Photoinduced Single-Molecule Magnet Properties in a Four-Coordinate Iron(II) Spin Crossover Complex

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S *Supporting Information*

ABSTRACT: The four-coordinate Fe(II) complex, PhB-(MesIm)$_3$Fe-N=PPh$_3$ (**1**) has been previously reported to undergo a thermal spin-crossover (SCO) between high-spin (HS, S = 2) and low-spin (LS, S = 0) states. This complex is photoactive below 20 K, undergoing a photoinduced LS to HS spin state change, as determined by optical reflectivity and photomagnetic measurements. With continuous white light irradiation, **1** displays slow relaxation of the magnetization, i.e. single-molecule magnet (SMM) properties, at temperatures below 5 K. This complex provides a structural template for the design of new photoinduced mononuclear SMMs based on the SCO phenomenon.

Figure 1. Schematic and ball-and-stick (from the single-crystal X-ray crystal structure)[10] views of PhB(MesIm)$_3$Fe-N=PPh$_3$ (**1**).

Light irradiation offers a method for switching the magnetic bistability of transition metal complexes, which may be manifested as spin-crossover (SCO),[1] single-molecule magnet (SMM)[2] or single-chain magnet (SCM)[3] properties. While light-induced SCO in molecular complexes is well-known,[4] similar activation of molecular magnets has so far been restricted to a few systems discovered in the past 3 years. Specifically, light irradiation of certain Fe(μ-CN)Co chains triggers an intermetallic electron transfer event between diamagnetic {Fe$^{II}_{LS}$-CN-Co$^{III}_{LS}$} and paramagnetic {Fe$^{III}_{LS}$-CN-Co$^{II}_{HS}$} states, switching their SMM or SCM behavior between on or off states.[5] More recently, it has been shown that the highest symmetry phase of the classic Fe(II) SCO salt, [Fe(1-propyltetrazole)$_6$](BF$_4$)$_2$, behaves as a single-molecule magnet in its photoexcited S = 2 state, the first example of SMM behavior arising from photoinduced SCO.[6] The development of molecules that show SMM resulting from photoinduced SCO has been thwarted by the fact that no complexes exhibiting both thermally induced SCO and SMM behaviors were known until very recently. The only example is an Fe(III) complex, (PNP)FeCl$_2$ (PNP = N[2-P(CHMe$_2$)$_2$-4-MeC$_6$H$_4$]$_2^-$), in which the S = 3/2 state shows SMM behavior as well as thermal SCO to a high temperature S = 5/2 state, however no photoinduced SCO was described.[7]

The slow relaxation of magnetization in a SMM originates from an energy barrier to its spin reversal (Δ) that is related to an uniaxial Ising-like magnetic anisotropy (D) acting on a high-spin ground state (S), $\Delta = |D|S^2$ (with $H = DS_z^2$).[2] While for a long time considerable efforts were focused on preparing polynuclear metal-ion complexes that maximize S, more recently alternate strategies toward increasing the magnetic anisotropy have been successful. One such strategy stems from the realization that low-coordinate environments can engender large uniaxial anisotropies, leading to the discovery of mononuclear iron complexes that display slow relaxation of their magnetization.[8,9] The prototypical example of this approach is the field-induced slow relaxation of the magnetization observed for four-coordinate, three-fold symmetric trigonal pyramidal iron(II) pyrrolide complexes.[8]

Concurrent with these developments in low-coordinate iron-based SMMs, we have recently shown that the low-coordinate Fe(II) phosphoraniminato complex PhB(MesIm)$_3$Fe-N=PPh$_3$ **1** (Figure 1) undergoes a reversible SCO between low spin (S = 0) and high spin (S = 2) states in solid state, with $T_{1/2}$ = 81 K.[10] The unique properties of this complex, in which a four-coordinate, three-fold symmetric iron center undergoes SCO, led us to hypothesize that it may display photoinduced SCO and possibly photoinduced SMM (Photo-SMM) behavior. In this contribution, we report our success in this endeavor, showing first, that the paramagnetic S = 2 state of **1** can be photoinduced below 20 K, and second, that low-temperature white light irradiation in the presence of an applied dc field results in SMM behavior. Intriguingly, the molecular architecture of **1** raises the prospect of modifying the magnetic performance through suitable synthetic modifications.
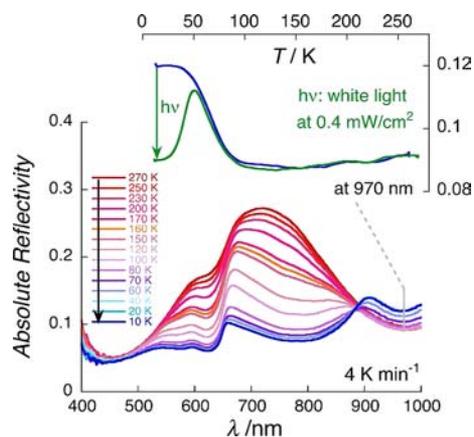
Figure 2. Optical reflectivity spectra of **1** at selected temperatures between 270 and 10 K (cooling mode) in the 400−1000 nm spectral range. The experiment was performed in the dark except during the spectrum acquisition (spectroscopic white light during 15 s, $P = 0.4$ mW/cm^2). Inset: Temperature dependence of the optical reflectivity at 970 nm of **1** between 270 and 10 K on cooling in the dark (blue) and after exposure to white light (2 h; $P = 0.4$ mW/cm^2) at 10 K (green).

