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Optically Switchable Molecular Solids: Photoinduced Spin-Crossover, Photochromism, and Photoinduced Magnetization

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ABSTRACT

A possible route to finding new optically switchable molecular solids is to investigate the photoeffects of compounds that exhibit an abrupt phase transition or hysteresis loop. Such compounds must possess at least bistable states that are separated by a potential barrier in free energy. In fact, on the basis of this idea, we have recently succeeded in identifying three kinds of optically switchable molecular compounds. These include an $\mathrm{Fe^{III}}$ spin-crossover complex exhibiting light induced excited spin state trapping effects and a $\mathrm{Cu^{II}}$ photochromic complex and an FeCo Prussian blue exhibiting photoinduced magnetization. It should be noted that abrupt phase transitions or phase transitions with a hysteresis loop are observed when cooperativity due to an intermolecular interaction operates within the crystals. This suggests that the introduction of intermolecular interactions such as $\pi-\pi$ interactions, hydrogen bonding, or an ion−dipole interaction might serve to achieve optical switching effects in molecular compounds.

1. Introduction

The development of novel molecular compounds whose physical properties can be controlled by external perturbations have recently been attracting great interest.[1−3] In particular, the design of optically switchable molecular compounds is one of the main challenges in molecular materials science because of their possible applications for optical memory.[1,3] However, the number of optically switchable molecular solids reported so far is not great. This is because the strategy that is required in order to achieve optical switching effects in the solid state has not been clarified as yet. Hence, the preparation of new optically switchable molecular compounds is still a challenging issue. Along these lines, we searched for new molecular compounds and have recently succeeded in developing several optically switchable molecular solids.[4−24] Here, we describe three examples of such phototunable molecular compounds. They are (1) the first observation of light-induced excited spin-state trapping for an $\mathrm{Fe^{III}}$ spin-crossover complex,[4−6] (2) photoinduced structural isomerization observed in $\mathrm{Cu^{II}}$ thermochromic complexes,[7,8] and (3) photoinduced magnetization observed in an FeCo Prussian blue[9−18]

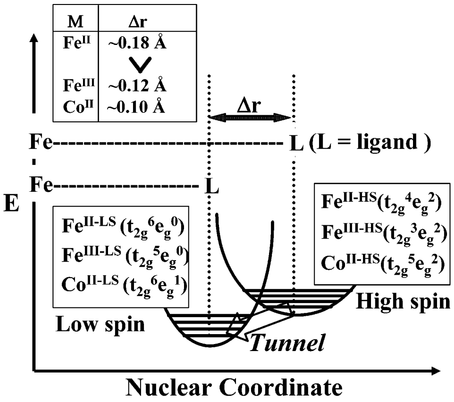

FIGURE 1. Schematic illustration of the difference (Δr) in the metal-to-ligand bond length between the high-spin and low-spin states. It has been believed that $\mathrm{Fe^{III}}$ and $\mathrm{Co^{II}}$ complexes can never show LIESST effects because the metastable high-spin states of the $\mathrm{Fe^{III}}$ and $\mathrm{Co^{II}}$ complexes are thought to be too easily relaxed back to the original low-spin state by tunneling effects due to the small structural change (Δr) compared with that of $\mathrm{Fe^{II}}$. It has been reported that Δr for $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$, and $\mathrm{Co^{II}}$ complexes are about 0.18, 0.12, and 0.10 Å, respectively.

2. First Observation of Light-Induced Excited Spin State Trapping for an $\mathrm{Fe^{III}}$ Complex: $\pi-\pi$ Interaction System[4−6]

Metal complexes with the electron configuration d^4 to d^7 can take two different spin states, i.e., the high-spin and low-spin states. In particular, when the ligand field is situated just within the critical region, the metal complex exhibits a thermally induced spin transition between the high-spin and low-spin states. Furthermore, it has been reported that the spin transition can be induced by illumination.[25] The photoinduced spin transition phenomena is called a light-induced excited spin state trapping (LIESST) effect. After this discovery, LIESST effects have been extensively studied.[26−30] However, until now, LIESST effects were only observed for $\mathrm{Fe^{II}}$ spin-crossover complexes, and there are no reports on the observation of the LIESST effect in $\mathrm{Fe^{III}}$ and $\mathrm{Co^{II}}$ molecular solids.[26] It has been thought that the different photoresponse derives from the difference in the metal-to-ligand bond length (Δr) between the high-spin and low-spin states. The Δr values for $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$, and $\mathrm{Co^{II}}$ spin-crossover complexes are shown in Figure 1. Because the e_g orbitals that are occupied in the high-spin state are antibonding in character, the chemical bond between the ligand and the metal of a high-spin species is relatively weak compared with that of a low-spin species. As a result, the ligand-to-metal bond length of the high-spin moieties is longer than that of the low-spin species. The characteristic property is that the difference, Δr, for $\mathrm{Fe^{III}}$ and $\mathrm{Co^{II}}$ is smaller than that for $\mathrm{Fe^{II}}$. It is thought that the shorter the relative horizontal

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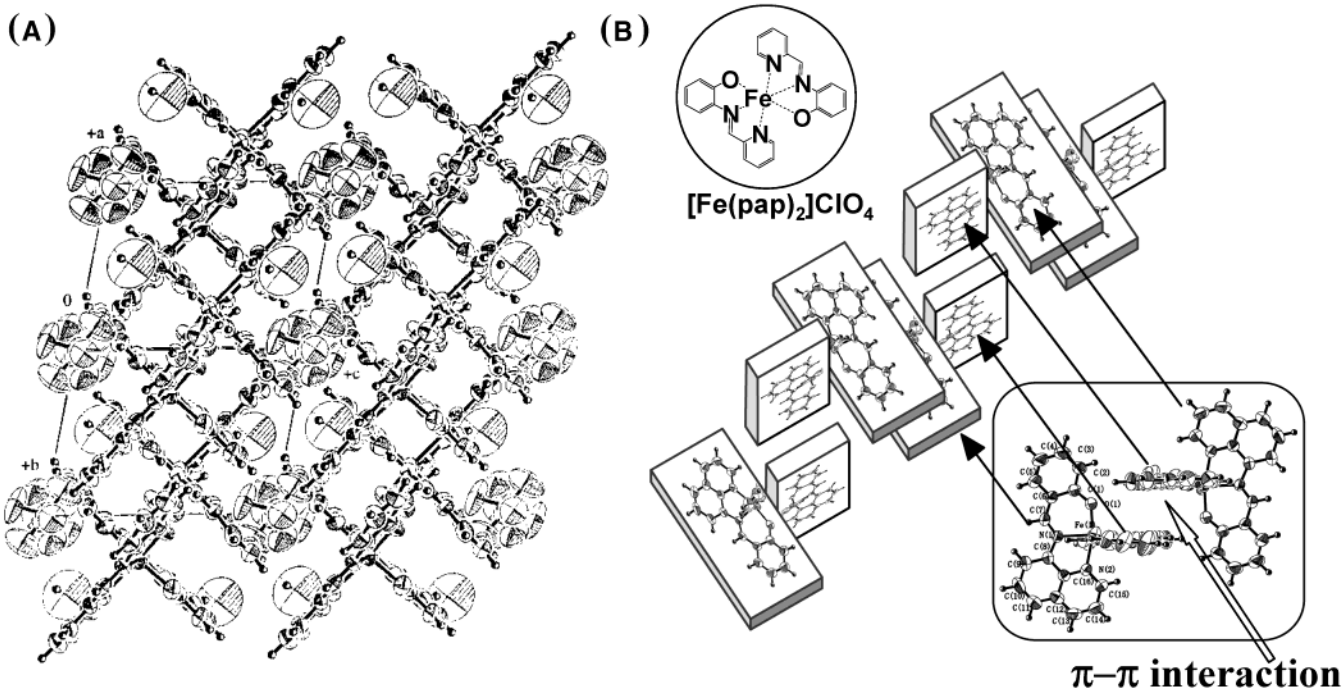

