Bistable Materials

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Reversible Thermally and Photoinduced Electron Transfer in a Cyano-Bridged {Fe_2Co_2} Square Complex**

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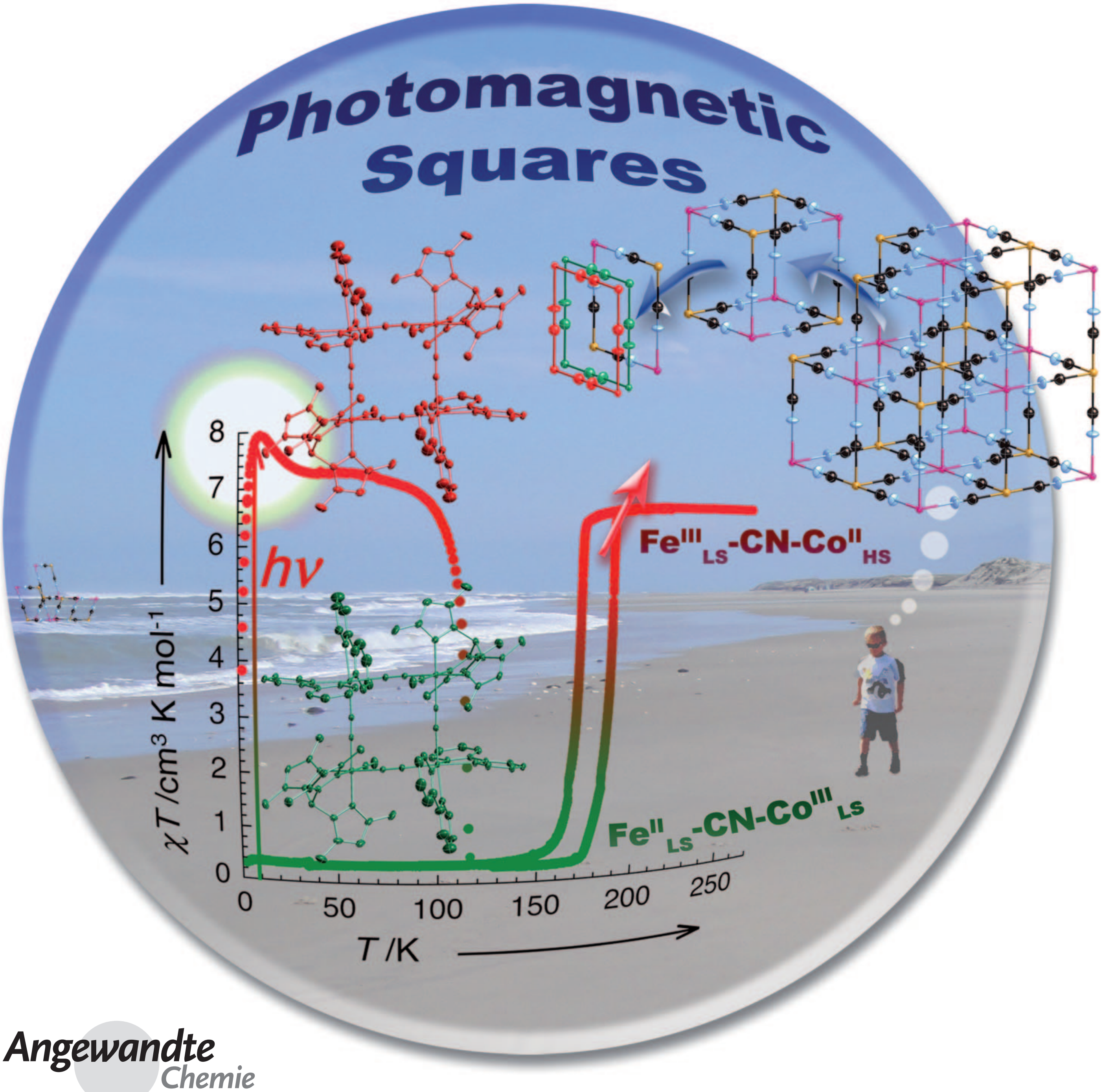

