A Photochromic Molecule-Based Magnet†

Sophie Bénard, Eric Rivière, and Pei Yu*

Laboratoire de Chimie Inorganique, Bât. 420, UMR 8613, Université Paris Sud, 91405 Orsay, France

Keitaro Nakatani and Jean François Delouis

PPSM, UMR 8531, Ecole Normale Supérieure de Cachan, 94235 Cachan, France

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A molecule-based magnet of formula (SP)MnCr$(ox)_3$·H_2O has been synthesized, where SP^+ stands for a new *N*-methylated pyridospiropyran cation and ox^{2-} represents the oxalate anion. The compound orders ferromagnetically at 5.5 K and exhibits crystalline-state photochromism. The main spectrokinetic data of the UV-induced open form of SP^+ are strongly modified in (SP)MnCr$(ox)_3$·H_2O as compared to those found in (SP)I. The reversible photoreaction of SP^+ does not modulate the critical temperature of the long-range ferromagnetic order in (SP)MnCr$(ox)_3$·H_2O but modifies in a significant way its hysteresis loop.

Introduction

Both organic photochromic molecules and molecule-based magnets have received much attention over the past decade for their potential applications.[1,2] In this context, design of molecule-based materials associating ferromagnetism with an organic photochromic component is of particular interest, because photoinduced structural changes via the organic photochrome may lead to photoresponsive magnets. Actually, other kinds of photomodulation of the magnetic behaviors have been recently reported in several molecule-based magnets and also in a hybrid organic−inorganic system.[3−5] On the other hand, the photochromic properties of the organic photochrome in such unusual systems are also interesting to study. With these aims in mind, we present in this work our approach to the design of a well-ordered 2D molecule-based magnet incorporating an organic photochrome.

The 2D oxalate (ox) bridged bimetallic salts AMM′$(ox)_3$ (A = bulky organic ammonium or phosphonium; M = Mn^{II}, Cu^{II}, Fe^{II}, Co^{II}, or Ni^{II}; M′ = Cr^{III}, Fe^{III}, or Ru^{III}) are known to behave as molecule-based magnets with T_c ranging from 5 to 44 K.[6−10] Moreover, the substitution of the simple ammonium or phosphonium, located between the magnetic layers $[MM'(ox)_3]_n^{n-}$ (shown in Scheme 1 (top) for M = Mn^{II} and M′ = Cr^{III}), proved to be an efficient way of introducing another property into these magnets.[11−13] We report herein the use of a cationic spiropyran (SP^+; Scheme 1, bottom) in the design of a novel system: (SP)MnCr$(ox)_3$·H_2O that associates the ferromagnetic properties of the $[MnCr(ox)_3]_n^{n-}$ layer with the photochromic properties of SP^+. In addition to the possible photomodulation of the magnetic behavior by the photoreaction of SP^+, this system may also, if crystallized in a noncentrosymmetric space group, give rise to highly interesting photoswitchable second-order nonlinear optical (NLO) properties.[14] Indeed, the two forms of spiropyrans generally have quite different molecular hyperpolarizabilities β.[15]

Experimental Section

^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer, and electronic spectra on a Varian Cary 5E spectrometer. The magnetic measurements were carried out on a Quantum Design squid magnetometer working in dc

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† Dedicated to the memory of Professor Olivier Kahn.

