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# Polynuclear Iron(II) Complexes with 2,6-Bis(pyrazol-1-yl)pyridineanthracene Ligands Exhibiting Highly Distorted High-Spin Centers

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#### Supporting Information

ABSTRACT: Two bis-tridentate ligands L1 and L2 that contain 2,6-bis(pyrazol-1-yl) pyridine N-donor embraces introduced on a anthracene-acetylene backbone were used for the synthesis of a tetranuclear compound [Fe<sub>4</sub>(L1)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·7CH<sub>3</sub>CN (1) and a hexanuclear compound  $[Fe_6(L2)_6](CF_3SO_3)_{12} \cdot 18CH_3NO_2 \cdot$  $9H_2O(2)$ . The polynuclear structures of both complexes were confirmed by X-ray diffraction studies, which revealed a [2 + 2]grid-like complex cation for 1 and a closed-ring hexagonal molecular architecture for the complex cation in 2. Although both compounds contain anthracene moieties arranged in a faceto-face manner, attempts at [4 + 4] photocyclization remain unsuccessful, which can be explained either by steric restraints or by inhibition of the photo-cycloaddition. Magnetic studies identified gradual and half-complete thermal spin crossover in



the tetranuclear grid 1, where 50% of ferrous atoms exhibit thermal as well as photoinduced spin state switching and the remaining half of iron(II) centers are permanently blocked in their high-spin state. On the contrary, the hexanuclear compound 2 exhibits complete blocking in a high-spin state. Analysis of the magnetic data reveals the zero-field splitting parameter  $|D| \approx$ 6-8 cm<sup>-1</sup> with a large rhombicity for all high-spin iron(II) atoms in 1 or 2. The electronic structures and the magnetic anisotropies were also investigated by the multireference CASSCF/NEVPT2 method, and intramolecular exchange interactions were calculated by density functional theory methods.

# INTRODUCTION

Spin crossover (SCO) coordination compounds exhibiting a competition between low-spin (LS) and high-spin (HS) states are one of the most exciting examples of molecular bistability. Among the transition metal complexes showing the SCO effect, the most intense variation of physical properties (i.e., change in magnetic moment, color, conductivity, or other physicochemical properties) has often been found in ferrous complexes with N-donor ligands.<sup>2</sup> SCO events in this class of complexes can be activated by different external stimuli (T, p,B,  $h\nu$ ), and their switching characteristics make them of interest in a variety of applications, including sensors, memory, and solid-state electronic devices. However, in practical applications, SCO should be ideally operated at room temperature and atmospheric pressure.<sup>1c,2</sup> Moreover, compared with thermally activated SCO, photoinduced SCO is

more attractive because light is a cheap and convenient trigger that is capable of alternating between LS and HS states by selective wavelengths with short response times and low power dissipation.<sup>3</sup> Two main concepts must be considered in this regard: (i) the reversible spin state photoconversion based on the direct irradiation of the coordination center, called a light induced excited spin state trapping (LIESST) effect<sup>4,5</sup> and (ii) the change of ligand field strength by light-induced isomerization of photosensitive substituents introduced on the ligand skeleton, called ligand driven light induced spin change (LD LISC).<sup>6</sup> While the lifetime of metastable HS or LS complexes formed by the direct LIESST mechanism is limited to cryogenic temperatures (usually T < 100 K), the photo-

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 Tetranuclear compound 1
 Hexanuclear compound 2

 [2+2] grid-like shape
 shape of hexagon

Figure 1. Molecular structures of bis-tridentate anthracene-bpp ligands L1 and L2 and their corresponding iron(II) polynuclear complexes 1 and 2.



**Figure 2.** Representations of the complex cation  $[Fe_4(L1)_4]^{8+}$  of 1 (a) and the complex cation  $[Fe_6(L2)_6]^{12+}$  of 2 (b) in the crystal structures. Visualization of the coordination of two L2 ligands with iron(II) coordination centers in the crystal structure of 2 (c) (orange – Fe, blue – N, red – O, gray – C).

isomerization of ligand moieties may lead to reproducible isothermal LS  $\leftrightarrow$  HS alternation even at ambient temperatures. The efforts of the last three decades in this field have therefore been focused on the preparation of SCO complexes with ligands containing light-sensitive stilbenes,<sup>7</sup> azabenzenes,<sup>8</sup> or diarylethenes moieties.<sup>9</sup> Surprisingly, there is a lack of SCO systems with anthracene photoisomerizable groups, despite their potential to carry out visible light [4 + 4] photocyclization, UV light (or thermal) cycloreversion, and the high thermal stability of the corresponding photoisomers (Figure S2, see Supporting Information).<sup>10-12</sup> To the best of our knowledge, there is only one report of an dinuclear copper(II) complex, in which light-induced reversible photoisomerization was employed for controlling magnetic properties.<sup>13</sup>

Our group has recently designed three novel bis-tridentate 2,6-bis(pyrazol-1-yl)pyridine (bpp) ligands that consist of two parallel 1,8-diethynylanthracene-bpp shoulders oriented to each other in a face-to-face fashion and connected to one of the central aromatic moieties: anthracene, 10-methoxyantracene, or anthraquinone.<sup>14</sup> Successful intramolecular photo-

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	Fe1	Fe2	Fe3	Fe4	2
Fe-N <sub>py1</sub>	1.919(6)	1.896(6)	2.134(6)	2.168(6)	2.157(5)
Fe-N <sub>pz1</sub>	1.968(7)	1.959(6)	2.188(7)	2.169(7)	2.182(7)
Fe-N <sub>pz2</sub>	1.980(7)	1.948(7)	2.181(7)	2.191(7)	2.192(8)
Fe-N <sub>py2</sub>	1.911(6)	1.877(6)	2.120(6)	2.150(6)	2.163(4)
Fe-N <sub>pz3</sub>	1.982(7)	1.952(6)	2.174(7)	2.150(6)	2.171(6)
Fe-N <sub>pz4</sub>	1.967(8)	1.965(7)	2.145(6)	2.199(9)	2.178(5)
$\Sigma / ^{\circ}$	84.5	86.1	157.3	173.0	194.2
Θ /°	290.4	276.2	491.9	517.9	587.3
$\phi$ /°	170.8(3)	171.7(3)	159.9(2)	151.5(3)	148.2(3)
9 /°	88.48	88.11	78.21	74.72	66.33
α /°	79.85(3)	80.35(3)	73.25(2)	72.75(3)	71.93(2)
φ /°	159.5(3)	160.5(3)	145.5(2)	143.5(2)	139.7(2)
S(OC-6)	2.420	2.172	7.289	8.871	11.447
S(TPR-6)	9.731	10.199	7.447	5.951	5.079