FIGURE 2. (A) Crystal structure for $[Fe(pap)_2]ClO_4\cdot H_2O$[4]. (B) Schematic illustration of the molecular arrangement of $[Fe(pap)_2]ClO_4\cdot H_2O$. The Fe complexes form $\pi-\pi$ stacking between molecules.

displacement of the low-spin and high-spin potential wells, the faster the tunneling becomes. Hence, it is believed that the metastable high-spin states of Fe^{III} and Co^{II} complexes can easily relax back to the original low-spin state by tunneling effects, even if the high-spin states could be induced by light. This means that the metastable state of Fe^{III} and Co^{II} complexes cannot be trapped even at low temperature.

However, it has been reported that several Fe^{III} and Co^{II} complexes exhibit a thermal hysteresis loop. For such compounds, just above the spin transition temperature $T_{1/2}\downarrow$ ($T_{1/2}\downarrow$ = the temperature at which there are 50% high-spin and 50% low-spin states) in the cooling mode within the hysteresis, the high-spin phase is a metastable one, and the low spin phase is a ground one. This means that the metastable high-spin state can be observed without being allowed to relax back to the more stable low-spin state via tunneling processes or a thermal activation process. This suggests that the observation of the LIESST effects is not necessarily an unexpected phenomenon, at least for Fe^{III} and Co^{II} complexes that exhibit thermal hysteresis or abrupt phase transitions. Hence, we aimed at producing an Fe^{III} LIESST compound. Naturally, it should be noted that the presence of a hysteresis loop is never directly related to the achievement of the LIESST effects, because these depend on the electronic structure of the excited states. Furthermore, it has been reported that a photoinduced metastable state is not completely consistent with the structure of a thermally accessible high-spin state.[31] However, there is a possibility that the metastable high-spin state can be trapped.

On the basis of this idea, we have investigated the photoeffects of the Fe^{III} complex $[Fe^{III}(pap)_2]ClO_4\cdot H_2O$ (where pap = N-2-pyridiyl-methylidene-2-hydroxyphenylaminato),[32] which exhibits a hysteresis loop. As shown in Figure 2, the Fe^{III} ions in the complex are coordinated by four nitrogen atoms and two oxygen atoms, i.e., N_4O_2. Furthermore, their crystal structure (Figure 2) shows that Fe^{III} molecules are bonded to each other by the $\pi-\pi$ interactions of their planar ligands, forming a one-dimensional network structure. The one-dimensional networks are finally assembled into a two-dimensional sheetlike structure.

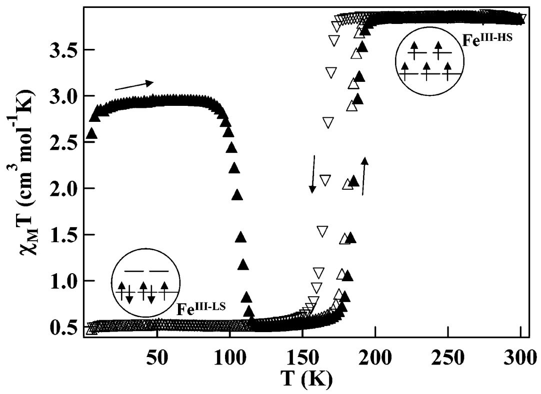

FIGURE 3. $\chi_M T$ vs T plots for $[Fe(pap)_2]ClO_4\cdot H_2O$.[4] The sample was cooled from 300 to 5 K (▽) and then warmed from 5 to 300 K (△) at a rate of 2 K min^{-1}. The sample was warmed at a rate of 2K min^{-1} after it had been quenched to 5 K (▲).

The magnetic properties of the complex are shown in Figure 3. The thermally induced spin transition appears at $T_{1/2}\downarrow = 165$ K on cooling and at $T_{1/2}\uparrow = 180$ K on heating ($T_{1/2}\uparrow$ = temperature for which there are 50% high-spin and 50% low-spin states in the heating mode). The hysteresis loop is about 15 K. The presence of the

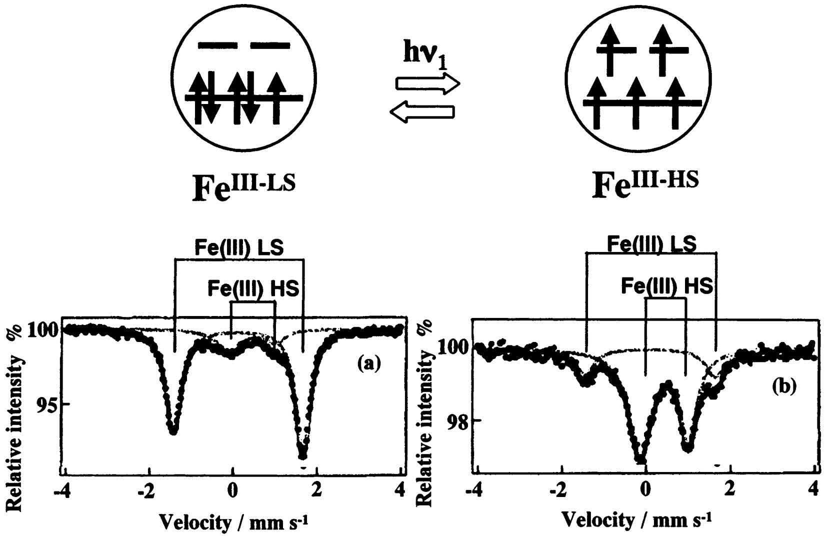

FIGURE 4. ^{57}Fe Mössbauer spectra for [Fe(pap)$_2$]ClO$_4$·H$_2$O at 13K.[4] (a) Spectrum before illumination. (b) Spectrum after illumination.

hysteresis loop in the spin transition curve originates entirely from cooperative effects. For this Fe^{III} complex, the cooperativity is thought to be derived from the intermolecular $\pi-\pi$ interactions of the ligands. Furthermore, as is described above, the presence of the hysteresis loop shows that the potential barrier separating the high-spin and low-spin phases is large enough to observe the metastable state in the temperature range between 165 and 180K. Hence, there is a possibility that the metastable state can be trapped on the bottom of the potential well at low temperature for this $\pi-\pi$ interaction system. It should be noted that π-stacking has been used for making cooperative spin crossover compounds.[33−35]

