Functional (Supra)Molecular Nanostructures



Habilitation à diriger des recherches

présentée par

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1. Resumé

L'auto-assemblage de nanostructures moléculaires fonctionnelles construites sur la base de liaisons hydrogène et de coordination a été étudié en solution, à l'état solide et sur à l'interface. En solution et à l'état solide, le contrôle de l'auto-assemblage hiérarchique a permis de construire des nanostructures moléculaires de complexité croissante. En effet des ligands organiques d'une structure tétranucléaire $[M^{II}_{4}L_{4}]$ adoptent un premier niveau d'organisation qui met en place des sites de coordination pour une organisation à un deuxième niveau. Ceci résulte en la formation de colonnes unidimensionelles et de superstructures en feuillet à deux dimensions. Par ailleurs, la coordination d'ion métalliques sur des surfaces métalliques s'est avéré générer un réseau infini à deux dimensions de stoechiométrie $([M^{II}_{2}L_{4/2}])_n$. Ainsi, des géométries de coordination peu usuelles ont été observées aux points de croisement à proximité des surfaces métalliques.

En solution et à l'état solide, plusieurs séries de grilles métalliques de composition $[M^{II}_{4}L_{4}]X_{8}$ (où M est un métal de transition) ont été synthétisées, et leurs propriétés optiques, magnétiques et électroniques étudiées extensivement. Ainsi les propriétés d'absorption visible des complexes tétranucléaires de Co^{II} dépendent du pH de la solution (incolore/ violet foncé). D'un point de vue magnétique, l'étude du couplage d'échange intramoléculaire des complexes tétranucléaires de Co^{II} a démontré leur comportement de méta-aimants moléculaires. Les complexes tétranucléaires de Fe^{II} sont, quant à eux, le siège d'une transition de spin conditionnée par la nature du ligand. Les complexes à ligands à fort champ demeurent diamagnétiques à bas champ, tandis que les ligands dont les propriétés stériques (et électroniques, dans une moindre mesure) assurent un champ plus faible promeuvent une transition de spin des complexes correspondants, activée par la température, la pression et la lumière. L'auto-assemblage hiérarchique des architectures complexes supramoléculaires favorise donc l'émergence de propriétés de spin à différents niveaux de complexité. Ainsi, chacun des deux niveaux de complexité structurale issus de l'assemblage séquentiel correspond à l'émergence de caractéristiques fonctionnelles liées à la modulation de la transition de spin.

Pour la première fois a été mise en évidence la tunneling quantique du moment magnétique anisotrope de mononucléaires complexes du type $[Ln(\mathbf{Pc})_2]^-$, ce qui définit une nouvelle classe d'aimants moléculaires à ion unique (SIMM). La barrière effective

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d'inversion de magnétisation a été déterminée (U_{eff} = 70 K), et la température de blocage (T_B) évaluée à 4.0 K est la plus haute de tous les SMMs reportés jusqu'alors.

Nos études dans le domaines électrochimiques ont montré que tous les complexes $[M^{II}_{4}L_{4}]X_{8}$ étudiés (où M est un métal de transition) en solution subissent des réductions à un électron localisées sur le ligand L. Les potentiels de réduction sont relativement bas et sont modulés par la nature du ligand. Plus généralement les systèmes étudiés ont les caractéristiques de dispositifs à niveaux électroniques multiples. La déposition des grilles $[Co^{II}_{4}L_{4}]X_{8}$ sur une surface de graphique offre un moyen de contrôler la topographie des arrangements supramoléculaires à zéro, une et deux dimensions, et ceci à l'échelle d'une molécule unique grâce à la technique STM. Par ailleurs, la probabilité de conduction par effet tunnel à travers un assemblage unique $[Co^{II}_{4}L_{4}]^{8+}$ a pu être détectée à l'échelle d'un cation.

Tous les systèmes (supra)moléculaires décrits dans ce travail représentent une voie d'accès au développement d'une électro-, spintro- et opto-tronique moléculaire.

2. Summary

The self-assembly of functional molecular nanostructures was investigated in solution, in the solid state, and at surfaces. Hydrogen bonding and metal ion coordination concepts were used to organize the supramolecular structures. Hierarchical self-assembly was studied rendering solid state molecular nanostructures with increasing complexity: Organic ligands were used in a first organization level to self-assemble tetranuclear $[M^{II}_{4}L_{4}]$ array structures, which preorganize the coordination site sets for second-level assembly steps resulting in a 1D columnar and in wall-like 2D layer superstructures. Furthermore, *in situ* metal ion coordination directly on metallic surfaces rendered infinite grid-like 2D network nanostructures with a $([M^{II}_{2}L_{4/2}])_n$ steochiometry. Unusual coordination geometries for the coordinated metal ion dimers were observed at the crossing points of the networks, where the metal ions are coordinated to organic ligands in close contact to the metallic surfaces.

In solution and in solid state, the optical, magnetic and electrochemical properties of different series of grid-type complexes of the general composition $[M^{II}_{4}L_{4}]X_{8}$ (with M = transition metal) were investigated thoroughly. Optically, Co^{II}₄-complexes displayed pHdependent absorption behaviour in the visible spectrum (pale-yellow to deep-violet) in solution. Magnetically, the intramolecular exchange coupling behaviour of Co^{II}₄-complexes was investigated and the results allowed them to be described as molecular metamagnets. The analogous Fe^{II}_4 -complexes exhibit evidence of the spin transition phenomena for the Fe^{II} -ions, whereby the emergence of the spin transition is directly coupled to the nature of the ligand. All ligand systems which favor strong ligand fields remain completely in the diamagnetic low spin state, while ligands which attenuate the ligand field by steric (and to a lesser extent electronic) effects exhibit spin transition behavior triggered by temperature, pressure and light. The hierarchical self-assembly of complex supramolecular architectures allows for the emergence of different spin transition properties at different levels of complexity. Thus, each of the two levels of structural complexity generated by the two sequential self-assembly steps corresponds the emergence of novel functional features due to the modulation of the intrinsic spin transition process.

For the first time, quantum tunneling of the strongly anisotropic magnetic moment of complexes of the type $[Ln(\mathbf{Pc})_2]^-$ was observed and a new class of so-called Single-Ion Molecular Magnets (SIMMs) is described. The effective barrier height determined for the

reversal of magnetization (U_{eff} = 70 K) and the blocking temperature (T_B = 4.0 K) are larger than the respective parameters for any other known Single Molecule Magnets (SMMs).

Electrochemically, all studied complexes $[M^{II}_{4}L_{4}]X_{8}$ (with M = transition metal) show multiple single-electron reductions in solution, whereby all reduction electrons are stored in molecular orbitals mainly localized on the ligands L. The reduction potentials are rather low and can be tuned by the nature of the ligands. In general, all investigated molecular systems show characteristics in solution typical for multilevel electronic devices. Depositing such $[Co^{II}_{4}L_{4}]X_{8}$ arrays onto graphite surfaces opens a way to control topographically (observed by STM techniques) the 0D, 1D and 2D arrangements of the supramolecules at the singlemolecule level. Furthermore, the tunnelling probability through an $[Co^{II}_{4}L_{4}]^{8+}$ array (mirroring its internal electronic properties) could be resolved on the single-molecule and single-ion level.

All of the (supra)molecular systems described in this work provide approaches to the development of (supra)molecular electro-, spintro-, and optotronics on the base of the functional properties of ensembles of molecules as well as those of a single molecule.

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3. Introduction

The function of a material depends both on the nature of its constituents and their mutual interactions and arrangement. The controlled fabrication, manipulation and implementation of nano-sized functional chemical entities into complex molecular architectures might provide a wide range of applications with great value for science and technology. The properties of nanostructured materials follow a bottom-up scale change from the nano- to the macrolevel with increasing structural and functional integration. The supramolecular self-organization approach enables a high degree of molecule-instructed structural organization within the nanoregime. Reversible noncovalent bonds mediate the controlled assembly and hierarchical growth of instructed, fully integrated and connected operational systems. Using such an approach, an impressive variety of structural motifs employing various self-assembly protocols has already been designed, e.g., helicates, catenates, grids, cages, dendrimers, rosettes, chains, ladders, rotaxanes etc.^[1]

The objective of the research studies concluded within this habilitation consists of the investigation and deliberate use of supramolecular self-organization and self-assembly of molecular systems (i) in solution with subsequent studies of the **bulk properties** as well as (ii) at well-defined surfaces and substrates. Both approaches are directed towards the long-term goal of controlled fabrication and manipulation of functional nanostructures and devices. The bottom-up self-assembly of supramolecular nanostructures relies pivotally on non-covalent interactions (metal coordination, hydrogen bonding, donor–acceptor π -interactions, van-der-Waals and electrostatic), which can be designed and investigated in molecular ensembles or, in some cases, directly at the single-molecule level. Furthermore, beyond one-step self-assembly concepts, the access to hierarchically organized functional nanostructures based on the modular construction of appropriately designed building blocks along self-assembly protocols containing multilevel-instructions was explored.

One possible way to address (supra)molecular nanostructures at the single-molecule level consists of organizing molecular systems at surfaces, where they could be approached and investigated by e.g. scanning probe or break junction techniques. Beside solution-based bulk self-assembly, three main concepts were used within this work to steer the construction of molecular nanostructures directly on surfaces: (A) A two-step approach starting with solution-based self-assembly of supramolecules followed by subsequent surface deposition. (B) The one-step surface-assisted self-assembly of hydrogen-bonded organic nanostructures

and (C) the surface-assisted coordination of metal ions by organic ligand systems out of the gas phase (Figure 1).



Figure 1: The main concepts to generate molecular nanostructures on surfaces: A) Solution-based self-assembly followed by subsequent deposition of the formed supramolecular systems. B) Surface-assisted hydrogen-bond based self-assembly from the gas (or liquid) phase C) Surface-assisted coordination chemistry. (spheres: metal ions or clusters, rods: organic molecules)

The functionalities of (supra)molecular architectures may derive from three principal routes: (i) the functionality may result as "emerging" property from the assembly of the bricks; (ii) the functionality may be encoded on the isolated bricks and persist as unchanged property in the self-assembled architecture or (iii) the two above mentioned approaches may also partially merge, since the molecular surroundings can alter or tune an original, "brick-based", functionality to a large extent and lead to the appearance of gradually new functional qualities. For example, supramolecular metal ion arrays cooperatively combine the properties of their constituent metal ions and ligands, exhibiting unique optical, electrochemical and magnetic behaviour.

The targeted functionalities within this work comprise **molecular magnetism**, **electronics**, **optotronics** and, more recently, opto-mechanical concepts of **molecular motion** and conformational changes at surfaces (Figure 2 and chapter 8.2.3.). The insights gained into supramolecular self-assembly contributes to the fabrication of novel functional nanoscale architectures and, in long term, their integration at a higher hierarchical level into the macroscopic surroundings. System parameters like temperature, photon and phonon irradiation, pressure, electric potential and tunnel current or chemical reactivity have been investigated as possible triggers for such future nanoscopic devices and engines. Furthermore, first experiments targeting the direct addressing of functionalities (starting with electronic) at the single-molecule level have been carried out and will be discussed.



Figure 2: Studied functionalities (molecular optotronics, magnetism and electronics) of (surpra)molecular nanostructures investigated within this habilitation in solution (left), in the solid state (centre) and at surfaces (right).

4. Molecular Self-Assembly

4.1. Solution-based Bulk Self-Assembly

Metallosupramolecular chemistry is an actively pursued area of research in supramolecular chemistry, which uses the interaction between organic ligands and metal ions to construct multicomponent and multinuclear coordination entities in the nanometer regime. It thus allows one to combine the properties of metal ions with those of the organic ligands in a defined structural frame with the potential for the cooperative generation of new properties not found in the individual components. The design of coordination compounds rests on the directing coordination instructions, which are based on the coordination geometry of the metal ion and the structure of the ligand's coordination sites.



Figure 3. Schematic (left) and chemical (right) representation of the self-assembly process of supramolecular [2x2] metal ion arrays from metal ions (spheres) and organic ligands (L^1 or L^2) in solution.

Transition metal coordination complexes of a [2x2] grid-type architecture comprise twodimensional arrays of metal ions connecting a set of organic ligands to generate a multiple wiring network.^[2] Structurally, this type of coordination requires strict perpendicular arrangements of the ligand planes at each metal centre (Figure 3). Given such a coordination environment around the metal centres, the linear and rigid extension of the ligand system from mono- to multitopicity will automatically lead to a grid-like two-dimensional coordination network with regularly arrayed metal ions. According to this general "leitmotif", grid-like metal ion arrays can in principle be prepared by careful prearrangement of the subunits using any set of metal ions and organic ligands possessing compatible coordination features. This requires ligands containing either bidentate or tridentate binding subunits in combination with metal ions possessing tetrahedral or octahedral (and in some cases bipyramidal) coordination geometry, respectively. General design principles for these structures involve thermodynamically driven synthesis of complex discrete objects from numerous molecular components in a single overall operation.

The construction of higher-order molecular architectures concerns the processes underlying the progressive complexification of matter through self-organization. The generation of organization levels of increasing complexity, diversity and functionality relies on a set of basic building blocks and subunits, interconnected through a multitude of relatively weak, non-covalent interactions (e.g. herein coordinative bonding, etc.) and rests on the progressive build-up of more and more complex entities by multiple, sequential and hierarchical self-organization steps that follow a conditional pathway, each step setting the base for the next one.

In recent years, more and more powerful self-assembly strategies have been developed for the controlled access to a variety of nano-sized objects of increasing complexity. Guided by the structural theme of the [2x2] metal ion array, we report herein on the hierarchical selfassembly of supramolecular architectures, which generate in a first self-assembly step new properties based on the spin-transition phenomenon and modulate this newly gained "collective" property during a second, higher ordered, self-assembly step (see chapter 6.1.). The structural organisation follows a component-module-architecture-hierarchy of increasing complexity (Figure 4).



Figure 4. Road map towards two-step hierarchically self-assembled architectures: From organic molecular components **A** and **B** to the molecular grid-like modules $[Fe^{II}_{4}A_{4}]^{8+}$ (1) and $[Fe^{II}_{4}B_{4}]^{8+}$ (2) and on to the 1-D architecture $\{[-Fe^{II}_{4}A_{4}]-(La^{III})_{4}\}_{n}^{11+}$ (3) and to the 2-D architecture $\{[-Fe^{II}_{4}B_{4}]-(Ag^{I})_{4}\}_{n}^{12+}$ (4).

By stepwise controlled coordination of the organic ligand systems **A** or **B**, the grid-like modules **1** and **2** and the corresponding column-and wall-like architectures **3** and **4** were generated in solution and structurally investigated in the solid state. The structure of the metal ion array $[Fe^{II}_{4}B_{4}]^{8+}$ (**2**) was determined by single crystal X-ray diffraction at 120 K (Figure 5) showing the monoclinic space group C2/c. It consists of a tetranuclear complex in which each of the Fe^{II} ions is in a pseudo-octahedral arrangement with a pronounced axial distortion. Each metal ion is surrounded by six nitrogen atoms from the pyrimidine and bipyridine units. The Fe-N bond lengths of d(Fe-N) = 1.898(6)-2.103(6) Å indicate that at 120 K all four Fe^{II} ions are in their LS state.^[3] The analytical data of complex $[Fe^{II}_{4}A_{4}]^{8+}$ (**1**) incorporating ligand **A** are very similar to those obtained for complex **2** and point to an identical composition $[Fe^{II}_{4}A_{4}]^{8+}$ as result of the first self-assembly step.



Figure 5. Top and side view of the x-ray single crystal structure of the metal ion array $[Fe^{II}_{4}B_{4}]^{8+}$ (2) (anions, solvent molecules, hydrogen atoms and the rotational disorder of the pyridine groups are omitted for clarity).

The generation of the second order coordination hierarchy was achieved by layering of an acetonitrile solution of of the tetranuclear unit $[Fe^{II}_4A_4]^{8+}$ (1) (as its CIO₄ salt) with a sixfold excess of a La(CIO₄)₃ in methanol resulting in deep-green, triangular-shaped crystals of supramolecular assembly product **3**. Elemental analysis of these crystals point to a {- $[Fe^{II}_4A_4]$ -(La^{III})}(ClO₄)₁₁ composition with additional sixteen water and two acetonitrile molecules. Single crystal X-ray investigations reveal a one-dimensional pillar-like motive involving aligned alternating $[Fe^{II}_4(A)_4]^{8+}$ and La³⁺ units (apparently interconnecting the tetranuclear Fe₄^{II} units in a linear fashion by the mediating coordination of one La³⁺ ion to two four-fold sets of 3-pyridyl groups above and below the molecular plan of the units). Unfortunately, due to the bad quality of the crystals, the resulting elevated R-factor of the data set prevent from a more detailed discussion of the molecular crystal structure of { $[Fe^{II}_4A_4]$ -(La^{III})₄}_n¹¹⁺ (**3**) (Figure 6).

To achieve a second order assembly of grid-like modules $[Fe^{II}_{4}B_{4}]^{8+}(2)$, a solution of its BF₄⁻-salt in acetonitrile was layered with a solution of methanol containing six equivalents of AgBF₄. After several weeks, pine-green prisms of compound **4** had grown at the diffusion interface of the two solutions. Single crystal X-ray diffraction studies at 120 K revealed that in compound **4** all eight exo-4-pyridyl groups of each $[Fe^{II}_{4}B_{4}]^{8+}$ unit were coordinated to Ag^I ions (Figure 7).



Figure 6: Structural motif concluded from the X-ray single crystal investigation of ${[Fe^{II}_{4}A_{4}]-(La^{III})_{4}}_{n}^{11+}$ (3) displaying the "column"-like 1D interconnection of two $[Fe^{II}_{4}A_{4}]^{8+}$ metal ion arrays by one Ln^{III} ion (green; disordered over two positions) (anions and solvent molecules are omitted for reasons of clarity).



Figure 7. X-ray single crystal structure of $\{[Fe^{II}_4B_4]-(Ag^I)_4-\}_n^{12+}$ (4) displaying the "brickwall"-like entanglement of the $[Fe^{II}_4B_4]^{8+}$ modules by the Ag^I ions (green) a) in the frontal elevation of the 2D "brickwall"-like network and b) in the cross section (anions and solvent molecules are omitted for reasons of clarity; carbon: grey, nitrogen: blue, iron: red).

The Ag^I ions are dicoordinated in an approximately linear coordination manner with d(Ag-N) = 2.130(12)-2.228(14) Å; $\alpha(\text{N-Ag-N}) = 166.4(7)^{\circ}$ and $168.8(8)^{\circ}$, and interconnect each tetranuclear $[\text{Fe}^{II}_{4}\mathbf{B}_{4}]^{8+}$ unit to four neighbouring units each time by two pyridine-Ag^I-pyridine bridges. Following this coordination scheme, an infinite coordination polymer is generated as a meander-like interwoven, two-dimensional network. Within this "brickwall"-like framework, the $[\text{Fe}^{II}_{4}\mathbf{B}_{4}]^{8+}$ -units are aligned in rows 2.15 nm apart, while the distance between two neighbouring "brickwalls" is around 1.56 nm (Figure 7).

The represented results show that self-assembly processes using suitably designed molecular components can be implemented to construct the metallo-supramolecular brick modules $[Fe_4A_4]^{8+}$ (1) and, $[Fe_4B_4]^{8+}$ (2), displaying both the structural prerequisites which enable 1 and 2 to undergo a second self-assembly process. This second process leads in both cases to a hierarchically ordered, either one-dimensional "column"-like $\{-[Fe^{II}_4A_4]-(La^{III})\}_n^{11+}$ (3), or two-dimensional "brickwall"-like $\{-[Fe^{II}_4B_4]-(Ag^I)_4\}_n^{12+}$ (4) architectures. The variation of the properties (herein magnetic) of the molecular architectures depending on progressing hierarchical levels of complexation will be shown in detail in chapter 6.1.

4.2. Surface-assisted Self-Assembly and Coordination

A) Surface deposition of pre-assembled supramolecules (in collaboration with Prof. P. Müller, University of Erlangen, Germany)

The controlled arrangement of supramolecular [2x2] metal ion arrays on surfaces might provide materials with addressable functional subunits smaller than the conventionally studied quantum dots. The sub-nanometer exploitation of the molecular properties requires a precise control of the positioning of the [2x2] metal ion arrays onto the surface. Such positioning processes might be steered by templating effects directed by weak van-der Waals interacting with the underlying substrate lattices. Successful attempts of the preparation of closely-packed, highly ordered monolayers of grid-like [2x2] metal ion arrays on pyrolytic graphite were reported before. Furthermore, it was shown, that single molecules within the full-coverage monolayer could be addressed destructively by removal with STM-tip manipulations.^[4]

Ongoing work towards low-dimensional arrangements of $[\text{Co}^{II}_4 L^1_4]^{8+}$ metal ion arrays has shown that in very dilute conditions, the supramolecules get trapped along the step edges of the highly ordered pyrolytic graphite after sputtering 10⁻⁴ mol l⁻¹ in acetonitrile solutions. Using this technique, it was possible to obtain continuous 1D chains of several hundred nanometers as well as 2D arrays of densely packed grid-like supramolecules depending on the concentration (Figure 8). The ordered 2D structures form spontaneously, growing outward from single nucleation points. This process might be viewed as the 2D equivalent of a crystallization process.



Figure 8. STM-images of samples generated by sputtering of acetonitrile solutions of $[Co^{II}_4L_4]^{8+}$ grid-like complexes at room temperature on graphite; left) an isolated molecule; centre) at low concentrations, the $[Co^{II}_4L_4]^{8+}$ complexes are ordered along graphite steps into 1D chains; right) following the same protocol, at higher concentrations, 2D arrangements made from $[Co^{II}_4L_4]^{8+}$ metal ion arrays could be obtained.

The so obtained free-standing molecular architecture (in contrast to the previously obtained densely-packed monolayers) of gridlike $[Co^{II}_{4}L_{4}]^{8+}$ metal ion were used as an experimental platform for the study of the electronic properties at the single-molecule level (see chapter 7.2.).

B) Surface-based Hydrogen-bonded Nanostructures (in collaboration with Prof. J. V. Barth EPF Lausanne, Switzerland)

Although relatively weak, Hydrogen-bonding interactions play a prominent role in organizing matter into hierarchical ordered complex structures. Their reversibility and relative structural flexibility together with the omnipresence of water as a preferred solvent enable them to play a key role especially in the self-organized metastable structures of living matter.

In material science, many examples have been used Hydrogen-bonding concepts to tune material structures as well as to generate functionalities. Recently, the weakness and reversibility of the Hydrogen bond was applied in the design of materials with self-adaptive properties and functionalities. Only few research work deals with the transfer of the mainly in bulk studies developed rules of Hydrogen bonding concepts to near-surface conditions on organic or metallic substrates.

The amide bond is one of the dominating hydrogen bonding groups in living matter as it interconnects amino acids in peptides. The maximisation of stabilization energy by the formation of configurations of a polypeptide chain with maximal number of -C=O---H-N-bonds (binding energy 21-42 kJ/mol per bond) leads to the fundamental secondary structural motifs as α -helix and β -sheet. ^[5]



Figure 9. Molecular structure of N, N-diphenyl-oxamide (**Oxamide**) (left) and 1D ribbon-like solid state structure of the molecule obtained by single crystal X ray diffraction studies (right).

In natural systems, the amid groups -C(=O)-NH- are distanced from each other by the amino acid backbone. Vicinal linking of two amide groups together with hydrophobic side blocking by phenyl substitution (as shown in the molecular structure of N, N- diphenyl-oxamide, **Oxamide**, in Figure 9) will generate an additional secondary hydrogen bonding motive (beside of the natural α -helix and β -sheet): the 1D linear ribbon. To test this concept, the **Oxamide** molecule was synthesized following literature protocols^[6] and investigated in the solid state by single crystal X-ray diffraction studies (Figure 9).^[7] Within the crystal lattice, the **Oxamide** molecule forms the 1D ribbon motive within by adapting a *s-trans* configuration around the central oxalic C-C-bond so enabling so the formation of two amide hydrogen bonds per molecule.

In order to prove the persistence of this ribbon hydrogen bonding motif under epitaxical conditions, the **Oxamide** was sublimed onto a clean gold (111) surface. Due to a weak absorbate-substrate interaction, the molecules order to molecular ribbons only below a temperature of 17 K. Within the accuracy of the STM data, basically the same structural features as found in the solid state (1.2 nm width, molecule-to-molecule distance within the chain of 0.5 nm) could be observed (Figure 10). Three different spatial orientations of the ribbons reflect the symmetry of the gold substrate. By the same token, templating effects of the underlying surface are apparently responsible for restricting the maximum lengths of the

ribbons to 20 nm, since the start and the end of each ribbon seems to be located on the crest of the gold elbow reconstruction.^[8] From the x-ray data it could concluded that efficient H-bond formation seems to be only possible if the phenyl rings are tilted by an angle of 23 ° (as found in the solid state). Apparently, the molecular **Oxamide** nanostructures at the surface show the identical molecule-molecule distances within the 1D ribbon as found in the solid state. This can be only explained if the tilting of the phenyl rings is also present in the surface nanostructures, which would result in a high-energy "entatic" state in the 1D ribbon.



Figure 10. Sublimation of the **Oxamide** molecule onto a gold (111) surface reproduces the 1D supramolecular ribbon motif by surface assisted H-bond formation.

2D molecular hydrogen-bonded architectures were obtained by the exploitation of the tendency for organic carboxylic acids to dimerize. In previous work, several research groups used purchasable mesitylic acid and its derivates to generate 2D hexagonal honeycomb motifs with three-fold geometry by self-assembly on graphite and on metallic substrates.^[9] In order to increase the diameter of the available cavities up to 1 nm, a phenyl ring extended version of mesitylic acid **ExMes** (4,4',4''-benzene-1,3,5-triyl-tri-benzoic acid) was synthesized following literature protocols (Figure 11).^[10]

The sample preparation and characterization have been conducted in an ultra-high vacuum (UHV) system providing well-defined conditions for the experiment. The UHV system (base pressure $\sim 3 \times 10^{-10}$ mbar) is equipped with a home-built UHV-STM operating at 5K. **ExMes** in powder form was deposited on an atomically flat clean Ag(111) surface by organic molecular beam epitaxy (OMBE) from a Knudsen-cell type evaporator with the temperature of the cell constantly held at 550 K during the evaporation. The Ag(111) surface was prepared by several cycles of sputtering with Argon ions and subsequent annealing at 850 K. The STM images were acquired at 5K in the constant current mode with bias voltages of 0.5 V.

The sublimation of the **ExMes** molecule onto a Ag(111) surface followed by short annealing at 270-300 K resulted into the formation of a regular 2D honeycomb network incorporating an array of cavities of 2.95 nm diameter (Figure 11). However, holding the deposition temperature of the molecules above 320 K resulted in the evolution of a second hydrogen bonding motif of closely-packed rows. Additionally, the phase I (open honeycomb network) can be transformed into phase II (closely-packed rows) by annealing at 320 K. The hydrogen bonding motif of phase II was not yet observed for mesitylic acid derivatives in the bulk. Investigations into the possibility to use the open cavities of phase I as quantum resonators or to fill them with suitable guest are under the way.



Figure 11. Sublimation of the **ExMes** molecule onto a Ag(111) surface results in the formation of two different 2D supramolecular hydrogen bonding motifs in depending on the deposition temperature: phase I (open honeycomb network) and phase II (close-packed rows).

C) Surface-assisted Coordination Chemistry (in collaboration with Prof. K. Kern, MPI-FKF Stuttgart, Germany)

As shown in chapter 4.2.A, the investigation of metal ion arrays within the nanometer regime follows conventionally a three step sequence: (i) the synthesis of the ligand molecules, (ii) the self-assembly into the supramolecular entities, and (iii) the controlled deposition or anchoring of the supramolecules on/at surfaces (Figure 12, left). However, this sequence is not a scientifically necessity, as it also reflects, at least partially, the historic background of an evolving interdisciplinary collaboration. A conceptually alternative route towards nano-sized metal ion arrays on surfaces is opened by the possibility of *in situ* self-assembly protocols emerging from metal ion coordination under near-surface conditions (Figure 12, right).^[11]



Figure 12. Schematic representations of the synthesis-self-assembly-deposition concept (left) and of the *in situ* surface-assisted coordination chemistry approach (right) used to construct surpamolecular nanostructures on surfaces (blue spheres: metal ions)

The infinite metal ion arrays were generated just by the cosublimation of organic dicarboxylic acid derivates and inorganic Iron(0) atoms on Cu(100) surfaces under ultra-high vacuum conditions. Technically, in a first step, the organic ligand *trans*-azobenzoic acid (**ADA**) was deposited by OMBE onto the Cu(100) surface. Subsequently, the metal atoms were evaporated on top of the formed (more or less complete) organic monolayer using electron beam evaporation. After a short annealing period (5 min at T = 450 K) to initiate the self-assembly process by the increased mobility of the molecular and ionic components on the surface, well-ordered regular structures emerged readily in domains of up to 50 nm size (Figure 13).



0.5 ML ADA / 0.1 ML Fe⁰, T = 300 / 450 K + 450 K post-anneal

Figure 13. Schematic representation and STM image of the result of the cosublimation of *trans*-azodibenzoic acid (ADA) and Fe atoms onto the Cu(100) surface.

The rectangular molecular assemblies shown in Figure 13 were obtained on the copper (100) surface at Fe/ligand ratios of about 0.5. Structurally; they consist of (i) dimeric Fe₂-nodes which are infinitely interconnected by (ii) an organic backbone of orthogonally arranged ligand linkers (Figure 14). The observed Fe-pairs in the cross positions of the network deserve some interest due to their coordination characteristics: Two Fe-centers are surrounded by two sets of two differently coordinating carboxylic groups; two of which are in a mono-dentate μ^2 -bridging mode and two in an apparently bidentate chelating mode. Overall, the coordination geometry of each of metal center is square-planar. However, since the resolution limits of the present STM data prevent a clear distinction between the mono- or bidentate coordination modes of the two chelating carboxylic groups, the exact determination of the coordination geometry is not possible in all cases.



Figure 14: Schematic representation and STM image of the coordination mode the infinite rectangular coordination network on Cu(100) surface with dimeric Fe₂-units at the crossing points of the grid-like network.

The Fe-O bond distances estimated from STM data are close to that of bulk materials $(d(Fe-O)= 1.9-2.3 \text{ Å})^{[12]}$ and the metal centers are held at a metal-metal distance of about d(Fe-Fe) = 5 Å. However, the observation of sometimes elongated Fe-O bonds might be indicative of a situation in which both ligand and metal centres are in close contact with the Cu(100) surface, which is then obviously acting a template. Thus, the underlying crystal lattice as well as the conduction band of the substrate might interfere structurally as well as electronically in the final positioning of the involved metal atoms relative to the organic ligands.

However, looking at the distinct $M_2L_{4/2}$ -stocheometry of the dimeric Fe₂-nods, it seems reasonable to reckon that the principle of electro-neutrality is still persisting also under interfacial conditions. Such a view would lead to the definition of two Fe(II) ions surrounded by four deprotonated, negatively charged carboxylic groups. The formation of such electroneutral 4+/4- units will depend critically on the smoothness of the deprotonation reaction, during which four carboxylic protons have to be reduced to two mole Hydrogen under simultaneous oxidation of the two Iron(0) centers. The gaseous Hydrogen could easily migrate into the UHV environment so favoring the accomplishment of the redox reaction. The local electro-neutrality around the dimeric Fe₂-knots may also explain the high thermal stability of the 2D networks up to 500 K (although they are not stable in the presence of ambient gases).

The further elucidation of the coordination characteristics of metal centers in close contact to metallic surfaces (coordination number, redox- and spin- state, metal-metal interactions, mirror charges, etc.) is under investigation and the results might advent a new

branch of "surface-assisted" metal coordination chemistry (maybe as extension of the more bulk- and solution-based, conventional "Werner-type" one). Together with other molecule-dealing STM-based surface manipulations (e.g. C-C bond formation, surface chirality)^[13] and new approaches towards nano-magnetism (e.g. spin-polarized STM),^[14] such "surface-assisted" coordination chemistry might constitute part of the future tool kit needed to put into reality directed construction and controlled manipulation of functional interfaces and operational surfaces.

5. Molecular Optotronics

5.1. pH-Modulated Absorption of Co₄L₄

The UV-vis spectra of the [2x2] metal ion arrays $[\text{Co}^{II}_4(\mathbf{L}^2)_4]^{8+}$ bearing acidic protons display reversible pH-modulation of the optical properties in solution. Due to the high accumulated charge of the complex cations, the eight N-H protons of the *bis*(hydrazone) ligands \mathbf{L}^2 (R¹=Ph) can be removed progressively and reversibly at relatively low pH values (below 7).^[15] The colour of the solution of $[\text{Co}^{II}_4(\mathbf{L}^2)_4]^{8+}$ changes from pale-yellow at low pH to orange and finally to deep-violet above neutral pH and repeated cycling indicates that the process is completely reversible (Figure 15).



Figure 15. The pH-induced color change (pale-yellow to deep-violett) and UV-vis spectra of complex $[Co^{II}_4(L^2)_4]^{8+}$ (R¹=Ph; acidic protons in red) in 50/50 vol% acetonitrile/buffer solution at pH 0.51; 0.75; 3.12; 3.79; 4.64; 5.53; and 7.22.

Furthermore, the $[Zn^{II}_4(\mathbf{L}^2)_4]^{8+}$ (R¹=Ph) complex exhibits an emission (originating from sandwich-like π - π -interactions of the phenyl substituents intercalated between two ligands \mathbf{L}^2), which depends on the protonation state.^[16]

6. Molecular Magnetism

6.1. Hierarchic Spin Transition (ST) Compounds (in collaboration with Prof. P. Gütlich, University of Mainz, Germany)

Bi- or multistability on the molecular level, as required e.g. for high density information storage devices, might be achieved by exploitation of changes in intrinsic molecular properties, such as conformational, spin, magnetic, electronic or photophysical states. Among the feasible effects, the spin transition (ST) phenomenon of Fe^{II} ions is one of the perspective processes to enable molecular memory due to the concomitance of possible "write" (temperature, pressure, light) and "read" (magnetic, optical) parameters (Figure 16).^[17] Such features provide access to the development of (supra)molecular spintronics.^[18]



Figure 16: Schematic representation of the spin transition phenomenon for octahedral coordinated Fe^{II} –ions (Δ_0 : ligand field splitting parameter; E_P : spin pairing energy; k_B : Boltzmann constant; T: temperature).

So far, predominantly mononuclear^[19] and only some binuclear^[20], one trinuclear^[21] and one pseudo-pentanuclear^[22] molecular Fe^{II} spin transition compounds have been investigated. Most investigations have concerned the influence of weak intermolecular interactions (H-bonding; π - π -stacking) on the cooperativity of the spin transition processes in the solid state. On the other hand, polymeric Fe^{II}-compounds involving 1,2,4-triazole and 1,2,3,4-tetrazole ligands have been subject of several investigations.^[23]

In order to widen the structural base of available molecular Fe^{II} -ST-systems, two series of [2x2] gridlike complexes $[Fe_4^{II}L_4](X)_8$ **1–8** (**L** = **C-J** X = PF₆, BF₄ or ClO₄) were synthesized and their ST properties were studied both in solution and in the solid state (Figure 17). ¹H-NMR and UV-Vis techniques were used in solution, while magnetic susceptibility, X-ray diffraction and Mössbauer investigations were carried out in the solid



state in order to reveal the influence of the nature of ligand \mathbf{L} on the magnetic behavior of the complexes.

Figure 17. Schematic representation of the two series of [2x2] Fe^{II}₄L¹₄ complexes 5-9 varying substituent R¹ and 10-12 varying substituent R² of L¹.

In a first series of compounds (compounds 5-9 $[Fe_4^{II}L_4^1](X)_8)$, the coordination sphere of the [2x2] grid-type complexes was varied by changing the substituent R¹ in the 2position of the pyrimidine of the incorporated ligands L¹ (L = C-G with R¹ = H, OH, Me, Ph, p-PhNMe₂). In a second series of compounds (compounds 10-12 $[Fe_4^{II}L_4^1](X)_8$), the ligands were additionally altered at the periphery. Thus, in complexes 10 and 11 S-ⁿpropyl groups were introduced in the 4`-position of the ligands (complex 10 $[Fe_4^{II}H_4](PF_6)_8$ and complex 11 $[Fe_4^{II}I_4](ClO_4)_8$). In complex 12, $[Fe_4^{II}J_4](BF_4)_8$, the peripheral pyridyl ring of the ligand backbone was exchanged by a 5´´-aminopyrazin-2´´yl group yielding ligand J (Figure 17).

The investigations have shown that the occurrence of spin transition in [2x2] gridlike complexes of the type $[Fe^{II}_4L^4](X)_8$ depends directly on the nature of the substituent R¹ in the 2-position of the ligand L¹. All compounds with substituents in this position favoring strong ligand fields (R¹ = H; OH) remain completely in the LS state at all temperatures studied. Only complexes bearing substituents which attenuate the ligand field by steric (and to a lesser extent electronic) effects ($R^1 = Me$; Ph) exhibit, although incomplete, a temperature triggered spin transition. The magnetic behavior was characterized in solution by ¹H-NMR and UV-Vis spectroscopy and in the solid state by X-ray, magnetic susceptibility and Mössbauer measurements (see exemplary complex **8** in Figure 18). In the case of complex **8**, it was equally shown that the switching between high and low spin state can also be triggered by light (leading to increased high spin populations at temperatures below 20 K) and by pressure (leading to an increase of the Fe^{II}(LS) fraction at ambient temperature).^[24]



Figure 18. General switching scheme between the Fe^{II} ion spin states in the gridlike [2x2] complex $[Fe^{II}_4(\mathbf{F})_4]^{8+}$ (8) triggered by temperature, pressure and light (left); the averaged Fe-N bond lengths in the 3 HS / 1 LS and in the 1 HS / 3 LS states determined by temperature dependent single crystal X-ray diffraction (middle), and the respective Moessbauer spectrum at 300 K and at 4.2 K showing the increase of the Fe^{II}(LS) fraction with decreasing temperature (right). ^[24]

In the solid state, very gradual and incomplete magnetic transitions without hysteresis seem to be typical for all investigated magnetically active compounds of the $[Fe^{II}_{4}L^{1}_{4}](X)_{8}$ [2x2] metal ion arrays. The presence of the substituent $R^{1} = Ph$ resulted in the most complete transition and further substitutions at the phenyl ring or in the 4'-position of

the ligand altered the spin transition behavior only marginally. Improving the intermolecular interaction between the tetranuclear centers by introduction of H-bonding between the grid units (compound **12**) increased the HS fraction over the whole temperature range, although the spin transition remained very gradual and incomplete.

The general result, that the substituent $R^1 = Ph$ produces the most complete spin transitions properties, while substituent R^2 can be varied without having direct influence on the spin transition properties of the $[Fe^{II}_4L^4]$ system, leads to the design of ligands **A** and **B**, where R^2 is a 4-pyridyl and 3-pyridyl group, respectively (see Figure 4). As shown in chapter 4.1., ligands **A** and **B** constitute the structural base for hierarchical self-assembly processes of, on first level, the gridlike complexes $[Fe^{II}_4A_4]$ (1) and $[Fe^{II}_4B_4]$ (2), respectively, and, on a higher level, of the molecular column- and wall-like architectures $\{[Fe^{II}_4A_4]-(La^{III})_4\}_n^{11+}$ (3) and $\{[Fe^{II}_4B_4]-(Ag^I)_4\}_n^{12+}$ (4) (see Figure 4).

The magnetic solid state investigations revealed that the spintronic modules **1** and **2** represent a collectively generated coordination [2x2] array displaying gradual spin transition behaviour (Figure 19). In the higher–order architectures **3** and **4**, the magnetic behaviour of the included $[Fe^{II}_{4}L^{1}_{4}]$ spintronic modules exhibits a progressive hindrance of the spin transition process with increasing dimensionality (Figure 19). Thus, the whole magnetic curve of the 1D "column"-like architecture **3** is shifted to higher temperature (in comparison to module **1**) by around 200 K. This can be interpreted as a increased preference for Fe^{II}(LS) at ambient conditions. In contrary, the 2D "wall"-like architecture **4** is blocked at a 2HS / 2LS situation and does not show any switching behaviour between Fe^{II}(HS) and (LS) states obviously due to increased steric hindrance in the interconnected, in comparison to the lattice structure of **2** much stiffer, 2D network.

The variation of the spin transition behaviour at different organisational levels, as realized in the coordination sequence from A/B to 1/2 to 3/4, show how the architectural parameters feed back actively on the intrinsic functionalities of complex supramolecular assemblies.



Figure 19. $\chi_M T/4$ *versus* temperature plots of a) the spintronic module $[Fe^{II}_4A_4](ClO_4)_8$ (1) and the 1D "column"-like assembly $\{-[Fe^{II}_4A_4]-(La^{III})\}_n(ClO_4)_{(11)n}$ (3) (top) and of the spintronic module $[Fe^{II}_4B_4](BF_4)_8$ (2) and the 2D "wall"-like architecture $\{-[Fe^{II}_4B_4]-(Ag^I)_4\}_n(BF_4)_{(12)n}$ (4) (bottom) displaying the progressive hindrance of the spin transition process going from 0D to 1D to 2D.

Ongoing investigations are directed towards the elucidation of the character of the cooperativity within and between the molecular building blocks and modules. In a farther-reaching perspective, architectures presenting spin state properties that may be switched by external triggers represent entries toward (supra)molecular spintronics.^[25]

6.2. Supramolecular Metamagnets (in collaboration with Prof. P. Müller, University of Erlangen, Germany)

In view of their structure, antiferro- or ferromagnetically coupled ring-like transition metal complexes are widely regarded as finite equivalents for 1D infinite magnetic chains, implying that physical concepts found for these chains should describe them too. Even-numbered, AF-coupled wheels are characterized by an S=0 spin ground state and previous magnetic studies revealed that $[Co^{II}_{4}L^{1}_{4}]$ with L=E or F (see Figure 17), which can be also considered ring-like molecules with n=4, behave exactly as an intramolecular antiferromagnetic (AF) exchange coupled molecular system with a S=0 ground state.^[26]

However, theoretical work has shown that in such systems excited magnetic states seem to be easily accessible.^[27] Additionally, the even-numbered ring-like AF-coupled molecular complexes might show large quantum effects, such as tunnelling of the Néel vector ^[28] or quantum coherence phenomena.^[29] Furthermore, very similar ring-like systems form a suitable series of objects to investigate the origins of magnetic anisotropy, partly because of their high symmetry.



Figure 20. Molecular structure of the grid-like [2x2] $[Co^{II}_4 E_4]$ complex (b) and the field dependence of the magnetic moment of a single crystal at 1.9 K for magnetic fields along the main axes showing the anisotropy in the magnetic saturation (a). The inset displays the magnetization curve of the powder sample.

Further magnetic studies of the $\text{Co}^{\text{II}}_{4}$ L₄ systems as function of temperature confirmed the general presence of intramolecular antiferromagnetic (AF) exchange interaction

independent of the substitution pattern of the involved ligands **L**. Subsequently recorded magnetisation curves on single crystals of $[Co^{II}_4E_4](BF_4)_8$ at 1.9 K revealed the following anisotropic situation: For magnetic fields perpendicular to the grid plane, the magnetization shows a behaviour reminiscent of a thermally broadened magnetization step due to a ground-state level crossing, as it is often observed in antiferromagnetic clusters.^[30] In contrast, the magnetic moments for applied fields within the plane of the Co^{II}_4 -wheel, increase linearly with equal slope as function of the magnetic field (Figure 20). No long-range ordering develops as intermolecular interactions are negligibly small preventing the system from undergoing a metamagnetic phase transition. However, the analysis of its magnetism can be completely recast in the language of metamagnetism, and in this sense it was proposed to call them examples for single-molecule metamagnets.^[31]

6.3. Single Ion Molecular Magnets (SIMMs) (in collaboration with Prof. P. Müller, University of Erlangen, Germany)

An exciting development in nanoscale magnetic materials occurred in 1993 when $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (hereafter Mn_{12}) was identified as a nanoscale magnet,^[32] the first to comprise discrete, magnetically non-interacting molecular units rather than a 3D extended lattice (as in metals and metal oxides, for example). The discovery initiated the field of molecular nanomagnetism and such molecules have since been termed single-molecule magnets (SMMs). They derive their special magnetic properties from the combination of a large spin (S) and an Ising (easy-axis) magneto-anisotropy exhibiting a negative zero-field splitting parameter (D), which gives rise to the superparamagnetic–like property of a barrier to magnetization relaxation (Figure 21). This class of compounds does not only display magnetisation hysteresis, but also quantum tunnelling of magnetisation (QTM)^[33] and quantum phase interference.^[34]

Usually, SMMs, like Mn₁₂ or Fe₈, consist of several magnetic ions coupled by strong intramolecular exchange interactions, resulting in a high spin ground state.^[35] Although considerable progress has been made in the synthesis of high-spin systems involving d-metal ions, restricted anisotropy terms have prevented, at least so far, from higher blocking temperatures.^[36] Since 4f-lanthanide ions posses, in comparison to 3d-metal ions, a much larger intrinsic anisotropy terms increase the tunnel splittings and shortcut the barrier resulting in reduced effective heights.^[37] Recently, Ishikawa et. al. reported on AC-

susceptibility measurements on powder samples of Dy^{3+} and Tb^{3+} double-decker complexes obtaining values for the effective barrier height of 28 cm⁻¹ (40 K) and 230 cm⁻¹ (330 K), respectively, which are significantly larger than those known for 3d-based SMMs.^[38]



Figure 21. Molecular structure (left), magnetic coupling scheme and hysteresis (right) of the Mn₁₂ family exhibiting magnetic hysteresis and quantum tunnelling of magnetization (QTM).^{[35][36]}

The Dysprosium double-decker compound $[Dy(\mathbf{Pc})_2]^ (TBA)^+$ (Pc = dianion of phthalocyanine; TBA = N(C₄H₉)₄⁺) was synthesized following a protocol described by Weiss et. al..^[39] The compound crystallizes in the monoclinic space group *P*2₁ with two formula units per elementary cell and with the following unit cell parameters: a = 11.41 Å, b= 22.44 Å, c = 13.44 Å, β = 107.46°. The molecular pseudo C₂-axes of the double-decker anions are aligned in a strictly parallel way along the crystallographic [100] axis and the n-butyl groups of the TBA-cations are structurally disordered over two positions, which have been refined with 50% occupancy each. In the crystal lattice, the molecules are arranged in infinite stacks with alternating double-decker anions [Dy(**Pc**)₂]⁻ and TBA⁺ cations (Figure 22). Within the stacks, the Dy³⁺-Dy³⁺ distance is with 11.4 Å noticeably shorter than the interstack distances (13.1 - 14.8 Å). Relatively weak C-H--- π (3.45 - 3.95 Å) were found between the butyl chains of the TBA⁺ cations and coordinating isoindoline groups and imine nitrogens of the Pc ligands.^[40] These interactions provides a possible relatively weak intermolecular exchange pathway between the [Dy(Pc)₂]⁻ molecules along the stacks via the TBA⁺ cations.



