Interplay between Magnetism and Photochromism in Spiropyran−$MnPS_3$ Intercalation Compounds

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N-Methylated pyridospiropyran cations SP-R^+ (R= Me, Ph) have been inserted into $MnPS_3$ by ion exchange to yield $Mn_{1-x}PS_3(SP\text{-}R)_{2x}$ intercalates. Thin transparent films of these materials have been processed, which exhibit photochromism due to spiropyran−merocyanin transformation. Intercalation considerably stabilizes the merocyanin form. When R = Me, the films are stable in the dark over months. Such a strong stabilization may be due to the formation of *J*-aggregates within the weakly polar interlayer medium of the $MnPS_3$ host lattice. The modifications of the basal spacing associated with photochromism have been characterized. One of the two intercalates (R = Me) acquires a spontaneous magnetization below about 40 K. Irradiation does not change T_c but considerably affects the hysteresis loop, increasing remanence and coercitivity.

Introduction

The synthesis of multifunctional, smart materials has become a very popular topic in recent years.[1−10] The strategy developed in our group for the design of such compounds is to make use of the composite character of layered intercalation compounds to bring together different properties.[11] Following this idea, the insertion of specific hyperpolarizable stilbazolium chromophores into layered $MnPS_3$ and more recently into bimetallic $MM'(C_2O_4)_3$ oxalates has afforded noncentrosymmetric organic−inorganic hybrid compounds that behave as NLO efficient magnets.[12,13] So far, however, despite the potential interest of such compounds, no interaction has been evidenced experimentally between the magnetization of a given material and its capability of generating second harmonic, although it has been recently suggested that such an interaction might be found in the study of the Faraday effect.[14] Attempts at gaining some control over the NLO properties by photoisomerizing the stilbazolium-type guest species have also led to disappointing results.

Therefore, active guest species of a different type should be considered. Recently a photochromic magnet containing spiropyran cations within bimetallic oxalate sheets has been synthesized. In this new compound, the hysteresis loop could be changed by irradiation.[15] The goal of the present work was to synthesize $MnPS_3$ intercalation compounds by incorporating photochromic guest molecules of the spiropyran family and to study their structural, magnetic, and photochromic properties under irradiation.

Although photochromism has received attention over about one century, it still constitutes an active field of research.[16] Photochromism in spiropyrans involves photocleavage of the C−O bond, which allows reversible switching between a colorless closed form (SP) and a strongly colored open merocyanin form (MC), as shown in Scheme 1.

The reversible SP ↔ MC conversion has drawn much attention as a possible process for information storage. The supporting medium exerts a strong influence on the ease of the conversion process and on the stability of the colored MC form. Traditional supporting media have been gel or polymer matrices,[17] Langmuir−Blodgett (LB) films, and micellar systems.[18,19] A few examples have also been reported, where the spiropyrans are

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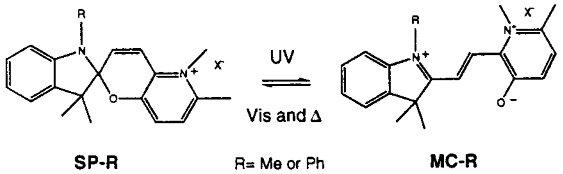
Scheme 1



inserted in the interlamellar space of a layered montmorillonite or LDH.[20] The formation of *J*- and *H*-aggregates of merocyanines within organic bilayers immobilized in clay matrices is highly interesting in the perspective of achieving NLO active arrangements.[21]

The MPS_3 layered semiconductors possess a unique intercalation chemistry.[22−25] They can incorporate a large variety of organic or inorganic cations in the interlayer space upon releasing metallic M^{2+} ions. Some of the MPS_3 compounds are colorless (M = Cd, Zn) or pale-green (M = Mn) and can serve as matrices suitable for optical purposes. A broad range of physical properties including ferrimagnetism, ferroelectricity, or second harmonic generation have been encountered.[26,27] A characteristic feature of the MPS_3 intercalation compounds is that the guest species usually fill up the interlayer galleries until they get close-packed, which may be useful in view of targeting high optical contrast if photochromic guest species switch between states of different colors. Of special interest is also the fact that the MPS_3 compounds (M = Mn, Cd) can be processed to yield intercalated transparent thin films well-adapted to light irradiations and UV−visible spectroscopy.[28]

Experimental Section

All chemicals and solvents were used as received unless otherwise stated. ^1H NMR experiments were carried out on a Bruker 200 MHz apparatus. Elemental analyses were performed by the Service de Microanalyse du CNRS in Gif sur Yvette, France. The two cationic spiropyrans selected in this work are those shown in Scheme 1 with methyl or phenyl substituents on the indoline ring, and noted hereafter as SP-Me and SP-Ph, respectively. The corresponding open merocyanine form will be noted MC-Me and MC-Ph.

Synthesis of the Cationic Spiropyrans. The synthesis of $(SP\text{-}Me)^+I^-$ was carried out as reported previously.[29] $(SP\text{-}Ph)^+I^-$ was prepared similarly by reacting 3-hydroxy-6-methyl-2-pyridinecarboxaldehyde in EtOH with 1-phenyl-3,3-dimethyl-2-methyleneindoline, followed by *N*-methylation of the pyridine ring with iodomethane in tetrahydrofuran (THF).[30] $(SP\text{-}Ph)^+I^-$ (recrystallized from CH_2Cl_2) was characterized by ^1H NMR and elemental analysis. ^1H NMR ($CDCl_3$): δ 1.40 (s, 3H), 1.50 (s, 3H), 2.85 (s, 3H), 4.33 (s, 3H), 5.33 (s, 2H), 6.50−7.70 (aromatic and ethylenic protons, 13H). Anal. Calcd (found) for $C_{25}H_{25}IN_2O{\cdot}0.9CH_2Cl_2$: C, 54.37 (54.40); H, 4.72 (4.74); N, 4.90 (4.72).