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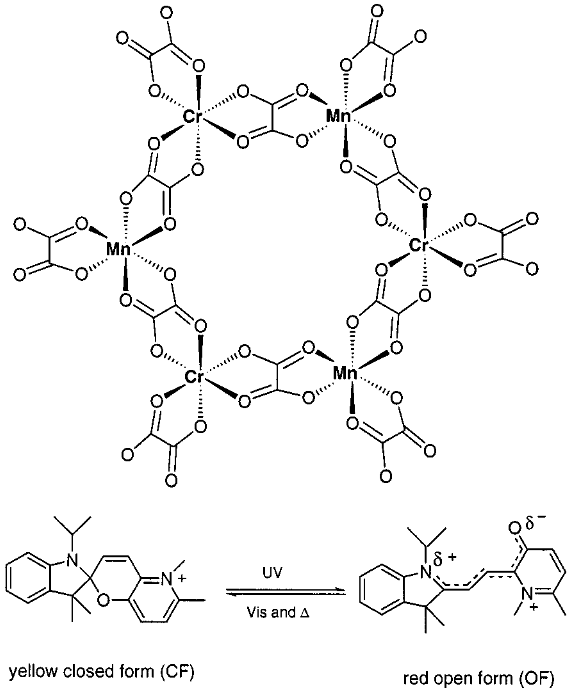
Scheme 1. (Top) Schematic Representation of the $[MnCr(ox)_3]_n^{n-}$ Layer and (bottom) Photoinduced Equilibrium of SP^+



Scheme 2. Synthesis of (SP)MnCr(ox)$_3$·H$_2$O

$$(SP)I \xrightarrow{AgCl} (SP)Cl \xrightarrow{K_3Cr(ox)_3.3H_2O}$$

$$(SP)_3Cr(ox)_3.4H_2O \xrightarrow{MnCl_2.4H_2O} (SP)MnCr(ox)_3.H_2O$$

mode. Elemental analyses were performed by the Service de Microanalyze du CNRS in Gif sur Yvette, France. Samples were irradiated either by the 365 nm line of a high-pressure Hg lamp (100 W) for UV−vis studies or by the third harmonic (355 nm, 80 mw/cm^2) of a nanosecond Nd:YAG pulsed (10 Hz) laser for the X-ray powder diffraction and magnetic studies.

Syntheses. (SP)MnCr(ox)$_3$·H$_2$O was obtained as a microcrystalline pale green powder in a three-step procedure according to Scheme 2. Any attempts to grow suitable single crystals for crystal structure determination were unsuccessful.

(SP)I. This compound was obtained as yellow microcrystalline powder according to the published method.[16] ^{1}H NMR (CDCl$_3$, 25 °C): 1.20 (s, 3H), 1.33 (s, 3H), 1.36 (d, J = 7 Hz, 3H), 1.43 (d, J = 7 Hz, 3H), 2.92 (s, 3H), 3.82 (q, J = 7 Hz, 1H), 4.53 (s, 3H), 6.50 (d, J = 11 Hz, 1H), 6.82 (d, J = 7 Hz, 1H), 6.91 (t, J = 7 Hz, 1H), 7.10 (d, J = 7 Hz, 1H), 7.18 (t, J = 7 Hz, 1H), 7.47 (s, 2H), 7.83 (d, J = 11 Hz, 1H). Elemental analysis calculated for $C_{22}H_{27}N_2OI$: C, 57.15; H, 5.89; N, 6.06; O, 3.46; I, 27.45. Found: C, 57.27; H, 5.77; N, 5.92; O, 3.47; I, 27.73. The slightly hygroscopic (SP)Cl was prepared by metathesis with AgCl in MeOH and used immediately for the next step.

(SP)$_3$Cr(ox)$_3$·4H$_2$O. By mixing 0.222 g (0.6 mmol) of (SP)Cl and 0.097 g (0.2 mmol) of K$_3$Cr(ox)$_3$·3H$_2$O, dissolved separately in a minimum of water, the intermediate (SP)$_3$Cr(ox)$_3$·4H$_2$O was obtained as a pale green powder (yield 90%). Elemental analysis calculated for $C_{72}H_{89}N_6O_{19}Cr$: C, 61.00; H, 6.44; N, 6.03; Cr, 3.73. Found: C, 61.48; H, 6.23; N, 5.97; Cr, 3.44.

