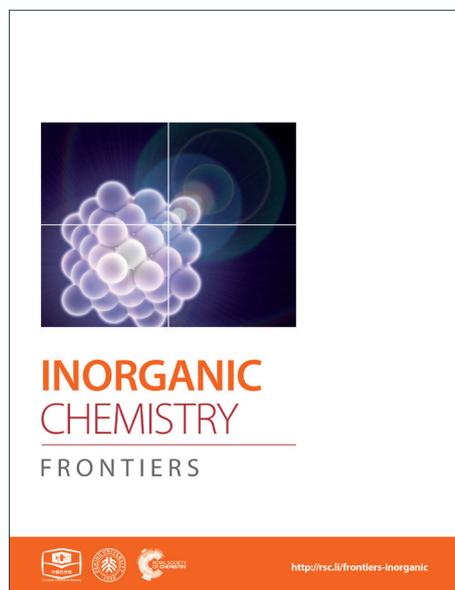
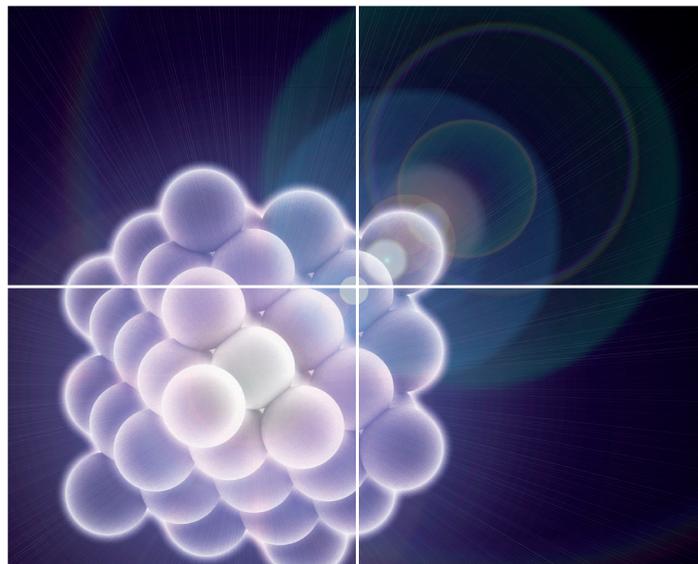


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COMMUNICATION

Investigation of light-induced electron-transfer-coupled spin transition in a cyanide-bridged [Co₂Fe₂] complex by X-ray diffraction and absorption measurements

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The light-induced electron-transfer-coupled spin transition (ETCST) behaviour in a cyanide-bridged [Co₂Fe₂] tetranuclear complex has been investigated in detail, using magnetic susceptibility measurements, single-crystal X-ray structural analyses and X-ray absorption spectroscopy.

Prussian blue (PB) and its analogues (PBAs) have recently attracted great interest resulting from their varied characteristics as functional materials.¹ In 1996, a cyanide-bridged CoFe PBA, K_{0.2}Co_{1.4}[Fe(CN)₆]·6.9H₂O, was reported to show light-induced magnetization from a paramagnetic [*ls*-Co^{III}-*ls*-Fe^{II}] phase to a ferrimagnetic [*hs*-Co^{II}-*ls*-Fe^{III}] phase (*ls* = low spin and *hs* = high spin), where light-induced charge transfer from Fe^{II} to Co^{III} ions caused *ls* to *hs* transitions to occur on the Co ions at low temperature.² This behavior and its thermally induced equivalent are described as electron-transfer-coupled spin transition (ETCST).³ Reverse ETCST was also achieved in the CoFe PBA by excitation of the Co^{II}→Fe^{III} charge transfer band. Since the discovery of the light-induced magnetization in CoFe PBAs, numerous heterometallic PBAs have been reported to show light-induced phase transitions,⁴ and a growing number of cyanide-bridged multinuclear complexes have been intensively investigated to explore the ETCST phenomenon at a molecular level. Light-induced ETCST in a discrete molecule was first reported in an octanuclear [Co₄Fe₄] complex,^{5a} and in subsequent reports, cyanide-bridged CoFe complexes with a range of nuclearities have been shown to exhibit similar behaviour.^{5b-5l} To the best of our knowledge, however, there have been only two reports of structurally characterized light-induced metastable states in the ETCST-active molecules.^{5e,5i} Additionally, the electronic structures of the light-induced states in the previous ETCST complexes were only investigated by magnetic susceptibility measurements, infrared spectra and diffuse reflectance spectroscopy on a bulk sample. X-ray absorption spectroscopy (XAS) is a useful technique to probe the electronic state of transition metal ions. We previously reported a cyanide-bridged tetranuclear complex, [Co₂Fe₂(CN)₆(tp*)₂(bpy*)₄](PF₆)₂·2MeOH (**1**) (tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate and bpy* = 4,4'-di-*tert*-butyl-2,2'-bipyridine), which exhibited two-step thermal ETCST and

