

Supporting Information for:

**Light switchable magnetism in a coordination polymer heterostructure combining the magnetic potassium chromiumhexacyanochromate with the light-responsive rubidium cobalthexacyanoferrate**

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Contains Experimental Section and Figures S1-S5.

**Experimental Section**

*Synthesis of CoFe-PBA@CrCr-PBA heterostructure:* A uniform batch of the CoFe-PBA particles was prepared as previously described.<sup>s1</sup> CoFe-PBA cores (20 mg; 0.07 mmol) were redispersed in 50 mL deionized water. CrCl<sub>2</sub> (25 mg; 0.20 mmol) dissolved in 25 mL of deionized water and an equal volume of an aqueous solution containing K<sub>3</sub>[Cr(CN)<sub>6</sub>] (75 mg; 0.23 mmol) were simultaneously added (45 mL/h using a peristaltic pump) to the core particle suspension under vigorous stirring. The mixture was covered and left stirring for 3 days. The particles were isolated by centrifugation at 9500 rpm for 10 min and subsequently washed with 150 mL of water. The product was isolated and air-dried.

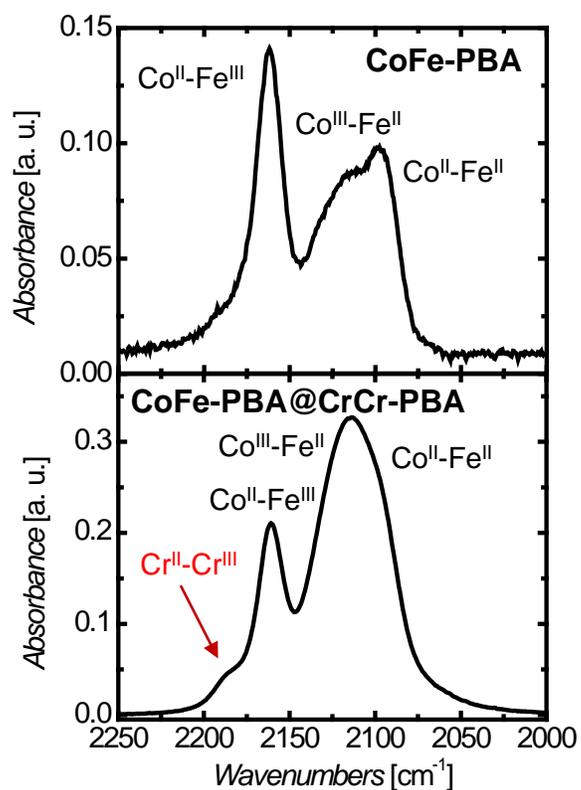
*{Rb<sub>0.2</sub>Co[Fe(CN)<sub>6</sub>]<sub>0.7</sub>}<sub>0.8</sub>@{K<sub>0.1</sub>Cr[Cr(CN)<sub>6</sub>]<sub>0.7</sub>}<sub>0.2</sub>·4H<sub>2</sub>O:* Reddish purple powder (26 mg; 10% yield). IR (KBr): 2185 (w, νCN, Cr<sup>II</sup>-NC-Cr<sup>II</sup>), 2165 (νCN, Co<sup>II</sup>-NC-Fe<sup>III</sup>), 2110 (broad, νCN, Co<sup>III</sup>-NC-Fe<sup>II</sup>, Co<sup>II</sup>-NC-Fe<sup>II</sup>) cm<sup>-1</sup>. EDS: 0.1:0.2:1.0:0.7:0.3 (K:Rb:Co:Fe:Cr); RbCoFe:KCrCr = 4.0. Anal. Calcd for: C, 17.26; H, 2.73; N, 20.13. Found: C, 17.55; H, 2.50; N, 19.70.