Synthesis of SP-Me and SP-Ph Intercalated $MnPS_3$ Powders. $MnPS_3$ powder was obtained by heating stoichiometric amounts of the elements at 700 °C, as previously described.[22] A pyridinium pre-intercalate $Mn_{1-x}PS_3(pyH)_{2x}$ was prepared by treating $MnPS_3$ (100 mg) with aqueous pyridinium chloride (500 mg in 10 mL of water) at room temperature for 1 h. After isolation and washing, the pale green powder was treated with a solution of 50 mg of the appropriate spiropyran iodide in 20 mL of methanol for 10 h at 60 °C. Brown solids were isolated in both cases.

Synthesis of SP-Me and SP-Ph Intercalated $MnPS_3$ Thin Films. Thin transparent films of a lithium $Mn_{1-x}PS_3Li_{2x}(H_2O)_n$ pre-intercalate were casted onto glass plates according to a sequence already described:[28] (i) intercalation of hydrated potassium ions into MPS_3 powder by ion exchange with an aqueous KCl solution; (ii) replacement of the K^+ ions by Li^+ ions by exchange with aqueous LiCl. The pale greenish solid was then isolated, washed with pure water, and separated by centrifugation. Upon washing the compound several times with deoxygenated water, a pale green colloidal solution was obtained. A few drops of this solution were then spread on glass (Pyrex) slides. Transparent thin films $Mn_{1-x}PS_3Li_{2x}(H_2O)_n$ ($x = 0.15$) about 10 μm thick were obtained after drying. Once dry the films were reasonably adherent, they were treated overnight with a 0.015 M solution of the SP-Me (or SP-Ph) iodide in MeOH at 20 °C, then washed with methanol, and dried at room temperature. In both cases, the films were pale yellow.

Measurements. X-ray powder diffraction patterns of the powders and of the thin films were recorded on a Siemens diffractometer with a Cu Kα ($\lambda = 1.540\ 51$ Å). Infrared spectra of powders were obtained on a FTIR Perkin-Elmer Spectrum 1000 spectrometer using KBr pellets (1:100). UV−visible absorption spectra were recorded between 800 and 300 nm either on solutions (initial spiropyran salts) or directly on the thin films using a Varian Cary 5E spectrophotometer.

Magnetic properties of the thin films were measured using a Quantum Design SQUID magnetometer. For this purpose, the films were cast on Kapton sheets. After intercalation, the materials could be easily removed as self-supported films which were introduced into a capsule. The weight of the sample was less than 1 mg. This procedure allowed measurement of the magnetic properties of the same film before and after irradiation.

Irradiations. Irradiations were carried out on thin films only. Visible light was generated by a 200 W Hg (Xe) lamp (LOT-Oriel) with a standard band-pass filter 550 FS80-25 (LOT-Oriel). Irradiations in the UV region were effected at 365 nm with a 100 W high-pressure Hg lamp.

Irradiation on the film was carried out directly inside the sample holder after removal of the top of the capsule.

Results

Characterization of Powders. Full intercalation of the spiropyrans SP-Me and SP-Ph into powdered $MnPS_3$ was ascertained by the appearance of sharp 00*l* X-ray reflections corresponding to interlayer distances of 13.97 and 13.38 Å for the SP-Me and SP-Ph intercalates, respectively (Table 1). Correlatively, the reflections of the pyridinium pre-intercalate (basal spacing, 9.5 Å) disappeared. Analysis of the elements gives composi-

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Table 1. Analytical Data and Interlayer Spacing for SP-R Intercalated MnPS$_3$

	chem anal (wt %)						
compd	Mn	P	S	C	H	N	spacing (Å)
$Mn_{0.89}PS_3[SP\text{-}Me]_{0.22}$ bulk	19.85	12.75	39.47	21.69	2.09	2.53	13.97
$Mn_{0.925}PS_3[SPPh]_{0.15}$ bulk	21.40	13.45	41.24	19.85	1.89	1.99	13.38
$Mn_{1-x}PS_3[SP\text{-}Me]_{2x}$ film							13.80
$Mn_{1-x}PS_3[SPPh]_{2x}$ film							13.18

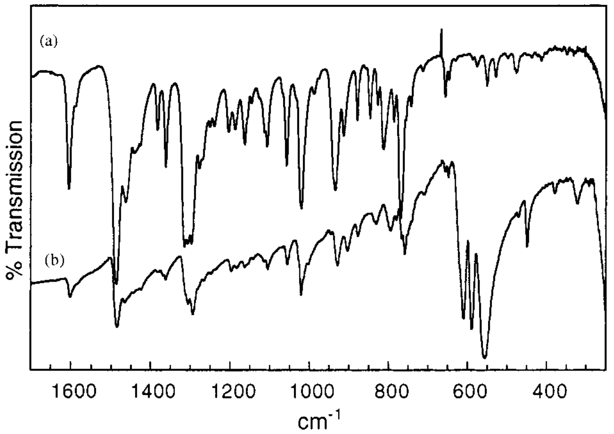

Figure 1. Infrared spectra of SP-Me (a) and $Mn_{0.89}PS_3$-$[SP\text{-}Me]_{0.22}$ (b) in KBr pellet.

tions close to $Mn_{0.89}PS_3[SP\text{-}Me]_{0.22}$ and $Mn_{0.925}PS_3$-$[SP\text{-}Ph]_{0.15}$, these figures being consistent with the composition of many intercalates with large guest species (Table 1).