light-induced ETCST behavior.⁶ Recently, it was also found that **1** exhibits X-ray induced ETCST, a process that was followed by XAS measurements. We report here a detailed investigation of the light-induced ETCST in **1** by means of single crystal X-ray diffraction (XRD) and XAS measurements upon light irradiation.

Light irradiation experiments using green and red lasers ($\lambda = 532$ and 808 nm) were performed on **1** in the SQUID magnetometer at 5 K, where a ground sample of **1** fixed on a transparent sheet was used to maximize the penetration length of the light. Note that **1** showed Fe^{II}→Co^{III} and Co^{II}→Fe^{III} intervalence charge transfer (IVCT) bands at 770 and 560 nm in its LS and HS states, respectively (Fig. S1).^{6a} The ground sample of **1** showed two-step thermal ETCST behavior in the temperature range of 330–5 K as it was cooled prior to light irradiation (Fig. 1). The ETCST behavior is sensitive to the sample preparation and the transition temperatures were slightly lower than those previously reported for a crystalline sample. Upon red light irradiation (808 nm) to the LS state, the $\chi_m T$ values abruptly increased, reaching saturation after 1.5 hours. After deactivating the light source, the $\chi_m T$ values increased gradually with increasing temperature, and a maximum value of 6.00 emu mol⁻¹ K was observed at 34 K, followed by a sudden decrease to almost zero at 85 K. XAS spectra measured at 15 K before and after red light irradiation confirmed that conversion to the metastable HS* state, as a result of light-induced ETCST, was completed (*vide infra*). Upon green light (532 nm) irradiation to the metastable HS* state, generated from the red light irradiation to the LS state, at 5 K, the $\chi_m T$ values decreased rapidly from 3.97 to 1.22 emu mol⁻¹ K, indicating the reversal of the visible-light-induced ETCST. Increasing the temperature caused an increase in $\chi_m T$ values to a maximum of 2.18 emu mol⁻¹ K at 34 K, at which temperature the reverse conversion ratio (HS*→LS) was estimated to be 64 % (= (6.00 - 2.18)/6.00). The incomplete reverse ETCST was understood as follows: green light (532 nm) irradiation led to a mixture of both (HS*→LS) and (LS→HS*) conversions. Irradiating the sample in the LS state with the green light resulted in spin conversion to the HS* state with a conversion ratio of 36%, meaning that green light irradiation to both the red light-excited HS* and ground LS states allowed the same photostationary state to be accessed. The

incomplete phase transition by green light was ascribed to the partial overlap of the broad $\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ IVCT ($\epsilon_{\text{max}} = 770 \text{ nm}$) band and the $\text{Co}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$ IVCT band ($\epsilon_{\text{max}} = 560 \text{ nm}$) (Fig. S1).^{6a} That is, the simultaneous green light excitation of the absorption bands corresponding to the two opposing IVCT processes led to the generation of a photostationary state, while red light (808 nm) irradiation excited only the $\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ IVCT band, and led to complete conversion to the HS* state. It should be noted that the forward (red) and reverse (green) light-induced ETCST could be repeatedly observed when the sample was exposed to alternating red and green light sources (Fig. 1, inset).

