From Intercalation to Aggregation: Nonlinear Optical Properties of Stilbazolium Chromophores−MPS_3 Layered Hybrid Materials

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A number of cationic chromophores derived from the stilbazolium skeleton have been synthesized and inserted into the transparent layered MPS_3 compounds (M = Mn, Cd, Zn). The NLO properties of the intercalates have been studied. Some of the materials are found to be active for second harmonic generation. UV−visible spectroscopy shows that some of the chromophores, once inserted, undergo strong intermolecular interactions and form J-type aggregates along the inorganic galleries, whereas others do not. Moreover, we have found that only those intercalates which contain aggregates are NLO active. The results allow us to understand, at least partially, why the centrosymmetrical MPS_3 host lattice can yield noncentrosymmetrical intercalates. The host lattice appears not so much to impose specific orientations upon the guest species as to favor chromophore aggregation.

Introduction

The design of new compounds often benefits from the joint efforts of both organic and material chemistry, the latter trying to assemble in the most efficient way the always-improving molecular units that the first provides. Although used in many other fields, this "brickwork" strategy can be extremely fruitful in the synthesis of compounds presenting nonlinear optical (NLO)[1−5] properties because of the considerable importance of the relative arrangement of molecules in the solid state.

The host−guest chemistry,[6,7] from inclusion[8−13] to intercalation,[14] has proven to be particularly promising, not only because of the versatility of already-known structures,[15] but also because of the possible synthesis of multiproperty materials.[16] Within this framework, the quite unusual ability of the MPS_3[17] layered compounds (where M is a metal in the +2 oxidation state) to insert reversibly cationic species,[18] and their optical transparency when M = Cd, Mn, and Zn, make them good candidates for the achievement of NLO-active materials. Moreover, the intercalation process, which involves the departure of M^{2+} intralayer cations from the host phase to counterbalance the electrical charge of the guest cations, may lead to composites that exhibit spontaneous magnetization at low temperature.[19,20]

As a matter of fact, we have previously reported[21,22] that intercalation of the cationic chromophore 4-[4-(dimethylamino)-α-styryl]-1-methylpyridinium iodide ($DAMS^+I^-$) into MPS_3 (M = Cd, Mn) gave rise to materials exhibiting second harmonic generation (SHG) efficiency as high as 750 and 350 times that of urea,

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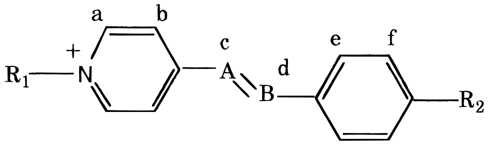
Scheme 1. Formula, Abbreviated Name, and Charge-Transfer (CT) Band Wavelength λ_0 Taken from UV−Vis Spectra Recorded in Ethanol for the Series of Stilbazolium Chromophores Synthesized



A=B	R1	R2		λ_0 (nm)
C=C	CH_3	$N(CH_3)_2$	DAMS	479
		NH_2	RNH2	462
		$N(C_2H_5)_2$	DEMS	492
		OCH_3	MOMS	386
		Cl	RCl	403
	CH_3CH_2	$N(CH_3)_2$	DAES	482
	$HO(C_2H_4)_2$		EOD	482
N=C	CH_3	$N(CH_3)_2$	IM1	438
C=N			IM2	507
N=N			DAZOP	552

respectively (at 1.34 μm). With the purpose of understanding how the centrosymmetric MPS_3 could lead to a noncentrosymmetric packing of chromophores, we have synthesized and intercalated a series of DAMS derivatives to try to sort out the relative importance of host−guest and guest−guest interactions.

Experimental Section

Synthesis and Characterization of the Guest Species. All the stilbazolium salts studied in this work (Scheme 1) were synthesized by condensation[23−25] of the 4-N-substituted picolinium iodide with the appropriate aldehyde in methanol, heating at reflux overnight in the presence of a catalytic amount of piperidine. Recrystallization generally led to highly colored needles.

