Photoinduced Electron Transfer

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Room-Temperature Photoinduced Electron Transfer in a Prussian Blue Analogue under Hydrostatic Pressure **

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The high technological demand for system miniaturization led to the "top–down" approach of the nanosciences. As the size of technological components progressively reaches that of the molecular level, the idea to use materials exhibiting intrinsically molecular properties becomes more and more appealing.[1–6] The use of light is one of the most promising ways to control various physical properties of organic[1], metal—organic, and coordination compounds[2a,c–e,3,4,6c] and this type of control could have future applications in the elaboration of molecular memories and switching devices.

Among these compounds, coordination compounds that exhibit photoinduced charge transfers and/or spin transitions involving the metallic d orbitals can have the following attributes: stability over successive cycles, short addressing times associated with such electronic transitions, full reversibility, and chemical stability. Although the photomagnetic properties of these compounds appear to have great potential for technological applications, the low relaxation temperature of the metastable state and therefore the low working temperature strongly limits their use in practical applications. To date, very few methods for enabling the photomagnetic effect to function at room temperature have been proposed: in 2002 Shimamoto et al. discovered that the low-temperature phase could be phototransformed into the high-temperature phase within the broad thermal hysteresis loop of a sodium derivative of a CoFe Prussian blue analogue (PBA);[7] later, Bozdag et al. reported a different kind of photomagnetic effect, which probably originates from a photoinduced structural distortion.[8] Herein, we demonstrate, using synchrotron-based energy-dispersive X-ray absorption spectroscopy, that a room-temperature photoinduced $Co^{III}–Fe^{II} \rightarrow (Co^{II}–Fe^{III})^*$ electron transfer occurs in the pressure-induced $Co^{III}–Fe^{II}$ state of a CoFe PBA that contains very few alkali metal cations. The results suggest an original and rational means for achieving room-temperature photomagnetic effects. By identifying the chemical conditions that allow the optically-triggered electronic switch to occur at room temperature, we have thus introduced a new perspective for the design of switchable materials at room temperature.

The face-centered cubic structure of CoFe PBAs can be represented by the chemical formula, $A_xCo_4[Fe(CN)_6]_{(8+x)/3}\square_{(4-x)/3}\cdot n\,H_2O$, where □ represents intrinsic $[Fe(CN)_6]$ vacancies, A is an alkali metal ion, and x is the number of alkali metal cations in one unit cell.[9] In switchable CoFe PBAs, the ground and metastable excited states are composed of $Co^{III}(LS)–Fe^{II}(LS)$ and $Co^{II}(HS)–Fe^{III}(LS)$ pairs, respectively (LS = low spin and HS = high spin).[4a,10–12] Owing to the oxidation and spin-state changes of the Co ions, the photoinduced $Co^{III}–Fe^{II} \rightarrow (Co^{II}–Fe^{III})^*$ electron transfer is accompanied by both a lengthening of the Co–ligand bonds (Co–N) and, importantly, an increase in the cell parameter.[10,11] In contrast to the structure of the Co coordination sphere, the structure of the $[Fe(CN)_6]$ entities, which are composed of low-spin Fe ions and strong covalent bonds, in both states are very similar.[11] A two-state model is usually used to explain the photomagnetic properties exhibited by CoFe PBAs (Figure 1).[3c–e] Upon irradiation at low temperature, the $Co^{III}–Fe^{II}$ ground state is converted into an excited state of the same spin multiplicity; the excited state then relaxes to the $(Co^{II}–Fe^{III})^*$ metastable state. The lifetime and the thermal-relaxation temperature of the metastable state depend on the energy barrier (E_{a1}) between both states, that is, they depend on the relative position of the potential wells.

The horizontal positions of the potential-energy curves depend on structural parameters and are therefore difficult to

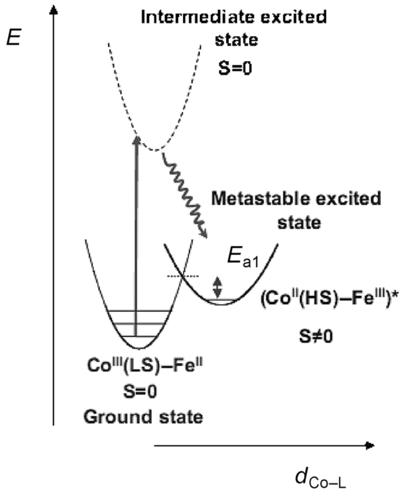

Figure 1. Schematic potential-energy curves of the $Co^{III}–Fe^{II}$ and $(Co^{II}–Fe^{III})^*$ states implied in the photomagnetic effect exhibited by CoFe PBAs ($d_{Co–L}$ represents the Co–ligand bond length).

