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Optical control of magnetization in a room-temperature magnet: V-Cr Prussian blue analog

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We report reversible photoinduced magnetic phenomena for a V-Cr Prussian blue analog ($T_c \sim 350$ K). This molecule-based magnet exhibits a decrease in magnetization upon illumination with UV light ($\lambda \sim 350$ nm) and reaches a metastable state that has a long lifetime at low temperatures ($>10^6$ s at 10 K). This photoexcited magnetic state totally recovers back to the ground state by warming above 250 K, and partially recovers with green light ($\lambda \sim 514$ nm) illumination. The effect of green light is triggered only when the sample is previously UV irradiated, suggesting a hidden metastable magnetic state. The photoinduced magnetic effects are proposed to originate from structural distortion that alters the magnetic exchange coupling and/or anisotropy.

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Molecule-based magnets are a relatively new class of materials targeting control of the magnetic properties at microscopic and/or molecular levels.[1,2] These magnetic materials are promising candidates for future applications of spin electronics due to their spin-resolved electronic structures[3] and chemical modulations of magnetic and electronic properties.[1,4] One of the unique properties of these systems is the magnetic bistability,[5,6] which may be controlled by optical excitations[7,8] and other external stimuli.[9,10] The optical control of magnetic properties in these systems add a new dimension for future applications of magnetoelectronics and optoelectronics. However, to date, the reported coexistence of long-range magnetic order and photoinduced magnetism have been limited to low magnetic ordering temperatures.[10] It is important to identify light-induced magnetic properties in a material that exhibits room-temperature magnetic ordering, and to address possible underlying mechanisms in order to develop materials with desired magnetic properties. Here, we report the first observation of reversible photoinduced magnetic phenomena in a V-Cr Prussian blue analog, one of the few room-temperature molecule-based magnets[11–13] developed so far.

The light-induced magnetic bistability was first reported in transition-metal complexes.[14] Since then there has been an increasing interest in optical control of magnetic properties both in organic and inorganic systems.[15,16] One of the extensively studied optically tunable molecule-based magnet family is Prussian blue analogs: $A_xM'_y[M''(CN)_6]_z \cdot nH_2O$ (A is an alkali metal ion, M' and M'' are transition-metal ions).[17–20] These cyanobridged bimetallic compounds have a face-centered-cubic lattice in which the transition metals are interconnected via CN bridges. The alkali-metal ions and water molecules are interstitial with respect to the extended network structure. $A_xCo_y[Fe(CN)_6] \cdot zH_2O$ has an ordering temperature (T_c) ~ 12 K and was reported to have light-induced changes between magnetic states with coexisting long-range magnetic ordering.[5,8,21] The photoinduced magnetism in $A_xCo^{III}_y[Fe^{II}(CN)_6] \cdot zH_2O$ originates from electron transfer between the Fe^{II} and Co^{III} ions that changes the total spin value.[8] Several other Prussian blue structured molecule-based magnets with $T_c < 50$ K also exhibit photoinduced magnetism.[20,22–25] Subsequent studies introduced optical control of magnetization in an organic-based magnet $Mn[TCNE]_2 \cdot z(CH_2Cl_2)$ (TCNE: tetracyanoethylene) that has a $T_c \sim 70$ K.[26] The effects of illumination for $Mn[TCNE]_2$ were attributed to change in bond lengths and angles of $[TCNE]^-$ which alter the exchange coupling between the spins of Mn ions and the organic radical. Recently photoinduced magnetism in a room-temperature molecule-based magnet has been achieved for $V(TCNE)_x (x \sim 2) (T_c \sim 400$ K), and was attributed to photoinduced change in magnetic anisotropy.[6,27] The photoinduced magnetic effects in $V(TCNE)_x$ were observed up to 200 K and only reversible upon heating the sample above 250 K.

Challenges still persist in the optical control of magnetism, as it requires both long-range magnetic order and sustained reversible illumination effects at high temperatures. In order to overcome these challenges, understand the photoinduced magnetism mechanisms, we sought to identify light-tunable magnets. In this study, we report reversible photoinduced magnetic phenomena in a V-Cr Prussian blue analog, which is a member of a family that exhibits ferrimagnetic ordering up to ~ 373 K.[11–13] The magnetization of V-Cr Prussian blue structured molecule-based magnet decreases upon UV-light excitation and partially recovers with green light excitation. The photoexcited state has a long lifetime at low temperatures suggesting light-induced trapping into a metastable state. The photoinduced magnetism cannot be explained by the electron-transfer model that is commonly observed in Prussian blue analogs[10,19,28] but is proposed to originate from structural distortion that changes magnetic exchange coupling and/or anisotropy. We also present detailed magnetic properties of the V-Cr Prussian blue analog in response to static and dynamic magnetic fields.