Figure 22. a) Schematic and b) single crystal X-ray structure of the $[Dy(Pc)_2]^-(TBA)^+$ molecule. c) Representation of the crystal packing diagram with the indicated intra- and interstack $Dy^{3+}-Dy^{3+}$ distances (arrows) and the most important C-H--- π interactions (dotted lines). The butyl groups of the TBA⁺ cation are structurally disordered and only one of the equivalent positions (50 % occupancy) is shown.

The magnetization of single crystal samples was investigated along the [100], [010], and [001] directions by SQUID measurements up to 5.5 T at 1.8 K. The magnetic data can be interpreted by the presence of an easy-magnetisation axis and a hard magnetic plane (Figure 23). A two parameter fit of the three magnetization curves along the three different orientations using the Hamiltonian (eq. 1 in Figure 23) gives $D = 3B^2_0 = -5.0$ K and $E = B^2_2 = 0.7$ K. The resulting barrier height of U = 281 K suggest SMM behaviour, although at much higher temperatures than observed (4K). However, a more realistic barrier height can be concluded from the energy separation between the two lowest levels of the ground state multiplet with $U_{eff} = 70$ K, which results following $T_B = U/ln(t/\tau_0) = 4$ K; a value close to the observed blocking temperature.

Single crystal magnetization measurements were also performed using 2DEG GaAs/GaAlAs hall sensors.^[41] At low temperatures, the magnetization *versus* magnetic field

curves show a pronounced step-like hysteresis up to a blocking temperature of $T_B = 4$ K. The observed steps can be explained by Quantum Tunneling of the magnetization (QTM) involving multiple anti-level crossings at close distance.^[42] The observed features of the broad steps in the hysteresis at finite fields can be explained by a complex interplay of intermolecular exchange, dipolar and hyperfine interactions.



Figure 23. a) The Hamiltonian used in the analysis of the b) direction-dependent magnetization data rendering the second order field parameters D = -5.0 K and E = 0.7 K. c) Single crystal hysteresis loop measurements for different temperatures along the easy axis ([100]) at different temperatures.

In conclusion, the Dysprosium *bis*-phthalocyanine compound, which consists of only one single metal ion, is the first member of the new class of Single-Ion Molecular Magnets (SIMMs). The value of the zero-field splitting parameter D = -5.0 K has been determined by anisotropy SQUID measurements on single crystals. The effective barrier height for the reversal of the magnetization $U_{eff} = 70$ K and the blocking temperature of $T_B = 4$ K are larger than for any other known SMM. Preliminary experiments on the Terbium analogues have shown even larger blocking temperatures.^[43]
7. Molecular Electronics

7.1. Multilevel Molecular Species (in collaboration with Dr. J.-P. Giesselbrecht, University of Strasbourg)

The drive to shrink electronic devices to the nano-level, has, in recent years, led to the design and investigation of molecular-scale components endowed with sensing, switching, logic, and information storage functions.^[44] Although the implementation of information processing with such devices faces hurdles in the development of logic architecture and intermolecular hook up schemes, molecular data storage and processing are subjects to active interest. Species suitable for molecular data storage (i) must possess two or more physicochemically distinct states that can be conveniently switched by application of external triggers (e.g. thermodynamic parameters or electro-magnetic fields) and (ii) should be addressable and switchable within the nanometer regime.

In this respect, interest for [2x2] grid-like molecular architectures might arise from an alternative encoding concept called "quantum cellular automata", in which molecules do not act as current switches but as structured charge containers.^[45] Envisioned first for quantum dots, binary information is encoded in the charge configuration of a cell composed of a small number of differently charged redox centres, which are electronically communicating within the entity but are not completely delocalised (Figure 24). Each cell has two degenerate ground states, which can be interconverted by an internal electron density redistribution (e.g. by the transfer of two or more electrons within the cell). The electrostatic interaction of two neighbouring cells (arranged in two- or three- dimensions) lifts the given degeneracy and results in "1" or "0" states. Remarkably, the intercellular information exchange is purely based on Coulomb interactions and involves no current flow. If such interaction can be realized, this approach may enable a general purpose computation, the "universal computer.^[46]

From the standpoint of nanochemistry, the cells can equally consist of molecular or supramolecular entities with an electronic delocalisation of the Robin-Day type II character between internal redox centres. Provided it is possible to achieve a fine-tuning of the intra- as well as intermolecular electronic and Coulomb interactions, tetranuclear metal ion coordination arrays arranged on surfaces (as shown in chapter 4.2.A) could represent particularly interesting candidates for "Molecular Cellular Automata", especially due to their

obvious structural similarity to the "charge containers" within the quantum dot cellular automata concept.



Figure 24. Schematic representation and working principle of "cellular automata" concept: a) Coulomb repulsion keeps the electron density (dark) at antipodal sites resulting in the degenerated "1" and "0" state. b) A wire of "cellular automata" can be formed by a one-dimensional arrangement of cells. The intercellular Coulomb interactions force all units into the same state. c) Working principle of a majority logic gate consisting of three inputs (A, B, C) which converge on an output (Maj(A;B;C;)).

In order to prove the suitability of [2x2] metal ion arrays for such and further novel data processing concepts, the electronic properties of a series of $[M^{II}_{4}L_{4}]$ -complexes were investigates in solution as well at surfaces. In solution, the electrochemical behavior of a family of tetranuclear grid-like oligopyridine complexes of the general formula $[M_{4}^{II}(L)_{4}]^{8+}$ displays well-resolved multiple one-electron reductions in all complexes investigated.^[47] Furthermore, the introduction of electron donating or attracting groups into the ligands tunes systematically the potential of the first reduction. As a consequence, one Co₄^{II} member of this family exhibits up to twelve well-resolved reversible one-electron processes at room temperature, which appears to be the most extended redox series known for well characterized molecular compounds (Figure 25).



Figure 25. Sequential twelve-electron reduction of a $[Co^{II}_4(\mathbf{F})_4]^{8+}$ array in dimethylformamide (DMF) at room temperature (left) and spectro-electrochemistry in acetonitrile of the same compound exhibiting the progressive increase of the ligand-based radical bands with increasing negative potential.

The rather low values of the redox potentials are of importance for the stability of the multi-electron species generated and thus for their possible applications as devices presenting multiple electronic levels. Spectro-electrochemical experiments revealed that the reductions take place on the coordinated ligands in all cases; no reduction of the metal centers was observed in the accessible potential range. Interestingly, the Co_4^{II} species exhibited an amazing regularity in the disposition of the reduction waves, as well as a remarkable stability and reversibility towards reduction (Figure 25). In contrast, all non- Co_4^{II} arrays (with $M^{II} = Fe^{II}$, Ru^{II}, Os^{II}, Zn^{II}, and Mn^{II}) were found to be more sensitive towards decomposition and to produce more complex reduction schemes. Obviously, the nature of the M^{II} ions in grid-like complexes plays a very important role for mediating electronic communication within the metallo-organic supramolecular array.

In order to understand the reasons for the very peculiar behaviour of the Co_4^{II} complexes, a theoretical model involving strongly-correlated electrons was developed. The model illustrates the interplay between electron addition and intramolecular spin coupling of localized magnetic moments at the Co^{II}-cornerstones and delocalized reduction electrons in ligand orbitals. As expected, the extra electrons injected into bridging ligand orbitals introduce a ferromagnetic (FE) spin correlation between the Co^{II} metal ions. However, for certain numbers of reduction electrons (n=3 or 5), sufficiently strong Coloumb interactions can stabilize an unexpected high *spin ground state* of S_{tot}=7/2. This finding is explained by

the occurrence of the Nagaoka mechanism,^[48] in which, due to the Pauli principle, a missing or an excess electron on the ligands (relative to half-filling of the LUMO) can be delocalized maximally, if the "background" of the remaining electrons is completely spin polarized. Such a mechanism might open novel ways to molecular high-spin states by the bridging ligand based reduction of AF-coupled metal ions in multinuclear complexes.^[49]

7.2. Current Induced Tunneling Spectroscopy on Co₄L¹₄ (in collaboration with Prof. P. Müller, University of Erlangen, Germany)

The structural elucidation of the coordination characteristics of metal centers and coordination compounds in close contact to metallic surfaces has been described in chapter 4.2.C, but in order to approach and eventually to use the functionalities of molecular nanostructures in devices, the influence and eventual feed-back of the environment (here the surface) on the physical properties of the molecules has to be investigated in detail.

As a test case for the property-environment relationship, we have chosen the grid-like $[Co^{II}_{4}L^{1}_{4}](BF_{4})_{8}$ molecules, those peculiar electronic properties in solution have been described in detail before (chapter 7.1.). An acetonitrile solution of $[Co^{II}_{4}L^{1}_{4}]^{8+}$ molecules was sputtered onto freshly cleaved graphite substrates at room temperature, where isolated or 1D arrangements could be used in spectroscopic investigations (Figure 26). In the constant current STM-mode, the molecules appeared as bright uniform spots without an internal structure, whereby no direct evidence for the presence of the BF₄-anions could be obtained. Apparently, at room temperature the electrostatically bound BF₄-anions show at room temperature a too fast kinetics to be observed in the STM set-up used.



Figure 26. left) STM-images in the current distance mode of the 1D arrangements of the $[\operatorname{Co}^{II}_{4}(\mathbf{F})_{4}]^{8^{+}}$ arrays on graphite at room temperature; right) Series of I-V spectra of three aligned $[\operatorname{Co}^{II}_{4}(\mathbf{F})_{4}]^{8^{+}}$ supramolecules.

In order to address the internal electronic properties of the deposited $[Co^{II}_{4}F_{4}]^{8+}$ metal ion arrays, Scanning Tunneling spectroscopic (STS) techniques were applied. CITS is current imaging tunneling spectroscopy and has been developed to perform scanning tunneling spectroscopy (STS) on a sample surface.^{[50][51]} The current voltage characteristics are recorded at every pixel position of the topography map. The current contrast changes significantly when at certain bias voltages new molecular energy levels come into play, thus enhancing the information obtained from topography alone. It was possible to extract a spatially resolved C_4 symmetric four-lobe feature of increased tunneling probabilities within the [2x2] metal ion array from the obtained tunneling I-V data. Comparison of the spectroscopic data with structural data obtained for the same molecule $[Co^{II}_4F_4](BF_4)_8$ from bulk X-ray diffraction studies, rendered the conclusion that the positions of the increased tunneling probabilities coincide with the positions of the Co^{II} cornerstone ions in the metal ion array (Figure 27).^[52]



Figure 27. (a) DFT calculation of electron density maps of 0.8 eV HOMO plotted together with the crystal structure, (b) and (c) simultaneously recorded topography and CITS image of $[\text{Co}^{II}_{4}\mathbf{F}_{4}]^{8+}$ metal ion array, and (d) 3d picture of a section (circle mark) of CITS image displaying increased tunnelling probability at the Co(II) cornerstones.

DFT calculations of electron density maps of 0.8 eV HOMO show that the molecular orbitals near the Fermi level are centred at the locations of the metal ions (Figure 27a).^[53] Comparison of STM topographic images (Figure 27 b) with single scan CITS current maps taken at $U_T = -400 \text{ mV}$ reveal a four-lobe structure of increased tunnelling probability (Figure 27 c; dark contrast) within the $[\text{Co}^{II}_4(\mathbf{F})_4]^{8+}$ metal ion array. The distance between the lobes is roughly 0.7 nm in accordance to the distance between neighbouring Co ions found in X-ray diffraction studies of the same molecule (Figure 27d).^[54] The weakest bonds within the [2x2] metal ion array, i.e. the supramolecular Co-N bonds, is situated, as shown in the DFT calculations, very close to the Fermi level of the molecule. It can be concluded that CITS-STS opens a spectroscopic possibility of direct addressing of metal ions within a supramolecule by their tunnelling characteristics through molecular orbitals with strong contributions of the internal coordinative bonds.

It is to be expect that single-molecule spectroscopic techniques such as CITS together with other molecule-dealing STM-based surface manipulations (e.g. molecular Kondo measurements),^[55] mechanically induced break junction techniques ^[56] and new approaches towards nano-magnetism (e.g. spin-polarized STM),^[57] might constitute part of the future tool kit needed to put into reality directed construction and controlled manipulation of fully electronically functional interfaces.

8. Current research8.1. List of Research Grants and Contracts

1. "*Molecular Magnetism*"

Priority Program of the "Deutsche Forschungsgemeinschaft (DFG)"

Coordinator:	Prof. H. Krüger, TU Kaiserslautern
Project (Ruben):	"Magnetic Lanthanide Carbamates"
Period:	01.03.2002 - 01.03. 2004

2. "MOLMEM- Highly-Integrated Molecular Electronic Elements"

Joint project of the **"Bundesministerium für Bildung und Forschung"** in collaboration with the Infineon AG and the Research Centres Jülich and Karlsruhe

Coordinator: Dr. M. Mayor; INT Karlsruhe

Project (Ruben): "Single-Molecule Transport Measurements of Transition Metal Complexes"

Period: 01.05. 2002 – 30.10.2005

3. *"FUN-SMARTs - Assembly and Manipulation of Functional Supramolecular Nano-Architectures at Surfaces*"

EUROCORE-SONS-Program of the **"European Science Foundation"**

Coordinator:	Dr. M. Ruben; INT Karlsruhe
Period:	01.12. 2003 - 30.11.2006
total volume:	1,6 Mill. €

4. "BIOMACH: Molecular Machines – Design and Nano-Scale Handling of Biological Antetypes and Artificial Mimics"

STREP im IV-Framework Programm der "European Commission"

Coordinator:	Dr. M. Ruben; INT Karlsruhe
Period:	01.03. 2004 - 30.03.2007
total volume:	2,3 Mill. €

5. "Kondo Molecules and Molecular Spintronics"

Project supported by the "Deutsche Forschungsgemeinschaft (DFG)"Coordinators:Dr. M. Ruben, INT Karlsruhe and Prof. H. Weber, University of ErlangenPeriod:01.04.2005 – 31.03. 2007total volume:two ½ Post-doc positions + 15 K€ consumables

8.2. Current Research Projects

8.2.1. Kondo-Molecules and Molecular Spintronics (Project supported by the Deutsche Forschungsgemeinschaft)

The interaction of metals and molecules is a field which has recently attracted increasing attention due to the appearance of molecular electronics. Thereby, two different electronic regimes are combined: (i) the electrons of a simple metal (e.g. gold) can be considered as non-interacting quasiparticles resulting in a quasi-continuous description of the density of states (DOS) at low temperatures, whereas (ii) the electrons in a molecule are commonly highly correlated and show discrete electronic levels.

In this project, we will create and investigate systems where a molecule on the surface induces electron correlations in the metal by controlled electron-metal interactions. In particular, the emergence of Kondo phenomena (or Abrikosov-Suhl resonances) in the metallic electron system by immobilization of spin-bearing coordination compounds (Ln and Co compounds) on (**A**) thin surfaces or between (**B**) nano-structured electrodes will be studied. Thereby, the main observable parameter will be (i) in the case of surfaces: the temperature and field dependence of the resistivity of a thin metal film (ii) in the case of nanostructured electrodes the I/V dependence of a current passing through the spin-bearing molecule (Figure 28).

A)		В)
spin scattering	double decker molecule	spin bearing molecule

Figure 28. Sketch of the two configurations where the Kondo effect is expected: left: (A) molecule on top of a gold film, right: (B) molecule contacted to two electrodes in a break junction setup.

The requirements of the molecules are delicate: on one hand, the free spin must survive when the molecule is in contact with the surface or the electrodes and on the other hand, the electronic coupling between the free spin and the conduction electrons must be sufficiently strong to make Kondo scattering efficient (and to keep the Kondo temperature in a convenient temperature range).

8.2.2. Shaping the Interface - Binary Metal Arrays (Fun-Smarts project supported by the European Science Foundation)

The design of low-dimensional molecule-based magnetic systems has become an attractive topic within the broad field magnetism. One of the advantages of this strategy is to the ability to include approaches from different research areas ranging from surface science to surpramolecular chemistry in order to fabricate surface-supported magnetic molecular architectures. The flexibility in the rational design of such a metal ion-organic ligand approach may allow the controlled introduction of different magnetic centres into the surface-supported architectures.

Based on the tetragonal network structures with Fe₂-dimers at the crossing points obtained using linear *bis*-carboxylic acid ligands in the surface-assisted self-assembly, as described in chapter 4.2.C, we would like to extend this strategy to build in a second metal ion rendering binary metal ion structures. Towards this goal, we have synthesized the 4,4'''-(1-dicarboxyphenyl)-substituted bipyrimidine system (**DCP**).^[59] We plan to coordinate two different metal ions by a two step surface-assisted coordination procedure: The first coordination step should introduce one metal as dimers at the crossing points of the formed network. The second metal will be subsequently introduced at the preorganized pyrimidine N-donor atoms by N-metal bond formation (Figure 29).



Figure 29. Representation of the generation of extended binary metal arrays using principles of surface-assisted coordination chemistry.

8.2.3. Moving the Nanoworld (BIOMACH project within the FP-IV-program of the European Commission)

In its simplest definition, a nanomotor is a nanoscale structure capable of converting energy to work. Approaching the nanometer regime requires new paradigms and concepts for fueling and controlling that pivotal conversion. The obvious challenge is to develop nanomachines whose motion can be externally controlled and that can be refueled continuously. In an explorative study, we would like, based on prevolously obtained results of our network, to investigate new concepts of powering the nanoworld.

Thus, a molecular device is envisioned in order to modulate a mechanical molecular translational motion triggered by light through a well described cis-trans isomerisation reaction of a 4,4'- dicarboxy-azobenzene. This isomerization reaction is well described in solution and bulk material,^[60] however has not yet been observed under near-surface conditions.



Figure 30. Sublimation of 4,4'-dicarboxy-azobenzene onto the surface and STMimages of the observed monolayer formation exhibiting the molecule as its *trans*-isomer at the Cu(100) surface.

In order to demonstrate our concept of near-surface isomerization, the compound 4,4'dicarboxy-azobenzene was synthesized following a modified protocol from the literature,^[56] The compound was then sublimed within a UHV-chamber onto a Cu(100) surface, where the monolayer formation was followed by STM techniques (Figure 30). Exclusively trans-domain formation could be observed. The conclusive irradiation experiments are in preparation in collaboration with MPI-FKF and scheduled for the next milestone.

9. Conclusion

(Supra)molecular nanostructures were self-assembled from organic and ionic bricks and their physical properties studied as ensembles of molecules as well at the single-molecule level.

1. The self-assembly of functional molecular nanostructures was investigated at different hierarchical levels in solution, in the solid state and at surfaces. Thereby, the hydrogen bonding concept could be transferred from solution and solid state to surface condition without further alterations, while using *in situ* metal ion coordination at surfaces caused deviations from the known conceptual base.

2. In solution and in the solid state, the physical properties of bulk self-assembled molecular nanostructures of different types were investigated considering especially optical, magnetic and electronic functionalities. Optically, reversible pH-dependent light absorption behaviour was found in solution. Magnetically, intramolecular exchange coupling and spin transition behaviour was found in the solid state for tetranuclear transition metal ion arrays, while quantum tunnelling of the strongly anisotropic magnetic moment could be observed in crystals of mononuclear Lanthanide double decker compounds (so called Single-Ion Molecular Magnets, SIMMs). Electronically, all investigated metal ion arrays show in solution characteristics typical for multilevel electronic devices.

3. The deposition of molecular nanostructures preformed in solution onto graphite surfaces enabled the STM imaging of the intramolecular tunnelling probabilities through one single molecule. However, the electronic properties found for the supramolecules deposited onto the surface mirror the electronic properties of the substrate-molecule couple under the boundary conditions of the experiment (STM set-up) rather than the electronic properties of an ensemble of the same molecules as found in the bulk or in solution. This result illustrates the importance of environmental feed-back processes on the physical properties of molecules during their implementation into devices.

All (supra)molecular systems described in this work provide approaches to the development of (supra)molecular electro-, spintro-, and optotronics on the base of the functional properties of ensembles of molecules as well as of a single molecule.

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A. Appendix

A.1. Publication List (publications attached to the habilitation, p. 56, in blue)

1. "Carbon Dioxide and Metal Centres: From Reactions Inspired by Nature to Reactions in Compressed Carbon Dioxide as Solvent"

D. Walther, M. Ruben, S. Rau; Coord. Chem. Reviews 1999, 67-100.

2. "Novel Polypyridyl Ruthenium Complexes Containing Oxalamidines as Ligands"

M. Ruben, S. Rau, A. Skirl, K. Krause, H. Görls, D. Walther, J. G. Vos, *Inorg. Chim. Acta* 2000, 206-214.

3. "A Benzimidazole Containing Ruthenium (II) Complex Acting as a Cation Driven Molecular Switch"

S. Rau, T. Büttner, C. Temme, M. Ruben, H. Görls, D. Walther, M. Duati, S. Fanni, J. G. Vos, *Inorg. Chem.* 2000, 1621-1624.

4. "Fixation of Carbon Dioxide by Oxalic Amidinato Magnesium Complexes: Structures and Reactions of Trimetallic Magnesium Carbamato and Related Complexes"

M. Ruben, D. Walther, R. Knake, H. Görls, R. Beckert, *Eur. J. Inorg. Chem.* **2000**, 1055-1060.

5. "Bis(R-bipyridyl)Ruthenium Bibenzimidazole complexes (R = H, Me or Bu^t): Supramolecular Arrangement via Hydrogen Bond, Photo- and Electro-Chemical Properties and Reactivity towards Carbon Dioxide"

S. Rau, **M. Ruben**, T. Büttner, C. Temme, S. Dautz, H. Görls, M. Rudolph, D. Walther, A. Brodkorb, M. Ducati, C. O'Connor, J. G. Vos, *Dalton Trans.* **2000**, 3649-3657.

6. "Spin Crossover in a Supramolecular Fe_4^{II} [2x2] Grid Triggered by Temperature, Pressure, and Light"

E. Breuning, **M. Ruben**, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegelius. K. Rissanen, *Angew. Chem. Int. Ed.* **2000**, 2504-2507.

7. "Multilevel Molecular Electronic Species: Electrochemical Reduction of a $[2\times 2]$ Co_4^{II} Grid-Type Complex by 11 Electrons in 10 Reversible Steps"

M. Ruben, E. Breuning, J.-P. Giesselbrecht, J.-M. Lehn, Angew. Chem. Int. Ed. 2000, 4139-4142.

8. *"Functional Supramolecular Devices:* $[M_4^{II}L_4]^{8+}$ -Grid-Typ Complexes as Multilevel Molecular Electronic Species "

M. Ruben, E. Breuning, M. Barboiu, J.-M. Lehn, J.- P. Giesselbrecht, *Chem. Eur. J.*, **2003**, *9*, 291-299.

9. "Synthesis of Ionisable [2x2] Grid-type Metallo Arrays and Reversible Protonic Modulation of the Optical Properties of the $[Co_4L_4]^{8+}$ Species"

M. Ruben, J.-M. Lehn, G. Vaughan, Chem. Comm. 2003, 1338-1339.

10. "Supramolecular Spintronic Devices: Spin Transitions and Magneto-Structural Correlations in $[Fe_4^{II}L_4]^{8+}$ [2×2]-Grid-Type Complexes"

M. Ruben, E. Breuning, J.-M. Lehn, V. Ksenofontov, F. Renz, P. Gütlich, G. Vaughan, *Chem. Eur. J.*, 2003, 9, 4422-4429.

11. "Magneto-Structural Correlations in Self-Assembled Spin-Transition Nano-Architectures of the $[Fe_4^{II}L_4]^{n+}$ [2×2]-Grid-Type"

M. Ruben, E. Breuning, J.-M. Lehn, V. Ksenofontov, F. Renz, P. Gütlich, G. Vaughan, *J. Magn. Magn. Mat.*, **2004**, 272-276, e715-e717.

12. *"Grid-Type Metal Ion Arrays: Functional Metallosupramolecular Devices"*

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A.2. Curriculum Vitae Mario Ruben

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A.2. Publications (related to this work)

Coordination on Surfaces

Squaring the Interface: "Surface-Assisted" Coordination Chemistry

Mario Ruben*

Keywords:

coordination chemistry · grid complexes · scanning probe microscopy · self-assembly

he potential of highly ordered metalion arrays to be used in molecular information storage and processing devices was recently highlighted.^[1] Among the set of possible architectures, twodimensional (2D) gridlike arrays of ionbased switchable elements have attracted particular interest due to their structural similarity to components of some of the newest information processing concepts.^[2,3] So far, the investigation of metal-ion arrays within the nanometer regime has comprised the following steps: the synthesis of the ligand molecules, the self-assembly into supramolecular entities, and the controlled deposition or anchoring of the supramolecules on or at surfaces (Figure 1, left), where the metal-ion arrays can be addressed by state-of-the-art singlemolecule techniques (generally AFMand STM-based).^[4] However, this sequence of synthesis, self-assembly, and deposition is not merely a scientifically necessity, since it also reflects, at least partially, the historic background of an evolving interdisciplinary collaboration of scientific groups anchored in chemistry and physics.

A conceptually alternative route towards nanosized metal-ion arrays on surfaces was developed recently (Figure 1, right). This straightforward selfassembly protocol is based on the nearsurface metal-ion coordination of simple ligand systems.^[5,7] Using such approach,

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Figure 1. Schematic representation of two approaches for the construction of molecular structures on surfaces. Left: the sequence of synthesis, self-assembly, and deposition. Right: surfaceassisted self-assembly.

the groups led by K. Kern, J. V. Barth, and N. Lin at the Max-Planck-Institut für Festkörperforschung in Stuttgart and at the École Polytechnique Fédérale in Lausanne generated a variety of infinite metal-ion arrays just by controlling the codeposition parameters for organic dicarboxylic acid derivatives such as terephthalic acid and iron(0) atoms on Cu(100) surfaces under ultra-high-vacuum (UHV) conditions.^[5]

In the first step the organic ligand was deposited by organic molecular beam epitaxy (OMBE) onto the Cu-(100) surface. Subsequently, the metal atoms were deposited on top of the formed (and more or less complete) organic monolayer by electron beam evaporation. After a short annealing period (5 min at T=450 K), during which self-assembly was initiated by the increased mobility of the molecular and ionic components on the surface, well-ordered regular structures emerged readily in domains of up to 50 nm in size (Figure 2).

The rectangular molecular assemblies shown were obtained on the copper(100) surface at an Fe/ligand ratio

of about 0.5:1. Structurally, they consist of dimeric Fe_2 nodes connected by an organic backbone of orthogonally arranged ligand linkers to form an infinite



Figure 2. a) STM image showing the 2D topography of the extended gridlike Fe-ligand network; b) high-resolution image of the same network indicating the positions of the organic ligands backbone (Fe atoms of the interconnecting Fe₂ nodes are represented as blue spheres).^[5]

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network. The observed Fe pairs in the cross positions of the network deserve some attention due to their coordination characteristics: The two Fe centers are surrounded by two sets of two differently coordinating carboxylate groups; two of these are in a monodentate μ^2 bridging mode and two in an apparently bidentate chelating mode (Figure 2b and Figure 3, MOCN-II). Overall, the coordination geometry of each of metal center is square-planar. However, since the resolution limits of the present STM data prevent clear distinction between the mono- and bidentate coordination modes of the two chelating carboxylate groups, the exact determination of the coordination geometry is not possible in all cases.

The Fe–O bond lengths estimated from the STM data are close to that in bulk materials (d(Fe-O) = 1.9-2.3 Å),^[6] and the metal-metal distance d(Fe-Fe)is about 5 Å. However, the observation of sometimes elongated Fe-O bonds might be indicative of a situation, in which both ligand and metal centers are in close contact with the Cu(100) surface, which is then apparently acting a template. Thus, the underlying crystal lattice along with the conduction band of the substrate might interfere structurally as well as electronically in the final positioning of the involved metal atoms relative to the organic ligands.

With regards to the ligands, nearedge X-ray adsorption fine structure (NEXAFS) studies have revealed that the ligand molecules are adsorbed with their phenyl rings almost parallel to the Cu(100) surface plane.^[5] This kind of metal-ligand contact is reminiscent of the donor-acceptor interaction of neutral arene rings and electron-rich metal centers, a classical coordination motif in coordination chemistry.^[8]

Since a strong interaction with the surface cannot be excluded, at least not at this stage, the discussion of the electronic properties (e.g. oxidation and spin states) of the coordination network components must involve rather unusual contributions like the electronic coupling of the metal centers to the substrate or possible counterbalancing of complex charges by mirror charges within the upper layers of the substrate. Only additional experimental data will clarify the picture and possibly support alternative interpretations such as the formation of neutral precomplexes composed of the ligand and the Cu(100) mentioned by the same authors in two previous articles.^[9]

However, considering the distinct M_2L_4 stoichiometry of the dimeric Fe₂ nodes, it seems reasonable to assume that the principle of electroneutrality also persists under near-surface conditions. This assumption would lead to the definition of two Fe^{II} ions surrounded by four deprotonated, negatively charged carboxylate groups. The formation of such electroneutral (4 + 4/) units will depend critically on the course of the deprotonation reaction, during which four protons are reduced to hydrogen molecules and simultaneously the two iron(0) centers are oxidized. The gaseous hydrogen could easily migrate into the UHV environment, thus driving the redox reaction to completion. The local

electroneutrality around the dimeric Fe_2 nodes may also explain the high thermal stability of the 2D networks (up to 500 K); however, they are not stable to ambient gases. Obviously, further investigations concerning the electronic nature of the metal centers and ligands are necessary, and the results will be awaited with great interest.^[5]

How the variation of the deposition parameters (e.g. ligand-to-metal ratio, annealing temperature) influences the formation of a set of different selfassembled modular structures was reported in more detail by the same authors in two further articles.^[7] Depending on the Fe⁰ concentration, different network structures were formed from the same organic ligand, terephthalic acid, on the Cu(100) surface: these ranged from isolated mononuclear "cloverleaf" complexes to infinite 2D "ladder" coordination polymers to the



Figure 3. Structural formulas and STM images of the different network motifs (cloverleaf, MOCN-I-III) obtained on the Cu(100) surfaces by variation of the Fe/L ratio and the annealing temperature.^[7a]

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Highlights

previously described gridlike 2D coordination polymers (Figure 3).^[7a]

At lower Fe concentrations the connectivity of the molecular network is achieved in part by additional hydrogen bonds between the aromatic H atoms of the phenyl ring and the oxygen atoms of the carboxylate groups. At higher Fe concentrations the formation of the dimeric Fe2-based structures predominates. In general, it was found that the amount of iron used must slightly exceed the theoretical value of the structural motif formed. This effect, which is even more pronounced at higher annealing temperatures, is attributed to the loss of Fe atoms/ions in collateral surface reactions such as decoration of substrate steps, formation of Fe islands, and Fe-Cu intermixing processes.

The further elucidation of the coordination characteristics of metal centers in close contact with metal surfaces (coordination number, redox and spin state, metal-metal interactions, mirror charges, etc.) might mark the beginning of a new branch of "surface-assisted" metal coordination chemistry (maybe as an extension of the more bulk- and solution-based, conventional "Wernertype"^[10] coordination chemistry). Together with other STM-based singlemolecule surface manipulations (e.g. C-C bond formation, generation of surface chirality)^[11,12] and new approaches towards nanomagnetism (e.g. spin-polarized STM),^[13] such surface-assisted coordination chemistry might constitute part of the future tool kit needed for the construction and controlled manipulation of functional interfaces and operational surfaces

Furthermore, the well-defined nanopores in these networks can be loaded with suitable substrates (e.g. C_{60}),^[5] which might be of importance for the design of many surface-dominated processes like heterogeneous catalysis and selective gas adsorption, and even for

the generation of optical metamaterials.^[14–16] Interestingly, the emergence of dimeric metal units is also strongly reminiscent of structural features observed around the catalytic centers of some types of enzymes.^[17]

It can be anticipated that the controlled design of functional surfaces by applying the principles of surface-assisted coordination chemistry not only opens new scientific perspectives but will also yield aesthetically appealing structures on surfaces that can be observed in real time.

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Reviews

Self-Assembly

Grid-Type Metal Ion Architectures: Functional Metallosupramolecular Arrays

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Recent advances in supramolecular coordination chemistry allow access to transition-metal complexes of grid-type architecture comprising two-dimensional arrays of metal ions connecting a set of organic ligands in a perpendicular arrangement to generate a multiple wiring network. General design principles for these structures involve the thermodynamically driven synthesis of complex discrete objects from numerous molecular components in a single overall operation. Such supramolecular metal ion arrays combine the properties of their constituent metal ions and ligands, showing unique optical, electrochemical, and magnetic behavior. These features present potential relevance for nanotechnology, particularly in the area of supramolecular devices for information storage and processing. Thus, a dense organization of addressable units is represented by an extended "grid-of-grids" arrangement, formed by interaction of grid-type arrays with solid surfaces.

1. Introduction

The drive to shrink electronic devices to the nano-level, has, in recent years, led to the design and investigation of molecular-scale components endowed with sensing, switching, logic, and information storage functions.^[1-3] Although the implementation of information processing with such devices faces hurdles in the development of logic architecture and intermolecular hook-up schemes,^[1] molecular data storage is subject to active interest, namely in view of the rapidly approaching upper limit in conventional magnetic data storage resulting from thermal erasure at the superparamagnetic limit. Species suitable for molecular data storage must 1) possess two or more physicochemically distinct states that can be conveniently switched by application of external triggers (e.g. thermodynamic parameters or electromagnetic fields) and 2) should be addressable and switchable within the nanometer regime. Toward this end, gridlike metal ion arrays, in which a set of metal ions is held in a regular network of organic ligands in a perpendicular arrangement (Figure 1), present several attractive features: 1) their redox, magnetic, and spin-state transitions are well-documented, 2) the welldefined two-dimensional (2D) arrangement of an exact number of metal ions resembles strongly the binary coded matrices and cross-bar architectures used in information



Figure 1. Molecular structures of several gridlike metal ion arrays that exhibit a regular network of perpendicular arranged organic ligands. $^{[4a,5a,6]}$

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storage and processing technology, and 3) they may be arranged into extended two-dimensional ensembles by deposi-

tion onto solid surfaces. The nuclearity and dimensionality of the gridlike metalloarrays are clearly based on the polytopic nature of the ligands and the ability of the metal to read and interpret the coordination options presented by the ligand in the most efficient way depending on its own coordination algorithm.

The two-dimensional (2D) grid motif was recently the architectural base of a molecular 64-bit logic and storage device.^[7a] The resulting architecture consists of two perpendicular sets of eight Pt wires (top and bottom). A bit of molecular memory (around 1000 molecules of an organic compound) is sandwiched at the crossing points between the higher and lower wire (Figure 2). The whole storage and switching units have an area of around 1 μ m² with a wire-to-wire distance of about 40 nm. Although, the working principles of such a device are still under discussion, it is possible to "write" and to "read" the information at different voltages.^[7b] Crossbar arrays based on nanowires may lead to addressable nanosystems.^[7c]

Further interest in gridlike molecular architectures might arise from an alternative encoding concept called "cellular

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Figure 2. A 64-bit molecular storage device. The crossed-wire structure of the memory shows the eight top and the eight bottom Pt wires (wire-to-wire distance ca. 40 nm).^[7a]



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Javier Rojo received his PhD degree under the supervision of Prof. J. C. Carretero at the University Autónoma, Madrid in 1995. He was a postdoctoral fellow with Prof. J.-M. Lehn at the Université Louis Pasteur in Strasbourg (1995–1998) and with Prof. L. W. McLaughlin at Boston College (1998– 1999). In January 2000, he joined the Carbohydrate Group at the Spanish Research Council (CSIC) in Seville where he is now a permanent research scientist. In 2001 he was awarded a "Ramón y Cajal" fellowship. His research interests include supramolecular chemistry and molecular recognition of carbohydrates.

automata", in which molecules do not act as current switches but as structured charge containers.^[8] Envisaged first for quantum dots, binary information is encoded in the charge configuration of a cell composed of a small number of differently charged redox centers, which are electronically communicating within the entity but are not completely delocalized (Robin-Day type II) (Figure 3). Each cell has two degenerate ground states, which can be interconverted by an internal electron density redistribution (e.g. by the transfer of two or more electrons within the cell). The electrostatic interaction of two neighboring cells (arranged in one, two, or three dimensions) lifts the given degeneracy and results in "1" or "0" states. Remarkably, the intercellular information exchange is purely based on Coulomb interactions and involves no current flow. If such interaction can be realized, this approach may enable a general purpose computation.^[9]

From the standpoint of nanochemistry, the cells can comprise molecular or supramolecular entities. Multinuclear metal ion coordination arrays present particularly attractive features in this respect. The main interest arises from a self-organization strategy involving appropriate ligands and metal ions, which allows close control of the structural and physical properties of the resulting assemblies. Recent progress in molecular self-assembly processes has opened the way to generate extended supramolecular structures by spontaneous, but controlled build-up from their components.^[3,10] Such self-fabrication techniques are of intense interest, due to the possibility of bypassing or complementing tedious (top-down) nanofabrication and nanomanipulation procedures.^[3]



Mario Ruben studied Chemistry in Germany and Spain. He obtained his PhD in 1998 at the University of Jena, Germany, under the supervision of Prof. D. Walther. A DAAD postdoctoral fellowship brought him to Prof. J.-M. Lehn's research group at the ISIS-ULP in Strasbourg, France, where he worked on supramolecular coordination compounds. Since 2001 he is a group leader at the Institute of Nanotechnology, Karlsruhe. His research interests involve functional molecule-based systems and their implementation into operational nanosystems. He is the

coordinator of several European networks (FUN-SMARTs; BIOMACH) dealing with molecular nanodevices.



Lindsay Uppadine obtained an M.Chem. degree from the University of Oxford in 1997. She stayed at Oxford for her doctoral research in the group of Prof. P. D. Beer, where she worked in the field of anion and ion pair recognition. She is currently a CNRS Postdoctoral Fellow in Prof. J.-M. Lehn's research group at the Université Louis Pasteur, Strasbourg.



Figure 3. Schematic representation and working principle of "cellular automata". a) Coulomb repulsion keeps the electron density (dark) at antipodal sites resulting in the degenerate "1" and "0" state. b) A wire of "cellular automata" can be formed by a one-dimensional arrangement of cells. The intercellular Coulomb interactions force all units into the same state. c) Working principle of a majority logic gate consisting of three inputs (A, B, C) which converge to an output (Maj(A;B;C;)).^[8]

2. General Concepts

Metallosupramolecular chemistry is an actively pursued area of research in supramolecular chemistry, which uses the interaction between organic ligands and metal ions to construct multicomponent and multinuclear coordination entities in the nanometer regime. It thus allows one to combine the properties of metal ions with those of the organic ligands in a defined structure with the potential for the generation of new properties not found in the individual components. A rich variety of metallosupramolecular architectures has been synthesized in the last few years, including helicates, rotaxanes, catenanes, and cages.^[10]

The design of gridlike metal ion arrays rests on the directing coordination instructions, which are based on the coordination geometry of the metal ion and the structure of the ligand's coordination sites. It requires perpendicular arrangements of the ligand planes at each metal center. Given such a coordination environment around the metal centers, the linear and rigid extension of the ligand system from mono- to multitopicity will automatically lead to a gridlike two-dimensional coordination network with regularly arrayed metal ions. According to this general "leitmotif", metal ion arrays can be prepared in principle by careful prearrangement of the subunits using any set of metal ions and organic ligands possessing compatible coordination features. This requires ligands containing either bidentate or tridentate binding subunits in combination with metal ions possessing tetrahedral or octahedral (and in some cases bipyramidal) coordination geometry, respectively (Figure 4).

Two-dimensional gridlike coordination complexes lead to a well-defined 2D arrangement of an exact number of metal ions. A number of square $[n \times n]$ and rectangular $[n \times m]$ grids with $n,m \le 4$ has been obtained for metal ions with tetrahedral as well as octahedral (and sometimes square-bipyramidal) coordination geometry (vide infra). Thus, a ligand with *n* coordination subunits is capable of forming a homoleptic $[n \times n]$ metalloarray, composed of 2n organic ligands and n^2 metal ions with an overall $[M_{(n^2)}L_{(2n)}]$ stoichiometry.^[11] Mixtures of different ligands containing unequal numbers of coordination subunits *n* and *m* may, in addition to square arrays, yield



Figure 4. General principles and building blocks for perpendicular arrangement of the ligand L about a metal center M. a) $[M(L)_2]$ units are formed with monotopic ligands (n=1); b) gridlike metal ion arrays $[M_4(L)_4]$ are formed with multitopic ligands (here n=2). Coordination geometry of the metal ions: \bigcirc tetrahedral, \bullet octahedral.

rectangular structures $[M_{(n\times m)}L_{(n+m)}]$ with a total of (n + m) organic ligands and $(n \times m)$ metal ions. In incomplete gridlike coordination compounds, the available coordination sites are not fully occupied thus generating several (p) subsets of $[n \times n]$ or $[n \times m]$ arrays within the same coordination compound (Figure 5).



Figure 5. Different types of grid-type metal ion arrays: a) squares $[n \times n]$, b) rectangles $[n \times m]$, and c) incomplete architectures $[p \times [n \times m]]$.

In designing such metal ion arrays, the choice of organic ligands follows the coordination chemistry of the metal ions to be incorporated. In most cases, the coordination number of the metal ion is 4 or 6, with tetrahedral or octahedral coordination geometries. Appropriate design of the systems requires the choice of a ligand that presents an adequate number of binding sites in the coordination subunit to satisfy the coordination sphere of the metal ion. Most of the ligands used for the construction of grids, so far, are listed in Figure 6.

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Figure 6. Ligands 1–20 employed in the self-assembly of gridlike metal ion arrays.

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Those based on nitrogen donor ligands (such as bipyridine or terpyridine) are the most common, but ligands with sulfurand oxo-bridging subunits have also been used.

Although some early examples can be identified,^[12] gridtype architectures have only recently experienced active and coherent development and are mainly based on tetrahedrally and octahedrally coordinated metal complexes of azaaromatic ligands containing bidentate or tridentate subunits.^[4-6, 13-26a]

In general, the matching information encoded in both the metal ions (nature, number, and disposition of electronic orbitals, charge, etc.) and in the organic ligands (number and nature of the donor atoms and the geometrical disposition, molecular conformations, rigidity, etc.) is interpreted during the self-assembly process and steers it to a mutually acceptable 2D architecture. All ligands shown in Figure 6 are chelating ligands, as their increased preorganization and stronger binding may result in cooperative effects during the self-assembly process. Furthermore, all these ligands contain rigid aromatic ring systems (mostly pyridine groups), which yield kinetically labile intermediates as well as thermodynamically stable end products with many M^I, M^{II}, and some M^{III} ions. The rigidity of these aromatic ring systems and their ability to participate in π - π interactions are further stabilizing factors for the gridlike array formation.

Energetically, the formation of the grid-motif competes with the generation of other types of structures (e.g. finite and infinite coordination oligo- and polymers). The defined gridlike array is favored enthalpically, since it maximizes the coordination site occupancy, as well as entropically, giving rise to the largest number of discrete entities. Furthermore, intercomponent interactions (π - π stacking, H-bonding) may contribute to achieving the correct alignment of all bricks.

Thus, the generation of grid-type arrays depends on three factors, which influence the self-assembly of metallosupramolecular architectures in general: 1) a robust set of coordination instructions that impose the correct (perpendicular) geometry and drive the process on the basis of the principle of maximal, optimally full, binding site occupancy;^[27] 2) internal orienting effects, such as steric factors that hinder the formation of undesired entities, or stabilizing interactions (e.g. stacking) that channel the assembly to the desired product; 3) external factors such as binding of solvent molecule(s), counterion(s), or other species present in the environment. In addition to the energetic parameters, entropy favors the formation of the largest number of products.

These different factors promote the formation of the discrete, "closed" grid architectures over polymetallic entities, which might in principle also form. In addition to entropy considerations, such polymers are disfavored energetically by the remaining free sites at the ends ("sticky ends") of the polymer chains, as well as by the marked steric crowding that would occur between ligands bound to vicinal sites.