Table 1. Donu Lenguis, Angles, and Distortion Parameters of the Reported Complexe	Table 1	1. Bond	Lengths.	Angles.	and Distortion	Parameters	of the	Reported	Complexes
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cyclization of the peripheral anthracenes and thermally activated decyclization have been observed in two earlier examples. However, the presence of anthraquinone in the molecular structure of the third ligand (Figure 1, L2) caused the inhibition of [4 + 4] photo-cycloaddition. Nevertheless, the topological molecular architecture of these ligands, aiming two parallel tridentate N-donor embraces oriented in the same direction, offers the formation of oligonuclear iron(II) complexes rather than coordination polymers.<sup>15</sup> In addition, the well-known family of iron(II)-bpp complexes often exhibits abrupt and room temperature thermal SCO accompanied by thermal hysteresis loops as well as photoinduced LS  $\leftrightarrow$  HS transitions (LIESST effect).<sup>16</sup> Thus, following the idea about the phototunable oligomeric SCO systems with regular molecular architectures, we report on the synthesis and the structural and magnetic characterization of  $\begin{bmatrix} 2 + 2 \end{bmatrix}$  grid-like tetranuclear and ring-shaped hexanuclear ferrous coordination compounds based on bis-tridentate anthracene-bpp ligands (Figure 1). The magnetic studies reveal half-complete and gradual SCO for the tetranuclear compound  $[Fe_4(L1)_4]$ -(CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·7CH<sub>3</sub>CN (1) and complete HS paramagnetic behavior for the hexanuclear compound  $[Fe_6(L2)_6]$ - $(CF_3SO_3)_{12}$ ·18CH<sub>3</sub>NO<sub>2</sub>·9H<sub>2</sub>O (2). The Ising-like model was utilized to analyze the SCO behavior in 1, and the zero-field splitting parameters of the HS Fe(II) atoms in 1 and 2 were extracted. The study is corroborated also by CASSCF/ NEVPT2 calculations and density functional theory (DFT) calculations.

# RESULTS AND DISCUSSION

**Synthesis and Structural Investigation.** Ligand L1 was prepared by a three-step synthetic protocol (see Supporting Information) starting from 1,8-dichloroantraquinone through the reduction to 1,8-dichloroanthracene, the formation of 1,8-diethynylanthracene by a Grignard reaction, and the consecutive deprotection of TMS groups. Finally, the introduction of 2,6-bis(pyrazol-1-yl)pyridine moieties was achieved by Pd-catalyzed Sonogashira coupling. The total yield exceeds 40%, which can be considered as reasonable given the complexity of the three-step synthesis, and it furnishes the ligand L1 on a rather useful scale of hundreds of milligrams. Ligand L2 was synthesized according to a previously reported synthetic procedure.<sup>14</sup> The reported

complexes were prepared by a reaction between the corresponding ligand and the iron(II) triflate in an equimolar ratio. The synthesis was carried out in a nitromethane/ acetonitrile solvent mixture (1:1) and resulted in the selfassembled formation of tetranuclear and hexanuclear compounds 1 and 2, respectively. Thus, as emphasized in the introduction, bis-tridentate ligands with two parallel tridentate N-donor embraces indeed offer the formation of oligomeric structures when coordinated with transition metals. In line with previous reports on tetranuclear ferrous complexes with miscellaneous bis-tridentate ligands,<sup>15</sup> compound  $\hat{1}$  forms the tetranuclear [2 + 2] grid complex cations (vide infra, Figure 2a). On the other hand, the self-assembly of L2 with iron(II) metal ions results in the formation of the closed ring-shaped hexanuclear complex cation (Figure 2b), which most probably shows higher thermodynamical stability than a possible tetranuclear grid architecture, as observed in 1. Single crystals were obtained by the slow diffusion of diisopropyl ether vapor into the respective solution of these compounds at room temperature. The UV-vis absorption spectra of both polynuclear complexes show a series of vibrationally spaced bands at wavelengths of  $\lambda = 360-480$  nm, which are typically attributed to  $\pi - \pi^*$  absorptions of the anthracene systems. Irradiation into these bands has been reported to lead to [4 + 4] photo-cyclization (Figure S2, see Supporting Information) of the anthracene rings.<sup>11,12</sup> However, in both cases, blue light irradiation ( $\lambda = 470 \text{ nm} \pm 50 \text{ nm}$ ) in an acetonitrile solution of 1 and 2 did not afford the formation of photoisomers, which can tentatively be explained by steric issues in the earlier case and by inhibition of [4 + 4] photocyclization in the latter case. From structural investigations, it is evident (vide infra) that the distances between opposite carbon atoms (9'...9'' and 10'... 10'') of two parallel anthracenes of 1 are more than 7 Å long, which makes the intramolecular [4 + 4] photo-cycloaddition impossible, even though both anthracenes are arranged in a face-to-face manner. Therefore, the steric problems concerning the realization of photoisomerization in the solution originate from the structure of the self-assembled tetranuclear complex cation itself. On the other hand, the distance between the two peripheral face-to-face arranged anthracenes in 2 are ideal (~3.5 Å; vide infra) in terms of intramolecular photocyclization. However, as previously reported in the case of uncoordinated L2,<sup>14</sup> photoisomerization is most probably

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inhibited by the presence of anthraquinone in the molecular structure of **2**.

The crystallographic investigation confirmed the polynuclear structures of both compounds 1 and 2. The single-crystal X-ray diffraction of 1 revealed a monoclinic  $P2_1/c$  space group at 100 K, and selected crystallographic parameters are given in Table S1 (see Supporting Information). The asymmetric unit consists of one cation  $[Fe_4(L1)_4]^{8+}$ , eight triflate anions, and seven acetonitrile solvent molecules. The shape of the complex cation  $[Fe_4(L1)_4]^{8+}$  is like a [2+2] grid, in which four L1 act as bis-tridentate ligands and coordinate four iron(II) metal centers (Figure 2a). The intramolecular distances between the iron(II) centers range from 8.05 to 8.67 Å. The anthracene moieties of the two neighboring parallel ligands are arranged in a face-to-face fashion at a distance of about 7.3 Å from each other and with the angles between the anthracene planes of  $14.2^{\circ}$  and  $11.0^{\circ}$ , respectively. Each iron(II) center is surrounded by six N donor atoms of two bpp moieties of opposite ligands L1. The Fe-N bond distances clearly distinguish two different coordination sites at 100 K (Table 1): Fe1 and Fe2 with average Fe-N distances of 1.94 Å are LS, while the bond lengths of the second couple (Fe3 and Fe4) are with 2.16 Å Fe-N indicative of the HS state. Selected angles of the coordination polyhedra (Table 2; Figure S6, see

