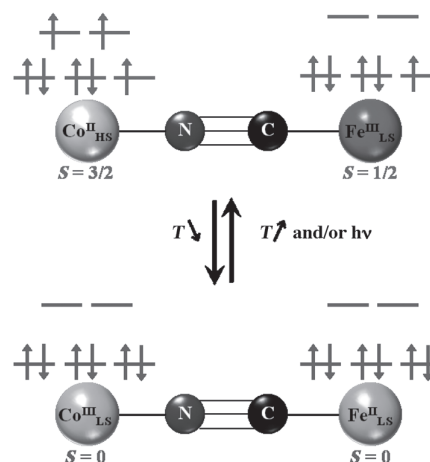


Controlling Thermally Induced Electron Transfer in Cyano-Bridged Molecular Squares: From Solid State to Solution

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The rational design of molecular systems that exhibit tunable optical and/or magnetic behavior as a function of external stimuli (temperature, electric or magnetic fields, light, pressure, etc.), is the subject of intense worldwide research activity to conceive high-performance molecule-based electronic devices. Promising applications are expected in numerous areas such as information processing, high-density recording media, molecular switches, sensors, and display devices.^[1,2] Among known switchable molecular systems, tunable optical and magnetic properties have been reported in many cyano-based materials such as Prussian Blue (PB) analogues.^[1,2c] In 1996, Hashimoto and co-workers reported the first Co/Fe PB analogue, $K_{0.2}Co_{1.4}[Fe(CN)_6] \cdot 6.9H_2O$, that showed photochemically controlled magnetic properties.^[3] Following this seminal work, a large series of Co/Fe PB analogues were synthesized, allowing for a more thorough understanding of the electron-transfer properties.^[4] These compounds contain $\{Fe(\mu-CN)Co\}$ motifs that exhibit a reversi-

ble metal-to-metal electron-transfer process, which converts diamagnetic $\{Fe^{II}_{LS}(\mu-CN)Co^{III}_{LS}\}$ into paramagnetic $\{Fe^{III}_{LS}(\mu-CN)Co^{II}_{HS}\}$ pairs (LS=low-spin, HS=high-spin; Scheme 1).^[3,4] During the past 15 years, chemists have investigated the synthesis of molecular magnetic and photoresponsive complexes through rational choices of cyano-based building blocks.^[5–10] This approach has been extremely successful, and various molecular architectures have been obtained with remarkable properties such as single-molecule magnet behavior,^[6] spin crossover,^[7] electron-transfer process,^[8] and photoinduced magnetism.^[8b–f,9]



Scheme 1. Thermally and photoinduced metal-to-metal electron transfer in $\{Fe^{II}_{LS}(\mu-CN)Co^{III}_{LS}\}$ and $\{Fe^{III}_{LS}(\mu-CN)Co^{II}_{HS}\}$ pairs.

Recently, we,^[8c] Oshio,^[8c,i] and Lescouëzec^[8d] reported tetranuclear cyano-bridged $\{Fe_2Co_2\}$ complexes that exhibit reversible thermally and photoinduced intramolecular electron-transfer in the solid state. In these systems, the optical and magnetic bistability can be tuned by the capping ligands^[8c–i] present on the metal ions, afford a range of crystal structures with variable long-range elastic interactions. In 2011, Oshio and co-workers^[8c] reported that the thermally induced electron-transfer process of their reported $\{Fe_2Co_2\}$ complex can be observed in butyronitrile solution and modulated by protonation. To probe whether the bistability of $\{Fe_2Co_2\}$ complexes can be transferred in a general manner to different solvents, we have oriented our effort to-