*Characterization.* IR spectroscopy was performed on a Nicolet 6700 Thermo Scientific spectrophotometer taking 16 scans per spectrum between 4000 and 400  $\text{cm}^{-1}$  with a resolution of 0.482  $\text{cm}^{-1}$ . Measurements were performed on powder samples (1 mg) mixed with KBr (200 mg) and pressed into a pellet at 20 MPa. Transmission electron microscopy (TEM) was performed on a JEOL-2010F high-resolution transmission electron microscope at 200 kV. The TEM samples were prepared by dropping 40  $\mu\text{L}$  of a water suspension containing 2 mg of product, dispersed by sonication, onto the grid (carbon film on a holey carbon support film, 400 mesh, copper from Ted-Pella, Inc.). Energy-dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments EDS X-ray Microanalysis System coupled to the high-resolution TEM. A total of four scans were recorded on different parts of the sample and then averaged to give relative atomic percentages for the metallic elements. Combustion analysis to determine carbon, hydrogen, and nitrogen (CHN) contents was performed at the University of Florida Spectroscopic Services Laboratory on an EA1108 CHNS-O manufactured by Fisons Instruments in 1995. The particle size distribution is determined from the size measurements of a minimum of 200 particles from multiple regions in one sample. The particle size is reported as the mean along with the standard deviation. The magnetic properties were investigated using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL7). The optical measurements were performed with the powder sample spread between two pieces of transparent tape and mounted in a homemade quartz optic sample rod<sup>s2</sup> connected to a tungsten halogen lamp (400 nm - 2200 nm) via a fiber optic patch cable. The field-cooled temperature dependence of the magnetization in the dark state was measured in an applied field of 100 G. After isothermal irradiation at 5 K and 100 G, irradiation was ceased and the long-lived light state established. The magnetization of the light state was measured on

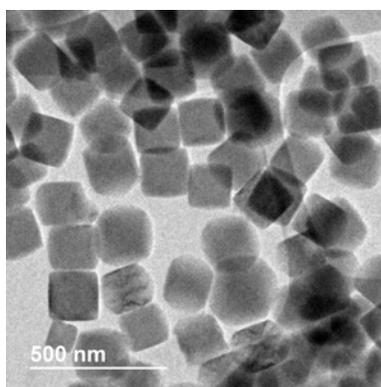
warming. The 80 K data were collected in the similar manner while only cooling the sample to 80 K. The sample measurement history affects the magnetic behavior to a certain extent. The power at the sample was around 4 mW. The CTIST region ( $T_{\uparrow} = 279$  K;  $T_{\downarrow} = 275$  K) was identified through the measurements of the sample in a gel cap inside a drinking straw using a commercial sample rod. The data were collected while cooling and warming in 100 G field in the 219 – 300 K region. The cooling rate for all the measurements was 2 K/min in the 100 - 300 K region and 3 K/min below 100 K.

(s1) Risset, O. N.; Quintero, P. A.; Brinzari, T. V.; Andrus, M. J.; Lufaso, M. W.; Meisel, M. W.; Talham, D. R. Light-Induced Changes in Magnetism in a Coordination Polymer Heterostructure,  $\text{Rb}_{0.24}\text{Co}[\text{Fe}(\text{CN})_6]_{0.74}@\text{K}_{0.10}\text{Co}[\text{Cr}(\text{CN})_6]_{0.70} \cdot n\text{H}_2\text{O}$  and the Role of the Shell Thickness on the Properties of Both Core and Shell. *J. Am. Chem. Soc.* **2014**, 136, 15660-15669.

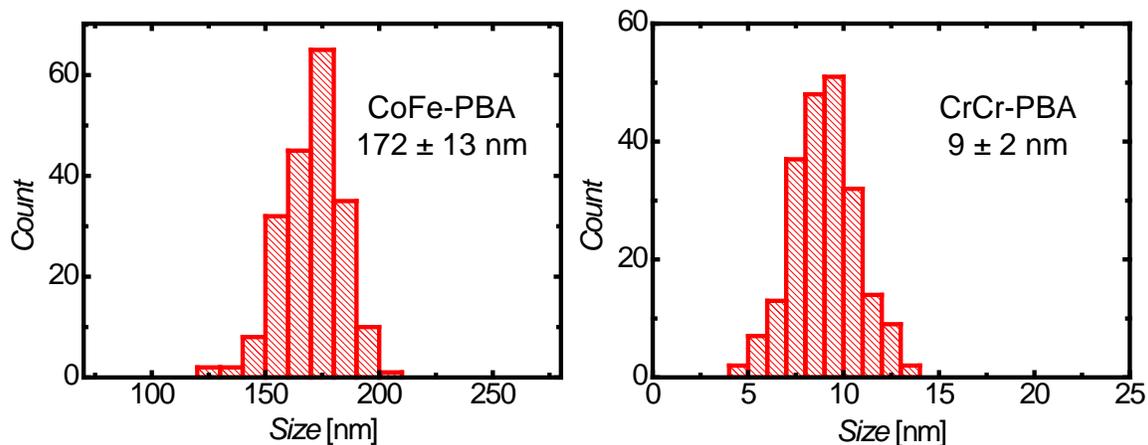
(s2) Knowles, E. S. Strain-Mediated Photomagnetic Effects in Heterostructured Nanoparticles of Prussian Blue Analogues, University of Florida, **2013**.