The spin transition was triggered by irradiating the sample with a Hg−Xe light source. The low-spin Fe^{III} complex has a broad absorption band in the visible region that can be attributed to the spin-allowed ligand-to-metal charge transfer (LMCT) transition. It has been reported that the excitation of the LMCT band results in the transient generation of high-spin Fe^{III} fractions.[36,37] Hence, for the excitation of the LMCT band, light with a wavelength of 400−600 nm that had passed through a combination of IR cutoff and green filters was used as the pump light. When the Fe^{III} complex was illuminated in a SQUID sample holder at 5 K, an increase in the magnetization value was clearly observed. This suggests that the LIESST effect was induced by light. To confirm this, we measured the Mössbauer spectra before and after excitation with light at 13 K (Figure 4). The Mössbauer parameters before illumination are isomer shift (I.S.) = 0.11 mms^{-1} and quadrupole split (Q.S.) = 3.08 mms^{-1}. This is consistent with the fact that Fe^{III} takes the low-spin state. On the other hand, when it is illuminated, the original wide quadrupole-split doublet was reduced, and new peaks appeared. The Mössbauer parameters after illumination are I.S. = 0.44 mms^{-1} and Q.S. = 1.14 mms^{-1}. This means that Fe^{III} takes the high-spin state. The magnetic and Mössbauer measurements clearly show that the LIESST effect was induced in the Fe^{III} complex for the first time. This can be expressed as

$$\mathrm{Fe^{III-LS}}(t_{2g}{}^{5}e_{g}{}^{0}) \leftrightarrows \mathrm{Fe^{II-HS}}(t_{2g}{}^{3}e_{g}{}^{2})$$

It is thought that the excited LMCT state relaxed back to the metastable high-spin state via the intermediate $^4T_1$ state.

It should be noted that this complex exhibits a frozen-in effect. That is, when the Fe^{III} complex is rapidly cooled from room temperature down to 5 K, the high-spin state is trapped without the spin transition proceeding from high-spin to low-spin (Figure 3). The trapping of the metastable high-spin state is consistent with the observation of the LIESST effects. Furthermore, the LIESST effects were also observed for the [Fe^{III}(pap)$_2$]PF$_4$·MeOH complex. This means that the previous prediction, i.e., "LIESST effect cannot be expected for Fe^{III} spin-crossover compounds",[26] might not be the case.

Let us mention why LIESST effects can be observed for the [Fe^{III}(pap)$_2$]ClO$_4$·H$_2$O compound, although this was not originally expected to be the case. As described above, the [Fe^{III}(pap)$_2$]ClO$_4$·H$_2$O compound exhibits a hysteresis loop, within which metastable high-spin or low-spin states can be observed. It is well-known that the hysteresis loop originates from cooperative effects. Hence, there is a possibility that cooperative interaction due to the $\pi-\pi$ interactions might play an important roll in observing the Fe^{III} LIESST effects at low temperature. Another possible reason is that the single configuration coordinate (SCC) model used for the description of the nonadiabatic relaxation of the LIESST process is a rather bad approximation for an Fe^{III} spin-crossover compound with an FeO$_2$N$_4$ core, and hence the observation of LIESST effects in an Fe^{III} spin-crossover compound is not unusual. Note that it has been reported that the SCC model becomes a rather bad approximation for Co^{II} systems.[26] Furthermore, we should note that Marcen et al. have reported that the relaxation temperature of the LIESST effects, T_c(LIESST), is not simply controlled by the horizontal and vertical displacements of the two potential wells, and hence other parameters such as the stiffness of the cage complex or the twisting motion between the ligand around the metal atom have to be investigated in more detail.[38]

Finally we would like to comment on the cooperative interaction. Recently, the relationship between cooperativity and LIESST effects has been discussed in detail.[38−43] However, to the best of my knowledge, the effect of the cooperativity on the LIESST process is still controversial. For example, Létard et al. have studied the relationship between thermally induced spin conversions and photoinduced high-spin to low-spin relaxation and observed that T_c(LIESST) is governed, at least in part, by the abruptness of the spin transition.[42] On this basis, they reported that a possible strategy for increasing the temperature range over which the photoinduced information can be retained consists of increasing the intermolecular interactions.[42] In contrast, more recently they reported that the T_c(LIESST) is insensitive to the cooperativity.[38] This means that the role of cooperativity on LIESST effects should be further investigated. However, in our opinion, cooperative interactions were at least in partly responsible for the LIESST effects that were observed in the present Fe^{III} compound, which exhibited an abrupt phase transition.

3. Photoinduced Structural Isomerization in a Cu^{II} Complex: Hydrogen Bonding System[7,8]

To search for new optically switchable molecular solids, we have focused on solid-state thermochromic complexes.[44,45] Thermochromic compounds have at least two different electronic states with different colors. This suggests that the two states can be switched by illumination as well as by thermal excitation. However, most of the solid state thermochromic complexes never show a photoinduced change in color. In other words, the number of metal complexes that can exhibit a color change induced by light, as in the case of the Fe^{II} LIESST compounds, is very small. On the other hand, we have recently discovered that a classical solid-state thermochromic complex, $[\text{Cu}^{II}(\text{dieten})_2](\text{X})_2$ ($\text{X} = \text{BF}_4$ and ClO_4), where dieten represents bis(*N*,*N*-diethylethylenediamine), exhibits a photoinduced structural isomerization.

The thermochromic properties of this Cu complex were first reported more than 60 years ago.[46] The crystal structures of the ClO_4 salt and the BF_4 salts have been reported by Grenthe et al.[47] and Narayanan et al.,[48] respectively. They show that $[\text{Cu}^{II}(\text{dieten})_2]^+$ molecules are bounded by ClO_4 or BF_4 species and undergo hydrogen bonding, forming a one-dimensional network with an alternate arrangement of $[\text{Cu}^{II}(\text{dieten})_2]^+$ molecules and anions (Figure 5).

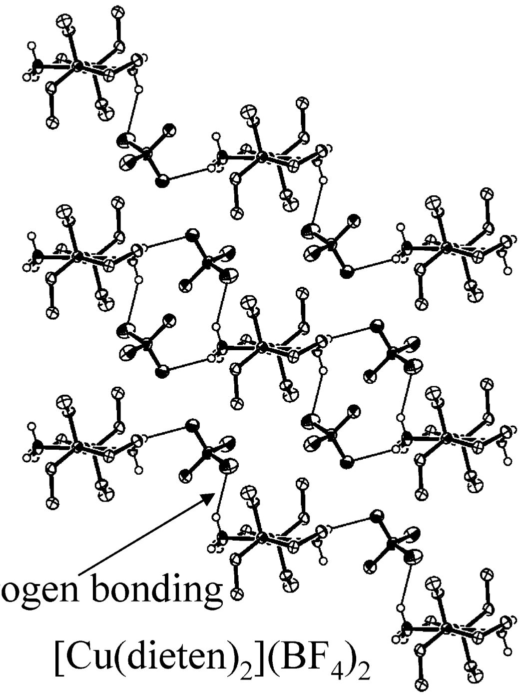

FIGURE 5. Crystal structure of $[\text{Cu}(\text{dieten})_2](\text{BF}_4)_2$.[47,48]