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wards more soluble compounds using functionalized bipyridine (bpy^{R}) ligands: $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]_2[\text{Co}(\text{bpy}^{\text{R}})_2][\text{OTf}]_2$ ($\text{Tp}^* = \text{tris}(3,5\text{-dimethyl})\text{pyrazolyl borate}$, $\text{bpy}^{\text{R}} = 4,4'\text{-R,R-2,2'}\text{-bipyridine}$ with $\text{R} = \text{alkyl groups}$, $\text{OTf} = \text{trifluoromethanesulfonate}$). Herein, we compare three different $\{\text{Fe}_2\text{Co}_2\}$ complexes: 1) $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]_2[\text{Co}(\text{DMF})_4][\text{OTf}]_2 \cdot 2\text{DMF}^{[10]}$ (**1**) that does not show electron transfer in the solid state or in solution; 2) $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]_2[\text{Co}(\text{bpy})_2][\text{OTf}]_2 \cdot 4\text{DMF} \cdot 2\text{H}_2\text{O}^{[8c]}$ (**2**) that displays electron transfer in the solid state and only in dilute CH_3OH or CH_3CN solutions; and finally, 3) $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]_2[\text{Co}(\text{bpy}^{\text{Me}})_2][\text{OTf}]_2 \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$ (**3**) ($\text{bpy}^{\text{Me}} = 4,4'\text{-dimethyl-2,2'}\text{-bipyridine}$) that exhibits electron transfer in the solid state and in a broad range of solvents. This work demonstrates and generalizes the possibility to transfer the solid-state properties of switchable $\{\text{Fe}_2\text{Co}_2\}$ complexes to solution, and thus opens up new possibilities to control molecular optical and magnetic behavior by tuning the energy of the electron-transfer process through variations in solvent composition and polarity.

Compound **3** was prepared by combining equimolar quantities of $[\text{Et}_4\text{N}][(\text{Tp}^*)\text{Fe}(\text{CN})_3]$ and $\text{Co}(\text{OTf})_2$ in DMF, followed by addition of bpy^{Me} (see the Supporting Information, Figure S1). It crystallizes in the triclinic $P\bar{1}$ space group as observed at 250 and 120 K (Table S1 in the Supporting Information) for which the crystal color changes from red to green, respectively. In structures of **3**, the cationic $\{\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\}$ core is nearly planar (Figure 1 and Figure S2 in the Supporting Information). At 250 K, the average Fe–C and Co–N_{CN} bond lengths are 1.921(8) and 2.095(5) Å (Table S2 in the Supporting Information), respectively,

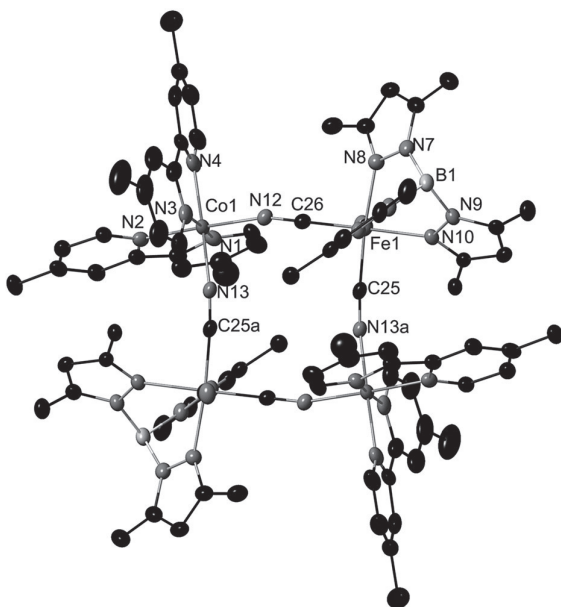


Figure 1. ORTEP-type view of the cationic part of **3** at 120 K with thermal ellipsoids at 30% probability level. Lattice solvents, anions, and hydrogen atoms are omitted for clarity.

which are in close agreement with those expected considering the valence sum bond analysis and charge compensation for high-spin Co^{II} and low-spin Fe^{III} metal ions. At 120 K the green crystal structure (Figure 1) reveals significantly shorter average Fe–C and Co–N_{CN} bond lengths of 1.887(4) and 1.930(3) Å, respectively. Although the Fe–C bond length is very similar to that observed at 250 K, as expected when $\text{Fe}^{\text{III}}_{\text{LS}}$ converts to $\text{Fe}^{\text{II}}_{\text{LS}}$, the Co–N bond lengths are characteristic of $\text{Co}^{\text{III}}_{\text{LS}}$ sites (Table S2 in the Supporting Information).^[8a–c] In the crystal packing, $\{\text{Fe}_2\text{Co}_2\}$ complexes are significantly better separated than in **2** by OTf^- and interstitial solvents at both 120 and 250 K (Figures S3 and S4 in the Supporting Information).