Table 2. CASSCF/NEVPT2 Calculated Parameters for HS Iron Atoms in 1 and 2

	Fe3 in 1 <sup>a</sup>	Fe4 in 1 <sup>a</sup>	Fe1 in 2				
ZFS and g parameters based on CASSCF/NEVPT2 calculations with $CAS(6,5)$							
$D (cm^{-1})$	-17.0	-13.6	7.08				
E/D	0.212	0.196	0.216				
$g_x$	2.063	2.051	2.067				
$g_y$	1.984	1.995	2.160				
gz	2.346	2.288	2.011				
$\Delta_{ m LFT} ( m cm^{-1})^{b}$	590	704	1374				
ZFS and g parameters based on CASSCF/NEVPT2 calculations with CAS(6,10)							
$D (cm^{-1})$	-15.9	-13.1	6.94				
E/D	0.227	0.207	0.216				
$g_x$	2.065	2.049	2.064				
$g_y$	1.979	1.989	2.159				
gz	2.336	2.286	2.008				
$\Delta_{ m LFT} ( m cm^{-1})^{b}$	575	665	1278				
ZFS and g parameters based on CASSCF/NEVPT2 calculations with CAS(10,12)							
$D (cm^{-1})$	-17.1	-14.4	7.15				
E/D	0.216	0.189	0.241				
g <sub>x</sub>	2.061	2.044	2.062				
$g_{y}$	1.976	1.985	2.171				
$g_z$	2.358	2.312	2.008				
$\Delta_{ m LFT}  \left( { m cm}^{-1}  ight)^{m{b}}$	523	586	1172				

 $^{a}$ The first excited state is relatively close to the ground state; thus, the spin Hamiltonian parameters must not be valid.  $^{b}$ The energy separation of the first excited ligand-field term.

Supporting Information) together with  $\Sigma^{17}$  and  $\Theta^{18}$  parameters, which are sensitive to the degree on Jahn–Teller distortion existing only in the HS iron(II) centers, therefore being excellent indicators of the spin state.<sup>19</sup> Furthermore, it is obvious that angular distortion parameters  $\Sigma$  and  $\Theta$  acquire double values for the HS iron(II) sites compared to the LS ones  $(\Delta\Sigma(\text{HS-LS})_{avg} \approx 80^\circ; \Delta\Theta(\text{HS-LS})_{avg} \approx 222^\circ)$ . The

dihedral angle between the least-squares planes of the two bpp moieties coordinating the same metal center  $\theta$  and the rotation of one bpp moiety with respect to the opposite one about the iron(II) atom  $\phi$  (N<sub>py</sub>-Fe-N<sub>py</sub>)<sup>19a</sup> (Figure S6, see Supporting Information) would acquire 90° and 180°, respectively, when the coordination polyhedron {FeN<sub>6</sub>} exhibits ideal octahedral symmetry.<sup>20</sup> Since the LS sites are less distorted than the HS sites due to the absence of Jahn-Teller distortion, their values are closer to the regular octahedron angles (Table 1), while the HS centers exhibit those angles significantly lower ( $\Delta \phi$ (HS-LS)  $\approx 16^{\circ}$ ;  $\Delta\theta$ (HS-LS)  $\approx 7^{\circ}$ ). A similar trend has also been observed in the case of the bite angle  $\alpha$  (N<sub>pz</sub>-Fe-N<sub>py</sub>) and clamp angle  $\varphi$  (N<sub>pz</sub>-Fe-N<sub>pz</sub>), which vary in the suggested ranges  $\alpha = 72-74^{\circ}$ ,  $\varphi = 150-140^{\circ}$  for HS centers, and  $\alpha =$ 79–81°,  $\varphi = 155-163^{\circ}$  for LS centers, respectively.<sup>19a</sup> The best way of classifying the geometry of the coordination polyhedron in 1 is to use the continues shape measures methodology proposed by Alvarez et al.<sup>21</sup> The results of the calculations (see Supporting Information, Table S2, Figure S5) show that the lowest deviations in both LS centers are for a regular octahedron (S(OC-6) = 2.4 and 2.2, respectively) and the second lowest for a trigonal prism shape (S(TPR-6) = 9.7)and 10.2, respectively). The HS coordination center Fe3 exhibits a comparable level of deviation from an octahedral and from a trigonal prism geometry (S(OC-6) = 7.3; S(TPR-6) =7.4). Interestingly, the HS polyhedron of Fe4 with the highest degree of angular distortion (i.e.,  $\Sigma$ ,  $\Theta$ ) shows the lowest deviation from a trigonal prism geometry (S(TPR-6) = 6.0)and the second lowest from an octahedral symmetry (S(OC-6))= 8.9). Neighboring tetranuclear complex cations are interconnected via weak  $\pi - \pi$  interactions, which are responsible for the formation of the one-dimensional (1D) chain along the a-c plane (see Supporting Information, Figure S7). Four anthracene moieties of two  $[Fe_4(L1)_4]^{8+}$  cations are arranged in a head-to-tail manner, with a distance of 3.8 Å between 9' and 10'' carbon atoms. According to this motive, two peripheral and two inner anthracenes, respectively, are almost linear to each other, and the angle between the peripheral and inner couple is around 11.1° (Figure S7, see Supporting Information). Such arrangement of anthracene units of neighboring complex cations of 1 is promising with respect to intermolecular [4 + 4] photo-cycloaddition; however, the blue light irradiation of the single crystals did not show any signature of photocyclization within a twomonth period of irradiation (see Supporting Information).

The hexanuclear compound **2** with the formula  $[Fe_6(L2)_6]$ - $(CF_3SO_3)_{12} \cdot 18(CH_3NO_2) \cdot 9(H_2O)$  crystallizes in a trigonal  $R\overline{3}$ symmetry, and the asymmetric unit consists of one ligand L2, one iron(II) central atom, two triflate anions, and the corresponding solvent molecules 3  $CH_3NO_2$  and 3/2  $H_2O$ . In the complex cation, the six ligands L2 coordinate six iron(II) centers and form a hexagonal closed ring shape of  $[Fe_6(L2)_6]^{12+}$  composition (Figure 2b). The intramolecular distance between the neighboring coordination centers is 8.26 Å, and each of them is surrounded by six nitrogen atoms of two bpp moieties originating from two opposite ligands L2(Figure 2c). Each coordinated ligand contains two anthracene rings packed in a face-to-face fashion with distances of 3.7 and 3.5 Å for 9'...9'' and 10'...10'' carbon atoms, respectively, and with the angle between their planes about 19.5°. Again, such packing of anthracene units usually supports the [4 + 4] photocycloaddition. However, in line with our previous results related to the photoisomerization attempts with the pure