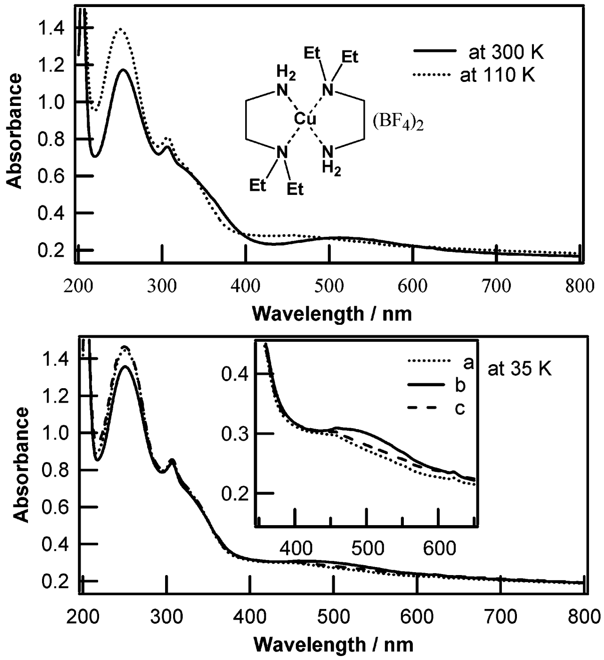

FIGURE 6. (Top) Temperature-dependent absorption spectra and chemical structure of $[\text{Cu}(\text{dieten})_2](\text{BF}_4)_2$.[7] (bottom) Spectra (a) before and (b) after illumination and (c) after thermal treatment to 150 K. Inset: expanded spectra from 350 to 650 nm.[7]

The Cu complex has absorption bands in the visible and UV regions. The absorption in the visible region is ascribable to the d−d transition, while that in the UV region is ascribable to the ligand-to-metal charge transfer (LMCT) band.[49] On cooling, the absorption peak in the visible region shifts from 515 nm at room temperature to 455 nm at 35 K (Figure 6). Single-crystal X-ray analysis shows that the copper atom is placed in a square-planar configuration in the low-temperature (red) phase and in a dynamically disordered, slightly tetrahedral-distorted configuration in the high-temperature (purple) phase, respectively.[47] This means that the color change is caused by a variation in the in-plane field strength. It should be noted that the phase transition involving the color change occurs abruptly, not gradually. This means that the two

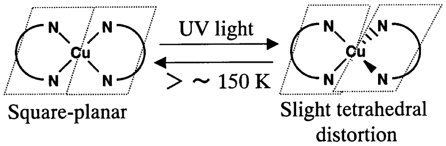

FIGURE 7. Schematic illustration of photoinduced structural isomerization in $[Cu(dieten)_2](BF_4)_2$.[7] The reverse process could be induced by thermal treatment or illumination with 532 nm light.

phases are separated by a potential barrier in free energy due to cooperative interactions. Hence, this suggests that the photoinduced phase can also be stabilized by the cooperativity resulting from the hydrogen bonding.

The effects of illumination on the Cu^{II} complex were investigated at low temperature. When the sample was illuminated by UV light (250−400 nm), the absorption peak at 455 nm shifted to longer wavelength in the UV spectra (Figure 6). The color change could be maintained at 35 K for more than several hours. This clearly shows that the metastable state could be induced by illumination and, in contrast to the conventional thermochromic compounds, the resultant metastable state, a local minimum in the potential well, could be trapped without showing appreciable decay at 35 K. By analogy to previous work, the change in the UV−vis spectra suggests that the UV-light illumination induces a transformation from a square-planar configuration to a slightly tetrahedrally distorted one around the copper atom (Figure 7). This idea is consistent with the fact that the Cu^{I} ions, which are generated transiently by exciting the LMCT band, favor the tetrahedral conformation rather than the planar structure. That is, the tetrahedrally distorted conformation, which might be generated in the excited LMCT state, was frozen after the back electron transfer from Cu^{I} to dieten was induced. It is thought that the unusually long-lived metastable state observed in the Cu complex was realized by the presence of a cooperative interaction by which the activation energy in the potential curve is enhanced. This finding suggests that, to find new optically switchable compounds, it is valuable to test those polymeric compounds exhibiting an abrupt phase transition.

4. Photoinduced Magnetization in an FeCo Prussian Blue: Ion−Dipole Interaction System[9−18]

In section 2, I described a photoinduced change in the magnetic properties.[4] However, this is a change at the single molecule level with respect to the magnetic properties, and the magnetic polarity of each molecule is completely random, which means that these systems are not magnets. In a true magnet, each magnetic polarity aligns ferromagnetically or antiferromagnetically. This means that, to design photomagnets, we should pay attention not only to the optical switching properties but also to the magnetic interactions between spin sources.

To create a photomagnet, we have focused on FeCo Prussian blue, where FeCo Prussian blue represents the Prussian blue analogues with Fe−CN−Co structures (Figure 8). FeCo Prussian blue has two proximal electronic states, i.e., $Fe^{II}-CN-Co^{III-LS}$ and its valence tautomer $Fe^{III}-CN-Co^{II-HS}$. It has been reported that a dinuclear FeCo complex, $[(NC)_5Fe-CN-Co(CN)_5]^{6-}$ has the $Fe^{II}-CN-Co^{III-LS}$ structure,[50] while the polymeric compound, $Co_{1.5}[Fe(CN)_6]\cdot xH_2O$, has the $Fe^{III}-CN-Co^{II-HS}$ structure. This suggests that the two states might be switched by some subtle external perturbation. Furthermore, a strong cooperativity is expected to operate due to the presence of the three-dimensional CN network. Hence, it is thought that the potential barrier separating these two phases is relatively large, potentially enabling the observation of a long-lived metastable state after illumination. Additionally, it is well accepted that the CN ligand can mediate magnetic interactions between spin sources. Hence, we can expect that the spins on the metal ions will align ferromagnetically or antiferromagnetically, resulting in the production of a ferro- or ferri-magnet below a critical temperature.

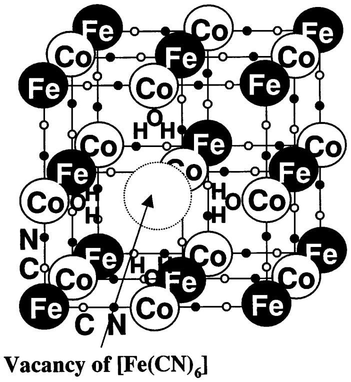

FIGURE 8. Structure of FeCo Prussian blue. It is thought that the vacancies at the $[Fe(CN)_6]$ site are surrounded by six water molecules. Interstitial alkali cations are omitted for clarity.