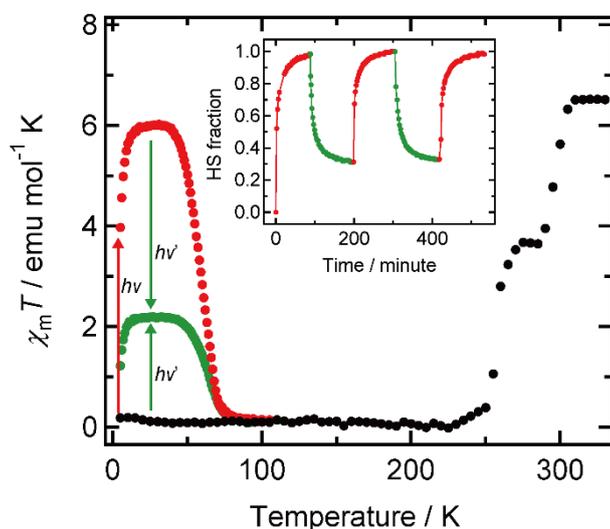


Fig. 1 $\chi_m T$ vs. T plot of **1** before (black) and after light irradiation. Red and green circles correspond to the susceptibility profiles after irradiation at $h\nu = 808 \text{ nm}$ or $h\nu = 532 \text{ nm}$ at 5 K, respectively. The inset displays a cycle process upon alternate irradiation at 808 nm (red) and 532 nm (green) at 5 K.

Single crystal X-ray crystallographic analyses of **1** before and after light irradiation at 808 nm were carried out at 24 K using a conventional X-ray diffractometer. Crystallographic data, and selected bond lengths and angles are listed in Tables S1 and S2, respectively. The molecular structure after visible-light irradiation is shown in Fig. 2(a). **1** crystallized in the monoclinic space group $C2/c$, and the complex cation has a square-shaped macrocyclic core, in which Co and Fe centers are alternately bridged by cyanide ions. The Fe ions are coordinated by tridentate tp^* ligands with facial configuration, and the remaining coordination sites are occupied by three cyanide carbon atoms. The two bidentate bpy^* ligands coordinate to the Co ion, while its remaining cis coordination sites are occupied by bridging cyanide ions with [Co-NC-Fe] bridging modes. Prior to visible-light irradiation, as previously reported,⁷ the average coordination bond lengths around the Co and Fe ions were 1.920(5) Å and 1.960(5) Å, respectively, characteristic of *ls* Co^{III} and *ls* Fe^{II} ions.^{5,6} After the sample was irradiated with 808 nm light for 1.5 hours, the crystallographic parameters changed and the cell volume increased by ca. 7%, suggesting the occurrence of a light-induced phase transition. The average coordination bond lengths after light irradiation changed to 2.12(1) and 1.97(1) Å for Co and Fe ions, respectively, and these values are in good agreement with those (Co: 2.113(4) Å, Fe: 1.964(5) Å) in the thermally generated HS state of **1** at 330 K.^{6b} The distortion of the coordination structure can be quantified by Σ parameters reported by P. Guionneau et al.⁸ The Σ values for the Co ion before and after visible-light irradiation were estimated as 45.3° and 68.1°, which are typical values for *ls* Co^{III} and

the *hs* Co^{II} ions, respectively (Fig. 2(b)).^{5,6} The observed structural changes revealed that the light-induced state is the metastable HS* state generated by light-induced ETCST of the LS state.

