

# Light-Induced Magnetization Changes in a Coordination Polymer Heterostructure of a Prussian Blue Analogue and a Hofmann-like Fe(II) Spin Crossover Compound

Corey R. Gros,<sup>†</sup> Marcus K. Peprah,<sup>‡</sup> Brian D. Hosterman,<sup>§</sup> Tatiana V. Brinzari,<sup>‡</sup> Pedro A. Quintero,<sup>‡</sup> Mariana Sendova,<sup>§</sup> Mark W. Meisel,<sup>\*,‡</sup> and Daniel R. Talham<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

<sup>‡</sup>Department of Physics and National High Magnetic Field Laboratory, University of Florida, Gainesville, Florida 32611-8440, United States

<sup>§</sup>Division of Natural Sciences, New College of Florida, Sarasota, Florida 32423, United States

## S Supporting Information

**ABSTRACT:** Coordination polymer thin film heterostructures of the Prussian blue analogue  $\text{Ni}_{1-b}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.7-n}\text{H}_2\text{O}$  (NiCr-PBA) and the 3D Hofmann-like spin crossover compound  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  {azpy = 4,4'-azopyridine} have been developed, and spin transition properties have been characterized via SQUID magnetometry and Raman spectroscopy. The magnetic response of the ferromagnetic NiCr-PBA layer ( $T_c \approx 70$  K) can be altered by inducing the LIESST effect (light-induced excited spin state trapping) in the coupled paramagnetic Fe(II) spin crossover material. Whereas an increase in magnetization is measured for the single-phase  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ , a decrease in magnetization is observed for the heterostructure. These results indicate the LIESST effect alone cannot account for the sign and magnitude of the magnetization change in the heterostructure, but the temperature profile of the magnetization shows that significant changes in the NiCr-PBA network are correlated to the spin state of the Hofmann-like SCO network.

Light-controllable magnetic materials are promising candidates for optically controlled or energy-assisted magnetic recording routes leading to orders-of-magnitude increases in information storage density.<sup>1–3</sup> Furthermore, photogeneration and control of spins can increase speeds in spintronics and spin-photonics based processing.<sup>4</sup> Despite these potentially high-impact payoffs, inducing and manipulating spins with light remains a considerable challenge that is currently materials-limited. Efforts to control magnetism with light go back nearly 50 years,<sup>5</sup> and much recent focus has centered on light-induced magnetization in II–VI and III–V dilute magnetic semiconductors, although the effects only persist for short times.<sup>6,7</sup> On the other hand, photoinduced magnetization resulting from localized charge transfer can persist for years in some coordination polymer systems, but the effects are restricted to low temperature.<sup>8,9</sup>

Recently, other work from our group described a new mechanism for switching magnetism with light involving

coordination polymer heterostructures, in which a light-sensitive component elastically couples across an interface to a nonphotoactive magnetic component altering its magnetization.<sup>10–12</sup> Members of the family of Prussian blue analogues,  $\text{A}_x\text{Co}_k[\text{Fe}(\text{CN})_6]_{1-n}\text{H}_2\text{O}$  (A is generally a monovalent alkali cation) are known to undergo a charge-transfer induced spin transition (CTIST).<sup>8,9,13</sup> When coupled to a magnetic analogue that is not photoactive, such as  $\text{Rb}_{0.8}\text{Ni}_{4.0}[\text{Cr}(\text{CN})_6]_{2.9}\text{H}_2\text{O}$  (NiCr-PBA), the NiCr-PBA magnetization can be significantly altered by phototriggering the CTIST in the CoFe-PBA lattice. The effect has been observed in both thin film and particle heterostructures and is most pronounced in heterostructures with dimensions on the order of 100–500 nm.<sup>10–12</sup> This new approach offers the opportunity to rethink light-controllable magnetism by separating the photoevent from the magnetic spins.

We report here a new photomagnetic heterostructure that for the first time uses something other than a CoFe-PBA as the photoactive component, thereby illustrating that the mechanism can be general. In previous examples, lattice changes associated with the CTIST elastically couple across the interface to realign magnetic domains in the magnetic component. When searching for alternative photoactive networks to couple to the magnetic PBA, coordination polymer spin crossover compounds involving  $\text{Fe}^{2+}$  become promising candidates, as alterations in metal–ligand bond lengths upon high-spin to low-spin transition lead to significant changes in unit cell dimensions.<sup>14,15</sup> If the low-spin to high-spin transition is induced via the LIESST effect (light-induced excited state spin trapping), the structural change can be used to elastically couple to the magnetic PBA to alter its magnetism. To demonstrate this idea, a thin film of the Hofmann-like SCO network  $\{\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}\}$  (azpy = 4,4'-azopyridine), recently reported by Agusti et al.,<sup>16</sup> was coupled to a thin film of NiCr-PBA ( $\text{Ni}[\text{Cr}(\text{CN})_6]_{0.7}\text{H}_2\text{O}$ ). Below the magnetic ordering temperature of the NiCr-PBA ( $T_c = 70$  K), a light-induced change in magnetization is observed. The sign and magnitude of the heterostructure magnetization change

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cannot be accounted for by the LIESST effect alone, but the temperature profile of the magnetization clearly shows that the changes in the NiCr-PBA network are correlated to the spin state of the Hofmann-like SCO network.