In addition to the assembly parameters mentioned so far, ligand substitutions provide the opportunity to fine-tune inherent functional properties (e.g. electronic, optical, magnetic, etc.). It is also possible to introduce a second coordination site on the ligand backbone, to enable multistep hierarchical organization of the self-assembly process.

It is crucial to note that the binding of metal ions to polyazaheterocyclic ligands involves major structural and energetical changes. Indeed, α, α' -connected aromatic azaheterocycles present a transoid orientation of the nitrogen sites around the $C(\alpha)$ – $C(\alpha')$ bond, which is more favorable than the *cisoid* orientation required for metal ion coordination by about 25-30 kJ mol⁻¹.^[26b] This feature has been implemented for designing heterocyclic "folding codons", in particular "helicity codons" that determine the shape of molecular strands.^[26c] Thus, the free uncoordinated ligands based on α, α' -linked bipyridine or terpyridine moieties adopt a *trans*oid conformation of the nitrogen atoms relative to the

large amounts of conformational energy, which must be overcompensated by the interaction energy resulting from metal ion binding (Figure 7). For example, the change from an all-transoid to an all-cisoid form of the bis(terpyridine) ligand **5a** costs about 100 kJ mol^{-1} per ligand (i.e. 400 kJ mol^{-1} in total on formation of the corresponding $[2 \times 2]$ M₄ grid complex), and energy costs in excess of 1500 kJ mol⁻¹ are attained on the self-assembly of the $[4 \times 4]$ Pb^{II}₁₆ grid (see Section 3.3)!

interheterocyclic C-C bond. The conversion of the alltransoid conformer into the energetically disfavored all-

cisoid one upon metal complexation occurs at the cost of

Figure 7. For the complete complexation, all binding sites of polyazaheterocyclic ligands must be present in the cisoid conformation. The required change in ligand conformation from all-transoid (uncoordinated ligand) to all-cisoid (coordinated ligand) is shown, for example, for the ligands 1a (left) and 5a (right).

In conclusion, the formation of gridlike architectures involves a subtle interplay of steric, enthalpic, and entropic effects, concerning both the ligand and the metal binding features. Thus, different metal ions and ligands can lead to the formation of different supramolecular coordination entities and self-assembly may result in several stable products partitioned under thermodynamic equilibrium. Only carefully designed systems of appropriate ligands and metal ions will lead to the self-assembly of gridlike metal ion arrays in a "programmed" fashion.

3. Grid-Type Metal Ion Arrays

3.1. [2×2] Metal Ion Arrays

The first report on the formation of $[2 \times 2]$ metal ion arrays based on tetrahedral coordination geometry involved



four *ditopic* ligands **1a** of the bis(pyridyl)pyridazine type arranged around four metal ions.^[13a] Both Cu_4^I and Ag_4^I ion arrays (Figure 8) assemble spontaneously when the metal and ligand components are mixed in a 1:1 stoichiometry.^[13]



Figure 8. Schematic representation of the self-assembly process of ligand **1 a** and tetrahedrally coordinating metal ions ($M = Ag^{l}$, Cu^{l}) leading to a [2×2] grid-type metalloarray [M_{4}^{l} (**1 a**)₄]⁴⁺.

The X-ray structure analysis of the $[Cu_4^I(\mathbf{1a})_4]^{4+}$ complex reveals a distorted rhombus with an almost planar arrangement of the metal ions in a distorted tetrahedral environment. The average Cu^I–N and Ag^I–N distances are about 2.0 and 2.3 Å, respectively, while the Cu^I–Cu^I distance is 3.57 Å and the Cu^I-Cu^I-Cu^I angles are approximately 79° and 101°.

An unusual self-assembled $[2 \times 2]$ metal ion array deviating from the general M₄L₄ stoichiometry was obtained by using the bis(phenanthroline)-based ligand **2c** and Cu¹ ions. In addition to the expected $[Cu_4^I(2c)_4]^{4+}$ scaffold, two additional, uncoordinated "guest" ligands **2c** were sandwiched in the upper and in the lower groove of the complex by multiple C-H-N and π - π interactions.^[14]

A $[2 \times 2]$ Cu₄^{II}L₄ metal ion array was obtained with the flexible ligand **3**; the two different ligand moieties are twisted by almost exactly 90° thus arranging the metal ions in a square-like fashion.^[15]

Ligand systems containing terpyridine-like coordination sites enable the arrangement of octahedrally coordinating metal ions: a number of late first- and second-row transition metal ions (e.g. Mn^{II} , Co^{II} , Fe^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II}) as well as some main group metal ions (e.g. Pb^{II}) have been introduced into gridlike arrays.^[4,6,16–17,24] The range of transition metals that can coordinate to ligand systems such as **5a** gives access to a wide variety of optical, electrochemical, photophysical, and magnetic properties. Furthermore, by using ligand system **5a**, these properties can be tuned by the choice of the different substituents R^1 , R^2 , and R^3 (Figure 9).

Ligand **5a** yields gridlike arrays of the metal ions with inter-metal distances of 6.0–6.5 Å between neighboring ions. The exchange of the central μ -pyrimidine group for an imidazole (**4**) or a pyrazole bridge (**6**) leads to only slightly shortened ion–ion distances.^[18,19] However, the use of oxoand sulfur-bridged ligands **9–12** (after deprotonation) resulted in more closely spaced metal ions with intermetallic distances of between 4.0 and 4.6 Å^[20–22] (e.g. 4.04 Å in the phenoxobridged metalloarray [Cu^{II}₄(**10**)₄]⁴⁺).



Figure 9. Schematic representation of the self-assembly of a $[2 \times 2]$ metal ion array from bis(terpyridine) ligands **5** a and octahedrally coordinating metal ions.

Ligand systems $15^{[23]}$ and 16 bearing acidic protons open the way to ionizable $[2 \times 2]$ arrays, whose self-assembly and properties can be influenced by the protonation state of the ligand (see Section 5.1.1 and 5.1.4).^[24,25]

X-ray structure analyses show that anions can be located within the central cage of the $[2 \times 2]$ architecture, although this is not a prerequisite for the stability of the gridlike structure. On the other hand, a direct coordinative involvement of the anions was found in the $[2 \times 2]$ array $[Pb_4^{II}(5a)_4]^{8+}$, where a triflate anion is directly coordinated to each Pb^{II} center to fulfill the coordinative requirements of the large Pb^{II} ion.^[17]

The controlled introduction of different metal ions at specific locations in a grid array is of great interest, because of the cross-over properties which may result from the presence of different metal ions in the same entity. Mixed ion $[2 \times 2]$ grid structures were obtained by a sequential synthesis protocol involving stereochemical features, for example, homochiral assembly of the intermediate *R* or *S* "corner" type intermediates (Figure 10). This self-assembly reaction is reminiscent of the "Coupe de Roi", in which an achiral object is divided into two identical homochiral components.^[26a]



Figure 10. Self-assembly of a chiral heterobimetallic $[2 \times 2]$ grid from two cornerlike homochiral precursors (R + R) or (S + S).^[26a] The resulting grid is achiral in the homometallic case ("Coupe de Roi" process) and chiral in the heterobimetallic case.

A $[2 \times 2]$ grid-type structure with two pairs of unlike metal ions may exist as either the *anti* or *syn* topoisomer. It is not possible to select a priori which form is generated by simply mixing together the components; however, the *anti* topoisomer, with diagonally located identical ions, can be obtained selectively from a precursor complex consisting of two terpyridine-type ligands (e.g. **5a**) and a strongly coordinating metal ion such as \mathbf{Ru}^{II} or \mathbf{Os}^{II} (to give for example $[\mathbf{M}^{II}(\mathbf{5a})_2]$). They contain two vacant sites, which combine with a second metal ion \mathbf{M}'^{II} of lower coordinative binding strength to yield a heterometallic $[2 \times 2]$ complex as the thermodynamic product. The combination of homochiral fragments leads to a C_2 -symmetric array (e.g. $[\mathbf{M}_1^{II}\mathbf{M}'_{II}^{II}(\mathbf{5a})_4]$) in a process displaying sponta-

neous chiral discrimination.

Such a methodology represents sequential self-assembly and introduces different metal ions in order of increasing coordinative lability. Thus, a system containing three different metal ions was isolated from an equimolar mixture of Ru^{II} and Os^{II} "cornerlike" fragments $[Ru^{II}(\mathbf{5a})_2]$ and $[Os^{II}(\mathbf{5a})_2]$ in the presence of Fe^{II} ions.^[26a]

An even more sophisticated, three-tiered synthesis, incorporating regioselective, redox, and chiroselective features, was used to construct $[Co_2^{III}M_2^{II}(15a)_4]$ grid-type arrays $(M^{II} = Co^{II}, Zn^{II}, Fe^{II})$ based on the bis(hydrazone)

ligand-type **15a** ($\mathbf{R}^2 = \mathbf{H}$ and Me, $\mathbf{R}_{left}^2 \neq \mathbf{R}_{right}^2$) containing both ionizable and nonionizable compartments.^[24b] As a consequence, the oxidation state of cobalt could be modified according to the charge on the hydrazone moiety.

The first stereoselective synthesis of a $[2 \times 2]$ metal ion array was achieved by using the chiral ligand system **8**. The "chiralization" of the parent ligand **7** was carried out by the introduction of pinene moieties, which gives access to both ligand diastereomers of **8** (only one is shown in Figure 6). The reaction of **8** with Zn^{II} ions delivers the tetranuclear (all- Δ)[Zn₄((*R*,*R*)-**8**)₄]⁸⁺ metal ion array as the major product in good diastereomeric excess.^[28]

3.2. [3 × 3] Metal Ion Arrays

The first $[3 \times 3]$ M₉ grid, $[Ag_9^I(\mathbf{1b})_6](OTf)_9$, was obtained in high yield by self-assembly of six equivalents of the tritopic ligand **1b** with nine equivalents of silver(i) ions.^[29] Because of the deviation of the coordinated ligand planes from the ideal $\gamma = 90^\circ$, the resulting $[3 \times 3]$ Ag₉ array forms a trapezoid with corners (angle Ag-Ag-Ag) of about 73° and 107°.

The self-assembly of ligand system **5b** with octahedrally coordinating metal ions gave mainly incomplete metal ion arrays (see Section 3.5).^[30a] Some evidence for $[3 \times 3]$ gridlike species was only obtained by electroscpray mass spectrometry in solution for the very large metal ions such as Pb^{II} or Hg^{II}.^[30b] The behavior of **5b** may be ascribed to ligand bending due to the pinching of the binding subunit on coordination of transition-metal ions.^[30c] Conversely, large metal ions such as Pb^{II} or Hg^{II} cause less pinching so that the ligand is less distorted from a linear arrangement, resulting in a less strained grid architecture.

The aromatic polytopic ligands **13** readily self-assemble with Mn^{II} , Cu^{II} , and Zn^{II} salts to produce nonanuclear [3 × 3] gridlike metal ion structures, in which the ligands are arranged in parallel sets and alkoxide bridging groups are

located between adjacent metal ions. Spectroscopic and other evidence indicate that similar metalloarrays are produced with Ni^{II}, Co^{II}, and Fe^{III} ions, but not with Pb^{II} ions.^[5,21] The cationic structures consist of a homoleptic $[M_9(13)_6]^{n+}$ complex in a roughly planar square array with metal-metal distances of about 4.0–4.3 Å (Figure 11).



Figure 11. Self-assembly of the $[3 \times 3]$ metal ion array $[Mn_{9}^{II}(13)_{6}]^{6+}$, the molecular structure of which is depicted on the right.^[5a]

3.3. [4×4] Metal Ion Arrays

The largest square grid reported to date, $[Pb_{I6}^{II}(\mathbf{5c})_8](OTf)_{32}$, is formed quantitatively from eight equivalents of the tetratopic tridentate ligand $\mathbf{5c}$ and sixteen equivalents of Pb^{II} ions.^[17] This remarkable species arises from the self-organization of 24 precursors and involves the formation of 96 coordination bonds. This example highlights the power of metallosupramolecular chemistry to create complex structures through self-assembly in a single operation.^[6]

The final composition of the $[4 \times 4]$ Pb₁₆ array consists of 8 molecules of ligand **5c**, 16 lead(II) ions, 16 triflate ions, and 8 coordinated water molecules; 16 further triflate ions and 1 molecule of water are located in close proximity. The eight ligands **5c** are arranged into two perpendicularly disposed sets of four outer and four inner ligands, resulting in a set of four $[2 \times 2]$ subgrids rather than a regular $[4 \times 4]$ grid (Figure 12).

The four inner ligands allow considerable overlap between the aromatic groups situated in a face-to-face stacking arrangement, with an average π - π stacking distance of 3.62 Å corresponding to the van der Waals contacts. The Pb^{II} ions form a saddle arrangement with an average Pb–Pb distance of 6.3 Å and average inner angles of 89.5°. The coordination polyhedron around the Pb^{II} ions reveals a hemidirected structure, and all of them present a distorted seven-, eight- or nine-coordinate geometry. The open faces of the metal ions are oriented towards the interior of the four $[2 \times 2]$ Pb^{II}₄ grid subsets and are occupied by one or two of the 16 internally coordinated triflate ions. Some of the internal triflate ions act as bridges between two adjacent Pb^{II} ions. Thus, each square of four Pb^{II} ions is linked on three sides by bridging triflate ions, whereby the remaining coordination sites at the Pb^{II} ions are filled with nonbridging triflate ions or water molecules.

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Figure 12. A $[4 \times 4]$ grid assembled from eight tetratopic ligands **5 c** and sixteen Pb^{II} ions: structure (a) and ball-and-stick model (b) of the $[Pb_{16}^{II}(5c)_{8}]$ framework. The framework with coordinated triflate anions and water molecules as ball-and-stick model (c) and as space-filling model (d).^[6]

3.4. Rectangular $[n \times m]$ Metal Ion Arrays with $(n \neq m)$

The construction of a rectangular grid involves the selfassembly of two ligands with a different number of coordination sites. In this case, however, the reactions with different ligands could lead to mixed homo- and heteroleptic products, as described, for example, for the reaction of the di- and tritopic ligands **1a** and **1b**, respectively, and AgCF₃SO₄.^[31a] When a 3:2:6 stoichiometric ratio of these components was used, a [2 × 3] grid was obtained as major compound (90%) in nitromethane solution, together with minor amounts of a [2 × 2] and a [3 × 3] grid (8% and 2%, respectively; Figure 13).



Figure 13. Synthesis of a $[2 \times 3]$ array from three ditopic ligands **1a**, two tritopic ligands **1b**, and six Ag¹ metal ions.^[31]

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This preferential assembly could be due to the lower stability of the metal-ligand coordination bonds at the central coordination site of the $[3 \times 3]$ grid as well as from solvation and thermodynamic parameters. In the $[2 \times 3]$ grid structure, the silver ions are arranged on a $[2 \times 3]$ rhombohedrally distorted rectangular matrix with an average Ag–Ag distance of 3.75 Å.^[31]

Rectangular $[2 \times 2] M^{II}$ arrays can be also obtained where ligands of type **12** (see Figure 6) coordinate in different conformations with different bridging groups.^[21a,31b,32]

3.5. Incomplete Metal Ion Arrays [p×[n×m]]

The self-assembly of the pentatopic ligand **1d** with Ag^I ions, aimed at constructing a [5 × 5] grid, ultimately led to the formation of two isolable polynuclear architectures: an incomplete grid-type species (Figure 14) and a quadruple-helicate, which crystallize side-by-side from an equilibrating mixture of the complexes in solution.^[33] Twisting around the central bond in the set of five parallel ligands releases a significant amount of strain so that a [2 × [2 × 5]] species is generated rather than the complete [5 × 5] grid.



Figure 14. The $[2 \times [2 \times 5]]$ Ag¹₂₀ grid assembled from nine pentatopic ligands 1d and twenty Ag¹ ions.^[33]

The X-ray structure analysis of the icosanuclear complex $[Ag_{20}^{I}(\mathbf{1d})_{9}]^{20+}$ reveals two $[2 \times 5] Ag_{10}^{I}$ rectangular subgrids located on opposite sides of an array of parallel ligands twisted into a *transoid* conformation across the central pyridazine–pyridazine bond, one above and one below the mean plane through the 20 Ag^I ions. This arrangement may be described as a "grid-of-grids" $[2 \times [2 \times 5]]$ with a distorted rhombohedral geometry of 23.3×23.3 Å, where within each column the average Ag^I–Ag^I separation is 3.73 Å along each

ligand and 3.93 Å between the inner Ag^I ion of each $[2 \times 5]$ column.^[33]

Attempted construction of $[3 \times 3]$ grid-type architectures with bis(terpyridine)-type ligands 5c revealed that in most cases only a $[2 \times 3]$ complex comprising five ligands and six metal ions could be obtained (Figure 15).^[30a] In these $[2 \times 3]$ structures, all sites are occupied by metals except for a vacant central row. Although some evidence for the formation of $[3 \times$ 3] grid-type complexes could be obtained for large metal ions, such as Hg^{II} and Pb^{II}, the enhanced ligand distortion for metal ions with smaller ionic radii becomes a decisive factor in determining the thermodynamically most stable complex, which in this case is the intermediate $[2 \times 3]$ grid-type structure with only a few of the central binding sites occupied. Thus, the predominant self-assembly of $[2 \times 3]$ architectures is a deviation from the "maximum coordination site occupancy" principle and is caused by ligand strain. Often in these cases, various other complexes representing incompletely assembled grids and cyclic structures were detected in lesser amounts.

The X-ray structure analysis of the $[2 \times 3]$ Co₆^{II} grid $[Co_6^{II}(\mathbf{5b})_5]^{12+}$ (R¹ = Ph) consists of five ligands arranged into two sets.^[30a] The first set includes three parallel ligands at a distance of 6.7 Å which are twisted into a *transoid* conformation about the two central pyrimidine-pyridine-pyrimidine C–C bonds. The central binding site of each is unoccupied. The second ligand set is composed of two units markedly warped, whose nitrogen atoms are fully coordinated and in a *cisoid* conformation. The Co^{II} ions are arranged into two rows of three ions with a Co–Co separation of 6.5 Å. The distance between two Co^{II} atoms in different rows is 13.8 Å.

A dodecanuclear metal ion array was obtained in the selfassembly of ligand **14** with Cu^{II} ions.^[34a] It is based on a $[4 \times 4]$ grid-motif, with an exclusive occupation of the peripheral coordination sites (leaving the inner four positions empty).



Figure 15. Two structures of the $[2 \times 3]$ incomplete grid architectures obtained by self-assembly of ligand **5b** and metal ions such as Co^{II}, Zn^{II} or Fe^{II[30a]}

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More recently, the same basic type of ligand system was used to generate a $[4 \times [2 \times 2]] Pb_{16}^{II}$ array.^[34b]

4. Mechanistic Features of the Self-Assembly Process

The nature of the emerging species during the self-assembly of the different grid-type complexes has been studied in solution and in the solid-state. A self-assembled collection of species is obtained upon mixing of the bis(bipyridine)-based ligand 2a and Cu^{I} ions. Detailed analysis of the resulting equilibrium mixture indicated the presence of



Figure 17. Self-assembly pathway for the $[3 \times 3]$ array $[Ag_9(\mathbf{1} \mathbf{b})_6]^{9+}$. The uncomplexed bipyridine-type sites are noted by an open square; they are expected to adopt the more stable *transoid* arrangement.^[36]

three major species: a double-helical architecture, a triangular complex, and square $[2 \times 2]$ grid complexes (Figure 16). These represent the output of a dynamic combinatorial library of supramolecular components, from which the double-helical complex could be trapped by crystallization.^[35] Very similar observations were made for ligand systems **7** with Zn^{II} ions, which yielded an equilibrium mixture of triangular and tetranuclear reaction products.^[28]



Figure 16. Self-assembly of an equilibrating mixture of the double-helical, triangular, and square $[2 \times 2]$ grid complexes from **2a** and Cu¹ ions. Gray bars correspond to ligands located on the underside.^[35]

The formation pathway of the $[3 \times 3]$ $[Ag_9^{I}(\mathbf{1b})_6]^{9+}$ metal ion array has been extensively studied by NMR spectroscopy.^[36] This self-assembly process involves several intermediates, which are generated at different metal/ligand stoichiometries. A mixture of several unidentified species is observed at low $Ag^{I}/(1b)$ ratios until $Ag^{I}/(1b) \approx 1:1$ is reached, when two complexes of $[Ag_n^{I}(\mathbf{1b})_n]^{n+}$ type are mainly present. They are characterized by an intertwined structure and a *transoid* arrangement of ligands. At Ag^I/ $(\mathbf{1b}) \approx 6.5$ a species $[Ag_6^{I}(\mathbf{1b})_5]$ has been identified which has three ligands in transoid form and two ligands in the all-cisoid form. Further addition of Ag^I ions leads to the conversion of this intermediate into the final $[Ag_9^{I}(\mathbf{1b})_6]^{9+}$ grid presumably through a $[Ag_6^{I}(\mathbf{1b})_5]^{6+}$ entity with all five ligands in the allcisoid form. These observations imply an overall positive cooperativity and a robust structure for the final $[3 \times 3]$ $[Ag_9^{I}(\mathbf{1b})_6]^{9+}$ complex (Figure 17).

The templating effect of certain anions upon the construction of metallosupramolecular nanostructures was clearly recognized for circular helicates and results from the operation of dynamic combinatorial diversity.^[37] The selfassembly of Ni^{II} or Zn^{II} ions with ligand **1e** in the presence of



 BF_4^- or ClO_4^- ions leads to the formation of the $[2 \times 2]$ grid

complexes (Figure 18).^[38] The metal ions have octahedral

coordination geometry, with four of the coordination sites occupied by two ligands and the other two positions by

Figure 18. Templating effect of the anions BF_4^- and SbF_6^- on the formation of metallosupramolecular nanoarchitectures with the ligand 1 e.

An anion is encapsulated within the cavity of these grids. Moreover, the ligands are disposed in an interwoven manner, giving rise to a chiral grid which could be spontaneously resolved as chiral crystals.^[38b] However, the self-assembly of the same ligand with Ni^{II} ions in the presence of a larger counterion such as SbF_6^- resulted in the formation of a molecular pentagon consisting of five ligands and five Ni^{II} ions (Figure 18).^[39]

As it has been stressed earlier, correct self-assembly implements both maximal site occupation and pathway selection (or orientation) by the introduction of appropriate substitution. The nature of the solvent and the concentration of reagents may also affect the output of the self-assembly process. For example, ligand **2a** ($\mathbf{R} = \mathbf{H}$) in the presence of Cu^{II} ions in a 1:1 ratio in acetonitrile gives equilibrating mixtures of a [2×2] grid and a hexagonal architecture (Figure 19).^[40] At increased concentrations in acetonitrile, the relative amount of hexamer increases. Its crystal structure revealed the presence of acetonitrile molecules and hydroxo groups bound to the Cu^{II} centers, which are therefore five-



Figure 19. Adaptive self-assembly of the $[2 \times 2]$ grid $[Cu_4^{II}(2a)_4]^{8+}$ and the hexameric cyclic complex $[Cu_6^{II}(2a)_6]^{12+}$ from ditopic ligand 2a (R=H) and Cu^{II} ions. The products exist in a solvent-dependent equilibrium.^[40]

coordinate. On the other hand, only the $[2 \times 2]$ metal ion array could be detected in nitromethane. Replacement of nitromethane by acetonitrile and vice versa indicated the reversible switching between a solution containing either the grid alone or an equilibrating mixture of the grid and the hexameric ring. This process displays three remarkable features: 1) self-assembly with substrate binding, 2) dynamic combinatorial structure generation, and 3) environmentsensitive behavior resulting in a process of adaptive selfassembly.^[40]

On the basis of the results obtained for many different grid self-assembly experiments, it can be stated that $[n \times n]$ grid-type complexes of high nuclearity may be disfavored by: 1) the imposition of a *cisoid* conformation for all ligands; 2) the bent, domelike shape in two perpendicular directions ("pinching-in") of the ligand; and 3) the presence of central metal ion coordination sites containing poorer donor atoms. On the other hand, they are favored by: 1) the trend towards establishing the highest number of coordination interactions and therefore towards maximum site occupancy; 2) maximization of stabilizing π - π contacts between ligands, and 3) the interaction with included anions or guest molecules. Thus, a subtle interplay between metal coordination, strain, and steric demand of the ligands as well as external factors, reaction conditions, and the nature of the counterions determines the product of the self-assembly.

5. Multistability and Addressability

High density information storage and informatics on the nanoscale may take advantage of a designed exploitation of intrinsic functional molecular properties and their modifications, such as size, multiplicity, and heteronuclearity as well as different redox, magnetic, or spin states. Planar multicenter transition-metal complexes appear to be very attractive candidates for the design of multilevel information storage devices, because they could fulfill intrinsically two important prerequisites for nanoscale memory devices: 1) multistability and 2) addressability.

5.1. Multistability 5.1.1. Redox States

The first report on the electrochemical properties of a $[2 \times 2]$ gridlike complex concerned the copper(I) complex $[Cu_4(1a)_4](BF_4)_4$, which exhibits seven reversible single-electron reduction waves.^[13a] The electrochemical behavior of a family of tetranuclear gridlike oligopyridine complexes of the general formula $[M_4^{II}(5a)_4]^{8+}$ displays well-resolved multiple one-electron reductions in all complexes investigated.^[41] Furthermore, the introduction of electron-donating or -attracting groups into the ligands tunes systematically the potential of the first reduction. As a consequence, one Co_4^{II} member of this family exhibits up to twelve well-resolved reversible one-electron processes at room temperature, which appears to be the most extended redox series known for well-characterized molecular compounds.^[41]

The rather low values of the redox potentials are of importance for the stability of the multielectron species generated and thus for their possible applications as devices presenting multiple electronic levels. Spectroelectrochemical experiments revealed that the reductions take place on the coordinated ligands in all cases; no reduction of the metal centers was observed in the accessible potential range. Interestingly, the Co₄^{II} species exhibited an amazing regularity in the disposition of the reduction waves, as well as a remarkable stability and reversibility towards reduction (Figure 20). In contrast, analogous $Mn_{\scriptscriptstyle 4}^{\rm II}$ arrays with $M^{\rm II}\!=\!$ Fe^{II}, Ru^{II}, Os^{II}, Zn^{II}, and Mn^{II} were found to be more sensitive towards decomposition and to produce more complex reduction schemes. The nature of the M^{II} ions in gridlike complexes plays a very important role for mediating electronic communication within the metalloorganic supramolecular array.^[41]

The oxidation of the manganese(II) $[3\times3]$ array $[Mn_9(\textbf{13})_6]^{6+}$ was studied by cyclic voltammetry and coulometry. $^{[21b]}$ A series of $Mn^{II} \rightarrow Mn^{III}$ oxidation waves was found,



Figure 20. Plot of the sequential 12-electron reduction of the $[Co_4^{II} (5a)_4]^{8+}$ array in dimethylformamide (DMF) at room temperature. Black line: cyclic voltammogram (CV); gray line: deconvolution of the CV; reference: Fc⁺/Fc. ^[41b]

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and the number of electrons per wave gave an insight into the sequence of oxidations in the array (Figure 21). A fourelectron oxidation event occurs at +0.61 V, tentatively assigned to simultaneous oxidation at the grid's four equivalent corners. Four additional oxidation waves at +0.92, +1.13, +1.33, and +1.53 V were attributed to the remaining edge-located Mn atoms, but oxidation of the central ion was not observed. Spectroscopic changes were correlated to an increasing proportion of positive charge on the array.

The protonation state of the ligand can also be used to manipulate the electrochemical properties of the gridlike array. For example, protonic modulation of redox properties has been achieved for ionizable $[2 \times 2]$ Co₄^{II} and $[2 \times 2]$ Co₄^{III} grids based on ligand **15 a** (R² = H).^[42]

Thus, the $[2 \times 2]$ Co^{II}₄ and $[3 \times 3]$ Mn^{II}₉ arrays are intriguing electron reservoirs, representing multiredox state electronic systems. Future studies may uncover a system presenting the features required for investigation into nanometric devices used for data representation, and addressable either locally, at a given metal or ligand site, or through the overall redox state (see Figure 21 and ref. [3a]).

5.1.2. Magnetic States

A new type of molecular material has recently emerged based on polynuclear metal complexes called "single-molecule magnets" (SMMs). SMMs possess slowly relaxing magnetic moments, a prerequisite for use in future magnetic information storage devices. This class of molecules exhibits a unique concomitance of both macroscopic (e.g. magnetism) and quantum regime properties (e.g. quantum tunneling) within monodispersed molecular entities.^[43]

The principal interest for potential use of SMMs as magnetic memory units arises from their size, undercutting the paramagnetic limit of conventional information storage materials, and from the presence of an energy barrier for the reversal of the direction of the molecular magnetization. The origin of magnetism in the SMMs is the spin(s) on individual metal ions, which couple to give rise to a high-spin ground state. The SMMs have an axial zero-field splitting, which leads to a double well potential with an energy barrier between "spin-up" and "spin-down" states. The final height U of the barrier is determined by $U = |D| S^2$, where D is the zero-field splitting parameter and S the resulting spin quantum number. Consequently, SMMs display hysteresis in their magnetic susceptibility versus external magnetic field loop (so far, only at very low temperature), which might be used in molecular data storage.^[44]

In conclusion, to achieve such molecular magnetic data storage, the respective molecule has to possess 1) a high total spin quantum number S and 2) a high Ising-type anisotropy

barrier arising from a negative zero-field splitting parameter D. A high spin quantum number S demands intramolecular ferromagnetic coupling of the involved metal ion spins. The commonly found antiferromagnetic coupling "destroys" the spin densities and renders completely antiferromagnetic-coupled molecules useless for magnetic information storage. Usable SMMs exhibiting AF coupling are molecular ferrimagnets, where the overall spin ground state is a result of the noncompensation of spins. A negative zero field splitting parameter D depends on the electronic nature of the metal ions involved (e.g. Mn^{III}) in combination with the low overall symmetry of the molecule.

The first and still most prominent example exhibiting SMM-like behavior was a spin cluster referred to in the literature as " Mn_{12} ".^[45] Later, other molecular compounds such as "Fe₈", "Fe₁₉", or " Mn_4 " joined the SMM family.^[46]

The ongoing search for SMMs exhibiting high anisotropy barriers (preferentially above room temperature to overcome the thermal fluctuation) is driving the increasing interest in the magnetic properties of spin bearing metal ion arrays. Thus, the $[2 \times 2]$ Co^{II}₄ entity was shown to represent an isolated magnetic domain, a model system for studying magnetic interactions in discrete entities.^[47] However, the whole series of $[2 \times 2]$ M_4^{II} ion arrays $[M_4^{II}(\mathbf{5a})_4]^{8+}$ $(M = Mn^{II}, Co^{II}, Ni^{II}, and$ Cu^{II}) exhibited exclusively weak antiferromagnetic intramolecular exchange couplings. Evidently, the µ-pyrimidine unit in ligand 5a is able to mediate antiferromagnetic but not the necessary ferromagnetic magnetic exchange couplings. The weak magnitude of the coupling parameter J can be attributed to the rather long metal-metal distances of around 6.5 Å.^[48] The change to the negatively charged µ-phenoxo bridging group in the $[2 \times 2]$ $[Cu_4^{II}(10^{-})_4]^{4+}$ compound leads to even weaker antiferromagnetic couplings.^[20]

Ferromagnetic exchange coupling was found in the μ alkoxo-bridged $[Cu_4^{II}(12)_4]^{4+}$ grid complex, but only antiferromagnetic couplings were observed for all further spinbearing ions assembled with the same ligand.^[21] Related to this work, the tritopic ligand **13** (X = CH) gave access to a ferromagnetically coupled Cu_8^{II} pin-wheel $[2 \times 2]$ gridlike complex (Figure 22).^[49]



Figure 22. Definition of the coupling constants J in $[2 \times 2]$ arrays (left), $[2 \times 2]$ "pin-wheel" arrays (middle), and $[3 \times 3]$ arrays (right).



Figure 21. Proposed oxidation sequence of manganese ions in the $[3 \times 3]$ metal ion array $[Mn_9(13)_6]^{6+}$ (\bigcirc Mn^{II}, \bullet Mn^{III}), based on experimental data.^[21b]

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The magnetic properties were thoroughly investigated for a series of nonanuclear [3×3] grid complexes incorporating doubly μ -O bridging ligands 13.^[21c] Some of the $[M_{0}^{II}(13)_{6}]^{n+1}$ systems exhibit magnetic features which can be interpreted as a combination between ferromagnetic and antiferromagnetic exchange processes. The relative contributions of ferromagnetic and antiferromagnetic coupling vary according to the temperature (e.g. the ferromagnetic behavior is more pronounced at low temperatures because all antiferromagnetic contributions are effectively coupled to a small spin (S=0)ground state). To explain the combined antiferromagnetic/ ferromagnetic coupling situation found in these metal ion arrays, the $[3 \times 3]$ grid can be considered as the sum of a ring of eight metal ions coupled to the central metal ion yielding two different exchange constants J_{ring} and $J_{central}$ (Figure 22). The $[Mn_9^{III}(13)_6]^{15+}$ system involves $|J_{ring}| \ge |J_{central}|$, and displays only antiferromagnetic behavior.^[5b] However, the orbital based magnetic orthogonality leads to the simultaneous observation of both exchange modes in the Cu^{II}₉ case, with dominant ferromagnetic exchange coupling at low temperatures.[5,50a]

There is currently no evidence for an anisotropic energy barrier in either the ferromagnetically coupled Cu_4^{II} grid arrays or the antiferromagnetically/ferromagnetically coupled Cu_9^{II} systems. However, a recent hint for magnetic anisotropy was given by the observation of metamagnetic-like behavior in antiferromagnetically coupled $[3 \times 3]$ Mn₉^{II} and $[2 \times 2]$ Co₄^{II} arrays.^[50b,c]

The investigation, understanding, and manipulation of magnetic coupling between metal ions in metallogrid complexes is a first step towards the potential use of gridlike arrays in information storage devices. The discovery of ferromagnetic coupling in some Cu^{II} arrays is encouraging, although ways to introduce a magnetic anisotropy barrier have still to be explored. The choice of donor atoms, bridging groups, paramagnetic metal ions, and systematic synthetic design strategies (in contrast to the mostly serendipitous syntheses of magnetic oxo clusters) might render such supramolecular metallogrid arrays well suited for magnetic data storage at the nanometric scale.

5.1.3. Electronic Spin States

Among the physical properties that may be considered for magnetic molecular data storage systems, the spin transition (ST) phenomenon between the low-spin (LS) and the highspin (HS) state of Fe^{II} ions is an attractive process to enable molecular memory effects.^[51] Spin transition systems possess an unique concomitance of possible "write" (temperature, pressure, light) and "read" (magnetic, optical) parameters.^[52] Investigations along these lines revealed ST behavior in several Fe^{II}₄ gridlike $[2 \times 2]$ arrays (e.g. $[Fe^{II}_4(5a)]^{8+}$). The internal spin states of the incorporated Fe^{II} ions could be switched between the diamagnetic (LS; S=0) and the paramagnetic (HS; S=2) state by applying external field triggers (temperature, pressure, light) on macroscopic samples.^[53]

The occurrence of ST in $[2 \times 2]$ gridlike ion arrays of the type $[Fe_4^{II}(\mathbf{5a})_4]^{8+}$ depends directly on the nature of the

substituent R^1 in the 2-position of ligand **5a**. All metal ion arrays with substituents R^1 favoring relatively strong ligand fields ($R^1 = H$; OH) remain entirely in the diamagnetic LS state throughout all studied temperatures. Only complexes bearing substituents R^1 that attenuate the ligand field by steric (and to a lesser extent electronic) effects ($R^1 = Me$, Ph) exhibit temperature triggered spin transition (Figure 23). The



Figure 23. General switching scheme between the Fe^{II} spin states in the $[Fe_4^{II}(5a)_4]^{8+}$ metal ion arrays triggered by temperature, pressure, and light. The averaged Fe–N bond lengths in the 3 HS/1 LS (top) and in the 1 HS/3 LS states (bottom).^[54]

magnetic switching behavior can be characterized in solution (by ¹H NMR and UV/Vis spectroscopy) and in the solid state (by X-ray structure analysis, magnetic susceptibility measurements, and Mössbauer spectroscopy). Very gradual and incomplete transitions without hysteresis seem to be typical for all investigated, magnetically active $[2 \times 2]$ Fe^{II}₄ arrays. Intramolecular cooperativity between the four iron centers was revealed, and improving the intermolecular interaction between the tetranuclear centers by introduction of hydrogen bonding between the grid units increased the HS fraction over the whole temperature range, although the spin transition remained very gradual and incomplete.^[54]

In a farther-reaching perspective, molecular architectures such as $[Fe_4^{II}(5a)_4]^{8+}$ present spin state properties that may be switched by external triggers, and may provide access to (supra)molecular spintronic devices.

5.1.4. Optical States

The UV/Vis spectra of the $[2 \times 2]$ metal ion arrays $[Co_4^{II}(15a)_4]^{8+}$ and $[Co_4^{II}(15b)_4]^{8+}$ both bearing acidic protons display reversible pH-modulation of the optical properties in
solution. Due to the high accumulated charge of the complex cations, the eight N–H protons of the bis(hydrazone) ligands **15** ($\mathbf{R}^1 = \mathbf{Ph}$; see Figure 6) can be abstracted progressively and reversibly at relatively low pH values (below 7).^[24a] The color of the solution of $[\mathbf{Co}_4^{II}(\mathbf{15a})_4]^{8+}$ ($\mathbf{R}^2 = \mathbf{H}$, $\mathbf{R}^3 = \mathbf{H}$) changes from pale-yellow at low pH to orange and finally to deep violet above neutral pH, and repeated cycling indicates that the process is completely reversible (Figure 24).



Figure 24. The color change and UV/Vis spectra of complex $[Co_4^{II}(15a)_4](BF_4)_8$ ($R^1 = Ph$; the abstracted acidic protons are labeled in red) depending on the pH of the acetonitrile/water solution.^[24a]

Furthermore, the $[Zn_4^{II}(15a)_4]^{8+}$ (R¹=Ph; R²=R³=H) complex exhibits an emission (originating from sandwich-like π - π interactions of the phenyl substituents intercalated between two ligands **15a**), which depends on the protonation state.^[55]

5.2. Two-Dimensional Ordering and Addressability 5.2.1. Two-Dimensional Self-Ordering in Crystals

Simple mononuclear metal complexes bearing H-bonding-donor and -acceptor sites are able to undergo hierarchical self-assembly processes. The same approach can also be applied to $[2 \times 2]$ grids, which can be organized into a chessboard-like 2D "grid-of-grids" arrangement (Figure 25). This strategy is a powerful alternative to the more laborious stepwise construction of high nuclearity metalloarrays.



Figure 25. Schematic representation of the two-step hierarchical self-assembly sequence to generate a 2D "grid-of-grids" pattern.

Such 2D-extended supramolecular arrays of precise architecture would be of special interest for addressing the metal ions individually. However, their formation and stabilization requires control over the various noncovalent interactions, so as to make them the thermodynamically preferred products and to avoid clusterlike structures as result of undesired interactions. The hierarchical self-organization of mononuclear metal complexes with the ligands **17** or **18**, which form self-complementary hydrogen bonds, illustrates the problems. Since the energies for the formation of the double hydrogen bonds are almost the same order of magnitude as the energies of crystal packing phenomena and π - π interactions, different thermodynamic products could be observed in these experiments.

The self-complementary aminopyrimidine units of the monotopic terpyridine-type ligand **17** lead to an infinite twodimensional gridlike structure of the corresponding $[Co^{II}(17)_2](PF_6)_2$ in the solid state.^[56] The complexes are connected by intermolecular double hydrogen-bonds between the amino groups and the noncoordinating pyrimidine nitrogen atoms. This creates a sinusoidal arrangement of the complexes, which are interwoven into a two-dimensional network (Figure 26). However, changing the counteranion from PF_6^- to BF_4^- causes a partial breakup of this grid motif leaving one quarter of the H-bonding sites unsaturated.

The extension of this methodology towards $[2 \times 2]$ gridlike complexes afforded 2D arrays representing dual levels of organization. The complex $[Co_4^{II}(19)_4](BF_4)_8$ was characterized by single-crystal X-ray diffraction.^[57] Although the presence of the aminopyrimidine units in the ligand should enable their metal complexes to generate hydrogen-bonded networks of grids, the hydrogen-bonding motif is only present



Figure 26. X-ray structure analysis of the mononuclear complex $[Co^{II}(17)_2](PF_6)_2$. The complex ions are arranged to give sinusoidal arrangements through the formation of double hydrogen-bonds. Top: Section with two complex ions with hydrogen boding contacts (ORTEP representation); middle: space-filling representation. Bottom: Infinite 2D gridlike metal ion array extracted from the crystal packing diagram.^[56]

in one dimension, leading to the formation of infinite onedimensional chains of grids. Neighboring complexes without hydrogen-bonding interactions show weak π -stacking between their ligands. Thus, $[Co_4^{II}(20)_4](BF_4)_8$ only generates a partially hydrogen-bonded network, because of the competition between hydrogen bonding and π - π stacking interactions.

The different structural outcomes of the mono- as well as the tetranuclear H-bonding approach illustrate the subtle energy interplay between H-bonding and crystal packing effects. This exemplifies a general problem found for this type of hierarchical self-assembly process.

5.2.3. Two-Dimensional Ordering at Surfaces and Single Molecule Addressing

One important factor in the exploitation of supramolecular architectures as components of functional devices is the ability to prepare ordered structures on solid surfaces. Recent advances in scanning probe techniques (STM, AFM) have enabled imaging and manipulation of surface-bound objects with molecular resolution.^[58] Thin films of metalloorganic grid complexes have been studied by these methods with the prospect that the resulting high density of active elements could be engineered into functional surfaces, for example, memory devices.

Highly stable monolayers of the cobalt(II) $[2 \times 2]$ complex $[Co_4^{II}(\mathbf{5a})_4]^{8+}$ were prepared on an atomically flat graphite surface (highly ordered pyrolytic graphite (HOPG)) by evaporation of dilute acetone solutions, yielding defect-free areas of up to 0.5 µm².^[59] The ordered structures form spontaneously, growing outward from single nucleation points; this process may be viewed as a two-dimensional crystallization. It was found that the orientation of the grids relative to the surface plane is controlled by the substitution pattern of ligand **5a**: the ligand with $R^1, R^2 = H$ and $R^3 = CH_3$ gave an edgewise orientation of grids with respect to the surface, while the ligand with $R^1 = CH_3$ and $R^2, R^3 = H$ resulted in flat tiles forming a superarray of $[2 \times 2]$ metallogrids. The superarray arrangement was reflected in an orthogonal 2.5 nm × 2.4 nm periodicity in the STM image (Figure 27 a).



Figure 27. a) STM image of the monolayer of $[Co_4^{"}(5 \mathbf{a})_4]^{8+}$ gridlike compounds on graphite. b) Hole in the monolayer produced by potentialinduced lifting of a single $[Co_4^{"}(5 \mathbf{a})_4]^{8+}$ molecule with the STM tip. c) Schematic representation of the disposition of the metalloarrays at the surface (top and side view).^[59]

A -500 mV voltage pulse applied to the STM tip (normally operated at below -50 mV for imaging) was employed to pluck a single grid from the monolayer, resulting in a square hole with the dimensions of a single gridlike complex (Figure 27b). This represents the first indication for the possibility of controlled addressing of the $[2 \times 2]$ metalloarrays using state-of-the-art technological devices. The migration rate of the hole was measured, and found to be 200 times slower than for a monolayer of cycloalkanes, reflecting strong adsorption to the graphite surface.^[60]

Analogous $[2 \times 2]$ gridlike Co^{II} complexes formed by bis(terpyridine)-derived ligands substituted with an additional *para*-pyridyl or n-propyl thia unit **5***a* were adsorbed as monolayers on graphite (HOPG). They gave rise to a weaker adsorption and higher mobility compared to the corresponding parent complex.^[61,62]

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Thin films of $[2 \times 2]$ Co₄^{II} metallogrids on gold surfaces have been prepared and imaged by in situ electrochemical deposition STM. Films of pure cobalt grid are poorly conductive (<10⁻⁶ S cm⁻¹), but upon doping with an excess of cadmium(II) ions, conductivity rises by four orders of magnitude to 10⁻² S cm⁻¹ resulting from additional electronic states in the material's insulating bandgap. While this increase is large, conductivity is still low relative to metallic conductors such as copper (10⁶-10⁸ S cm⁻¹).^[63] [2 × 2] Co₄^{II} grid complexes have been included in thin films^[64a] and may serve as components^[64b] for metallosupramolecular polymers providing novel properties to the polymeric network.^[64c] Recently, a Mn₉^{II} grid (derived from a ligand similar to **13**; Figure 6) was similarly investigated on a Au(111) surface.^[65]

A two-step process of an air-water interfacial reaction between free ligand **1a** ($\mathbf{R} = \mathbf{Ph}$) and \mathbf{Ag}^{I} ions contained in the aqueous subphase led to the formation of a [2×2] \mathbf{Ag}_{4}^{I} grid complex, followed by its self-assembly into an oriented crystalline monolayer. On surface compression, the original monolayer underwent a transition to a crystalline bilayer, almost retaining the initial in-plane arrangement.^[66]

A single report of thin film preparation employing grids of higher order concerns the silver(I) $[3 \times 3]$ complex $[Ag_9(1b)_6]^{9+}$. Self-assembly of the grids was achieved at the air-water interface by spreading uncomplexed ligand 1b on an aqueous solution of silver(I) triflate. This gave ordered crystalline films of 13–20 Å thickness that could be transferred successfully onto quartz slides.^[67] Grazing incidence X-ray diffraction (GIXD) revealed that grid orientation in the films could be controlled by varying the substituents of ligand 1b: the grids lie parallel to the surface when R = Ph, but "stand up" normal to the air-water interface when $R = CH_3$. Thus, the formation of metallogrid monolayers represents a twofold self-assembly sequence; conventional synthetic techniques are only employed for preparation of the ligand.

