Photoinduced Modifications of the Magnetization of a Stilbazolium−$MnPS_3$ Layered Intercalate

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Stilbazolium-type cations 4-[4-(diethylamino)-α-styryl]-1-methylpyridinium (noted DEMS) have been inserted into layered $MnPS_3$ by ion exchange. Transparent, self-supported thin films of approximate composition $Mn_{0.8}PS_3Li_{0.2}(DEMS)_{0.2}(H_2O)_n$ have been processed using a colloidal aqueous dispersion of $Mn_{1-x}PS_3(Li)_{2x}$ as an intermediate. Irradiation of these films at 550 nm results in the dramatic modification of their magnetic properties, characterized by the irreversible loss of the spontaneous magnetization. This photomagnetic effect is tentatively ascribed to structural disorder induced by limited photoreaction of the DEMS chromophores. Irradiation of nondispersed, lithium-free powdered samples of $Mn_{1-x}PS_3(DEMS)_{2x}$ intercalates also show photomagnetic effects similar in nature but less pronounced, and thermally reversible under ambient conditions.

Introduction

There has been growing interest over recent years in the synthesis of new multifunctional materials.[1−9] This area encompasses many compounds that simultaneously possess several properties such as magnetism, conductivity, nonlinear optical (NLO) properties, photochromism, etc.[8,9] Most interesting, some materials have been designed whose properties interact with each other, leading to unusual processes such as the photoinduced switching of optical nonlinearities[10] or the photoinduction of magnetization in heterometallic cyanides.[11] A strategy applied in our group to the design of new multifunctional materials consists of utilizing the natural nanostructuration of layered intercalation compounds to achieve intimate contact between a magnetizable inorganic host lattice and a photoactive organic species.[12] Along this line, we have recently reported on the substantial interplay between magnetism and photochromism in spiropyran-$MnPS_3$ and spiropyran-$MM'(C_2O_4)_3$ inclusion compounds.[13,14] In both compounds, the photoinduced switching of the spiropyran molecules was accompanied by a marked broadening of the magnetic hysteresis loop of the intercalate.

Cis−trans photoisomerizable molecules, such as stilbene or azobenzene derivatives, have been widely used as photoactive species.[15,16] Quite recently, azo dye molecules (e.g., DR1) grafted on gels have even been shown to be capable of effecting reptation motions under polarized irradiation and thereby achieve matter transportation.[17] Such spectacular effects suggest that structural changes should occur in the neighborhood of cis−trans chromophores when the latter are excited. We have shown a few years earlier that inserting hyperpolarizable, stilbazolium-like DAMS species (Scheme 1) into $MnPS_3$ enforced spontaneous poling of the chromophores and resulted in strong second-order optical nonlinearity.[6] A straightforward idea was to attempt at photoisomerizing the chromophores with the hope that the NLO efficiency could vary. Unfortunately, photoisomerizing the inserted DAMS species has proven to be unfeasible so far, probably because these dye molecules form stable J-aggregates, which precludes any reorientational motion.[12,18]

In the present work, a cis−trans photoisomerizable stilbazolium-like chromophore (DEMS, Scheme 1) that

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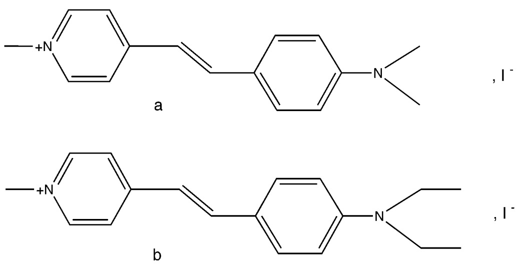
Scheme 1. (a) DAMS,I; (b) DEMS,I



does not aggregate and absorbs in the visible range has been inserted between magnetic MnPS$_3$ slabs. We describe below the photophysical behavior of the inserted DEMS chromophores and its relation with the magnetic properties of the intercalate.

Experimental Section

All chemicals and solvents were used as received. Elemental analyses were performed by the service de microanalyze du CNRS.