A sample of nominal $K_{1.54}V^{II}_{0.77}V^{III}_{0.08}[Cr^{III}(CN)_6](SO_4)_{0.16} \cdot 3.1H_2O$ (**1**) composition as determined by x-ray photoemission spectroscopy was synthesized as previously reported.[12] Like other members of this family, **1** is highly structurally disordered and inhomogeneous. In addition to conventional defects in Prussian blue structure, **1** incorporates SO_4^{2-} ions. For photoinduced magnetism studies, samples were prepared inside a glove box by dispersing and grinding **1** powder in

O_2-free Nujol oil that is chemically inert and commonly used for mull preparation for IR spectroscopy. The dispersion of **1** was then filtered through a 10 μm filter. Due to filtering, the mass of the dispersed samples of **1** could not be determined. The samples were then sealed in quartz tube under vacuum, in order to prevent oxidation. The dc magnetization was measured with a Quantum Design Magnetic Property Measurement System (MPMS-XL) magnetometer. For ac susceptibility measurements Quantum Design Physical Property Measurement System (PPMS) 6000 with an ACMS option was used. Illumination of the sample for both ac and dc magnetization studies is provided through fiber optic cables that are integrated to sample holders. For light illumination at 514 nm single line and 350 nm UV multiline, an argon laser (Coherent Innova 300) was used. UV-vis optical absorption of **1** was probed with a Varian 5000 spectrometer.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations (samples were cooled down from 275 K) of both powder sample and Nujol dispersed sample of **1** are similar to those previously reported for compositionally related ferrimagnets[11,12] ($T_c \sim 350$ K). The high magnetic ordering temperature was proposed to originate from the strong antiferromagnetic interaction between the t_{2g}-like spins of $V^{II}(S=3/2)$, $V^{III}(S=1)$, and $Cr^{III}(S=3/2)$ via the bridging cyanides.

Despite the room-temperature magnetic ordering, no photoinduced magnetism study for V-Cr Prussian blue analogs have been reported. To perform a photomagnetic study, Nujol dispersed samples of **1** were used. Dispersing and grinding in oil reduces the grain size, which allows light penetration into a larger fraction of the sample. In addition to dispersed samples, thin pressed powder samples of **1** were studied for photoinduced magnetism. Although photoinduced magnetism was observed in the powder samples, detailed photoinduced magnetization studies could not be done due to the weak magnetic signal resulting from the limited sample amount. The ZFC and FC magnetization data for both the powder and dispersed samples display similar behavior at low temperatures (Fig. 1). The ZFC and FC magnetizations of both samples exhibit a strong irreversibility below 25 K indicating an intrinsic magnetic property of **1**. Moreover, the temperature at which the ZFC magnetization deviates from FC magnetization (irreversible temperature, T_{irr}) shifts to lower temperatures with increasing applied magnetic field. Both the strong irreversibility and the magnetic field dependent T_{irr} suggests that the spins start to freeze, and the system enters a spin-glasslike state from the ferrimagnetic state at low temperatures. In dispersed samples, the ZFC and FC magnetizations show a peak at around 200 K at low magnetic fields and start to diverge as the temperature is lowered further [Fig. 1(b)]. The presence of the peak and divergence can be explained by the freezing of the Nujol oil ($T_f \sim 200$ K) in which the magnetic grains (diameter <10 μm) were dispersed. Freezing of the oil fixes the segregated magnetic particles at random orientations with respect to their easy axis and increases the magnetic anisotropy. Therefore, the magnetization is suppressed at low magnetic fields and a higher magnetic field is needed to overcome the anisotropy. When the applied magnetic field is larger than 300 Oe, no suppression in magnetization is observed below 200 K. Above the freezing temperature of Nujol oil, the magnetic particles can rotate with the magnetic field and ZFC and FC magnetizations merge even at low magnetic fields.