The rational design of molecule-based materials that exhibit tunable magnetic and optical properties that vary as a function of external stimuli is currently a topic of worldwide research activity.[1,2] Cyanometalates, in particular Co/Fe Prussian blue compounds, are among the most celebrated class of compounds that exhibits these bistable properties, with the first example reported by Hashimoto in 1996.[3] These 3D Co/Fe solids are composed of $\{Fe(\mu\text{-}CN)Co\}$ linkages and possess nonstoichiometric defect lattices. Diamagnetic $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$ pairs are reversibly converted into paramagnetic $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ units by thermally and light-induced electron transfer (LS = low-spin, HS = high-spin),[3–14] and concomitant changes in their magnetic and optical properties are observed.[3]

We reasoned that model complexes of photoactive Prussian blue compounds may be prepared using a building block approach, where molecular precursors are allowed to self-assemble towards a common structural archetype.[15] Judicious choice of the ancillary ligands on the transition-metal ions allow the simultaneous tuning of the solubility, and electronic and steric properties of the precursors. As part of our efforts to design $\{FeCo\}_n$ complexes, we recently reported the first molecular system that mimics the optical and magnetic bistablity seen in Co/Fe Prussian blue compounds.[15] Within the octanuclear $\{Fe_4Co_4\}$ complex, thermally and optically induced intramolecular electron transfer reversibly interconverts $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$ and $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ units at approximately 250 K, and long photostationary lifetimes (10 years at 120 K) are found; surprisingly no other $\{Fe_nCo_m\}$ complexes[16–20] are reported to exhibit similar bistability.

In order to understand the role that crystal packing and nuclearity play in modulating the properties of $\{FeCo\}_n$ complexes, we prepared tetranuclear $\{Fe_2Co_2\}$ units using sterically demanding pyrazolylborates such as tris(3,5-dimethyl)pyrazolyl borate (Tp*). Herein, we report a new tetranuclear cyanometalate complex, $[\{(Tp^*)Fe^{III}(CN)_3\}_2\{Co^{II}(bpy)_2\}_2][OTf]_2\cdot 4\,DMF\cdot 2\,H_2O$ (**1**; bpy = 2,2′-bipyridine, OTf = trifluoromethanesulfonate), which exhibits reversible thermally and photoinduced electron transfer.

The $\{Fe_2Co_2\}$ complex can be prepared by two general routes. The first route is treatment of $[NEt_4][(Tp^*)Fe(CN)_3]$ with $Co^{II}(OTf)_2$ in DMF to initially afford the DMF solvate $[\{(Tp^*)Fe^{III}(CN)_3\}_2\{Co^{II}(DMF)_4\}_2][OTf]_2\cdot 2\,DMF$;[21a,b] **1** was obtained by subsequent addition of bpy. The second route is the simultaneous reaction of $[NEt_4][(Tp^*)Fe^{III}(CN)_3]$,[21b] $Co^{II}(OTf)_2$, and bpy in a 1:1:2 ratio in DMF; this reaction afforded **1** as red needles from DMF/diethyl ether mixtures.

Single-crystal X-ray studies at 230 K reveal that **1** crystallizes in the triclinic $P\bar{1}$ space group.[22,23] Adjacent Fe and Co ions reside in alternate corners and are linked by cyanide ligands to form $\{Fe(\mu\text{-}CN)Co\}$ pairs; each Fe center bears one terminal cyanide ligand that adopts an *anti* orientation relative to the $\{Fe_2(\mu\text{-}CN)_4Co_2\}$ plane (Figure 1).[22] The average Co–N bond distance of approximately 2.11(1) Å indicates that Co^{II}_{HS} ions are present, thus dictating by charge balance that the Fe sites are trivalent.[15,22] The $\{Fe_2(\mu\text{-}CN)_4Co_2\}$ core is nearly planar and the Fe1-C-N angles range between 175.9(5) and 178.8(5)°. Nevertheless, the C1-Fe1-C2A angles (86.0(2)°) and Fe···Fe (7.583(2) Å) and Co···Co (6.954(2) Å) contacts indicate that **1** adopts a