Synthesis of DEMS Iodide. The synthesis of the 4-[4-(diethylamino)-α-styryl]-1-methylpyridinium (DEMS) iodide has already been reported.[12]

Intercalation of DEMS in MnPS$_3$ Powder. MnPS$_3$ powder was obtained by heating stoichiometric amounts of the elements at 700 °C, as previously described.[19] A two-step procedure was used to insert DEMS cations: a pyridinium pre-intercalate $Mn_{1-x}PS_3(pyH)_{2x}$ was first prepared by treating MnPS$_3$ (200 mg) with an ethanolic solution of pyridinium chloride (1 g in 10 mL of ethanol) over 48 h at room temperature.[20] After isolation and washing, the pale green powder was treated with a solution of 200 mg of DEMS iodide in 10 mL of methanol for 48 h at 80 °C in a sealed evacuated Pyrex tube. The dark red powder was washed several times with methanol until the solution remained clear.

Synthesis of DEMS-Intercalated Mn_{1-x} PS$_3$ Thin Films. Transparent (pale green) thin films of a lithium $Mn_{1-x}PS_3Li_{2x}(H_2O)_y$ pre-intercalate were casted onto glass plates and Kapton sheets according to a procedure already described.[13,21] The films, about 1-μm thick, were then treated overnight with a 0.015 M solution of DEMS iodide in MeOH at room temperature, then washed with methanol, and dried. The films remained transparent on reaction but their color turned red-pink. Self-supported films of the DEMS−MnPS$_3$ compound automatically detached themselves when formed on Kapton substrate.

Characterization. The X-ray diffraction patterns of the powder and of the thin films were recorded on a Siemens diffractometer fitted with a Cu anticathode filtered by a nickel film (Kα radiation). The powder was spread on a flat sample holder and the films were studied on their glass or Kapton support. In all cases preferential orientation, due to the platelet shape of the grains, resulted in considerably enhanced intensity of the 00*l* reflections.

Magnetic properties were measured using a Quantum Design SQUID magnetometer. The powder was spread on double-coated tape fixed on cardboard, whereas the self-supported films were directly fixed on the tape. In both cases the mass of the sample was <1 mg. Each series of magnetic measurements carried out at various stages of irradiation was always performed on the *same* sample.

UV−visible absorption spectra of the intercalates were obtained between 800 and 350 nm with a Cary 5E spectrophotometer. Only thin films were studied, directly on their own glass plate support.

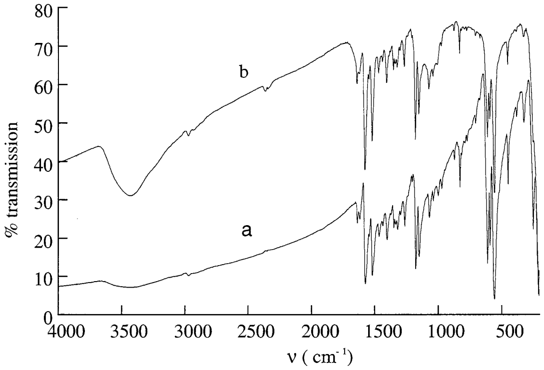


Figure 1. Infrared spectra of DEMS−MnPS$_3$ intercalate powder (a) and DEMS−MnPS$_3$ intercalate film (b).

Irradiation. Irradiations were carried out on both powders and thin films of the DEMS intercalates. Irradiations of the samples devoted to spectroscopic studies were effected by means of a 200-W Hg(Xe) lamp (LOT-Oriel) fitted with standard band-pass filter 550FS80-25 and 340FS25-25 (LOT-Oriel). Irradiations of samples devoted to magnetic measurements were effected inside the SQUID chamber by means of an optical fiber guiding the radiation generated by a 100-W halogen lamp (visible range) or a 75-W deuterium lamp (UV range). The same standard band-pass filters as above were used.