Infrared spectra of the compounds showed numerous bands assignable either to the organic species or to the MnPS$_3$ host lattice. The asymmetric P−S stretching mode, which appears as an intense band at 570 cm^{-1} in the pristine compound, is split into two components (at 605 and 555 cm^{-1}) in the pyridinium pre-intercalate. In the case of the two spiropyran intercalates, the P−S band is even split into three components at 610, 585, and 555 cm^{-1}, as shown in Figure 1.

The splitting of the P−S band in the spectra of the intercalates arises from the occurrence of Mn^{2+} intralayer vacancies, which renders certain P−S bonds inequivalent. However, when the amount of vacancies is lower than 1/6, some of the P$_2$S$_6$ units of the layers are surrounded by six M^{2+} ions as in the pristine pure phase; hence, these six P−S are equivalent and vibrate at a frequency close to that in the pristine phase.

Characterization of the Films. The X-ray diffraction pattern of the spiropyran intercalated thin films are reported in Figure 2a, b and showed sharp intense 00*l* peaks, up to 004 on the diffractogram of (SP-Ph)−MnPS$_3$.

However, the basal spacings are found to be slightly smaller (by about 0.2 Å) than the spacing of the corresponding powdered samples. No confusion can occur with the spacing of the hydrated lithium intercalated films (11.5 Å). The very small amount of matter in the films precluded chemical analysis by traditional techniques. In this paper, we will assume that the samples processed as thin films have the same composition as the powdered samples. The pale yellow color of the films is consistent with the presence in both cases of the spiropyran (close form) inserted within the galleries. The photochromic properties described below have been studied on thin films rather than on powdered samples for the following reasons: (i) thin films are quite transparent and, hence, the whole volume can be effectively irradiated; (ii) the UV−visible spectra of the films have a much higher quality because of very little diffusion. Nevertheless, a qualitative study of the powdered samples show that they present very similar photochromic properties.

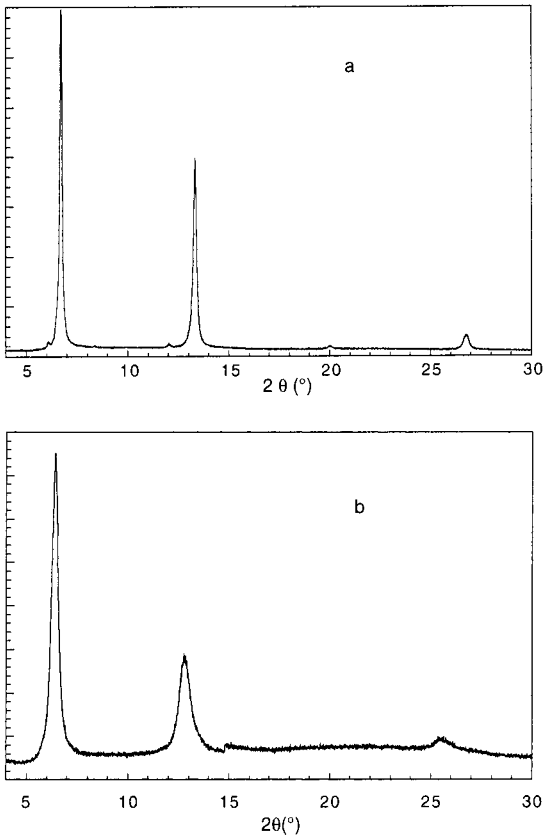

Figure 2. X-ray diffraction pattern of the (SP-Ph)−MnPS$_3$ intercalate (a) and the (SP-Me)−MnPS$_3$ intercalate films (b).

Photochromic Properties of SP-Me and SP-Ph Solutions. The photochromic properties of SP-Ph iodide in solution were compared to those previously reported for SP-Me iodide. Prior to any irradiation, the solutions (0.04 M in methanol) were colorless, and their spectra showed only one band centered in both cases around 350 nm, characteristic of the closed form of the spiropyrans. Upon irradiation at 365 nm, the solutions rapidly turned red-pink for SP-Me and pink-violet for SP-Ph . The spectra after irradiation are presented in Figure 3.

They show two absorption bands: the former one at 350 nm plus a new one at a wavelength dependent on the substituent (531 nm for R = Me, 572 nm for R = Ph). The new band in the visible region is characteristic of the merocyanin forms MC-Me and MC-Ph. The thermally unstable MC forms return to the initial SP forms both thermally and photochemically upon visible

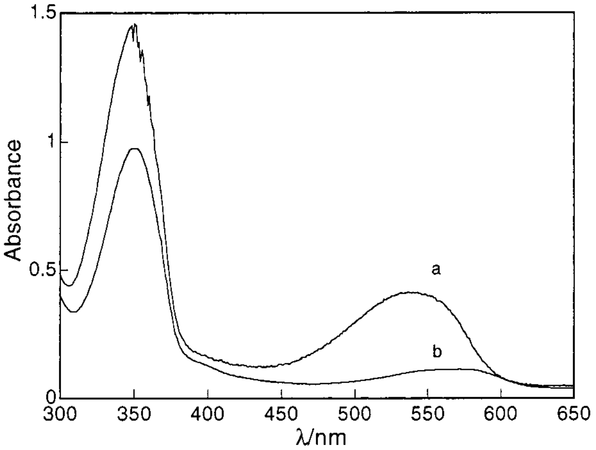

Figure 3. Electronic absorption spectra of SP-Me (a) and SP-Ph (b) in methanolic solution (0.04 M).