(SP)MnCr(ox)$_3$·H$_2$O. (SP)$_3$Cr(ox)$_3$·4H$_2$O (0.140 g, 0.1 mmol) was dissolved in 25 mL of methanol and 1 mL of water. To this solution was added 0.020 g (0.1 mmol) of MnCl$_2$·4H$_2$O in 5 mL of methanol. The mixture was stirred for 10 min, after which a microcrystalline pale green powder was collected, washed with methanol, and dried under vacuum (yield 56%). Elemental analysis calculated for $C_{28}H_{27}N_2O_{13}CrMn \cdot H_2O$: C, 46.42; H, 4.03; N, 3.87; Cr, 7.18; Mn, 7.58. Found: C, 46.64; H, 3.81; N, 3.85; Cr, 7.07; Mn, 7.40.

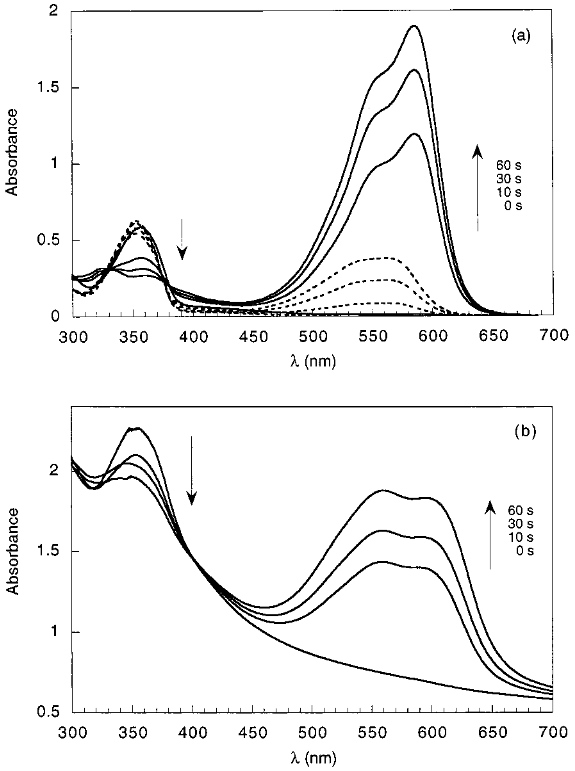


Figure 1. (a) Electronic absorption spectral changes of (SP)I in ethanol solution (dashed lines) and chloroform solution (solid lines) at 5×10^{-5} mol.L^{-1} and room temperature, upon UV irradiation (365 nm). (b) Electronic absorption spectral changes of (SP)I in KBr pellet upon UV irradiation (365 nm).

Results and Discussion

Photochromic Properties: (SP)I. As we have recently reported for similar compounds,[16] (SP)I was found to display both solution and crystalline-state photochromism (Figure 1). Its photochromism in both states is based on a UV light-induced equilibrium between a yellow closed form and a deep red open form (Scheme 1, bottom). At room temperature the thermally less stable open form returns slowly to the closed form in the dark, while this process is considerably accelerated with visible light irradiation. The main UV−vis data of closed and open forms of (SP)I as well as the thermal ring closure rate (k) of the latter (obtained by monitoring the thermal decay of the visible absorption band associated to the open form) are summarized in Table 1.

These data are comparable to those reported for its analogues.[16] However, an important difference has to be pointed out. In ethanol solution and in the crystalline state, the thermal ring closure process of the open form of (SP)I does not revert back to the closed form by following a single-exponential equation, and a biexponential equation [$A(t) = A_0e^{-kt} + A_1e^{-k't}$] is necessary to correctly fit the experimental data. One has to keep in mind that for spiropyran molecules the so-called open form itself is often an equilibrium mixture of geometrical

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Table 1. Spectral and Kinetic Data of (SP)I

	λ_{max} (nm)				
	CF	OF	k (s^{-1})	k' (s^{-1})	A_0/A_1
solution (chloroform)	357	555,[a] 587	1.3×10^{-5}		
solution (ethanol)	353	542,[a] 561	4.5×10^{-5}	3.6×10^{-8}	3.98
crystalline state	352	560, 597	1.6×10^{-4}	1.1×10^{-5}	0.22

[a] Shoulder.

