of 1-aminoindoles that could formerly be synthesized by only limited methods.[23] This methodology also allows sequential reactions of this new cyclization and known palladium-catalyzed reactions with nucleophilic reagents in a single procedural operation to furnish indole derivatives with substituents on the carbocyclic rings. Indole derivatives that are not functionalized at both the 2- and 3-positions could be synthesized by using arylacetaldehyde hydrazones as substrates. Such compounds are important for the synthesis of more elaborate indole derivatives, because these positions can be easily functionalized by several methods.[5a,b] Furthermore, this methodology can be extended to the construction of six-membered ring systems such as 4*H*-quinolines.

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

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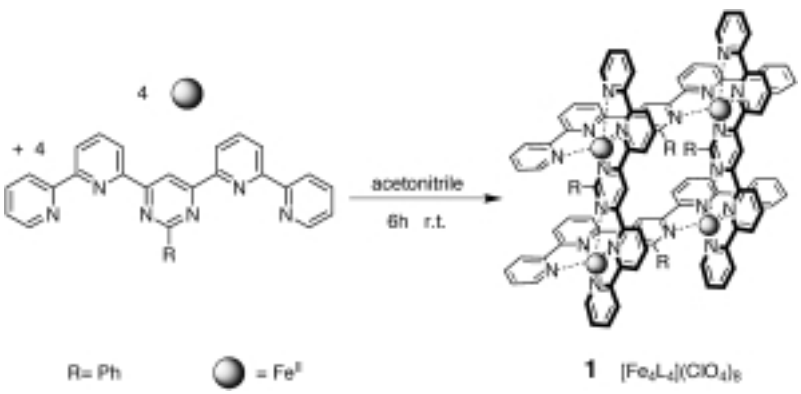
enable a highly efficient information storage.[1] Towards this end, a promising and challenging field of research is the study of spin crossover (SC) compounds.[2] The phenomenon of spin crossover between low-spin (LS) and high-spin (HS) states is one of the most appealing examples of molecular bistability.[3,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

It has been shown that molecular systems of the [2 × 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 × 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 Fe_4^{II} [2 × 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 $Fe(ClO_4)_2 \times 6H_2O$ 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 ^{1}H 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 (Δ_{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

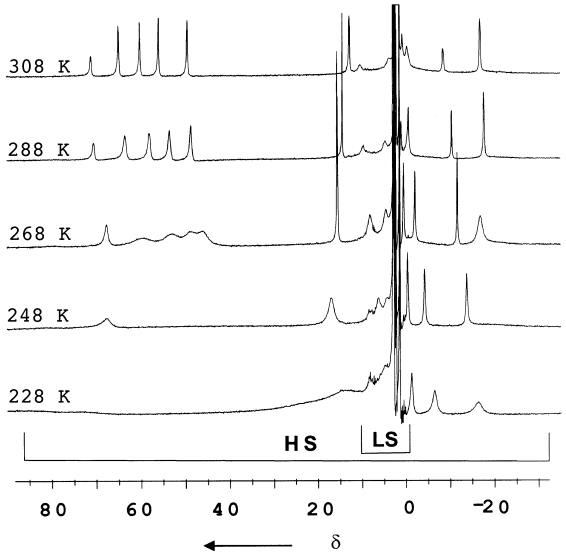


Figure 1. Variable-temperature ^{1}H NMR studies of **1** exhibiting the increase of LS fraction at the expense of the HS fraction on lowering the temperature (in [D_6]acetone/[D_6]acetonitrile).

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

At room temperature, $\chi_M T/4$ is equal to 2.5 cm^3 K 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 cm^3 K mol^{-1}. On lowering the temperature, $\chi_M T/4$ progressively decreases reaching a value of 1.4 cm^3 K 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 BF_4^- 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 cm^3 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.

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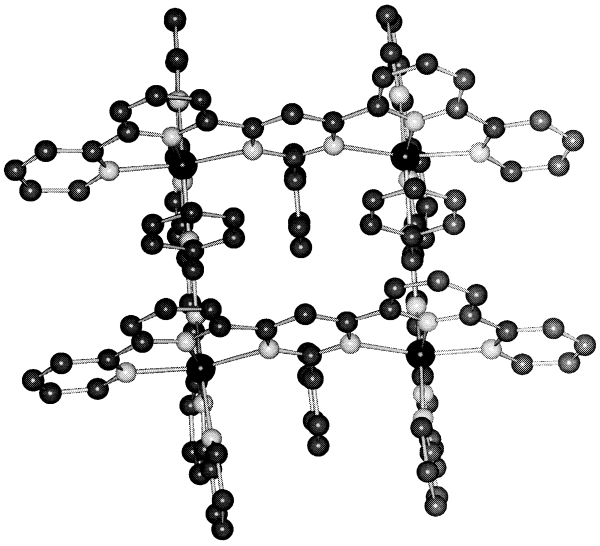

Figure 2. Molecular structure of the cation of **1** at 293 K (anions and solvent molecules are omitted for clarity). The structure of **1** has also been determined at 100 K. The averaged Fe–N distances [Å]: 1) at 293 K: 2.19(1) (HS), 2.17(1) (HS), 2.07(1) (HS/LS), 2.17(1) (HS); 2) at 100 K: 2.20(1)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