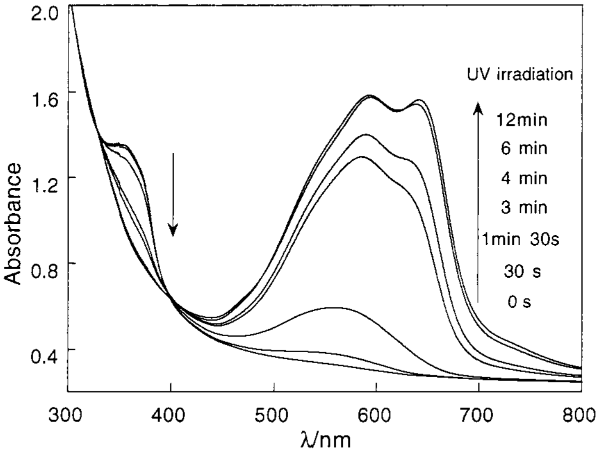

Figure 4. Electronic absorption spectral changes of (SP-Me)–$MnPS_3$ intercalate thin film upon UV irradiation (365 nm).

light irradiation. In polar and protic solvent such as MeOH, the merocyanin form MC-Ph was found to revert back to the SP form much faster than MC-Me, leading to the weak absorbance observed for the phenyl-substituted compound in Figure 3.

Photochromism of (SP-Me)–$MnPS_3$ Intercalate Thin Films. Prior to irradiation, the UV–vis spectrum of a pale yellow thin film of the SP-Me intercalate only shows one absorption band centered at 360 nm, clearly indicating that the guest species are under their SP (closed) form. The spectra after various irradiation times (at 365 nm) are shown in Figure 4: upon irradiation, the initial pale-yellow color rapidly turns to violet in a first step (traces from 30 to 90 s) and then becomes intense blue in a second step (traces from 3 to 12 min).

Right after the very first seconds of irradiation, a broad band centered at 560 nm appears. Upon further irradiation, the intensity of this band grows and its λ_{max} progressively shifts up to 590 nm, while a second band appears at 640 nm. The relative intensity of the new band progressively increases until it dominates. Comparison of the low- and high-energy side profiles indicates that the 640 nm band is significantly sharper than the 590 nm band. The occurrence of two bands appearing at different times means the presence of two distinct species, namely, merocyanin MC-Me guest species under two different states. Examination of Figure 4 also

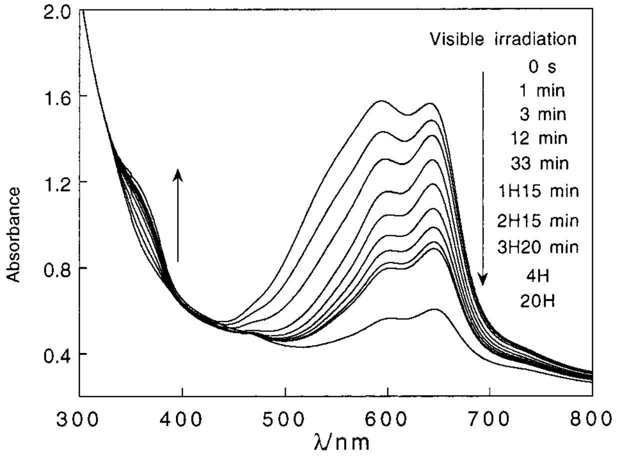

Figure 5. Electronic absorption spectral changes of (SP-Me)–$MnPS_3$ intercalate thin film upon visible irradiation (550 nm).

shows that as the visible (MC-Me) bands grow, the intensity of the UV (SP-Me) band decreases, generating an isobestic point at 395 nm. This isobestic point is correlated to the existence of the SP and MC forms, and it may seem inconsistent with MC under two forms. However, the intensity of the low-energy band is negligible at 395 nm.

The kinetics of the relaxation was followed in the dark by monitoring the decay of the absorbance $A(t)$ at the two peaking wavelengths, 590 and 640 nm as a function of time. The decay is extremely slow. Typically, the absorbance decreases by about 1% over the first day after irradiation (at both wavelengths), and the film remains strongly colored after standing several months in the dark.

Irradiation of a deep blue sample by visible light (range 550 ± 40 nm) for several hours enhances color fading but does not permit recovery of a noncolored state after 20 h of continuous irradiation. A few spectra taken after various irradiation durations (550 ± 40 nm) are shown in Figure 5. Furthermore, an irradiated film heated at 110 °C in the dark over 24 h displays an absorption spectrum similar to the one obtained after 20 h of visible irradiation.

Therefore, the film clearly does not revert back along the same way as it became colored: the intensities of the two (590 and 640 nm) bands decrease simultaneously without any significant shift. Nevertheless, if the film is re-irradiated at 365 nm, the band at 590 nm again starts growing before the 640 nm one.

Photochromism of (SP-Ph)–$MnPS_3$ Intercalate Thin Films. The UV–vis spectrum of a pale yellow thin film of this intercalate prior to irradiation also shows a single absorption band centered at 360 nm. Under irradiation at 365 nm, the film rapidly turns to blue. The absorption spectra after various irradiation times are shown in Figure 6.