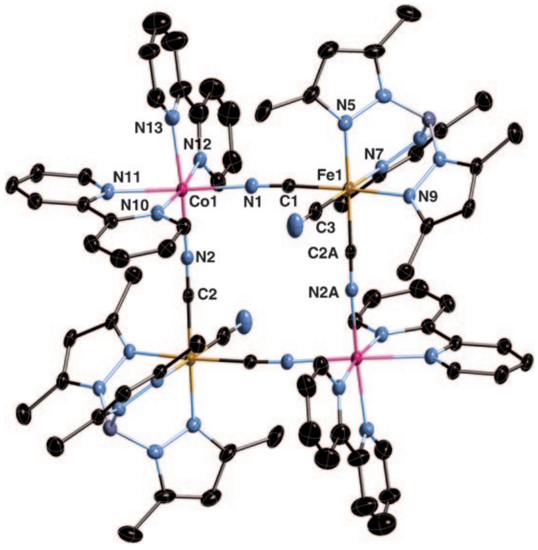

Figure 1. ORTEP-type view of cationic portion of **1** at 230 K with thermal ellipsoids at 30% probability. Lattice solvent molecules, anions, and hydrogen atoms are omitted for clarity. C black, Co pink, Fe yellow, N blue, B gray.

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distorted square structure. Hydrogen-bonding interactions are present between the lattice water and DMF molecules and the OTf$^-$ ions. Terminal cyanide ligands (O1W···N3, 2.930(1) Å) form chains along the *c* axis, and close bpy π–π contacts (ca. 3.35 Å) are found along the *b* axis.[22]

The solid-state IR spectrum of **1** at 298 K contains intense $\tilde{\nu}_{BH}$ (2542 cm^{-1}) and $\tilde{\nu}_{CN}$ (2154 and 2130 cm^{-1}) stretching absorptions. The highest energy $\tilde{\nu}_{CN}$ stretches are ascribed to $\{Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}\}$ units while those at approximately 2120 cm^{-1} correspond to the terminal cyanide ligands.[15,21a] Upon cooling from 298 to 130 K, the $\tilde{\nu}_{BH}$ stretch shifts to 2520 cm^{-1}, and new $\tilde{\nu}_{CN}$ stretches (2102, 2081, 2069, and 2044 cm^{-1}), which are characteristic of $\{Fe^{II}_{LS}(\mu\text{-CN})Co^{III}_{LS}\}$ pairs, appear (Figure 2, left).[3–16] The original (298 K) spectrum is restored upon reheating. Consistent with the IR data, UV/Vis spectra indicate that the optical properties also change with temperature (Figure 2, right). At 213 K, a broad and intense absorption, which is attributed to a spin- and Laporte-allowed ligand-to-metal charge transfer, is found at around 525 nm. Below approximately 180 K, a new low-energy absorption appears at around 845 nm while the higher-energy absorption concomitantly disappears.[15,22]