Results

Characterization of Powders of DEMS Intercalate. Full intercalation of the DEMS species into MnPS$_3$ powder was ascertained by the appearance of sharp 00*l* X-ray reflections corresponding to an interlayer distance of 12.5 Å, and correlatively by the disappearance of the reflections of the pyridinium−MnPS$_3$ pre-intercalate (interlayer spacing 9.9 Å). When compared with the spacing of pristine MnPS$_3$ (6.5 Å), the spacing value (12.5 Å) strongly suggests that the DEMS species are located in an essentially “edge on” orientation, the aromatic rings being nearly perpendicular to the MnPS$_3$ slabs. Intercalation by the DEMS species is also obvious from the IR spectra of the compound, which display numerous bands assignable to the DEMS species or to the MnPS$_3$ host lattice. The asymmetric $\nu(PS_3)$ stretching mode is split into three components at 556, 590, and 610 cm^{-1} (see Figure 1a). This splitting arises from the occurrence of Mn^{2+} intralayer vacancies which renders P−S bonds inequivalent.[22]

Elemental analysis data leads to the composition $Mn_{0.86}PS_{2.9}(DEMS)_{0.23}$ in reasonable agreement with the usual $Mn_{1-x}PS_3(DEMS)_{2x}$ formula expected for a monocharged guest cation. (C: 18.14%, H: 2.08%, N:2.77%, P:13.07%, S:38.97%, Mn: 19.91%)

Characterization of Thin Films of the DEMS Intercalate. The X-ray diffraction pattern of $Mn_{1-x}PS_3Li_{2x}$ ($x \sim 0.20$) thin films after exchange with DEMS species also showed sharp, intense 00*l* peaks corresponding to an interlamellar distance of 12.87 Å slightly larger than that (12.5 Å) of the above-described powdered DEMS intercalate. The infrared spectrum of the film is essentially identical to that of the DEMS powdered intercalate (Figure 1b), but it shows an

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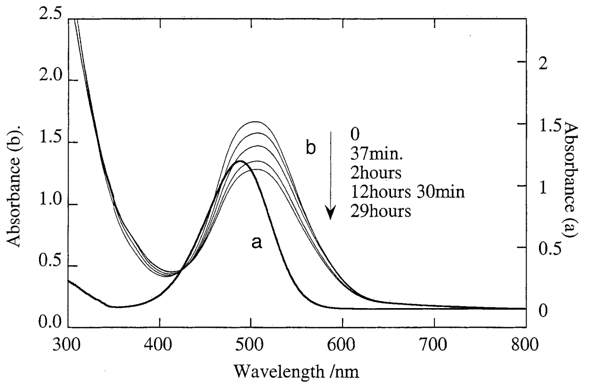

Figure 2. UV–visible absorption spectra of DEMS,I in solution (0.68 × 10^{-4} M) in methanol (a) and of $MnPS_3$ film intercalated with DEMS,I (b).

additional broad, quite intense band around 3600 cm^{-1} that denotes the presence of a significant amount of inserted water molecules. Due to the very small mass of the films (<1 mg), only the Li content of the DEMS intercalated thin films has been measured. The value found (0.7%) provides an estimation of the molar ratio of 0.18 Li per $Mn_{1-x}PS_3$ unit group. A significant amount of hydrated lithium ions therefore remains present in the films of DEMS intercalate, about as much as DEMS itself. This feature is not surprising in view of the fact that the DEMS species are much bigger than the lithium ions. Due to insufficient space, the interlayer region cannot accommodate 0.4 DEMS species, which would be necessary if the $2x = 0.4$ lithium ions contained in the $Mn_{1-x}PS_3Li_{2x}(H_2O)_n$ intermediate were to be fully exchanged (the above powder samples only contains 0.23 DEMS). In conclusion, the films have an approximate composition $Mn_{0.8}PS_3Li_{0.2}(DEMS)_{0.2}(H_2O)_n$.

Irradiation of Samples. For the sake of clarity, it should be kept in mind that the irradiated thin films have been studied by both UV–visible *and* magnetic measurements, whereas irradiated powdered samples have been the subject of magnetic studies only. The main reason is that thin films are very transparent to UV–visible radiation, which ensures complete "in depth" irradiation and convenient study by UV–visible spectroscopy, whereas powdered samples are much thicker, which renders effective irradiation of the heart of the grains uncertain and furthermore yields spectra of poor quality.

Photochromic Properties of DEMS in Solution. The photochromic properties of pure DEMS iodide were studied in methanolic solution (0.68 10^{-4} M). Prior to any irradiation, the spectrum of the solution (reported on Figure 2a) showed an intense charge-transfer band at 488 nm ($\epsilon = 17\,772$ cm^{-1} mol^{-1}), in relation to the red color of the solution.