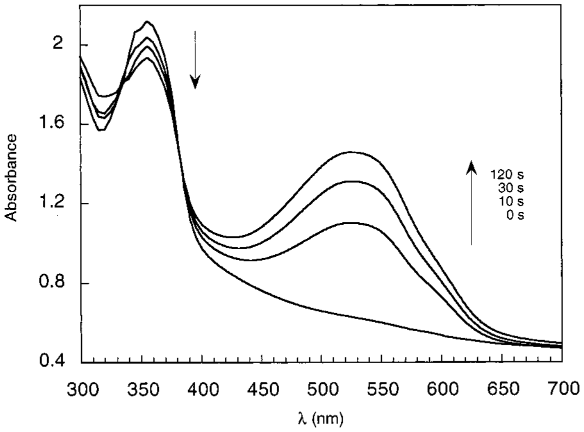

Figure 2. Electronic absorption spectral changes of (SP)-$MnCr(ox)_3 \cdot H_2O$ in KBr pellet upon UV irradiation (365 nm).

conformations,[17] so a possible explanation for this deviation from first-order kinetics in the present case could well be the presence of at least two such conformations of the open form with different thermal ring closure rates.

Another important aspect of the crystalline state photochromism is the photoinduced structural changes. As observed for its analogues,[16] the X-ray powder patterns of (SP)I taken after various UV irradiation times revealed an important and irreversible decrease of intensity of all initial peaks, indicating that the photoreaction in (SP)I induces significant and permanent disorder in its crystal structure. This result is not surprising given the geometrical difference between the closed and photoinduced open forms.

(SP)MnCr(ox)3·H2O. Both the intermediate $(SP)_3Cr(ox)_3 \cdot 4H_2O$ and $(SP)MnCr(ox)_3 \cdot H_2O$ were found to show crystalline-state photochromism. Before UV irradiation, the closed form is thermally stable in both compounds as in (SP)I. The UV−vis spectral evolution of $(SP)MnCr(ox)_3 \cdot H_2O$ upon UV irradiation is given in Figure 2 as an example. This remarkable anion-independent photochromic behavior is not unexpected because the photoactive part lies solely on the cation. However, the anion, which can be viewed as playing a matrix-like role toward the cationic photochrome in such a compound, may have notable effects on the spectrokinetic data of the open form. For instance, the absorption bands of the open form in $(SP)MnCr(ox)_3 \cdot H_2O$ are significantly blue-shifted in comparison to those in (SP)I. Since in solution the open form of SP^+ exhibits negative solvatochromism, this blue shift is probably due to the more ionic and polar environment surrounding SP^+ in $(SP)MnCr(ox)_3 \cdot H_2O$ than in (SP)I. On the other hand, most (about 90%) of the UV-induced open species in $(SP)MnCr(ox)_3 \cdot H_2O$ are found to be thermally stable in the dark, and only a small part of them return to the initial closed form with kinetic constants similar to those found in (SP)I ($k = 3.7 \times 10^{-4}$ s^{-1} and $k' = 2.7 \times 10^{-5}$ s^{-1}). Such strong environment-sensitive behaviors of the open form are well documented for other spiropyrans in various matrices.[18−20] In the present case, the thermal stabilization of the photoinduced open form is probably due to important interactions between the polar zwitterionic open form (Scheme 1, bottom) and the anionic layers. However, the closed form can be easily restored either slowly under normal laboratory lighting conditions or quickly with visible light irradiation (550 nm). In other words, both the open and closed forms are thermally stable in $(SP)MnCr(ox)_3 \cdot H_2O$.