Solid-state reflectivity and magnetic properties confirm that intramolecular electron-transfer, inferred from X-ray diffraction studies, has occurred in **3** (Figures S5 and S6 in the Supporting Information). At room temperature, the reflectivity data collected for **2**^[8c] and **3** are superimposable with a strong broad absorption between 500 and 700 nm (absolute reflectivity at 550 nm $R_{550} = 0.02$) and a high reflectivity above 700 nm ($R_{800} = 0.32$, Figure S5 in the Supporting Information). Between 280 and 150 K, the sample becomes strongly absorbent above 700 nm ($R_{800} = 0.02$), the hallmark signature of the thermally induced electron transfer between Co^{II} and Fe^{III} ions. Upon further cooling (below 120 K), compound **3** becomes more reflective in the near-infrared region as expected for a photoconversion (induced by the reflectivity source light) of the $\{\text{Fe}^{\text{II}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{III}}_{\text{LS}}\}$ into $\{\text{Fe}^{\text{III}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{II}}_{\text{HS}}\}$ units. Magnetic susceptibility data (Figure S6 in the Supporting Information) confirm that **3** exhibits a complete thermally and photoinduced electron-transfer process: 1) the paramagnetic $\{\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}\}_2$ state is observed in the dark between 280 and 240 K, or after photoexcitation below 120 K ($\chi T = 6.5 \text{ cm}^3 \text{ K mol}^{-1}$), and 2) in the dark, the diamagnetic $\{\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}\}_2$ state is detected below 120 K ($\chi T = 0.51\text{--}0.08 \text{ cm}^3 \text{ K mol}^{-1}$ from 120 to 1.8 K). Thus, although **1** remains in its paramagnetic $\{\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}\}_2$ state above 1.8 K, and **2** shows a first-order phase transition with a thermal hysteresis of 18 K (at 0.4 K min^{-1}) between 186 and 168 K, associated with an electron-transfer process,^[8c] compound **3** displays a thermally reversible electron-transfer conversion at approximately $T_{1/2} = 174 \text{ K}$.^[11] This result suggests the presence of significantly fewer elastic interactions between complexes in the crystal structure of **3** than for **2**. This assumption is confirmed by a comparative structure analysis at 250 K, which highlights an increase of the $\pi\text{--}\pi$ contact distances between bpy^{Me} in **3**, certainly due to the steric influence of the methyl group in the *para*-position of bpy^{Me} ligands (Figures S3 and S4 in the Supporting Information; centroid-to-centroid distances of 3.9 and 4.4 Å for **2** and **3**, respectively).

To examine the possibility of transferring the solid-state properties of these switchable $\{\text{Fe}_2\text{Co}_2\}$ molecules to fluid solutions, the solubility of the three complexes and the properties of the resulting solutions have been studied. As expected, methyl functionalization of the bipyridine ligands affords a higher solubility for **3** in different solvents in com-

Table 1. Solubility and qualitative tests of electron-transfer for solutions of **1**, **2**, and **3**.^[a]

Solvents/Polarity, P' ^[12]	1	2	3
Nitromethane/6.8	red	×	red-green
Methanol/6.6	red	red-green	red-green
Acetonitrile/6.2	red	red-green	red-green
Ethanol/5.2	red	×	red-green
Acetone/5.1	red	red	red-green
Nitrobenzene/4.5	red	×	red
Tetrahydrofuran/4.2	red	×	×
Chloroform/4.1	red	red	red
Dichloromethane/3.4	red	red	red-green