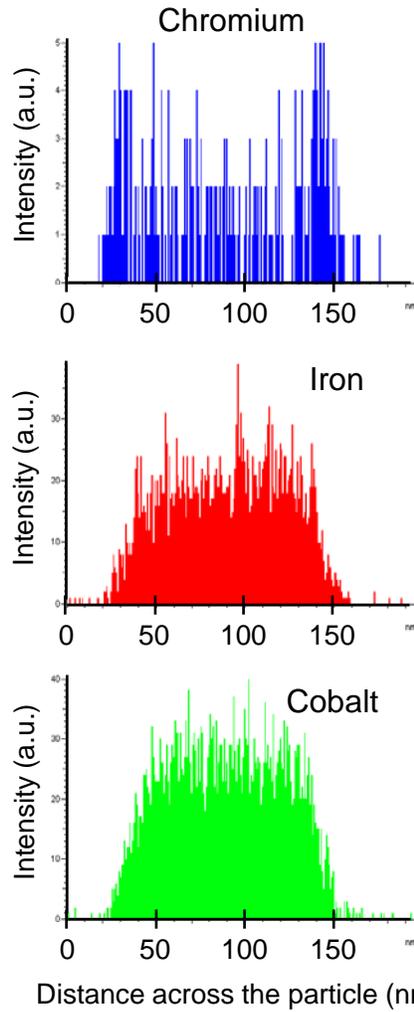
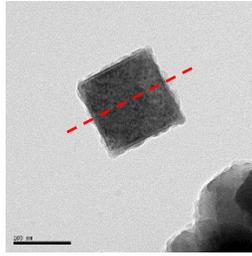
**Figure S1.** FT-IR spectra for CoFe-PBA cores (top) and CoFe-PBA@CrCr-PBA heterostructures (bottom). For the heterostructures, a signal appears at 2185 cm<sup>-1</sup>, characteristic of CrCr-PBA. Furthermore, a change occurs in the oxidation states of the transition metals in CoFe-PBA upon growth of CrCr-PBA nanoparticles.



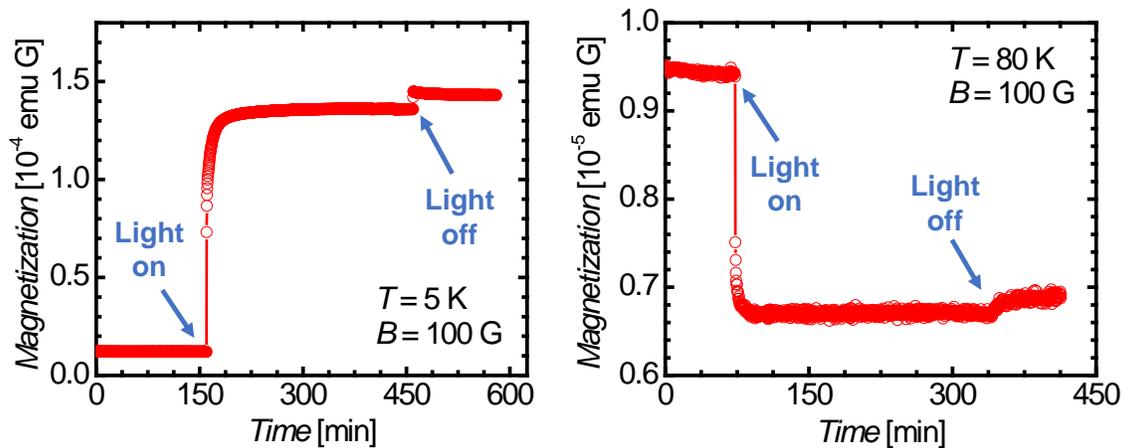
**Figure S2.** TEM image of CoFe-PBA particles. Scale bar is 500 nm.



**Figure S3.** Size dispersion for CoFe-PBA cores and CrCr-PBA nanoparticles in CoFe-PBA@CrCr-PBA heterostructures. The particle size is reported as the mean along with the standard deviation.



**Figure S4.** EDS line scan on an individual CoFe-PBA@CrCr-PBA particle. Data represent the counts for each element detected as a function of the position of the electron beam across the particle. EDS line scans confirm the growth of CrCr-PBA nanoparticles on the CoFe-PBA core.



**Figure S5.** Left: Time dependence of the magnetization upon irradiation at 5 K. The light was turned on at 160 min and turned off at 460 min, several hours after the magnetization reaches saturation. Right: Time dependence of the magnetization upon irradiation at 80 K. The light was turned on at 73 min and turned off at 342 min, several hours after the magnetization reaches saturation.