Figure 3. Temperature dependence of the χT product in the dark at 1000 Oe between 120 to 1.8 K for a polycrystalline sample of **1** in cooling (blue) and heating (red) modes at 0.3 K/min, and after irradiation under white light at 10 K for 18 h (green). Inset: time evolution of the χT product during irradiation with a white light source at 10 K and 1000 Oe ($P = 0.3$ mW/cm^2).

Previously, we investigated the SCO process in complex **1** by temperature-dependent magnetometry and Mössbauer spectroscopy of a sample crystallized from toluene.[10] In this work, we find similar results for a sample of **1** crystallized from THF, with $T_{1/2} = 81$ K (Figure S1 in Supporting Information [SI])[11] being same as previously reported. The SCO process was also monitored through the thermal evolution of the solid-state optical reflectivity spectrum. At room temperature, three bands are observed at 970, 620, and 440 nm. Cooling from 270 to 100 K results in a smooth decrease in the absolute reflectivity over most of the spectrum (Figure 2), revealing a significant increase in the absorbance and strong thermochromism of **1** with the growth of a new band around 780 nm (Figure S2 in SI). Below 100 K, the observed spectral changes between 500 and 1000 nm mainly originate from the SCO phenomenon with the equilibrium between the two spin states leading to the appearance of an isosbestic point at 890 nm (Figures 2 and S2 in SI). The thermal evolution of the absolute reflectivity at 970 nm allows the SCO phenomenon to be probed over the whole temperature range (Figures 2 and S3 in SI) and is in agreement with the χT vs T data (Figure 3). Heating the sample leads to a complete reversal of these spectral changes, and therefore, as with the magnetic data, there is no thermal hysteresis associated with the SCO. Irradiating the sample with white light (0.4 mW/cm^2) at 10 K for 2 h results in the reappearance of the spectrum associated with the HS state (Figure S4 in SI). The HS state is metastable, and increasing the temperature (at 4 K min^{-1}) to 40 K results in recovery of the spectrum for the thermodynamically favored LS state (inset Figure 2). Thus, the optical reflectivity reveals the high photosensitivity of **1** (at least at the sample surface) with white light irradiation leading to formation of a metastable HS state at 10 K.

The photoinduced SCO was also investigated by dc magnetic measurements (Figure 3). Irradiating the sample with white light (0.3 mW/cm^2) at 10 K for 18 h causes the χT product to increase from 0.1 to 2.7 cm^{3}K/mol (inset, Figure 3), consistent with photoinduced LS-to-HS state conversion of a large majority (>70%) of the bulk sample. Heating the metastable photogenerated HS state in the dark from 2 to 120 K causes the

Figure 4. Frequency dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) components of the ac susceptibility for **1** recorded at 2.3 K at dc fields between 0 and 3000 Oe. Measurements were conducted with a 3 Oe ac field oscillating between 1 and 1500 Hz and with continuous white light irradiation ($P = 5 \mu$W/cm^2). The solid lines are the best fits of the data using a generalized Debye model. Inset: Field dependence of the characteristic frequency at 2.3 K for **1** deduced from the $\chi''(\nu)$ plots (main figure).

χT product to decrease abruptly between 18 and 26 K, at which temperature all the material is in its thermodynamically favored LS state.[12] The optical reflectivity and photomagnetic data therefore establish that **1** is the first example of a four-coordinate complex that displays light-induced LS-to-HS spin-crossover, which is usually observed in six-coordinate Fe(II) complexes containing nitrogen-based donors.[1,4] Importantly, **1** does not decompose upon irradiation as evidenced by the fully reversible thermal behavior of the optical and magnetic properties following irradiation. However, in contrast to other photomagnetic complexes, where relaxation from the metastable HS state to the stable LS state typically occurs between
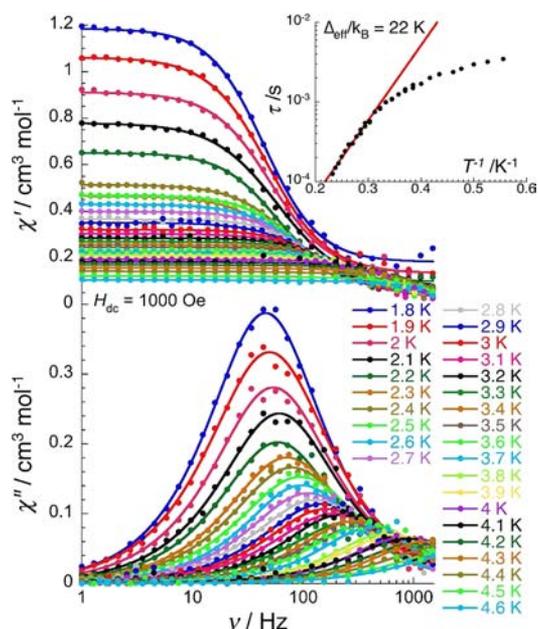
Figure 5. Frequency dependence of the in-phase (top, χ') and out-of-phase (bottom, χ'') susceptibility recorded on a polycrystalline sample of **1** at temperatures between 1.8 and 4.6 K. Measurements were made in the presence of an applied dc field of 1000 Oe and with continuous white light irradiation ($P = 5$ μW/cm^2). The solid lines are the best fits of the data using a generalized Debye model. Inset: Temperature dependence of τ plotted as τ vs $1/T$ for **1** deduced from ac measurements at 1000 Oe (main figure). The red solid line corresponds to the least-squares fit of the data to an Arrhenius law (see text).

