

Persistent Photoinduced Magnetism in Heterostructures of Prussian Blue Analogues

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Photoswitching of magnetic response is a growing field because of the increasingly diverse materials available.^{1–3} Persistent photoinduced magnetism (PPIM), wherein long-lived changes in magnetization remain intact for periods of weeks or more after irradiation, is an important example. PPIM has been identified in several molecule-based magnetic systems. Some organic-based magnetic semiconductor thin films^{4–6} provide examples, as do compounds that exhibit a variety of spin-crossover effects,^{1,7} including charge-transfer-induced spin transitions (CTIST).^{7,8} Much recent excitement has focused on a series of cyanometallate coordination polymers, Prussian blue analogues (PBAs),^{9,10} for which CTIST leads to long-range magnetic order.^{11–13} This coexistence of PPIM and long-range magnetic order is desirable from a technological standpoint to ease detection of changes in state, although to date the effect has been restricted to low temperatures.

The present report describes the fabrication of cyanometallate PBAs into **ABA** heterostructured films. The heterostructure leads to new behavior, in this case PPIM at temperatures not previously observed in either of the constituents. In the **ABA** heterostructures, (Figure 1), **A** is ferromagnetic $\text{Rb}_{0.8}\text{Ni}_4[\text{Cr}(\text{CN})_6]_{2.9} \cdot n\text{H}_2\text{O}$ (Ni–Cr PBA; $T_C \approx 70$ K), and **B** is ferrimagnetic $\text{Rb}_{0.7}\text{Co}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$ (Co–Fe PBA; $T_C \approx 18$ K), which is known to be photomagnetic. The heterostructures show two striking features not observed in the homogeneous phases (Figure 2). First, there is a significant increase (from 18 to 70 K) in the temperature at which persistent photoinduced changes in the magnetically ordered state are observed. Second, the magnetization decreases with light, in contrast to the normal photoinduced increases known for this family of compounds. The results suggest a new mechanism for PPIM whereby photoinduced changes in one lattice alter the magnetic response of the other. These thin films are among the first examples of nanometer-scale coordination polymer heterostructures,¹⁴ and our results further demonstrate that such structures can lead to new phenomena.

The mechanism of PPIM in the bulk Co–Fe PBA involves light-induced electron transfer from $\text{Fe}^{\text{II}}(\text{LS}, S = 0)$ to $\text{Co}^{\text{III}}(\text{LS}, S = 0)$, yielding long-lived metastable $\text{Fe}^{\text{III}}(\text{LS}, S = 1/2) - \text{CN} - \text{Co}^{\text{II}}(\text{HS}, S = 3/2)$ pairs that couple antiferromagnetically, giving rise to a net increase in magnetization in the ferrimagnetic state below 18 K.^{11–13} The electron transfer and change in spin state also lead to a change in lattice constant, which increases by ~ 0.2 Å upon the transition from the low-spin (LS) state to the high-spin (HS) state.^{15,16} On the other hand, the ferromagnetic Ni–Cr PBA is not known to be photomagnetic. However, its magnetic response has a dramatic pressure dependence in low fields, where decreases of $\sim 50\%$ in the magnetization can be induced by the application of a hydrostatic pressure of 0.8 GPa.¹⁷ The photomagnetic response of the heterostructure indicates that the structural change in the Co–Fe

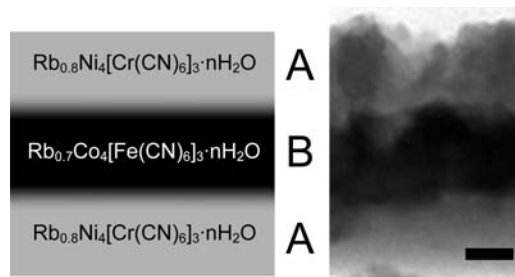


Figure 1. **ABA** heterostructure. (left) Schema of the heterostructure using a shading gradient between layers to illustrate regions at the interfaces where mixing of the two phases can occur. (right) TEM micrograph showing a cross-section of a microtomed sample. The scale bar is 100 nm. The film was fabricated using 40 deposition cycles for each layer (see the SI).

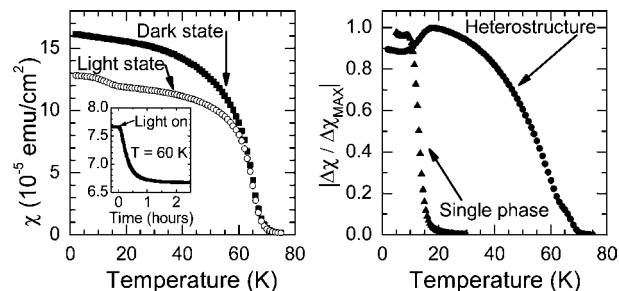


Figure 2. Photoinduced magnetism. (left) Field-cooled magnetic susceptibility $\chi(T)$ in a 100 G field oriented parallel to the surface of the film, where $\chi(T)$ is normalized to the area of the film: (■) data prior to irradiation (i.e., the dark state); (○) data acquired after 5 h of irradiation with white light but with the light subsequently off (i.e., the PPIM state). Inset: time dependence of $\chi(T = 60$ K), with the start of irradiation at $t = 0$. (right) Absolute value of the photoinduced change in χ , $\Delta\chi = \chi(\text{dark}) - \chi(\text{light})$, normalized to the maximum value: (●) data for the heterostructure from the left panel; (▲) data for a single-phase Co–Fe PBA thin film taken from ref 20.