[a] × = insoluble at 298 K; all the complexes are insoluble in diethyl ether, ethyl acetate, toluene, hexane, and water.^[13] “Red” color at all temperatures suggests the absence of electron transfer; “red-green” colors at 290 and 77 K indicates an electron transfer. P' is the solvent polarity index.^[12]

parison to **2** (Table 1). Consistent with our assumption, intramolecular electron-transfer remains operative in dilute solutions of **2** and **3**, whereas those containing **1** do not exhibit changes in their optical properties (in other words solutions/solids are red between 298 and 77 K) despite a higher solubility in all solvents examined. As shown in Table 1, compound **2** is slightly soluble in organic solvents and electron transfer is observed only in acetonitrile and methanol solutions.

For compound **3**, the color change occurs in the majority of the solvents tested (Table 1), with the exception of chloroform and nitrobenzene in which it is sparingly soluble.^[13] The thermochromism observed in solutions of **3** has been quantitatively studied by UV/Vis spectroscopy. A broad absorption band is centered at 470 nm in addition to a small shoulder at approximately 560 nm (Figure 2). The intense 470 nm absorption corresponds to a spin- and Laporte-allowed ligand-to-metal charge-transfer (LMCT) transition,^[8b,14] whereas the shoulder at 560 nm may be attributed to a $\text{Co}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$ metal-to-metal charge-transfer (MMCT) transition.^[8b] With decreasing temperature, the absorption band at 560 nm decreases progressively in intensity as a new absorption band, characteristic of the $\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ MMCT, concomitantly appears around 770 nm (Figure 2, top). Therefore, the spectroscopic data unambiguously demonstrate that the thermal conversion of $\{\text{Fe}^{\text{III}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{II}}_{\text{HS}}\}$ into $\{\text{Fe}^{\text{II}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{III}}_{\text{LS}}\}$ pairs occurs in solution. Furthermore, the presence of an isosbestic point at 630 nm confirms that only two species are involved in the interconversion process. The temperature dependence of the $\{\text{Fe}^{\text{III}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{II}}_{\text{HS}}\}$ and $\{\text{Fe}^{\text{II}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{III}}_{\text{LS}}\}$ fractions (r), shown in Figure 2 (bottom), can be deduced from the thermal variation of the 560 and 770 nm absorptions, respectively. As expected, the two fractions cross each other at 0.5, defining a $T_{1/2}$ temperature that is approximated^[15] to range from 180 to 240 K (180 K in dichloromethane, 190 K in acetone, 220 K in acetonitrile, and 240 K in methanol). The r versus T data, shown in Figure 2 and Figure S7 in the Supporting Information, are well-fitted to the ideal solution model^[16] with enthalpy changes, ΔH , between 45 (CH_2Cl_2) and 63 kJ mol^{-1} (CH_3OH and $(\text{CH}_3)_2\text{CO}$) and the above $T_{1/2}$