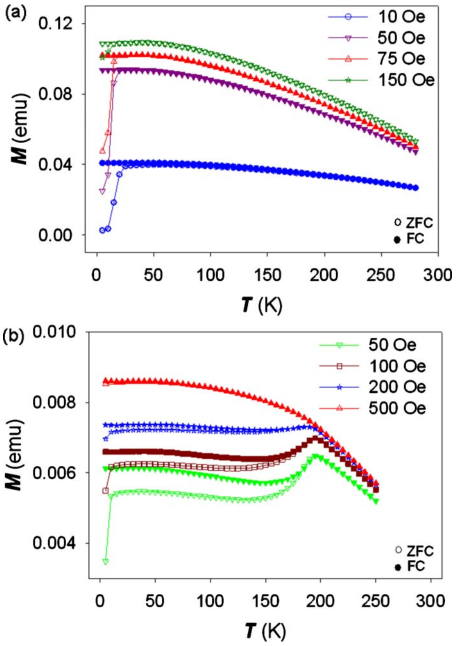

FIG. 1. (Color online) ZFC and FC magnetizations at different applied magnetic fields for (a) powder sample and (b) Nujol-dispersed sample of **1**. At low T (<25 K) and low H, both powder and dispersed samples display strong irreversibility between ZFC and FC magnetizations. In the dispersed sample an additional bifurcation is observed at around 200 K.

In order to identify the spin-glasslike state in **1**, in addition to ZFC/FC irreversibility and magnetic field dependent T_{irr}, frequency dependency of ac susceptibility and slowing down of the spin dynamics should be verified. The temperature dependences of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities exhibit frequency-dependent peaks for powder samples of **1** and shoulders for Nujol dispersed samples of **1** below 25 K. The suppressed ac susceptibility peak in the Nujol-dispersed samples of **1** may be attributed to the high blocking energy due to freezing of the Nujol oil around 200 K, as observed in the dc magnetization. For the Nujol-dispersed sample of **1**, τ_c was determined from complex ac susceptibility (Fig. 2),

$$\chi = \chi' + i\chi'' = \chi_s + \frac{\chi_0 + \chi_s}{1 + (i\omega\tau_c)^{1-\alpha}} \tag{1}$$

through a Cole-Cole analysis, where α is the distribution width of relaxation times around the median, and χ_0 and χ_s are the isothermal ($\omega=0$) and adiabatic ($\omega \to \infty$) susceptibilities, respectively.[29] Here, τ_c corresponds to the frequency exhibiting the maximum of χ'' at a fixed temperature and the Cole-Cole analysis allows us to extract τ_c when the frequency of χ''_{max} is close to or inside the measurement window ($11 \leq f \leq 10\,000$ Hz). For **1** dispersed in Nujol oil, τ_c increases with decreasing temperature [inset Fig. 2(b)] demonstrating the slowing down of the spin dynamics below 25 K, as expected in spin glasses.[30] Moreover, α is estimated to be

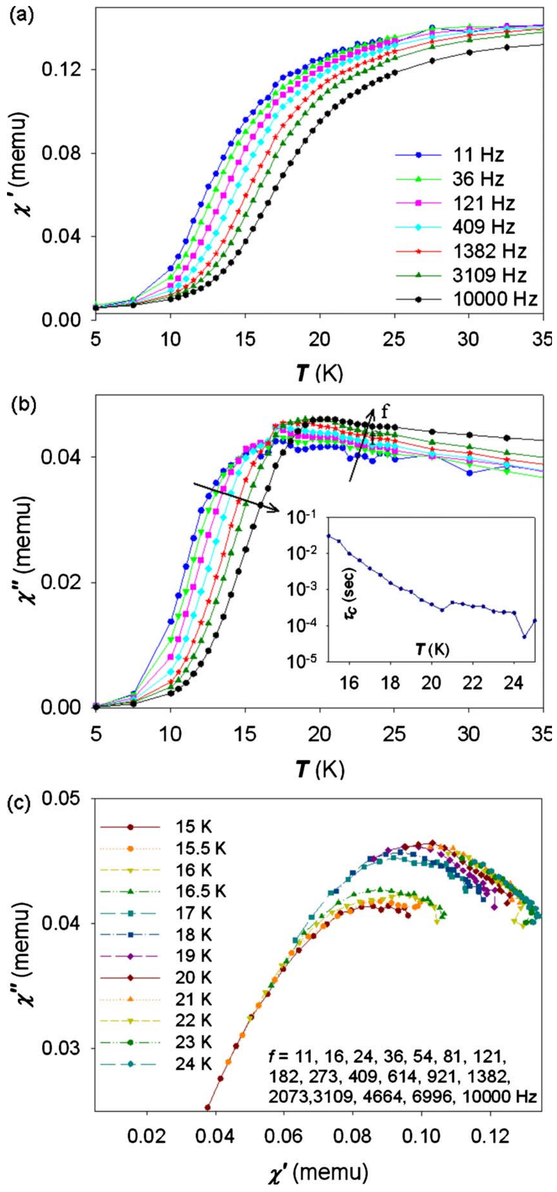

FIG. 2. (Color online) (a) χ' and (b) χ'' ac susceptibilities for frequencies $11 \le f \le 10\,000$ Hz for **1** dispersed in Nujol oil. Inset (b); temperature dependence of mean spin-relaxation time, τ_c, for **1**. (c) Cole-Cole plot (χ' vs χ'') of Nujol-dispersed sample of **1** at different temperatures.