The two Schiff bases were synthesized by dissolving the appropriate neutral amine and aldehyde in toluene, the mixture being heated at reflux for about 36 h. A Dean−Stark trap was used to facilitate the removal of water. After recrystallization, the 4-*N*-methyl iodide salts were obtained by reaction over 12 h with a slight excess of methyl iodide in dried dichloromethane heated at reflux.

The azo compound was obtained by a two-step process, starting with the formation of the diazo derivative of the 4-aminopyridine in an acidic (2:1 phosphoric acid 85%−nitric acid 65%) solution of sodium nitrite. This solution was then slowly added to *N*,*N*-dimethylaniline in a 30% phosphoric acid solution, and the mixture subsequently neutralized with sodium carbonate. The whole process had to be carried out between −5 and +5 °C, mostly because of the facile decomposition of the diazo form. The resulting orange precipitate was washed with water, dried, and recrystallized in ligroine. Methylation was then achieved following the procedure described above.

^1H NMR spectra of all species were recorded in $CDCl_3$. Using the designation described in Scheme 1, a typical spectrum for the C=C-containing derivatives has the following characteristics: δ 8.85 (d, $J = 7$ Hz, 2H, Ha), 7.9 (d, $J = 7$ Hz, 2H, Hb), 7.65 (d, $J = 16$ Hz, Hc), 7.55 (d, $J = 9$ Hz, 2H, He), 6.85 (d, $J = 16$ Hz, 2H, Hd), 6.7 (d, $J = 9$ Hz, 2H, Hf). The R_1 and R_2 protons were detected in the δ 1.0−5.0 domain. For those compounds where the double bond is modified, the spectra remained essentially the same except for the H_c and H_d signals: for IM1, only H_d appeared at δ 8.45; for IM2, H_c appeared at δ 8.65, and the azo derivative obviously showed none.

All the derivatives were also identified using infrared spectroscopy. Moreover, the study of the visible absorption spectra of $10^{-4}/10^{-5}$ M solutions showed an intense ($\epsilon \approx 4 \times 10^4$ L mol^{-1} cm^{-1} in ethanol) charge-transfer (CT) band presenting a large solvatochromic effect consistent with the high values of the molecular hyperpolarizability β expected for this family of chromophores. In the solid state, the iodide phases diluted in KBr pellets present a broad and slightly asymmetric band.

Synthesis of the Intercalates. Pure MPS_3 (M = Cd, Mn, Zn) compounds were synthesized by heating stoichiometric mixtures of the elements (purity 99.9%) in sealed evacuated quartz ampules, following already-described procedures.[17] Unless being small or highly charged, cationic species do not enter easily MPS_3 host lattices: the interlamellar space usually needs to be preexpanded using a solvated, highly mobile cation such as pyridinium or tetramethylammonium. Two routes have been followed in this work: either a one-step process (method 1) where the mobile cation is added in very small quantities to the solution containing the chromophore to be inserted, or a two-step process (method 2) where the preintercalated phase is isolated before being treated with the chromophore solution.

Method 1 was used with $CdPS_3$ and $ZnPS_3$, adding a few milligrams of pyridinium (pyH^+) chloride to a 10 cm^3 ethanolic solution containing 300 mg of chromophore in the presence of 100 mg of MPS_3 powder. The mixture was heated at 130 °C in a sealed evacuated Pyrex tube. Reaction durations varied from 3 days for the $CdPS_3$ intercalates to 1 night with $ZnPS_3$. $MnPS_3$ was first treated with a concentrated aqueous solution of tetramethylammonium chloride for 1 h and then washed and dried. The resulting $Mn_{1-x}PS_3(Me_4N)_{2x}(H_2O)_y$ preintercalate ($x \approx 0.15$) was then treated overnight following the procedure described above. In both cases, the final highly colored powder was washed several times with ethanol until the solution remained clear. Carefully distilled dried ethanol had to be used for the intercalation of the water-sensitive Schiff bases and the azo derivative.