**Figure 3.** Magnetic data for compound 1. The temperature dependence of the effective magnetic moment measured at B = 0.1 T with a zoom-in into the low temperature region shown in the inset (left) and the reduced isothermal magnetizations measured at T = 1.8, 3, 4, and 5 K (right). The empty circles represent the experimental data points, and the black full line represents the best fit calculated with eq 1 using D = +6.8 cm<sup>-1</sup>, E/D = 0.28, g = 2.35, zj = 0.068 cm<sup>-1</sup>. The blue full line represents the best fit calculated with eqs 4–5 using  $g_{\text{HS}} = 2.38$ ,  $\Theta_{\text{HS}} = -1.48$  K,  $\Delta = 704$  K,  $r_{\text{eff}} = 14$ , and  $\gamma = 48$  K.

ligand L2,<sup>14</sup> the blue light irradiation of single crystals of 2 has neither brought any evidence for a solid-state intramolecular photocyclization. At 180 K, the Fe-N bond distances acquire an average value of around 2.17 Å, typical for the HS state. Angular distortion parameters  $\Sigma$  and  $\Theta$  as well as the selected angles of the coordination polyhedra (Table 2; Figure S6, see Supporting Information) indicate a pronounced Jahn-Teller effect, and according to Halcrow and co-workers, their extremely high values situate compound 2 to the group of permanently HS iron(II)-bpp complexes where SCO is disfavored or prohibited.<sup>19</sup> Continues shape measures (Table S2, see Supporting Information) indicate severe deviation from all considered symmetries. Surprisingly, the coordination polyhedra of all six crystallographically equivalent iron(II) centers are like a trigonal prismatic shape (S(TPR-6) = 5.1), while the second lowest symmetry measure parameters for the expected octahedral symmetry (S(OC-6) = 11.4) indicate already pronounced divergence. This can be attributed to the double axial distortion quantified by an extremely low clamp angle  $\varphi$ .<sup>21d</sup> Molecules of crystal water create a hydrogenbonded network  $(d(O \cdots O) = 2.79 \text{ Å})$  in the central cavity of the hexanuclear wheel  $[Fe_6(L2)_6]^{12+}$ , and some other weak contacts between lattice solvent molecules and triflate anions are present as well. Careful investigation of supramolecular packing of the neighboring complex cations has not revealed any significant noncovalent interactions between them.

**Magnetic Properties.** The temperature and field-dependent magnetic data on the tetranuclear compound 1 are shown in Figure 3. The value of the  $\chi T$  measured at 400 K is 14.1 cm<sup>3</sup> K mol<sup>-1</sup>, close to the theoretical value of 12.0 cm<sup>3</sup> K mol<sup>-1</sup> (with g = 2.0 for four non-interacting HS iron(II) atoms showing a S = 2 ground spin state). Upon cooling, the  $\chi T$  product starts to decrease at ca. 330 K, reaching a plateau of 8.4 cm<sup>3</sup> K mol<sup>-1</sup> at ca. 100 K and manifesting the presence of the SCO phenomenon in 1. This experimental value corresponds to the two iron(II) atoms in HS state and the two iron(II) atoms in LS state for which the theoretical  $\chi T$  is 6.0 cm<sup>3</sup> K mol<sup>-1</sup>. The presence of half-complete SCO in 1 with a transition temperature determined at  $T_{1/2} = 236$  K agrees with the results from the structural investigations (vide supra), where two LS and two HS iron(II) centers were established in

one tetranuclear complex unit at 100 K. Further cooling down to 2 K causes a decrease in the product function of up to 5.0  $cm^3$  K mol<sup>-1</sup>, which can be ascribed to the zero-field splitting of HS iron(II) atoms and eventually to weak exchange interactions. The magnetic anisotropy is also evident from the isothermal magnetization measurements undertaken at the lowest temperatures, where  $M_{\rm mol}/N_{\rm A}\mu_{\rm B}$  reaches a value of 6.8 at B = 7 T and T = 1.8 K, much lower than theoretical limit  $M_{\rm mol}/N_{\rm A}\mu_{\rm B} = 2 \times g \times S = 8$ . Compound 1 also exhibits photoinduced SCO upon the red-light irradiation (637 nm), causing an increase in the  $\chi T$  product from 7.3 cm<sup>3</sup> K mol<sup>-1</sup> to 8.8 cm<sup>3</sup> K mol<sup>-1</sup> at 10 K. The  $\chi T$  product of the photoexcited metastable HS fraction increases with further temperaturesweeping in the dark and reaches the maximum  $9.5 \text{ cm}^3 \text{ K}$ mol<sup>-1</sup> at 35 K, corresponding to about 70% of HS iron(II) centers. Subsequent increase of the temperature leads to thermal relaxation back to the LS state, which is completed above 80 K. The rather gradual character of the thermal HS  $\rightarrow$ LS relaxation made the calculation of the T(LIESST)temperature impossible.

To estimate the magnetic anisotropy of these HS iron(II) atoms, the low temperature data below 30 K, unaffected by SCO, were fitted with the following spin Hamiltonian

$$\hat{H} = D(\hat{S}_{z}^{2} - \hat{S}^{2}/3) + E(\hat{S}_{x}^{2} - \hat{S}_{y}^{2}) + \mu_{B}Bg\hat{S}_{a} - zj\langle\hat{S}_{a}\rangle\hat{S}_{a}$$
(1)

where the single-ion zero-field splitting parameters D and E, the isotropic g-factor, and the molecular field correction zjparameters are present. The  $\langle S_a \rangle$  is the thermal average of the molecular spin projection in the *a* direction of the magnetic field, defined as  $\mathbf{B}_a = B \cdot (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ , with help from the spherical coordinate system. The molar magnetization in *a*-direction of magnetic field can then be numerically calculated as

$$M_{a} = -N_{\rm A} \frac{\sum_{i} \left(\sum_{k} \sum_{l} C_{ik}^{+} (Z_{a})_{kl} C_{li}\right) \exp(-\varepsilon_{a,i}/kT)}{\sum_{i} \exp(-\varepsilon_{ai}/kT)}$$
(2)

where  $Z_a$  is the matrix element of the Zeeman term for the *a* direction of the magnetic field and *C* refers to the eigenvectors resulting from the diagonalization of the complete spin



**Figure 4.** Magnetic data for compound **2**. Temperature dependence of the effective magnetic moment measured at B = 0.1 T (left) and reduced isothermal magnetizations measured at T = 1.8, 3, 4, and 5 K (right). The empty circles represent the experimental data points. The black full line represents the best fit calculated by eq 1 using D = +7.8 cm<sup>-1</sup>, E/D = 0.31, g = 2.14, zj = 0.14 cm<sup>-1</sup>,  $\chi_{TIP} = 20 \times 10^{-9}$  m<sup>3</sup> mol<sup>-1</sup>.