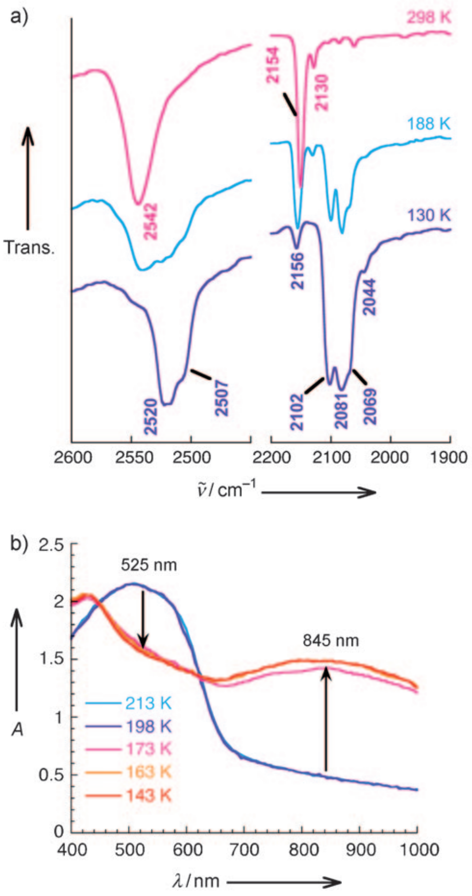

Figure 2. a) Infrared spectra of **1** (Trans. = transmittance) at 298, 188, and 130 K (cooling rate of 1 K min^{-1}). Spectra are vertically offset for clarity. (right) Solid-state UV/Vis spectra of **1** (*A* = absorbance) with cooling between 213 and 143 K (cooling rate of 5 K min^{-1}).

Solid-state reflectivity data between 260 and 10 K also confirm the optical changes seen in the UV/Vis spectra (Figure 3, top). Upon cooling **1**, an abrupt decrease in the absolute reflectivity at 800 nm (R_{800}) is seen, and changes from 0.8 at 240 K to 0.11 at 160 K (Figure 3, bottom). As the temperature is further reduced, the R_{800} value increases to 0.16 at 10 K. Upon heating, R_{800} recovers a value of 0.8 at 260 K but two thermal hystereses are revealed below 130 K and between 160 and 200 K, thus signaling that photo- and thermally induced behaviors, respectively, are operative. The photoexcitation properties of **1** were studied by cooling samples to 10 K in the dark, followed by white-light irradiation (50 μW cm^{-2}). Surprisingly, after 4 hours, the R_{800} value is nearly saturated and the resulting spectrum is nearly identical to that recorded at 220 K.[22] Upon heating, the photogenerated state rapidly decays around 130 K (Figure 3, bottom, green) and is reminiscent of the photoactive Co/Fe cyanometalates.[12–15,24,25] Therefore, this behavior is certainly induced by electron transfer that converts $\{Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}\}$ linkages, which exist at room temperature or below 130 K with irradiation, into $\{Fe^{II}_{LS}(\mu\text{-CN})Co^{III}_{LS}\}$ units below approximately 170 K.

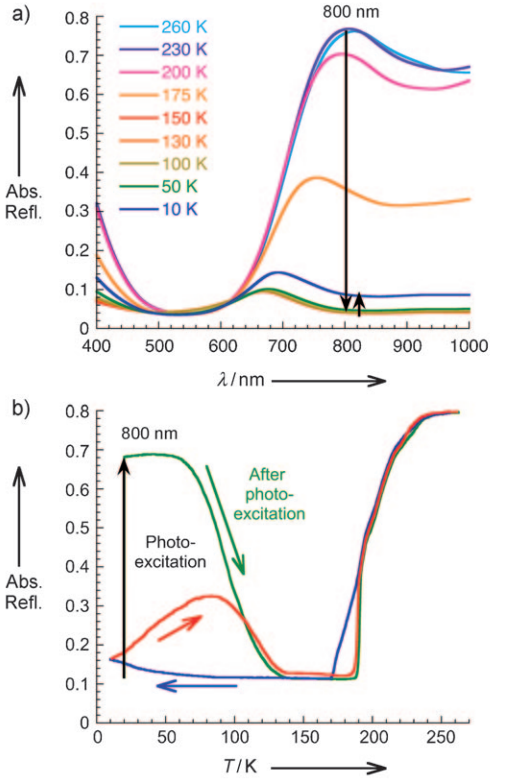

Figure 3. a) Surface reflectivity spectra of **1** upon cooling from 260 to 10 K (4 K min^{-1}). b) Absolute reflectivity (Abs. refl.) at 800 nm with cooling (blue), heating (red), and heating after 4 h of white light irradiation (50 μW cm^{-2}) at 10 K (green).