The X-ray powder diffraction pattern of the intercalates were recorded using a Siemens diffractometer. The powder was spread on a sample holder, and preferential orientation (due to the platelet shape of the grains) resulted in considerably enhanced intensity of the 00L reflections. Infrared spectra were obtained using a Perkin-Elmer 883 spectrometer and the KBr pressed disk sampling.

The UV−visible absorption spectra were recorded between 800 and 350 nm. Samples were diluted from 0.1 to 1% in dry KBr powder, carefully ground, and pressed as pellets. Pure KBr was used as a reference for the double-beam mode of the Cary 5E spectrophotometer.

Nonlinear Optical Measurements. The measurements of SHG intensity were carried out using the Kurtz−Perry powder technique,[26] using a picosecond Nd:YAG pulsed (10 Hz) laser operating at 1.064 μm. A few measurements were also carried out at 1.54 μm. Samples were microcrystalline powders previously sieved below 100 μm and squeezed between two glass plates. The appearance of a green light (532 nm) under the laser irradiation was indicative of the tested compound efficiency; after passing through the appropriate filters, the transmitted signal was detected by a photomultiplier and read on an ultrafast Tektronix 7834 oscilloscope. The

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Table 1. Elemental Analysis of a Series of MPS_3 Intercalates

proposed formulation	%C	%H	%N	%O	%M	%P	%S
$Cd_{0.91}PS_3$(DAZOP)0.18	10.85	1.23	3.65		37.91	11.12	35.64
calculated	11.09	1.13	3.70		37.49	11.35	35.25
$Cd_{0.92}PS_{2.7}$(MOMS)0.16	11.25	0.91	0.87	0.95	40.62	10.96	30.63
calculated	11.17	0.90	0.87	0.99	40.07	11.0	33.90
$Cd_{0.90}P_{0.97}S_3$(EOD)0.2	14.03	1.48	1.96	1.39	36.37	10.56	33.54
calculated	14.52	1.51	1.99	1.14	35.97	10.68	34.20
$Mn_{0.92}PS_3$(DAZOP)0.16	11.63	1.4	3.71		22.15	14.15	47.91
calculated	12.44	1.27	4.14		23.37	14.32	44.46
$Mn_{0.89}PS_3$(IM1)0.22	15.16	1.79	4.28		23.09	13.51	42.31
calculated	17.35	1.75	4.05		21.02	13.45	42.17
$Mn_{0.90}PS_3(IM2)_{0.20}$	16.28	2.08	3.71		25.00	13.88	41.24
calculated	16.27	1.64	3.79		22.33	13.99	41.98
$Mn_{0.86}PS_3$(DAMS)0.28	21.67	2.22	3.17		19.20	12.84	38.98
calculated	22.29	2.22	3.25		19.57	12.83	39.84

Table 2. SHG Efficiencies (Referred to Urea) of the Powdered Intercalates Using a 1.064 μm Laser Radiation (L Indicates Signals under the 0.001 Limit of Detection)

	$CdPS_3$	$MnPS_3$	$ZnPS_3$
DAMS	1 (1500[a])	0.5	0.01
DAZOP	0.5	0.2	0.05
IM2	0.2	0.1	
IM1	L	L	
MOMS	L (0.1[a])	0.001	0.05
DEMS	L (0.1[a])	L	0.005
preintercalated phases	0.001 (1[a]) [with pyH]	L [with Me_4N]	0.01 (10[a]) [with pyH]
freshly prepared pure phases	0.001	L	0.001
pure phases after few weeks	0.001(1[a])	L	0.05

[a] Measurements using a 1.54 μm laser radiation.

SHG of a sieved urea sample was firstly measured as the reference value.