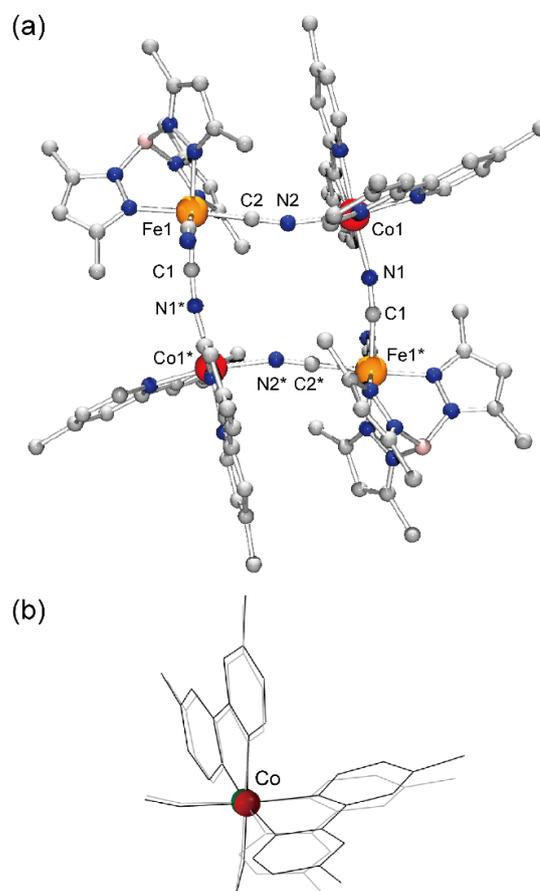


Fig. 2 (a) Molecular structure of **1** in the light-induced metastable HS* state. The *tert*-butyl groups on bpy^* and hydrogen atoms were omitted for clarity. (b) The core structures around the Co ion before (gray) and after (black) visible-light irradiation at 808 nm. The structural change is due to the electronic state changes in Co ion through the light-induced ETCST in **1**.

Co and Fe K-edge XAS spectra were recorded on a single crystal of **1** to investigate the electronic state changes of the metal ions upon light-induced ETCST. **1** showed absorption edges at 7.729 (*ls* Co^{III}) and 7.126 keV (*ls* Fe^{II}) at 15 K,⁷ where the absorption edge corresponds to the inflection point at the onset of the K-edge absorption peak.⁹ The XAS spectra of **1** at 15 K agrees well with previously reported spectra of **1** in the LS state.^{7,10} When a single crystal of **1** in the LS state was irradiated by 808 nm light for 30 minutes at 15 K, the Co absorption edge shifted to lower energy (7.724 keV), while the Fe absorption edge showed a slight shift to higher energy (7.128 keV), suggesting the generation of metastable HS* state (Fig. 3 and Fig. S2). The resultant Co and Fe K-edge spectra for the HS* state are in accord with those for thermally generated HS state. The XRD and XAS measurements revealed that the molecular structure and electronic state of the light-induced HS* is almost the same as the thermally generated HS state. Note that the XAS spectra of the light-induced HS* state shifted back to the LS spectra upon heating to 100 K, confirming the occurrence of thermal relaxation (Fig. S3).

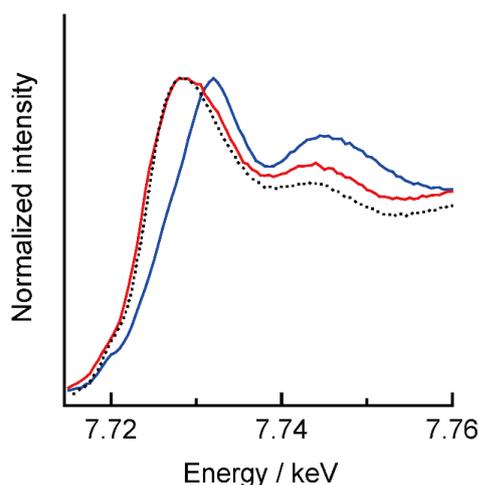


Fig. 3 Co K-edge XAS spectra of **1** before (blue) and after (red) 808 nm irradiation at 15 K. The black dashed line represents the thermally generated HS state.

In summary, we investigated the structural and electronic state changes upon visible-light irradiation of **1** by single-crystal XRD and XAS measurements. As a result, both molecular structure and electronic state of the light-induced HS* state were coincident with the thermally generated HS state. Furthermore, the reversible magnetic susceptibility changes were demonstrated by alternate irradiation with red and green lasers.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental and crystallographic details and XAS spectra. CCDC 992600 (after light irradiation)]. See DOI: 10.1039/c000000x/

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- It should be noted that the relative small energy shift of Fe K edges associated with the thermal and light-induced ETCST were attributed to the small structural changes between the *ls* Fe^{III} and the *ls* Fe^{II} ions.