

Photochromism and Photomagnetism of a 3d–4f Hexacyanoferrate at Room Temperature

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S Supporting Information

ABSTRACT: Polycyanometallate compounds with both photochromism and photomagnetism have appealing applications in optical switches and memories, but such optical behaviors were essentially restricted to the cryogenic temperature. We realized, for the first time, the photochromism and photomagnetism of 3d–4f hexacyanoferrates at room temperature (RT) in $[\text{Eu}^{\text{III}}(18\text{C}6)(\text{H}_2\text{O})_3]\text{Fe}^{\text{III}}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ (18C6 = 18-crown-6). Photoinduced electron transfer (PET) from crown to Fe(III) yields long-lived charge-separated species at RT in air in the solid state and also weakens the magnetic susceptibility significantly. The PET mechanism and changing trend of photomagnetism differ significantly from those reported for known 3d–4f hexacyanoferrates. This work not only develops a new type of inorganic–organic hybrid photochromic material but opens a new avenue for RT photomagnetic polycyanometallate compounds.

Photochromic species exhibit not only color change but variation of diverse physicochemical properties in the reversible manner.¹ For the latter, one of the most appealing is photoswitchable magnetism, the so-called photomagnetism, which may find potential applications in optical information storage² and medical service.³ As candidates that may exhibit both photochromism and photomagnetism in the solid state, polycyanometallate compounds, especially Prussian Blue analogues (PBAs), were thought to offer the most promising perspectives.⁴ After the pioneering work of Sato et al.,⁵ photoinduced magnetization concentrated on PBAs has been widely studied.⁶ It is best to realize photomagnetism around RT for practical applications. Unfortunately, most PBAs exhibit photomagnetism below liquid nitrogen temperature and only very few samples around room temperature (RT).⁷

It has become a great challenge to improve the photomagnetic temperature of PBAs through changing the metal centers considering their limited selectivity. Instead, some research groups have aimed to inorganic–organic hybrid polycyanometallate compounds for their tailored properties and good crystallinity.⁸ In 2003, we reported the synthesis and crystal structure of the cyanide-bridged 3d–4f heterobimetallic compound $[\text{Nd}^{\text{III}}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}^{\text{III}}(\text{CN})_5] \cdot \text{H}_2\text{O}$ (**NdFeDMF**; DMF = *N,N*-dimethylformamide).⁹ Somewhat after, Einaga et al. found this compound showed a surprisingly large increase in magnetic susceptibility upon illumination with

UV light at temperature below 50 K.¹⁰ Subsequently, other similar 3d–4f heterobimetallic hexacyanoferrates (4f metals: La, Ce, Nd, Sm, Gd, Tb, or Yb) or hexacyanocobaltates (4f metal: Nd) were also found or predicted to exhibit photomagnetic properties, no matter if the two metal centers are bridged by the cyano group or not.¹¹ It was thought that these findings might open up a new domain for developing molecule-based magnetic materials.¹⁰

However, photoinduced magnetization of the established 3d–4f hexacyanoferrates is still not achieved at RT until now. In addition, the photoresponsive mechanisms for these compounds remain ambiguous. Einaga et al. regarded that a photoinduced ligand-to-metal charge transfer (LMCT) process from the cyano group to the Fe(III) center could explain the photomagnetic behavior of **NdFeDMF** according to the UV–vis, IR, and X-ray powder diffraction (PXRD) data. Even so, it is hard to understand why the valence of the Fe^{III} center was the same after irradiation and the fact that $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ is silent itself upon illumination.^{11g} Iversen et al. raised another completely different mechanism, on the basis of photo-crystallography and time-dependent DFT calculation.^{11e} They thought a photoinduced LMCT process from the cyano group to the Nd^{III} center was more reasonable. Still, this mechanism cannot tell us why the Fe^{III} center is not reduced in advanced, considering its more positive standard reduced potential than that of the Nd^{III} center ($\varphi^\theta(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$, $\varphi^\theta(\text{Nd}^{3+}/\text{Nd}^{2+}) = -2.7 \text{ V}$ vs SHE). Also, the radical signal for the cyano group should be able to be observed through electron spin resonance (ESR) determination, but this data is lacking. Consequently, much effort is needed to illuminate the detailed mechanism.