When the solution was irradiated at 500 nm (outside the spectrophotometer), no change in the spectra occurred, whatever the exposure time. Our experimental setup did not allow irradiating the solution directly in the spectrophotometer. Following the suggestion of a referee, this experiment was repeated using a sample of DEMS hexafluorophosphate instead of iodide, to ensure that the nonreactivity of DEMS iodide was not due to an electron transfer from the iodide anion, but identical result as observed.

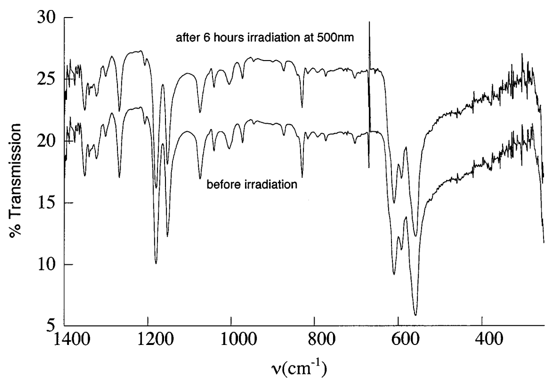

Figure 3. Infrared spectra of DEMS–$MnPS_3$ intercalate thin film before and after 6 h of irradiation at 500 nm.

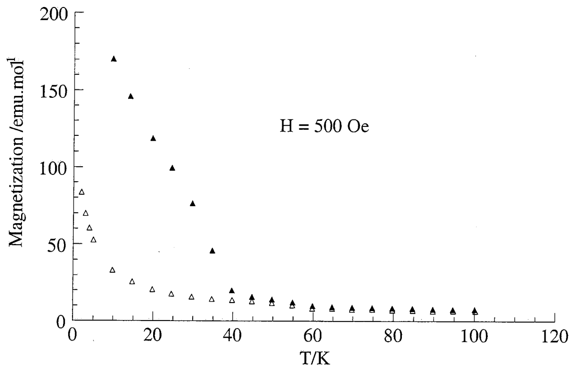

Figure 4. Temperature dependence of field cooled magetization (FCM) in a field of 500 Oe for DEMS–$MnPS_3$ intercalate film before irradiation (filled triangle) and after 4 h of irradiation at 500 nm (empty triangles).

Photochromic Properties of DEMS–$MnPS_3$ Thin Films. The absorption spectra of the $Mn_{0.8}PS_3Li_{0.2}(DEMS)_{0.2}(H_2O)_n$ thin films after various irradiation times are shown in Figure 2b. Before any irradiation, the charge-transfer band due to the inserted chromophore appears at $\lambda_{max} = 504$ nm, a value very slightly red-shifted (by 16 nm) with respect to the methanolic solution. When the film was irradiated at 500 nm, the intensity of this band slowly decreased and the series of spectra shows an isobestic point at 427 nm. A photostationary state is reached after several hours of irradiation. Examination of the irradiated thin films by X-ray diffraction revealed that the interlamellar distance had not significantly changed. The reflections remained sharp, indicating that no long-range disorder occurred. Furthermore, the FTIR spectrum (reported in Figure 3) of a self-supported film did not show any significant change upon irradiation, a feature that strongly suggests that a vast majority of the intercalated stilbazolium ions cations remain.

Magnetic Properties of DEMS –$MnPS_3$ Thin Film. The temperature dependence of the magnetization of a $Mn_{0.8}PS_3Li_{0.2}(DEMS)_{0.2}(H_2O)_n$ thin film cooled under a field of 500 Oe was recorded before and after irradiation (a smaller field could not be used because of the very small amount of matter in the film). The results are shown in Figure 4.

Before any irradiation, the field-cooled magnetization (FCM) showed a steep increase below 40 K, due to the onset of spontaneous magnetization in the sample, commonly observed for the $MnPS_3$ intercalates.[22]

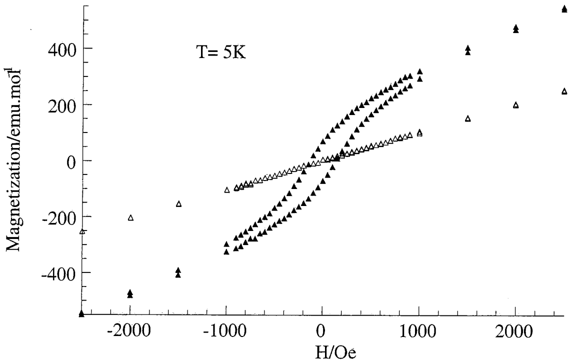

Figure 5. Hysteresis loop of the DEMS−MnPS$_3$ intercalate film at 5 K before irradiation (filled triangles) and after visible (500 nm) irradiation (empty triangles).