6. Conclusion and Outlook

The synthetic accessibility by self-assembly of two-dimensionally arrayed switchable elements of nanometric size complements theoretical developments in molecular information storage and processing.^[1,2] Gridlike metal ion architectures are attractive in this context for several reasons. For example, grid-type arrays can behave as multilevel electronic species, triggered by electrochemical, magnetic, and optical parameters. In addition, it has been shown that single grid units on surfaces are addressable within the nanometer regime. It is important to recognize the challenges that remain in order to combine these two main features in a working functional device by detecting, controlling, and addressing the electronic or magnetic states of individual grids or even ions, for instance in 2D monolayers. The information-representing metastable states must be sufficiently robust to permit room-temperature operation. The question of implementation and integration of possible devices with the supporting frame (wiring, pinning, powering) has yet to be addressed.

A sense for the potential of information storage using (supra)molecular memory elements can be obtained by contrasting the density of magnetic disk and CD-ROM technologies (~ 10^8 bits cm⁻²) with the estimated storage capacity of DNA (10^{21} bits cm⁻³ corresponding to ~ 10^{10} bits cm⁻²). The cationic metalloarrays, deposited on surfaces, have shown external dimensions in the order of 25 × 25 Å and a closely packed 2D array; with one data bit stored per [2 × 2] matrix, they would lead to a potential surface data storage density of about 10^{12} bits cm⁻².

Gridlike arrays display "ion dot" type features, by analogy with semiconductor quantum dot arrays.^[3a] One may remark that "ion dots" are of much smaller size than quantum dots. It has been pointed out that "... such architectures may foreshadow multistate digital supramolecular chips for information storage in and retrieval from inscribed patterns that might be addressable by light or electrically. Different states could, in principle, be characterized either by different local features at a given x, y coordinate, in ion dot fashion, or by specific overall optical or oxidation levels. Inducing ± 1 redox changes at specific locations in a single unit would then correspond to a sort of single electronics at ion dots."^[3a]

In conclusion, the power of self-assembly to create ordered nanostructures of intriguing technological potential has been underlined through the investigation of metalloorganic grid complexes. It has been stressed that selforganization represents a self-fabrication process, allowing in principle one to bypass tedious nanofabrication procedures.^[3] Considering the panoramic properties of transition-metal compounds, and the small collection of metals and ligands that have as yet been incorporated into metallogrid or other types of architectures, there can be little doubt that a very wide set of nanosize devices and materials with a rich palette of properties will spring from novel metal–ligand combinations for the benefit of the development of supramolecular electronics, spintronics, and optotronics.^[68]

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Synthesis of ionisable $[2 \times 2]$ grid-type metallo-arrays and reversible protonic modulation of the optical properties of the $[Co_4^{II}L_4]^{8+}$ species

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The new bis-hydrazone based ligands A and B form ionisable $[2 \times 2]$ grid-type transition metal complexes whose properties may be modulated by multiple protonation/deprotonation as shown by the reversible change in optical properties of the $[Co_4^{II}L_4]^{8+}$ complexes depending on their protonation state.

Two-dimensional grid-like coordination complexes have attracted increasing interest for the last decade since a welldefined 2-D arrangement of an exact number of metal ions suggests possible uses in information storage and processing technology.¹ A number of square²⁻⁴ [$n \times n$] and rectangular⁵ [$n \times m$] grids with $n, m \le 4$ have been obtained for metal ions with tetrahedral² as well as octahedral coordination geometry. Of special interest are complexes undergoing reversible switching processes of optical, magnetic⁶ and redox⁷ properties triggered by external parameters like temperature, pressure, light, magnetic or electric potential.

We present herein the synthesis of a new type of bishydrazone based ligands **A** and **B** and their conversion into the $[2 \times 2]$ grid-like complexes $[Co_4^{II}A_4](BF_4)_8$ **1** and $[Co_4^{II}B_4](BF_4)_8$ **2** (Schemes 1 and 2) which show optical switching with intense reversible colour changes depending on the pH of the solution.[†]

The introduction of a hydrazone group into a terpyridine (terpy) unit gives easy synthetic access to long helical chains⁸ as well as to multiple terpy-type ligands and their complexes presenting ionisable N–H sites.⁹ This protocol was applied to



Scheme 1 Synthesis of ligands A and B.



the synthesis of ligands A and B, analogs of the bis-terpy type ligands described earlier.³ The isomeric ligands A and B were synthesised by condensation of one equivalent of the respective pyrimidine brick with two equivalents of the respectively substituted pyridine compound in a 1 : 1 solution of EtOH-CH₃Cl and in the presence of molecular sieves (95 and 90% yield respectively, Scheme 1). In analogy to the previously reported formation of grid-type complexes,³ ligands A and B react with transition metal ions of octahedral coordination (such as Zn^{II}, Co^{II}, Fe^{II} and Mn^{II}) to generate tetranuclear $[2 \times 2]$ grid-type complexes.⁹ Thus, the compounds $[Co_4^{II}A_4](BF_4)_8$ 1 and $[Co_4^{II}B_4](BF_4)_8 2$ were obtained in quantitative yields by the equimolar reaction of $Co(BF_4)_2$ with **A** or **B** in dry acetonitrile under reflux for 6 hours. Because of their design, both ligands A and B steer the metal ions into square-like arrangements and simultaneously introduce pH-sensitive NH functionalities into the complexes (Scheme 2).

Crystals of $[Co_4^{II}A_4](BF_4)_8$ 1 were obtained from a buffer/ acetonitrile solution at pH 5.29 and a single crystal X-ray diffraction study was carried out. Unfortunately, detailed structural analysis was prevented by the low quality of the refined data. Nevertheless, the data set obtained allowed us to conclude that the complex presented the expected $[2 \times 2]$ gridlike structure. Additionally, no anions were found, which argues for the loss of all eight protons in accordance with the spectroscopic investigations at the applied pH.

More precise structural insight was gained from the single Xray structure of the structurally analogous $[Mn_4^{II}A_4](ClO_4)_8$ **3** complex (Fig. 1),‡ which revealed a tetranuclear complex with four metals in an octahedral N₆ environment. The ligands are found in an almost ideal alignment in perpendicular and parallel directions. The distance between the pyrimidine rings of two parallel ligands averages 7.0 Å. The phenyl substituents are perpendicularly twisted with respect to the pyrimidine rings and are sandwiched between the two opposite ligands at a distance of d = 3.5 Å as found for other $[2 \times 2]$ $[M_4^{II}L_4]^{8+}$ complexes.³ Because these crystals were grown from an anhydrous nitromethane solution, all eight anions (and so presumably all eight N–H protons) were still present.

In addition to the synthetic aspects, ligands **A** and **B** present the interest that in their grid complexes $[M_4^{II}L_4]^{8+}$ the high positive charge should render the eight hydrazone N–H protons (two per ligand) acidic, thus allowing protonic modulation of



Fig. 1 Side (left) and top (right) views of the X-ray structure of $[Mn_4^{II}A_4](CIO_4)_8$ 3 (protons, anions and solvent are omitted for clarity).

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the properties (optical, redox, magnetic, *etc.*) of these complexes, up to a fully deprotonated, overall neutral species.¹⁰

The pH-dependency of $[Co_4^{II}A_4](BF_4)_8 \mathbf{1}$ was studied by UVvis spectroscopy in a 50/50 vol% mixture of acetonitrile and Britton-Robinson buffer.¹¹ Fig. 2 shows the spectroscopic changes observed when the pH of a solution of 1 was increased in a stepwise manner. Starting from low pH (0.51-3.79), a new peak at $\lambda = 527$ nm emerges progressively at the expense of the main peak at $\lambda = 378$ nm. Intermediately, a third peak at $\lambda =$ 450 nm evolves and disappears at pH values between 3 and 5.5. From moderately acidic to neutral pH values (4.64-7.22) the band at $\lambda = 527$ nm ($\varepsilon = 42 \times 10^3$ cm² mol⁻¹) surmounts all remaining peaks in intensity and exhibits saturation behaviour at pH values above 7. Subsequent decrease of the pH reestablishes the low pH spectra and repeated cycling indicates that the process is completely reversible. The colour of the solution changes from pale-yellow at low pH to orange and finally deep-violet above neutral pH (Fig. 3).

A very similar spectroscopic behaviour is observed on titration of a 4.5×10^{-7} M solution of 1 in anhydrous acetonitrile with water exhibiting saturation above 3 vol% of water.

Likewise, the UV-vis spectra of $[Co_4^{II}B_4](BF_4)_8 \ 2$ displays reversible pH modulation of the optical properties. However, 2 exhibits already in the fully protonated state at low pH an absorption band in the visible range ($\lambda = 421$ nm) which decreases as a more intense band at $\lambda = 620$ nm emerges and saturates at neutral pH by progressive titration. The colour of complex 2 changes from blue to deep-green and the process is completely reversible. The analogous $[Zn_4^{II}L_4]^{8+}$ complexes exhibit a similar pH dependency of the spectrocopic properties (between colourless at acidic pH and dark-blue above neutral pH) indicating the primary involvement of ligand orbitals in such pH modulation processes. In addition, the $[Zn_4^{II}L_4]^{8+}$ complexes exhibit also an emission at $\lambda_{max} = 452$ nm, which might be tuned by pH modulation.

In conclusion, due to the high accumulated charge of the $[Co_{I}^{II}L_{4}]^{8+}$ complex cations, the eight N–H protons can be abstracted progressively and reversibly in solution at relatively low pH (below about 7). Further investigations concerning the protonic modulation of the redox^{12a} and magnetic^{12b} properties of this new class of grid-like compounds are in progress. In view of the remarkable properties (magnetic,⁶ electronic,⁷ and optical) of $[2 \times 2]$ grid-type complexes of transition metal ions, the hydrazone-type ligands **A** and **B** give access to medium dependent modulation of the physical properties of their complexes through reversible protonation/deprotonation processes. Such a feature is of great interest from the perspective of

Fig. 2 UV-vis spectra of a 4.5×10^{-7} M solution of $[Co_4^{II}A_4](BF_4)_8$ 1 in buffer/acetonitrile 50/50 vol% at pH 0.51; 0.75; 3.12; 3.79; 4.64; 5.53 and 7.22.



Fig. 3 Colour change of $[Co_4^{II}A_4](BF_4)_8$ 1 at different pH.

addressing functional metallo-supramolecular devices through external triggers.

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Notes and references

[†] Ligands **A** and **B** were fully characterised by ¹H and ¹³C NMR; FAB-MS and elemental analysis.

Synthesis of complexes: A suspension of the ligand (19.8 µmol) and of the respective Co^{II} - (or of the respective Mn^{II} -) salt (19.8 µmol) in ACN (1.5 mL) was heated until the ligand was completely dissolved. The solution was stirred under reflux for 6 h. The complex was isolated by addition of diisopropyl ether to the solution until a precipitate formed. The precipitate was collected, washed with diisopropyl ether and dried *in vacuo* resulting in quantitative yields.

 $[Co_4^{II}A_4](BF_4)_8, 1: {}^{1}H-NMR (d_3-ACN): \delta = 215.9, 197.9, 187.3, 63.1, 59.2, 57.2, 11.2, 9.4, 8.1, 6.7, 6.3, -17.3; FAB-MS: <math>m/z = 2158.3 [M - 4BF_4]^+, 2071.1 [M - 5BF_4]^+, 1982.2 [M - 6BF_4]^+, 1893.2 [M - 7BF_4]^+, 1806.2 [M - 8BF_4]^+, 903.1 [M - 8BF_4]^{2+}]; elemental analysis calc. (%) for C_{88}H_{68}B_8N_{32}F_{32}Co_4: C 42.21, H 2.74, N 17.90; found C 42.03, H 2.67, N 17.79.$

 $[\mathrm{Co}_4^{\mathrm{I}}\mathbf{B}_4](\mathrm{BF}_4)_8,$ **2:** ¹H-NMR (d₃-ACN): δ = 238.5, 142.3, 119.8, 116.1, 66.8, 64.5, 51.4, 12.1, 11.4, 8.4, 8.1, 6.2; FAB-MS: m/z = 1805.4 [M - 8BF₄]⁺, 903.2 [M - 8BF₄]²⁺]; elemental analysis calc. (%) for C₈₈H₆₈B₈N₃₂F₃₂Co₄: C 42.21, H 2.74, N 17.90; found C 41.45, H 2.53, N 17.64.

[‡] *Crystal data*: [Mn₄^{II}A₄](ClO₄)₈, 120 K, triclinic, *P*Ī, *a* = 17.7576(12), *b* = 17.9133(12), *c* = 24.6470(15) Å, *α* = 80.381(1), *β* = 84.562(3), *γ* = 70.980(3)°, *V* = 7301.1(8) Å³, *Z* = 2, *D_c* = 1.564 g cm⁻³, *θ_{max}* = 14.06°, μ (0.42753 Å) = 0.312 mm⁻¹. 38752 collected reflections, 14971 unique reflections [5838 *I* > 2 σ (*I*)] were used for refinement. The final *R* values were *R* = 0.1155, *wR*² = 0.2765 [*I* > 2 σ (*I*)], *R* = 0.1393, *wR*² = 0.2902 (all data) for 2010 parameters and 361 restraints. The highest electron density on the final difference map was 1.266 e Å⁻³. CCDC reference number 207377. See http://www.rsc.org/suppdata/cc/b3/b303922f/ for crystallographic data in CIF or other electronic format.

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Spin Crossover in a Supramolecular Fe_4^{Π} [2 × 2] Grid Triggered by Temperature, Pressure, and Light^{**}

Esther Breuning, Mario Ruben, Jean-Marie Lehn,* Franz Renz, Yann Garcia, Vadim Ksenofontov, Philipp Gütlich,* Elina Wegelius, and Kari Rissanen

In memory of Oliver Kahn

The development of advanced materials and devices for nanotechnology requires systems that form switchable domains on the molecular or supramolecular level, so as to

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enable a highly efficient information storage.^[1] Towards this end, a promising and challenging field of research is the study of spin crossover (SC) compounds.^[2] The phenomenon of spin crossover between low-spin (LS) and high-spin (HS) states is one of the most appealing examples of molecular bistability.^[3, 4]

It has been shown that molecular systems of the $[2 \times 2]$ grid type with exactly four precisely located transition metal ions are accessible by self-organization.^[5, 6] With respect to potential addressability, such architectures can be ordered on surfaces in regularly packed domains of monolayers, and even single molecules can be manipulated by means of scanning tunneling microscopy (STM).^[7] The transition metal ions in $[2 \times 2]$ grid-like structures are situated in an octahedral ligand field. Introduction of sterically demanding substituents attenuates the ligand field strength to a magnitude that enables SC behavior for certain metal ions. Herein, we present the first triply switchable system, the Fe⁴₁ $[2 \times 2]$ grid **1**, in which SC can be triggered by temperature, light, and pressure.

 $[Fe_4L_4](ClO_4)_8$ (1) was synthesized by spontaneous assembly from the ligand 4,6-bis(2',2"-bipyrid-6'-yl)-2-phenyl-pyrimidine^[8] (L) and Fe(ClO₄)₂ × 6H₂O in acetonitrile at room temperature, followed by precipitation with diethyl ether. The composition of **1** was confirmed by FAB mass spectrometry and elemental analysis.



Indications of SC behavior in solution were first obtained in the course of ¹H NMR investigations (Figure 1). At 308 K, **1** exhibits the number of signals expected for a symmetrically coordinated ligand, in a range from $\delta = -20$ to 130, typical for paramagnetic HS species.^[9] Upon stepwise cooling to 228 K, several peaks between $\delta = 0$ and 10, that is the typical region for diamagnetic LS species, emerge at the expense of the paramagnetic peaks, ending up in a mainly diamagnetic situation.

The structure of **1** was determined by single-crystal X-ray diffraction at 293 K and 100 K (Figure 2).^[10] The investigation reveals a tetranuclear complex in which each of the Fe^{II} ions is in a pseudooctahedral arrangement with a pronounced axial distortion ($\Delta_{ax} = ca. -0.1$ Å). Each metal ion is surrounded by six nitrogen atoms arising from the pyrimidine and bipyridine units. Since the Fe–N bond lengths differ considerably between the HS and LS case ($\Delta d = 0.2 - 0.3$ Å), the averaged

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Figure 1. Variable-temperature ${}^{1}H$ NMR studies of 1 exhibiting the increase of LS fraction at the expense of the HS fraction on lowering the temperature (in [D₆]acetone/[D₆]acetonitrile).

bond lengths can be directly related to the actual spin state of each Fe^{II} ion. At room temperature, three of the Fe^{II} ions stay in the HS state (d(Fe-N) = 2.086(5) - 2.287(4) Å) with the

fourth exhibiting bond lengths intermediate between both states (d(Fe-N) = 1.977(5) - 2.162(4) Å). At 100 K, three of them are between the LS and HS state but closer to the LS state (d(Fe-N) = 1.895(6) - 2.117(5) Å), while the fourth remains in the HS state (d(Fe-N) = 2.116(6) - 2.282(5) Å). This decrease in bond lengths, which is significantly larger than the thermal contraction, indicates clearly a SC behavior from HS to LS for some Fe^{II} ions. The same space group $P\overline{1}$ for **1**, is retained at both temperatures; there is no crystallographic phase transition.

The magnetic properties of **1** are represented in Figure 3a in the form of the $\chi_M T/4$ versus *T* curve, in which χ_M is the molar magnetic susceptibility, corrected for diamagnetic con $z = -3578 \times 10^6$ cm³ mol⁻¹) using Pascal's con-

tributions ($\chi_D = -357.8 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$) using Pascal's constants, and *T* is the temperature.

At room temperature, $\chi_M T/4$ is equal to 2.5 cm³K mol⁻¹ and thus in the range of values expected for three HS Fe^{II} ions and one LS Fe^{II} ion, since the spin-only value for a Fe^{II} ion in the HS state (S = 2) is 3.0 cm³K mol⁻¹. On lowering the temperature, $\chi_M T/4$ progressively decreases reaching a value of 1.4 cm³K mol⁻¹ at 30 K; below this temperature, $\chi_M T/4$ drops down. This can be attributed to zero-field splitting. No hysteresis was observed.

We also investigated the magnetic properties of the BF₄⁻ salt of **1** under pressure (because of the hazard of explosion with perchlorate salts). Pressure dramatically affects the SC curve, decreasing the $\chi_M T/4$ values over the whole temperature range (e.g. by 0.5 cm³ K mol⁻¹ at 300 K and 8.4 kbar). This corresponds to a shift of the SC curve to higher temperatures as a result of the lower volume for the LS Fe^{II} ions.



Figure 2. Molecular structure of the cation of 1 at 293 K (anions and solvent molecules are omitted for clarity). The structure of 1 has also been determined at 100 K. The averaged Fe–N distances [Å]: 1) at 293 K: 2.19(1) (HS), 2.17(1) (HS), 2.07(1) (HS/LS), 2.17(1) (HS); 2) at 100 K: 2.20(1) (HS), 2.01(1) (LS/HS), 1.99(1) (LS/HS), 2.01(1) (LS/HS).



Figure 3. a) Calculated (circles) and experimental (squares) $\chi_M T/4$ versus T plots for a powder sample of **1** (calculated $\chi_M T/4$ values derived from molar fractions); b) HS (squares) and LS (points) molar fractions plotted versus T showing the thermally induced SC; c) LIESST (light-induced excited spin state trapping; irradiation at $\lambda = 514$ nm at 4.2 K) and LITH (permanent irradiation at $\lambda = 514$ nm under variation of temperature). All molar fractions are calculated from Mössbauer spectra.

The very gradual increase of $\chi_M T/4$ versus *T* suggests a practically noncooperative one-step SC situation with a residual HS fraction at low temperature.^[2] The Mössbauer effect, a microscopic tool, has been used to probe the spin and oxidation states of the metal ions (Figure 4).^[11] At 4.2 K, two doublets are found: the first one with an isomer shift of $\delta = 0.402(6) \text{ mm s}^{-1}$ (relative to α -iron) and a quadrupole splitting of 1.37(1) mm s⁻¹, is typical for Fe^{II} ions in the LS state, the second one with an isomer shift of $\delta = 1.090(8) \text{ mm s}^{-1}$ and a quadrupole splitting of 2.17(1) mm s⁻¹ typical for Fe^{II} ions in the HS state.^[11] Taking equal Lamb–Mössbauer factors for both spin states, the LS and HS molar fractions are



Figure 4. Selected ⁵⁷Fe Mössbauer spectra for **1** at various temperatures and after irradiation at $\lambda = 514$ nm at 4.2 K (LIESST).

approximately equal to the area fractions giving a population of 54 and 46%, respectively, at 4.2 K (Figure 3b). Upon increasing the temperature, the LS doublet loses intensity in favor of the HS doublet. At 300 K, the HS and LS states are observed in populations of 80 and 10%, respectively. This unambiguously indicates the occurrence of SC behavior. Above 193 K, an additional small signal appears, growing in intensity with increasing temperature. This could be attributed either to a new species, most likely Fe^{III} in the HS state, or it could be based on a texture effect,^[11] where the extra signal would result from the data reduction procedure assuming equal area fractions of the Fe^{II} HS doublet.^[12]

Compound 1 can also be switched by light (LIESST effect)^[13] as documented in the Mössbauer spectra in Figure 4. Irradiating the sample with green light ($\lambda = 514$ nm, 15 mW cm⁻²) at 4.2 K results in an increase of the population of the HS state from 46 to 70% (Figure 3 c). Switching back to the LS state with red light, that is the reverse LIESST effect,^[2] cannot be achieved because of the unfavorable position of the Fe^{II} LS MLCT bands.

Mössbauer spectra have also been recorded in the heating and cooling mode under permanent irradiation ($\lambda = 514$ nm, 15 mW cm⁻²) and revealed a light-induced thermal hysteresis (LITH,^[14] Figure 3c). The occurrence of the LITH effect implies the presence of cooperativity among the Fe^{II} centers. Therefore, the Boltzmann-shaped SC curve observed by magnetic susceptibility measurements (Figure 3a) is due to the macroscopic compensation between long-range (mainly intermolecular) and opposite directed short-range (mainly intramolecular) interactions. This indicates unambiguously intramolecular cooperativity. Therefore, the four Fe^{II} centers within the tetranuclear grid unit communicate and cannot display the same SC behavior. This excludes a single-step and implies a multistep SC process, which has been already discussed for two-step SC compounds.^[2] However, the multiple steps are not resolved macroscopically. This is attributed to the disorder of the anions and solvates around the tetranuclear grid cations, as indicated by the X-ray crystal structures, inasmuch as even the second HS Fe^{II} at 100 K is distributed over three coordination sites. This disorder contributes to a smooth SC curve, hiding the multistep character of the spin transition. We believe that this problem could be overcome by ordering the present system on a surface as a monolayer.^[7]

The present results show that, in addition to the potential addressability of the $[2 \times 2]$ grid system,^[7] this supramolecular entity can also be switched by several external perturbations. In particular, the Fe₄^{II} [2×2] grid **1** represents a unique prototype of a multiply switchable multilevel device presenting three magnetic levels (3HS/1LS, 2HS/2LS and 1HS/3LS) and driven by three different triggers (temperature, pressure, and light). Future work may allow improvements in the multistability of such systems and achieve further manipulations (e.g. applying an electric potential), in order to explore possible applications of $[2 \times 2]$ grid-type systems in information storage and nanotechnology.

Experimental Section

A solution of L^[8] (20.3 mg, 44 mmol) and Fe(ClO₄)₂·6H₂O (15.9 mg, 44 mmol) in acetonitrile (5 mL) was stirred at room temperature for 6 h. Compound **1** was isolated as a dark green solid by precipitation with diethyl ether in quantitative yield. For ⁵⁷Fe Mössbauer experiments, samples were enriched by 33 % of ⁵⁷Fe^{II}. The BF₄ salt of **1** was synthesised by the same procedure using Fe(BF₄)₂·6H₂O. The obtained product exhibits identical spectroscopic properties as **1**. ¹H NMR (200 MHz, [D₃]acetonitrile, 298 K): $\delta = 126.1, 67.6, 61.2, 55.8, 52.0, 47.1, 14.1, 9.2, 6.1, 0.3, -0.2, -8.4, -15.5;$ FAB-MS (NBA): *m/z*: 2776.7 [*M* - ClO₄]⁺; 2677.6 [*M* - 2ClO₄]⁺; 2578.6 [*M* - 3ClO₄]⁺; 2478.7 [*M* - 4ClO₄]⁺; 2378.7 [*M* - 5ClO₄]⁺; 2578.6 [*M* - 3ClO₄]⁺; 1388.8 [*M* - 2ClO₄]²⁺; 1289.3 [*M* - 3ClO₄]²⁺; 1283.8 [*M* - 4ClO₄]²⁺; 1189.4 [*M* - 5ClO₄]²⁺; 1248.8 [*M* - 4ClO₄]²⁺; 1276.7; elemental analysis calcd (%) for C₁₂₀H₁₀₆N₂₄Cl₈Fe₄O₄₅: C 46.33, H 3.43, N 10.80; found: C 46.54, H 3.72, N 10.41.

The magnetic measurements were carried out with a Foner susceptometer working in the 4.2-300 K temperature range. The applied magnetic field was 1 Tesla. A hydrostatic high-pressure cell with silicon oil as the pressure transmitting medium has been used. The pressure determination was achieved by using the known pressure dependence of a superconducting transition of an inner tin manometer.

Mössbauer spectra were recorded in transmission geometry with a Co/Rh source kept at room temperature and a conventional spectrometer operating in the constant-acceleration mode. The samples were sealed in a plexiglass sample holder and mounted in a helium-bath cryostat for temperature variation between 4.2 and 300 K. The spectra were fitted to Lorentzian-shaped lines using a nonlinear iterative minimization routine (MOSFUN). For the LIESST experiments, approximately 20 mg of the polycrystalline compound was placed in a disc-shaped polished PMMA container (ca. 3 cm² surface). The sample was irradiated at 4.2 K with an Ar-ion laser (514 nm, 15 mWcm⁻²) for 20 min within the cavity of the Mössbauer spectrometer.

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- [10] X-ray structural analysis of 1: A suitable dark green crystal (0.5 \times $0.4 \times 0.2 \text{ mm}$) of $[C_{120}H_{80}N_{24}Fe_4]^{8+} \cdot 8 \text{ClO}_4^{-} \cdot 9 \text{CH}_3\text{CN} \cdot 1.25 \text{H}_2\text{O}$ was obtained from acetonitrile-diisopropyl ether. The data were measured both at 293.0(2) K and 100.0(2) K using the same crystal. Both data were recorded with a Nonius Kappa CCD diffractometer using graphite-monochromated radiation [λ (MoK_{α}) = 0.71073 Å]. The data were processed with Denzo.^[15] $L_{\rm P}$ correction was applied. The absorption correction was made with SORTAV^[16]. Structure solution was done by direct methods^[17] and refinement against $F^{2,[18]}$ The hydrogen atoms were calculated at their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and were refined as riding atoms. Compound 1 at 293 K: triclinic, $P\bar{1}$, a = 17.7037(3), b = 18.4101(2), c = 25.0629(4) Å, a = 16.4101(2)85.7672(9), $\beta = 82.2308(7)$, $\gamma = 65.3290(8)^{\circ}$, V = 7353.5(2) Å³, Z = 2, $\rho_{\text{calcd}} = 1.473 \text{ g cm}^{-3}, \quad 2\theta_{\text{max}} = 55.84^{\circ}, \quad \mu(\text{Mo}_{\text{K}\alpha}) = 0.619 \text{ mm}^{-1}, \quad T_{\text{min}} = 0.619 \text{ mm}^{-1}$ 74.7%, $T_{\text{max}} = 88.6$ %. A total of 87837 collected reflections, 34383 unique reflections [15896 $I > 2\sigma(I)$] were used for refinement. The final R values were R = 0.102, $wR^2 = 0.251 [I > 2\sigma(I)]$, R = 0.213, $wR^2 = 0.314$ (all data) for 1898 parameters. A final difference map displayed the highest electron density of 1.02 e Å⁻³, which is located near to disordered ClO₄⁻ ions. Compound **1** at 100 K: triclinic, $P\overline{1}$, a =17.2936(3), b = 18.0917(3), c = 24.7836(5) Å, a = 85.1273(11), $\beta =$ 82.0435(12), $\gamma = 64.9006(9)^{\circ}$, $V = 6951.3(2) \text{ Å}^3$, Z = 2, $\rho_{\text{calcd}} = 1.558 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.84^{\circ}$, $\mu(\text{Mo}_{\text{Ka}}) = 0.655 \text{ mm}^{-1}$, $T_{\text{min}} = 73.5 \%$, $T_{\text{max}} = 88.0\%$. A total of 91012 collected reflections, 32258 unique reflections [19824 $I > 2\sigma(I)$] were used for refinement. The final R values were R = 0.1150, $wR^2 = 0.2770 [I > 2\sigma(I)]$, R = 0.1771, $wR^2 = 0.1771$ 0.3148 (all data) for 1905 parameters. A final difference map displayed the highest electron density of 2.37 e Å⁻³, which is located near to iron atoms, disordered ClO₄⁻ ions and acetonitrile molecules. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140266 and CCDC-140267. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Magneto-structural correlations in self-assembled spin-transition nano-architectures of the $[Fe_4^{II}L_4]^{n+}$ [2 × 2]-grid-type

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Abstract

The magnetism of a series of tetranuclear complexes of the $[Fe_4^{II}L_4](BF_4)_8 [2 \times 2]$ -grid-type was investigated, revealing the occurrence of spin-transition (ST) behavior within this class of compounds. The phenomenon depends directly on the nature of the substituent R¹ of the ligand L. All Fe^{II} ions in compounds with R¹ substituents favoring strong ligand fields (R¹ = H; OH) remain completely in the diamagnetic low-spin state. Only the complex bearing R¹ = Ph exhibits thermally induced ST behavior.

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Keywords: Supramolecular chemistry; Iron complexes of N ligands; Magnetic susceptibility; Spin transition

Among the accessible physical effects, the spin transition (ST) phenomenon of Fe^{II} ions is one of the perspective processes to enable molecular memory effects due to the concomitance of possible "write" (temperature, pressure, light) and "read" (magnetic, optical) parameters [1].

In a previous communication, a $[2 \times 2]$ grid-type Fe^{II}₄ complex (1 herein) has been described as the first tetranuclear compound exhibiting ST properties, generated by a consequent application of self-assembly on ST-systems [2].

Since self-assembled tetranuclear $[Fe_4^{II}L_4]^{n+}$ [2 × 2]grid-type species appeared to be a promising new class of ST compounds, a series of complexes $[Fe_4^{II}L_4](BF_4)_n$ **1–3** (**L** = **A**, n = 8; **B**⁻, n = 4; and **C**, n = 8) was synthesized and their magnetic properties were studied both in solution and in the solid state. Within the series of compounds **1–3** $[Fe_4^{II}L_4](BF_4)_n$, the coordination sphere and so the strength of the ligand field of the Fe^{II} ions was varied by changing the substituent **R**¹ in the 2-position of the pyrimidine of the incorporated ligands **L** (**L** = **A**, **B**, and **C** with **R**¹ = **H**, **O**⁻, and Ph; Scheme 1).

First evidence for a different magnetic behavior of the incorporated Fe^{II} ions in compounds 1–3 was found in the room temperature ¹H-NMR spectra: complexes 1 and 2 exhibit only signals in the region expected for diamagnetic Fe^{II} low spin (LS) complexes ($\delta = 0$ –10 ppm). In contrast, complex 3 shows peaks spread across a wide range ($\delta = -20$ to 80 ppm) indicating the

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Fig. 1. 1 H-NMR spectra of compounds 1 (top) and 3 (bottom) in [D₃]-acetonitrile (asterisk).

presence of paramagnetic species (Fig. 1). This strong shift of peaks in the proton NMR spectra is caused by the high local field typical for incorporated Fe^{II} high spin (HS) ions [3]. Furthermore, the absence of coupling patterns can be attributed to broadening by increased relaxation rates near the strong polar fields of the Fe^{II}(HS) ions.

In solid state, the X-ray investigations of both complexes **2** and **3**, show pseudooctahedral N₆-surroundings for all Fe^{II}-ions (Fig. 2). The averaged Fe–N bond lengths can be used as an indicator for the spin state, since the population of the anti-bonding e_g^* orbitals in the HS case causes an elongation of the bond length by ca. 0.2 Å [3]. Thus, complex **2** shows at 120 K four identical Fe^{II}–N bond distances of d (Fe^{II}–N) = 1.95 Å, close to those characteristic of the Fe^{II}(LS) state [3].² Complex **3** exhibits at low



Fig. 2. Top (left) and side (right) view of the single crystal X-ray investigation of complex 2 (anions, solvent molecules, and hydrogen atoms are omitted for clarity).



Fig. 3. Magnetic susceptibility versus temperature plot of complex 3 at two different pressures.

temperature also three Fe^{II} -ions with LS characteristics, while the fourth one remains at bond lengths typically observed for the $Fe^{II}(HS)$ state. Following the same argumentation, we can conclude that complex **3** presents at 293 K a situation pointing to three HS and one LS Fe^{II} sites.

The solid state magnetic properties of the complexes 1–3 were examined directly by magnetic susceptibility measurements. The diamagnetic compounds 1 and 2 did not show any magnetic moment. The magnetic properties of 3 are represented in Fig. 3 in form of the $\chi_M T/4$ versus *T* curve, χ_M being the molar magnetic susceptibility, corrected for diamagnetic contributions ($\chi_D = -357.8 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$) using Pascal's constants, and *T* the temperature.

At room temperature, $\chi_{\rm M} T/4$ is equal to 2.9 cm³ K mol⁻¹ and thus in the range of values expected for four HS Fe^{II} ions, since the spin-only value for a Fe^{II} ion in the HS state (S = 2) is 3.0 cm³ K mol⁻¹. On lowering the temperature, $\chi_{\rm M} T/4$ progressively decreases reaching a value of 1.4 cm³ K mol⁻¹ at

²Crystallographic data under CCDC reference number: 213092.

30 K; below this temperature, $\chi_M T/4$ drops down. This can be attributed to zero-field splitting [4]. No hysteresis was detected, which is in line with the very gradual ST apparently arising from very weak cooperative interactions [5].

We also investigated the magnetic properties of **3** under pressure. Pressure dramatically affects the SC curve, decreasing the $\chi_{\rm M}T/4$ values over the whole temperature range (e.g. by 0.5 cm³K mol⁻¹ at 300 K and 8.4 kbar). This corresponds to a shift of the SC curve to higher temperatures as a result of the lower volume for the LS Fe^{II} ions.

The occurrence of ST in $[2 \times 2]$ grid-like complexes of the type $[Fe_4^{II}L_4](BF_4)_n$ depends directly on the nature of the substituent R^1 in the 2-position of the ligand L. Compounds 1 and 2 with substituents in this position favoring strong ligand fields $(R^1 = H; O^-)$ remain completely in the LS state at all temperatures studied. Only the complex 3 bearing a substituent which attenuates the ligand field sufficiently by steric effects ($\mathbb{R}^1 = \mathbb{P}h$), exhibits, although incomplete, temperature triggered spin transition.

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Supramolecular Spintronic Devices: Spin Transitions and Magnetostructural Correlations in $[Fe_4{}^{II}L_4]^{8+}$ [2 × 2]-Grid-Type Complexes

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Abstract: The magnetism of a series of tetranuclear complexes of the $[Fe^{II}_{4}L_{4}](X)_{8}$ [2 × 2]-grid-type was investigated, revealing the occurrence of spin transition behavior within this class of compounds. The phenomenon depends directly on the nature of the substituent R^{1} in the 2-position on the central pyrimidine group of the ligand L. All Fe^{II} ions in compounds with R^{1} substitu-

ents favoring strong ligand fields (R^1 = H; OH) remain completely in the diamagnetic low-spin state. Only complexes bearing R^1 substituents attenuat-

Keywords: iron • magnetic susceptibility • Mössbauer spectroscopy • N ligands • spin transition • supramolecular chemistry ing the ligand field by steric (and to a lesser extent electronic) effects (R^1 = Me; Ph) exhibit spin transition behavior triggered by temperature. In general, gradual and incomplete transitions without hysteresis were observed for magnetically active complexes. The systems described provide approaches to the development of (supra)molecular spin-tronics.

Introduction

The next frontier in data storage, just before entering the realm of the quantum effects, lies in the nanodomain of the molecule. Molecular systems, which are capable of undergoing externally triggered transitions between two or more different states have attracted increasing interest during the last decades in view of their potential for future applications.^[1] Such bi- or multistability at the molecular level, as required for high density information storage devices, might be achieved by exploitation of changes in intrinsic molecular properties, such as conformational, spin, magnetic, electronic,

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or photophysical states. Among the feasible effects, the spin transition (ST) phenomenon of Fe^{II} ions is one of the perspective processes to enable molecular memory effects due to the concomitance of possible "write" (temperature, pressure, light) and "read" (magnetic, optical) parameters.^[2a] Such features provide access to the development of (supra)-molecular spintronics.^[3]

So far, predominantly mononuclear^[2] and only some binuclear,^[4a] one trinuclear,^[4b] and one pseudo-pentanuclear^[4c] molecular Fe^{II} spin transition compounds have been investigated. Most investigations have concerned the influence of weak intermolecular interactions (hydrogen bonding; $\pi - \pi$ stacking) on the cooperativity of the spin transition processes in the solid state. On the other hand, polymeric Fe^{II} compounds involving 1,2,4-triazole and 1,2,3,4-tetrazole ligands have been subject of several investigations.^[5]

In a previous communication, a $[2 \times 2]$ grid-type Fe₄^{II} complex (**4** herein) was described as the first tetranuclear compound exhibiting ST properties,^[6] generated by a consequent application of self-assembly on ST systems.

Self-assembly processes open the way to generate functional supramolecular devices by spontaneous, but controlled buildup from their components.^[7] Such self-fabrication techniques are of particular interest, due to the possibility of bypassing tedious nanofabrication and nanomanipulation procedures.^[8]

Furthermore, previous publications reported on particular magnetic and electrochemical properties of analogous $[Co_4{}^{II}L_4]^{8+}$ [2 × 2] grid species.^[9, 10]

Since self-assembled tetranuclear $[Fe_4^{II}L_4]^{8+}$ [2 × 2] gridtype species appeared to be a promising new class of ST compounds, a series of complexes $[Fe_4^{II}L_4](X)_8 \mathbf{1-8} (L=\mathbf{A}-\mathbf{H}; X=\mathbf{PF}_6^-, \mathbf{BF}_4^- \text{ or } ClO_4^-;$ see Scheme 1) was synthesized and their ST properties were studied both in solution and in the solid state. ¹H NMR and UV/Vis techniques were used in solution, while magnetic susceptibility, X-ray diffraction and Mössbauer investigations were carried out in the solid state to reveal the influence of the nature of ligand L on the magnetic behavior of the complexes.



Scheme 1. Ligands A-H and $[2 \times 2]$ grid complexes 1-8.

In a first series of compounds (compounds 1-5 [Fe₄^{II}L₄](X)₈), the coordination sphere of the [2 × 2] grid-type complexes was varied by changing the substituent R¹ in the 2-position of the pyrimidine of the incorporated ligands L (L=A-E with R¹=H, OH, Me, Ph, *p*-PhNMe₂). In the

Abstract in French: Une série de complexes 1-8 de type grille $[2 \times 2]$, $[Fe^{II}_{4}L_{4}](X)_{8}$, a été synthétisée et leurs propriétés magnétiques ont été étudiées, révélant des phénomènes de transition de spin pour les ions Fe^{II} dans ces complexes. Ce comportement est directement dépendant de la nature du substituent R^1 en position 2 sur le noyau pyrimidine du ligand L. Tous les composés avec un substituent R¹ donnant champ de ligand fort ($R^1 = H$, OH) restent complètement dans l'état de spin bas. Les complexes n'ayant que de substituents qui affaiblissent le champ de ligand par des effets stériques (ou dans une moindre mesure électroniques) ($R^{l} = Me$, Ph) montrent une transition de spin induite par la température. Généralement, des transitions très graduelles et incomplètes ne présentant aucune hystérésis, ont été observées pour les composés magnétiquement actifs. Les systèmes décrits représentent une voie d'accès au développement d'une spintronique moléculaire.

second series of compounds, the ligands were additionally altered at the periphery. In complexes 6 and 7 S-*n*-propyl groups were introduced in the 4'-position of the ligands (complex 6 [Fe₄^{II}F₄](PF₆)₈;^[11] and complex 7 [Fe₄^{II}G₄](ClO₄)₈). In complex 8, [Fe₄^{II}H₄](BF₄)₈, the peripheral pyridyl ring of the ligand backbone was exchanged by a 5"-aminopyrazin-2"yl group yielding ligand H (Scheme 1).

Results

Synthesis: The synthesis of the ligands has been described elsewhere (see Experimental Section). The $[Fe_4{}^{II}L_4]^{8+}$ $[2\times2]$ grid-type complexes 1-8 (Scheme 1) were generated by selfassembly from the corresponding metal salt and ligand in acetonitrile or methanol solution. For the complexes 1, 2, and $6^{[11]}$ even rather long reaction times (2-3 days under reflux, in the case of 2 under deprotonation of ligand B) do not drive the self-assembly process to completion. Therefore, in these cases, further purification steps became necessary (1, 6: column chromatography; 2: recrystallization) and delivered the pure compounds in modest yields (1: 8%; 2: 23%; 6: 18%^[11]). On the other hand, the self-assembly of complexes 3-5, 7, and 8 was accomplished after only 2-6h at room temperature giving quantitative yields without further purification. In these cases, the crude products showed correct analytical data and were directly used in the subsequent investigations.

¹H NMR spectroscopic analysis: At room temperature, solutions of Fe₄^{II} complexes 1, 2, and 6 give rise to the usual diamagnetic ¹H NMR spectra with typical shifts between $\delta = 0$ and 10 ppm. All other complexes (3-5, 7, and 8) exhibit shifts over a wide range, between $\delta = -20$ and +150 ppm (so-called paramagnetically shifted spectra). Characteristic spectra for both cases are depicted in Figure 1 for complexes 1 and 3. The number of signals observed coincides in all cases with the expected number of signals of the respective, symmetrically coordinated, ligands. No coupling patterns have been observed for the paramagnetic shifted peaks.

On the stepwise decrease of the temperature of the solutions of complexes exhibiting paramagnetic behavior, new peaks between $\delta = 0$ and 10 ppm emerge at the expense of the paramagnetically shifted peaks finally reaching an almost completely diamagnetic situation at low temperatures (228 K). Temperature-dependent ¹H spectra of complex **4** [Fe₄^{II}**D**₄](ClO₄)₈ were described earlier in a temperature range from 308 K to 228 K.^[6]

UV/Vis spectroscopy: The absorption spectra of compounds 1–8 in acetonitrile show two strong absorption bands in the UV region and, in addition, several weak and broad absorption bands in the visible region (Figure 2). However, the most remarkable feature is that all compounds with a R^1 =H or OH (1, 2, and 6) exhibit absorption bands in the visible range with absorption coefficients $\varepsilon = 2.5 - 3.5 \times 10^4 \text{M}^{-1} \text{ cm}^{-1}$ superior to those of complexes with R^1 =Me, Ph, or *p*-Ph-NMe₂ (3–5, 7, and 8, with $\varepsilon = 0.5 - 1.8 \times 10^4 \text{M}^{-1} \text{ cm}^{-1}$) at room temperature.

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Figure 1. ¹H NMR spectra in CD_3CN of complex **1** (bottom) and of complex **3** (top, the asterisk marks the solvent signal).



Figure 2. a) UV/Vis spectra of complex **4** in acetonitrile between 0° C and 60° C; b) extinction coefficient ε as a function of the temperature.

Increasing the temperature of the solutions of complexes 3-5 and 7 and 8 in acetonitrile resulted in a strong decrease of the corresponding absorption band, while the intensity remained completely unchanged for compounds 1, 2, and 6. As an example, Figure 2 depicts the temperature-dependent behavior of complex 4, $[Fe_4^{II}D_4](CIO_4)_8$, for which an almost linear change in intensity with temperature is observed in the range between 273 and 333 K.

Single-crystal X-ray investigations: Crystals of compound **7**, $[Fe_4^{II}G_4](ClO_4)_8$, were grown by diffusion of diisopropyl ether into a solution of the complex in acetonitrile. The structure of **7** was determined at 120 K and yielded a monoclinic space group $P2_1/c$. It was not possible, however, to use the same crystal for data collection at 298 K, apparently due to a phase transition.

The investigation reveals a tetranuclear complex with four inequivalent Fe^{II} ions in a pseudo-octahedral N₆ environment. The ligands are found in an almost ideal alignment in perpendicular and parallel directions (Figure 3). The distance between the pyrimidine rings of two parallel ligands averages 7.0 Å, whereby the peripheral pyridine rings of the ligands are slightly bent inside. The substituents R¹ are perpendicularly twisted with respect to the pyrimidine rings and are sandwiched between the two opposite ligands in a distance of d = 3.5 Å. This distance is an argument for an effective π -stacking between the respective pyridine groups of the ligands and the R¹ = phenyl substituents.