Figure 5. Molecular fragment of 2, comprising an Fe1 atom derived from the experimental X-ray geometry used for CASSCF/NEVPT2's calculation, also showing the principal axes of the D-tensor with the arrows (x-axis is green, y-axis is violet, and z-axis is red).

Hamiltonian matrix. The inclusion of zj means that an iterative procedure needs to be applied.<sup>22</sup> Then, the averaged molar magnetization of the powder sample can be calculated as the integral (orientational) average

$$M_{\rm mol} = 1/4\pi \int_0^{2\pi} \int_0^{\pi} M_a \sin\theta \,\,\mathrm{d}\theta \mathrm{d}\varphi \tag{3}$$

Both temperature and field dependent data were fitted simultaneously, which resulted in  $D = +6.8 \text{ cm}^{-1}$ , E/D = 0.28, g = 2.35,  $zj = 0.068 \text{ cm}^{-1}$ , and similarly, a good fit was also found for the negative D-parameter:  $D = -5.9 \text{ cm}^{-1}$ , E/D = 0.33, g = 2.35,  $zj = -0.019 \text{ cm}^{-1}$ . The results suggest the axial type of the magnetic anisotropy and the presence of weak exchange or dipolar interactions.

The spin crossover behavior of **1** is quantitatively described by an Ising-like model based on the following Hamiltonian<sup>23</sup>

$$\hat{H} = \frac{\Delta}{2}\hat{\sigma} - \gamma \langle \sigma \rangle \hat{\sigma} \tag{4}$$

where  $\Delta$  is the energy difference between HS and LS states,  $\gamma$  is the cooperativeness, and  $r_{\text{eff}}$  is the effective degeneracy ratio between HS and LS states. This model enables to calculate the

temperature dependence of the mole fraction of the HS state  $\chi_{\text{HS}}$ , which is the next step used to calculate the molar susceptibility of 1 as

$$\chi_{\rm mol} = 2\chi_{\rm HS} + 2x_{\rm HS}\chi_{\rm HS} + 2(1 - x_{\rm HS})\chi_{\rm LS}$$
(5)

taking into account that two iron atoms remain in an HS state and the next two iron atoms undergo spin crossover. The molar susceptibility of the HS state  $\chi_{\rm HS}$  was calculated by the Curie–Weiss equation, and  $\chi_{\rm LS}$  equals zero. Finally, the parameters  $\Delta \gamma$ ,  $r_{\rm eff}$   $g_{\rm HS}$ , and  $\Theta_{\rm HS}$  (per one iron atom) were varied during the fitting procedure. The best fit was found with these parameters:  $g_{\rm HS} = 2.38$ ,  $\Theta_{\rm HS} = -1.48$  K,  $\Delta = 704$  K,  $r_{\rm eff} =$ 14 and  $\gamma = 48$  K (Figure 3). The fitted *g*-factor is close to that found by the spin Hamiltonian in eq 1, and the negative Weiss constants mostly reflect the zero-field splitting of the HS iron(II) atoms. The microscopic parameters of the Ising-like model were then utilized to calculate the enthalpy and the entropy of the spin transition as  $\Delta H = N_{\rm A}\Delta = 5.85$  kJ mol<sup>-1</sup> and  $\Delta S = R \ln r_{\rm eff} = 21.9$  J K<sup>-1</sup> mol<sup>-1</sup>, with a transition temperature of  $T_{1/2} = \Delta H/\Delta S = 266$  K. These parameters adopt typical values for iron(II) SCO compounds.



**Figure 6.** Graphical output of the CASSCF/NEVPT2 calculations with CAS(6,5) for the mononuclear molecular fragments of **1** and **2**. Plot of the d-orbitals splitting calculated by ab initio ligand field theory (AILFT) (left), low-lying ligand-field terms (middle), and ligand-field multiplets (right). The singlet, triplet, and quintet spin states are shown in red, green, and blue, respectively.

The temperature and field-dependent magnetic data of the hexanuclear compound **2** are depicted in Figure 4. The value of the  $\chi T$  product measured at 300 K is 23.4 cm<sup>3</sup> K mol<sup>-1</sup>, which is slightly higher than the theoretical value of 18.0 cm<sup>3</sup> K mol<sup>-1</sup> (with g = 2.0 for six noninteracting HS iron(II) atoms with S = 2 ground spin state). The monotonical decrease of  $\chi T$  down to ca. 30 K can probably be ascribed to the temperature-independent paramagnetism (TIP), and the drop of  $\chi T$  to 14.0 cm<sup>3</sup> K mol<sup>-1</sup> at T = 2 K is due to the zero-field splitting and weak exchange interactions among the paramagnetic atoms. This finding is also apparent from the isothermal magnetization measurements undertaken at the lowest temperatures, where  $M_{\rm mol}/N_A\mu_{\rm B}$  adopts values of 17.6 at B = 7 T and T = 1.8 K, which is much lower than the theoretical limit  $M_{\rm mol}/N_A\mu_{\rm B} = 6 \times g \times S = 24$ .

Therefore, the magnetic data of **2** were treated with a spin Hamiltonian in eq 1, and as a result, two parameter sets are obtained: (i)  $D = +7.8 \text{ cm}^{-1}$ , E/D = 0.31, g = 2.14,  $zj = 0.14 \text{ cm}^{-1}$ ,  $\chi_{\text{TIP}} = 20 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ , and (ii)  $D = -7.6 \text{ cm}^{-1}$ , E/D = 0.33, g = 2.15,  $zj = 0.11 \text{ cm}^{-1}$ ,  $\chi_{\text{TIP}} = 19 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ . Obviously, both sets are able to satisfactorily describe the experimental data with  $|D| \approx 8 \text{ cm}^{-1}$  and limiting rhombic anisotropy  $E/D \approx 1/3$ ; thus, the determination of the sign of the *D*-parameter from the experimental data is inconceivable.