The sample was subsequently warmed to 300 K and irradiated at 500 nm *inside the SQUID* over 4 h and then the FCM was again recorded on cooling to 5 K. No steep magnetization "uprise" was observed any longer around 40 K. Irradiating the sample at room temperature therefore modifies the intercalate in such a way that the onset of spontaneous magnetization has been suppressed. To establish whether the irradiated intercalate would thermally relax, that is, recover its initial properties, the film was taken out of the SQUID and abandoned for 1 week under ambient conditions. A subsequent study of the sample revealed that the magnetic transition did not reappear.

The study of the magnetic hysteresis on the nonirradiated sample was carried out at 5 K by cycling the external field between +5000 and −5000 Oe. The hysteresis loop (shown in Figure 5) is characterized by a coercitive field of 300 Oe. After irradiation, the magnetization linearly depends on the field strength and hysteresis is no longer observed.

It is worth noting that irradiations effected at low temperature (10 K) instead of 300 K do not affect at all the magnetic properties.

Magnetic Properties of DEMS-Intercalated MnPS$_3$ Powder. Experiments similar to those described above have also been performed on powdered samples of the $Mn_{0.86}PS_{2.9}(DEMS)_{0.23}$ intercalate. Results are substantially different: (a)The FCM of the nonirradiated compound, recorded under a field of 500 Oe, shows a steep increase on cooling below 40 K (see Figure 6). (b) After a 4-h irradiation (500 nm) of the powder at room temperature, the FCM still exhibits a steep increase below 40 K (in contrast to the film), but the magnetization is significantly smaller than before irradiation. At this stage, annealing the sample at room temperature turned out to bring modifications that strongly depended on the conditions. (c) After staying 1 h *inside* the SQUID under reduced helium pressure at 300 K, the sample exhibited the same FCM plot as in case (b); hence, no relaxation had occurred. In contrast, when the sample was kept for 1 h *outside* the SQUID under ambient conditions at 300 K, the FCM plot was superimposable to the initial one before irradiation (case a); hence, the compound had structurally relaxed and could again acquire magnetization.

The effect of irradiation on the hysteresis loop was also studied at 5 K by cycling the external field between +5000 and −5000 Oe. Results are shown in Figure 7. Before irradiation, a quite broad hysteresis loop was observed with a coercitive field of 700 Oe (the magnetization reaches 240 emu/mol of Mn for $B = 5000$ Oe). After the sample was irradiated for over 4 h *inside* the SQUID at 300 K, the hysteresis loop recorded at 5 K exhibited a much smaller saturated magnetization (120 emu/mol of Mn for $B = 5000$ Oe) but the coercitive field was unchanged.

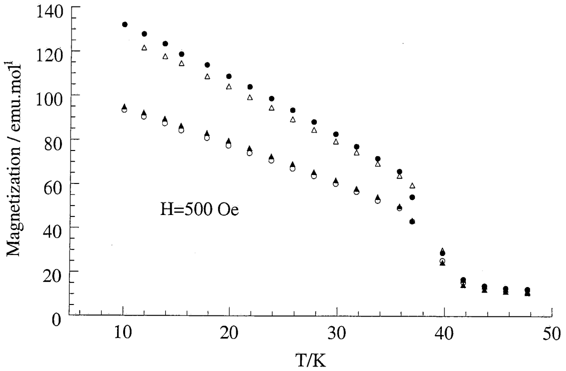

Figure 6. Temperature dependence of field cooled magnetization (FCM) in a field of 500 Oe for DEMS−MnPS$_3$ intercalate powder before irradiation (empty triangles), after 4 h of irradiation at 500 nm (empty rounds), after 1 h of relaxation into the SQUID (filled triangles), and after 1 h of irradiation outside the SQUID (filled circles).