Results

All the cationic chromophores synthesized in this work were found to form intercalates with the three MPS_3 compounds studied (M = Mn, Cd, Zn). The X-ray diffraction patterns of the M = Mn and Cd intercalates showed sharp 00L reflections, but those of the $ZnPS_3$ intercalates displayed broader peaks, indicating poorer crystallinity. Disappearance of the 001 reflection of the preintercalates was taken as a criterion for complete insertion of the chromophores. All the intercalates present basal spacings between 12.5 and 13 Å (Table 1) to be compared with the 6.5 Å spacing of the unintercalated phases.[17] Such an increase suggests that the stilbazolium species are inserted so that the two aromatic rings stand nearly perpendicular to the MPS_3 layers.

Elemental analysis data of selected intercalates of $MnPS_3$ and $CdPS_3$ (obtained from the CNRS analytical service) are gathered in Table 1. As shown for the DAZOP intercalates, the inserted amount of a given guest species is essentially the same for both $MnPS_3$ and $CdPS_3$ intercalates. When comparing the stoichiometry of different intercalates, it appears that the DAMS content is significantly higher than the other ones. No analytical data have been obtained for the $ZnPS_3$ intercalates yet.

The infrared spectra of the intercalates generally show numerous bands in the 2000−800 cm^{-1} area which can be readily assigned to the chromophore species, plus an intense band consisting of two or three sharp components in the range 600−550 cm^{-1}. This feature is the classical signature of intercalation in these systems and it has been assigned to the ν(P−S) asymmetric stretching band which occurs as a degenerate single band at 570 cm^{-1} in pristine MPS_3, the degeneracy being lifted as a consequence of the occurrence of intralamellar vacancies due to the departure of a fraction of the M^{2+} during intercalation.

Second-Order NLO Activity. The efficiencies of all the intercalates for second harmonic generation are gathered in Table 2. All values are expressed with respect to urea used as a reference. Only the intercalates of $MnPS_3$ and $CdPS_3$ with DAMS, DAZOP, and the imine noted IM2 were found to exhibit SHG, with efficiencies at 1.06 μm of the same order of magnitude as urea or slightly lower. However, these efficiencies are certainly lower than the true values because of autoabsoption effect. The DAMS intercalate of $CdPS_3$ has also been also studied at 1.54 μm and the SHG efficiency is more than 1000 times larger. For technical reasons the other intercalates have not been studied so far. All intercalates prepared with the other guest species (Scheme 1) do not exhibit any significant SHG signal. We have checked that the pristine Mn- and $CdPS_3$ phases as well as the preintercalates used do not generate any significant signal. It is worth mentioning that a strong red fluorescence was observed when irradiating at 1.06 μm the DAMS, RNH2, and DEMS intercalates.

The case of $ZnPS_3$ deserves a few comments. In the first place, the $ZnPS_3$/DAMS and $ZnPS_3$/DAZOP intercalates exhibit only very weak efficiency, in sharp contrast to the corresponding Mn- and $CdPS_3$ intercalates of these two chromophores. In the second place, we found that while freshly synthesized pristine $ZnPS_3$ was not efficient, older $ZnPS_3$ that has been stored for a few months unprotected from the ambient atmosphere did. This is experimental evidence that $ZnPS_3$ undergoes a slow transformation that may be related to the fact that the Zn^{2+} ions are easily hydrolyzed.

UV−Visible Spectra. The absorption spectra of DAMS iodide in ethanolic solution and in the solid state are shown in Figure 1a. The intense charge-transfer band of the DAMS species appears considerably broadened and somewhat red-shifted in the solid state. The absorption spectra of the DAMS species once inserted in the three MPS_3 host lattices (M = Mn, Cd, Zn) are shown in Figure 1b. A striking feature is the strong deformation of the band in the $CdPS_3$ and $MnPS_3$ intercalates and the appearance of a strong narrow band around 580 nm, which is red-shifted by 100 nm with respect to the band observed in ethanolic solution. In contrast, the $ZnPS_3$/DAMS spectrum is very close to the spectrum of solid DAMS iodide. The broad band ex-