Each component of the thin film heterostructure was deposited using sequential adsorption methods that have frequently been used for both PBA films<sup>10,11,17</sup> and Hofmann-like thin films<sup>18–20</sup> (see Supporting Information (SI) for details). The NiCr-PBA was deposited from aqueous precursor solutions at room temperature yielding a polycrystalline film ~200 nm thick. The deposition is terminated with the addition of hexacyanochromate ions that provide a nitrogen-functionalized surface to promote the coordination of iron ions and begin nucleation of the Hofmann-like network. Subsequent Hofmann network deposition was performed in ethanolic precursor solutions at low temperature (–78 °C) to reduce ligand desorption,<sup>18</sup> thus allowing for the controlled growth of a 3D network with an average thickness of approximately 50 nm. The successful deposition of the film on the substrate is seen via SEM (Figure 1a). With the use of XPS (Figure 1), the layered structure of the film is confirmed upon deposition of each component, in which the emergence of the surface Fe(azpy)[Pt(CN)<sub>4</sub>] signals and a decrease of underlying NiCr-

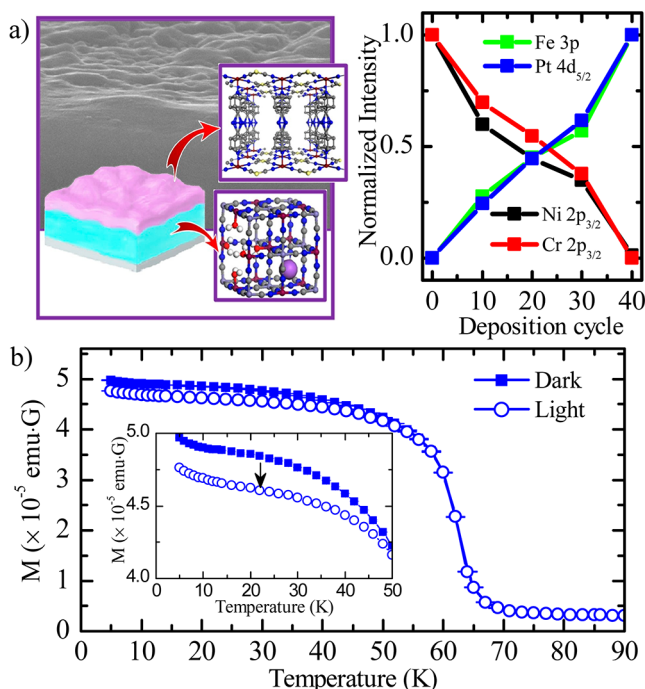
PBA signals are observed. Additional XPS, SEM, and ATR-FTIR data supporting the composition and topography of the layered structure are presented in the SI.

The field-cooled magnetic response of the heterostructure before irradiation shows the typical features of a NiCr-PBA film, with ferromagnetic ordering below 70 K (Figure 1).<sup>10</sup> Since the thin Fe(azpy)[Pt(CN)<sub>4</sub>] layer is paramagnetic, it does not contribute significantly to the magnetic signal of the heterostructure sample (vide infra) in a small field (10 mT). Upon photoirradiation with white light at low temperature, a decrease in the overall magnetization of the heterostructure is observed (Figure 1, SI Figure S8). After turning the light off, this reduced magnetization is maintained and upon warming persists up to 60 K, slightly below the ordering temperature of the NiCr-PBA phase. The NiCr-PBA material is known to not be photoactive (SI Figure S9), but the Hofmann-like material is capable of undergoing a LIESST effect.<sup>16</sup> Consequently, photoirradiation of the Hofmann layer influences the magnetic response of the NiCr layer, similar to the persistent photoinduced magnetization changes seen previously in mixed PBA heterostructures containing photoactive components.<sup>10–12,21</sup>