**Theoretical Calculations.** The multireference ab initio calculations based on the state-averaged complete active space self-consistent field method (SA-CASSCF) were carried out to inspect the electronic structure of the iron atoms in compounds 1 and 2. Therefore, the ORCA software<sup>24</sup> was used in the CASSCF calculation with the active space defined for six electrons in five d-orbitals, CAS(6,5). Additionally, dynamic electronic correlation was handled by using the NEVPT2 method. These calculations were undertaken on the mononuclear molecular fragments extracted from the experimental X-ray structures of 1 and 2 by replacing the anthracene units with methyl groups as shown in Figure 5. Figure 6 summarizes the obtained results for 1 and 2. The atomic positions of the hydrogen atoms were optimized using the B97-3c method.<sup>25</sup>

The ab initio ligand field theory (AILFT) was used to calculate the energy of the d-orbitals as depicted in Figure 6 (left). In perfect  $O_h$  symmetry, the d-orbitals split into two sets of  $t_{2g}$  and  $e_g$  orbitals separated by the energy of 10Dq, but due to the lower symmetry of the coordination polyhedron, the degeneracy of these orbitals is removed. By averaging the

energies of the three former  $t_{2g}$  and two former  $e_g$  orbitals, the estimates of 10Dq were calculated as 17 405  $\text{cm}^{-1^5}$  for Fe1 of 1, 18 956 cm<sup>-1</sup> for  $\hat{F}e2$  of 1, 7480 cm<sup>-1</sup> for Fe3 of 1, 6768 cm<sup>-1</sup> for Fe4 of 1 and 6248 cm<sup>-1</sup> for Fe1 of 2. Thus, the ratio for the 10Dq<sup>LS</sup>/10Dq<sup>HS</sup> is approximately 2.3–2.8 in 1. Subsequently, the CASSCF/NEVPT2 ligand field terms are shown in Figure 6 (middle), where the large energy splitting of the d-orbitals results in the singlet ground state of the Fe1 and Fe2 atoms in 1 originating from the <sup>1</sup>A<sub>1</sub> state, and the Fe3 and Fe4 atoms in 1 and the Fe1 in 2 have the three lowest quintet states originating from the splitting of  ${}^{5}T_{2}$  state in ideal  $O_{h}$  symmetry. The first excited quintet terms have energy separations of 590  $cm^{-1}$  in Fe3 of 1, 704  $cm^{-1}$  in Fe4 of 1, and 1374  $cm^{-1}$  in Fe1 of 2. In the case of the Fe1 and Fe2 atoms in 1, the first excited singlet terms suitable for the LIESST effect have energies of 16881 and 18135 cm<sup>-1</sup>, respectively, in reasonable agreement with the energy of  $637 \text{ nm} (15700 \text{ cm}^{-1})$  used for the photoexcitation in 1.<sup>3b</sup> After the spin-orbit coupling was incorporated, the ligand-field terms (LFT) are split into the ligand-field multiplets (LFM), as plotted in Figure 6 (right). The application of the zero-field splitting spin Hamiltonian to the quintet ground states enabled us to extract the ZFS D and E parameters, and g-tensor parameters are summarized in Table 2. The utilization of the effective Hamiltonian theory resulted in relatively large and negative D-parameters for Fe3 and Fe4 in 1 with large rhombicity,  $E/D \approx 0.2$ . However, the presence of close lying excited states means that the spin Hamiltonian approach is no longer valid, and more elaborated theoretical models incorporating the orbital angular momentum should be utilized. This could also explain the large difference between ab initio calculated as D = -13.6/-17.0 $cm^{-1}$  and the fitted averaged *D*-parameter,  $D = 6.8/-5.9 cm^{-1}$ . On the contrary, the ab initio calculations for Fe1 in 2 show a good agreement between the calculated ( $D = 7.08 \text{ cm}^{-1}$ ). Furthermore, the fitted  $(D = 7.8/-7.6 \text{ cm}^{-1})$  ZFS parameters and the large energy of the first excited state also validate the utilization of the spin Hamiltonian. The calculated principal axes of the D-tensor are visualized in Figure 5. Furthermore, the double-shell effect, which is supposed to be important for late 3D-metals, was accounted for by enlarging the active space to 10 d-orbitals (3d + 4d). Remarkably, this approach (CAS(6,5) vs CAS(6,10)) has only a minor impact on the derived D and E ZFS parameters and g-factors (Table 2). In line with previous studies,<sup>26</sup> we extended the active space with two  $\sigma$ -type orbitals to CAS(10,12), and again, there were only



Figure 7. Molecular fragment  $[Fe_6(L2)_6]^{12+}$  of 2 and B3LYP calculated spin isodensity surface for the HS state (left) and the broken-symmetry spin state (right) with a cutoff value of 0.005 e-bohr<sup>-3</sup>. The positive and negative spin densities are represented by the yellow and cyan surfaces, respectively. The hydrogen atoms are omitted for clarity.

minor changes in the ZFS parameters, as listed in Table 2. A comparison of all ligand-field terms and multiplets for all three active space choices is plotted in Figure S8 (see Supporting Information).

Finally, the DFT calculations were applied to 2 to evaluate the superexchange interactions among the Fe atoms, because the fitting of the experimental magnetic data suggests nonnegligible ferromagnetic interactions ( $zj = 0.14 \text{ cm}^{-1}$ ). Therefore, the broken symmetry approach was used for the proposed spin Hamiltonian

$$\hat{H} = -J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_4 \cdot \mathbf{S}_5 + \mathbf{S}_5 \cdot \mathbf{S}_6 + \mathbf{S}_1 \cdot \mathbf{S}_6)$$
(6)

where J is the isotropic exchange parameter among the adjacent iron atoms. Then, Ruiz's approach was employed to derive the following relationship

$$J = \Delta/90 \tag{7}$$

where  $\Delta$  is the energy difference between the brokensymmetry spin state and the HS spin state,  $\Delta = \varepsilon_{\rm BS} - \varepsilon_{\rm HS}$ . Herein, the well-established B3LYP functional was used to calculate these spin states, for which the spin densities are shown in Figure 7, which resulted in  $\Delta = 2.984$  cm<sup>-1</sup> and consequently, J = 0.033 cm<sup>-1</sup>. Thus, these calculations support the weak ferromagnetic interactions mediated by the anthracene-bpp L2 ligand in 2.

# CONCLUSION

In conclusion, we have successfully prepared two new polynuclear iron(II) complexes with bis-tridentate ligands containing two 2,6-bis(pyrazol-1-yl)pyridine N-donor moieties introduced on an acetylene-anthracene skeleton. Magnetic investigations revealed the presence of a half-complete SCO in the tetranuclear compound and HS behavior in the hexanuclear compound. Structural investigations confirmed the polynuclear structures of both compounds. In line with magnetic properties, X-ray diffraction studies reveal two iron(II) centers in HS state and another two in LS state in the tetranuclear [2 + 2] grid-like complex. Inspection of the symmetry in the coordination polyhedra revealed severe angular deviation from the expected octahedral shape for

those iron(II) sites, which are permanently retained in the HS state. Even higher angular distortion was found to be present in the hexanuclear complex 2. We can conclude that the pronounced structural deviation of the coordination polyhedra stabilizes the HS state of iron(II) centers. An analysis of the magnetic properties revealed the zero-field splitting parameter |  $D \approx 6-8 \text{ cm}^{-1}$  with large rhombicity  $(E/D \approx 0.28-0.33)$  for all HS iron(II) atoms in 1 or 2, indicating the axial type of the magnetic anisotropy. The Ising-like model was applied to analyze the SCO behavior of 1, providing estimates in spin transition enthalpy and entropy, with the spin transition temperature being  $T_{1/2}$  = 266 K. The electronic structure and magnetic anisotropy were also investigated by means of multireference CASSCF/NEVPT2 methods, confirming the ground spin state properties for all iron atoms in 1 and 2 and also revealing the substantial magnetic anisotropy of the involved HS iron(II) atoms. The non-negligible weak ferromagnetic exchange in 2 was also substantiated by the DFT level using well-established B3LYP functional.