All Fe–N bond lengths are different at each Fe^{II} ion, generally exhibiting longer bond lengths to the less basic pyrimidine nitrogen atoms than to the pyridine nitrogen sites. The internal pyridine nitrogen atoms present slightly shorter bonds than their peripheral equivalents. These differences in bond lengths result in an overall axial distortion of the coordination N₆ octahedron ($\Delta_{ax} \approx -0.1$ Å).

The single X-ray investigation of $[Fe_4^{II}D_4](CIO_4)_8$ (4) was reported previously for temperatures of 100 K and 298 K.^[6] The same space group, $P\bar{1}$, was retained at both temperatures; no crystallographic phase transition was observed. Complex 4 presented at both temperatures structural features similar to those obtained for complex 7 (rectangular shape, sandwiched phenyl substituent, π -stacking).

The average Fe–N bond lengths of **7** at 120 K show that two of the Fe^{II} ions have distances of about d=2.15 and 2.16 Å, while the other two are considerably shorter (d=2.07 and 1.99 Å, Table 1).

In comparison, the average Fe–N bond lengths of $4^{[6]}$ present the following picture. At low temperature, three Fe^{II} ions exhibit shorter bond lengths of d = 1.99 - 2.01 Å, while the fourth remains at a longer distance of d = 2.20 Å. Increasing the temperature of complex 4 to room temperature reverses the situation: three of the Fe^{II} ions exhibit now longer distances of d = 2.17 - 2.19 Å, while the fourth remains with a short bond distance of d = 2.07 Å.

Magnetic susceptibility measurements: Complexes 1, 2, and 6 remain diamagnetic over the whole temperature range between 4 K and 300 K, while for the other complexes investigated, the magnetic moments change with the temper-





Figure 3. Top (a) and side view (b) of the single-crystal X-ray investigation of complex 7; some of the S-*n*-propyl chains are disordered (anions, solvent molecules, and hydrogen atoms are omitted for clarity).

ature. The magnetic properties of two series of these complexes are represented in Figure 4 and 5 in the form of $\chi_M T/4$ versus *T* plots. $\chi_M T/4$ refers to the molar magnetic susceptibility (χ_M) times temperature (T) normalized to one Fe^{II} ion and corrected for diamagnetic contributions, $\chi_D = -357.8 \times 10^6 \text{ cm}^3 \text{ mol}^{-1}$ using Pascal's constants.^[12]

All magnetic plots present gradual slopes without hysteresis loops. Another common feature is the strong drop of the $\chi_M T/4$ values for all magnetic curves below 30 K.

In the first series of complexes 3-5, the substituent R^1 was varied from methyl via phenyl to *para*-dimethylaminophenyl. This results in similar plot shapes but different maxima of the susceptibility at room temperature (Figure 4).

Table 1. Average Fe–N bond lengths in Å for the perchlorate salts of **4** (at 173 K and 293 K) and of **7** (at 120 K).

	4 ^[6] 293 K	4 ^[6] 173 K	7 120 K
Fe1-N	2.19	2.20	2.164(5)
Fe2-N	2.17	2.01	2.148(5)
Fe3–N	2.07	1.99	2.067(6)
Fe4-N	2.17	2.01	1.986(6)

In a second series of the complexes 4, 7, and 8 the pyrimidine substituent was maintained (R^1 =Ph), while the peripheral substitution pattern (4: R^2 =H; 7: R^2 =SⁿPr; 8: introduction of a 5"-aminopyrazin-2"yl ring) was varied. The ligand variations modified the shapes of the magnetic susceptibilities versus temperature plots, while the maxima at room temperature remained relatively unchanged (Figure 5).

Mössbauer spectroscopy: The Mössbauer effect, a microscopic tool, was used to probe the spin states and oxidation states of the metal ions.^[13] Complex **6**, $[Fe_4^{11}F_4](PF_6)_8$, exhibits a doublet with an isomer shift $\delta = 0.178$ (0.093) mm s⁻¹ (relative to Fe/Rh) and a quadrupole splitting of 1.197 (1.173) mm s⁻¹ shown at 4.2 K (300 K), which remains constant over all the temperature range from 10 K to 300 K (Figure 6a). An additional small signal arises at 330 K from an impurity in the detector window (10 % at 300 K).

The same investigation using complex **4**, $[Fe_4^{II}D_4](CIO_4)_8$, resulted in the observation of two doublets at 4.2 K: one with an isomer shift $\delta = 0.402(6) \text{ mm s}^{-1}$ and a quadrupole splitting of 1.37(1) mm s⁻¹, and a second with an isomer shift of $\delta =$ 1.090(8) mm s⁻¹ and a quadrupole splitting of 2.17(1) mms⁻¹ (Figure 6b). Taking equal Lamb – Mössbauer factors for both signals, the area fraction of these signals is 54 and 46%, respectively. Upon increasing the temperature, the first doublet loses intensity in favor of the second doublet, yielding



Figure 4. $\chi_M T/4$ versus T plots of complexes 3–5: Influence of the variation of the substituent R¹ (R¹ = Me, Ph, p-PhNMe₂) on the magnetism.

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Figure 5. $\chi_M T/4$ versus *T* plots of complexes **4**, **7**, and **8**: Variation of the peripheral substituents of the ligands (maintaining substituent $R^1 = Ph$).



Figure 6. Mössbauer spectra of a) 6 and b) 4 at various temperatures.

a 10 to 80% ratio at 300 K. As also found for 6, above 193 K an additional small signal emerges due to impurity in the detector window (10% at 300 K).

Discussion

The characteristics observed during the self-assembly process subdivide the complexes 1-8 into two classes of compounds. All complexes with $R^1 = H$ or OH (1, 2, and 6) show slow formation kinetics and result in low yields. In contrast, all complexes with $R^1 = Me$, Ph, or *p*-PhNMe₂ undergo selfassembly in a short time with quantitative yields of the respective products 3-5, 7, and 8. Clearly, the substituent R^1 close to the coordinating pyrimidine nitrogen donor atoms plays a predominant role in the kinetics of the self-assembly process, while changes in other, more peripheral, ligand positions influence the reaction parameters to a much lesser extent.

As known from other Fe^{II} -ligand systems, the introduction of sterically demanding substituents in the neighboring position of a coordinating nitrogen provokes the (partial) transition of Fe^{II} ions from the low-spin ground state into the high-spin state (vide infra).^[14, 15] The differences in reaction times and yields of the self-assembly processes may be related to the fact that the kinetics of ligand exchange of Fe^{II} ions in the low-spin (LS; $t_{2g}^6 e_g^0$) and high-spin (HS; $t_{2g}^4 e_g^2$) state differ markedly. Similar observations were reported on Fe^{II} ions in the gas phase, but have not yet been described for Fe^{II} ions in solution.^[16] It is known from ligand field theory, that the "closed shell" Fe^{II}(LS) state is kinetically more inert than the "open shell" HS state, thus leading to slower ligand exchange. As reversibility of the bond formation is essential for the self-assembly process, the formation of the final [2 × 2] grid structure is inhibited, resulting in slow and incomplete reactions. The introduction of bulky R¹ substituents results in an "open shell" HS configuration at reaction temperature by attenuation of the ligand field and thus drives the selfassembly process to completion in much shorter times.

All ¹H NMR spectra illustrate the formation of highly symmetric structures in agreement with the proposed $[2 \times 2]$ grid-like motif. The number of signals, in combination with the composition of the complexes obtained by mass spectroscopy, elemental analysis and X-ray investigations, allows the

unambiguous assignment of the $[2 \times 2]$ grid-type nature for both dia- and paramagnetic complexes.

Figure 1 illustrates the effect of incorporation of Fe^{II}(LS) or Fe^{II}(HS) ions on the room-temperature ¹H NMR spectra: all complexes (**1**, **2**, and **6**) with Fe^{II}(LS) ions exhibit only signals in a region expected for diamagnetic complexes ($\delta =$ 0-10 ppm). In contrast, those of the paramagnetic complexes (**3**–**5**, **7**, and **8**), show peaks spread across a wide range ($\delta = -20-180$ ppm). The strong shift of peaks in the proton NMR spectra is caused by the high local field typical for paramagnetic Fe^{II}(HS) ions.^[17] Furthermore, the absence of coupling patterns can be attributed to broadening by increased relaxation rates

near the strong polar fields of the Fe^{II}(HS) ions. Because of these two features, non-diagnostic shifts and absence of any coupling patterns, an assignment of the peaks was only achieved for some of the signals by cross comparison of the differently substituted complexes 3-5, 7, and 8, however, not conclusively and completely for all signals.

Temperature-dependent ¹H NMR investigations confirmed the proposed spin transition behavior of paramagnetically shifted complexes in solution.^[6] Upon stepwise cooling from 308 to 208 K, the paramagnetically shifted peaks are first broadened, later disappearing in favor of new signals found in the "diamagnetic" region of the spectrum. This process was proven to be completely reversible. Thus, in solution the course of the spin transition can be described by a Boltzmann approach with a temperature-dependent distribution over the HS and LS states.

The room-temperature electronic spectra of all compounds **1–8** show qualitatively similar features with two main transitions bands in the UV and two in the visible region. The two transitions in the UV region can be attributed to ligand-centered $\pi - \pi^*$ transitions of the pyridine and the pyrimidine groups. In the visible region, the two distinct maxima coincide with the Fe^{II}(LS)–pyridine MLCT band, as

also observed in $[Fe(tpy)_2](PF_6)_2$ ($\lambda_{max} = 518 \text{ nm}$).^[18] The Fe^{II}(LS) – pyrimidine MLCT transition is found at significantly longer wavelengths, since the pyrimidine LUMO is of lower energy than the pyridine LUMO, such that the respective MLCT has a smaller band gap.

The subdivision of the investigated compounds into diaand paramagnetic compounds is also mirrored by the absorption coefficients derived from the MLCT bands. All diamagnetic complexes (1, 2, and 6) show values close to the sum of those of four mononuclear $[Fe(tpy)_2]^{2+}$ segments ($\varepsilon =$ 9200 M⁻¹ cm⁻¹).^[18] In contrast, all paramagnetic compounds exhibit dramatically decreased absorption coefficients at room temperature. This can be explained by the involvement of occupied antibonding e* orbitals in the Fe^{II}(HS) state, which leads to elongated Fe-N bonds and reduced overlap integrals and consequently to very weak or undetectable MLCTs under standard conditions.^[19] Evidently, the observed intensities of the MLCT bands originate almost exclusively from Fe^{II}(LS) to ligand transitions. Thus, the comparison of the absorption coefficients of dia- and paramagnetic complexes gives already a first rough estimate of the ratio of $Fe^{II}(LS)$ and (HS) ions at room temperature in solution.

In addition, as shown for compound **4** in Figure 2, the absorption coefficients of the paramagnetic complexes decrease almost linearly with increasing temperature, thus indicating the transformation of visible light-absorbing Fe^{II} (LS) ions into "colorless" Fe^{II} (HS) ions.

The X-ray investigations of both complexes $4^{[6]}$ and 7, show pseudooctahedral N₆ surroundings for all Fe^{II} ions. All four ions are crystallographically inequivalent in each structure and exhibit very different Fe–N bond lengths. The Fe–N bond lengths do not only vary considerably between the four Fe^{II} ions within one complex, but also for the respective six bonds around each of the four coordination centers. These deviations are due to the differences in π -basicity of the pyridine and of the pyrimidine nitrogen atoms on the one hand and due to small distortions originating from the electronic structure of the d⁶ HS systems on the other hand.^[20]

The average Fe–N bond lengths can be used as an indicator for the spin state, since the population of the antibonding e_g^* orbitals in the HS case causes an elongation of the bond length by about 0.2 Å.^[21] Thus, at 100 K in complex **4** three of the four metal ions show bond lengths close to those characteristic of the Fe^{II}(LS) state, while the fourth remains at bond lengths typically observed for the Fe^{II}(HS) state.^[6] Following the same argumentation, we can conclude that complex **7** presents at 120 K a situation pointing to two HS and one LS Fe^{II} sites with a last one in between (d(Fe–N) = 2.06 Å). The latter can be interpreted by the occurrence of disorder over the sites within the averaging of the bond lengths over the coherence wavelength.

At 298 K, the crystal structure of **4** indicates that three of the Fe^{II} ions are in a HS situation, while the fourth exhibits once more a bond length apparently between the LS and HS state.^[6] The differences in the average bond lengths in **4** and **7** at low temperatures as well as the bond length change on increasing the temperature in **4** indicate clearly a spin transition behavior of the paramagnetic complexes in the solid state.

The solid-state magnetic properties of the present complexes were examined directly by magnetic susceptibility measurements. The paramagnetic complexes 3-5, 7, and 8 were studied in two different ligand variation series, while the compounds 1, 2, and 6 are diamagnetic. In general, all paramagnetic complexes present very gradual and incomplete spin transitions with a sharp decrease of the magnetic moment below 30 K due to the zero-field splitting of the Fe^{II}(HS) ion.^[22] No hysteresis was detected, which is in line with the very gradual spin transition apparently arising from very weak cooperative interactions.^[2]

In the first series 3-5, the substitution of R¹ resulted in very similarly shaped magnetic curves, but with different maximum values of susceptibilities $\chi_M T/4$ at room temperature. In the case of compound **3** (R = methyl) a value of $\chi_M T/4 = 1.5 \text{ cm}^3 \text{K} \text{ mol}^{-1}$ indicates a magnetic situation close to the presence of 2LS/2HS in one molecule, while compounds **4** and **5** exhibit room temperature $\chi_M T$ values closer to a 1LS/3HS situation ($\chi_M T/4 = 1.9$ and 2.5 cm³K mol⁻¹).

The second series (4, 7, and 8), where R^1 = phenyl is conserved but the peripheral ligand sphere varies, yields slightly higher $\chi_M T$ values at room temperature (close to a 1LS/3HS situation for 4 and 8 and a 2LS/2HS for 7), but shows clear differences in the change of $\chi_M T$ with temperature. Complex 8, which may undergo intermolecular hydrogenbonding interactions, shows the biggest $\chi_M T$ values and the smallest slope of all investigated compounds within the temperature range studied. On the contrary, compound 4 displays a more structured progression, while complex 7 presents a pronounced magnetic plateau up to 150 K and a small, but continuous slope at temperatures above 150 K. However, the highest experimental $\chi_M T$ values in both series remain below the theoretical spin-only value of a Fe^{II} ion in the high spin state ($\chi_M T/4 = 3.2 \text{ cm}^3 \text{ K mol}^{-1}$).

The Mössbauer spectra were investigated for one diamagnetic and one paramagnetic compound as typical examples. Compound **6** shows a doublet of $Fe^{II}(LS)$ at all temperatures investigated. On the other hand, compound **4** presents two doublets at T=4.2 K with characteristics typical for $Fe^{II}(LS)$ (small isomeric shift and small quadrupole splitting) and $Fe^{II}(HS)$ (large isomeric shift and large quadrupole splitting) under the given symmetric environments. The low-temperature spectrum accounts for a 3LS/1HS situation, while at high temperature the reverse situation is observed. This confirms once more a thermally induced spin transition for the paramagnetic compounds.

Conclusion

The occurrence of spin transition in $[2 \times 2]$ grid-like complexes of the type $[Fe^{II}_{4}L_{4}](A)_{8}$ depends directly on the nature of the substituent R¹ in the 2-position of the ligand L. All compounds with substituents in this position favoring strong ligand fields (R¹=H; OH) remain completely in the LS state at all temperatures studied. Only complexes bearing substituents which attenuate the ligand field by steric (and to lesser extent electronic) effects (R¹=Me; Ph), exhibit, although incomplete, temperature triggered spin transition.

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The magnetic behavior was characterized in solution by ¹H NMR and UV/Vis spectroscopy and in the solid state by X-ray, magnetic susceptibility, and Mössbauer measurements. Very gradual and incomplete transitions without hysteresis seem to be typical for all investigated, magnetically active compounds of the $[Fe^{II}_{4}L_{4}](X)_{8} [2 \times 2]$ grid-type. The presence of the substituent $R^{1} = Ph$ resulted in the most complete transition and further substitutions at the phenyl ring or in the 4'-position of the ligand altered the spin transition behavior only marginally. Improving the intermolecular interaction between the tetranuclear centers by introduction of hydrogen bonding between the grid units increased the HS fraction over the whole temperature range, although the spin transition remained very gradual and incomplete.

The question of cooperativity within and between the molecular building blocks is being investigated. Moreover, further work is being directed toward the construction of larger functional architectures using grid-like building blocks in extended hierarchic self-assembly processes.

In a farther-reaching perspective, architectures presenting spin state properties that may be switched by external triggers represent entries toward (supra)molecular spintronics.^[3]

Experimental Section

Magnetic measurements: The magnetic measurements were carried out with a Foner susceptometer and a SQUID Magnetometer (Quantum Design) working in the 4.2-300 K temperature range. The applied magnetic field was 1 T.

Mössbauer spectra: Mössbauer spectra were recorded in transmission geometry with a Co/Rh source kept at room temperature and a conventional spectrometer operating in the constant-acceleration mode. The samples were sealed in a plexiglass sample holder and mounted in a heliumbath cryostat for temperature variation between 4.2 and 300 K. The spectra were fitted to Lorentzian-shaped lines using a nonlinear iterative minimisation routine (MOSFUN).

X-ray structural analysis of complex 7: A suitable pine-green prism ($0.02 \times$ $0.02\times 0.04~mm)$ of $[C_{144}H_{128}N_{24}S_8Fe_4]^{8+}\cdot 8\,ClO_4^{-}\cdot 3\,CH_3CN\cdot 5\,H_2O$ was obtained from acetonitrile-diisopropyl ether. The data were recorded at 120.0(2) K on Beamline ID11 at the ESRF. Phi rotation images (1s per frame) were recorded with a Bruker Smart 6500 camera and a Si(111) monochromated wavelength of 0.45085 Å. The data were integrated with the Bruker data reduction suite Saint and the absorption correction applied via SADABS. Structure solution was performed by direct methods $(SHELXS)^{[23]}$ and refinement against F^2 (SHELXL).^[24] The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and were refined as riding atoms. Due to the poor diffracting power of the crystal and the consequent low number of strong observations, geometric constraints were applied in order to keep the data/parameter ratio acceptable. Many of the thiol side chains and one of the perchlorate ions were disordered between different sites.

Complex 7: (at 120 K) monoclinic, $P2_1/c$, a = 26.266(2), b = 19.930(2), c = 33.801(4) Å, $\beta = 110.378(5)^\circ$, V = 16587(3) Å³, Z = 4, $\rho_{calcd} = 1.344$ g cm⁻³, $2\theta_{max} = 22.4^\circ$, $\mu(0.45085$ Å) = 0.317 mm⁻¹. A total of 38325 collected reflections, 10188 unique reflections [5838 with $I > 2\sigma(I)$] were used for refinement. The final *R* values were R = 0.121, $wR^2 = 0.325$ [$I > 2\sigma(I)$], R = 0.187, $wR^2 = 0.364$ (all data) for 1294 parameters and 2249 restraints. The highest electron density on the final difference map was 0.671 e Å⁻³.

CCDC-205093 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033; or deposit@ccdc.cam.uk).

Synthesis

General: All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. The following solvents were distilled prior to use: tetrahydrofuran (THF) and diethyl ether from sodium and benzophenone, and dimethyl sulfoxide (DMSO) from calcium hydride under argon. All organic solutions were routinely dried over magnesium sulfate or sodium sulfate and solvents were removed under vacuum using a rotary evaporator. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 spectrometer at 200 MHz and 50 MHz, respectively. Flash chromatography was performed using neutral alumina (activity 2). FAB mass spectra were performed on a Fisons TRIO-2000 (Manchester) and a Micromass AUTOSPEC-M-HF spectrometer using 3-nitrobenzylic alcohol as matrix. Microanalyses were carried out by the Service de Microanalyse, Faculté de Chimie, Strasbourg. Melting points were measured on a digital electrothermal apparatus and are uncorrected.

Ligands: The synthesis of ligands $\mathbf{A}_{2}^{[25]} \mathbf{C}_{25}^{[26]} \mathbf{D}_{27}^{[27]} \mathbf{E}_{27}^{[11]} \mathbf{G}_{27}^{[10b]}$ and $\mathbf{H}^{[28]}$ is described elsewhere. Ligand **B** was synthesized by using Stille-type coupling procedures following the reactions depicted in Scheme 2.



Scheme 2. Reaction scheme for the synthesis of ligand **B**: i) $[Pd(PPh_3)_4]$ (cat.), toluene; ii) NaOBn, BnOH; iii) excess CF₃SO₃H, toluene.

6-(Tributylstannyl)2,2'-bipyridine^[26](970 mg, 2.1 mmol), 2,4,6,-trichloropyrimidine (200 mg, 1.09 mmol), and $[Pd(PPh_3)_4]$ (153 mg, 0.22 mmol) were combined in DMF (5 mL), flushed with argon, and heated under reflux for 48 h. The solvent was evaporated and the resulting brown crude material was washed with methanol several times. The product 4,6bis(2',2"-bipyrid-6'-yl)-2-chloropyrimidine remained as a white powder in 60 % yield (270 mg, 0.65 mmol).

4,6-Bis(2',2"-bipyrid-6'-yl)-2-chloropyrimidine (85 mg, 0.2 mmol) was suspended in benzylic alcohol (30 mL), and NaOBn (0.28 mL, 1M in methanol) was slowly added. The suspension was heated at 120 °C until all solid had disappeared resulting in a dark yellow solution. The solvent was removed in vacuo and the remaining crude product dissolved in toluene. This solution was treated with an excess of triflic acid (10 mL) under reflux for 2 h. The resulting solid was filtered and suspended three times in *n*-hexane (10 mL) immersing it each time into a ultrasound bath for about five minutes. The remaining solid was recrystallized twice from methanol yielding 45 mg of a white powder (0.11 mmol, 55%).

Ligand C: 4,6-bis(2',2"-bipyrid-6'-yl)-pyrimid-2-one: ¹H NMR (200 MHz, $[D_6]DMSO$, 298 K): $\delta = 8.81$ (d, J = 5.1 Hz, 2H), 8.74 (d, J = 8.1 Hz, 2H), 8.61 (d and s, J = 7.7 Hz 3H), 8.50 (d, J = 6.82 Hz, 2H), 8.23 (t, J = 8.1 Hz, 2H), 8.15 (t, J = 7.66 Hz, 2H), 7.62 (t, J = 5.1 Hz, 2H), 4.77 ppm (s, 1H); ¹³C NMR: not determined due to insufficient solubility ; FAB-MS: m/z: 405.0 $[M^+]$; elemental analysis calcd (%) for C₂₄H₁₆N₆O: C 71.28, H 3.99, N 20.78; found: C 70.78, H 3.81, N 19.09.

Complexes: The synthesis of complexes $\mathbf{1}^{[25]}$ $\mathbf{4}^{[8]}$ $\mathbf{6}^{[27]}$ and $\mathbf{8}^{[28]}$ was carried out following literature protocols.

Complex 2: A suspension of the ligand **B** (30 mg, 74 µmol) in anhydrous methanol (3 mL) was treated with NaOMe (74 µL of a 1m solution in methanol). After dissolution of the ligand, the metal salt Fe(BF₄)₂ · 6H₂0 (25 mg, 74 µmol) was added and the deep blue solution was heated under reflux for 48 h. The solvent was evaporated and the remaining blue solid was recrystallized from methanol to yield complex **2** as blue, thin needles (36 mg, 17 µmol; 23 %). ¹H NMR (200 MHz, CD₃CN, 298 K): δ = 8.73 (d, 2H), 8.46 (s and d, 3H), 8.05 (d, Hz, 2H), 7.82 (d, 2H), 7.48 (t, 2H), 6.62 (t,

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2 H), 6.38 ppm (t, 2 H); ¹³C NMR: (due to insolubility not possible); FAB-MS: m/z: 2097.1 [$M^+ - BF_4$], 2011.1 [$M^+ - 2BF_4$], 1924.1 [$M^+ - 3BF_4$], 1852.1 [$M^+ - 4BF_4$]; UV/Vis (CH₃CN, nm, 298 K)(ε in 10⁴ m⁻¹ cm⁻¹): λ = 312 (134), 383 (155), 569 (37), 694 (28), 753 (29); elemental analysis calcd (%) for C₉₆H₆₀B₄F₁₆N₂₄O₄Fe₄ · 4 CH₃OH: C 51.94, H 3.31, N 14.54; found: C 50.87, H 3.45, N 13.83.

Complexes 3, 5, and 7: A suspension of the ligand (19.8 μ mol) and the respective Fe^{II} salt (19.8 μ mol) in CH₃CN (1.5 mL) was heated shortly until the mixture was dissolved completely. The solution was stirred for 12 h at room temperature (in the case of solubility problems under reflux). The complex was isolated by evaporation of the solvent or addition of diisopropyl ether to the solution until a precipitate formed. The precipitate was collected, washed with diisopropyl ether and dried in vacuo. The crude product was used directly for the measurements without further purification.

 $\begin{array}{l} Complex \ \textbf{3}\colon ^1\text{H}\ \text{NMR}\ (200\ \text{MHz}, \text{CD}_3\text{CN}, 298\ \text{K})\colon \delta = 140.9, 63.1, 50.4, 44.8, \\ 41.5, 38.4, 11.0, 8.0, -8.5\ \text{ppm}; \text{FAB-MS}\colon m/z\colon 2430.1\ [M^+ - 2\ \text{ClO}_4],\ 2330.2\\ [M^+ - 3\ \text{ClO}_4],\ 2231.4\ [M^+ - 4\ \text{ClO}_4],\ 2031.7\ [M^+ - 5\ \text{ClO}_4];\ UV/\text{Vis} \\ (\text{CH}_3\text{CN}, \text{nm}, 298\ \text{K})\ (\varepsilon\ \text{in}\ 10^4\ \text{m}^{-1}\text{cm}^{-1})\colon \lambda = 274\ (95),\ 332(100),\ 346\ (102), \\ 512\ (10),\ 585\ (17),\ 651(5);\ \text{elemental}\ analysis\ calcd\ (\%)\ \text{for} \\ \text{C}_{100}\text{H}_{72}\text{Cl}_8\text{N}_{24}\text{O}_{32}\text{Fe}_4\cdot 5.5\ \text{H}_2\text{O}\colon \text{C}\ 44.18,\ \text{H}\ 3.04,\ \text{N}\ 12.36;\ \text{found}\colon \text{C}\ 42.34, \\ \text{H}\ 3.13,\ \text{N}\ 11.17. \end{array}$

Complex **5**: ¹H NMR (200 MHz, CD₃CN, 298 K): δ = 141.2, 78.0, 70.6, 64.6, 55.5, 50.3, 16.3, 7.6, 4.9, 3.7, -6.8, -17.0 ppm; FAB-MS: *m/z*: 2773.9 [*M*⁺ - 2BF₄], 2687.6 [*M*⁺ - 3BF₄], 2600.3 [*M*⁺ - 4BF₄]; UV/Vis (CH₃CN, nm, 298 K) (ε in 10⁴m⁻¹ cm⁻¹): λ = 385 (108), 623(13); elemental analysis calcd (%) for C₁₂₈H₁₀₀B₈F₃₂N₂₈Fe₄· 2 CH₃CN · 6 H₂O: C 50.14, H 3.82, N 13.49; found: C 49.93, H 4.07, N 12.17.

 $\begin{array}{l} Complex \ \textbf{7}: \ ^{1}\text{H}\ \text{NMR}\ (200\ \text{MHz},\ \text{CD}_3\text{CN},\ 298\ \text{K}): \ \delta = 151.9,\ 77.2,\ 72.0,\ 67.0, \\ 60.1,\ 54.0,\ 18.2,\ 9.0,\ 8.2,\ -0.1,\ -9.8;\ \text{FAB-MS}:\ m/z:\ 3370.6\ \left[M^+ - \text{CIO}_4\right], \\ 3270.3\ \left[M^+ - 2\ \text{CIO}_4\right],\ 3171.2\ \left[M^+ - 3\ \text{CIO}_4\right],\ 3071.3\ \left[M^+ - 4\ \text{CIO}_4\right];\ \text{UV/Vis} \\ (\text{CH}_3\text{CN},\ \text{nm},\ 298\ \text{K})(\varepsilon\ \text{in}\ 10^4\ \text{m}^{-1}\ \text{cm}^{-1}): \ \lambda = 289\ (89),\ 349\ (110),\ 572\ (9),\ 646 \\ (7);\ \text{elemental analysis calcd}\ (\%)\ \text{for}\ \ C_{144}\text{H}_{128}\text{Cl}_8\text{N}_{24}\text{O}_{32}\text{S}_8\text{Fe}_4\cdot\ 3\ \text{CH}_3\text{CN}\cdot \\ 5\text{H}_2\text{O}:\ C\ 48.41,\ \text{H}\ 4.06,\ \text{N}\ 10.37,\ \text{S}\ 7.03;\ \text{found}:\ C\ 49.43,\ \text{H}\ 4.21,\ \text{N}\ 8.61,\ \text{S}\ 7.10. \end{array}$

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Hierarchical Self-Assembly of Supramolecular Spintronic Modules into 1D- and 2D-Architectures with Emergence of Magnetic Properties

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Abstract: Hierarchical self-assembly of complex supramolecular architectures allows for the emergence of novel properties at each level of complexity. The reaction of the ligand components **A** and **B** with Fe^{II} cations generates the $[2 \times 2]$ grid-type functional building modules **1** and **2**, presenting spin-transition properties and preorganizing an

array of coordination sites that sets the stage for a second assembly step. Indeed, binding of La^{III} ions to **1** and

Keywords: functional emergence • metallosupramolecular grids • selfassembly • spin transition • supramolecular chemistry of Ag^{I} ions to 2 leads to a 1D columnar superstructure 3 and to a wall-like 2D layer 4, respectively, with concomitant modulation of the magnetic properties of 1 and 2. Thus, to each of the two levels of structural complexity generated by the two sequential self-assembly steps corresponds the emergence of novel functional features.

Introduction

A major present thrust in supramolecular chemistry concerns the processes underlying self-organization, the goals being to understand their origin and operation, to induce the emergence of novel properties at each level of complexity, and to achieve their implementation in artificial functional systems.^[1]

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The generation of organization levels of increasing complexity, diversity and functionality relies on a set of basic building blocks and subunits, interconnected through a multitude of relatively weak, non-covalent interactions (e.g. hydrogen, van der Waals and coordinative bonding, etc.).^[1,2] It rests on the progressive build-up of more and more complex entities by multiple, sequential and hierarchical self-organization steps, following a conditional pathway, each step setting the base for the next one. Hierarchical self-organization^[3,4] may be driven by more or less pronounced positive cooperativity, up to a phase change, such as the formation of a liquid crystalline or a solid state.

In recent years, more and more powerful self-assembly strategies have been developed for the controlled access to a variety of nano-sized objects of increasing complexity. Much work was addressed to the understanding and manipulation of the parameters which give access to a variety of nano-architectures, in particular of metallo-supramolecular type, such as rods, squares, circles, cages, clamps, emphasizing mainly structural aspects like size, symmetry and chirality of the products.^[5] Less attention has been paid to self-assembled architectures exhibiting discrete functional properties (switching, moving etc.).^[6]

Such functional architectures may derive from three principal routes: i) the functionality may result as "emerging" property from the assembly of the building modules; ii) the functionality may be encoded on the isolated modules and persist as unchanged property in the self-assembled architecture or iii) the two approaches above may also partially

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merge, since the molecular surroundings can alter or tune an original, "module-based", functionality to a large extent and lead to the gradual appearance of new functional features.^[7-9]

Herein, we report on the hierarchical self-assembly of the magnetic molecular architectures **3** and **4**. It involves in a first step the assembly of the ligand components **A** and **B** and Fe^{II} ions into the supramolecular spintronic modules^[9b] **1** and **2**, displaying magnetic properties based on the spintransition phenomenon and preorganizing an array of binding sites that sets the stage for a second step. This newly gained "collective" property is modulated through a subsequent, higher order self-assembly process induced by binding of a new set of cations and generating the 1D and 2D architectures **3** and **4**, respectively. The structural and magnetic properties of the four architectures **1–4** were investigated in detail at the two hierarchical organisation levels.

Results and Discussion

Synthesis and structures of the $[2 \times 2]$ grid-type complexes $[Fe_4^{II}L_4]^{8+}$, 1 and 2: It has been shown that tetranuclear molecular systems of the $[2 \times 2]$ grid type with four precisely located transition metal ions are accessible by self-organisation and exhibit interesting electrochemical, magnetic and optical properties.^[8,9] The nature of the substitutions of the ligand can induce for $M^{II} = Fe$ the occurrence of spin transition in the $[Fe_4^{II}L_4]^{8+}$ units.^[9]

We designed ligand components **A** and **B**, which should be able to undergo two hierarchical self-assembly steps through the stepwise coordination of different metal ions, such as Fe^{II} and La^{III} (for **A**) or Fe^{II} and Ag^{I} (for **B**), generating first the respective $[2 \times 2]Fe_4^{II}$ grids, as building modules, and interconnecting thereafter these units via coordination of a second type of metal ion. In a earlier study, a related ligand contained sites for a second assembly step through hydrogen bonding.^[10] The synthesis and first results of the coordination behaviour of the ligands **A** and **B** were reported earlier.^[11]

Abstract in French: L'autoassemblage hiérarchisé d'architectures supramoléculaires conduit à l'émergence de nouvelles propriétés à chaque niveau de complexité. La réaction des ligands A et B avec des cations Fe^{II} génère des modules fonctionnels de type grille [2×2], I et 2, qui présentent des propriétés de transition de spin, et prédisposent un ensemble de sites de coordination pour une deuxième étape d'assemblage. En effet, la complexation d'ions La^{III} par I et d'ions Ag^{I} par 2 conduit respectivement à une superstructure colonnaire 3ID et à un arrangement en feuillet 2D, avec une modulation concomittante des propriétés magnétiques de I et 2. Ainsi, à chaque niveau de complexité structurale généré par les deux étapes d'autoassemblage séquentiel, correspond l'émergence de nouvelles propriétés fonctionnelles.



The compounds, $[Fe_4A_4](BF_4)_8$ (1) and $[Fe_4^{II}B_4](BF_4)_8$ (2), were obtained by assembly from the corresponding ligand **A** or **B** and $[Fe(BF_4)_2] \times 6H_2O$ in acetonitrile at reflux for eight hours, followed by precipitation with diisopropyl ether (Figure 1). The composition of 1 and 2 was confirmed by FAB-mass spectrometry and elemental analysis. No evidence for higher-mass polymeric products was found in ESmass spectrometry investigations.

The ¹H NMR spectra of **1** and **2** at 298 K both exhibit fourteen singlets covering a range from $\delta = -10$ to 150 ppm. The number of signals is indicative of $C_{2\nu}$ symmetry of the coordinated ligands **A** or **B** and of a hindered rotation of the phenyl groups with free rotation of the pyridine units. The spread-out chemical shift domain covered by the signals results from paramagnetic contact shifts of Fe^{II}(HS) ions.^[12]

The structure of $[Fe_4^{II}B_4]^{8+}$ (2) (as the perchlorate compound) was determined by single crystal X-ray diffraction at 120 K (Figure 2). It consists of a tetranuclear complex in which each of the Fe^{II} ions is in a pseudo-octahedral arrangement with a pronounced axial distortion. Each metal ion is surrounded by six nitrogen atoms from the pyrimidine and bipyridine groups. The Fe–N bond lengths of d(Fe-N)=1.898(6)-2.103(6) Å indicate that at 120 K all four Fe^{II} ions are in their LS state.^[9] A single chloride anion, coming presumably from impurities of the [Fe(ClO₄)₂]×6H₂O salt used, is bound in the central cavity of the [Fe^{II}₄B₄]⁸⁺ cation, while the remaining seven ClO₄ anions are found together with solvent and water molecules in the crystal lattice around the complex cation.

The four ligands **B** are bound to the Fe^{II} ions by their terpyridine-type coordination sites formed from lateral four pyridine and the central pyrimidine groups, while the eight 4-pyridyl units point orthogonally above and below the main molecular plane containing the four metal ions. The central C–C axes connecting the terpy moieties with the *exo*-directed 4-pyridines deviate by 5.2 up to 29.5° from ideal orthogonality. As a consequence, all pyridine groups are slightly bent outside, and the free nitrogen atoms are easily accessible for further coordination.

The first self-assembly process incorporates the four ligands **B** in the complex $[Fe_4^{II}B_4]^{8+}$ (2) and, at the same time, pre-organizes them in a disposition which enables further



Figure 1. Two-step hierarchical self-assembly of metallosupramolecular architectures with emergence of magnetic properties. From ligands **A** and **B** to the magnetic $[2\times2]$ grid-type building modules $[Fe_4^{II}\mathbf{A}_4]^{8+}$ (1) and $[Fe_4^{II}\mathbf{B}_4]^{8+}$ (2) (self-assembly I), and on to the columnar 1-D architecture $\{[-Fe_4^{II}\mathbf{A}_4]^{-}(La^{III})_4\}_n^{11+}$ (3) and the wall-like 2-D architecture $\{[-Fe_4^{II}\mathbf{B}_4]^{-}(\mathbf{A}g^{I})_4\}_n^{12+}$ (4) (self-assembly II). Red spheres: Fe^{II}, green spheres (top): La^{III}, green spheres (bottom) Ag^I. Bottom: emerging magnetic properties.



Figure 2. Top and side view of the $[2 \times 2]$ grid-type complex $[Fe_4^{II}B_4]^{8+}$ (2) in the crystal structure (anions, solvent molecules, hydrogen atoms and the rotational disorder of the pyridine groups are omitted for clarity).

metal ion coordination to the building module generated, for a higher order second self-assembly step.

The analytical data for the complex $[Fe_4^{II}A_4]^{8+}$ (1) are very similar to those obtained for complex 2 (see Experimental Section) and point to an identical composition.

Synthesis and structures of the extended coordination architectures {[$Fe_4^{II}A_4$]-(La^{III})₄]_n¹¹⁺ (3) and {[$Fe_4^{II}B_4$]-(Ag^{I})₄]_n¹²⁺ (4): The generation of a second order coordination assembly was achieved by connecting the tetranuclear grid modules [$Fe_4^{II}A_4$]⁸⁺ (1) through binding of lanthanum(III) ions. The reaction was performed by layering an acetonitrile solution of 1 (as its ClO₄⁻ salt) with a six-fold excess of a [La(ClO₄)₃] in methanol resulting in deep-green, triangular-shaped crystals of assembly 3. Elemental analysis of these crystals point material. The structure of the cationic $[Fe_4^{II}B_4]^{8+}$ subunits within **4** is of $[2\times 2]$ grid type, very similar to that determined for **2** with Fe–N bond lengths of d(Fe-N)=1.890(7)-2.092(6) Å, indicating the presence of exclusively Fe^{II}(LS) ions at 120 K. All eight *exo*-4-pyridyl groups of each $[Fe_4^{II}B_4]^{8+}$ unit were coordinated to Ag^I ions (Figures 1 and 3). Attempts to dissolve the complex in polar solvents (DMF, DMSO) resulted in the break-up of **4** into the tetranuclear $[Fe_4^{II}B_4]^{8+}$ units and solvated Ag^I ions.

The Ag^I ions are dicoordinated in an approximately linear coordination manner with d(Ag-N) = 2.130(12)-2.228(14) Å; $\alpha(N-Ag-N) = 166.4(7)$ and $168.8(8)^{\circ}$, and interconnect successive tetranuclear [Fe^{II}₄**B**₄]⁸⁺ units through four pyridine–Ag^I–pyridine bridges. Following this coordination scheme, an infinite coordination polymer is generated

to a $\{-[Fe_4^{II}A_4]-(La^{III})\}(ClO_4)_{11}$ composition with additional sixteen water and two acetonitrile molecules. Single crystal X-ray investigations reveal an one-dimensional columnar motif involving aligned alternating $[Fe_4^{II}(\mathbf{A})_4]^{8+}$ and coordinated La^{III} ions. The data reveal the tetranuclear Fe4II modules, interconnected in a linear fashion by the coordination of a La^{III} ion to two four-fold sets of 3-pyridyl groups above and below the Fe^{II}₄ plane of two neighbouring modules. Unfortunately, due to the bad quality of the crystals and despite several attempts to improve the quality of the data, the resulting elevated R factor does not allow a more detailed discussion of the molecular structure of $\{[Fe_4^{II}A_4] (La^{III})_4\}_n^{11+}$ (3). However, the overall motif described above is secure.

To achieve a second order assembly of module $[Fe_4^{II}B_4]^{8+}$ (2), a solution of its BF_4^- salt in acetonitrile was layered with a solution of methanol containing six equivalents of AgBF₄. After several weeks, pine-green prisms of compound 4 had grown at the diffusion interface of the two solutions. The overall composition of the compound was determined as $\{[Fe_4^{II}B_4]-(Ag^{I})_4\}(BF_4)_{10}(SiF_6)$ by elemental analysis and its structure was determined by X-ray investigations of the crystalline



Figure 3. X-ray single crystal structure of $\{[Fe_4^{II}B_4]-(Ag^{I})_4]_n^{12+}$ (4) displaying the wall-like 2D interconnection of the $[Fe_4^{II}B_4]^{8+}$ [2×2] grid-type building modules (red) by the Ag^I ions (green): a) cross section; b) frontal elevation of the 2D wall-like array (anions and solvent molecules are omitted for clarity; carbon: grey, nitrogen: blue, iron: red).

as a meander-like interwoven, two-dimensional network (Figure 3). Within this wall-like array, the $[Fe_4^{II}B_4]^{8+}$ building modules are aligned in rows at 2.15 nm apart, while the distance between two neighbouring "walls" is about 1.56 nm. The central and peripheral cavities within the $[Fe_4^{II}B_4]^{8+}$ units, but not the hollow space around the Ag^{I} ions, are filled with the BF_4^{-} anions and solvent molecules (Figure 3).

Magnetic properties of the units 1 and 2 and of the assemblies 3 and 4: The magnetic properties of module $[Fe_4^{II}A_4](ClO_4)_8$ (1) and of the extended assembly $\{-[Fe_4^{II}A_4] (La^{III})$ (ClO₄)_{(11)n} (**3**) are represented in Figure 4a as $\chi_M T/4$ versus T plots, χ_M being the molar magnetic susceptibility, corrected for diamagnetic contributions ($\chi_D = -357.8 \times$ $10^{-6}\,\mathrm{cm^3mol^{-1}})$ using Pascal's constants, and T the temperature. At room temperature, $\chi_M T/4$ of **1** is equal to $3.2 \text{ cm}^3 \text{Kmol}^{-1}$, close to the spin-only value expected for four high-spin Fe^{II} ions. On lowering the temperature, $\chi_M T/4$ progressively decreases reaching a value of 1.2 cm³K mol⁻¹ at 30 K, calling for the presence of one to two HS Fe^{II} (a situation already found in other $[Fe_4^{II}L_4]^{8+}$ units).^[9a] Below this temperature, $\chi_M T/4$ drops, which can be attributed to zerofield splitting of the Fe^{II}(HS) ions.^[13] The very gradual increase and the absence of any hysteresis in the $\chi_M T/4$ versus T plot suggests that the cooperative interactions accompanying spin transition are rather weak. This was already observed for other members of this class of compounds and is apparently characteristic for the spin transition behaviour of these systems.^[9,14] The magnetic properties of **1** (as well as of 2, below) emerge from the assembly and are absent in the components, the ligands and metal ions.

Upon aligning the $[Fe_4^{II}A_4]^{8+}$ modules into the one-dimensional coordination polymer $\{-[Fe_4^{II}A_4]-(La^{III})\}_n(ClO_4)_{(11)n}$ (3), the unit-based spin transition behaviour persists, but the whole magnetic curve is shifted towards stabilization of the LS state (Figure 4a). At low temperature, below 50 K, a pla-

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teau with almost no remaining magnetic moment and the absence of any Fe^{II}(HS)-based zero-field splitting indicates a completely diamagnetic situation only involving four Fe^{II}(LS) (each with S=0). At room temperature, a maximum value of $1.8 \text{ cm}^3 \text{ K mol}^{-1}$ evokes an incomplete spin transition in accordance with the shift of T_c to higher temperatures.

The magnetic properties of module $[Fe_4^{II}B_4](BF_4)_8$ (2) and its assembly $\{-[Fe_4^{II}B_4]-(Ag^{I})_4\}_n(BF_4)_{(12)n}$ (4) are represented in Figure 4b. At room temperature, $\chi_M T/4$ for 2 is equal to 2.4 cm³K mol⁻¹ and thus in the range of values expected for three HS and one LS



Figure 4. $\chi_M T/4$ versus temperature plots of a) the module $[Fe_4^{II}A_4](CIO_4)_8$ (1) and the columnar assembly $\{[Fe_4^{II}A_4]-(La^{III})\}(CIO_4)_{(11)n}$ (3); b) the module $[Fe_4^{II}B_4](BF_4)_8$ (2) and the wall-like assembly $\{-[Fe_4^{II}B_4]-(Ag^I)_4]_n(BF_4)_{(12)n}$ (4).