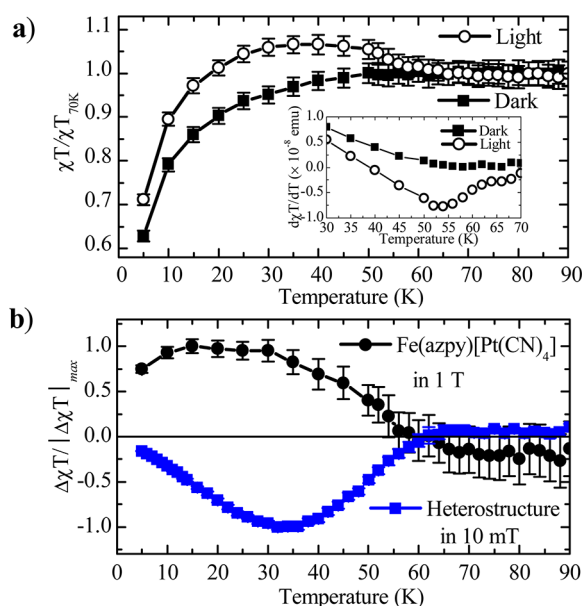
Although the photoactivity of the heterostructure correlates with the LIESST effect of the Fe(azpy)[Pt(CN)<sub>4</sub>] layer, the sign of the change contradicts the magnetization increase normally associated with a LS to HS transition (SI Figure S7). Magnetization vs temperature before and after irradiation for a Fe(azpy)[Pt(CN)<sub>4</sub>] film alone appears in Figure 2, showing the increase in magnetization upon irradiation that is expected as the light generates HS iron centers in the spin transition compound. Typical LIESST behavior<sup>15</sup> is observed as the increased magnetization persists after irradiation with a  $T(\text{LIESST}) \sim 53$  K (Figure 2). As the Hofmann-like compound is not magnetically ordered, the signal is significantly weaker than that for the heterostructure, so the data in Figure 2 are for a thicker film (>1 μm) measured in a much higher field (1 T) in order to detect the magnetization above the background signal of the supporting substrate.

By comparing the difference plots before and after irradiation (Figure 2b) for both the single-phase Fe(azpy)[Pt(CN)<sub>4</sub>] and the NiCr-PBA/Fe(azpy)[Pt(CN)<sub>4</sub>] heterostructure, striking similarities between the temperature profiles are revealed. The temperature regime for which the heterostructure experiences a light-induced decrease in magnetization mimics the Hofmann-like network HS trapping and relaxation behavior, implying a correlation between the two events in the heterostructure. Furthermore, the magnetization decrease in the heterostructure suggests that the photoinduced change is more than simply an additive effect of the Hofmann material independent of the NiCr-PBA, but rather results from the coupling of the two materials via the interface to perturb the NiCr-PBA magnetic response.

As a possible cause of the photoinduced magnetization change in the heterostructure, we might consider that the transition from the LS to the HS state of iron centers in the Fe(azpy)[Pt(CN)<sub>4</sub>] network produces spins at the interface that are able to align antiferromagnetically through cyanide bridges to the Cr<sup>3+</sup> ions at the PBA surface. If this mechanism was the source of the magnetic decrease, however, the disappearance of the effect would be evident at temperatures that reflect the strength of the Fe<sup>2+</sup>-NC-Cr<sup>3+</sup> coupling. Typically, iron hexacyanochromate PBA networks magnetically order below 25 K.<sup>22,23</sup> Thus, the presence of a significant



**Figure 1.** (a) SEM image and scheme (left) of the heterostructure film cross section illustrating the deposition of a continuous film on the substrate, along with normalized XPS data illustrating the layered architecture of the heterostructure by monitoring the Hofmann deposition on top of the NiCr film. The increase of Fe 3p and Pt 4d<sub>5/2</sub> signals is observed (normalized to final peak intensities) as well as the decrease of the underlying Ni 2p<sub>3/2</sub> and Cr 2p<sub>3/2</sub> signals (normalized to final peak intensities) as the Hofmann layer is deposited, emphasizing the layered structure of the components within the film. (b) The field-cooled, low-field (10 mT) magnetization of the heterostructure before (dark) and after (light) irradiation for 3 h and with the light then off depicting the LIESST-induced decrease in magnetization exhibited by the heterostructure. A photoinduced decrease is observed up to 60 K, which is slightly below the magnetic ordering temperature of the NiCr-PBA layer.