around 0.72–0.85, that is consistent with previous reports for spin glasses.[31] A power-law fitting of the mean relaxation time $[\tau_c \propto \tau_0 (T/T_g - 1)^{-z\nu}]$ gives $T_g \sim 12.3$ K, $z\nu \sim 4.5$ (in the range of typical spin glasses[30]) and $\tau_0 \sim 5 \times 10^{-5}$ s. Here, τ_0 is much smaller than the typical values ($\sim 10^{-8} - 10^{-11}$ s) for canonical spin-glass systems, reflecting evolution of cluster spin-glass order from correlated spins. Similar τ_0 values were reported previously for cluster spin-glass systems.[31] Moreover, because of the observed reentrance behavior (transition from ferrimagnet to spin-glasslike state) cluster glass behavior is expected in **1**.[30,32]

Upon optical excitation of **1** in Nujol oil with multiline UV light ($\lambda \sim 350$ nm) for 60 h at 10 K, the FC magnetization decreases $\sim 2\%$ [Fig. 3(a)]. The observed change in magnetization is an order of magnitude smaller than that for $A_x\text{Co}_y[\text{Fe(CN)}_6] \cdot z\text{H}_2\text{O}$ (Ref. 5) suggesting that the photoinduced effects occurred only in the restricted (disordered and/or inhomogeneous) regions of **1**. The FC magnetization sustains its photoinduced value for a long time ($>10^6$ s) after illumination. This lifetime of the photoexcited state is similar to the previously reported lifetimes in $A_x\text{Co}_y[\text{Fe(CN)}_6] \cdot z\text{H}_2\text{O}$,[8] and suggests that the system is trapped in a metastable state. Partial recovery from the photoinduced state is observed when the system is excited with monochromatic 514 nm green light [see Fig. 3(b)]. The lack of full recovery upon illumination with green light might be due to smaller penetration depth and limited accessibility of 514 nm light compared to 350 nm light. The effect of 514 nm light is only observed when the sample is previously UV irradiated, reflecting a "hidden" photoexcited metastable state induced by illumination with UV light. Similar reversible photoinduced magnetic effects are reported for $A_x\text{Co}_y[\text{Fe(CN)}_6] \cdot z\text{H}_2\text{O}$.[8]

Full recovery from the photoinduced state to ground state is observed without any degradation when the system is heated above 250 K. Thermal activation ($T > 250$ K) allows the system to relax back to its initial state from the metastable state. The temperature and magnetic field dependences of the dc magnetization for the initial ground state, photoexcited state, and fully recovered ground state in the dispersed sample are shown in Figs. 3(c) and 3(d).

The $\chi'(T)$ and $\chi''(T)$ data at 3330 Hz are displayed in Figs. 3(d) and 3(e) for the ground and photoinduced states of the dispersed sample. Optical excitation of **1** with UV light for 60 h substantially decreases both χ' and χ'' (as much as 25% and 40%, respectively) and shifts the peak to lower temperatures. The shoulders in the temperature dependence of χ' and χ'' at ~ 200 K are also attributed to an increased magnetic anisotropy due to freezing of the oil in which **1** was dispersed.

The photoinduced magnetism in most Prussian blue analogs such as $A_x\text{Co}_y[\text{Fe(CN)}_6] \cdot z\text{H}_2\text{O}$ was attributed to electron transfer between the transition-metal ions.[10,19,28] However, this electron-transfer model cannot explain the reversible photoinduced effects in **1**, as the total spin value remains unchanged within this model after optical excitation. Moreover, photoinduced effects in conventional Prussian blue analogs are triggered by visible light (450–650 nm) illumination, which excites the charge-transfer band. In contrast, no change in the magnetization was observed for **1** when illuminated by visible light ($\lambda = 488$, 514, or 650 nm). The fact that the initial photoinduced effect is initiated by UV light suggests that the observed reversible photoinduced magnetism is due to ligand to metal charge transfer (LMCT). This LMCT will change the electron distribution between the metal and ligand, and may result in structurally distorted metastable state in **1**. Similar LMCT-induced structural distortions and photoinduced magnetism were previously reported for cyanobridged $3d$-$4f$ heterobimetallic complexes.[33,34] Another possible explanation for photoinduced magnetism might be local heating due to UV light radiation, which allows magnetic grains to rotate in an applied magnetic field in the Nujol. However, this can be excluded since the grain rotation leads to an increase in the