Another notable difference between $(SP)MnCr(ox)_3 \cdot H_2O$ and (SP)I concerns the photoinduced structural changes. In contrast to the large crystal structure modifications observed for (SP)I, the X-ray powder data did not reveal any significant changes that would accompany the UV-induced color change in the layered structure of $(SP)MnCr(ox)_3 \cdot H_2O$. Indeed, the interlayer separation (d = 9.60 Å) was not affected by the ring opening of SP^+. Furthermore, no significant broadening and intensity decrease of the Debye−Scherrer diffraction lines could be observed on the irradiated sample. However, no definitive conclusion can be drawn because small structural changes cannot be easily detected by the Debye−Scherrer method. Several factors may contribute to the result. First, the oxalate bridged metal layer $[MnCr(ox)_3]_n^{n-}$ and its packing certainly dominate the X-ray powder diffraction; second, it is possible that the geometrical differences between the closed and UV-induced open forms of SP^+ in $(SP)MnCr(ox)_3 \cdot H_2O$ are not large enough to perturb significantly the inorganic layers, even though some weak and local layer deformations cannot be excluded.

Magnetic Properties: Before UV Irradiation. The magnetic properties of $(SP)MnCr(ox)_3 \cdot H_2O$, shown in Figure 3 in the form of an $\chi_M T$ versus T plot and the thermal dependence of M at low-temperature regions (χ_M being the molar magnetic susceptibility and M the molar magnetization), are characteristic of weak ferromagnetic interactions between Mn^{II} and Cr^{III} and a long-range ferromagnetic order with T_c = 5.5 K. This behavior, comparable to those reported for known $AMnCr(ox)_3$,[6,7,9] confirms that $(SP)MnCr(ox)_3 \cdot H_2O$ has the expected layered magnetic structure with cationic SP^+ located in between.

After UV Irradiation. Now let us look at what effects the photochromism of SP^+ has over the magnetic properties of $(SP)MnCr(ox)_3 \cdot H_2O$. To ensure a maximum of photoconversion of the closed form of SP^+ to its open form, a thin layer of powder sample squeezed between two glass plates was irradiated at room temperature with a UV laser (355 nm) until no further color change was observed. The T_c of the resulting red powder was

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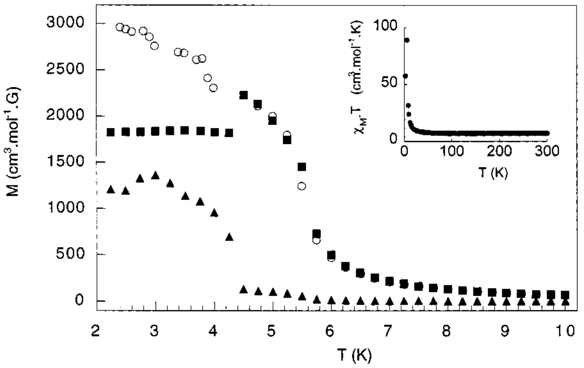

Figure 3. Temperature dependence of magnetization M for (SP)MnCr(ox)$_3$·H$_2$O before irradiation: (○) field-cooled magnetization (FCM) (30 G); (▲) remnant magnetization (RM); (■) zero field-cooled magnetization (ZFCM). The inset shows the temperature dependence of $\chi_M T$ for (SP)MnCr(ox)$_3$·H$_2$O.

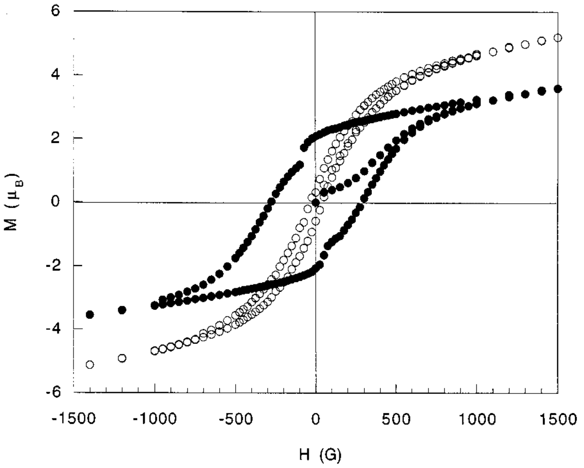

Figure 4. Hysteresis loops of (SP)MnCr(ox)$_3$·H$_2$O before (○) and after (●) UV irradiation (355 nm).

found to be not significantly different from that of the initial sample. This result is not surprising, because the T_c of such a system depends mainly on the magnetic interactions within each [MnCr(ox)$_3$]$_n^{n-}$ layer, which, according to the aforementioned X-ray powder data, was not significantly affected by the interconversion of the two forms of SP$^+$ located in between.