Further evidence that electron transfer occurs in **1** was found in a series of magnetic studies. Between 270 and 175 K, the χT product remains nearly constant at 6.8 cm^3 K mol^{-1} in good agreement with the presence of a 2:2 ratio of Fe^{III}_{LS} ($S = ^1/_2$, $g \approx 2.6$) and Co^{II}_{HS} ($S = 3/2$, $g \approx 2.4$) ions.[15] When the temperature was lowered (at a rate of 0.4 K min^{-1}), the χT

values abruptly decreased at around 168 K, and reached a minimum value of 0.4 $cm^3 K mol^{-1}$ at 120 K, thus confirming that intramolecular electron transfer generates diamagnetic $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$ units (Figure 4). As expected, this phenomenon is thermally reversible when the samples are heated above approximately 186 K. Consistent with magnetic and reflectivity data, enthalpic peaks are seen at 169 and 190 K in differential scanning calorimetry (DSC) thermograms (scan rate of 1 $K min^{-1}$), thus suggesting that a first-order transition occurs at 177 K.[22]

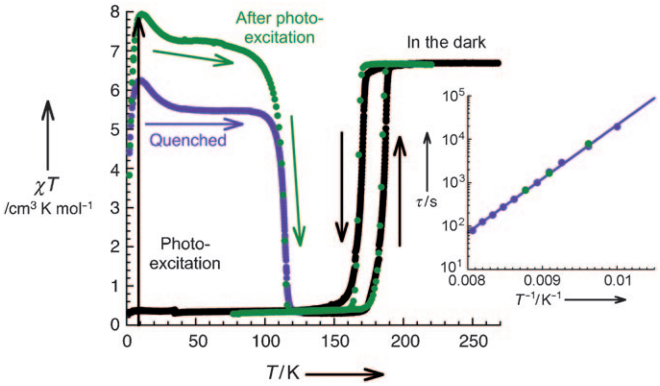

Figure 4. χT vs. T data for **1** (at 0.4 $K min^{-1}$, with χ defined as the molar magnetic susceptibility and equal to M/H; M = magnetization and H = external magnetic field): in the dark (black, 0.1 T), after thermal quench (purple, 0.1 T), and after irradiation (green, 1 T, 3 $mW cm^{-2}$). Inset: τ vs. $1/T$ plot for thermally quenched (purple) and irradiated (green) samples. The solid line is a fit of the data to an Arrhenius law.

Under white-light irradiation (3 $mW cm^{-2}$) at 10 K, the χT values quickly increased and reached a maximum of 7.9 $cm^3 K mol^{-1}$ after 4–5 hours, thus suggesting that $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ pairs are photogenerated.[22] Upon heating in the dark from 2 to 10 K, the χT product increased from 3.8 to 7.9 $cm^3 K mol^{-1}$, thus signaling that magnetic anisotropy and/or intermolecular antiferromagnetic interactions are present in the photoinduced phase (Figure 4). In the 10–70 K range, the χT product decreased slightly towards 7.2 $cm^3 K mol^{-1}$, thus suggesting that intramolecular Fe^{III}_{LS}–Co^{II}_{HS} ferromagnetic couplings are operative. Consistent with reflectivity studies, the photogenerated metastable state readily converts into the thermodynamic $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$ state near 120 K. It is worth noting that the metastable $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ phase can be also obtained by fast cooling from 298 K to 10 K ($>$ 50 $K min^{-1}$). Not surprisingly, the thermally quenched and photogenerated phases exhibit nearly identical magnetic data. However, the χT values are consistently lower in quenched phase, therefore suggesting that light irradiation is a more efficient means to obtain the metastable $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ phase. At fixed temperatures, the relaxation of the metastable phase can be followed by the time decay of χT. The relaxation time τ (deduced using stretched exponential laws) is independent of the sample preparation (by light irradiation or rapid cooling),[22] and follows an Arrhenius law (Figure 4, inset): $\tau = 9.1\times10^{-9}\exp(2854/T)$. Relaxation times of (190 ± 20) s and (145 ± 15) years are estimated at 120 and 70 K, respectively.