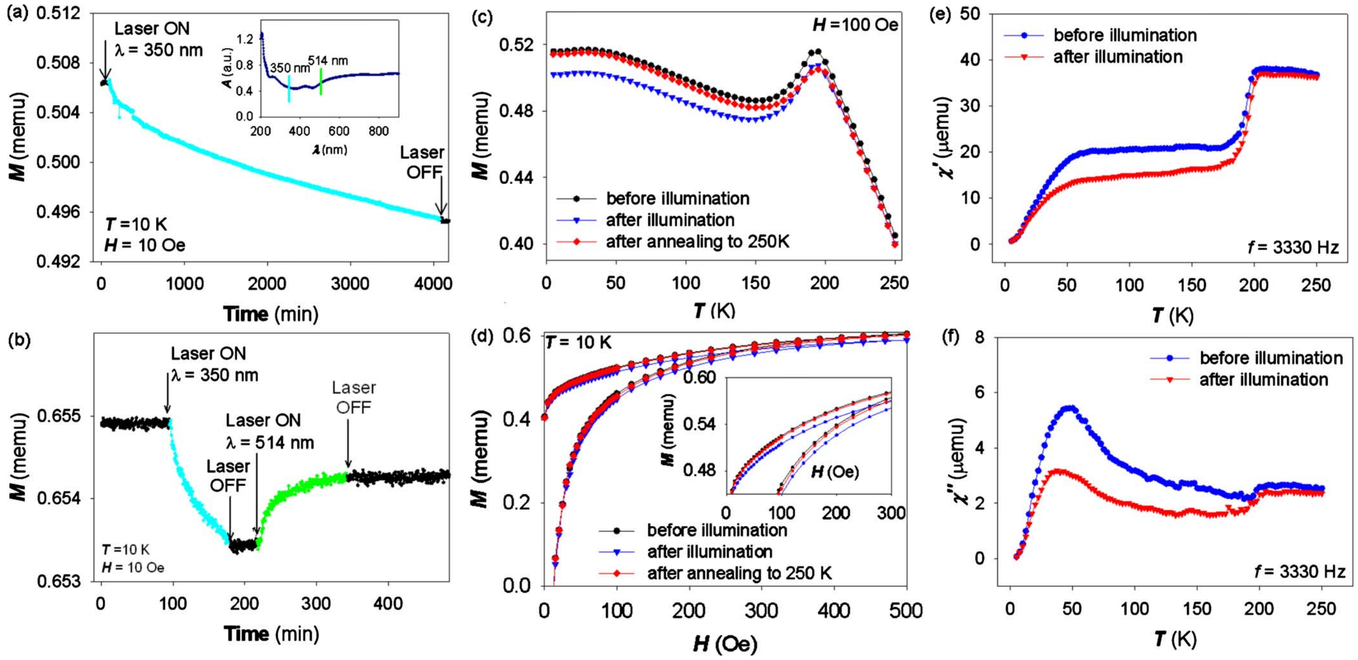

FIG. 3. (Color online) (a) Decrease in the FC magnetization upon excitation with UV light for **1** dispersed in Nujol oil. Inset: UV-vis spectrum of **1**. (b) Partial recovery of magnetization upon subsequent illumination with 514 nm light from a photoexcited state. (c) Temperature and (d) field dependence of magnetization before illumination, after illumination for 60 h with UV light and after heating the sample up to 250 K, for **1** dispersed in Nujol. (e) χ' and (f) χ'' for the ground and photoinduced states (UV light excitation for 60 h) for **1** dispersed in Nujol at 3330 Hz. The light intensity is $\sim 12\ \mathrm{mW/cm^2}$ for both illuminations with 350 and 514 nm radiation.

magnetization. Here, we propose that the photoinduced effects are due to structural distortion in ligand-metal bond length and the symmetry of the molecule by LMCT that changes the exchange coupling and/or magnetic anisotropy.

In conclusion, we report reversible photoinduced magnetization in a room-temperature molecule-based magnet (**1**). Illumination with UV light suppresses magnetization, whereas subsequent illumination with green light partially recovers the magnetization. The effects of illumination are maintained up to 200 K but are completely erased when the sample is heated above 250 K. This reversible photoinduced magnetism is proposed to originate from LMCT-induced structural change which alters the exchange coupling and/or magnetic anisotropy in **1**. Our study suggests the possibility of developing new forms [such as nanoparticles, Langmuir-Blodgett (LB) films] of optically tunable room-temperature magnet **1**.

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