After a few seconds, a broad band around 600 nm appears. As the band grows, its center shifts to about 613 nm, and two poorly resolved maxima can be observed at 591 and 634 nm. The shape of the overall band remains quite symmetric. Therefore, in contrast to the former case it is not obvious whether a second component related to another type of MC form appears. Upon standing in the dark after irradiation, the color fading takes place much faster than in the former

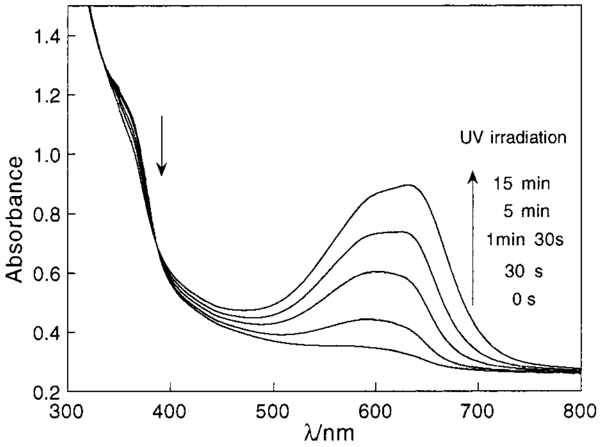

Figure 6. Electronic absorption spectral changes of (SP−Ph)-MnPS$_3$ intercalate thin film upon UV irradiation (365 nm).

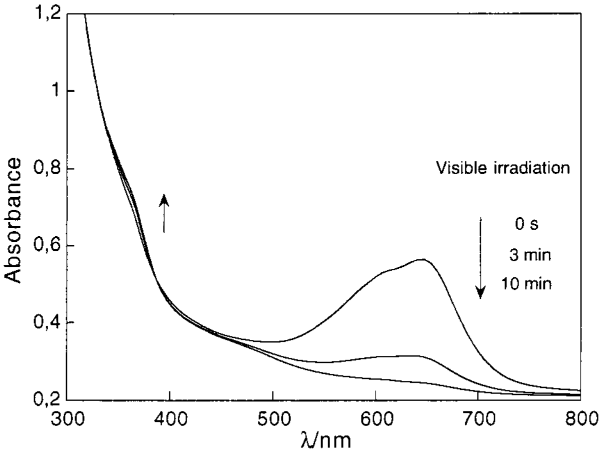

Figure 7. Electronic absorption spectral changes of (SP-Ph)−MnPS$_3$ intercalate thin film upon visible irradiation (550 nm).

SP-Me intercalate. The loss of absorption is about 10% over 1000 min at room temperature. More precisely the data for the decay at 613 nm could be fitted by a monoexponential equation with a time constant 2×10^{-3} min^{-1}. Finally, shining visible light (550 ± 40 nm range) greatly enhances the rate of decay and allows an intense blue film to revert to a colorless state shown in Figure 7 within about 10 min. Furthermore, an irradiated film returns to a colorless state after being heated at 110 °C for 30 min.

Structural Modifications Related to Photochromism. It was of interest to determine whether the molecular SP ↔ MC interconversions that result from UV and visible irradiation were accompanied by modifications of the interlayer distance. The values of the basal spacing of thin films of the SP-Me and SP-Ph intercalates have been measured after UV irradiation (intense blue state) and then after decolorizing (as completely as possible) by visible irradiation.

The angular position of the 002 reflection of SP-Me intercalated MnPS$_3$ thin films at different stages of irradiation is represented in Figure 8, and the values of the basal spacing are shown in Figure 9.

It is clear from Figure 9a that the initial value of the basal spacing for the never-irradiated sample cannot be compared with the subsequent ones. Upon sequences of UV and visible irradiations, the basal spacing cycles between two recurrent values separated by about 0.15 Å. Visible irradiation (closure step) causes the basal spacing to decrease, whereas UV irradiation (opening step) results in an increase. The same measurements have been carried out for SP-Ph intercalated MnPS$_3$ film. The evolution of the position of the 002 reflection is shown in Figure 10, and the variations of the basal spacing are represented in Figure 9b.

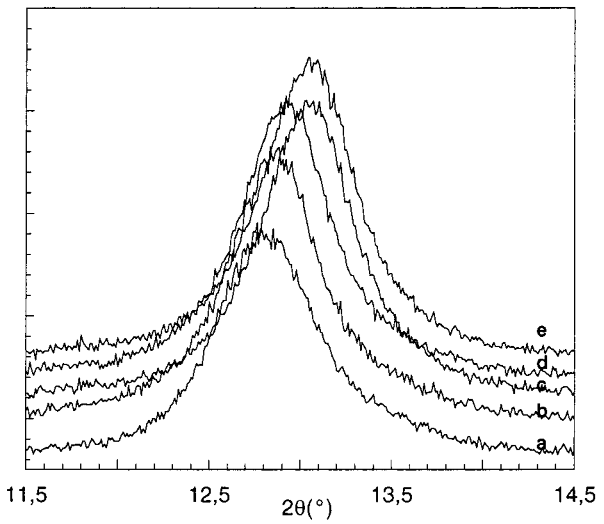

Figure 8. Angular position of the 002 reflection of X-ray diffraction pattern of the (SP-Me)−MnPS$_3$ intercalate thin film at different stages of irradiation: no irradiation (a), first UV irradiation (b), first visible irradiation (c), second UV irradiation (d), and second visible irradiation (e).