We also tried to control the magnetic and spin state properties by light. Ferrous complexes with potential SCO properties containing photoactive anthracene moieties offer the possibility of [4 + 4] photoisomerization. However, due to steric problems in the case of tetranuclear compound or the inhibition of the photo-cycloaddition mechanism caused by the presence of anthraquinone in the hexanuclear compound, both complexes exhibit innocent behavior independently upon the wavelength selected for irradiation. Thus, further careful molecular design is necessary for the synthesis and successful photo-isomerization of the next iron(II) SCO complexes containing the anthracene photoisomerizable units.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03432.

Synthesis and structural, magnetic, and computational details (PDF)

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# Accession Codes

CCDC 1862242–1862243 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) (a) See recent reviews and references therein: Spin-Crossover Materials: Properties and Applications; Halcrow, M. A., Ed.; John Wiley & Sons Ltd: Chichester, 2013. (b) Special Issue: "Spin-Crossover Complexes". Murray, K. S.; Oshio, H.; Real, J. A., Eds.; Eur. J. Inorg. Chem. 2013, 574–1067. (c) Bousseksou, A.; Molnar, G.; Salmon, L.; Nicolazzi, W. Molecular spin crossover phenomenon: recent achievements and prospects. Chem. Soc. Rev. 2011, 40, 3313–3335. (d) Spin Crossover in Transition Metal Compounds I – III, Topics in Current Chemistry 233 – 235; Gütlich, P., Goodwin, H. A., Eds.; Springer: Berlin/Heidelberg, 2004.

(2) Šalitroš, I.; Madhu, N. T.; Boča, R.; Pavlik, J.; Ruben, M. Roomtemperature spin-transition iron compounds. *Monatsh. Chem.* **2009**, *140*, 695–733.

(3) (a) Létard, J.-F.; Chastanet, G.; Guionneau, P.; Desplanches, C. Optimizing the Stability of Trapped Metastable Spin States. In *Spin-Crossover Materials: Properties and Applications*; Halcrow, M. A., Ed.; John Wiley & Sons Ltd: Chichester, 2013; pp 475–507. (b) Šalitroš, I.; Pavlik, J. Light-Induced Excited Spin State Trapping. In *Encyclopedia of Physical Organic Chemistry*; Wang, Z., Ed; John Wiley & Sons, Inc.: Hoboken, NJ, 2017; pp 3083–3180.

(4) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. Light-induced excited spin state trapping in a transition-metal complex: The hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system. *Chem. Phys. Lett.* **1984**, *105* (1), 1–4.

(5) Hauser, A.; Gütlich, P.; Spiering, H. High-spin - low-spin relaxation kinetics and cooperative effects in the hexakis(1-propyltetrazole)iron bis(tetrafluoroborate) and  $[Zn_{1-x}Fe_x(ptz)_6]$ -(BF<sub>4</sub>)<sub>2</sub> (ptz = 1-propyltetrazole) spin-crossover systems. *Inorg. Chem.* **1986**, 25, 4245–4248.

(6) Boillot, M.-L.; Zarembowitch, J.; Sour, A. Ligand-Driven Light-Induced Spin Change (LD-LISC): A Promising Photomagnetic Effect. In *Spin Crossover in Transition Metal Compounds II*; Topics in Current Chemistry 234; Gütlich, P., Goodwin, H. A., Eds.; Springer: Berlin/Heidelberg, 2004; pp 261–276.

(7) Takahashi, K.; Hasegawa, Y.; Sakamoto, R.; Nishikawa, M.; Kume, S.; Nishibori, E.; Nishihara, H. Solid-State Ligand-Driven Light-Induced Spin Change at Ambient Temperatures in Bis-(dipyrazolylstyrylpyridine)iron(II) Complexes. *Inorg. Chem.* **2012**, *51* (9), 5188–5198.

(8) Hasegawa, Y.; Kume, S.; Nishihara, H. Reversible light-induced magnetization change in an azobenzene-attached pyridylbenzimidazole complex of iron(II) at room temperature. *Dalton Trans.* **2009**, 280–284.

(9) Rösner, B.; Milek, M.; Witt, A.; Gobaut, B.; Torelli, P.; Fink, R. H.; Khusniyarov, M. M. Reversible Photoswitching of a Spin Crossover Molecular Complex in the Solid State at Room Temperature. *Angew. Chem., Int. Ed.* **2015**, *54*, 12976–12980.

(10) Becker, H.-D. Unimolecular photochemistry of anthracenes. *Chem. Rev.* **1993**, *93*, 145–172.

(11) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. Photodimerization of anthracenes in fluid solution:structural aspects. *Chem. Soc. Rev.* **2000**, *29*, 43–55.

(12) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. Photodimerization of anthracenes in fluid solutions: (part 2) mechanistic aspects of the photocycloaddition and of the photochemical and thermal cleavage. *Chem. Soc. Rev.* **2001**, *30*, 248–263.

(13) Castellano, M.; Ferrando-Soria, J.; Pardo, E.; Julve, M.; Lloret, F.; Mathoniere, C.; Pasán, J.; Ruiz-Pérez, C.; Canadillas-Delgado, L.; Ruiz-García, R.; Cano, J. Photoswitching of the antiferromagnetic coupling in an oxamato-based dicopper(II) anthracenophane. *Chem. Commun.* **2011**, *47*, 11035–10983.

(14) Salitroš, I.; Fuhr, O.; Gál, M.; Valašek, M.; Ruben, M. Photoisomerization of Bis(tridentate) 2,6 Bis(1H pyrazol 1 yl)-pyridine Ligands Exhibiting a Multi anthracene Skeleton. *Chem. - Eur. J.* **2017**, 23, 10100–10109.