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tune. To control the switching properties in a rational way, it seems easier to tune the vertical energy gap between the two states. To increase the relaxation temperature, one has to increase the E_{a1} energy-barrier value. The relative energy levels of the Co^{III}–Fe^{II} and $(Co^{II}–Fe^{III})^*$ states depend on the relative position of the potentials of the $Co^{III/II}$ and $Fe^{III/II}$ redox couples. Recently, we showed that these redox potentials depend on the transfer of electron density from the $[Fe(CN)_6]$ entities to the Co ions along the Co–NC–Fe linkages.[13a] A strengthening in the interactions between these two species usually lowers the potential of the $Co^{III/II}$ redox couple and stabilizes the Co^{III}–Fe^{II} state.[13] Therefore, to reduce the energy gap between the two states in photomagnetic CoFe PBA, one has to weaken the interactions between the $[Fe(CN)_6]$ entities and the Co ions.

This can be achieved through chemical means by decreasing the proportion of $[Fe(CN)_6]$ entities in the structure. Several years ago, we showed that it is indeed possible to control the relaxation temperature through chemical means in a series of cesium derivatives of chemical formula $Cs_xCo_4[Fe(CN)_6]_{(8+x)/3}\cdot n\,H_2O$. When the proportion of alkali metal cation decreases, which also corresponds to a decrease in the number of N-bonded cyanide ligands in the Co coordination sphere, the thermal relaxation temperature increases.[3e] But, the magnitude of the switching properties (number of Co–Fe switching pairs) also decreases[3e] so that a CoFe PBA that contains a very small proportion of alkali metal cations and the lowest amount of $[Fe(CN)_6]$ entities (referred to as $\mathbf{A_0}$ below), unfortunately, does not show any switching properties.[3d,14] $\mathbf{A_0}$ is essentially composed of Co^{II}(HS) and Fe^{III}(LS) ions whatever the temperature.[3d,14]

Nevertheless, under applied pressure, which strengthens the interactions between the $[Fe(CN)_6]$ entities and the Co ions, $\mathbf{A_0}$ undergoes a total piezo-induced $Co^{II}(HS)–Fe^{III} \rightarrow Co^{III}(LS)–Fe^{II}$ electron transfer at room temperature.[15–17] With the lowest possible amount of $[Fe(CN)_6]$ entities in the structure, the energy barrier between the potential-energy curves and the thermal-relaxation temperature are expected to be at their highest.

$\mathbf{A_0}$ was placed in a diamond anvil cell and a pressure of 2.1 GPa (enough to induce a total $Co^{II}(HS)–Fe^{III} \rightarrow Co^{III}(LS)–Fe^{II}$ electron transfer) was applied.[16] The Co and Fe K-edge XANES spectra of $\mathbf{A_0}$ at 2.1 GPa before and after irradiation in the visible range are shown in Figure 2. At 2.1 GPa before irradiation, the absorption maxima are at 7728 eV and 7130 eV at the Co and Fe K-edges, respectively. These energy positions are the signatures of Co^{III}(LS) and Fe^{II}(LS), respectively, in CoFe PBAs.[10–12] As previously shown, at 2.1 GPa, $\mathbf{A_0}$ is essentially composed of Co^{III}(LS) and Fe^{II}(LS) ions.[15,16] Furthermore, a previous variable-pressure X-ray diffraction study of $\mathbf{A_0}$ has shown that the piezo-induced $Co^{III}(LS)–Fe^{II}$ state is well-crystallized and is characterized by a weak cubic to rhombohedral distortion.[16]

At 2.1 GPa, the Co and Fe K-edges XANES spectra of $\mathbf{A_0}$ before and after irradiation in the visible range (Figure 2) are different. The spectral change can be unambiguously attributed to irradiation because no change was detected when $\mathbf{A_0}$ was placed in the dark for a long period of time at the same pressure. At the Co K-edge, the irradiation of the sample at 2.1 GPa, induces both a 2 eV shift of the absorption maximum towards lower energy and a shift of the first EXAFS oscillation towards lower energy. Such changes in the absorption spectrum have been attributed to the $Co^{III}(LS)–Fe^{II} \rightarrow Co^{II}(HS)–Fe^{III}$ electron transfer in CoFe PBAs in other contexts.[10–12] The shift of the absorption maximum is consistent with a decrease of the Co oxidation state from III to II; the shift of the first EXAFS oscillation to lower energy is consistent with a lengthening of the Co–ligand bond, a change that is associated with the $Co^{III}(LS) \rightarrow Co^{II}(HS)$ transformation. The experiment has been repeated several times at the Co K-edge and the same spectrum was obtained after irradiation, thus demonstrating the reproducibility of the photoinduced transformation. At the Fe K-edge, the irradiation induces a 1 eV shift of the absorption maximum towards higher energy without other changes to the spectrum. This shift is the signature of the $Fe^{II}(LS) \rightarrow Fe^{III}(LS)$ transformation in CoFe PBAs, and thus the observation of this shift