PBA layer couples to the Ni–Cr PBA, leading to the change in magnetization.

We previously observed PPIM in nanometer-scale thin films of the Co–Fe PBA (Figure 2).^{18–20} In those studies, single-component films ranging in thickness from ~ 10 to ~ 400 nm were prepared from aqueous solutions of the precursor ions at room temperature using sequential adsorption methods.^{18–20} The **ABA** heterostructures in Figure 1, with a layer thickness of ~ 200 nm, were prepared using similar methods [for details, see the Supporting Information (SI)]. The ability to deposit layers with finite controllable thickness allows the influence of the interface to coexist with the pure phases, making each component susceptible to mechanical changes of the other.

After the heterostructured film is cooled in the dark state, photoexcitation causes a significant decrease in its magnetization

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(Figure 2). Close examination of the temperature dependence of the magnetic response shows two distinct signals, one near the bulk T_C of the Co–Fe PBA (~ 18 K) and the other near the bulk T_C of the Ni–Cr PBA (~ 70 K). Strikingly, the ability to photoinduce large changes in the magnetism exists above the ordering temperature of the Co–Fe PBA and extends up to the ferromagnetic transition temperature of the Ni–Cr PBA, indicating that there is a magnetization change in the Ni–Cr PBA layers in response to the light absorbed by the Co–Fe PBA layer. The photoinduced change in magnetization has different signs for the two networks. There is a decrease in magnetization of the Ni–Cr PBA layers, which order near 70 K, and an increase in the magnetization of the Co–Fe PBA layer below 18 K. Since there is more Ni–Cr PBA in the heterostructure and its net moment is larger, the photoinduced decrease dominates. The time evolution of the magnetization during illumination shows that the photoinduced changes have similar time constants at different temperatures (see the SI).

Despite the photoinduced decrease, new spins were being generated in the Co–Fe PBA layer of the ABA films. This interpretation was confirmed by an increase in the magnetization at high magnetic fields (see the SI). Therefore, the molecular-level mechanism whereby optical absorption leads to CTIST is the same as previously known for the Co–Fe PBA, and the decrease in magnetization does not result from a diminution of the number of moments.²¹

Pressure studies of the magnetic properties of the Ni–Cr PBA $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ by Zentkova et al.¹⁷ revealed important pressure-induced changes in magnetization with only a slight alteration of T_C . The ferromagnetic exchange coupling arises from the partially occupied e_g orbitals of the Ni^{2+} sites and partially occupied t_{2g} orbitals of the Cr^{3+} sites. Since the orbital overlap is essentially zero, the exchange constant, J , and therefore T_C , should not be affected by pressure. However, pressure can induce structural changes that alter the orientation of the transition-metal octahedron, thereby canting the moments.¹⁷ For $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, even relatively small pressure changes induce large field-cooled magnetization changes in the low-temperature ordered (or cluster glass) state. In the heterostructures, the magnetization of the Ni–Cr PBA components responds to the mechanical stress induced by bond length changes associated with the CTIST of the photoactive Co–Fe PBA layers.

The mixing of ions at the interface between the two phases could also provide a mechanism whereby CTIST lead to a decrease in magnetization,²² but the effect is expected to be small in these heterostructures because of the large regions of unmixed PBA. Ions from the two phases mix at the interface, forming Cr–CN–Co and Fe–CN–Ni superexchange pathways in addition to the Cr–CN–Ni and Fe–CN–Co pathways present in the pure phases. If the direction of the photogenerated Fe^{III} and Co^{II} moments is determined by the stronger ferromagnetic $\text{Fe}^{\text{III}}\text{---CN---Ni}^{\text{II}}$ superexchange experienced by the Fe^{III} sites in mixed environments at the interface, a net decrease in magnetization will result. This concept was demonstrated previously in specific mixed-metal PBA compositions, $\text{Na}_x\text{Ni}_{1-x}\text{Co}_x[\text{Fe}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$, for which photogenerated spins lead to a decrease in magnetization.²² However, the size of the photoinduced decrease demonstrated in Figure 2 for the heterostructures is too large to be associated with the photogenerated Co–Fe spin pairs located only in the interface. Furthermore, this mechanism cannot explain the observation that the photoinduced decrease in magnetization occurs up to the ordering temperature of the Ni–Cr PBA phase.

In summary, heterostructured films consisting of two different Prussian blue analogues, one ferromagnetic with a high T_C and the

other photoactive, have been fabricated for the first time, and this novel arrangement leads to persistent photoinduced changes in magnetization at elevated temperatures. The new behavior is not seen in either pure phase and requires the unique heterostructure arrangement that generates an interface between them. Simple mixing of ions in a three-dimensional lattice does not give the same result and in fact serves to greatly suppress the amount of Co–Fe material that is bistable.^{22–24} Heterostructures based on coordination polymers are largely unexplored,¹⁴ and these results provide an example of new phenomena arising from engineered coordination polymer-based structures that may motivate the rational design of additional systems with new applications.

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Supporting Information Available: Description of the synthesis protocol and characterization procedures; FT-IR spectra; TEM and EDS scans; low-field magnetic susceptibility plots with the external field parallel and perpendicular to the films; time evolution of the magnetization during irradiation at 5, 45, and 60 K; and full magnetic hysteresis loops at 2 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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