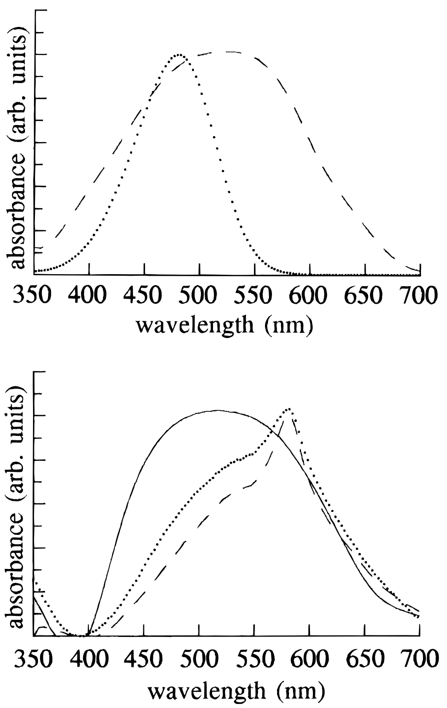

Figure 1. (a, top) UV−vis spectra of DAMS in ethanol (dotted line) and DAMS$^+$I$^-$ (dashed line) in KBr pellets. (b, bottom) UV−vis spectra of CdPS$_3$/DAMS (dotted line), MnPS$_3$/DAMS, (dashed line) and ZnPS$_3$/DAMS (plain line) in KBr pellets.

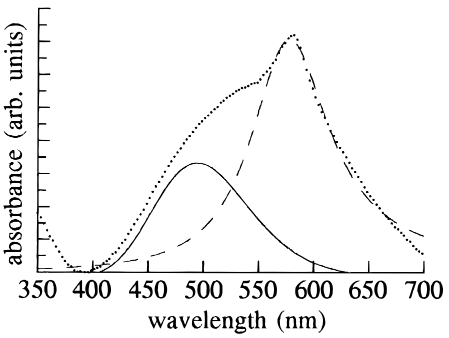

Figure 2. CdPS$_3$/DAMS UV−vis band (dotted line) as the superposition of a broad band at 500 nm (plain line) and a narrow one at 570 nm (dashed line).

hibits no structure and is red-shifted only by 30 nm with respect to the ethanolic solution maximum.

An attempt to decompose the CdPS$_3$/DAMS spectrum (Figure 2) revealed the possibility of analyzing it as the superposition of two bands, a first broad one centered around 500 nm (which could be identified as the band already observed) and an intense narrow one at 570 nm.

Keeping in mind the above-described results, all other MnPS$_3$ and CdPS$_3$ intercalates synthesized in this work can be classified in two families according to their UV−visible spectra:

(i) The intercalates of DAZOP (Figure 3) and IM2 (Figure 4), whose strongly deformed and shifted spectra bear a strong resemblance to the spectrum of the CdPS$_3$/DAMS intercalate.

(ii) All the other intercalates, for which no deformation or structure of the CT band was observed in either CdPS$_3$ or in MnPS$_3$ (Figures 5 and 6). Nevertheless, the IM1 intercalate seems to be a frontier case: although its spectrum (shown in Figure 7) is strongly perturbed, its band shape is somewhat different from the band shape of the three (DAMS, DAZOP, IM2) intercalates.

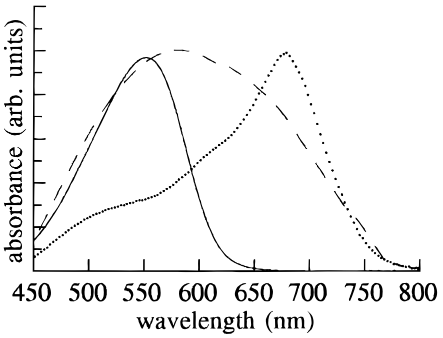

Figure 3. UV−vis spectra of DAZOP in ethanol (plain line), of DAZOP$^+$I$^-$ (dashed line) and CdPS$_3$/DAZOP (dotted line) in KBr pellets.