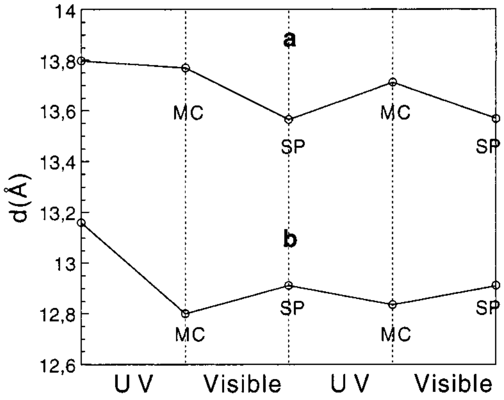

Figure 9. Variation of the basal spacing of (SP-Me)−MnPS$_3$ intercalate (a) and (SP-Ph)−MnPS$_3$ intercalate films (b) upon sequences of UV and visible irradiations.

Considering again the initial value separately, the basal spacing also cycles between two recurrent values separated by only 0.1 Å. Interestingly enough, the expansion/contraction steps are inverted with respect to the former intercalate. UV irradiation of the SP-Ph intercalate (opening step) causes a contraction, whereas visible irradiation (closure) causes an expansion. These X-ray diffraction experiments have been reproduced twice, using compounds formed by independent syntheses.

Magnetic Properties of the Intercalates. *SP-Me Intercalated MnPS*$_3$. The temperature dependence of the magnetic susceptibility χ of $Mn_{0.89}PS_3[SP\text{-}Me]_{0.22}$ (powdered sample) over the temperature range 4−300 K is shown in Figure 11 as $1/\chi = f(T)$. The data show a Curie−Weiss behavior with antiferromagnetic interac-

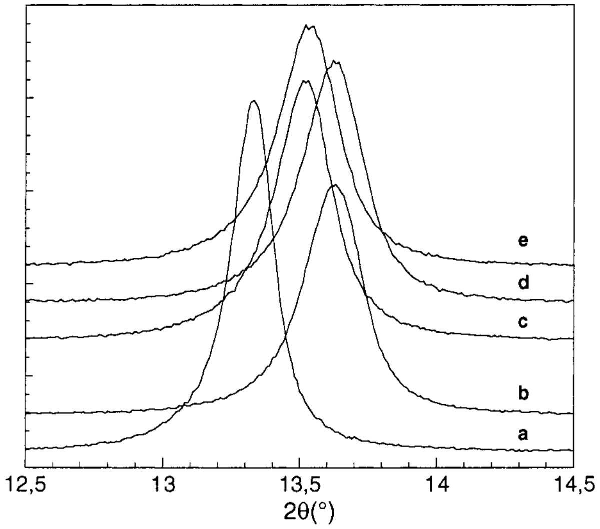

Figure 10. Angular position of the 002 reflection of X-ray diffraction pattern of the (SP-Ph)$-$MnPS$_3$ intercalate thin film at differents stages of irradiation: no irradiation (a), first UV irradiation (b), first visible irradiation (c), second UV irradiation (d), and second visible irradiation (e).

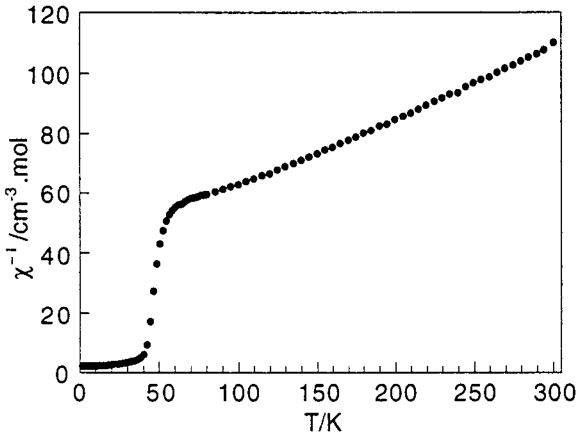

Figure 11. Temperature dependence of the reciprocal magnetic susceptibility χ^{-1} for Mn$_{0.89}$PS$_3$[SP-Me]$_{0.22}$.

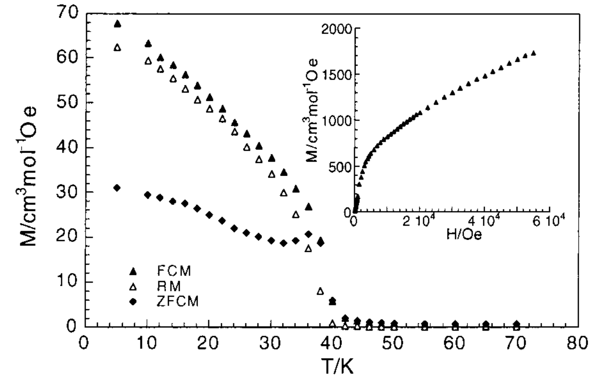

Figure 12. Temperature dependence of field cooled magnetization (FCM), remnant magnetization (RM), and zero field cooled magnetization (ZFCM) in a field of 30 Oe for (SP-Me)$-$MnPS$_3$ intercalate film before irradiation. The insert shows the dependence of the magnetization versus the applied field at 10 K.