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Fe^{II} ions; it decreases on lowering the temperature reaching a value of $1.4 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ at 30 K, calling for the presence of two Fe^{II}(HS). The magnetic data show a very gradual and, in comparison with **1**, a very incomplete spin transition process as already observed for other members of this class of compounds.^[9]

The magnetic behaviour of the two-dimensional, wall-like assembly **4** {[$Fe_4^{II}B_4$]-(Ag^I)₄}_n(BF_4)_{(12)n} is shown in Figure 4b. At room temperature, $\chi_M T/4$ of **4** is equal to 1.4 cm³K mol⁻¹ which is significantly lower than found for the constituting complex **2** itself and points at a magnetic situation involving two Fe^{II}(LS) and two Fe^{II}(HS) ions. On lowering the temperature the magnetic moment of **4** remains almost unchanged before showing a slight increase to $\chi_M T/4$ = 1.5 cm³K mol⁻¹ at T=30 K. Below that temperature, once more, a sharp drop due to the zero field splitting of Fe^{II}(HS) ions is observed.^[13]

The spin transition in the assembly 4 is, in comparison with module 2, inhibited over the whole temperature range studied, possibly due to steric hindrance in the interconnected, two-dimensional network. Since the conversion of $Fe^{II}(LS)$ to $Fe^{II}(HS)$ is accompanied by a volume increase, each spin transition would have to expand against the, more rigid, 2D network of 4.^[14,15] As a result, the magnetic moment remains close to the value of the non-bridged "monomer" 2 at low temperature (30 K). The observed slight decrease of the $\chi_{\rm M}T$ versus T curve between 300 and 150 K may be due to weak antiferromagnetic intramolecular interaction as already observed in the analogous $[Co_4^{II}L_4]^{8+}$ compounds.^[8b] The increase of χT below about 150 but above 30 K, might result from ferromagnetic intermolecular exchange coupling between the neighbouring 2D-networks (Figure 4b), although such coupling should be very weak over a distance of 15 Å.

Conclusion

The present results show that hierarchically ordered self-assembly processes using suitably designed molecular components can be implemented to construct the metallosupramolecular $[2 \times 2]$ grid-type modules $[Fe_4A_4]^{8+}$ (1) and $[Fe_4B_4]^{8+}$ (2), presenting spin transition behaviour and displaying a collectively generated coordination array, that prepares the structural prerequisites enabling 1 and 2 to undergo a second self-assembly process. This second process leads in both cases to an extended architecture displaying either a one-dimensional columnar $\{-[Fe_4^{II}A_4]-(La^{III})\}_n^{11+}$ (3), or a two-dimensional wall-like $\{-[Fe_4^{II}B_4]-(Ag^{I})_4\}_n^{12+}$ (4) arrangement. In both higher-order architectures, the magnetic behaviour of the $[Fe_4^{II}L_4]^{8+}$ modules exhibits a progressive hindrance of the spin transition process with increasing dimensionality.

The generation and variation of a certain molecular functionality (here magnetism) at different organisational levels, as realized here in the supramolecular spintronic modules 1/2 and arrays 3/4, show how the architectural parameters feed-back actively on intrinsic functionalities of complex supramolecular assemblies. It relates to the progressive build-up of functional nanostructured supramolecular devices by sequential self-organization, with concomitant emergence of novel (optical, electronic, magnetic) properties at different levels of system complexity.^[1]

Experimental Section

Synthesis of complexes 1 and 2: A solution of ligand $\mathbf{A}^{[11]}$ (30 mg, 48 µmol) (or $\mathbf{B}^{[11]}$) and [Fe(BF₄)₂]×6H₂O (16 mg, 48 µmol) in acetonitrile (50 mL) was stirred under reflux for 12 h. Complex 1 (or 2) was isolated, respectively, as dark green solid by precipitation with diisopropyl ether in quantitative yields (18.0 mg).

The ClO₄ salts of **1** and **2** were synthesized by the same procedure by using $[Fe(ClO_4)_2] \times 6H_2O$. The products obtained exhibit identical spectroscopic properties as the BF₄ salts.

[Fe^{II}₄A₄](BF₄)₈ (1): ¹H NMR (200 MHz, CD₃CN, 298 K): δ =118.6, 62.4, 55.2, 49.9, 47.3, 42.8, 14.5, 7.8, 7.1, 5.6, 4.3, 4.0, 0.7, -7.3; FAB-MS (NBA): *m*/z: 3132.4 [*M*-3BF₄]⁺, 3046.5 [*M*-4BF₄]⁺, 2959.6 [*M*-5BF₄]⁺, 2871.5 [*M*-6BF₄]⁺; UV/Vis (acetonitrile, ε in 10³ cm²mol⁻¹): λ =274 (189), 365 (41.6), 497 (14.8), 662 nm (15.3); elemental analysis calcd (%) for C₁₆₀H₁₀₄N₃₂B₈Fe₄F₃₂×19H₂O: C 51.45, H 3.83, N 12.00; found: C 51.47, H 3.36, N 11.70 (for the perchlorate salt C₁₆₀H₁₀₄N₃₂Cl₈Fe₄O₃₂× 3CH₃CN×4H₂O: C 54.05, H 3.31, N 13.29; found: C 54.80, H 3.52, N 13.18.).

$$\begin{split} & [\mathbf{Fe}_4^{\mathsf{H}}\mathbf{B}_4](\mathbf{BF}_4)_8 \ \textbf{(2):} \ ^{1}\mathsf{H} \ \mathsf{NMR} \ (200 \ \mathsf{MHz}, \ \mathsf{CD}_3\mathsf{CN}, \ 298 \ \mathsf{K}): \ \delta = 145.0, \ 109.8, \\ & 60.4, \ 52.7, \ 47.6, \ 45.9, \ 41.3, \ 13.5, \ 8.1, \ 4.0, \ 3.6, \ 3.5, \ -1.4, \ -6.6; \ \mathsf{FAB-MS} \\ & (\mathsf{NBA}): \ \mathit{m/z}: \ 3284.9 \ [\mathit{M}-\mathsf{BF}_4]^+, \ 3219.8 \ [\mathit{M}-2\mathsf{BF}_4]^+, \ 3131.8 \ [\mathit{M}-3\mathsf{BF}_4]^+, \\ & 3045.8 \ [\mathit{M}-4\mathsf{BF}_4]^+, \ 2958.8 \ [\mathit{M}-5\mathsf{BF}_4]^+, \ 2871.8 \ [\mathit{M}-6\mathsf{BF}_4]^+; \ \mathsf{UV/Vis} \ (acetonitrile, \ \varepsilon \ in \ 10^3 \ \mathrm{cm}^2\mathrm{mol}^{-1}): \ \lambda = 271 \ (147), \ 335 \ (62.4), \ 380 \ (57.0), \ 496 \\ & (9.7), \ \ 666 \ \mathrm{nm} \ \ (8.7); \ \ elemental \ \ analysis \ \ calcd \ \ (\%) \ \ for \\ & \mathsf{C}_{160}\mathsf{H}_{104}\mathsf{N}_{32}\mathsf{B}_8\mathsf{F}_{32}\mathsf{Fe}_4 \times 6 \ \mathsf{CH}_3\mathsf{CN} \times 5 \ \mathsf{H}_2\mathsf{O}: \ \mathsf{C} \ 55.40, \ \mathsf{H} \ 3.57, \ \mathsf{N} \ 14.27; \ found: \\ & \mathsf{C} \ 55.18, \ \mathsf{H} \ 3.43, \ \mathsf{N} \ 13.94 \ \ (for \ the \ perchlorate \ salt \ \mathsf{C}_{160}\mathsf{H}_{104}\mathsf{N}_{32}\mathsf{Cl}_8\mathsf{Fe}_4\mathsf{O}_{28} \times \\ & 10 \ \mathsf{CH}_3\mathsf{CN} \times 2 \ \mathsf{H}_2\mathsf{O}: \ \mathsf{C} \ 55.77, \ \mathsf{H} \ 3.59, \ \mathsf{N} \ 15.18; \ found: \ \mathsf{C} \ 55.40, \ \mathsf{H} \ 3.63, \ \mathsf{N} \\ 15.11). \end{split}$$

Synthesis of assemblies 3 and 4

 $\label{eq:constraint} \begin{array}{l} \label{eq:constraint} \left\{ -\left[Fe_4^{II}A_4 \right] - \left(La^{III} \right) \right\}_n (CIO_4)_{(11)n} (3) : A solution of 1 (as its CIO_4^- salt; 5 mg, 1.43 \mu mol) in CH_3CN was layered with a solution containing a six-fold excess of [La(CIO_4)_3] (3.8 mg, 8.6 \mu mol) in methanol (3 mL). After two days, triangle-shaped dark-green prisms of compound 3 were found floating on the solution. An amount of 5.2 mg (1.3 \mu mol, 92 %) of the crystalline material of 3 was collected and directly used in the structural and magnetic investigations. Elemental analysis calcd (%) for C_{100}H_{104}N_{32}Fe_4LaCl_{11}O_{44} \times 2 CH_3CN \times 16 H_2O: C 45.79, H 3.33, N 11.07; found: C 44.90, H 3.41, N 10.58. \end{array}$

[-[Fe₄^{II}B₄]-(Ag¹)₄]_n(BF₄)_{(12)n} (4): A solution of 2 (5 mg, 1.47 μmol) in CH₃CN was layered with a solution of a six-fold excess of AgBF₄ (1.8 mg, 8.84 μmol) in methanol (3 mL). After several weeks right-angled pine-green prisms of compound **4** were found at the diffusion interface of the two solutions. An amount of 4.8 mg (1.1 μmol, 75%) of the crystal-line material of **4** was collected and directly used in the structural and magnetic investigations. Elemental analysis calcd (%) for C₁₆₀H₁₀₄N₃₂Fe₄Ag₄B₁₀SiF₄₆×12 CH₃CN×2H₂O: C 47.34, H 3.11, N 13.20; found: C 46.95, H 3.22, N 13.01.

Magnetic measurements: They were carried out with a SQUID magnetometer working in the 4.2–300 K temperature range. The applied magnetic field was 1 Tesla. FAB mass spectra were performed on a Fisons TRIO-2000 (Manchester) and a Micromass AUTOSPEC-M-HF spectrometer using 3-nitrobenzylic alcohol as matrix. Microanalyses were carried out by the Service de Microanalyse, Faculté de Chimie, Strasbourg.

X-ray structural analysis of 2 and 4: The data for both compounds were recorded at 120.0(2) K on Beamline ID11 at the European Synchroton Research Facility in Grenoble. Phi rotation images (1 s per frame) were

recorded with a Bruker Smart 6500 camera and a Si(111) monochromated wavelength of 0.45085 Å. The data were integrated with the Bruker data reduction suite Saint and the absorption correction applied via SADABS. Structure solution was performed by direct methods (SHELXS) and refinement against F^2 (SHELXL). The hydrogen atoms were refined with a riding model. As the small size, poor diffracting power of the crystals and volatility of the incorporated solvent molecules led to a low number of strong observations, geometric constraints were applied in order to keep the data/parameter ratio acceptable. The final structures are relatively low resolution and quality, contain disordered counterions and solvent molecules and probably lack further solvent molecules, the positions of which could not be resolved.

The perchlorate salt of 2 was recrystallized by vapour diffusion of benzene into a nitromethane solution of 2 and the obtained green crystals were used in the X-ray investigations.

X-ray structural data for 2: A suitable pine-green prism $(0.02 \times 0.02 \times 0.04 \text{ mm})$ of 2 $[C_{160}H_{104}N_{32}Fe_4]^{8+} \times 7 \text{CIO}_4 \times \text{CI}^- \times 7 \text{CH}_3\text{NO}_2 \times 6 \text{H}_2\text{O}$ was obtained from nitromethane/benzene. Complex 2 (at 120 K) monoclinic, C2/c, a=17.346(2), b=40.015(6), c=31.120(4) Å, $\beta=99.150(6)$, V=21326(5) Å³, Z=4, $\rho_{calcd}=1.324$ g cm⁻³, $2\theta_{max}=28.36^\circ$, $\mu(\text{MO}_{Ka})=0.241 \text{ mm}^{-1}$. 70634 reflections were collected of which 12315 were unique; 10676 of these had $I > 2\sigma(I)$. The final *R* values were R=0.1120, $wR^2=0.2588$ [$I > 2\sigma(I)$], R=0.1271, $wR^2=0.2662$ (all data) for 1348 parameters and 434 restraints. A final difference map displayed the highest electron density of 0.983 e Å⁻³.

Crystals of **4** were obtained by layering a solution of the BF_4^- salt of **2** in acetonitrile with a solution of methanol containing six equivalents of AgBF₄. After several weeks, pine-green prisms of compound **4** had grown at the diffusion interface of the two solutions.

X-ray structural data for 4: Green prisms $(0.01 \times 0.01 \times 0.03 \text{ mm})$ of $[C_{160}H_{104}N_{32}Fe_4Ag_4]^{12+} \times 10BF_4^{-} \times 1SiF_6^{2-} \times 2CH_3CN \times 4H_2O$ were obtained from acetonitrile/methanol. Complex **4** (at 120 K) monoclinic, *C2/c*, *a*=17.0199(11), *b*=43.104(3), *c*=30.9306(18) Å, β =99.981(3), *V*=22348(2) Å^3, *Z*=4, ρ_{calcd} =1.276 g cm⁻³, $2\theta_{max}$ =24.68°, $\mu(Mo_{K\alpha})$ = 0.365 mm⁻¹. Of 42249 collected reflections, 11311 were unique and 8279 had *I* > $2\sigma(I)$. The final *R* values were *R*=0.1200, *wR*²=0.2879 [*I* > $2\sigma(I)$], *R*=0.1528, *wR*²=0.3050 (all data) for 1470 parameters and 2844 restraints. Although the SiF_6²⁻ anions were not introduced initially, they probably form by reaction with the glass container when BF_4⁻ ions are present and are incorporated in the crystals. This is not uncommon (see for instance ref. [10]).

CCDC-238750 (2) and -238751 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033; or email: deposit@ccdc.cam.ac.uk.

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Quantum Tunneling of the Magnetization in the Dysprosium Double-Decker Complex

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Magnetization hysteresis of dysprosium double-decker single crystals was observed below a blocking temperature of 4K. The very large anisotropy of rare-earth ions has two opposing effects on the barrier height for reversal of the magnetization: The strong axial anisotropy results in a very large ligand-field splitting, whereas the large transversal anisotropy shortcuts the barrier. Since the double-decker molecules contain only one lanthanide ion, they represent a new class of singlemolecule magnets, which we denominate as single-ion molecular magnets. The observed steps in the hysteresis are due to quantum tunneling of the magnetization. We interpret these steps and related features in terms of intermolecular exchange, dipole-dipole and hyperfine interactions.

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At low temperatures, some organometallic molecules show magnetization hysteresis. Unlike classical magnets this behavior is not based on a cooperative long-range order of spins, but on the properties of a single molecule. The magnetic anisotropy barrier $U = |D| S^2$ between the $m = \pm S$ ground states slows down magnetic relaxation in these single-molecule magnets (SMMs). Hence, below the blocking temperature $T_B = U/ln(t/\tau_0)$, magnetic field measurements exhibit hysteresis loops. In the low temperature regime, the spins are localized in the anisotropy double well minima and can only escape by quantum tunneling of the magnetization (QTM) [1]. Usually, SMMs like Mn_{12} and Fe_8 consist of several magnetic ions coupled by strong intramolecular exchange interactions, resulting in a high-spin ground state [2]. Although considerable progress has been made in the synthesis of highspin systems, anisotropy has been the limiting factor in achieving increased blocking temperatures [3]. Since 4f lanthanide ions possess a much stronger anisotropy in comparison to 3d metal ions, they might provide larger barrier heights. However, strong transverse anisotropy terms increase the tunnel splittings and therefore shortcut the barrier. This results in a reduced effective barrier of the system [4]. Recently, Ishikawa et al. reported ac susceptibility measurements on powder samples of Dy³⁺ and Tb^{3+} lanthanide double-decker complexes [5]. They obtained effective barrier heights of 28 $\text{cm}^{-1}(40 \text{ K})$ and $230 \text{ cm}^{-1}(330 \text{ K})$, respectively. Therefore, these complexes are interesting candidates for SMMs with large blocking temperatures.

In this letter, we present the first single-crystal magnetization measurements of the Dysprosium double-decker molecule and provide evidence that these molecules are SMMs with a blocking temperature of 4 K. Lanthanide double-decker complexes are the first members of a new class of SMMs, that consist of only one metal ion per molecule. We denote them as single-ion molecular magnets (SIMMs). These molecules show a step-like hystere-



FIG. 1: Representation of the lattice structure of $[Pc_2Dy]^-$ TBA⁺ showing a stack-like packing of the $[Pc_2Dy]^-$ anions and TBA⁺ cations. The intra- and interstack Dy^{3+} - Dy^{3+} distances (arrows) and the most important intermolecular C-H··· π interactions (dotted lines) are indicated. The structural disorder of the butyl groups of the TBA⁺ is omitted for clarity and only one of the two equivalent positions (50% occupancy) is shown.

sis due to QTM. The steps and related features are explained by a coaction of intermolecular exchange, dipolar and hyperfine interactions.

The Dysprosium double-decker compound $[Dy(Pc)_2]^- TBA^+$ (Pc²⁻ = dianion of phthalocyanine; $TBA^+ = N(C_4H_9)_4^+)$ was synthesized following a protocol described by Weiss et al. [6]. The compound crystallizes in the monoclinic space group $P2_1$ with two double-deckers per unit cell, the cell parameters being a = 11.41 Å, b = 22.44 Å, c = 13.44 Å and $\beta = 107.46^{\circ}$ [7]. The molecular pseudo C_2 axes of the double-decker anions are aligned in a strictly parallel fashion along the crystallographic [100]-axis. In the crystal lattice, the molecules are arranged in infinite stacks with alternating $[Dy(Pc)_2]^-$ and TBA⁺ ions (see Fig. 1). Along these stacks, the Dy³⁺-Dy³⁺ distance between next neighbors



FIG. 2: The second order ligand-field parameters have been determined by a two parameter fit of three magnetization curves along the [100], [010], and [001] directions.

is noticeably shorter (11.4 Å) than in any other direction (13.1 Å-14.8 Å). Weak C–H··· π interactions (C– π distance 3.55-3.95 Å) were found between the butyl groups of TBA⁺ and coordinating isoindoline groups of the Pc^{2–} ligands [8]. These interactions provide a possible intermolecular exchange pathway between the double-decker molecules along the stacks via the TBA⁺ cations.

The 4f⁹ configuration of the Dy³⁺ ion results in a spin S = 5/2, angular momentum L = 5 and Landé-factor $g_J = 4/3$. Due to the strong spin-orbit coupling, the total angular momentum J = 15/2 ground-state multiplet is energetically well separated from the excited multiplets. Thus the magnetic properties of $[Dy(Pc)_2]^-$ can be described by the following Hamiltonian incorporating Zeeman, zero-field splitting terms and hyperfine interaction:

$$\mathcal{H} = \mathcal{H}_{crystal\,field} + \mathcal{H}_{Zeeman} + \mathcal{H}_{hyperfine}$$
(1)
$$= \sum_{q=0,2} B_2^{\mathbf{q}} \mathbf{O}_2^{\mathbf{q}} + \sum_{q=0,2,4} B_4^{q} \mathbf{O}_4^{\mathbf{q}} + \sum_{q=0,2,4,6} B_6^{q} \mathbf{O}_6^{\mathbf{q}}$$
$$+ g_J \mu_B \mu_0 \mathbf{J} \cdot \mathbf{H}$$
$$+ A_J \mathbf{J} \cdot \mathbf{J}$$

where B_k^q are the ligand-field parameters, $\mathbf{O}_k^{\mathbf{q}}$ are the equivalent Stevens operators, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, \mathbf{J} is the total angular momentum operator, \mathbf{H} is the applied field, A_J is the hyperfine constant and \mathbf{I} is the nuclear spin operator.

The magnetization of single crystal samples was measured along the [100], [010], and [001] directions by SQUID measurements up to 5.5 T at 1.8 K. In order to estimate the barrier height, we restrict our analysis to the second order ligand-field parameters. The fourth



FIG. 3: Hysteresis loop measurements for different temperatures along the easy axis. The sweep direction is indicated by arrows. Step 3 and the corresponding thermally activated step 1 are broadened due to closely spaced multiple anti-level crossings over a wide range.

and sixth order ligand-field terms, the intermolecular and the hyperfine interaction are neglected in this first approximation. A two parameter fit of three magnetization curves along the different orientations gives $D = 3B_2^0 = -$ 5.0 K and $E = B_2^2 = 0.7$ K (see Fig. 2). The resulting barrier height of U = 281 K suggests SMM behavior of $[Dy(Pc)_2]^-$ at temperatures far above 4 K. However, a more realistic value is given by the energy separation between the two lowest levels of the ground state multiplet $U_{eff} = |D| (2J-1) = 70$ K. This value corresponds to the effective barrier height determined by Ishikawa et al. [5] and is in accordance with the observed blocking temperature of 4 K (see Fig. 3). Thus, we conclude that the barrier is shortcut at the first excited level of the ground-state multiplet by large tunnel splittings.

Single crystal magnetization measurements were also performed using 2DEG GaAs/GaAlAs Hall sensors [9]. At low temperatures, the magnetization versus magnetic field curves show a pronounced step-like hysteresis up to a blocking temperature of about 4 K (see Fig. 3). The hysteresis loop was measured at different temperatures, sweep rates and orientations with respect to the easy axis. The width of the hysteresis increases with decreasing temperature and increasing sweep rate. For sweeps in positive field directions, one large sharp step (labeled 2) at 0 T and a second large broadened step (labeled 3) at about 0.3 T can be observed. With increasing temperature, a third broadened step (labeled 1) emerges at about -0.3 T. In the following, we will show that these steps are caused by QTM involving closely-spaced multiple anti-level crossings.

Measurements at different temperatures and sweep rates revealed a fine structure of step 2 (see Fig. 4a, 4b). It consists of many nearly equidistant peaks at certain fields, which are shifted towards negative fields with increasing temperature. These shifts are caused by thermally activated QTM [10] in the presence of the large hyperfine interactions of lanthanides, which provide equidistant avoided level-crossings over a large scale. Similar substructures have been observed in $LiY_{0.998}Ho_{0.002}F_4$ [4]. In natural Dy, there are three isotopes with $A_J = -5.2 \text{ mK} (19\%), A_J = 7.3 \text{ mK} (25\%)$ and $A_J = 0$ (56%) and nuclear spin I = 5/2. At the resonant field values $H_n = n A_J / (2 g_J \mu_B)$, tunneling transitions may occur $(-5 \le n \le 5)$. For clarity, only the level crossings for $A_J = 7.3$ mK are indicated in figure 4 by dotted lines. Although the observed peaks are in good agreement with these field values, the isotopes with $A_J = -$ 5.2 mK might also be involved in the tunneling processes. The intermolecular dipolar interactions mainly broaden the hyperfine peaks. Depending on the spin arrangements, the dipolar energy is distributed between 0 and 42 mK. The resulting distribution width of about 5 mT corresponds to the line broadenings observed in Fig. 4a, 4b. We point out, that the observed substructures and correlated features unambiguously prove that step 2 is caused by QTM on the electro-nuclear level scheme. Our results show, that the observed steps in the hysteresis of SMMs generally should be caused by multiple level crossing due to hyperfine interaction. Using the Landau-Zener method [11], the size of the effective tunnel splitting $\Delta_{-15/2,+15/2}$ for the multiple processes was measured for different sweep rates in the range 1 - 38 mT/s. The tunnel splitting is given by the saturation value in the limit of fast sweep rates $(\pi \Delta^2/(2\hbar g_J | m - m' | \mu_0 \frac{dH}{dt}) \ll 1)$. It was shown [11] that a reasonable value for this limit is given by the tunneling probability P < 0.04. Due to the strong anisotropy of lanthanides and the resulting large tunnel splittings, very fast sweep rates are necessary to reach this limit. Hence, we did not reach this saturation value. However, our measurements give a lower limit for the tunnel splitting of $\Delta_{-15/2,+15/2} > 1.5 \,\mu\text{K}$. By extrapolation of the measured data, we expect even a much larger value on the order of 10^{-5} K. Avoided level-crossings at excited levels should be even larger and result in the observed barrier reduction mechanism. The large range at which the subpeaks show a strong temperature dependence cannot be explained by the hyperfine splitting of the ground state. Since the barrier is shortcut at the first excited magnetic level, hyperfine splitted intermolecular levels should be involved. In the following discussion of steps 1 and 3, we will show that intermolecular exchange interactions are the crucial factor.

In Figure 5 it can be seen, that the broad peak 3 is composed of numerous closely spaced subpeaks. With increasing sweep rate, the average position is shifted to higher fields and the total width gets larger. The related thermally activated step 1 shows the same basic features. Due to its smaller height, the substructures are even less pronounced. This can only be explained by a



FIG. 4: The first derivative of the magnetization curves for sweeps in positive field direction are presented for different temperatures and sweep rates. The observed peaks are caused by closely spaced avoided level crossings and are broadened by dipolar intermolecular interactions. (a) Thermally activated QTM causes the peaks to shift to lower fields with increasing temperature. (b) Due to decreasing tunneling probability with increasing sweep rate, the peaks at positive fields become more pronounced for faster sweeps.



FIG. 5: First derivative of the magnetization curves at different temperatures for sweeps in the positive field direction.

series of closely spaced level crossings over a wide range. For SMMs, level crossings between the 2J+1 magnetic levels, occur at the field values $H_n = \pm n D/(\mu_B g_J)$ for n=0,1,2,...,2J-1. The first magnetic level crossing at non-zero field occurs at $H_1 = \pm 5.2$ T, which shows that step 3 and 1 cannot be caused by this mechanism. Thus, we conclude that steps 3 and 1 originate from level crossings due to intermolecular interactions. It has been shown, that such weak interactions are not negligible, since they result in additional steps in the hysteresis due to tunneling transitions [12]. The intermolecular exchange interaction along the direction of stacks is responsible for the field values of these steps. In order to explain the thermally activated step 1, the coupling must be ferromagnetic. Intermolecular interactions result in additional level crossings in the level scheme. Assuming an isotropic Heisenberg coupling, characteristic level crossings around zero-field are given by the fields

$$H_q = \pm q \frac{JC}{\mu_B g_J},\tag{2}$$

where J is the total angular momentum and C is the intermolecular coupling constant. We introduced the intermolecular coupling parameter q. The possible values for q are fractional numbers depending on the intermolecular coupling scheme. Equation 2 is applicable, if all couplings are of about equal strength as in case of the chainlike coupled double-deckers. Considering a coupling between one double-decker and its two nearest neighbors along the stack, the possible values are $q = \frac{1}{2}, 1, 2$. By taking into account the splitting of levels due to hyperfine interaction, we obtain additional crossings around these fields. However, the number of crossings is still insufficient to explain the features of the broad steps. Including the coupling to the next nearest neighbors along the chain, we obtain the possible values $q = \frac{1}{4}, \frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{3}{2}, 2, 3$. This assumption is reasonable due to the strength of the coupling energy $CJ^2 \approx 3$ K between two double-deckers. Note that similar behavior was recently observed for intermolecular chainlike coupled 3d SMMs, but with more discrete steps due to much smaller broadening by hyperfine and dipolar interactions [13]. Assuming a realistic value of the coupling strength of C = 30 mK for such interactions, the width of the broad steps can be explained qualitatively. Additional crossings due to hyperfine interaction around the intermolecular levels can explain the smooth shape of these steps.

In conclusion, we have shown that the Dy doubledecker, which consists only of one metal ion, is the first member of the new class of SIMMs. The value of the zero-field splitting parameter D = -5.0 K has been determined by anisotropy SQUID measurements on single crystals. The effective barrier height for reversal of the magnetization $U_{eff} = 70$ K and the blocking temperature $T_B = 4.0$ K is larger than for any other known SMM. Preliminary experiments on the Tb double-deckers show even much larger blocking temperatures [13]. We showed that the observed steps in the hysteresis are due to QTM involving multiple anti-level crossings at close distance. The estimated order of the effective tunnel splitting $\Delta_{-15/2,+15/2} \approx 10^{-5}$ K corresponds to the large anisotropy of lanthanide complexes. The observed features of the broad steps in the hysteresis at finite fields could be traced back on a complex interplay between ferromagnetic intermolecular exchange, dipolar and hyperfine interactions.

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Multilevel Molecular Electronic Species: Electrochemical Reduction of a $[2 \times 2] \operatorname{Co}_{4}^{II}$ Grid-Type Complex by 11 Electrons in 10 Reversible Steps**

Mario Ruben, Esther Breuning, Jean-Paul Gisselbrecht,* and Jean-Marie Lehn*

The search for high-density information storage devices has stimulated an increasing interest in molecules exhibiting multistable behavior.^[1] Multistability can be achieved by several means by exploiting changes in intrinsic molecular properties such as spin state,^[2] conformation,^[3] or redox state.^[4] For instance, fullerenes and nanotubes have attracted wide interest in view of their potential in the design of new materials and electronic devices based on their unusual electrochemical behavior (reversible single-electron reductions and semiconducting properties).^[5] Multicenter transition metal complexes with different redox states are very attractive candidates for the design of multilevel electronic systems. Thus, for instance, polynuclear metal complexes of polypyridine ligands present several reversible multielectron steps.^[6]

We have described recently a new class of polypyridinederived, multinuclear metal complexes of the $[2 \times 2] M_4^{II}$ gridtype (M = transition metal),^[7, 8] which have been found to present a range of interesting structural^[7] and physicochem-

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ical (electrochemical,^[7a] magnetic^[9]) properties. Here we report on the exceptional electrochemical and spectroelectrochemical properties of one specific member of this family, complex **1**, $[Co_4L_4](BF_4)_8$, which was synthesized from ligand



L (L=4,6-bis(2',2"-bipyrid-6'-yl)-2-phenylpyrimidine^[10]) and Co(BF₄)₂ · 6H₂0 as described before.^[7b] The redox behavior of **1** has been investigated in solution (DMF) by cyclic and steady-state voltammetry (Table 1).

Cyclic voltammetry carried out at -20 °C gives rise to a cyclic voltammogram (CV) consisting of ten well-resolved, completely reversible reduction steps on the available potential window (Figures 1 a and b). Nine reduction steps are still



Figure 1. CV (a) and semidifferential convolution of one CV curve (b) of **1** in a 0.1m solution of Bu_4NPF_6 in DMF at -20 °C on a glassy carbon working electrode at a sweep rate of 1 V s⁻¹.

observed at room temperature, one less than at low temperature because of the restricted potential window at that temperature.

Analysis of the peak characteristics shows that the peak potentials are independent of the scan rates $(10-1000 \text{ mV s}^{-1})$ and that the cathodic and anodic peak current ratio (I_{pc}/I_{pa}) for each step is unity. Each peak current is also proportional to the square root of the scan rate, as expected for a reversible process. Thus, subsequent chemical reactions can be excluded. The shape and amplitude of the first reduction peak are indicative of the overlap of two one-electron transfers.

Steady-state voltammetry at the rotating disc electrode gives rise to seven well-resolved reduction waves, further ones being less well defined. The wave amplitudes indicate that the first reduction step involves two electrons, whereas the remaining steps present one electron each. Careful examination of the first reduction step, which presents a log-plot slope of 90 mV $(lg[(I/I_d - I)] = f(E); I_d = diffusion current)$ and twice the amplitude of a one-electron reduction, results in the assignment of two overlapping one-electron steps separated by about 40 mV.^[11]

Based on these results, we can conclude that ten wellresolved, reversible reduction steps involving eleven electrons are observable in **1** at -20 °C. As far as we are aware, this represents the highest reported number of well-characterized, resolved and reversible one-electron reductions on a molecular compound. For example, the fullerenes C₆₀ and C₇₀ exhibit only six reversible single-electron reductions spread over a larger potential window and located at much more negative potentials (from -0.98 V to -3.26 V).^[5]

At -1.95 V, we observe a small additional signal which can be attributed, by comparison, to the reduction of some uncoordinated ligand. This additional signal already appears during the first scan and does not increase on continued scanning. Even the use of pure crystalline material of 1 could not prevent the presence of the additional signal. However, exhaustive electrolysis as carried out by spectroelectrochemical investigations (see below) only slightly increases this signal. Thus, we attribute it to a trace of the uncoordinated ligand present in solution in equilibrium with compound 1 independent of the electrochemical studies. Indeed, investigations concerning the stability of the reduced species indicate that even after 20 repeated scans to -2.73 V, the obtained CV remained superimposable with the first scan. In comparison, the homologous Fe_4^{II} and Zn_4^{II} grid-type compounds as well as the mononuclear $[Co(terpy)_2]^{2+}$ (after threefold reduction; terpy = 2,2':6',2''-terpyridine) showed fast decomposition under identical conditions.^[12]

Basically the same voltammetric pattern is observed in acetonitrile, but with a limited number of observable waves due to the lower solubility of the reduced species of 1 in this solvent. However, an oxidation wave corresponding to the

Table 1. Redox potentials *E* and redox potential separations ΔE of **1** observed in a 0.1M solution of Bu₄NPF₆ in DMF on a glassy carbon working electrode at -20 °C (all potentials given versus ferrocene).

` 1	0		,								
Red. step	1	2	3	4	5	6	7	8	9	10	11
$E [V] \Delta E [V]$	- 0.59	-0.63 0.04	$-0.78 \\ 0.15$	$-1.02 \\ 0.24$	-1.35 0.33	$-1.60 \\ 0.35$	-1.85 0.25	- 2.11 0.26	-2.40 0.29	- 2.61 0.21	- 2.73 0.12

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transfer of four electrons at +1.0 V could be detected only by steady-state voltammetry in acetonitrile. This wave is widely spread out and has a log-plot slope of 300 mV. Such behavior is indicative of a kinetically slow process of the Co^{II}/Co^{III} redox couple, occurring stepwise on the four metal centers of the complex. Slow electron transfer rates have been observed on encapsulated metal ions in bulky and dendrimeric structures.^[13]

Spectroelectrochemical studies were carried out on **1** up to the seventh reduction step (Figure 2). The evolution of the spectrum during the first four steps is in agreement with ligand-centered reductions: the initial $\pi - \pi^*$ band of the



Figure 2. Electronic spectra of 1 and its electrochemically generated reduced forms in a 0.1 m solution of Bu₄NPF₆ in DMF at 298 K.

unreduced ligand at 370 nm decreases subsequently and two broad bands appear at 550 nm and around 800 nm. These lowenergy bands can be attributed to intraligand $\pi - \pi^*$ transitions from the new SOMOs (monoanion) to the first and the second new LUMOs (monoanion) of the reduced ligands.^[14] The initial spectrum could be recovered by stepwise oxidation of the generated heptaanion, indicative of the high stability of the reduced species.

Semiempirical PM3 molecular orbital calculations^[15] showed that the LUMO of the uncoordinated, neutral ligand is mainly centered on the pyrimidine ring. The double coordination of the pyrimidine in **1** strongly stabilizes this molecular orbital. Thus, the first four reducing electrons should be mainly localized on the bridging pyrimidine rings of the ligands. One notes that, starting with the fifth reduction, the two low-energy bands increase further, but are shifted remarkably to lower energies. Thus, the second series of four electrons is also localized on the ligand (at least up to the observable seventh electron). The red shift of the new intraligand bands can be attributed to an electronic destabilization of the corresponding HOMOs of the ligands, as a

consequence of the two electrons introduced onto the pyrimidine orbital.

In general, the gradual evolution of the intensities of the new bands expresses a proportionality with the number of reducing electrons (only the seventh step is slightly larger because of the involvement of some uncoordinated ligand). The shift of the bands to lower energies in the course of reduction is also an indication for an electronic coupling of the reduced ligands. This is also confirmed by the increasing differences between the values of the first four reduction waves in the CV ($\Delta E(1-2) = 0.04$ V; $\Delta E(2-3) = 0.15$ V; $\Delta E(3-4) = 0.24$ V). Because of the small separation between the first and the second reduction, it can be concluded that the first two reductions concern two parallel ligands and that these electrons are coupled only to a very small extent. The next two reductions occur at the remaining two ligands and the negative charge on the ligands is increasingly delocalized over the complex. We assume that up to twelve electrons could be introduced into compound 1, but the last one is probably taken up at a potential too negative to be observed.

As far as we are aware, this study presents the highest number of well-resolved, completely reversible reductions of a molecular compound. Additionally, the ten successive reduced species derived from **1** exhibit a remarkable stability in solution. Investigations concerning the reduction behavior of $[2 \times 2]$ Co₄^{II} grid-type compounds deposited as monolayers^[16] on graphite are in progress. They should in particular allow one to examine the potential use of the reported extraordinary electrochemical behavior of this class of compounds in future information storage devices.^[17]

Experimental Section

The electrochemical studies were carried out in a 0.1 M solution of Bu₄NPF₆ in DMF in a classical three-electrode cell connected to a computerized electrochemical device AUTOLAB (Eco Chemie B.V. Holland). The working electrode was a glassy carbon disc (3 mm diameter), the auxiliary electrode a platinum wire, and the reference electrode an aqueous Ag/AgCl electrode. The measurements were carried out by cyclic and steady-state voltammetry (rotating-disc electrode). Under our experimental conditions, ferrocene, used as internal standard, was oxidized at +0.45 V versus Ag/AgCl. Spectroelectrochemical studies were carried out in a home-made borosilicate glass cell placed in a diode array UV/vis spectrophotometer HP 8453 (Hewlett Packard). A platinum grid (1000 mesh) was placed in the optical pathway (about 0.1 mm) of the OTTLE cell (OTTLE = optically transparent thin-layer electrode). The auxiliary electrode was a platinum wire and the reference electrode was an aqueous Ag/AgCl electrode.

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Repetitive Application of Perfluoro-Tagged Pd Complexes for Stille Couplings in a Fluorous Biphasic System**

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The recovery and reuse of expensive catalysts is an important topic in catalytic processes. Thus, in homogeneous catalysis the use of liquid biphasic systems has attracted a great deal of attention. Examples include the aqueous biphasic Ruhrchemie/Rhône-Poulenc process,^[1] catalytic reactions in supercritical carbon dioxide,^[2] catalysis in molten salts,^[3] and use of fluorous biphasic systems (FBS).^[4]

In the FBS concept, first reported by Horváth and Rábai,^[5] owing to the perfluorinated ligands on the organometallic catalyst it is soluble in a fluorous phase (e.q. n-C₆F₁₄, C₇F₁₆, C₆F₁₃Br, CF₃C₆F₁₁). The reaction is carried out in a two-phase mixture consisting of a perfluorinated solvent and an organic solvent (toluene, hexane, acetonitrile). Such a two-phase system often becomes homogeneous at elevated temperature. Lowering the temperature after reaction leads to reformation of the two phases; the organic phase contains the product, the fluorous phase the catalyst to be reused.

This new concept has been applied to a number of catalytic reactions such as hydroformylation of alkenes,^[5] oligomerization of ethylene,^[6] hydroboration of alkenes,^[7] oxidation of aldehydes,^[8] thioethers,^[8] and alkanes,^[9] epoxidations,^[8, 10–12] Wacker oxidation of alkenes,^[13] rhodium-catalyzed carbenoid reaction,^[14] palladium-catalyzed allylic nucleophilic substitution,^[15] cross-coupling of arylzinc bromides with aryl iodides,^[16] and the Heck reaction.^[17]

Here, we report on the synthesis of three new fluoro-tagged bis-triphenylphosphanepalladium complexes and their application to the Stille cross-coupling reaction,^[18] with the goal of reusing the catalyst for subsequent cross-couplings.

Fluoro-tagged phosphanes 1a-c were synthesized with slight modifications of the original procedures^[16, 19] (Scheme 1 a, b). Replacement of the iodine substituent of *m*- or *p*iodoaniline by the perfluoro tag followed by bromination of the diazonium intermediate delivered the corresponding bromobenzene with the fluoro tag in the *m*- or *p*-position, respectively. Br-Li exchange and reaction with PCl₃ yielded the desired phosphanes **1a** and **1b**. To the best of our knowledge, **1b** has not been reported in the literature. Phosphane **1c** was prepared starting from 1,4-dibromobenzene (Scheme 1b). Reaction of the corresponding Grignard compound with C₈F₁₇CH₂CH₂I was applied to introduce the perfluoro tag. Br-Li exchange and reaction with PCl₃ led to

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Functional Supramolecular Devices: $[M_4^{II}L_4]^{8+}$ [2 × 2]-Grid-Type Complexes as Multilevel Molecular Electronic Species

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Abstract: The $[M_4^{II}L_4]^{8+}[2 \times 2]$ -grid-type complexes 1-8 present a set of features of particular interest for potential applications. All complexes exhibit multiple reduction levels at low reduction potentials paired with rather high stability. The modulation of the reduction potentials is possible by introduction of appropriate substituents on the ligands. The Co^{II}₄ complexes 1-5 present a remarkable regularity in the disposition of the reduction levels, indicating the ability of the Co^{II} sites to transmit electronic interactions between reduced ligands. In general, all investigated molecular systems 1-8 show characteristics typical for multilevel supramolecular electronic devices.

Introduction

Fundamental physical constraints as well as economics are expected to limit continued miniaturization in electronics by conventional top-down manufacturing during the next one to two decades.^[1] Bottom-up approaches to electronics, in which the functional electronic structures are assembled from well-defined nanoscale building blocks, such as carbon nano-tubes,^[2] semiconducting nanowires^[3] and/or molecules,^[4] have the potential to go far beyond the limits of conventional manufacturing. Of particular interest and great potential are approaches based on self-assembly processes capable of generating functional supramolecular devices by spontaneous but controlled build-up from their components, thus bypassing tedious nanofabrication and nanomanipulation procedures.^[5]

Scaling down electronic processes to the molecular level raises the question of controlling electron distribution in

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et de Chimie-Physique du Corps Solide UMR 7512, CNRS-Université Louis Pasteur 4, rue Blaise Pascal, 67000 Strasbourg (France) molecules. Multistability on the molecular level, as required for high-density information storage devices on the nanoscale, might be achieved by exploitation of changes in intrinsic molecular properties, such as the redox state. Multicenter transition-metal complexes with different redox states appear to be very attractive candidates for the design of multilevel electronic devices.^[6]

The redox chemistry of polynuclear oligopyridine complexes has been investigated extensively and was reviewed recently.^[7] Most electrochemical studies deal predominantly with metal-metal interactions mediated through a bridging ligand. Rather few papers provide a detailed analysis of reduction processes,[8] which may carry a wealth of information regarding the electronic interactions taking place in complexes, mainly between ligand-based redox centers. Such interactions among electrons localized on ligands are expected to be of the same order of magnitude as those between metal centers (at least, if the ligands are bound to the same metal center). Their detailed analysis opens the way to a better understanding of these multielectron species as potential components of metallo-supramolecular electronic devices. A prerequisite consists in the accurate determination of the localization of electronic changes in the individual redox steps.

Gridlike tetranuclear $[M_4^{II}L_4]^{8+}$ metal complexes with four octahedral coordination centers are accessible by self-assembly of a transition-metal ion and an appropriate bis-tridentate organic ligand in solution.^[9] Such $[2 \times 2]$ -grid species with $M = Co^{II}$ or Fe^{II} exhibit interesting magnetic behavior.^[10] In addition, Co_4^{II} complexes have been shown to present unique electrochemical properties.^[9a, 11] Related features are found in

Keywords: cyclic voltammetry • N ligands • supramolecular chemistry • UV/Vis spectroscopy

a $[2 \times 2]\text{-grid-type}$ compound based on four tetrahedral Cu^{I} sites. $^{[12]}$

The $[M_4^{II}L_4]^{8+}$ [2 × 2]-grid-type complexes **1**–**8** (Scheme 1) were generated by self-assembly from the corresponding metal salt and ligand in acetonitrile solution. Their NMR and mass spectroscopic properties were in agreement with their structure following the characterizations described earlier.^[9] The products obtained could be used directly for the electrochemical investigations without further purification.



Scheme 1. Structure of the ligands $\mathbf{A} - \mathbf{E}$ (left) and of the [2 × 2] grid-type complexes $\mathbf{1} - \mathbf{8}$ (right).

A first series of five $[Co_4{}^{II}L_4][BF_4]_8$ complexes (1-5), involving variation of ligand L, was investigated to reveal the influence of ligand substitutions on the electrochemical behavior.

The influence of the nature of the metal ion on the electrochemical properties was studied by means of a second series of four complexes $[M_4^{II}L_4][X]_8$ keeping the same ligand $L = \mathbf{B}$, but varying the metal ion: $[Co_4^{II}\mathbf{B}_4][BF_4]_8$ (2),

Abstract in French: Une série de complexes 1-8 de type grille $[2 \times 2]$, $[M^{II}_{4}L_{4}]X_{8}$ (avec M = Mn, Fe, Co, Zn; L = A - E, $X = BF_{4}^{-}$, ClO_{4}^{-} , $CF_{3}SO_{3}^{-}$) a été synthétisée et leurs propriétés électrochimiques et spectro-électrochimiques ont été étudiées. Tous ces complexes présentent des réductions monoélectroniques multiples localisées sur les ligands et sont stables à la réduction. Les potentiels de réduction peuvent être modifiés par le choix de la nature des substituents. Les complexes du Co^{II} 1-5 possèdent des niveaux de réduction également espacés mettant en évidence l'aptitude de ces ions à transmettre l'interaction électrochimique entre les ligands. L'ensemble de ces propriétés donne aux complexes 1-8 le caractère de dispositifs fonctionnels supramoléculaires à niveaux électroniques multiples.

 $[Fe_4^{II}B_4][BF_4]_8$ (6), $[Zn_4^{II}B_4][CF_3SO_3]_8$ (7), and $[Mn_4^{II}B_4]-[CIO_4]_8$ (8).

We present here an extended investigation of the electrochemical behavior of these grid-like $[M_4{}^{II}L_4]^{8+}$ complexes 1-8 incorporating differently substituted ligands L and various first row transition metal ions M^{II} . In addition, spectroelectrochemical experiments have been performed to confirm the assignment of the redox sites.