In this work, we studied the photoresponsive properties of a known 3d–4f hexacyanoferrate with a crown ligand, $[\text{Eu}^{\text{III}}(18\text{C}6)(\text{H}_2\text{O})_3]\text{Fe}^{\text{III}}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ (**1**; 18C6 = 18-crown-6).¹² The crown ligand was selected because we and other groups have found that ligands containing oxygen atoms can be used as effective electron donors to prepare compounds with electron-transfer (redox) photochromism at RT.¹³ The Eu element was chosen considering its relative easier one-electron reduction ($\varphi^\theta(\text{Eu}^{3+}/\text{Eu}^{2+}) = -0.35 \text{ V}$ vs SHE) compared with that of Nd^{III}. It is imaginable the Eu^{III} ion should be reduced after irradiation, if the mechanism raised by Iversen et al. is applicable in our case. Interestingly, photochromic phenomenon and photomagnetic properties at RT were observed for **1**.

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To the best of our knowledge, such optical behaviors have not been reported for 3d–4f polycyanometallates. Moreover, the PET mechanism and changing trend of photomagnetism for **1** differ significantly from those reported in the known 3d–4f hexacyanoferrates.^{10,11}

Compound **1** was synthesized by the reported procedure.¹² The phase purity of their crystalline samples was checked by PXRD and elemental analyses (see the Experimental Section and Figure S1 in the Supporting Information (SI)). The molecular structure of **1** contains one isolated $[\text{Eu}^{\text{III}}(18\text{C}6)(\text{H}_2\text{O})_3]^{3+}$ cation, one $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ anion, and two lattice water molecules (Figure 1).

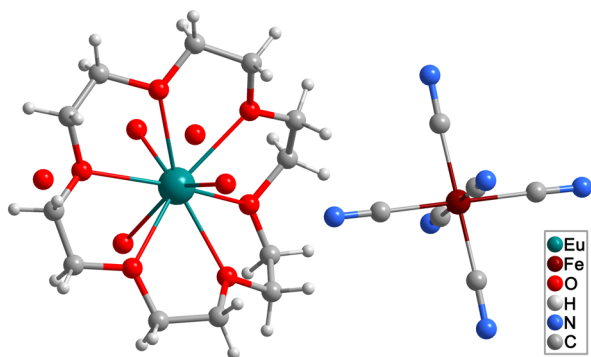


Figure 1. Molecular structure of **1**. Hydrogen atoms for water molecules are omitted for clarity.

Upon irradiation by a 300 W Xe lamp (ca. 908 mW/cm²) at RT, the fresh yellowish green sample of **1** (denoted as **1G** hereafter) underwent clear color change from yellowish green to orange in air or under N₂ atm (Figure 2). The

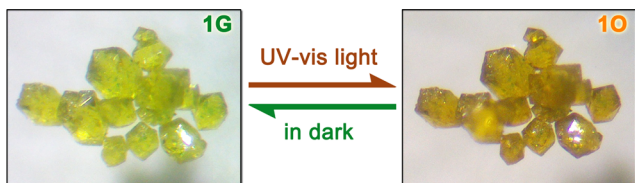


Figure 2. Photochromism of **1** at RT.

photoresponsive wavelength is below 420 nm. Such a wavelength-dependent character demonstrates that the coloration proceeds through a photon mode instead of a photothermal fashion. The orange sample, denoted as **1O** hereafter, could slowly reverse transformation to **1G** in air or under N₂ atm after 5–6 days in dark condition. The transformation could also be completed in 2 h by annealing at 75 °C. PXRD data verified that there was no obvious structural difference between **1G** and **1O** (Figure S1).

After coloration, two new absorption bands emerged at about 470 and 518 nm, which belong to $^1A_1 \rightarrow ^1T_2$ ¹⁴ and $^1A_1 \rightarrow ^1T_{1g}$ ¹⁵ transitions for Fe^{II}, respectively (Figure 3). After decoloration, they disappeared again. Such a change in the UV–vis spectrum was not observed in NdFeDMF.¹⁰ As depicted in Figure 4, several absorption bands in the IR spectra also changed significantly during the photochromic process. Upon irradiation, the $\nu(\text{CN})$ stretching band at 2123 cm⁻¹ for the $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ ion¹⁶ decreased gradually in intensity and became tiny when the time reached 80 min. On the contrary, the $\nu(\text{CN})$ stretching band at 2055 cm⁻¹ and the F1u $\delta(\text{Fe}^{\text{II}}-$