The FeCo Prussian blue can be synthesized via an electrochemical route[10,11] or by a simple solution reaction of $CoCl_2$ and $A_3[Fe(CN)_6]$ (A = alkali cation).[9,16−18] The stoichiometry of the FeCo Prussian blue can basically be expressed by $A_{2y}Co_{1.5-y}[Fe(CN)_6]\cdot zH_2O$. An important characteristic of the FeCo Prussian blue is that it exhibits a thermally induced phase transition involving electron transfer between Fe and Co ions. For example, the electrochemically synthesized compound $A_{0.4}Co^{II-HS}_{1.3}[Fe^{III}(CN)_6]\cdot 5H_2O$ (A = Na) exhibited the following phase transition at around 260 K[11]:

$$A_{0.4}Co^{II-HS}_{1.3}[Fe^{III}(CN)_6] \leftrightarrows A_{0.4}Co^{II-HS}_{0.3}Co^{III-LS}[Fe^{II}(CN)_6]$$

This means that following electron-transfer proceeds in the compounds

$$Fe^{III}(t_{2g}{}^5e_g{}^0)-CN-Co^{II-HS}(t_{2g}{}^5e_g{}^2) \leftrightarrows Fe^{II}(t_{2g}{}^6e_g{}^0)-CN-Co^{III-LS}(t_{2g}{}^6e_g{}^0)$$

The phase transition is an entropy-driven process. The observation of the thermally induced switch between the two states is consistent with the view that the FeCo Prussian blue has two proximal electronic states, i.e., $Fe^{II}-$

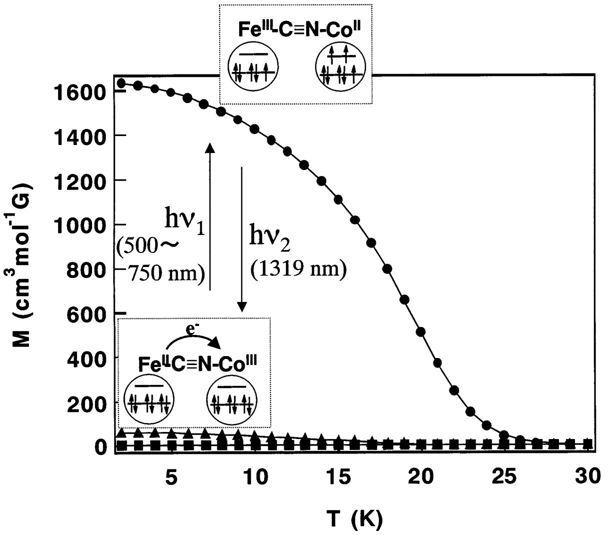

FIGURE 9. Field-cooled magnetization vs temperature curves at $H = 5$ G (■) before light illumination, (●) after visible light ($h\nu_1$) illumination, and (▲) after near-IR light ($h\nu_2$) illumination.[10] The FCM plots after visible light illumination showed an abrupt break around 26 K, i.e., $T_C = 26$ K. The enhancement of the magnetization could almost be reverted back to the original level by near-IR light illumination.

CN$-$Co^{III-LS} and Fe$^{III}-$CN$-$Co^{II-HS}. Furthermore, the phase transition is accompanied by a hysteresis loop.[11,16−18] The largest hysteresis width observed for the FeCo Prussian blue is 40 K. The presence of a hysteresis loop derives from cooperative effects. The abrupt spin transition with hysteresis shows that the potential barrier separating the two phases is large enough to observe supercooling and superheating phenomena. Hence, there is a possibility that the metastable state can be trapped on the bottom of the potential well at low temperature for this three-dimensional ion−dipole interaction system.

The effects of illumination on FeCo Prussian blue were investigated by exciting the charge-transfer band from Fe^{II} to Co^{III-LS}. Figure 9 shows the Field-cooled magnetization (FCM) versus temperature plots of electrochemically synthesized $A_{0.4}Co^{II-HS}{}_{0.3}Co^{III-LS}[Fe^{II}(CN)_6]\cdot 5H_2O$.[10] Before illumination, the magnetization value is small, and there are no abrupt breaks between 340 and 2 K because it is a paramagnetic material. On the other hand, excitation of the CT band from Co^{II-HS} to Fe^{III} with a Hg−Xe lamp at 5 K induced an increase in the magnetization value. After illumination, the FCM plots showed an abrupt break around 26 K, meaning that the compound turns magnetic below 26 K.[10] Additionally the plot of M versus H after illumination did exhibit hysteresis loops (Figure 10)[10,14] The Mössbauer,[51] IR,[14,17] X-ray-absorption fine-structure (XAFS),[13,15] and UV−vis spectra[14,16] show that the Fe^{II}-$(t_{2g}{}^6e_g{}^0)$−CN−Co$^{III-LS}(t_{2g}{}^6e_g{}^0)$ state transferred to the Fe^{III}-$(t_{2g}{}^5e_g{}^0)$−CN−Co$^{II-HS}(t_{2g}{}^5e_g{}^2)$ state. This can be expressed as

$$A_{0.4}Co^{II-HS}{}_{0.3}Co^{III-LS}[Fe^{II}(CN)_6] \rightarrow A_{0.4}Co^{II-HS}{}_{1.3}[Fe^{III}(CN)_6]$$

The change persisted for periods of several days when the sample was maintained at 5 K. The metastable state reverted back to the ground state at around 130 K. Furthermore, the reverse process could be induced by illumination with near-IR light at 5 K. This is the first reported example of a molecular photomagnet, which is different from a change in the magnetic properties at the single molecule level.

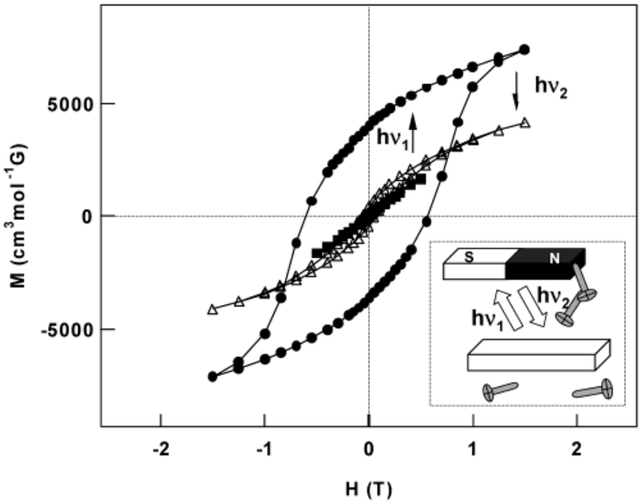

FIGURE 10. Hysteresis loops at 2 K (■) before illumination, (●) after visible light ($h\nu_1$) illumination, and (△) after near-IR light ($h\nu_2$) illumination.[10]

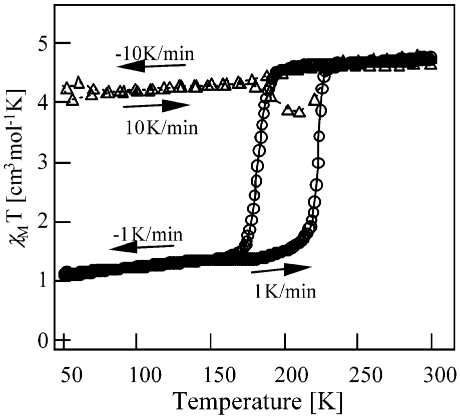

FIGURE 11. Temperature dependence of the magnetization of $Na_{0.34}Co^{II-HS}{}_{1.33}[Fe^{III}(CN)_6]\cdot 4.5H_2O$.[16] When it was cooled from room temperature to 5 K at a rate of 10 K/min, the high-temperature phase with the Fe^{III}-CN-Co^{II-HS} structure was trapped without relaxing back to the low-temperature phase with the Fe^{II}-CN-Co^{III-LS} structure. On the other hand, when it was cooled at a rate of 1 K/min, a phase transition accompanied by a thermal hysteresis was induced. The transition temperatures were $T_{1/2}\downarrow = 180$ K and $T_{1/2}\uparrow = 220$ K.