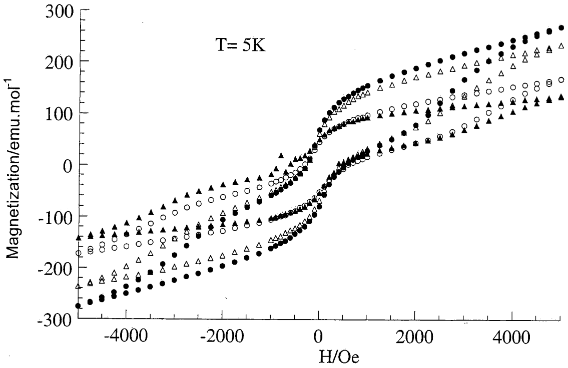

Figure 7. Hysteresis loop of the DEMS−MnPS$_3$ intercalate powder at 5 K before irradiation (empty triangles), after 4 h of irradiation at 500 nm (filled triangles), after 1 h of relaxation into the SQUID (empty circles), and after 1 h of irradiation outside the SQUID (filled circles).

Annealing the sample for 1 h at 300 K *inside* the SQUID did not cause any change of the hysteresis loop. In contrast, leaving the sample for 1 h at 300 K *outside* the Squid caused the hysteresis loop to recover its initial characteristic features (250 emu/mol of Mn at $B = 5000$ Oe).

A Blank: Irradiation of the Me_4N−MnPS$_3$ Nonphotoactive Intercalate. It was important to make sure that the photoinduced changes of the magnetic properties of the DEMS−MnPS$_3$ intercalates were really due to the presence of photoactive guest species, all the more as the magnetization finds its origin in the manganese spin structure of the host lattice.

For this purpose, we have submitted a sample of a tetramethylammonium Me_4N−MnPS$_3$ intercalate thin film prepared by the same procedure as the DEMS−MnPS$_3$ films to 4 h of irradiation at 500 nm and to 3 h of irradiation at 365 nm (where the host lattice is known to absorb strongly). This particular intercalate was

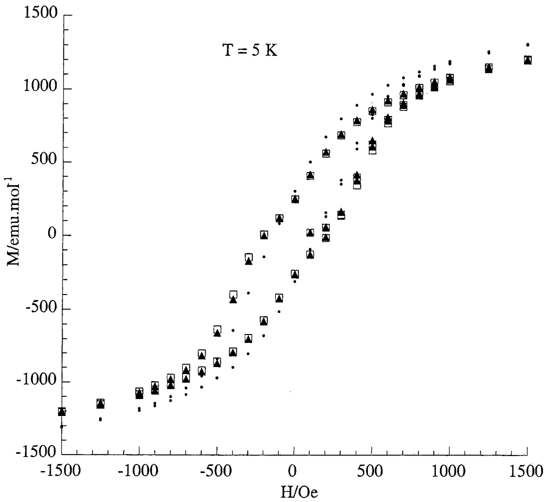

Figure 8. Hysteresis loop of the $Me_4N^+{-}MnPS_3$ intercalate film at 5 K before irradiation (filled triangles), after 4 h of irradiation at 500 nm (empty squares), and after 3 h of irradiation at 350 nm (filled circles).

selected for its similar interlayer distance (11.8 Å) and because it exhibits the strongest magnetization among the $MnPS_3$-based magnets.[22]

In all cases, no significant change of the magnetic data of the $Me_4N{-}MnPS_3$ compound could be detected after irradiation (Figure 8).

Discussion

Photochemistry of the Stilbazolium Chromophores. The photochemistry of stilbazole and stilbazolium derivatives in solution[23,24] and within lamellar phases[25−27] has been the subject of a number of studies. Molecular cations analogous to DEMS exhibit very little photoisomerization in solution, a feature consistent with the present results. On the other hand, Sawaki et al. have shown that UV-irradiation of *trans*-stilbazolium species intercalated in Saponite clay layers led to almost complete conversion of the chromophore into a mixture of trans and cis isomer and dimers formed by photocycloaddition, the latter process being favored by the specific relative orientation of the inserted stilbazolium species.