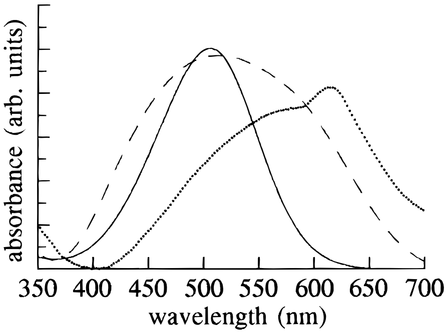

Figure 4. UV−vis spectra of IM2 in ethanol (plain line), of IM2$^+$I$^-$ (dashed line) and CdPS$_3$/IM2 (dotted line) in KBr pellets.

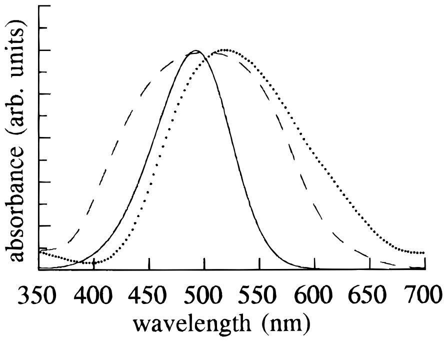

Figure 5. UV−vis spectra of DEMS in ethanol (plain line), of DEMS$^+$I$^-$ (dashed line) and CdPS$_3$/DEMS (dotted line) in KBr pellets.

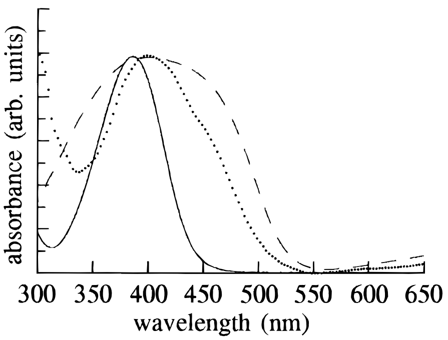

Figure 6. UV−vis spectra of MOMS in ethanol (plain line), of MOMS$^+$I$^-$ (dashed line) and CdPS$_3$/MOMS (dotted line) in KBr pellets.

Discussion

CdPS$_3$ and MnPS$_3$ Intercalates. Our previous discovery that the DAMS intercalates of Cd- or MnPS$_3$ were spontaneouly active materials for second-order NLO raised a number of questions. The most fundamental one was the reason why an initially centrosym-

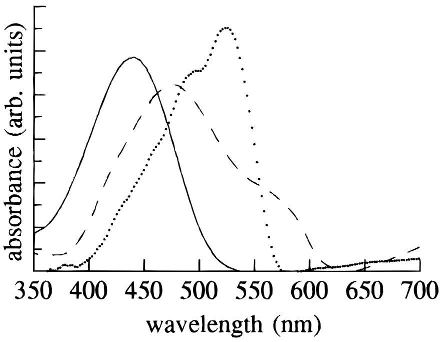

Figure 7. UV−vis spectra of IM1 in ethanol (plain line), of $IM1^+I^-$ (dashed line), and $CdPS_3$/IM1 (dotted line) in KBr pellets.

metrical[27] layer host lattice should lead to an acentric intercalate. It was therefore interesting to examine the NLO properties of other intercalated chromophores to try to sort out the essential factors. As discussed below, the fact that nearly all intercalates obtained with modified DAMS species are NLO inactive will lead to the conclusion that the acentric packing of the DAMS chromophores inserted into MPS_3 cannot simply result from a general direct orientional effect exerted by the host lattice. However, this work also shows that some other chromophores give NLO-active intercalates, therefore demonstrating that the DAMS intercalate is not a unique case.

The stilbazolium-type chromophores constitute an already well-known and widely studied[1,28−30] family of molecular compounds having high second-order hyperpolarizabilty. The chromophores synthesized in this work derive from three types of modifications carried out on the DAMS skeleton: (i) Those modifications where the NMe_2 donor group has been changed, either for very different functions (methoxy or halogeno groups) or for much closer forms (amino and diethylamino groups); (ii) those where the pyridinium acceptor group is grafted with ethyl or ethanol groups to favor possible hydrogen bonds between molecules in the host lattice; (iii) those in which the central C=C double bond is changed for an azo or imine group.