50 and 80 K,[1b] relaxation in four-coordinate **1** happens at a significantly lower temperature (i.e., ~23 K at 0.4 K/min). Thus, the photoinduced HS state in **1** has a smaller energy barrier to relaxation than conventional Fe(II) SCO complexes.

Simple molecular orbital considerations predict the HS ($S = 2$) state of **1** to be magnetically anisotropic.[8−10] This consideration, along with the observed photomagnetic properties of **1** (vide supra), prompted us to investigate the magnetization dynamics of the photoinduced HS state. Since this photogenerated state was observed to rapidly decay above 2.5 K, the magnetization dynamics were measured in the presence of continuous white light irradiation.[13] Low-power (5 μW/cm^2) irradiation was used to minimize thermal heating (measured at 0.4 K below 5 K). In these conditions and in zero dc field, the ac susceptibility does not show an out-of-phase component above 1.8 K for ac frequencies up to 1.5 kHz. However, similar to other mononuclear Fe(II) SMMs,[8,9] application of a dc field leads to the detection of a single-mode out-of-phase signal (Figure 4), revealing the slow dynamics of the magnetization in the photoinduced HS state of **1**.

The field dependence of the characteristic relaxation frequency reveals that the relaxation time, τ, is maximum for an optimum applied dc field of 1000 Oe (inset Figure 4) indicating a competition between the thermally activated and quantum tunneling relaxation regimes. Variable frequency ac susceptibility data were thus collected under 1000 Oe between 1.8 to 5 K (Figure 5). Relaxation times were extracted by fitting the ac data to the generalized Debye model. The τ vs T^{-1} Arrhenius plot (inset Figure 5) shows a linear region above 3 K where the magnetization relaxation is thermally activated with a

pre-exponential factor, τ_0, of 8.7×10^{-7} s and an energy gap of 22(1) K (15 cm^{-1}) leading to rough an estimation of D_{Fe}/k_B around −5.5 K (3.8 cm^{-1}). Due to the possible influence of the quantum tunneling of the magnetization (QTM) even above 3 K, these energy gap and D_{Fe} values are certainly underestimated.[14] For instance, in other pseudotetrahedral Fe(II) complexes, negative D values as large as ~−72 K (−50 cm^{-1}) have been reported.[8,9a,15] Below 3 K, τ becomes progressively temperature independent as expected in the vicinity of a QTM regime with a quantum time estimated at about 4×10^{-3} s.

In summary, we have described a four-coordinate Fe(II) spin-crossover complex that behaves as a photoinduced single-molecule magnet (Photo-SMM). While this behavior is currently only observed below 5 K under an applied dc field, it is likely that the synthetic flexibility inherent in the design of the complex will provide the opportunity to tailor both the photomagnetic and magnetization dynamics properties. Studies to investigate the impact of the phosphine moiety of the phosphoraniminato ligand on the photomagnetic behavior are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(11) The x_{HS} vs T plot was fitted using a regular solution model including the presence of elastic interactions between Fe(II) complexes, giving ΔH = 6.5 kJ/mol, ΔS = 79.7 J/K/mol, and W = 1.17 kJ/mol. These parameters are slightly different from those reported in ref 10, where elastic interactions were not considered.

(12) The photoinduced HS state relaxes at different temperatures due to the different heating rates of the two techniques: 4 K/min for reflectivity measurements and 0.4 K/min for magnetic measurements.

(13) Initial measurements revealed a decay in the intensity of the photoinduced ac mode in the dark. This susceptibility relaxation was minimized by using continuous white light irradiation (P = 5 μW/cm^2).

(14) The curvature of the τ vs $1/T$ plot observed below 3 K is indicative of a crossover between the thermally activated and the QTM regimes of relaxation. Thus, the energy gap of the activated regime has been estimated from data above 3 K. Nevertheless, due to the quantum effects which are minimized but still probably effective above 3 K, this energy gap is expected to be lower than the theoretical value of a purely thermally activated regime.

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