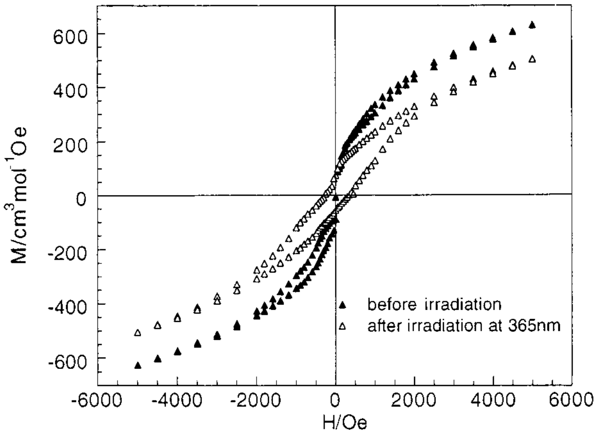

Figure 13. Hysteresis loop of the (SP-Me)$-$MnPS$_3$ intercalate film at 10 K before irradiation and after UV (365 nm) irradiation.

tions above about 100 K. Nonlinearity in the intercalate plots develops as the temperature is lowered, until around a critical temperature T_c (about 45 K) a very large increase of the susceptibility is observed, indicating the onset of a spontaneous bulk magnetization. Further studies have been carried out on thin films only.

The temperature dependence of the magnetization M of a nonirradiated thin film of the intercalate has been measured under a very low field. Data are shown in Figure 12.

The field-cooled magnetization (FCM) observed on cooling under 30 Oe shows a steep increase when T falls below 40 K. Then the field is switched off at 5 K and the sample allowed to warm. The remnant magnetization is quite strong and steadily decreases until it vanishes at T_c. The zero field cooled magnetization (ZFCM) was obtained by cooling from 100 to 5 K in zero field and then warming up under 30 Oe. The ZFCM slightly increases on warming in the vicinity of T_c and drops rapidly at T_c. The dependence of magnetization versus the applied magnetic field has been measured at 10 K, and the data are shown in Figure 12. The magnetization rises steeply as the field is increased and reaches a regime characterized by a constant slope rather than a plateau. Saturation is not attained even at 5 T. The search for hysteresis was carried out by cycling the external field between +5000 and $-$5000 Oe. The data are represented on Figure 13. They show that virtually no hysteresis occurs.

Irradiating the film with UV light until it becomes deep blue results in significantly different magnetic data. The temperature dependence of the magnetization shows that the critical temperature T_c has not been affected. However, the dependence of M on an applied magnetic field is significantly modified. The M(H) plot of the irradiated sample lies below the plot of the nonirradiated sample. If the applied field is again cycled between +5000 and $-$5000 Oe, a much broader hysteresis loop is obtained with a coercitive field (Hc) about 400 Oe (Figure 13). To appreciate whether these effects are reversible, the film was irradiated further by visible light for 20 h. As already mentioned above, the film remains slightly colored after such a long irradiation period, but a large fraction of MC-Me species have reverted to SP-Me. Correlatively, the width of the hysteresis loop measured after the “visible” irradiation is significantly smaller, as shown in Figure 14.

SP-Ph Intercalated MnPS$_3$. The magnetic properties of the Mn$_{0.925}$PS$_3$[SP-Ph]$_{0.15}$ intercalate have been also studied; however, this intercalate does not acquire any

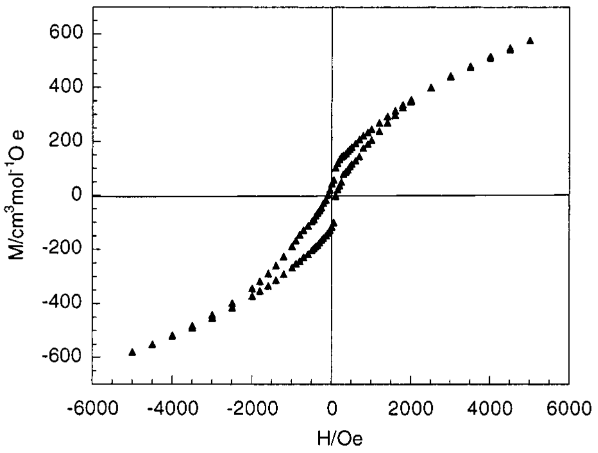

Figure 14. Hysteresis loop of the (SP-Me)−$MnPS_3$ intercalate film at 10 K after 20 h visible (550 nm) irradiation.

spontaneous magnetization at low temperature, and it behaves rather as an antiferromagnet before and after UV irradiation.

Discussion

Photochromism. The whole set of irradiation experiments carried out on the SP-Me and SP-Ph intercalates shows that the SP ↔ MC conversions still occur within the interlayer galleries, but that they are considerably affected by the constraints brought by the MnPS3 host lattice. In particular, the rate of back-conversion of the merocyanin form toward the spiropyran form is dramatically diminished, to such an extent that the process is almost blocked for SP-Me intercalate.

We examine more closely the photoresponse of each intercalate. Upon UV irradiation, intercalated SP-Me species give rise to a first type of merocyanin SP-MC form, characterized by $\lambda_{\max} = 580$ nm. As the "concentration" of this form increases, a second type of MC appears. This second form is considerably red-shifted ($\lambda_{\max} = 640$ nm) and the absorption band narrower. These features suggest that the MC-Me species could form *J*-aggregates when their "concentration" becomes important. This suggestion appears quite sensible, because aggregates often form when highly conjugated dyes having strong dipolar moments are introduced in media of weakly polar character such as many polymers.[31] The interlayer space of the MPS_3 host lattice is a weakly polar medium and the formation of *J*-aggregates of certain stilbazolium and pyrilium dyes within the MPS_3 galleries has already been demonstrated.[12,32] Moreover the formation of *J*- and *H*-aggregates of merocyanines within organic bilayers immobilized in clay matrices has also already been observed.[21] The high stability of the inserted MC forms and their difficulty to revert to the SP form constitute another argument in favor of aggregation.