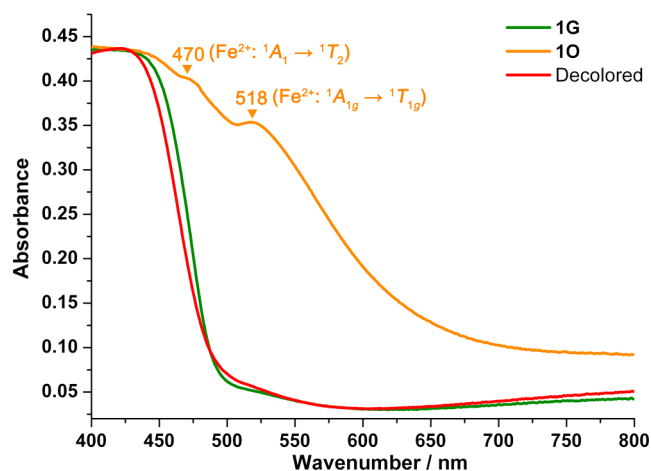


Figure 3. UV–vis spectra of **1G**, **1O**, and the decolored sample.

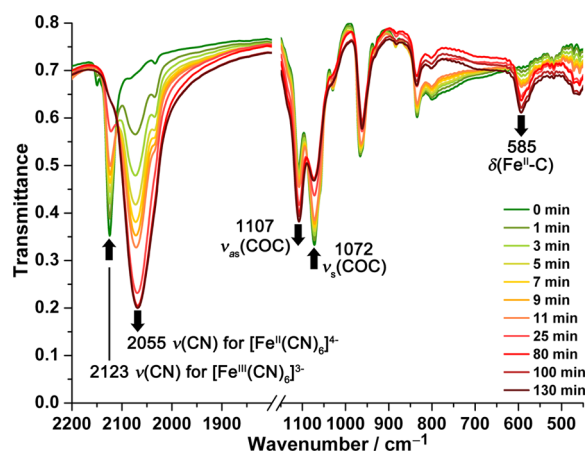


Figure 4. Evolution of the IR spectrum of **1** in the KCl matrix upon irradiation.

C) band at 585 cm⁻¹ for the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ion increased clearly in intensity.¹⁶ Both UV–vis and IR data demonstrate the photoreduction of Fe^{III} to Fe^{II}.

Then, how about the Eu^{III} ion during the photochromism of **1**? A photoluminescence study showed that **1G** exhibits a structured broad emission band in the range of 400–550 nm and three sharp peaks at 592 ($^5D_0 \rightarrow ^7F_1$), 615 ($^5D_0 \rightarrow ^7F_2$), and 698 ($^5D_0 \rightarrow ^7F_4$) nm for Eu^{III} (Figure S2). After irradiation for 2 h, the broad band dropped dramatically, but no new peaks for Eu^{II} emerged. Note that the emission band of Eu^{II} usually falls in the 400–550 nm range.¹⁷ This result excludes photoreduction of Eu^{III}, which does not correspond to the mechanism raised by Iversen et al.^{11d–g}

As mentioned before, $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ is silent to light in the solid state.^{11g} In addition, we found that $[\text{Eu}^{\text{III}}(18\text{C}6)(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ¹⁸ did not show any color change and generates radical signals in its ESR spectrum upon irradiation by the 300 W Xe lamp (Figure S3). Therefore, the PET of **1** should occur between the $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ anion and the $[\text{Eu}^{\text{III}}(18\text{C}6)(\text{H}_2\text{O})_3]^{3+}$ cation. A clear change happened in ESR spectra of **1** after illumination (Figure 5): the positions of bands for Fe^{III} were somewhat changed, but a new single-line radical signal at $g = 2.03$ emerged prominently.¹⁹ At the same time, the IR peaks of COC in 18C6 for **1** varied markedly after irradiation. It has been documented that the symmetric and asymmetric stretching bands of COC will be enhanced and