**Figure 2.** (a) Magnetic response exhibited by a single phase  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  film before (dark) and after irradiation (light) at 5 K, acquired in a field of 1 T and plotted as the magnetic susceptibility times temperature normalized to the value detected at 70 K. The “light” measurement is taken after the light is turned off. The photoinduced LS to HS transition is consistent with the LIESST effect observed in similar Fe(II) SCO compounds.<sup>16</sup> The observed  $T(\text{LIESST})$  defined as the minimum of the derivative plot (inset) occurring at  $T = 53$  K. (b) The differences (light–dark) of the magnetic responses (in part a) of the single-phase  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  in 1 T and the NiCr/ $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  heterostructure in 10 mT, highlighting the temperature regions in which population and relaxation of the photoinduced high spin state occur in the single-phase spin crossover material and the associated light-induced effect on the heterostructure.

magnetization decrease up to 60 K in the heterostructure is not sufficiently explained by interfacial antiferromagnetic interactions. Furthermore, the magnitude of the decrease for a 200 nm NiCr-PBA layer implies that the magnetic perturbation likely penetrates beyond the surface layer of the NiCr-PBA, involving depths of several unit cells.

Our current understanding is the structural change associated with the spin-state transition of the  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  couples to the NiCr-PBA, resulting in a magnetomechanical effect<sup>24,25</sup> in a portion of the PBA network that experiences domain distortion/realignment.<sup>21</sup> Spin transitions in Fe(II) complexes are well-known to undergo relatively large structural changes within the  $[\text{FeN}_6]$  coordination sphere as a consequence of the promotion or removal of electrons to or from antibonding  $\text{Fe } e_g$  orbitals, resulting in Fe–N bond length changes of approximately 0.2 Å.<sup>26,27</sup> Linkages at the film interface couple the networks, so structural changes in the LIESST-active  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  layer influence the NiCr-PBA. Upon cooling, the  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$  thermally transitions to the LS state (Figure S7), undergoing a lattice contraction that alters the underlying NiCr-PBA near the interface (these elastic coupling effects have been seen in mixed PBA heterostructures, where they are easier to quantify).<sup>28</sup> More specifically, this alteration distorts domains in the interface-strained region from highly anisotropic to less anisotropic forms. With further cooling below 70 K, the “altered” NiCr-PBA domains magnetically order with their moments more aligned with the magnetic field.

At base temperature, the application of light leads to the HS state of the Hofmann-like layer via the LIESST effect, and the associated structural changes relax the interface-strained domains, which reassume their original level of anisotropy with their moments less aligned with the applied magnetic field. Even slight structural changes can be enough to reorient magnetic anisotropy axes, in this case causing them to reorient away from the applied field direction, leading to a net decrease in magnetization. Upon warming, the trapped HS state of the Hofmann-like lattice relaxes at  $T(\text{LIESST})$  bringing the structures of the networks, and therefore the magnetization, back to the conditions similar to those established when the NiCr-PBA was first cooled below its ordering temperature.

Further support for this mechanism comes by comparing the temperature profile of the light-induced effects (Figure 2) of the PBA–Hofmann heterostructure to that of the mixed-PBA heterostructure reported previously.<sup>10</sup> In the mixed-PBA heterostructure, the optical CTIST of the CoFe-PBA relaxes in the vicinity of 140 K, well above the NiCr-PBA ordering temperature, so the light-induced state alters the magnetization of the NiCr-PBA up to its  $T_c$  near 70 K. On the other hand, the Hofmann  $T(\text{LIESST})$  of  $\sim 53$  K is below  $T_c$  of the NiCr-PBA. As a consequence, the photoeffects of the heterostructure diminish before the ordering temperature is reached.

The magnitude of the change is associated with the extent of strain induced at the interface and the depth to which it has an effect, as well as by the size of magnetic domains. The measured photoinduced magnetization changes suggest the perturbed region extends beyond just the ions at the interface and involves reorienting domains several unit cells deep.<sup>21,28</sup> Compared to other magnetic PBA lattices, the NiCr-PBA appears to be more susceptible to interface effects and may be related to the significant pressure-dependence of the NiCr-PBA magnetic response.<sup>29,30</sup>

In summary, a Hofmann-like spin crossover compound was coupled with a nickel hexacyanochromate Prussian blue analogue to develop a new type of coordination polymer heterostructure in which a light-induced change in one network induces a magnetization change in the other. For the first time, the interface-mediated photoinduced magnetization change in coordination polymer heterostructures is observed with structurally different materials, demonstrating that this mechanism for switching magnetism with light can be general.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Includes a description of film deposition, instrument details and characterization via ATR-FTIR, SEM, Raman, XPS, and SQUID irradiation measurements of the heterostructure,  $\text{Fe}(\text{azpy})[\text{Pt}(\text{CN})_4]$ , and NiCr-PBA control sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

[talham@chem.ufl.edu](mailto:talham@chem.ufl.edu)  
[meisel@phys.ufl.edu](mailto:meisel@phys.ufl.edu)

### Notes

The authors declare no competing financial interest.



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