Finally, single-crystal X-ray studies of **1** obtained at 230 K or after rapid cooling to 90 K are virtually identical and reveal average Co–N distances (2.11 Å) and N-Co-N angles that are consistent with the presence of $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ units.[22] To avoid crystal fracture that arises from the first-order phase transition, we followed a thermal treatment protocol employed in the magnetic studies: the crystal was quenched from 300 to 90 K, warmed from 90 to 120 K (at 0.4 $K min^{-1}$), and kept at 120 K for 24 h to allow for complete and slow conversion to the thermodynamic phase. The data collected at 120 K show a marked decrease in the average Co–N distance (ca. 0.10 Å), which is consistent with the conversion of $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ into $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$. Moreover, the unit cell shrinks significantly and smaller bpy π–π contacts (ca. 0.03 Å) are found between adjacent $\{Fe_2Co_2\}$ complexes.[22]

In summary, combined structural, spectroscopic, magnetic, and optical measurements demonstrate unambiguously that **1** undergoes thermally and photoinduced magnetic and optical bistability as the result of intramolecular electron transfer that reversibly converts $\{Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}\}$ into $\{Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}\}$ pairs. This bistability is only observed in the solid state, thus highlighting the important role of weak intercomplex interactions (hydrogen bonds and close bpy π–π contacts) and their ability to control temperature and light-induced changes within Co/Fe Prussian blue compounds and $\{FeCo\}_n$ complexes.

Experimental Section

Synthesis of **1**: $[NEt_4][(Tp^*)Fe(CN)_3]\cdot H_2O$[21b] (165 mg, 0.3 mmol) was treated with $Co(OTf)_2$ (107 mg, 0.3 mmol) in wet DMF (5 mL) under argon to afford a red solution that was allowed to stir for 2 h. Bpy (94 mg, 0.6 mmol) was subsequently added and the mixture stirred for 10 min and filtered. The red filtrate was layered with Et_2O (25 mL) and allowed to stand 7 days. The resulting red crystals were filtered and dried under vacuum for 2 min at 300 K. Crystals of **1** suitable for X-ray diffraction were obtained after 30 days a 1:10 ratio of the crude reaction solution and Et_2O in an H tube. Yield: 0.211 g (64.1 %). IR (Nujol, 300 K): $\tilde{\nu} = 2542$ (m, $\tilde{\nu}_{BH}$), 2154 (s, $\tilde{\nu}_{CN}$), 2130 cm^{-1} (w, $\tilde{\nu}_{CN}$); UV/Vis (DMF): λ_{max}/nm (ε/$M^{-1} cm^{-1}$) 415 (1538); UV/Vis (CH_3CN): 465 (1479); elemental analysis calcd (%) for $C_{90}H_{108}B_2Co_2F_6Fe_2N_{30}O_{12}S_2$: C 48.45, H 4.88, N 18.83; found: C 48.20, H 4.56, N 18.75.

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[22] See the Supporting Information.

[23] Crystal data for (**1**): $C_{90}H_{108}B_2Co_2F_6Fe_2N_{30}O_{12}S_2$, $M_W = 2231.36$, triclinic, space group $P\bar{1}$, $a = 13.6803(9)$, $b = 13.8388(9)$, $c = 14.779(1)$ Å, $\alpha = 99.628(4)$, $\beta = 93.452(4)$, $\gamma = 108.240(4)°$, $V = 2600.9(3)$ Å^3, $T = 230(2)$ K, $Z = 1$, $\mu = 0.710$ mm^{-1}, $\rho_{calcd} = 1.425$ Mg m^{-3}, $R1 = 0.0682$, $wR2 = 0.1705$. CCDC 765354 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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