As in the case of the $[Fe^{III}(pap)_2]ClO_4\cdot H_2O$ complex, FeCo Prussian blue exhibited frozen-in effects.[16] That is, when the $Na_{0.34}Co^{II-HS}{}_{1.33}[Fe^{III}(CN)_6]\cdot 4.5H_2O$ is cooled from room temperature to 5K at a rate of 10 K/min, the high-temperature phase with the Fe^{III}-CN−Co^{II-HS} structure was trapped without relaxing back to the low-temperature phase with the Fe^{II}−CN−Co^{III-LS} structure (Figure 11). This observation is consistent with the view that the achievement of a long-lived metastable state is related to the presence of a strong intermolecular interaction operating within the crystals. Furthermore, it has been reported that

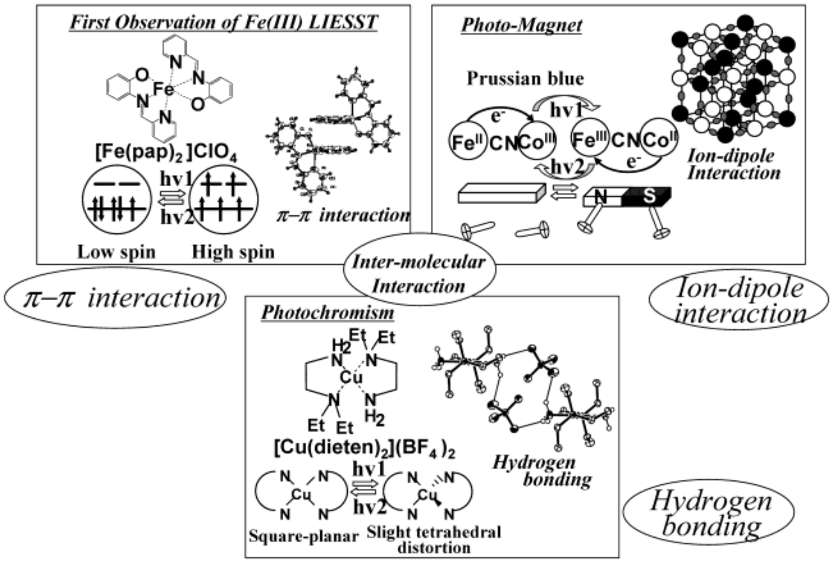

FIGURE 12. Optically switchable molecular solids. The cooperativity due to $\pi-\pi$ interactions, hydrogen boning, and ion−dipole interaction might play an important role in trapping the photoinduced metastable state for these polymeric systems.

the thermal relaxation after illumination does not follow the exponential law, with the sigmoidal shape typical of a self-accelerated process.[52] By analogy to the relaxation behavior observed for LIESST complexes, the sigmoidal relaxation suggests the operation of cooperative effects within the crystal. This observation also supports the idea that an intermolecular interaction due to the three-dimensional CN network plays an important role in trapping the photoinduced metastable state.

It is important to note that several other groups have also recently studied the photomagnetic properties of FeCo Prussian blue from both the theoretical[53−57] and experimental viewpoints.[52,58,59] It has been reported that the presence of structural disorder, i.e., vacancies on [Fe(CN)$_6$] sites, plays an important roll in the photoeffects of the FeCo Prussian blue.[57]

Furthermore, we should note that several other optically switchable molecular magnets have been recently reported.[60,61] Additionally, Kawamoto et al. recently proposed a new strategy to design optically switchable systems, i.e., the design of nanosuperstructures consisting from two kinds of bistable materials with opposite relative stabilities.[62]

5. Summary

In summary, I have shown that several molecular solids exhibit optical switching effects. These are an Fe^{III} spin-crossover complex exhibiting light-induced excited spin state trapping effects, a Cu^{II} photochromic complex, and an FeCo Prussian blue exhibiting photoinduced magnetization. To find such new optically switchable compounds, it seems to be valuable to examine the photoeffects of polymeric compounds that exhibit an abrupt phase transition or hysteresis loop. This is because the cooperative interaction resulting from the polymeric structure allows one to separate the two states in free energy by creating a potential barrier, potentially enabling the observation of the long-lived metastable state.

It should be noted that the design of polymeric structures using noncovalent bonds such as the $\pi-\pi$ interaction, hydrogen bonding, and ion−dipole interactions are currently attracting great attention in the discipline of supra-molecular chemistry. This suggests that optically switchable compounds might be designed rationally by combining knowledge from the fields of supramolecular chemistry and photochemistry (Figure 12).

References

(1) Feringa, B. L. Molecular Switches; Wiley-VCH: Weinheim, Germany, 2001.
(2) Sato, O.; Iyoda, T.; Fujishima, A., Hashimoto, K. Electrochemically Tunable Magnetic Phase Transition in a High-T_c Chromium Cyanide Thin Film. *Science* **1996**, *271*, 49−51.
(3) Gütlich, P.; Garcia, Y.; Woike, T. Photoswitchable Coordination Compounds. *Coord. Chem. Rev.* **2001**, *219*−*221*, 839−879.
(4) Hayami, S.; Gu, Z.-Z.; Shiro, M.; Einaga, Y.; Fujishima, A.; Sato, O. First Observation of Light Induced Excited Spin State Trapping for an Iron(III) Complex. *J. Am. Chem. Soc.* **2000**, *122*, 7126−7127.
(5) Hayami, S.; Gu, Z.-Z.; Einaga, Y.; Fujishima, A.; Sato, O. Iron(III) Spin-Crossover Compounds with a Wide Apparent Thermal Hysteresis around Room Temperature. *J. Am. Chem. Soc.* **2001**, *123*, 11644−11650.
(6) Juhasz, G.; Hayami, S.; Sato, O.; Maeda, Y. Photo-Induced Spin Transition for Iron(III) Compounds with $\pi-\pi$ Interactions. *Chem. Phys. Lett.* **2002**, *364*, 164−170.
(7) Takahashi, K.; Nakajima, R.; Gu, Z.-Z.; Yoshiki, H.; Fujishima, A.; Sato, O. Unusually Long-Lived Light-Induced Metastable State in a Thermochromic Copper(II) Complex. *Chem. Commun.* **2002**, 1578−1579.
(8) Yokoyama, T.; Takahashi. K.;Sato, O. A New Meatsatble Photo-induced Phase of Cu(II) Ethylenediamine Complexes Studied by X-ray-absorption Fine-structure Spectroscopy. *Phys. Rev. B*, in press.
(9) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Photoinduced Magnetization of a Cobalt Iron Cyanide. *Science* **1996**, *272*, 704−705.
(10) Sato, O.; Einaga, Y.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Reversible Photoinduced Magnetization. *J. Electrochem. Soc.* **1997**, *144*, L11−L13.
(11) Sato, O.; Einaga, Y.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Cation Driven Electron-Transfer Involving a Spin Transition at Room Temperature in a Cobalt Iron Cyanide Thin Film. *J. Phys. Chem. B* **1997**, *101*, 3903−3905.
(12) Einaga, Y.; Gu, Z.-Z.; Kobayashi, Y.; Sato, O.; Iyoda, T.; Ambe, F.; Hashimoto, K.; Fujishima, A. Mössbauer Study on Characterization of $Co[Fe(CN)_5NH_3]\cdot xH_2O$. *Hyperfine Interactions* **1998**, *116*, 159−166.