However, as far as the hysteresis loop is concerned, much more pronounced changes were observed between the initial and irradiated samples as shown in Figure 4. The coercive field (H_{coer}) as well as the remnant magnetization value (M_R) were raised in a spectacular way by UV irradiation, passing from $H_{coer} = 40$ G and $M_R = 0.3\mu_B$ (Bohr magneton) for the nonirradiated sample to $H_{coer} = 290$ G and $M_R = 2\ \mu_B$ for the irradiated one. It is also important to point out that strictly similar results were obtained with samples that, after being UV-irradiated, were submitted to visible light irradiation or allowed to stand several days in the dark. In other words, the changes in H_{coer} and M_R are irreversible with regard to the reversible photoreaction of SP$^+$ in (SP)MnCr(ox)$_3$·H$_2$O.

The small H_{coer} and low M_R of the nonirradiated sample are usual for the crystalline (SP)MnCr(ox)$_3$·H$_2$O with only isotropic spin carriers (Mn^{II} and Cr^{III}), while the large enhancements of M_R and H_{coer} for the irradiated sample are probably attributable to the photoinduced defects in the crystal structure, that render more difficult the Bloch wall displacements of ferromagnetic domains below T_c.[21]

To make sure that the hysteresis loop change does result from the photochromism of SP$^+$ and not from undesired laser-induced effects on the oxalate-bridged magnetic layer [MnCr(ox)$_3$]$_n^{n-}$, a "blank" experiment was carried out on a sample of (Nbu$_4$)MnCr(ox)$_3$, known to possess a similar T_c and coercive field.[6,9] UV irradiation of the sample under identical conditions as those used for (SP)MnCr(ox)$_3$·H$_2$O did not give any detectable changes in either its T_c or its hysteresis loop. On the other hand, the crystallization water molecule in (SP)MnCr(ox)$_3$·H$_2$O seems to be retained after UV and visible irradiation since the IR spectra of the nonirradiated and irradiated sample were found to be identical. On the basis of these data, the origin of the crystal structure defects can probably be attributed to the photoreaction of SP$^+$ that would lead to some disorders between the layers and probably also to some small and local deformations of layer [MnCr(ox)$_3$]$_n^{n-}$ as well.

NLO Properties. By use of the Kurtz−Perry powder technique,[22] neither the pale green form nor the red form of (SP)MnCr(ox)$_3$·H$_2$O was found to show any detectable second harmonic generation (SHG) activity at 1.907 μm radiation. Given the potentially large difference of hyperpolarizabilities β between the closed and open forms of SP$^+$, absence of SHG activity in both forms is probably attributable to a centrosymmetric or pseudocentrosymmetric arrangement of SP$^+$ in the structure of (SP)MnCr(ox)$_3$·H$_2$O, which would prevent any bulk SHG activity.

Conclusion. We describe in this work a new cationic spiropyran, (SP)I, and its use in the elaboration of (SP)MnCr(ox)$_3$·H$_2$O, a novel multiproperty system that orders ferromagnetically at 5.5 K and displays crystalline-state photochromism. In contrast to (SP)I, both the closed and photoinduced open forms of SP$^+$ in (SP)MnCr(ox)$_3$·H$_2$O are found to be thermally stable, making the system a potential candidate for optical switching and data storage. From the viewpoint of magnetic properties, although no modulation of the magnetic behaviors is achieved by the reversible photoreaction of the organic photochrome in such a system, UV irradiation transforms the initially very soft magnet to a much harder one by increasing considerably its coercive field as well as the remnant magnetization. This spectacular change in the hysteresis loop is ascribed to the photoinduced crystal structure defects through the photoreaction of SP$^+$. We are currently investigating other magnetic systems incorporating organic photochromes in search of greater synergistic effects between magnetic and photochromic properties.

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