An aggregation model would also account for the fact that the basal spacing of the SP-Me intercalate increases when the SP species open up. Aggregation involves $\pi-\pi$ interactions between stacked guest molecules. Since the axes of the stacks run along the layers' planes, aggregation should then tend to orient molecular planes upright (perpendicular to the layers), increasing the basal spacing. Finally, aggregation is also consistent with the fact that guest species within the MPS_3 lattice are close packed.

The photoresponse of the SP-Ph intercalate is somewhat different from that of its SP-Me analogue. Although the absorption band that grows upon UV irradiation is centered at about 630 nm, it should not be concluded that the molecules are aggregated. Indeed, the band of MC-Ph in solution does appear at a longer wavelength than the band of MC-Me (see Figure 3). The absence of aggregation might also explain that the merocyanin state MC-Ph is less stabilized than that of MC-Me: the reverse process is at least 10 times faster, and it can be completed by irradiation in the visible. Furthermore, the basal spacing of the SP-Ph intercalate varies upon irradiation in an opposite manner as compared to its SP-Me analogue. Such behavior can actually be easily understood. If the MC-Ph species do not aggregate when the UV photons open up the SP form, there are no reasons why the basal spacing should increase. The MC form being more flexible than the SP form, the guest layer probably relaxes under the influence of the host−guest ionic packing forces. A factor responsible for nonaggregation of the intercalated MC-Ph species may be the bulky phenyl group that prevents the molecules to orient themselves in the proper manner.

Influence of Irradiation on the Magnetic Properties of (SP-Me)−$MnPS_3$. The magnetic properties of $MnPS_3$ and of many $MnPS_3$ intercalates is a well-documented matter.[33−38] $MnPS_3$ behaves as a 2-D Heisenberg antiferromagnet which orders magnetically below a critical temperature close to 78 K. The spins 5/2 are located at the corners of a honeycomb lattice.[39−41] Intercalating the host lattice with molecular cations often results in the appearance of a spontaneous magnetization. The basic reason is that although the interaction between adjacent metallic sites remains antiferromagnetic, the loss of Mn^{2+} ions accompanying intercalation generates intralayer vacancies.[42,43] In certain cases, those vacancies spontaneously form an ordered superstructure on one of the two antiparallel spin sublattices, which results in spin imbalancing. For example the tetramethylammonium intercalate $Mn_{1-x}PS_3(Me_4N)_{2x}$ ($x = 1/6$) reaches a saturated magnetization $M_{\text{sat.}}$ close

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to 4000 emu/mol of Mn (that is 1/6[NgβS]).[43] In other cases $M_{\mathrm{sat.}}$ is weak or zero when the manganese vacancies are located more or less randomly.

The manganese deficit in (SP-Ph)−$MnPS_3$ intercalate is very small, about 7.5% (Table 1). Therefore, the vacancies are "diluted" and therefore tend to be located quite randomly on the metallic sites. This may be part of the reason why this intercalate does not acquire any spontaneous magnetization at low temperature. In contrast, (SP-Me)−$MnPS_3$ intercalate acquires a (relatively weak) spontaneous magnetization below about 45 K. The initial steep increase of magnetization in the M(H) curve is not followed by a clear saturation regime; this indicates a complex behavior and the presence of many defects and disorder.

The most interesting feature concerning the magnetic properties of (SP-Me)−$MnPS_3$ intercalate is obviously the influence exerted by irradiation on the hysteresis loop. UV irradiation causes a significant broadening and flattening of the hysteresis loop; hence, remanence and coercitivity are gained. Interesting enough, a similar effect has been recently reported on a spiropyran containing bimetallic layered oxalate (SP-Me)[MnCr(ox)$_3$].[15] This photomagnetic effect has been ascribed to the numerous structural defects created by the irradiation process. Actually, it is well-known that defects tend to prevent Bloch walls from moving freely. In this oxalate material, the loop remained broad even after the merocyanin forms had reverted to spiropyran forms upon applying visible irradiation.

In the present case of the (SP-Me)−$MnPS_3$ intercalate, the broadening of the hysteresis loop that follows UV irradiation is at least partially reversible upon irradiation of visible light. Because the MC → SP back-transformation was not complete after 20 h of visible irradiation, it cannot be said whether the broadening of the loop would be fully reversible if the MC → SP back-tranformation were complete. Nevertheless, the partial reversibility that has been evidenced means that the defects associated with irradiation have a subtle nature; they might consist of heterogeneities due to the boundaries between domains where aggregation prevails and other domains. More work is necessary if a more precise description is to be aimed at.

Conclusion

In the perspective of synthesizing new multiproperty materials exhibiting some synergy, intercalation of cationic spiropyran into layered $MnPS_3$ represent an interesting approach. Intercalates can be synthesized and processed as thin films which exhibit photochromic properties and spontaneous magnetization at low temperature. The photochromic properties are interesting in themselves because intercalation considerably stabilizes the merocyanin form, especially MC-Me. Such a strong stabilization may be due to the formation of *J*-aggregates of the merocyanin forms within the weakly polar interlayer medium. Stable photochromic films may be of interest for information storage. The interest is reinforced by the onset of spontaneous magnetization at low temperature and by the interaction between photochromism and magnetic properties. The coercitivity gained thanks to the photochromic effects would allow a "magnetic copy" of the information stored to be read optically. Although the magnetic aspect remains of academic interest because of the low critical temperature, it nevertheless turns out that a strategy based on intercalation can lead to original materials when compared to other types of organic−inorganic hybrids.

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