(13) Yokoyama, T.; Ohta, T.; Sato, O.; Hashimoto, K. Characterization of Magnetic Materials of CoFe Cyanides by X-Ray-Absorption Fine-Structure Spectroscopy. *Phys. Rev. B* **1998**, *58*, 8257−8266.

(14) Sato, O.; Einaga, Y.; Iyoda, T.; Fujishima, A.; Hashimoto, K. Photo-Induced Long-Range Magnetic Ordering of a Cobalt−Iron Cyanide. *Inorg. Chem.* **1999**, *38*, 4405−4412.

(15) Yokoyama, T.; Kiguchi, M.; Ohta, T.; Sato, O.; Einaga, Y.; Hashimoto, K. Local Structure of a Trapped Photo-Excited State of a FeCo Cyanide Studied by X-ray-absorption Fine Structure Spectroscopy. *Phys. Rev. B* **1999**, *60*, 9340−9346.

(16) Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. Photochromic Behavior Based on Spin Transition on a Cobalt−Iron Polycyanide. *Mol. Cryst. Liq. Cryst.* **2000**, *344*, 95−100.

(17) Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. Control of Charge-Transfer Induced Spin Transition Temperature on Cobalt−Iron Prussian Blue Analogues. *Inorg. Chem.* **2002**, *41*, 678−684.

(18) Liu, H.-W.; Matsuda, K.; Gu, Z.-Z.; Takahashi, K.; Cui, A.-L.; Nakajima,R.; Fujishima A.; Sato, O. Reversible Valence Tautomerism Induced by a Single-Shot Laser Pulse in a Cobalt−Iron Prussian Blue Analogue. *Phys. Rev. Lett.* **2003**, *90*, 167403−1−167403−4.

(19) Hayami, S.; Gu, Z.-Z.; Einaga, Y.; Kobayashi, Y.; Ishikawa, Y.; Yamada, Y.; Fujishima, A.; Sato, O. A Novel LIESST Iron(II) Complex Exhibiting a High Relaxation Temperature. *Inorg. Chem.* **2001**, *40*, 3240−3242.

(20) Sato, O.; Hayami, S.; Gu, Z.-Z.; Seki, K.; Nakajima, R.; Fujishima, A. Photo-Induced Long-Lived Intramolecular Electron Transfer in a Co Valence Tautomeric Complex. *Chem. Lett.* **2001**, 874−875.

(21) Yokoyama, T.; Okamoto, K.; Nagai, K.; Ohta, T.; Hayami, S.; Gu, Z.-Z.; Nakajima, R.; Sato, O. Photo-Induced Magnetized State of $Co(DTBSQ)(DTBCat)(phen)\cdot C_6H_5CH_3$ Studied by X-ray Absorption Spectroscopy. *Chem. Phys. Lett.* **2001**, *345*, 272−276.

(22) Sato, O.; Hayami, S.; Gu, Z.-Z.; Takahashi, K.; Nakajima, R.; Seki, K.; Fujishima, A. Photo-Induced Valence Tautomerism in a Co Compound. *J. Photochem. Photobiol. A: Chem.* **2002**, *149*, 111−114.

(23) Sato, O.; Hayami, S.; Gu, Z.-Z.; Takahashi, K.; Nakajima, R.; Fujishima, A. Photo-Induced Reverse Valence Tautomerism in a Metastable Co Compound. *Chem. Phys. Lett.* **2002**, *355*, 169−174.

(24) Sato, O.; Hayami, S.; Gu, Z.-Z.; Takahashi, K.; Nakajima, R.; Seki, K.; Fujishima, A. Photo-Reversible Valence Tautomerism in a Co Compound. *Phase Transitions* **2002**, *75*, 779−785.

(25) Decurtins, S.; Gütlich, P.; Kohler, 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*, 1−4.

(26) Gütlich, P.; Hauser, A.; Spiering, H. Thermal and Optical Switching of Iron(II) Complexes. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024−2054.

(27) Gütlich, P.; Garcia, Y.; Goodwin, H. A. Spin Crossover Phenomena in Fe(II) Complexes. *Chem. Soc. Rev.* **2000**, *29*, 419−427.

(28) Hauser, A.; Vef, A.; Adler, P. Intersystem Crossing Dynamics in Fe(II) Coordination Compounds. *J. Chem. Phys.* **1991**, *95*, 8710−8717.

(29) Vef, A.; Manthe, U.; Gütlich, P. Hauser, A. Intersystem Crossing Dynamics in the Spin-crossover Systems [M: $Fe(pic)_3]Cl_2\cdot$Sol (M=Fe or Zn, Sol= MeOH or EtOH). *J. Chem. Phys.* **1994**, *101*, 9326−9332.

(30) Hauser, A. Intersystem Crossing in Iron(II) Coordination Compounds-A Model Process Between Classical and Quantum-Mechanical Behavior. *Comment Inorg. Chem.* **1995**, *17*, 17−40.

(31) Tayagaki, T.; Tanaka, K. Photoinduced Phase Transition to a New Macroscopic Spin-Crossover-Complex Phase. *Phys. Rev. Lett.* **2001**, *86*, 2886−2889.

(32) Oshio, H.; Kitazaki, K.; Mishiro, J.; Kato, N.; Maeda, Y.; Takashima, Y. New Spin-Crossover Iron(III) Complexes With Large Hysteresis Effects and Time-Dependence of Their Magnetism. *J. Chem. Soc., Dalton Trans.* **1987**, 1341−1347.

(33) Real, J. A.; Gallois, B.; Granier, T.; Suez-Panamá, F.; Zarembowitch, J. Comparative Investigation of the Spin-Crossover Compounds $Fe(btz)_2(NCS)_2$ and $Fe(phen)_2(NCS)_2$ (Where btz = 2,2′-Bi-4,5-dihydrothiazine and phen = 1,10-Phenanthroline). Magnetic Properties and Thermal Dilatation Behavior and Crystal Structure of $Fe(btz)_2(NCS)_2$ at 293 K and 130 K. *Inorg. Chem.* **1992**, *31*, 4972−4979.

(34) Létard, J. F.; Guionneau, P.; Codjovi, E.; Lavastre, O.; Bravic, G.; Chasseau, D.; Kahn, O. Wide Thermal Hysteresis for the Mononuclear Spin-Crossover Compound Cis-bis(thiocyanato) bis[N-(2′-pyridylmethylene)-4-(phenylethynyl)anilino]iron(II). *J. Am. Chem. Soc.* **1997**, *119*, 10861−10862.

(35) Zhong, Z.-J.; Tao, J.-Q.; Yu, Z.; Dun, C.-Y.; Liu, Y.-J.; You, X.-Z. A Stacking Spin-Crossover Iron(II) with a Large Hysteresis. *J. Chem. Soc., Dalton. Trans.* **1998**, 327−328.

(36) Schenker, S.; Hauser, A. Low-Temperature Tunneling in the Spin-State Relaxation Dynamics of Iron(III) Spin-Crossover Compounds. *J. Am. Chem. Soc.* **1994**, *116*, 5497−5498.

(37) Schenker, S.; Hauser, A.; Dyson, R. M. Intersystem Crossing Dynamics in the Iron(III) Spin-Crossover Compounds $[Fe(acpa)_2]PF_6$ and $[Fe(Sal_2tr)]PF_6$. *Inorg. Chem.* **1996**, *35*, 4676−4682.