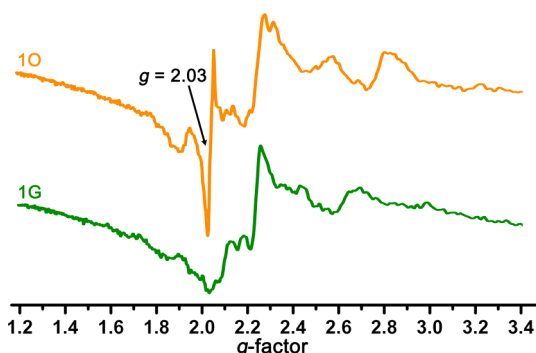


Figure 5. EPR spectra of 1G and 1O recorded in the X band at RT.

weakened, respectively, when the free 18C6 molecule coordinates to a metal center.^{16,20} For **1**, upon irradiation, the symmetric stretching band at 1072 cm⁻¹ for COC was weakened, while the asymmetric one at 1107 cm⁻¹ enhanced (Figure 4). Clearly, the illumination makes the Eu^{III}-O(18C6) coordination bond turn weak. This means that the electron density on O atoms of 18C6 decreases, that is, the O atoms lose electrons. Consequently, we infer that the photochromism of **1** at RT is caused by PET from crown to Fe^{III}, which results in the formation of crown radicals and Fe^{II} centers.

The magnetic studies have been performed on powdered crystalline sample of **1** before and after irradiation at RT by a diode pumped solid state (DPSS) laser (355 nm; 90 kHz; 23 ns pulse width; ca. 60 mW/cm²; spot size, ca. 5 cm²). As shown in Figure 6, the value of $\chi_M T$ at 300 K before irradiation is 2.22

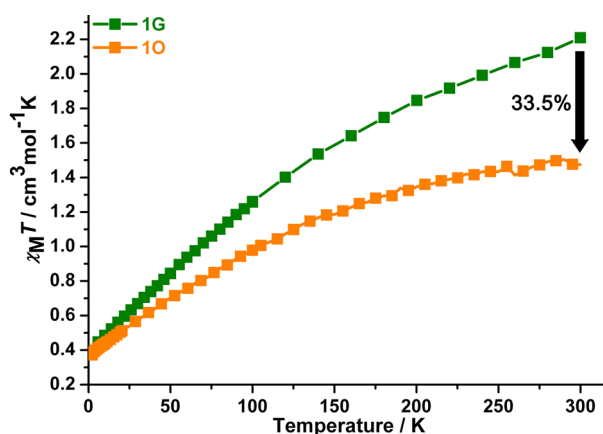


Figure 6. $\chi_M T$ versus temperature (T) for 1G and 1O at $H = 5000$ Oe.

cm³·mol⁻¹·K, in line with those reported for known Eu-Fe complexes with one Fe^{III} ion and one Eu^{III} ion.²¹ The monotonous increase of $\chi_M T$ value on heating shows a typical characteristic occurrence of thermally populated excited states of Eu(III).²² After illumination by the DPSS laser at RT for 10 min, the $\chi_M T$ value at 300 K fell by 33.5%. This magnitude is much larger than that of NdFeDMF (<3%) reported by Iversen et al.^{11g} The photoinduced change trend of $\chi_M T$ of **1** is just the opposite of that of NdFeDMF.^{1b,11d,eg} It has been proved that Eu-Fe complexes show very weak or negligible magnetic interactions.^{11c,21} Therefore, the falling of $\chi_M T$ at 300 K for **1** after coloration may be attributed to the stronger antiferromagnetic interaction between the crown radical and the Eu^{III} ion in **1O**, or/and the larger magnetic contribution of Fe^{III} in **1G** than that of the crown radical in **1O** because of the orbital

angular momentum of Fe^{III}. The more detailed magnetic behaviors need to be further studied in the future.

In summary, we succeeded in observing photochromism and photomagnetism in 3d-4f hexacyanoferrates at RT for the first time. The photoresponsive mechanism has been well elucidated on the basis of UV-vis, IR, ESR, and photoluminescence data. This work not only develops a new type of inorganic-organic hybrid photochromic material but opens a new avenue for RT photomagnetic polycyanometallate compounds.

■ ASSOCIATED CONTENT

📄 Supporting Information

This material is available free of charge at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05320.

Experimental details and Figures S1-S3 (PDF)

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Notes

The authors declare no competing financial interest.

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