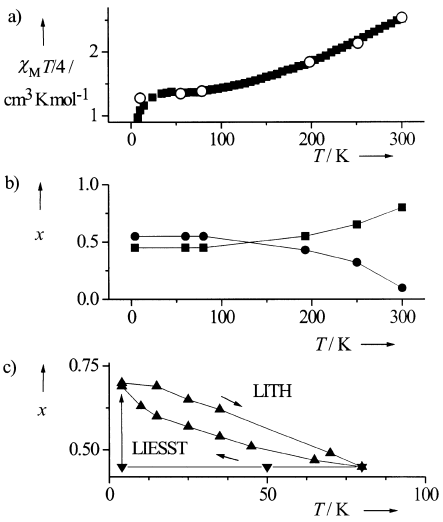

Figure 3. a) Calculated (circles) and experimental (squares) $\chi_M T/4$ versus T plots for a powder sample of **1** (calculated $\chi_M T/4$ values derived from molar fractions); b) HS (squares) and LS (points) molar fractions plotted versus T showing the thermally induced SC; c) LIESST (light-induced 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 $\delta = 0.402(6)$ 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 $\delta = 1.090(8)$ 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

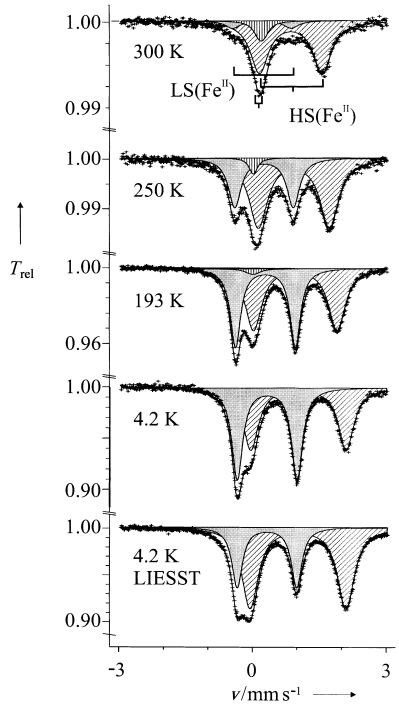

Figure 4. Selected ^{57}Fe Mössbauer spectra for **1** at various temperatures and after irradiation at $\lambda = 514$ nm at 4.2 K (LIESST).

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 3c). 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

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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 Fe_4^{II} $[2 \times 2]$ 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 $Fe(ClO_4)_2 \cdot 6H_2O$ (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 ^{57}Fe Mössbauer experiments, samples were enriched by 33% of $^{57}Fe^{II}$. The BF_4 salt of **1** was synthesised by the same procedure using $Fe(BF_4)_2 \cdot 6H_2O$. The obtained product exhibits identical spectroscopic properties as **1**. ^1H NMR (200 MHz,[D$_3$]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 $[M-ClO_4]^+$; 2677.6 $[M-2ClO_4]^+$; 2578.6 $[M-3ClO_4]^+$; 2478.7 $[M-4ClO_4]^+$; 2378.7 $[M-5ClO_4]^+$; 2378.3 $[M-6ClO_4]^+$; 1338.8 $[M-2ClO_4]^{2+}$; 1289.3 $[M-3ClO_4]^{2+}$; 1238.8 $[M-4ClO_4]^{2+}$; 1189.4 $[M-5ClO_4]^{2+}$; 1140.9 $[M-6ClO_4]^{2+}$; UV/Vis (acetonitrile, nm): $\lambda = 379$ ($\pi-\pi^*$); 622 (MLCT); elemental analysis calcd (%) for $C_{120}H_{106}N_{24}Cl_8Fe_4O_{45}$: 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 cm^2 surface). The sample was irradiated at 4.2 K with an Ar-ion laser (514 nm, 15 mW cm^{-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 ($0.5 \times 0.4 \times 0.2$ mm) of $[C_{120}H_{80}N_{24}Fe_4]^{8+} \cdot 8ClO_4^- \cdot 9CH_3CN \cdot 1.25H_2O$ 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 [$\lambda(MoK_\alpha) = 0.71073$ Å]. The data were processed with Denzo.[15] L_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, $\alpha = 85.7672(9)$, $\beta = 82.2308(7)$, $\gamma = 65.3290(8)^\circ$, $V = 7353.5(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.473$ g cm^{-3}, $2\theta_{max} = 55.84^\circ$, $\mu(Mo_{K\alpha}) = 0.619$ mm^{-1}, $T_{min} = 74.7\%$, $T_{max} = 88.6\%$. 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 ClO_4^- ions. Compound **1** at 100 K: triclinic, $P\bar{1}$, $a = 17.2936(3)$, $b = 18.0917(3)$, $c = 24.7836(5)$ Å, $\alpha = 85.1273(11)$, $\beta = 82.0435(12)$, $\gamma = 64.9006(9)^\circ$, $V = 6951.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.558$ g cm^{-3}, $2\theta_{max} = 55.84^\circ$, $\mu(Mo_{K\alpha}) = 0.655$ mm^{-1}, $T_{min} = 73.5\%$, $T_{max} = 88.0\%$. A total of 91012 collected reflections, 32258 unique reflections [19824 $I > 2\sigma(I)$] were used for refinement. The final R values were $R = 0.1150$, $wR^2 = 0.2770$ [$I > 2\sigma(I)$], $R = 0.1771$, $wR^2 = 0.3148$ (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 ClO_4^- 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 CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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