(15) (a) Ruben, M.; Breuning, E.; Lehn, J.-M.; Ksenofontov, V.; Renz, F.; Gütlich, P.; Vaughan, G. B. M. Supramolecular Spintronic Devices: Spin Transitions and Magnetostructural Correlations in  $[Fe_4^{II}L_4]^{8+}$  [2 × 2] Grid Type Complexes. Chem. - Eur. J. 2003, 9, 4422-4429. (b) Breuning, E.; Ruben, M.; Lehn, J.-M.; Renz, F.; Garcia, Y.; Ksenofontov, V.; Gütlich, P.; Wegelius, E.; Rissanen, K. Spin Crossover in a Supramolecular Fe<sub>4</sub><sup>II</sup>  $[2 \times 2]$  Grid Triggered by Temperature, Pressure, and Light. Angew. Chem., Int. Ed. 2000, 39, 2504-2507. (c) Matsumoto, T.; Newton, G. N.; Shiga, T.; Hayami, S.; Matsui, Y.; Okamoto, H.; Kumai, R.; Murakami, Y.; Oshio, H. Two-dimensional quasi-freestanding molecular crystals for highperformance organic field-effect transistors. Nat. Commun. 2014, 5, 3865-3868. (d) Schäfer, B.; Greisch, J.-F.; Faus, I.; Bodenstein, T.; Šalitroš, I.; Fuhr, O.; Fink, K.; Schünemann, V.; Kappes, M. M.; Ruben, M. Divergent Coordination Chemistry: Parallel Synthesis of  $[2 \times 2]$  Iron(II) Grid-Complex Tauto-Conformers. Angew. Chem., Int. Ed. 2016, 55, 10881-10885.

(16) (a) Pritchard, R.; Lazar, H.; Barrett, S. A.; Kilner, C. A.; Asthana, S.; Carbonera, C.; Létard, J.-F.; Halcrow, M. A. Thermal and light-induced spin-transitions in iron(II) complexes of 2,6-bis(4halopyrazolyl)pyridines: the influence of polymorphism on a spincrossover compound. *Dalton Trans.* **2009**, 6656–6666. (b) Chastanet, G.; Tovee, C. A.; Hyett, G.; Halcrow, M. A.; Létard, J.-F. Photomagnetic studies on spin-crossover solid solutions containing two different metal complexes,  $[Fe(1-bpp)_2]_x[M(terpy)_2]_{1-x}[BF_4]_2$ (M = Ru or Co). *Dalton Trans.* **2012**, 41, 4896–4902. (c) Rajadurai, C.; Fuhr, O.; Kruk, R.; Ghafari, M.; Hahn, H.; Ruben, M. Above room temperature spin transition in a metallo-supramolecular coordination oligomer/polymer. *Chem. Commun.* **2007**, 2636–2638.

(17) (a) Guionneau, P.; Marchivie, M.; Bravic, G.; Létard, J.-F.; Chasseau, D. Structural Aspects of Spin Crossover. Example of the  $[Fe^{II}L_n(NCS)_2]$  Complexes. In Spin Crossover in Transition Metal Compounds II; Topics in Current Chemistry 234; Gütlich, P., Goodwin, H. A., Eds.; Springer: Berlin/Heidelberg, 2004; pp 97– 128. (b)  $\sum = \sum_{i=1}^{12} (|\varphi_i - 90|)$ , Figure S6 (see SupportingInformation)for the explanation of  $\Sigma$  parameter.

(18) (a) Halcrow, M. A. Structure:function relationships in molecular spin-crossover complexes. *Chem. Soc. Rev.* 2011, 40,

# **Inorganic Chemistry**

4119–4142. (b)  $\Theta = \sum_{i=1}^{24} (|\theta_i - 90|)$ , Figure S6 (see Supporting Information) for the definition of  $\Theta$  parameter.

(19) (a) Halcrow, M. A. Iron(II) complexes of 2,6-di(pyrazol-1yl)pyridines—A versatile system for spin-crossover research. *Coord. Chem. Rev.* **2009**, 253, 2493–2514. (b) Berdiell, I. C.; Kulmaczewski, R.; Halcrow, M. A. Iron(II) Complexes of 2,4-Dipyrazolyl-1,3,5triazine Derivatives—The Influence of Ligand Geometry on Metal Ion Spin State. *Inorg. Chem.* **2017**, 56, 8817–8828.

(20) Schramm, F.; Meded, V.; Fliegl, H.; Fink, K.; Fuhr, O.; Qu, Z.– R.; Klopper, W.; Finn, S.; Keyes, T. E.; Ruben, M. Expanding the Coordination Cage: A Ruthenium(II)–Polypyridine Complex Exhibiting High Quantum Yields under Ambient Conditions. *Inorg. Chem.* **2009**, *48*, 5677–5684.

(21) (a) Alvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M. Continuous symmetry maps and shape classification. The case of six-coordinated metal compounds. New J. Chem. 2002, 26, 996–1009. (b) Alvarez, S. Relationships between Temperature, Magnetic Moment, and Continuous Symmetry Measures in Spin Crossover Complexes. J. Am. Chem. Soc. 2003, 125, 6795–6802. (c) Alvarez, S. Distortion Pathways of Transition Metal Coordination Polyhedra Induced by Chelating Topology. Chem. Rev. 2015, 115, 13447–13483. (d) Kershaw Cook, L. J.; Mohammed, R.; Sherborne, G.; Roberts, T. D.; Alvarez, S.; Halcrow, M. A. Spin state behavior of iron(II)/ dipyrazolylpyridine complexes. New insights from crystallographic and solution measurements. Coord. Chem. Rev. 2015, 289–290, 2–12. (22) Boča, R. Theoretical Foundations of Molecular Magnetism; Elsevier: Amsterdam, 1999.

(23) (a) Bari, R. A.; Sivardiere, J. Low-Spin-High-Spin Transitions in Transition-Metal-Ion Compounds. *Phys. Rev. B* 1972, *5*, 4466–4471.
(b) Wajnflasz, J. Etude de la transition Low Spin, High Spin dans les complexes octaédriques d'ion de transition. *Phys. Status Solidi B* 1970, *40*, 537–545. (c) Boča, R.; Linert, W. Is There a Need for New Models of the Spin Crossover? *Monatsh. Chem.* 2003, *134*, 199–216.

(24) (a) Neese, F. The ORCA program system. WIREs Comput. Mol. Sci. 2012, 2, 73–78. (b) Neese, F. Software update: the ORCA program system, version 4.0. WIREs Comput. Mol. Sci. 2018, 8, No. e1327.

(25) Brandenburg, J. G.; Bannwarth, C.; Hansen, A.; Grimme, S. B97-3c: A revised low-cost variant of the B97-D density functional method. *J. Chem. Phys.* **2018**, *148*, 064104.

(26) (a) Pierloot, K.; Phung, Q. M.; Domingo, A. Spin State Energetics in First-Row Transition Metal Complexes: Contribution of (3s3p) Correlation and Its Description by Second-Order Perturbation Theory. J. Chem. Theory Comput. 2017, 13, 537–553. (b) Ashley, D. C.; Jakubikova, E. Ray-Dutt and Bailar Twists in Fe(II)-Tris(2,2'bipyridine): Spin States, Sterics, and Fe–N Bond Strengths. Inorg. Chem. 2018, 57, 5585–5596.