In response to any change of the i and ii types carried out on the DAMS molecular structure, the SHG efficiency of the $MnPS_3$ and $CdPS_3$ intercalates dramatically dropped to zero. In contrast, the third type of substitution gave two active intercalates.

To explain the striking difference in SHG signals observed, it is first necessary to compare the chromophores from a molecular point of view. The molecular quadratic hyperpolarizability β can be approximated using the two-state model[1] which is known to be particularly well adapted to the donor−acceptor type of chromophores. In this model, β is expressed by the relation

$$\beta \propto \Delta\mu \; f \frac{1}{W_0^{\,3}} \frac{\lambda^4}{(\lambda^2 - 4\lambda_0^{\,2})(\lambda^2 - \lambda_0^{\,2})}$$

where $\Delta\mu$ is the difference between the dipole moments of the ground and excited states, f the oscillator strength, W_0 the energy of the first transition corresponding to λ_0 and λ the wavelength of the laser radiation. This relation can also be written as

$$\beta = \beta_0 F(\lambda)$$

where the β_0 factor is independent of λ. Solvatochromic studies on the synthesized chromophores were carried out using the Varma and Groenen method[31] to approximate this parameter, leading to a maximum ratio of 50 between the lowest value (MOMS) and the highest (DEMS), so that the differences in β_0 cannot account for the wide gap observed in SHG efficiencies of the intercalates.

To deal with the influence of λ is more difficult because as λ_0 gets closer to $\lambda/2$, the increase of the $F(\lambda)$ factor is in competition with the reabsorption of the second harmonic radiation. This happens to be the case for most compounds absorbing in the 500−550 nm wavelength range, which therefore interact with the 532 nm green emitted second harmonic. Nevertheless, despite very close λ_0 values, it is clear that the NLO properties of DEMS, RNH_2, EOD, and DAES intercalates are very different from those reported for DAMS.

As the observed discrimination does not seem to be controlled by the molecular hyperpolarizability β, we have to seek its origin in the packing mode of the chromophores. The second-order NLO properties are described by the macroscopic $\chi^{(2)}$ hyperpolarizability. As a tensor, $\chi^{(2)}$ depends on the relative orientation of chromophores in the solid state and is known to equal zero for a centrosymmetric packing.[1−3] However, due to the extreme difficulty of obtaining true monocrystals of the intercalated phases, it is out of reach to get refined crystal structures. X-ray studies did not allow us to detect structural changes from one intercalate to another other than small differences in the host interlayer space. Infrared spectra in the studied range of wavenumbers only display internal vibrational modes which are rather insensitive to the intermolecular packing. Elemental analysis only indicates that the content of inserted DAMS species is somewhat higher than the content of the other chromophores.

In sharp contrast, the UV−visible spectra of the intercalates reflect the existence of two kinds of chromophore packings. The three intercalates exhibiting high SHG signals also present a strongly perturbed charge-transfer band, whereas those which are NLO inactive merely display spectra very close to the spectra of the chromophores in their pure solid iodide form. The deconvolution of the strongly structured band supports the coexistence of two species inside the interlamellar space. In fact, this band shape is very well-known and has been reported as characteristic of J aggregates[32] (or Scheibe aggregates). This phenomenon, described as the formation of dimers or higher polymers, is known to occur in Langmuir−Blodgett films,[33−35] polymers,[36,37]