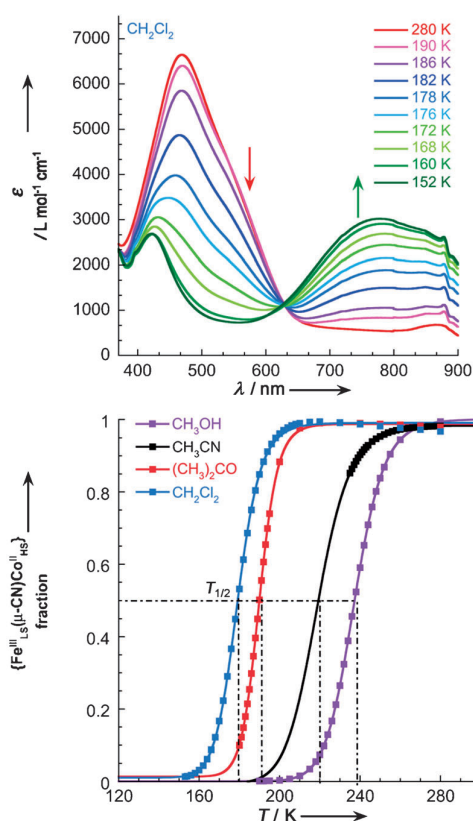


Figure 2. Top: UV/Vis spectra for **3** in CH_2Cl_2 in cooling mode from 280 to 152 K (at $0.2\text{--}0.3 \text{ K min}^{-1}$). Bottom: Temperature dependence of the $\{\text{Fe}^{\text{III}}_{\text{LS}}(\mu\text{-CN})\text{Co}^{\text{II}}_{\text{HS}}\}$ fraction estimated from the absorption intensities at the MMCT band ($\approx 560 \text{ nm}$) for **3** in different solvents; solid lines are the fits to the ideal solution model.^[16]

value corresponding to entropy variations, $\Delta S = \Delta H/T_{1/2}$, between 220 (CH_3CN) and 330 $\text{J K}^{-1} \text{mol}^{-1}$ ($(\text{CH}_3)_2\text{CO}$).^[16] These results confirm that the intramolecular electron-transfer processes in **3** persist in solution (as evidenced by their electronic transitions), and that they are strongly solvent-dependent.

Additional evidence in support of intramolecular electron-transfer was also found in magnetic data collected for dilute solutions of **3**. Regardless of solvent, the χT product at room temperature is essentially the same around $6.6 \text{ cm}^3 \text{K mol}^{-1}$ in agreement with the presence of paramagnetic $\{\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}\}_2$ complexes. With decreasing temperature, the χT product rapidly decreases to small values (0.26 to $0.35 \text{ cm}^3 \text{K mol}^{-1}$, Figure 3), consistent with the presence of diamagnetic $\{\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}\}_2$ complexes as the majority species. As already observed by UV/Vis spectroscopy, the electron-transfer process is strongly influenced by the solvent. In particular, $T_{1/2}$ values, precisely evaluated for **3** at 186(1), 199(1), 231(1), and 250(1) K in dichloromethane, acetone, acetonitrile, and methanol solutions, respectively, are found to increase with solvent polarity (Table 1),^[12] mirroring the trend seen in UV/Vis data. It is worth mentioning that for **2** the $T_{1/2}$ values of 198(1) and 206(1) K, found in acetonitrile

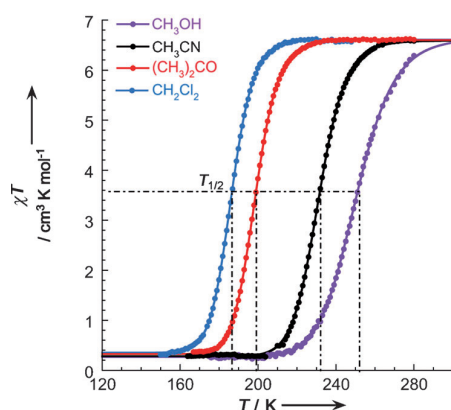


Figure 3. χT versus T data for **3** (with χ defined as molar magnetic susceptibility and equal to M/H) in methanol, acetonitrile, acetone, and dichloromethane solutions (0.4 K min^{-1} , 1 T; solid lines are fits to the ideal solution model^[16]).

and methanol, respectively (Figure S8 in the Supporting Information), are significantly lower than for **3**, although in solid state the two complexes possess an almost identical $T_{1/2}$. The χT versus T data (Figure 3) for **3** are also in good agreement with the ideal solution model,^[16] which allows ΔH to be estimated at 52(1), 56(1), 65(1), and 53(1) kJ mol^{-1} in CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$, CH_3CN , and CH_3OH (the corresponding ΔS values are 274(10), 282(10), 282(10), and 208(10) $\text{J K}^{-1} \text{mol}^{-1}$, respectively). These thermodynamic parameters and $T_{1/2}$ values are similar to those recently reported by Oshio and co-workers,^[8c] and are significantly higher in solution than in the solid state for **3** ($T_{1/2} = 174(1) \text{ K}$, $\Delta H = 20(1) \text{ kJ mol}^{-1}$, and $\Delta S = 116(10) \text{ J K}^{-1} \text{mol}^{-1}$) probably due to the higher symmetry of the complexes in solution, which induces a more degenerate paramagnetic state.^[17] To further illustrate the easy tuning of the optical and magnetic properties in this system, compound **3** was dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solutions. Figure 4 shows that $T_{1/2}$ is linearly depen-