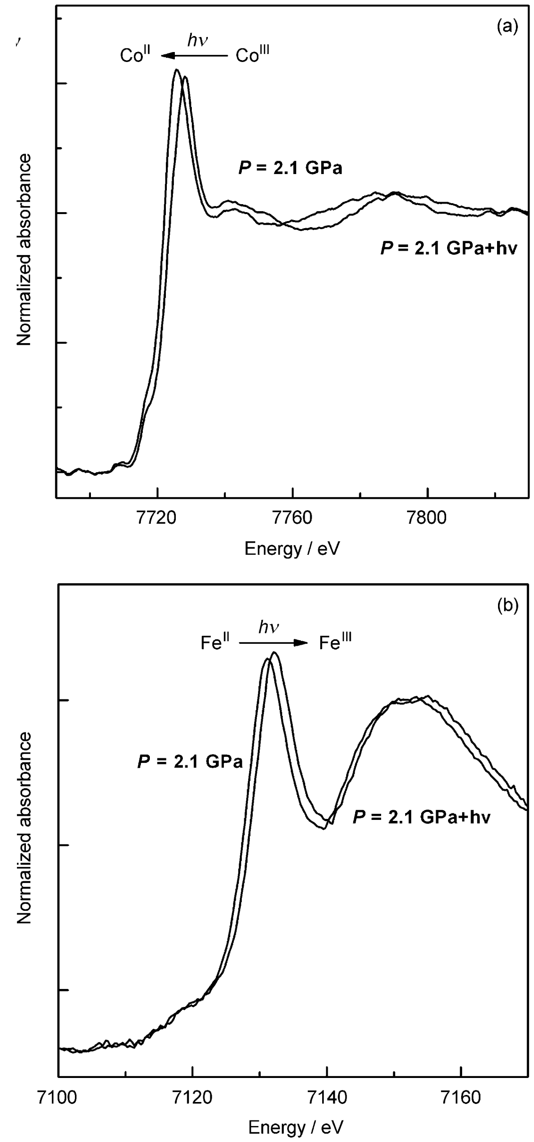

Figure 2. Co K-edge (a) and Fe K-edge (b) spectra of $\mathbf{A_0}$ recorded at 2.1 GPa before (P = 2.1 GPa) and after irradiation (P = 2.1 GPa + hv).

confirms the photoinduced electron transfer.[10–12] The small difference between the spectra at the Fe K-edge is due to the following: the Fe ion being in the same spin state in both states, the very similar structures of the $Fe(CN)_6$ entities, and the real charges of the Fe ions in both states being similar, a characteristic that is possible because the overall charge can be spread over the six cyanide ligands. After irradiation, the XANES spectra remained unchanged for hours, an observation that indicates that $\mathbf{A_0}$ is trapped in the photoinduced $(Co^{II}–Fe^{III})^*$ metastable state at room temperature (see the Supporting Information, S1). The above data obtained by a local probe of both metallic ions are direct evidence of the photoinduced $Co^{III}(LS)–Fe^{II} \rightarrow (Co^{II}(HS)–Fe^{III})^*$ electron transfer in the pressure-induced state of $\mathbf{A_0}$ at room temperature. Work is in progress to fully characterize the structure of this room-temperature photoinduced state.

A photoinduced electron transfer at room temperature has been detected in a CoFe polycyanide. The room-temperature-operating photoswitchable state was created under hydrostatic pressure. This work introduces an original way to access room temperature photomagnetic materials and opens new perspectives for the design of photoswitchable molecular compounds that operate at room temperature.

Experimental Section

The synthesis of $\mathbf{A_0}$ is described in Refs. [14] and [18]. The compound was characterized by elemental analysis and powder X-ray diffraction (see the Supporting Information, S2 and S3). The combination of variable hydrostatic pressure, in situ irradiation, and selective probe of the electronic structure of the transition-metal ions by XANES measurements at the Co and Fe K-edges has been made possible by the use of a diamond anvil cell, a green laser (532 nm $P = 10\,mW\,cm^{-1}$), and the energy-dispersive mode available on the new XAS ODE beamline (see the Supporting Information, S4).[19,20] We carefully checked that the X-ray beam does not damage the compound in any of its states.

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