Results

Electrochemical reduction of $[M_4^{II}L_4][X]_8$ complexes 1–8: The electrochemical behavior of complexes $[M_4^{II}L_4][X]_8 \mathbf{1-8}$ $(M^{II}=\text{Co}, \text{Fe}, \text{Zn}, \text{Mn}; L=\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}, \text{ or } \mathbf{E}; X=BF_4^-, \text{CF}_3\text{SO}_3^-, \text{CIO}_4^-)$ was investigated in dimethylformamide (DMF) and acetonitrile (ACN) by cyclic (CV) and steadystate voltammetry on a glassy carbon disc electrode.

An extended sweep width over a large potential range was only accessible in DMF. However, in this solvent, slow decomposition by decomplexation within hours or minutes could be observed for several compounds by UV-visible spectroscopy. For this reason, all electrochemical studies were carried out only on freshly prepared solutions in a range of concentration of 5×10^{-4} M.

In ACN, no decomplexation was observed, neither during electrochemical studies nor by UV-visible spectroscopy. Indeed, the complexes have been proved to be more stable in this solvent. However, the low solubility of the electrochemically generated reduced species prevented investigations at more negative potentials.

Variation of the ligand L—Complexes 1–5: All Co_4^{II} complexes **1–5** in DMF give rise to seven well-resolved reduction waves during steady-state voltammetry in the available potential range. Analysis of the amplitude and of the logplot slope indicates that the first reduction always presents the characteristics of two overlapping reversible one-electron reductions separated by 40 to 80 mV. In contrast, all following waves are well-separated, reversible one-electron transfers (log-plot slope for each step close to 60 mV, as expected for a reversible one-electron transfer).

Cyclovoltammetry of complexes $[Co_4^{II}L_4][BF_4]_8 \ 1-5$ in DMF at room temperature reveals well-resolved, multiple single-electron processes with complete reversibility for each compound (Table 1). Closer inspection of the redox potentials of complexes 1-5 in DMF exhibits, within the given similarity, a slight dependence of the electrochemical behavior on the ligand substitutions.

The CV of complex $[Co_4^{II}A_4][BF_4]_8$ (1) exhibits nine oneelectron reduction steps at room temperature. In comparison, the reduction of $[Co_4^{II}B_4][BF_4]_8$ (2) under identical conditions leads to the same number of reduction steps, but with the first reduction potential slightly shifted to more positive values $(\Delta E_{1/2} = +60 \text{ mV})$. Thus, substitution of the proton by a phenyl group in the 2-position of the pyrimidine causes a positive shift of the first reduction potential. However, this shift is less pronounced in the following reductions and was rather unexpected on the basis of the known inductive effects

Table 1. Redox potential *E* of the $[Co_4^{II}L_4][BF_4]_8$ complexes **1**-**5** in dimethylformamide (DMF) or acetonitrile (ACN) (0.1 M Bu₄NPF₆, glassy carbon electrode, versus Fc⁺/Fc).

Reduction				Complex			
step	1 DMF	1 ACN	2 DMF	2 ACN	3 DMF	4 DMF	5 DMF
1	-0.65	-0.54	- 0.59	-0.50	-0.45	-0.43	-0.65
2	-0.71	-0.58	-0.63	-0.58	-0.50	-0.47	-0.69
3	-0.92	-0.68	-0.78	-0.76	-0.63	-0.60	-0.82
4	-1.31	-0.90	-1.02	-1.01	-0.75	-0.82	-1.02
5	-1.57	-1.29	-1.32	-1.36	-1.03	-1.10	-1.37
6	-1.82	-1.55	-1.60	-1.61	-1.24	-1.30	-1.57
7	-2.04	$-1.77^{[a]}$	-1.85	$-1.76^{[a]}$	-1.45	-1.50	-1.82
8	-2.26		-2.11		-1.62	-1.70	-1.95
9	-2.40		-2.40		-1.89	-1.92	-2.07
10			$-2.61^{[b]}$		-2.05	-2.12	-2.32
11			$-2.73^{[b]}$		-2.12		
12					-2.20		

[a] Irreversible reduction: cathodic peak potential. [b] At - 20 °C.

of the substituents. Decreasing the temperature to -20 °C resulted in an enlargement of the available potential window, thus giving rise to two additional reduction steps close to the electrolyte discharge.

The introduction of two electron-attracting ester groups per ligand into the 4'-position yields complex $[Co_4^{II}C_4][BF_4]_8$ (3), which bears a total of eight ester groups. The CV of 3 displays a very pronounced shift of the first reduction potential (Figure 1 top; $\Delta E_{1/2} = +200$ mV). This shift is even larger for the subsequent reduction steps and is increasing from step to step (all values relative to complex 1). The complex $[Co_4^{\Pi}D_4][BF_4]_8$ (4) bears both substitutions, a phenyl ring on the pyrimidine unit and the carboxymethyl groups in the 4'position of the ligand. This leads to an even larger positive shift of the first reduction potential ($\Delta E_{1/2} = +220 \text{ mV}$ relative to 1, Figure 1 bottom). On introduction of thio-npropyl groups into the 4'-position of the ligands in $[Co_4^{II}E_4][BF_4]_8$ (5), the reduction potentials are close to those of the unsubstituted compound 1. Apparently, the electronic influences of the four phenyl and the eight thio-n-propyl groups compensate each other in 5, resulting in an electronic situation very similar to that of the reference compound 1.

In ACN, complexes **1** and **2** give rise to a maximum of only seven reduction steps, whereas sharp peaks were observed on the reverse scan, whose shapes are characteristic for anodic redissolution processes. Evidently, the more reduced species are no longer soluble in ACN and precipitate on the electrode surface. However, CV in ACN carried out only to the sixth one-electron reduction give curves corresponding to wellresolved, reversible electron exchange. For completeness, the values for compounds **1** and **2** obtained in ACN are also given in Table 1.

Variation of the metal ion M^{II}—Complexes 2, 6–8: In a second series, the electrochemistry of four complexes $[M_4^{II}B_4][X]_8 2$, **6–8** containing different first-row transition-metal ions (with $M = Co^{II}$, Fe^{II}, Zn^{II}, and Mn^{II}, $X = BF_4^-$, ClO₄⁻, or CF₃SO₃⁻) and the ligand **B** was investigated (Table 2). The Fe₄^{II} and Zn₄^{II} compounds **6** and **7** turned out to be less stable in DMF than the corresponding Co₄^{II} compound **2**; however, the first CV scan allowed the correct determination of the redox potentials



Figure 1. Cyclic voltammetry (bold: scan rate = 0.1 V s^{-1}) and its semi-

derivative deconvolution (thin) of $[Co_4^{II}C_4]^{8+}$ (top) and $[Co_4^{II}D_4]^{8+}$ (bottom) in DMF + 0.1M Bu₄NPF₆ (potentials given versus ferrocene).

Table 2. Redox potential *E* of the $[M_4^{II}B_4][X]_8$ complexes **2** and **6–8** in dimethylformamide (DMF) or acetonitrile (ACN) (0.1M Bu₄NPF₆, glassy carbon electrode, versus Fc⁺/Fc).

Reduction		Complex									
step	2 DMF	2 ACN	6 DMF	6 ACN	7 DMF	7 ACN	8 DMF	8 ACN			
1	- 0.59	-0.50	-0.60	-0.53	-0.67	-0.60	_[c]	-0.60			
2	-0.63	-0.58	-0.65	-0.57	-0.72	-0.68	_[c]	-0.68			
3	-0.78	-0.76	-0.77	-0.70	-0.87	-0.83	_[c]	-0.82			
4	-1.02	-1.01	-0.85	-0.80	-0.92	-0.91	_[c]	-0.92			
5	-1.32	-1.36	-1.45	-1.29	-1.51	-1.36	_[c]	-1.57			
6	-1.60	-1.61	-1.55	-1.40	-1.60	-1.51	_[c]	-1.67			
7	-1.85	$-1.76^{[b]}$	-1.75	$-1.50^{[b]}$	-1.78	$-1.61^{[b]}$	_[c]	$-1.82^{[b]}$			
8	-2.11		-1.89		-1.91						
9	-2.40		-2.45		-2.50						
10	$-2.61^{[a]}$		$-2.60^{[b]}$		-2.65						
11	$-2.73^{[a]}$										

[a] Irreversible reduction: cathodic peak potential. [b] Adsorption peaks. [c] Decomposition.

despite the presence of free ligand (arrows in Figure 2), resulting from partial decomplexation (Figure 2 top and bottom). In contrast, complex $[Mn_4^{II}B_4](ClO_4)_8$ (8) decomposed completely in DMF exhibiting only the reduction peak of the decomplexed ligand ($E_{1/2} = -1.95$ V). The use of ACN

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Figure 2. Cyclic voltammetry (bold: scan rate = 0.1 V s⁻¹) and its semiderivative deconvolution (thin) of $[Fe_4^{\Pi}B_4]^{8+}$ (top) and $[Zn_4^{\Pi}B_4]^{8+}$ (bottom) in DMF + 0.1M Bu₄NPF₆ (potentials given versus ferrocene; arrows indicate reduction of free ligand resulting from partial decomplexation).

allowed the correct determination of the redox potentials of this compound in the restricted potential range as already described before for this solvent. Because of the stability problems within this series, all reduction potentials of complexes 6-8 are also given for the more stabilizing solvent ACN (Table 2). Similarly to compounds 1-5, the CVs of complexes 6-8 provide multiple one-electron reduction schemes with complete reversibility of all observed reduction waves. Thus, $[Fe_4^{II}B_4][BF_4]_8$ (6) in DMF exhibits nine reversible reduction waves; however, they are not equally distributed over the potential range as observed for the CoII complexes 1-5 (Figure 2 top). After the first set of four reductions with an internal wave separation of a maximum of $\Delta E_{1/2} = 120$ mV, the onset of the second set occurs only after a potential shift of $\Delta E_{1/2} = 600$ mV. Equally, after the second set of one-electron reductions, the third one starts only after a potential shift of around $\Delta E_{1/2} = 500$ mV, but now the following reductions are disturbed by electrolyte discharge processes.

Because of the nonreducibility of its metal centers, the complex $[Zn_4^{II}B_4][CF_3SO_3]_8$ (7) constitutes an especially interesting variation within the series (Figure 2 bottom). It presents a redox behavior very similar to that found for the Fe₄^{II} complex 6. One may conclude that the observed

reductions take place at the same redox sites in both complexes. Also, the corresponding Mn_4^{II} complex 8 exhibits a comparable CV in the restricted potential range of ACN with clustering of the reduction waves as found for 6 and 7.

Spectro-electrochemical investigations: The electrochemical results described above suggest that the electronic characteristics of the gridlike compound are dominated by the electrochemical properties of the ligands. To determine the location of the injected electrons, we carried out spectro-electrochemical investigations on complexes $[Co_4^{\Pi}B_4][BF_4]_8$ (**2**) and $[Fe_4^{\Pi}B_4][BF_4]_8$ (**6**).

The UV-visible spectra of **2** were observed progressively up to the seventh reduction step (Figure 3 top). The evolution of the spectra during the first four one-electron reductions shows the progressive appearance of two new bands with maxima at 550 nm and around 800 nm, the smaller one of which at 550 nm shows some structuring. Simultaneously, the initial $\pi - \pi^*$ band of the unreduced ligand **B** at 370 nm decreases. Further reduction beyond the fourth electron equivalent results in a increase of the intensity of the two new bands proportional to the number of accepted electrons. The observation of the reduction process beyond the seventh





Figure 3. Time-resolved UV-visible spectra during stepwise reduction of $[Co_4^{II}B_4]^{8+}$ (top) in DMF + 0.1M Bu₄NPF₆ for the six first reduction steps, and of $[Fe_4^{II}B_4]^{8+}$ (bottom) in CH₃CN + 0.1M Bu₄NPF₆ for the four first reduction steps.

electron was not possible due to technical limitations of the experimental setup.

Because of its low stability in DMF, the complex **6** was investigated in ACN, restricting so the observation of reduction only up to the fourth electron. Once more, the striking feature of the spectrum obtained is the appearance of a broad low-energy band with a maximum at 846 nm, now covering the initial MLCT band of **6** at 662 nm. Simultaneously, a small structured band with two maxima at 497 and 565 nm emerges. At the same time, as found in **2**, the initial $\pi - \pi^*$ band of the unreduced ligand at 366 nm decreases and is shifted towards lower energies. The overall features of the reduction spectra in **6** resemble strongly those observed in the analogous Co₄^{II} compound **2**.

In both experiments, the initial spectrum could be regenerated quantitatively by stepwise reoxidation of the electrogenerated reduced species (hepta-anion of 2 in DMF, tetraanion of 6 in ACN). In view of the longer timescale of the spectro-electrochemical experiments, this is a remarkable indication for the absence of side reactions during the reduction of 2 and 6.

Electrochemical oxidation of complexes 1–8: Under the present experimental conditions, none of the complexes **1–8** allowed the detection of well-defined oxidation steps by CV in DMF. Nevertheless, rotating disc voltammetry of **2** in ACN provides a long oxidation step corresponding to the transfer of four electrons at about +1.0 V. This step is widely spread out and has a log-plot slope of 300 mV. Such behavior is indicative of a kinetically slow process of the M^{III}/M^{II} redox couple, occurring stepwise on the four metal ions of the complex. Slow electron-transfer rates seem to be inherent for encapsulated metal ions in bulky and dendrimeric structures and have been observed already in other systems.^[13, 14]

However, a previous investigation of complex $[Co_4^{II}A_4][BF_4]_8$ (1) with a different experimental setup (saturated calomel electrode (SCE) in DMF) exhibited analyzable oxidation signals.^[9a] Thus, compound 1 underwent a first oxidation at $E_{1/2} = +0.46$ V, followed by a two-electron oxidation at $E_{1/2} = +0.66$ V and by a fourth wave at $E_{1/2} = +0.91$ V (all values referred to SCE).

Discussion

Electrochemical features: The electrochemical experiments of both series (variation of either ligand L or metal ion M^{II}) resulted in multiple single-electron reduction processes exhibiting a good reversibility for all waves. The first series of complexes 1-5 shows that a systematic tuning of the first reduction potential is feasible by introduction of electrondonating or -attracting substitutents on the ligand. The influence of each functional group can be evaluated qualitatively by comparing the first reduction potentials of complexes 1-5. The phenyl group in the 2-position of the pyrimidine, although suffering a hindered conjugation with the rest of the ligand by intramolecular constraints,^[10b] acts still inductively as an electron-withdrawing substitutent under these conditions and shifts the reductions of the complexes 2 and **4** to more positive potentials ($\Delta E_{1/2} = +50$ to +60 mV). As expected, the ester group has the strongest effect on the first reduction potential ($\Delta E_{1/2} = +160$ to +200 mV), while the thio-*n*-propyl group leads only to a small shift towards more negative values. This behavior reflects basically the differences in their Hammett parameters of COOMe and thio-*n*-propyl groups ($\sigma_{\rm p} = 0.45$ and 0.03).^[15]

The marked positive shift caused by the eight electronattracting ester groups enables the observation of an increased number of reduction waves. Thus, reduction of complex **3** gives rise to twelve well-resolved one-electron waves even at room temperature. This represents the highest number of well-characterized, resolved and reversible oneelectron reductions displayed by a molecular compound, reported so far. One may note that a tetranuclear $[2 \times 2]$ -gridtype Cu₄^I complex was found to have seven reduction potentials.^[12] Also, the fullerenes C₆₀ and C₇₀ exhibit six,^[16] the dinuclear compound $[{Ru(bpy)_2}_2(\mu-bpym)]^{4+}$ eight,^[8b] and the mononuclear $[Ru\{4,4'-(EtOOC)_2bpy\}]^{2+}$ compound ten^[8c] reversible single-electron reductions in a comparable or larger potential window.

Within the second series (compounds 2, 6-8), multiple oneelectron reductions are observed as in the first series, but exhibiting a "clustering" of the reduction waves into sets of four reductions for $M^{II} = Fe^{II}$, Zn^{II} , Mn^{II} , in contrast to the regular change in potentials found for $M^{II} = Co^{II}$.

The similarity in number and pattern of the reduction steps in both series and the results of the UV-visible spectroscopic experiments (vide infra) are strong indications for ligandcentered reduction.

Compared with the mononuclear complexes $[M^{II}(tpy)_2]^{2+,[17, 18]}$ the onset of the reduction processes of complexes **1–8** is strongly shifted towards positive values. This shift is in particular remarkable in complex **6**, whose first reduction potential is found at a 0.88 V more positive value than the complex $[Fe^{II}(tpy)_2]^{2+}$ under similar experimental conditions. Since reductions at very low potentials represent a more easy access to and an enhanced stability of the reduced species, this electrochemical feature is of special importance for potential applicability of such species.

Scheme 2 represents the possible main electron repulsion interactions taking place in the symmetrical $[M_4L_4]$ species. J_R expresses the repulsive interaction between the reduction electron(s) on a given bridging ligand and the further incoming electrons. J_{LL}^s represents the interaction between the electrons located on ligands bound to the *same* metal center, whereas J_{LL}^D is the analogous interaction for parallel ligands bound to *different* metal ions and situated on opposite sides in the complex. J_{MM}^B and J_{MM}^{TS} denote the interaction between the metal centers mediated through bridging ligands and occurring directly through space, respectively. These J values are not exactly accessible electrochemically, because only differences in half-wave potentials are measured experimentally. Nevertheless, the changes $\Delta E_{1/2}$ are roughly reflecting the changes in magnitudes of the repulsion terms.^[19]

The first two reduction waves of complexes 1-8 are always found in very close proximity, as consequence of the almost simultaneous reduction of two parallel ligands. $\Delta E_{1/2}$ values between the first and the second reduction ($\Delta E_{1/2} = 40-$



Scheme 2. Electronic interaction parameters in a $[2 \times 2]$ -grid-type complex. For definitions, see text.

80 mV) reflect rather small J_{LL}^{D} interactions. The electronic interactions mediated through one unreduced ligand and two interjacent metal centers seem to be similarly small for all investigated complexes.

In the case of the Fe₄^{II}, Zn₄^{II}, and Mn₄^{II} complexes **6**–**8**, the reduction waves are "clustered" into three sets of four reductions, with an internal spacing within the set of $\Delta E_{1/2} = 50-200 \text{ mV}$ and a potential shift of $\Delta E_{1/2} = 560-650 \text{ mV}$ between successive sets (Table 2, Figure 2). This is the behavior one may expect. Indeed, the first gap inserts between the fourth and the fifth reduction, where each of the four ligands has already accepted one electron, so that incoming electrons have to overcome the repulsive interaction $J_{\rm R}$ with the electron already present on the same ligand. This repulsion is normally reflected in the amount of spin-pairing energy in polypyridine ligands found to be about $\Delta E_{1/2} = 600-700 \text{ mV}.^{[19]}$

In marked contrast, all Co₄^{II} complexes **1**–**5** show a regular spacing of $\Delta E_{1/2} = 130-390$ mV for all subsequent reductions occurring at ligands bound to the same metal ion as an already reduced ligand, (Table 1; Figure 1). This even spacing of the one-electron processes over the whole potential range is indicative of electronic communication J_{LL}^{s} between the ligand centered redox sites through the interjacent common Co^{II} ion. Remarkably, the J_{R} interaction appears to be decreased in these Co₄^{II} complexes relative to the others, and to have become similar in magnitude to J_{LL}^{s} . Closer inspection of the CVs indicates that there is nevertheless a limited potential shift ($\Delta E_{1/2} = 140-390$ mV) after each fourth reduction, noticeably smaller, however, than the 560–650 mV observed for complexes **6**–**8** containing no Co^{II} sites.

Evidently, the differences in the magnitude of the $J_{\rm R}$ interaction between the Co₄^{II} compounds **1**–**5** and the other complexes **6**–**8** reflect the ability of the interjacent M^{II} ions to mediate $J_{\rm LL}^{\rm s}$ interactions (equally expressed by larger $J_{\rm LL}^{\rm s}$ values for the Co₄^{II} compounds of $\Delta E_{1/2} = 130-390$ mV for **1**– **5** compared to $\Delta E_{1/2} = 50-200$ mV for **6**–**8**). A better mediating ability of the interjacent Co^{II} ions between the reduced ligand anions should lead to a certain electronic coupling over the complex, thus reducing the repulsion for incoming further electrons. These features portray electronic interactions between ligand-centered redox sites mediated through "bridging metals", in contrast to the well-investigated metal-metal interactions through "bridging ligands".^[20]

The previously reported oxidation of compound $[Co_4^{II}A_4][BF_4]_8$ (1) gives additional access to the metal-metal interactions J_{MM}^{B} and $J_{\text{MM}}^{\text{TS}}$.^[9a] The one-two-one sequence evokes a preference of successive oxidations of adjacently located Co^{II} centers. Consequently, the second two-electron step would represent the simultaneous oxidation of two diagonally situated Co^{II} ions expressing a through-space J_{MM}^{TS} interaction, which is apparently too small to be determined. On the other hand, the separation between the first and second two-electron steps and thereafter between the twoelectron and the last oxidation step should represent the electronic J_{MM}^{B} interaction of two adjacent Co^{II}-ions through the bridging pyrimidine group of the ligand. Thus, the $J_{\rm MM}^{\rm B}$ values of $\Delta E_{1/2} = 200$ and 250 mV indicate substantial electronic interaction between two adjacent metal centers, corresponding to a medium strong comproportionation constant of $K_{\rm com} = 1.7 - 2.4 \times 10^3$.^[20]

Electronic spectra: Although carried out in different solvents, the spectral behavior of the Co_4^{II} complex **2** and of the Fe_4^{II} complex **6** during reduction is similar (Figure 3). As reduction proceeds, a broad spectral band around 800 nm and a smaller, more structured band around 550 nm emerge, while at the same time the band below 400 nm decreases progressively. Additionally, the MLCT transition around 620 nm in compound **6** disappears or is covered by the new bands. All changes in intensity occur almost linearly with the number of electrons added.

The two new emerging low-energy bands in **2** and **6** can be assigned, by comparison with the absorption spectra of the mono-reduced form of uncoordinated bipyrimidine (bpym) in DMF (two bands with $\lambda_{max} = 500$ and 800 nm) and of coordinated bipyrimidine in mono-reduced [Fe(bpym)₃]²⁺ (two bands with $\lambda_{max} = 510$ and 1020 nm), to intraligand $\pi^* - \pi^*$ transitions from the new SOMOs (mono-anion) to the first and the second new LUMOs (mono-anion) of the four monoreduced **B**⁻ radical anions.^[18, 21]

Interestingly, the emerging bands in the absorption spectra of **6** exhibit a linear increase in intensity of the radical bands (without any additional perturbations of the spectra) even beyond the fourth electron added. This is in line with the formation of a dianion \mathbf{B}^{2-} , similar to bpym²⁻ observed in the reduction of μ -bipyrimidine in [{Ru(bpy)_2}_2(\mu-bpym)]^{4+,[8c]}

The band of the nonreduced ligand in **2** and **6** located below 400 nm can be assigned to the $\pi - \pi^*$ transition of the ligand **B**. Consequently, its intensity decreases on progressive population of the LUMO of the coordinated ligand by the reducing electrons.

It is worth mentioning that all intraligand reduction bands, increasing and decreasing, experience a subsequent shift to lower energies on progressive reduction, especially beyond the fourth reduction. This red shift can be associated with an electronic destabilization of the corresponding HOMOs of the ligands, as a consequence of the second electron introduced into the ligand orbitals. No evidence for low-lying interligand and intervalence transitions has been found. Also, aggregate formation at the used concentrations (less than 5×10^{-4} M) can be excluded by the spectroscopic data.

Conclusion

The electrochemical behavior of the family of tetranuclear gridlike oligopyridine complexes 1-8 of the general formula $[M_4{}^{II}L_4]^{8+}$ displays well-resolved multiple one-electron reductions for all compounds independent of the nature of ligands A-E and of the coordinated metal ions M^{II} .

Introduction of electron-donating and -attracting groups into the ligands systematically tunes the potential of the first reduction. As a consequence, reduction of complex $[Co_4^{II}B_4][BF_4]_8$ (3) exhibits up to twelve well-resolved reversible one-electron processes at room temperature; this appears to be the most extended redox series known for well-characterized molecular compounds.

The rather low values of the redox potentials are of importance for the stability of the generated multielectron species and thus for their possible applications as devices presenting multiple electronic levels. For the Co_4^{II} complexes the repulsive interaction parameter J_R is unusually small, and comparable to the electronic interaction J_{LL}^{S} between two neighboring ligands through an interjacent metal ion. Since J_R was found for the non- Co_4^{II} compounds in the expected range, this difference displays an ability of the Co^{II} ion (relative to Fe^{II}, Zn^{II}, and Mn^{II}) to better mediate electronic interactions. This is also confirmed by slightly larger J_{LL}^{S} values for all investigated Co_4^{II} complexes. Thus, the ability of different M^{II} ions to act as "bridging metals" for electronic interactions seems to be responsible for the differences in the pattern of the reduction scheme.

Spectro-electrochemical experiments revealed that the reductions take place on the coordinated organic ligands, independent of the nature of the metal ions involved. No indication for reduction of the metal centers was observed in the accessible potential range.

The oxidation of complex $\mathbf{1}^{[9a]}$ reveals a medium strong J_{MM}^{B} interaction between adjacent metal centers mediated by the pyrimidine groups of the ligands, while the electronic $J_{\text{MM}}^{\text{TS}}$ interaction between nonadjacent metal centers through space is too small to be determined.

Further study of the nature of the radical anions L^{-} and of the dianions L^{2-} and their interplay with the different open spin-bearing metal ions (implicating even spin-crossover phenomena),^[10b] requires magnetic and EPR investigations of the reduced species.

In conclusion, the grid-type complexes 1-8 present a set of features of particular interest for potential applications as supramolecular electronic devices: 1) multiple reduction levels, 2) ease of reduction, 3) stability towards reduction, 4) modulation of the reduction potentials by appropriate substituents on the ligands, and 5) in the case of the Co^{II} species, regularity in disposition of the reduction levels.

Experimental Section

Electrochemistry: The electrochemical studies were carried out on 5.10⁻⁴ M solutions of complexes 1-8 in DMF + 0.1M Bu₄NPF₆ or in ACN + 0.1M Bu₄NPF₆ in a classical three-electrode cell connected to a computerized electrochemical device AUTOLAB (Eco Chemie B.V. Holland). The working electrode was a glassy carbon disc (3 mm diameter), the auxiliary electrode a platinum wire, and the pseudoreference electrode a silver wire. The measurements were carried out by cyclic voltammetry and by steadystate voltammetry (rotating disc electrode). In our experimental conditions all potentials are referred versus ferrocene, used as an internal standard. DMF and acetonitrile (both Aldrich, spectroscopic grade) were dried over molecular sieves 4 Å prior to use. The measurements were carried out at room temperature and in some cases at -20°C. Spectro-electrochemical studies were carried out in a home made borosilicate glass cell with an optical pathway length of 0.1 mm placed in a diode array UV/Vis spectrophotometer HP8453 (Hewlett Packard). The OTTLE cell was a platinum grid (1000 mesh) placed in the optical pathway. The auxiliary electrode was a platinum wire and the reference electrode was an aqueous Ag/AgCl electrode. Under the described experimental conditions, ferrocene, which was used as internal standard in all measurements, was oxidized at +0.45 V.

Synthesis: All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. The following solvents were distilled prior to use: tetrahydrofuran (THF) and diethyl ether from sodium and benzophenone, and dimethyl sulfoxide (DMSO) from calcium hydride under Ar. All organic solutions were routinely dried over magnesium sulfate or sodium and solvents were removed under vacuum using a rotary evaporator. ¹H and ¹³C NMR spectra were recorded on a Bruker AC200 spectrometer at 200 MHz and 50 MHz, respectively. Flash chromatography was performed by using neutral alumina (activity 2). FAB mass spectra were performed on a Fisons TRIO-2000 (Manchester) and a Micromass AUTOSPEC-M-HF spectrometer using 3-nitrobenzylic alcohol as matrix. IR data were collected on Perkin–Elmer 1600 Series FTIR spectrometer. Microanalyses were carried out by the Service de Microanalyse, Faculté de Chimie, Strasbourg. Melting points were measured on a digital electrothermal apparatus and are uncorrected.

Ligands: The synthesis of ligands **A** and **B** was described earlier.^[22, 10b] Ligands **C** and **D** were synthesized by using Stille-type coupling procedures following the reactions depicted in Scheme 3.



Scheme 3. i) Sn₂Me₆, [Pd(PPh₃)₄] (cat.); ii) [Pd(PPh₃)₄] (cat.).

2-Bromo-4-(methylcarboxylate)-6-(pyrid-2'-yl)pyridine: 2-(Tributylstannyl)pyridine^[23] (672 mg, 1.83 mmol), 2,6-dibromo-4-(methylcarboxylate)pyridine^[24] (700 mg, 2.37 mmol), and [Pd(PPh₃)₄] (137 mg, 0.19 mmol) were combined in toluene (10 mL), flushed with Ar, and heated under reflux for 39 h. The mixture was poured into KF (10 mL saturated solution) and, after addition of Et₂O, was stirred for 2 h. The precipitate was filtered and the phases were separated. The aqueous phase was extracted with Et₂O (2 \times 40 mL). The combined organic phases were washed with $H_2O~(1\times30~\text{mL})$ and dried over MgSO4, and the solvent was evaporated. The product was purified by column chromatography on silica by using hexane/EtOAc (3:1 v/v) as eluant to give 2-bromo-4-(methylcarboxylate)-6-(pyrid-2'-yl)pyridine as a white powder. Yield: 221 mg (0.75 mmol, 41 %); m.p. 142 °C; ¹H NMR (200 MHz, CDCl₃, 298 K): $\delta = 3.99$ (s, 6H; CH₃), 7.36 (ddd, J =7.6, 4.9, 1.2 Hz, 1H; H⁵), 7.84 (td, J = 7.9, 1.8 Hz, 1H; H⁴), 8.04 (d, J =1.2 Hz, 1 H; H³ or H⁵), 8.42 (dt, J = 7.9, 1.2 Hz, 1 H; H³), 8.70 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H; H⁶), 8.91 ppm (d, J=1.2 Hz, 1H; H³ or H⁵); ¹³C NMR $(50 \text{ MHz}, \text{ CDCl}_3, 298 \text{ K}): \delta = 52.8, 119.1, 121.4, 124.5, 127.2, 136.9, 140.6,$ 141.9, 149.2, 153.5, 158.1, 164.2 ppm; EI-MS: *m*/*z*: 293.9 [*M*⁺], 233.9 [*M*⁺

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COOMe]; IR (KBr): $\tilde{\nu} = 3007$, 2956, 1732, 1585, 1550, 1433, 1381, 1310, 1242, 1118, 994, 977, 813, 763, 731, 664 cm⁻¹; elemental analysis calcd (%) for C₁₂H₉BrN₂O₂: C 49.17, H 3.09, N 9.56; found: C 49.43, H 3.41, N 9.20.

4,6-Bis[4'-(methylcarboxylate)-6'-(pyrid-2''-yl)pyrid-2''-yl)pyridine (Ligand C): 2-Bromo-4-(methylcarboxylate)-6-(pyrid-2'-yl)pyridine (211 mg, 0.72 mmol), hexamethyldistannane (259 mg, 0.79 mmol), and [Pd(PPh₃)₄] (42 mg, 0.036 mmol) were combined in tolucen (5 mL), flushed with Ar and heated under reflux for 30 min. The solvent was evaporated and the crude stannylated product was used for the following coupling reaction without further purification. ¹H NMR (200 MHz, CDCl₃, 298 K): δ = 0.41 (s, 9H; Sn(CH₃)₃), 3.96 (s, 3H; CH₃), 7.81 (td, *J* = 7.9, 1.8 Hz, 1H; H⁴), 8.00 (d, *J* = 1.5 Hz, 1H; H³ or H⁵); FAB-MS (NBA): *m/z*: 379.2 [*M*⁺].

4-(Methylcarboxylate)-6-(pyrid-2'-yl)-2-(trimethylstannyl)pyridine

(812 mg, 2.15 mmol) and 4,6-dibromopyrimidine (250 mg, 0.76 mmol) were combined in toluene (10 mL), degassed, and [Pd(PPh₃)₄] (48 mg, 0.042 mmol) was added. The solution was flushed with Ar and heated under reflux for 24 h. The precipitate was filtered off, washed with MeOH and acetone and dried in vacuo to give **C** as an off-white powder. Yield: 350 mg (0.69 mmol, 91 %); m.p. > 300 °C; ¹H NMR (200 MHz, CDCl₃/CF₃COOD, 298 K): $\delta = 4.11$ (s, 6H; CH₃), 8.20 (t, J = 5.8 Hz, 2H; H^{4''} or H^{5''}), 8.55 (d, J = 7.3 Hz, 2H; H^{3''}), 8.65 (t, J = 8.8 Hz, 2H; H^{4''} or H^{5''}), 8.55 (d, J = 7.3 Hz, 2H; H^{3''}), 8.65 (t, J = 8.8 Hz, 2H; H^{4''} or H^{5''}), 8.76 (d, J = 1.1 Hz, 2H; H^{3'} or H^{5'}), 9.34 (d, J = 5.8 Hz, 2H; H^{6''}), 9.39 (d, J = 1.1 Hz, 2H; H^{3'} or H^{5'}), 9.54 (d, J = 1.5 Hz, 1H; H⁵), 9.94 ppm (d, J = 1.1 Hz, 1H; H²; l^{3C} NMR (50 MHz, CDCl₃/CF₃COOD, 298 K): $\delta = 105.8$, 111.4, 171, 122.8, 142.7, 143.3, 148.0, 159.5, 160.4, 161.2, 162.1, 163.9 ppm; FAB-MS: $m_i z$: 505.1 [M^+ +H]; IR (KBr): $\tilde{r} = 1733$, 1580, 1537, 1431, 1376, 1349, 1235, 1111, 1068, 761, 683 cm⁻¹; elemental analysis calcd (%) for C₂₈H₂₀N₆O₄: C 66.66, H 4.00, N 16.66; found: C 66.62, H 3.72, N 16.68.

4,6-Bis[4'-(methylcarboxylate)-6'-(pyrid-2"-yl)pyrid-2'-yl)-2-phenylpyrimidine) (Ligand D): 4-(Methylcarboxylate)-6-(pyrid-2'-yl)-2-(trimethylstannyl)pyridine (244 mg, 0.65 mmol), 4,6-dichloro-2-phenylpyrimidine (73 mg, 0.32 mmol), and $[PdCl_2(PPh_3)_2]$ (18 mg, 0.026 mmol) were combined in anhydrous DMF (5 mL), degassed, flushed with Ar, and heated to $100\,^\circ\text{C}$ for 46 h. The solvent was evaporated and the residue taken up in MeOH/ acetone (1:1 v/v). The precipitate was centrifuged off, washed with MeOH/ acetone, and dried in vacuo. The residue was dissolved in boiling CHCl3 and filtered, and the solvent was evaporated to give ligand D as an off-white powder. Yield: 90 mg (0.16 mmol, 44% over 2 steps); m.p. >250 °C (decomp); ¹H NMR (200 MHz,CDCl₃, 298 K): $\delta = 4.09$ (s, 6 H; CH₃), 7.39 (dd, J = 6.4, 4.9 Hz, 2H; H⁵"), 7.60 – 7.63 (m, 3H; H^{meta} and H^{para}), 7.91 (td, $J = 6.7, 1.5 \text{ Hz}, 2 \text{ H}; \text{H}^{4''}$, 8.75 – 8.86 (m, 6 H; H^{ortho}, H^{3''} and H^{6''}), 9.14 (d, J = 1.2 Hz, 2 H; H^{3'} or H^{5'}), 9.24 (d, J = 1.5 Hz, 2 H; H^{3'} or H^{5'}), 9.64 ppm (s, 1 H; H⁵); ¹³C NMR (50 MHz, CDCl₃, 298 K): $\delta = 52.8$, 111.7, 121.0, 121.3, 121.9, 124.4, 128.6, 131.0, 136.8, 137.5, 139.9, 149.4, 154.9, 155.1, 156.7, 163.5, 164.4, 165.7, 168.7 ppm; HR-FAB-MS: m/z calcd for $C_{34}H_{25}N_6O_4$: 581.193729; found: 581.193730 [*M*⁺+H]; IR (KBr): $\tilde{\nu}$ = 3065, 2955, 1732, 1560, 1543, 1364, 1254, 1231, 756, 734, 684, 665 cm⁻¹; elemental analysis calcd (%) for C₃₄H₂₄N₆O₄: C 70.34, H 4.17, N 14.47; found: C 69.81, H 4.17, N 14.08

4,6-Bis[6'-(pyrid-2"-yl)-4'-(thio-*n***-propyl)pyrid-2'-yl]-2-phenylpyrimidine** (**Ligand E**): Ligand **E** was synthesized by using Potts' synthesis protocol (Scheme 4);^[24] the bis-Michael acceptor was synthesized according to the literature.^[25] 2-Acetylpyridine (0.43 g, 3.56 mmol) and the bis-Michael acceptor (1.00 g, 1.78 mmol) in THF (50 mL) were added to a stirred solution of potassium *tert*-butoxide (0.80 g, 7.12 mmol) in THF (30 mL) under Ar. The resulting red solution was stirred at room temperature for



Scheme 4. i) tBuOK, THF, RT; ii) NH₄OAc, AcOH.

16 h. Glacial acetic acid (10 mL) and ammonium acetate (5 g) were added. The mixture was heated under reflux for 2 h, cooled, and poured into water (200 mL), and the product was extracted with chloroform. The combined organic phases were washed with sat. NaHCO₃ and water, and dried over Na₂SO₄; the solvent was evaporated. The product was isolated by column chromatography (alumina, chloroform) as an off-white solid that was recrystallized from acetone to afford **E** (0.50 g, 0.81 mmol) as a white powder in 45 % yield. ¹H NMR (200 MHz, CDCl₃, 298 K): δ = 1.17 (t, *J* = 7.3 Hz, 6 H), 1.87 (sext, *J* = 7.3 Hz, 4 H), 3.18 (t, *J* = 7.3 Hz, 4 H), 7.37 (m, 3 H), 7.82 (dt, *J* = 7.6, 1.5 Hz, 2 H), 8.40 (d, *J* = 1.5 Hz, 2 H), 8.52 (d, *J* = 1.5 Hz, 2 H), 8.70 (m, 6 H), 9.54 ppm (s, 1 H); ¹³C NMR (50 MHz, CDCl₃, 298 K): δ = 13.7, 22.2, 32.9, 118.5, 118.8, 121.5, 124.0, 128.4, 128.6, 136.6, 149.2, 152.0, 155.1, 155.8, 163.9 ppm; elemental analysis calcd (%) for C₃₆H₃₂N₆S₂: C 70.56, H 5.26, N 13.71, S 10.47; found: C 70.25, H 5.22, N 13.64, S 10.18.

Complexes: The synthesis of complexes 1,^[9a] 2,^[9b] 6,^[10b] and 7^[9b] was carried out following literature protocols. A typical protocol for the synthesis of complexes 3, 4, 5, and 8 is as follows: A suspension of the ligand (19.8 µmol) and the metal salt (19.8 µmol) in ACN (1.5 mL) was briefly heated until the mixture was dissolved completely. The solution was stirred for additional 12 h at room temperature (in the case of solubility problems under reflux). The complex was isolated by evaporation of the solvent or addition of diisopropyl ether (5 mL) to the solution until a precipitate formed. The precipitate was collected, washed with diisopropyl ether, and dried *in vacuo*. The crude product was used directly for the measurements without further purification.

Complex 4: ¹H NMR (200 MHz, [D₃]ACN, 298 K): $\delta = 0.5$, 8.3, 42.0, 62.7, 63.8, 82.5, 117.3, 151.0 ppm; FAB-MS: m/z: 2774.4 [$M^+ - 2BF_4$], 2687.6 [$M^+ - 3BF_4$], 2601.0 [$M^+ - 4BF_4$], 2514.4 [$M^+ - 5BF_4$]; elemental analysis calcd (%) for C₁₃₆H₉₆N₂₄O₁₆Co₄B₈F₃₂: C 53.59, H 3.17, N 11.07; found: C 50.01, H 3.07, N 10.57.

Complex 5: ¹H NMR (200 MHz, [D₃]ACN, 298 K): $\delta = -19.3$, 1.9, 3.5, 8.0, 10.2, 13.1, 13.3, 21.5, 22.3, 40.6, 51.5, 73.7, 140.9, 167.6 ppm; FAB-MS: m/z: 3208.5 [$M^+ - 2BF_4$], 3121.5 [$M^+ - 3BF_4$], 3033.6 [$M^+ - 4BF_4$], 2946.6 [$M^+ - 5BF_4$], 1560.3 [$M^{2+} - 3BF_4$], 1516.8 [$M^{2+} - 4BF_4$], 1473.3 [$M^{2+} - 5BF_4$]; elemental analysis calcd (%) for C₁₄₄H₁₂₈N₂₄S₈Co₄P₈F₃₂: C 50.45, H 3.87, N 10.08; found: C 50.04, H 3.50, N 9.71.

Complex 8: ¹H NMR (200 MHz, [D₃]nitromethane, 298 K): $\delta = 1.32$ (br), 8.5 ppm (br); FAB-MS: m/z: 2673.9 [$M^+ - 2 \operatorname{ClO}_4$], 2574.8 [$M^+ - 3 \operatorname{ClO}_4$], 2474 [$M^+ - 4 \operatorname{ClO}_4$], 2376.9 [$M^+ - 5 \operatorname{ClO}_4$], 1286.9 [$M^+ - 5 \operatorname{BF}_4$]²⁺; elemental analysis calcd (%) for C₁₂₀H₈₀N₂₄Cl₈Mn₄O₃₂: C 50.15, H 3.81, N 11.69; found: C 50.24, H 2.98, N 12.39.

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Charge-induced maximal spin states of a polynuclear transition-metal complex

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We theoretically investigate the ground state spin of a polynuclear transition-metal complex as a function of the number of added electrons taking into account strong electron correlations. Our phenomenological model of the so-called $[2 \times 2]$ -grid molecule incorporates the relevant electronic degrees of freedom on the four transition-metal centers (either Fe²⁺ or Co²⁺) and the four organic bridging ligands. Extra electrons preferably occupy redox orbitals on the ligands. Magnetic interactions between these ligands are mediated by transition-metal ions and vice versa. Using both perturbation theory and exact diagonalization we find that for certain charge states the maximally attainable total spin (either $S_{tot} = 3/2$ or $S_{tot} = 7/2$) may actually be achieved. Due to the Nagaoka mechanism, all unpaired electron spins couple to a total maximal spin, including unpaired electron spins on the metal-ions in the case of Co²⁺. The parameters are chosen to be consistent with cyclovoltammetry experiments in which up to twelve redox states have been observed. The above effect may also be realized in other complexes with an appropriate connectivity between the redox sites. The maximal spin states of such a charge-switchable molecular magnet may be experimentally observed as spin-blockade effects on the electron tunneling in a three-terminal transport setup.

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I. INTRODUCTION

The synthesis and investigation of molecule based magnets have been active areas of research for almost a decade [1, 2]. Today molecule based magnets offer a variety of chemical and magnetic properties which have potential applications in a wide range of systems. Photo-magnetic (e.g. $K_{0.4}Co_{1.3}[Fe(CN)_6]$) or spin-crossover magnetic substances (e.g. Fe(o $phenanthroline)_2(NCS)_2)$ offer potential applications in switchable devices. Polynuclear transition-metal complexes are particularly attractive in the effort to design molecules with magnetic centers which couple either ferro- or antiferromagnetically. Interesting quantum tunneling effects were reported for ferromagnetic molecules, e.g. Mn_{12} [3] and Fe_8 [4]. Antiferromagnets are of interest also due to effects associated with the Néel-vector [5-7]. One interesting class of highly-designable complexes is the $[M \times M]$ -grid structure which is formed by selfassembly [8–11]. It consists of M^2 transition-metal centers which are positioned by two perpendicular arrays of rod-like ligands, each with M coordination sites. The transition-metals typically lie in a plane due to symmetric positioning of the ligands. Several realizations of these supramolecules exist which exhibit a variety of magnetic and electrochemical properties, which can be manipulated via sidegroup substitutions. In this paper we focus in particular on the $[2 \times 2]$ -grid depicted in Figure 1. It consists of four organic ligands (bis(bipyridyl)bipyrimidine) and four transition-metal ions (e.g. Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} or Zn^{2+} [12]). Each metal-ion is situated in an approximately octahedral environment of nitrogen atoms. The total charge 8+ of the complex is countered by anions, e.g. BF_4^- . The $Co^{2+}-[2 \times 2]$ -grid exhibits an impressive twelve reversible reduction steps



FIG. 1: Structure of the $[2 \times 2]$ -grid-type complex.

in solution in a cyclic voltammetry at T = 253K [12]. It is also possible to trap and identify these complexes on a graphite surface in a controlled way [13]. Furthermore, in $\operatorname{Co}^{2+}-[2\times 2]$ -grids the spin of each metal-ion was found to be S = 1/2 at low temperature and their intramolecular magnetic coupling was demonstrated to be antiferromagnetic [14].