(38) Marcen, S.; Lecren, L.; Capes, L.; Goodwin, H.; A. Létard, J. F. Critical Temperature of the LIESST Effect in a Series of Hydrated and Anhydrous Complex Salts $[Fe(bpp)_2]X_2$. *Chem. Phys. Lett.* **2002**, *358*, 87−95.

(39) Hauser, A. Cooperative Effects on the HS-LS Relaxation in the $[Fe(ptz)_6](BF_4)_2$ Spin-Crossover System. *Chem. Phys. Lett.* **1992**, *192*, 65−70.

(40) Hauser, A.; Jeftic, J.; Romstedt, H.; Hinek, R.; Spiering, H. Cooperative Phenomena and Light-Induced Bistability in Iron(II) Spin-Crossover Compounds. *Coord. Chem. Rev.* **1999**, *192*, 471−491.

(41) Létard, J. F.; Capes, L.; Chastanet, G.; Moliner, N.; Létard, S.; Real, J. A. Kahn, O. Critical Temperature of the LIESST Effect in Iron-(II) Spin Crossover Compounds. *Chem. Phys. Lett.* **1999**, *313*, 115−120.

(42) Capes, L.; Létard, J. F.; Kahn, O. Photomagnetic Properties in a Series of Spin Crossover Compounds $[Fe(PM\text{-}L)_2(NCX)_2]$ (X=S, Se) with Substituted 2′-Pyridylmethylene-4-amino Ligands. *Chem. Eur. J.* **2000**, *6*, 2246−2255.

(43) Ogawa, Y.; Koshihara, S.; Koshino, K.; Ogawa, T.; Urano, C.; Takagi, H. Dynamical Aspects of the Photoinduced Phase Transition in Spin-Crossover Complexes. *Phys. Rev. Lett.* **2000**, *84*, 3181−3184.

(44) Bloomquist, D. R.; Willett, R. D. Thermochromic Phase Transitions in Transition Metal Salts. *Coord. Chem. Rev.* **1982**, *47*, 125−164.

(45) Sone, K.; Fukuda, Y. *Inorganic Thermochromism*; Springer: Berlin, 1987.

(46) Pfeiffer, P.; Glaser, H. Kupferkomplexsalze mit N-alkylierten Athylendiaminen. *J. Prakt. Chem.* **1938**, *151*, 134−144.

(47) Grenthe, I.; Paoletti, P.; Sandstrom, M.; Ginkberg, S. Thermochromism in Copper(II) Complexes. Structure of the Red and Blue-Violet Forms of Bis(N,N-diethylethylenediamine)copper(II) Perchlorate and the Nonthermochromic Violet Bis(N-ethylethylenediamine)copper(II) Perchlorate. *Inorg. Chem.* **1979**, *18*, 2687−2692.

(48) Narayanan, B.; Bhadbhade, M. M. X-Ray Structure of Thermochromic Bis(N, N.-Diethylethylenediamine)copper(II) Tetrafluoroborate. *J. Coord. Chem.* **1998**, *46*, 115−123.

(49) Kennedy, B. P.; Lever, A. B. P. Charge-Transfer Spectra of Bis-(diamine)copper(II) Complexes and Their Correlation with Other Electronic, Vibronic, and Thermodynamic Properties. *J. Am. Chem. Soc.* **1973**, *95*, 6907−6913.

(50) Hester, R. E.; Nour, E. M. Resonance Raman and Infrared Studies of Cyanide-bridged Dimetal Complexes. *J. Chem. Soc., Dalton Trans.*, **1981**, 939−941.

(51) Einaga, Y.; Sato, O.; Iyoda, T.; Kobayashi, K.; Ambe, F.; Hashimoto, K.; Fujishima, A. Electronic States of Cobalt Iron Cyanide by ^{57}Fe Mössbauer Spectroscopy. *Chem. Lett.* **1997**, *3*, 289−290.

(52) Goujon, A.; Roubeau, O.; Varret, F.; Dolbecq, A.; Bleuzen, A.; Verdaguer, M. Photo-Excitation from Dia- to Ferri-Magnetism in a Rb-Co-Hexacyanoferrate Prussian Blue Analogue. *Eur. Phys. J. B* **2000**, *14*, 115−124.

(53) Gutsev, G. L.; Reddy, B. V.; Khanna, S. N.; Rao, B. K. Jena, P. Optically Induced Magnetism in Cobalt Iron Cyanide. *Phys. Rev. B* **1998**, *58*, 14131−14134.

(54) Yoshizawa, K.; Mohri, F.; Nuspl, G.; Yamabe, T. Analysis of Photoinduced Magnetization in a (Co, Fe) Prussian Blue Model. *J. Phys. Chem. B* **1998**, *102*, 5432−5437.

(55) Nishino, M.; Yamaguchi, K.; Miyashita, S. Switching Dynamics between the Metastable Ordered Magnetic State and a Nonmagnetic Ground State: Possible Mechanism for Photoinduced Ferromagnetism. *Phys. Rev. B* **1998**, *58*, 9303−9311.

(56) Kawamoto, T.; Asai, Y.; Abe, S. Ab Initio Calculations on the Mechanism of Charge Transfer in Co−Fe Prussian-Blue Compounds. *Phys. Rev. B* **1999**, *60*, 12990−12993.

(57) Kawamoto, T.; Asai, Y.; Abe, S. Novel Mechanism of Photoinduced Reversible Phase Transitions in Molecule-Based Magnets. *Phys. Rev. Lett.* **2001**, *86*, 348−351.

(58) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Moulin, M. C. C.; Verdaguer, M. Photoinduced Ferrimagnetic Systems in Prussian Blue Analogues $C^{I}_{x}Co_4[Fe(CN)_6]_y$ (C^{I} = Alkali Cation). 1. Conditions to Observe the Phenomenon. *J. Am. Chem. Soc.* **2000**, *122*, 6648−6652.

(59) Pejakovic, D. A.; Manson, J. L.; Miller, J. S.; Epstein, A. J. Photoinduced Magnetism, Dynamics, and Cluster Glass Behavior of a Molecule-Based Magnet. *Phys. Rev. Lett.* **2000**, *85*, 1994–1997.

(60) Ohkoshi, S.; Yorozu, S.; Sato, O., Iyoda, T.; Fujishima, A.; Hashimoto, K. Photoinduced Magnetic Pole Inversion in a Ferro-ferrimagnet: $(Fe^{II}_{0.40}Mn^{II}_{0.60})_{1.5}Cr^{III}(CN)_6$. *Appl. Phys. Lett.* **1997**, *70*, 1040–1042.

(61) Pejakovic, D. A.; Kitamura, C.; Miller, J. S.; Epstein, A. J. Photoinduced Magnetization in the Organic-Based Magnet $Mn(TCNE)_x \cdot y(CH_2Cl_2)$. *Phys. Rev. Lett.* **2002**, *88*, 057202-1–057202-4.

(62) Kawamoto, T.; Abe, S. Conceptual Design of Nanostructures for Efficient Photoinduced Phase Transitions. *Appl. Phys. Lett.* **2002**, *80*, 2562–2564.

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