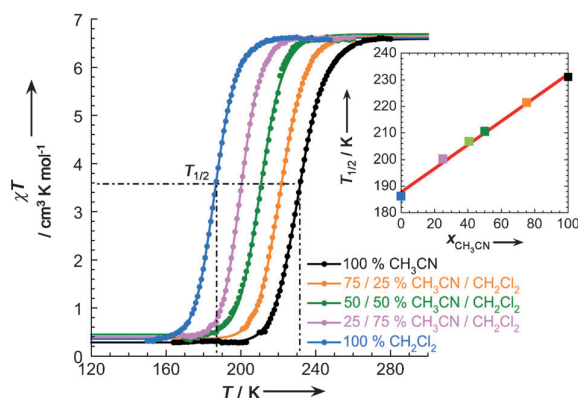


Figure 4. χT versus T data for **3** for $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solutions of **3** (0.4 K min^{-1} , 1 T; solid lines are fits to the ideal solution model^[16]). Inset: $T_{1/2}$ versus $x_{\text{CH}_3\text{CN}}$ plot. The solid line is the best linear regression fit of the data.

dent on the solvent molar fraction ($T_{1/2} = 0.45x_{\text{CH}_3\text{CN}} + 187$), allowing remarkable fine tuning of the electron-transfer process between 186(1) and 231(1) K obtained for the pure solvents.

In summary, a new $\{\text{Fe}_2\text{Co}_2\}$ complex, $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]_2[\text{Co}(\text{bpy}^{\text{Me}})_2]_2[\text{OTf}]_2 \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$, was synthesized, and its solid state optical and magnetic properties were described in the frame of an intramolecular metal-to-metal electron transfer. Due to methyl functionalization of the ligand, which results in good solubility of this complex, the thermally induced switchable behavior, as was observed in the solid state, has been transferred to dilute solutions. Remarkably, a fine tuning of the electron transfer and associated magnetic and optical properties in solution is demonstrated over a broad range of temperatures by simply adjusting the solvent composition and polarity.

Experimental Section

Synthesis of 3: Treatment of $[\text{NEt}_4][(\text{Tp}^*)\text{Fe}(\text{CN})_3] \cdot \text{H}_2\text{O}$ (165 mg, 0.3 mmol) with $\text{Co}(\text{OTf})_2$ (107 mg, 0.3 mmol) in wet DMF (5 mL) under argon afforded a red solution that was allowed to stir for 2 h. Addition of bpy^{Me} (114 mg, 0.6 mmol) and stirring for 20 min followed by filtration gave a red filtrate that was layered with Et_2O . Yield: 0.25 g (75.7%); IR (KBr pellet): $\tilde{\nu} = 2545$ (m; BH), 2151 (s; CN), 2117 (w; CN) cm^{-1} ; elemental analysis calcd for $\text{C}_{92}\text{H}_{108}\text{B}_2\text{Co}_2\text{Fe}_2\text{N}_{28}\text{O}_9\text{S}_2$: C 50.70, H 5.00, N 18.00; found: C 50.36, H 4.94, N 18.13.

Solutions of **3** were prepared from dried crystals dissolved in organic solvents at concentrations between 4 and $8 \times 10^{-5} \text{ mol L}^{-1}$, and between 1 and $3 \times 10^{-3} \text{ mol L}^{-1}$ for UV/Vis and magnetic measurements, respectively. The chosen concentrations for the magnetic measurements were determined after multiple tests down to 77 K to avoid precipitation of powder and/or crystals during cooling down.

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