We have developed a phenomenological stronglycorrelated electron model which represents the important spin and charge degrees of freedom that play a role in both the redox chemistry and the magnetic interactions of $[2 \times 2]$ -grid complexes. We include the strong electrostatic interactions between electrons localized on the metal-ions and the ligands as well as the weak tunneling of electrons between them. A crucial feature of our model is that the orbital and charging energies on the ligands and ions are very different, a situation common in transition-metal complexes. We are interested in how the electron spins on the molecule couple to form the total magnetic moment and how this coupling is affected by total electron number which can be electrically controlled in a three terminal transport setup (which is not considered here). The metal-ions mediate the coupling between electrons on the ligands and vice versa. We also want to study the effect of an unpaired electron spin on a mediating metal-ion on the ligand-ligand spin coupling, which will in turn determine the total spin formed by the ion and ligand subsystems. Two simple cases are therefore considered, assuming each ion is in a low-spin state: either S = 0, Fe²⁺, or $\overline{S} = 1/2$, Co²⁺. The Coulomb interaction also generates direct exchange coupling between unpaired electrons on ligands and metal-ions which we also take into account. We focus on how the spins couple to a magnetic moment of large magnitude due to strong Coulomb and kinetic effects depending on the total charge. We do not consider effects on smaller energy scales which determine the preferred direction of the magnetic moment.

As expected, an antiferromagnetic coupling between the metal-ion and ligand subsystems prevails for most total charge numbers. Extra electrons added to the bridging ligands introduce a ferromagnetic spin correlation between the metal-ions if the latter have a spin. However, we find that near half-filling of the four ligand orbitals sufficiently strong Coulomb interactions can stabilize a maximal spin ground state ($S_{tot} = 3/2$ for Fe²⁺ and 7/2 for Co^{2+}) by the Nagaoka mechanism [15]. Due to the Pauli principle a missing or excess electron on the ligands (relative to half-filling) can be delocalized maximally when the "background" of the remaining electrons is completely spin-polarized. In our model this effect is most easily achieved for a Fe²⁺- $[2 \times 2]$ - grid. For a Co^{2+} -[2 × 2]-grid the spins of electrons localized on the bridging metal-ions counteract the Nagaoka mechanism. However, the direct exchange coupling between unpaired electrons on the neighboring ligands and metal-ions cooperates with the Nagaoka mechanism [16]. The resulting maximal spin is however more than twice as large as for Fe^{2+} . The charge-sensitive spin-polarization requires a strong local Coulomb charging effect and metal-toligand charge-transfer (MLCT) barrier. The former can be achieved chemically by introducing electron-donating sidegroups on the ligands [12]. The electrochemical experiments [12] were performed near room temperature where thermal occupation of high-spin excited states of the metal-ions becomes possible. Generalization of our model to incorporate the high-spin states of the ions is, however, nontrivial since vibrational degrees of freedom of the nuclear framework are involved in their stabilization [17]. This is beyond the scope of the present paper where we focus on low temperature behavior.

Experimental detection of sublattice and total magnetization as a function of the number of added electrons would be of great interest. In particular, we propose electron transport through the complex in a three terminal

setup. In a gate voltage range where the ligand orbitals are near half-filling the large change in ground state spin $(\Delta S_{\text{tot}} = 3/2 \text{ (Fe}^{2+}), \text{ resp. } \Delta S_{\text{tot}} = 7/2 \text{ (Co}^{2+}))$ may be revealed through the spin-blockade effect [18]. We have investigated this transport problem in detail for a simple generic model n [19]. The goal of the present paper is to derive and investigate the effective model, in particular the effect of bridging metal-ions with a spin. Experiments in semiconductor heterostructures show that a transport current can couple through the spin-blockade effect to electron spins localized in a quantum dot and subsequently to nuclear spins in the local environment via the hyperfine interaction [20]. This offers an interesting perspective for single-molecule transport where the immediate nuclear environment of the device can be controlled at the level of chemical synthesis.

The paper is organized as follows. In section II we discuss the minimal set of orbitals involved in electron addition processes and the intramolecular magnetic coupling. This serves as a motivation for the correlated electron model which we introduce in section III. In section IV we discuss a perturbative treatment of the ion-ligand tunneling in this model to gain a simple understanding of the role of spin degrees of freedom on the ions. We obtain the ground states and low energy total-spin excitations in sections V A and V B. We discuss the electron addition energies and the modulation of the ground state spin as a function of the number of added electrons. We conclude with a discussion of implications for electron tunneling experiments in section VI.

II. ELECTRONIC STRUCTURE

We can expect that the dominant molecular orbitals (MOs) at the Fermi energy are either *d*-like orbitals from the metal 2+ ions or π -orbitals from the ligands. The electrochemical experiments [12] indicated that additional electrons occupy orbitals localized mostly on the *ligands*, which is not uncommon for polypyridine complexes [21].

Let us first consider the individual metal-ions which are coordinated by six nitrogen atoms. In a ligand-field picture, an octahedral coordination of each metal-ion in the grid would cause their *d*-orbitals to split up into two shells, t_{2g} (d_{xy}, d_{xz}, d_{yz}) and e_g ($d_{x^2-y^2}, d_{z^2}$). However, the symmetry of the local environment is lower and results in a small splitting of the levels in each shell. The different orbital occupations for Fe²⁺ and Co²⁺ are shown in Figure 2. In the case of Fe²⁺ in its low-spin configuration the t_{2g} shell is closed and the e_g orbitals are empty. In the case of Co²⁺ there is an additional unpaired electron in the lowest of the two e_g orbitals.

The highest occupied molecular orbitals of the ligands are mostly of π character as ab-initio calculations show. The important point is that the empty or singly occupied e_g -orbitals on the metal-ions have different approximate symmetry (σ). This means we can consider lig-



FIG. 2: Orbital configuration of transition metal-ions and ligands.



FIG. 3: Geometry of transition-metal $[2 \times 2]$ -grid consisting of metal-ion orbitals (small circles), Fe²⁺ (left) and Co²⁺ (right), connected by ligands (large circles). The hopping t, orbital energies E, ϵ and Coulomb charging U, V, u, v, w and direct exchange energy F are shown schematically.

ands and metal-ions weakly coupled systems and discuss the tunneling of electrons between them. The remaining question is whether extra electrons prefer to occupy the metal-ion *d*-orbitals or the ligand π -orbitals. As far as charging effects are concerned, one expects that the onsite energy *U* on the metal ions is larger than the on-site energy *u* on the ligands because orbitals are more contracted on the metal-ions. Furthermore, electrons would favor positions between two positively charged ions, i.e. on the bridging ligand. This is in line with the interpretation of the cyclovoltammetry experiments [12]. The main difference in our model between the $\operatorname{Co}^{2+}/\operatorname{Fe}^{2+}-[2 \times 2]$ grids will thus be the presence/absence of an localized, unpaired electron in an orbital of the metal-ion bridging the two ligands (Figures 2, 3).

III. CHARGING MODEL

We model the $[2 \times 2]$ -grid complex by four metal (Fe²⁺ or Co²⁺) and four ligand sites with one spin-degenerate orbital per site (Figure 3). The following Hamiltonian then captures the features of the electronic degrees of

freedom discussed in section II:

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$$H = H_{\rm T} + H_{\rm L} + H_{\rm Fe/Co} + H_{\rm dir} + H_{\rm V},$$
 (1)

$$H_{\mathsf{T}} = \sum_{\langle i,j \rangle} \sum_{\sigma} t \, A^{\dagger}_{i,\sigma} a_{j,\sigma} + h.c.$$
 (2)

$$H_{\mathsf{L}} = \sum_{j=1}^{4} (\epsilon n_{j} + u \, n_{j,\uparrow} n_{j,\downarrow} + v \, n_{j} n_{j+1}) + w \sum_{j=1}^{2} n_{j} n_{j+2}$$
(3)

$$H_{\mathsf{Fe/Co}} = \sum_{i=1}^{4} (EN_i + UN_{i,\uparrow}N_{i,\downarrow})$$
(4)

$$H_{\mathsf{dir}} = F \sum_{\sigma,\sigma'} \sum_{\langle i,j \rangle} A^{\dagger}_{i,\sigma} a^{\dagger}_{j,\sigma'} A_{i,\sigma'} a_{j,\sigma}$$
$$= -2F \sum_{\langle i,j \rangle} (\mathbf{S}_{i} \mathbf{s}_{j,j} + \frac{1}{4} N_{i} n_{j})$$
(5)

$$H_{\mathbf{V}} = V \sum_{\langle i,j \rangle} N_i n_j. \tag{6}$$

Operators and variables (except t, F, V) in lower/upper case relate to the metal-ion/ligands and it is implicitly understood that all indices appearing run from 1 to 4 (e.g. $j + 1 \rightarrow 1$ for j = 4). $\langle i, j \rangle$ denotes a summation over nearest neighbor metal-ions (i = 1 - 4) and ligands (j = 1 - 4). The Fermion operator $a_{j,\sigma}^{\dagger}(a_{j,\sigma})$ creates (destroys) an electron on ligand site j = 1 - 4 with spin projection $\sigma = \pm 1/2$. The occupation number operator is defined as usual $n_{j,\sigma} = a_{j,\sigma}^{\dagger} a_{j,\sigma}$ and $n_j = \sum_{\sigma} n_{j,\sigma}$. Similar definitions hold for the metal-ion $(A_{i,\sigma}, N_{i,\sigma})$ $A_{i,\sigma}^{\dagger}A_{i,\sigma}, N_i = \sum_{\sigma} N_{i,\sigma}$). $S_i = \frac{1}{2} \sum_{\sigma,\sigma'} A_{i,\sigma}^{\dagger} \tau_{\sigma,\sigma'} A_{i,\sigma'}$, where τ is the vector of Pauli matrices, is the electron spin of a metal-ion and $\mathbf{s}_{j,k} = \frac{1}{2} \sum_{\sigma,\sigma'} a^{\dagger}_{j,\sigma} \boldsymbol{\tau}_{\sigma,\sigma'} a_{k,\sigma'}$, is an operator related to the ligands. The tunneling term (2) describes hopping between ligand and metal-ions. For a D_{2d} symmetric molecular structure the hopping matrix elements t are independent of sites. In the following we choose t = 1 and all energies are expressed in units of t. The ligand-part of the Hamiltonian in (3) consists of a spin independent orbital energy ϵ , the classical Coulomb repulsion terms on the ligand (u) and between adjacent (v) and the opposite ligands (w). Due to decreasing overlap with distance we have $u > v/2 \ge w$ (e.g. for Fe^{2+} $u \approx 4v \approx 0.3 eV$ and $v \approx 2w$ [12]). Equation (4) describes the isolated metal-ion orbitals with energy E. For the metal-ions we only consider the short-range interaction U because the orbital overlap between two ions is much smaller than that between two ligands. In order to describe the spin coupling of metal-ion and ligand electrons correctly, we include the direct exchange (5)with F > 0, which is known to stabilize ferromagnetic states even when it is weak [16] (see sections IV and V). For consistency the metal-ligand charging energy (6) also needs to be incorporated. In general $F \lesssim V$ are of the



FIG. 4: Energy diagram: Example of a charge transfer from one ligand to another ligand by virtual occupation of $\mathrm{Fe}^{2+}/\mathrm{Co}^{2+}$ -ion state in the middle. Note that the MLCT barrier $\Delta = \epsilon - E$ is negative in the case of Fe^{2+} and positive in the case of Co^{2+} . Also, for Fe^{2+} the doubly occupied state with energy E + U can be neglected in the perturbation theory.

same order. However, in the regime of interest the particle number on the metal-ions is fixed $(N = 0 \text{ for } \text{Fe}^{2+}, N = 4 \text{ for } \text{Co}^{2+}, \text{ cf. section II})$, so the second term in (5,6) yield a constant. In Figure 3 these interactions are schematically indicated.

We study the parameter regime where the first eight extra electrons will occupy the ligands as in the experiment [12]. (To describe more than 8 reduction steps more than one orbital per ligand has to be taken into account. This is not our purpose here.) For Fe^{2+} we must then assume that the two charge states of the ligand lie below the Fe^{2+} orbital energy E:

$$Fe^{2+}: \epsilon < \epsilon + u < E < E + U \tag{7}$$

For Co^{2+} the two charge states of the ligand lie *between* the singly and doubly occupied states of the metal-ion:

$$\operatorname{Co}^{2+} : E < \epsilon < \epsilon + u < E + U \tag{8}$$

The orbital energy difference $\Delta = \epsilon - E$ is associated with metal-ion to ligand charge transfer (MLCT) between unoccupied metal-ion and ligand sites. In the case of Fe²⁺ $\Delta < 0$ and in the case of Co²⁺ $\Delta > 0$.

IV. PERTURBATION THEORY - EFFECTIVE MODEL

In the limit $|\Delta| \gg |t|$ (Fe²⁺), resp. $\Delta, U - \Delta \gg |t|$ (Co²⁺) the charge transfer between ligands and metalions is suppressed. In order to gain qualitative insight the fluctuations of the orbital occupation around zero (Fe²⁺) or one (Co²⁺) can be treated using 2nd order Brillouin-Wigner perturbation theory (equivalent to a Schrieffer-Wolff transformation [22]). We thereby eliminate the charge degrees of freedom on the metal-ion sites and incorporate their effect in an effective tunnel coupling between the ligands. An example of a virtual process giving rise to this coupling is shown in Figure 4. In the resulting effective model each metal-ion site is thus either entirely eliminated (Fe²⁺) or characterized by a pure spin degree of freedom (Co²⁺). This model contains the low energy properties of the mobile electrons on the $[2 \times 2]$ -grid. As a result we are left with the effective Hamiltonian (up to a constant):

$$H_{\mathsf{Fe}}^{\mathsf{eff}} = \sum_{\langle jk \rangle} \sum_{\sigma} T a_{j,\sigma}^{\dagger} a_{k,\sigma} + H_{\mathsf{L}}$$
(9)

$$H_{\mathsf{Co}}^{\mathsf{eff}} = \sum_{\sigma,i} \sum_{j,k=i,i+1} \left\{ (K + J\sigma\tau_{i}^{z})a_{j,\sigma}^{\dagger} a_{k,\sigma} + J\tau_{i}^{+\sigma}s_{j,k}^{-\sigma} + (K + (J - F)\sigma\tau_{i}^{z})n_{j,\sigma} + (J - F)\tau_{i}^{+\sigma}s_{j,j}^{-\sigma} \right\}$$
$$+ H_{\mathsf{L}} = \sum_{i} \sum_{j,k=i,i+1} \left\{ (J - F\delta_{j,k})\tau_{i} \mathbf{s}_{j,k} + \sum_{\sigma} K a_{j,\sigma}^{\dagger} a_{k,\sigma} \right\}$$
$$+ H_{\mathsf{L}}$$
(10)

The coupling constants T, K and J are

$$T = \frac{t^2}{2\Delta}$$

$$K = \frac{1}{2}\left(\frac{t^2}{\Delta} - \frac{t^2}{U - \Delta}\right)$$

$$J = \frac{1}{2}\left(\frac{t^2}{\Delta} + \frac{t^2}{U - \Delta}\right).$$
(11)

For Fe²⁺ the effective Hamiltonian is the extended Hubbard model on four ligand sites with effective hopping matrix element T. In contrast, for Co^{2+} we retain an eight site model: the effective Hamiltonian couples the spin and charge on the four ligands to the spin on the four metal-ions. The first two terms in (10) describe tunneling between ligands with (J) and without spinflip (K). The next two terms describe fluctuations of the charge and spin on the ligands. The exchange coupling J > 0, which is counteracted by the direct ferromagnetic exchange F > 0, favors a correlated ground state where the ligand and metal-ion spins are coupled antiferromagnetically. This coupling always dominates over the tunneling amplitude $K: J > |K| \ge 0$ and K even vanishes for $\Delta = \frac{U}{2}$. The sign of K depends on whether $\Delta < \frac{U}{2}(K > 0)$ or $\Delta > \frac{U}{2}(K < 0)$ and determines whether the amplitude K + J for the tunneling of electrons with spin σ parallel to the local spin on the metal-ion S_i is enhanced/suppressed relative to the amplitude K - J for spin antiparallel to S_i .

We point out that the effective Hamiltonian (10) for Co^{2+} contains no explicit interaction term between the metal-ion spins: all interactions are mediated by the electrons on the ligands. In order to describe the electron addition effects on the metal-ion spin coupling our second-order perturbation theory suffices. In the absence of extra electrons on the ligands, only in fourth-order perturbation theory a weak effective antiferromagnetic Heisenberg exchange interaction between the spins on the metal-ions appears. This superexchange is mediated by an empty intermediate ligand orbital. The four site Heisenberg-model with this effective coupling has been

studied in [14] and agrees with intramolecular coupling found experimentally. As soon as a ligand orbital contains one electron, the weak fourth order effect is superseded by the second order coupling incorporated in the effective Hamiltonian (10).

V. ADDITION ENERGIES AND SPIN STATES

We now present the results for the effective Hamiltonian (9),(10) (perturbation theory) and the full Hamiltonian (1). We first study the addition energy spectra which reflect mainly the electrostatic effects and then focus on the spin properties of the ground states and lowest lying excited states as a function of the number of *added* electrons n.

A. \mathbf{Fe}^{2+} -grid

To highlight the effect of the electrostatic interactions, we first consider the *noninteracting* limit of the effective 4-orbital model (9) for Fe^{2+} $(u, v, w \ll |T|)$. Of the four eigenstates the lowest one lies at energy $\epsilon - 2|T|$, two states are orbitally degenerate at ϵ (due to the 4-fold symmetry axis) and the highest state lies at $\epsilon + 2|T|$. Electron addition in this case would give rise to a pair of twofold degenerate peaks with a fourfold degenerate peak in between. This is in clear qualitative disagreement with the experiments [12]. The addition spectrum can only be understood by including the interactions u > v > w > |T|in our effective model (9). The first electron reduces one of the four ligands. The next one goes onto the opposite ligand in order to minimize the Coulomb interaction. The third and fourth electrons reduce the adjacent ligands. For the next four electrons this sequence of processes is repeated, each time doubly occupying a ligand orbital. We thus have two sets of four reduction peaks separated by a large gap of order u. Each set of four consists of two pairs of closely spaced peaks (distance w) separated by a moderate gap 2v - w < u. The tunneling between equivalent ligands only weakly affects this picture. In Figure 5 we plot the addition energies as a function of the tunneling amplitude t.

Now we discuss the ground state spin as successive electrons are added to the ligands. Filling the levels in the *noninteracting* case of the effective model (9) $(u, v, w \ll |T|)$ according to the Pauli principle the ground state spin is $S_{\text{tot}} = 1/2$ for odd particle number n. For even n = 2, 6 the ground state spin is $S_{\text{tot}} = 0$, whereas for half-filling $(n = 4) S_{\text{tot}} = 0$ and $S_{\text{tot}} = 1$ are degenerate. In the presence of interactions charge fluctuations are suppressed. For $u \gg |T|$ this gives rise at n = 4 to a Heisenberg antiferromagnet with a singlet ground state (Figure 6).

For sufficiently large $u > u_{th}^{Fe}$ (Figure 7) the ground state spin for odd n = 3, 5 is enhanced from the noninteracting value $S_{tot} = 1/2$ to the maximal possible value



FIG. 5: Addition energy of Fe^{2+} - $[2 \times 2]$ -grid as function of tunneling t (in units of w) for $u = 15, v = 3, w = 1, \Delta = -50, U = 100$ calculated from the full model 1. For $|t| < |\Delta|$ we are in the perturbative regime where no spin is localized on the Fe^{2+} site and the effective model (9) applies. We reproduce the addition energy spectrum measured in [12] where the spacings between the ground state energies with different n are due to electrostatic interactions.



FIG. 6: Ground-state spin as function of the number of electrons n added to the ligands for $u > u_{\rm th}$ (dashed blue line = ${\rm Fe}^{2+}$, black line = ${\rm Co}^{2+}$ without direct exchange) and for $u < u_{\rm th}$ (dotted red line in both cases).

 $S_{\text{tot}} = 3/2$ (Figure 6). Now the tunneling between the ligands plays a decisive role. Because double occupation is suppressed, a single hole/electron (relative to the half-filled state n = 4) can maximally gain kinetic energy when the background of the other electrons is fully spin polarized. This ferromagnetic alignment competes with the antiferromagnetic spin coupling due to superexchange processes. Which process dominates depends on the strength of the onsite repulsion u relative to the hopping |T| i.e. $u_{\text{th}}^{\text{Fe}} \propto |T|$. The gap between maximal spin ground state and lowest excited state saturates at a value



FIG. 7: Fe²⁺-[2 × 2]-grid: Ground-excited state gap as function of u for n = 3, $\Delta = -10$, v = 2.25, w = 1. For $u > u_{\rm th} \approx 4.15$ the ground state has maximal spin.

 $\sim 2|T|$ independent of u due to the kinetic origin of the effect. This is the underlying mechanism for the Nagaoka theorem [15] which guarantees that the ground state has maximal spin if u is larger than some positive threshold value. It applies to the effective model (9) because it fulfills a certain connectivity condition for the lattice, namely that a so-called "exchange loop" exists which is no longer than four sites [23, 24]. This implies that all basis states with common S_{tot}^z are connected with each other via nonvanishing matrix elements of (9) [24]. In order to attain an observable effect one should have a moderate T on the one hand, and on the other hand the onsite interaction u must be enhanced with increasing T. The latter can be achieved by a chemical modification of the ligands that draw charge density in the ligand LUMO orbitals. Taking typical parameters [12] $|\Delta| \approx 1 eV, t \approx 10^{-1} eV, \Delta E_{\text{Nag}} \approx 10^{-2} eV$, we estimate $u_{\rm th} \approx 1 eV$ which is reasonable.

We have checked that the interactions v, w increase the critical value u_{th}^{Fe} for the Nagaoka state but do not destroy it [16]. We have also analyzed the effect of disorder by making the ligand sites inequivalent through different MLCT barriers Δl . As expected, the Nagaoka state is stable if the change in the MLCT barrier Δ is smaller than |T|. Otherwise, due to the localization of electrons the Nagaoka effect, which is of kinetic nature, is suppressed. We expect disorder effects to be relatively weak since the ligands and the metal-ions form a highly symmetric grid of equivalent centers.

B. \mathbf{Co}^{2+} -grid

The addition energy spectrum which we obtain for the Co^{2+} -grid is qualitatively the same as for the Fe²⁺-grid since electrostatic interactions dominate. In the experiment [12] the reduction peaks corresponding to the first three electrons are similar to those of Fe²⁺, in agreement with our model. However, the next five peaks exhibit

roughly a constant spacing ~ 0.25-0.3eV, corresponding to the charging of one big "island" with better screening. This would require in our model to artificially change the parameters to $u \approx v \approx w \approx 0.3eV$ beyond n = 3. Obviously effects become important which are not included in our electronic low temperature model, e.g. adding electrons could result in a change in the molecular geometry which will lead to different electrostatic interactions. Also at the high experimental temperatures individual Co^{2+} ions may be in the high-spin state where the π symmetric t_{2g} -orbitals are singly occupied. These can couple more strongly to the ligand orbitals and increase metal-ligand charge transfer. Here we are interested in the low temperature regime however and assume low-spin (S = 1/2) Co²⁺ ions.

The spin properties of the eigenstates of the effective model (10) without direct exchange interaction, i.e. F =0, are qualitatively similar to Fe^{2+} (Figure 6) and will be considered first. We have a singlet ground state at halffilling (n = 4), and a Nagaoka maximal-spin ground state near half-filling (n = 3, 5) for sufficiently large charg-ing $(U > u > u_{\text{th}}^{\text{Co}})$. At half-filling n = 4 the antiferromagnetic Néel-state has the largest weight in the ground state. The electron spins on the metal-ions couple ferromagnetically due to the presence of electrons on the ligands and and vice versa. This is to be contrasted to the situation at n = 0 where the metal-ion spins couple antiferromagnetically and at n = 4 for the Fe²⁺-[2 × 2]-grid, where the electron spins on adjacent ligands couple antiferromagnetically. The total spins of the metal-ion and ligand sublattice couple antiferromagnetically to a singlet ground state. The appearance of the Nagaoka state at n = 3,5 has a different origin than in the Fe²⁺-[2×2]-grid since we have exchange loops longer than four sites. We do, however, have a bipartite lattice and hopping occurs only between the ligand and metal-ion sublattices. This is also a sufficient condition for the Nagaoka theorem to apply [16, 24].

The four spins on the bridging Co^{2+} metal-ions cause two quantitative differences from the case of Fe^{2+} . Firstly, the maximal spin value attained in the Nagaoka state is simply larger, $S_{tot} = 7/2$. Secondly, the threshold value of u_{th}^{Co} for the appearance of this state is dramatically increased, $u_{\rm th}^{\rm Co} \approx 10^4$ in both the full and effective models. This is due to the antiferromagnetic exchange coupling Jbetween the metal-ion and ligand sublattices. This suppression of ferromagnetism can however be understood by considering two extreme limits. In the limit where two sublattices are equivalent ($\Delta = 0, u = U$) Nagaoka's mechanism is ineffective because the exchange paths are to long (> 4 sites, [24]). This implies that with decreasing Δ a higher $u_{\rm th}^{\rm Co}$ is required to stabilize the Nagaoka state. In the opposite limit where the sublattices are well separated in energy $(\Delta, U - \Delta \gg |t|)$, the effective model (10) applies and $u_{\text{th}}^{\text{Co}}$ is decreased. The maximal spin state can still be achieved when U is sufficiently increased for *fixed* Δ , such that $t \ll \Delta \ll U/2$ we have $K \approx -J$: tunneling of electrons with spins antiparallel to the metal spins is



FIG. 8: Co^{2+} - $[2 \times 2]$ -grid: Ground-excited state gap as function of u for n = 3, $\Delta = 10, U = 100, v = 2.25, w = 1$ and three different values for the direct exchange F = 0.06, 0.065, 0.07. The non-monotonic behavior of the gap is due to several level crossings until the Nagaoka state is the ground state (beyond the rightmost zero). The direct exchange "kicks" the system into the Nagaoka state: the threshold value $u_{\text{th}}^{\text{Co}}$ is reduced when $F \to J = 0.06$. Even for smaller F > 0 one still needs $u > u_{\text{th}}^{\text{Co}}$ to drive the system into the maximal spin ground state.

suppressed, favoring a polarized ground state. However, the splitting ΔE is decreased due to the small effective coupling constants.

The neglect of any (even small) direct exchange represents an unbalanced treatment of the magnetic coupling, since the Nagaoka mechanism and the direct exchange are known to cooperate to stabilize maximal spin states [16]. Even when it is weak, $F \approx J$, the direct exchange leads to a dramatic reduction of the threshold Coulomb energy for achieving the Nagaoka state to values more close to those found above for Fe²⁺: $u_{\rm th}^{\rm Co} \sim 5$ (Figure 8) and the gap between ground and excited state increases again. Furthermore it is possible that an enhanced direct exchange stabilizes a maximal spin state even at half-filling n = 4. Still the spin can be switched from 0 to 7/2 by going from n = 2 to n = 3 (or from n = 5 to n = 6). The excitation gap ΔE as function of u(Fig. 8) saturates at values of the order of 0.2J. In this limit the direct exchange "kicks" [16] the system into the Nagaoka state. For $F \gg J$ the ferromagnetic coupling exceeds the exchange coupling and the resulting ground state is always ferromagnetic, independent of u indicating the Nagaoka mechanism is not relevant anymore.

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VI. CONCLUSION

We have analyzed a strongly-correlated electron model for a $[2 \times 2]$ -grid complex with four transition-metal centers (either Fe^{2+} or Co^{2+}) to illustrate the interplay between electron addition and intramolecular spin coupling. Our model contains both localized magnetic moments and delocalized electrons, in contrast to the customary description of molecular magnets. We have based our model on the addition energy spectra of the experiments in Ref.[12], the crucial input being that the extra electrons occupy ligand orbitals. We found large changes in the total spin, $\Delta S_{\text{tot}} > 1/2$, of the molecule upon variation of the total electron number due to the Nagaoka mechanism. The large charging energies on the ligands required for the high spin states can be tuned chemically by adding electron-donating groups to the ligands. Localized spins on the mediating metal ions (Co^{2+}) counteract the Nagaoka effect, but the direct exchange coupling with the neighboring ligands can compensate for this. The total spin in the Nagaoka state for the Co^{2+} complex is therefore more than twice as large as for the Fe^{2+} complex. Low temperature electron tunneling experiments can access the change of the molecular spin as a function of added charge. Spin-blockade effects [18] will dominate the single-electron tunneling around transitions between charge states with maximal spin [19]. Also, the $S_{tot} = 1/2$ Kondo effect usually expected for odd n = 3,5 will also be suppressed. In any case the Nagaoka mechanism lowers maximal spin states in energy. Even as low lying total-spin excitations Nagaoka states have clear transport fingerprints due to spin-selection rules [19]. Other molecular complexes can also show the above behavior. It is essential that the connectivity of the electron-accepting centers is appropriate [16, 24] for the Nagaoka mechanism to be effective.

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History of Science

Color Theory in Science and Art: Ostwald and the Bauhaus**

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Keywords:

art and science \cdot biographies \cdot history of science \cdot Ostwald, Wilhelm

The outstanding but controversial position of Wilhelm Ostwald as a scientist and philosopher was highlighted exhaustively last year, in this journal among others, to mark the 150th anniversary of his birth.^[1] Yet among the many diverse activities Ostwald engaged in during his life, his artistic work and its impact on his philosophical ideas has generally been overlooked. During his scientific life, and especially after his formal retirement in 1906, he dedicated much time and energy to artistic endeavors. His favorite leisure activities were painting, playing the viola, and writing poetry. But Ostwald's interest in the arts was not incidental to his scientific and philosophical theories; rather, the two were interwoven. This is particularly evident in his work on color, which exerted a marked influence on the industry and fine art of his own period. Little has been said about the interac-

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[**] We thank Ms. Gretel Brauer, the granddaughter of Wilhelm Ostwald, Großbothen, for her invaluable advice and help in locating the documents that provided the basis for this article. Furthermore, we would like to thank Prof. L. Beyer, University of Leipzig, Ms. Eckert from the Bauhaus-Archiv in Berlin, and Ms. Witzel from the Berlin-Brandenburgischen Akademie der Wissenschaften, Berlin, for their constructive help. tion of Ostwald's ideas with fine art, and here we hope to close this gap somewhat by describing an historically rare mutual concordance between science and the arts, in which Ostwald and the personalities of the Bauhaus school of art, architecture, and design appear as the main actors.

The Bauhaus School

The Bauhaus School was founded in 1919 by the architect Walter Gropius under the utopian slogan "The building of the future". It sought to train a new type of artist, capable of reaching beyond the confines of academic specialization and of bridging the gulf between fine art and the traditional crafts. In essence, Gropius wanted to remove the long-standing distinction between the pure and the applied (something that surely resonates with scientists today). To achieve that, he recognized the necessity of establishing new teaching methods in his school. This was the goal he strove towards during the first period of the Bauhaus in Weimar; but after a somewhat anarchic beginning, the mission of practical training was reiterated when the school relocated, for political reasons, to Dessau in 1925. In the 1919 Bauhaus manifesto, Gropius wrote: "Architects, painters, and sculptors must once again come to know and comprehend the composite character of a building, both as an entity and in terms of its various parts. Then their work will be filled with that true architectonic spirit which, as 'salon art', it has lost."^[2]

It soon became clear that this reconciliation of art and crafts could not be backward-looking (in the way that it had been in the British Arts and Crafts movement), but needed to embrace the reality of a technical civilization, with its incipient methods of mass manufacturing. In short, the aesthetic of the artist had to be installed in the factory and workplace. In 1923, the Bauhaus acknowledged this with a new motto: "Art and technology-a new unity". The design standards promoted at the school would thenceforth recognize the demands of industry in both its functional and aesthetic aspects. The Bauhaus workshops produced prototype artifacts for mass production, ranging from individual household lamps to complete dwellings.[2]

From 1921, every student of the Bauhaus was required to take a compulsory "preliminary course" (Vorkurs) before entering into a workshop of his choice, where he would be taught both practical and artistic skills in a unified manner. Ever since its foundation, the school was able to attract talented artists and craftsmen, acquiring an extraordinary collection of personalities that made the Bauhaus a thriving center of European art. Its illustrious gallery of teachers ("masters") and pupils favored late Expressionism and early Abstraction (Figure 1), and together they helped to define the course of artistic modernism. They included the painters Wassily Kandinsky, Paul Klee, Oskar Schlemmer, Johannes Itten, Lyonel Feininger, and Josef Albers, the architects Gropius himself and, in the late phase, Ludwig Mies van der Rohe and Marcel Breuer, and the photographers László Moholy-Nagy (also an accomplished painter) and Andreas Feininger. Students flocked to the school to study with these famous names, although Gropius



Figure 1. The masters on the roof of the Bauhaus building in Dessau. From the left: Josef Albers, Hinnerk Scheper, Georg Muche, László Moholy-Nagy, Herbert Bayer, Joost Schmidt, Director Walter Gropius, Marcel Breuer, Wassily Kandinsky, Paul Klee, Lyonel Feininger, Gunta Stölzl, and Oskar Schlemmer.^[2]

discovered that they tended to arrive with dreams of becoming fine artists rather than being content to turn out designs for factories.

Several masters of the Bauhaus were intensely interested in theories of color and its relation to form. Such "constructivist" work took place mainly in the courses directed by Itten, Kandinsky, and Klee, and to a lesser extent with Schlemmer, Moholy-Nagy, and Albers. There was a strong feeling that color composition could be pursued in an objective, "scientific" way. Itten, who was responsible for devising the preliminary course, believed that colors could be assigned definite and universal emotional values, an idea that he pursued with something akin to dogmatic mysticism (Figure 2, left). Klee made reference in his teachings to standard ideas about color taken from the theories of Goethe and the works of the

French painter Eugène Delacroix, which stressed the use of complementary pairs (red–green, blue–orange, yellow–violet). But he was always wary of too much theory: "Of course we may use it for a bit, but we hardly have any need for a theory of colors. All the infinite mixtures will never produce an emerald green, a Saturn red, a cobalt violet."^[3] In other words, Klee felt that the characteristic hues of these materials engendered profound emotional effects that could not be dissected, laid out, and analyzed on color tables and charts.

But it was Kandinsky who was responsible for most of the color teaching at the Bauhaus. He experienced the condition of synesthesia, a neurological confusion of the senses in which two different sensations can be triggered by the same stimulus. This commonly results in an association of color with sound, so that certain timbres or pitches



Figure 2. Two examples of color systems invented by Itten at the Bauhaus (left) and by Ostwald (right).^[6,7]

create a sense of color. So it is not surprising that Kandinsky believed that "color directly influences the soul"that a carefully chosen arrangement of colors could pluck the heartstrings of the emotions as deliberately as a pianist strikes chords on the keyboard. The task was then to identify the psychological meanings of different colors, which Kandinsky tried to establish by "scientific" tests. He issued a questionnaire^[4a] in which participants were asked to match the three primary colors (red, yellow, blue) to particular forms (circle, square, triangle)^[5]—with somewhat inconclusive results.

Thus the Bauhaus, standing at the intersection of art, design, and industry, turned out to be very receptive to all kinds of systematic approaches to art, including those that claimed to have a foundation in science.

Ostwald's Color System in Theory and Practice

Wilhelm Ostwald (Figure 3) was an enthusiastic amateur painter during most of his lifetime, especially after he retired from his academic career. He considered painting and drawing to be a form of "physical and psychic recovery", and his first explicit reference to these activities was in 1884, when he painted during a journey.

After 1904, he undertook such painting excursions nearly every year (Figure 4). His artistic efforts, which were generally naturalistic and traditional (even, for their time, conservative), were, however, not simply a form of relaxation but an expression of his closely intertwined scientific and philosophical preoccupations, guided by his enormous intellectual curiosity. Since his childhood, Ostwald had used his interest in and knowledge of chemistry to synthesize pigments for use in art.

Around 1914, Ostwald begun to develop a systematic theory of color as well as a quantitative color science, culminating in the publication of several books and publications on the topic between 1917 and 1922—most notably, *The Colour Primer* (original German version, 1917).^[9] Ostwald's most important contribution to color theory was the role he assigned to gray as a key

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Figure 3. Portrait of Wilhelm Ostwald by A. Klamroth (pastel, 1904).^[8a]

coordinate of "color space" (Figure 2, right). His attempts to map this space were influenced by the work of the American artist and teacher Albert Munsell, whom Ostwald met in 1905. Munsell tried to quantify and standardize colors according to the parameters of hue (roughly speaking, the dominant wavelength), saturation (the intensity or "richness" of the color), and brightness (which can be crudely equated with the shade of gray the color gives in a black and white photo).^[4b] The last of these parameters was particularly important to Ostwald. He believed that a scale of perceptually equal steps in the brightness of a color could be achieved by adding black and white in ratios that followed a logarithmic progression. This, he said, provided a scheme for achieving perfect tonal balance and harmonious color composition in a painting. The idea of "harmony" in painting was one much discussed by Renaissance artists, and no doubt goes back even further. It alludes to the skill of combining colors so that no part of the composition stands out glaringly in relation to others. This is not necessarily a naturalistic device; even in their



Figure 4. One of the artistic products of Wilhelm Ostwald's annual excursions: the painting *Clouds and Waves* from 1913.^[8a]

abstract works, painters like Klee and Kandinsky show an awareness of the need for harmony to lend unity to their pictures. Ostwald was, at face value, offering a foolproof set of rules for achieving such harmony (and he was quite prepared to criticize famous works of art which violated them).

Ostwald used his fame as a chemist and Nobel laureate to impress his color theory on the German paint industry. In 1912 he joined the Deutsche Werkbund, an organization dedicated to introducing standardization into industrial design, and in 1914 he arranged an exhibition of commercial paints and dyes at a Werkbund exhibition in Cologne. Eventually Ostwald established his own pigment factory near Leipzig, which operated from 1920 to 1923.

While at first Ostwald directed his artistic endeavors towards the "accurate" reproduction of nature, after 1915 his paintings reveal his experiments on how his color theories should be put into practice (Figure 5). In other words, he was trying to create art from a scientific standpoint, which ultimately led him towards the notion of the "ideal" painting constructed according to principles of his color theory. He spoke about this idea in a lecture at a congress of the Werkbund in Stuttgart in 1919; but such a rigid program for art was rejected by most contemporary artists.^[10] In the same period Ostwald did little to endear himself to those of an artistic sensibility by announcing that Titian had once used a blue "two tones too high".^[11]

Ostwald and the Bauhaus

Thus Ostwald was prepared to convert the artistic world to his ideas on color. Having encountered him on several previous occasions (for example, in the Werkbund), Walter Gropius seems



Figure 5. Two examples of Ostwald's artistic work before (left) and after (right) being influenced by his own color theory.^[8a,9]

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to have approached him in late 1926 with a view to arranging a visit to the Bauhaus. In a letter to Ostwald on November 20, 1926, Gropius says "...enclosed you will find a small brochure describing how the teaching of form and color is organized within our institute... On November 4th we are going to inaugurate our new institute building. I send you an invitation and I would be very pleased to meet you again."^[12] Ostwald's reaction is recorded by his daughter Grete in her diary of December 1926: "He is so fascinated by a brochure written by Gropius that he even decided to visit it [the Bauhaus] on the occasion of the inauguration of its new buildings. Beauty = Law, this is what Gropius has also understood, and he [WO] is interested in how this can fit with Kandinsky and in particular with Klee. Indeed, it transpired that Gropius is the constructive head, but is indifferent to color. Unfortunately, it was only possible to exchange some brief words with him. On the other hand, he had a heated discussion and lunch together with a painter with a Polish name..., who is constructing paintings out of squares and rectangles."^[13]

Beginning with the meeting on December 4, 1926, there was an intense exchange of letters and books between Ostwald on one side and Gropius, Moholy-Nagy, and the designer and typographer Herbert Bayer on the other. Grete's diary mentions on February 28, 1927, that *"he* [WO] *is looking forward to the promised Bauhaus week"*.^[13] This week was first scheduled for the beginning of April 1927, but was later postponed so that it finally took place on June 10–15, 1927, in Dessau.

In a letter to his wife Helene written on June 10, 1927, Ostwald says that he arrived in Dessau in the morning and was invited to stay with Gropius in one of the recently erected school buildings in the famous Bauhaus style. After taking lunch with Gropius and his wife, the two men were clearly intent on entering into intense discussion: "...going a long distance together...",^[14] as Ostwald put it. This is confirmed by an entry in the diary of Gropius's wife Ise concerning the same day: "Ostwald has arrived... he behaves very brightly and naturally here, and his intensity does not slow down for a moment."^[15]

In the afternoon Ostwald gave his introductory talk and reported to his wife that 120 people attended, including "the professors, except for Klee ... it might be disconcerting for him to meet me".^[14] Ise Gropius recorded on June 12, 1927, that Ostwald was giving daily talks which were well received by the Bauhaus pupils, and she praises Ostwald's brio and vitality.^[15]

What kind of lectures did he give there? In her diary entry for the June 13, 1927, Ise mentions that "Ostwald gave his last lecture about his tenet of harmony. As big as the impact of his tenet of order has been, the opposition to his tenet of harmony is of comparable size. I too believe that it is wrong to apply his tenet of color to painters..."[15] Later she refers to a "color organ" that Ostwald gave to the Bauhaus, which attracted interest from Bayer and Hinnerk Scheper, the designer who had devised the color scheme for the new building in Dessau.^[15,16] The connection between music and color has ancient origins, and it shaped Isaac Newton's division of the visible spectrum into seven rainbow colors. The connection was particular evident to the synesthetic Kandinsky (Figure 6), as well as to the Russian composer Alexander Scriabin, who had the same condition and composed in color for a "keyboard of light". Ostwald explored these notions in a 1925 manuscript "Musical Art and the Art of Light".^[16]

The tenets of color, order, and harmony to which Ise Gropius refers

might be related to Ostwald's lecture manuscripts "The Euphonies of the World of Colors" (presumably 1927), "The General Order of Forms into Regular Networks—A Contribution to the Harmony of Forms" (presumably 1927), and "The Harmothek" (1926). All of these documents are still available in Ostwald's written estate.^[16]

Ostwald's Impact on the Artistic World

The reaction at the Bauhaus to Ostwald's talks was mixed. He made a strong impression as a personality, but there was considerable skepticism towards his theories. It wasn't the first time the artists had encountered them. of course-Ostwald's ideas had been a topic of debate at least since the publication of The Colour Primer, and Gropius referred to them in the catalogue of the Bauhaus exhibition of 1923. Kandinsky had been initially ambivalent about Ostwald's color theory, but had become more sympathetic to it by 1925; nonetheless, his color course after 1927 was not entirely uncritical of Ostwald's framework. Klee, meanwhile, remained unwilling to be fettered by any scientific theory of color. He had come across Ostwald's ideas as early as 1904, when he had read the chemist's Malerbriefe (Letters to a Painter). He once commented on these theories in the most acerbic and dismissive terms: "That which most artists have in common, an



Figure 6. Wassily Kandinsky's painting *Jocular Sounds* from the artist's Bauhaus years (1929); virtually every element in the painting is adapted from music notation. (Copyright VG Bild-Kunst, Bonn, 2004).

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Essays

aversion to color as a science, became understandable to me when a short time ago I read Ostwald's theory of colors. I gave myself a little time to see if I could succeed in getting something of value from it but instead was only able to get a few interesting thoughts... To hold that the possibility of creating harmony using a tone of equal value should become a general rule means renouncing the wealth of the soul. Thanks but no thanks."^[3]

Schlemmer, who must have been present in Dessau in 1927, echoed these sentiments: "Ostwald's color building is a typical scientific result; artistically it is nonsense."[10] Ise Gropius likewise drew the conclusion that "he [WO] knows nothing whatsoever about the painters. although he is able to define 'the painter' in theory absolutely correctly. But if he stands next to him, he does not recognize him."[15] Yet it must be said that Ostwald's color theory was rather positively received by Piet Mondrian and his colleagues in the "De Stijl" group in the early 1920s. The Colour Primer was enthusiastically reviewed in the group's journal in 1918, and Ostwald is said to have become something of a "cult figure" for them. Mondrian's work with simple primary colors bears some evidence of Ostwald's influence.^[4a,1b]

During the months after the visit, Gropius kept in close contact with Ostwald, who sent several of his pigments, binders, and books to Dessau. On June 28, 1927, Gropius asked Ostwald to join the advisory board of the Bauhaus, to which Ostwald replied two days later: *"With thanks and joy I accept the honor of entering onto the board of trustees... I would like to add that I do not consider this membership a hollow formality, but I ask you to contact me whenever I can be useful to the Bauhaus..." (Figure 7).^[17]*

Such a collaboration could have been as fruitful as it would have been controversial—but apparently it did not develop to Ostwald's own satisfaction. In August 1928, one year after the lectures, Gropius had to reassure Ostwald in a letter that *"it is not true, as you believe, that your lectures have not left any trace at the Bauhaus. I know that Scheper has dealt with them intensively and is using your systems in his courses."*^[18] Shortly after this assurance, Joost Schmidt contacted Ostwald to ask for

Wilhelm Oftwald . Großbothen (Sa aufraty von Prof. , Keles

Figure 7. Fascimile of the first page of Ostwald's response to the invitation to join the Bauhaus board of trustees.^[17]

explanatory material, which he planned to use in the course of his classes dealing with advertising techniques, and he even seems to have visited Ostwald in Großbothen to that purpose.^[19] But there is no record of further visits by Ostwald after 1928, and he died in 1932, the year before the school, a center of "degenerate art", was closed by the Nazi regime. Its artistic stars were scattered across the world, several of them finding refuge in the USA. There, abstract expressionism was to establish color as the central constructive component of modern art, largely in isolation from any consensual theory about how color should be used or what it "meant". But at least the American artists' later engagement with the industrial materials championed by Ostwald was a matter of choice. After the closure of the Bauhaus, Oskar Schlemmer was forbidden to exhibit his work in Germany, and was reduced to making a living by testing materials for a paint company.

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