In the present study, less energetic radiation (500 nm) was used as compared to the above-mentioned work. Careful examination of the FTIR spectra of self-supported thin films of $MnPS_3$/DEMS before and after irradiation did not show any detectable significant change. As the bands due to DEMS are clearly visible on the spectra, this means that there is either no photoreaction of the DEMS species or a very limited one that we missed because of insufficient sensitivity. The unchanged X-ray diffractograms after irradiation means that no long-range disorder occurs.

In contrast, the slight decrease of the intensity of the UV−visible absorption band, associated with an isosbestic point, suggests that part of the DEMS species is transformed into another form. We tentatively suggest that a very limited fraction of the initial *trans*-DEMS chromophores turns into the cis form. This is not necessarily in contradiction with the absence of IR spectral modification, provided the extent of photoreaction is limited, all the more as the *cis*-form must have an IR spectrum very similar to that of the trans form.

Magnetic Properties of the DEMS−$MnPS_3$ Intercalate. Before discussing how irradiation can affect the magnetic properties, it is useful to recall why many $MnPS_3$ intercalates behave as magnets below a critical temperature T_c. Pristine $MnPS_3$ actually orders antiferromagnetically below around 78 K.[28] Below 78 K, the Mn^{2+} ($S = {}^5\!/_2$) spins are arranged on the corners of a honeycomb lattice in such a way that each spin "up" is surrounded by three spins "down" and vice versa.[29,30] When cationic species are being inserted into the lamellar phase, electroneutrality is preserved thanks to the loss of Mn^{2+} ions. Intralayer manganese vacancies are thus created, which are not randomly distributed, but instead order in such a way as to destroy the balance betrween the two (up and down) spin sublattices. The strongest saturated magnetization M_{sat} recorded so far is $M_{sat} = {}^1\!/_6 N_{Av} g\beta S$, a value reached in the case of the tetramethylammonium intercalate $Mn_{5/6}PS_3[Me_4N]_{2/6}$. In this compound, evidence has been found for a superlattice being formed by the guest ions, and therefore it may be assumed that the "chemical force" driving spin vacancy ordering is simply the electrostatic interaction between *positively charged* guest species and *negatively charged* vacancies.[22,31,32] In this model, it is then obvious that the net value of M_{sat} will strongly depend on both the amount of vacancies and on the geometry of the ordering. M_{sat} should vanish if the vacancies are located randomly. We therefore come to the idea that a change of the positions of the cationic guest species should affect the distribution of the Mn^{2+} vacancies (provided they can move) and hence M_{sat}. In the case of the two DEMS intercalates investigated in this work, M_{sat} is quite weak, about 250 emu/mol of Mn, which is 10 times less than that in the Me_4N intercalate. According to our model, this means that the Mn vacancies—and hence the underlying guest cations—are far from being perfectly ordered.

At this point, it must be emphasized that there is not a direct relation between the photoreaction of a guest species and the fate of the magnetic transition of the host lattice. For example, we have shown recently that irradiating a spiropyran−$MnPS_3$ intercalation compound readily caused a complete spiropyran to merocyanin switch, yet the magnetic transition was not at all suppressed; its coercitivity was even larger.[9]

Therefore, one must admit that the mechanism by which the irradiation of $Mn_{08}PS_3Li_{0.2}(DEMS)_{0.2}(H_20)_n$ annihilates the magnetic transition involves subtle factors which are not unambiguously identified at

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present. We tentatively suggest that the *limited* photoreaction taking place between the host layers introduces local defects which still increase the random character of the Mn vacancies because the latter are already *very poorly ordered* in this intercalate before irradiation. The more dramatic photomagnetic effect displayed by the thin film, as compared to the bulk powder, may be due to the co-intercalation of lithium and water molecules that may facilitate structural flexibility and rearrangement.

Conclusion

In the quest for hybrid, multifunctional materials exhibiting synergy or “cross-fertilization”, intercalation chemistry brings new synthetic opportunities that may be very useful, especially when dealing with properties that require strong cooperativity. Following our previous demonstration that an inserted photochromic spiropyran could affect the magnetic coercitivity of the intercalate, this work shows that another kind of photoactive molecule allows one to achieve the photoinduced decrease of a magnetic moment. Further work is in progress to design analogous materials in which the photomagnetic effect would entirely take place at low temperature, in the range where the materials remain ferrimagnetic.

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