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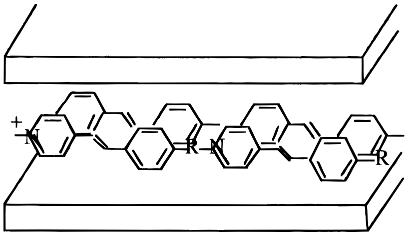
Scheme 2. Schematic Structure of Aggregated Chromophores in the Interlamellar Space of $CdPS_3$ or $MnPS_3$



sol−gel matrixes,[38] at the surface of gypsum or mica,[39] in concentrated solution[40,41] and is widely used in photographic process.[42] Moreover, formation of J aggregates has been reported to induce SHG properties because of the resulting noncentrosymmetric packing of the interacting chromophores.[43,44] The proposed mechanism involves an anionic chromotrope, which in our case may be the negatively charged sulfur layers, which favors the highly charged polymeric state. From a structural point of view, a calculation model has been developed[45−47] in order to correlate the band shift with the relative arrangement of molecular dipoles in interaction, using a brickwork concept. Although this theory can hardly be used for MPS_3 intercalates because of the difficulty of defining in a precise way the monomer absorption wavelength, the red-shift character and the order of magnitude (≈100 nm) of the shift lead to a hypothetical structure consistent with the values of the basal spacing, which suggest that the average molecular planes of the guest chromophores stand essentially “edge on” with respect to the host lattice slabs (Scheme 2), so that $\pi-\pi$ interactions between the chromophore rings can develop. Furthermore, it can be readily understood that the aggregation process is very geometry dependent so that slight modifications at both ends of the rings may inhibit possible interactions between two or more molecules, whereas replacement of the central C═C double bond by N═N or C═N would not. It should also be pointed out that these aggregates must have a sufficient size of coherence (around 1 μm) for effective SHG to occur: too small, uncorrelated aggregates would reintroduce a statistical center of symmetry and cancel SHG. This may be the explanation for the peculiar behavior of the imine IM1 intercalates, in which the chromophores appear to be aggregated, at least to some extent, but yet turn out to be NLO inactive.

$ZnPS_3$ Intercalates. The $ZnPS_3$ intercalates turn out to be rather different. In contrast to the $CdPS_3$ and $MnPS_3$ compounds, they all show small but nonzero SHG signals that do not depend much on the inserted molecule. For instance, insertion of pyridinium (a very low β species) into $ZnPS_3$ yields an intercalate which has about the same efficiency as the $ZnPS_3$/DAMS intercalate. Correlatively, the UV−visible spectra of all $ZnPS_3$ intercalates do not show any structure of the charge-transfer band, indicating that no aggregation occurs in these materials. Therefore the SHG signals detected can be attributed to the host phase. This is probably related to some change of the host lattice that occurs during the insertion reactions and which confers some noncentrosymmetry to the phase but precludes aggregation of the inserted chromophores. Actually even pure aged $ZnPS_3$ generates a significant SHG signal (0.05 times urea). The layered MPS_3 phases are known to crystallize in the monoclinic $C2/m$ centrosymmetric space group[27] so that no SHG properties would be expected. This turns out to be true for pure $MnPS_3$ and $CdPS_3$ and also for freshly synthesized $ZnPS_3$ but not for a sample of $ZnPS_3$ kept in air for a few weeks. These facts seem to indicate that slow hydrolysis of $ZnPS_3$ occurs that may be responsible for its unexpected behavior ($ZnPS_3$ is known to be particularly sensitive toward hydrolysis). The fact that none of the $ZnPS_3$ intercalates exhibit a signal stronger than the pure aged $ZnPS_3$ may be explained by the low crystallinity of these compounds (as seen by X-ray) which precludes any aggregation of the DAMS, DAZOP, and IM2 species.

Conclusion

In conclusion, this work significantly extends the very first results that the MPS_3/DAMS structure was NLO active. Moreover, it permits an appreciation of the relative importance of the guest−host and interchromophore interactions. The noncentrosymetric packing of certain inserted chromophores seems to arise from J-aggregate formation. However the host lattice may also have some importance, for instance, through its crystallinity.

Finally, although it appears that intercalation in MPS_3 layered phases is not a general method to obtain SHG-active materials, it may be also mentioned that chromophores oriented and aggregated over large distances might have large third-order NLO susceptibilities.[1]

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