MATERIALS CHEMISTRY COMMUNICATION

Second harmonic generation of dye aggregates in bentonite clay

Thibaud Coradin,[a] Keitaro Nakatani,[b] Isabelle Ledoux,[c] Joseph Zyss[c] and René Clément*[a]

[a]Laboratoire de Chimie Inorganique, U.R.A. 420, Université Paris-Sud, 91405 Orsay, France

[b]P.P.S.M., Ecole Normale Supérieure de Cachan, U.R.A. 1906, avenue du Pdt Wilson, 94235 Cachan, France
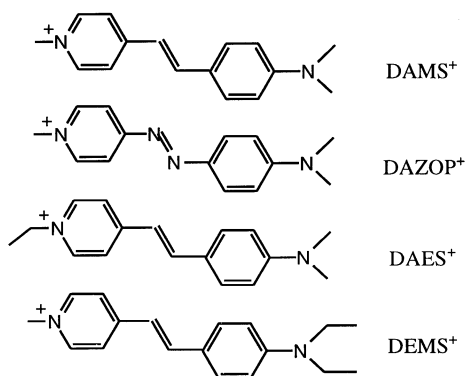
[c]France Telecom CNET Centre Paris B, Laboratoire de Bagneux, 196, avenue Henri Ravera, 92220 Bagneux, France

Intercalation of stilbazolium chromophores in a bentonite clay leads to the formation of dye aggregates exhibiting second harmonic generation properties.

The use of organic–inorganic hybrid materials has already been extremely fruitful for producing new compounds with non-linear optical (NLO) properties.[1–4] We have recently reported that intercalation of stilbazolium chromophores in the hexathiohypodiphosphate MPS_3 layered phases can give rise to NLO-active materials.[5,6] A model involving the formation of dye J-aggregates in the interlamellar space of the host was then suggested.

In order to study the influence of the nature of the host lattice on the chromophore packing and its possible contribution to the NLO properties, we have undertaken the insertion of the same dyes in bentonite, a cation-exchangeable clay. In contrast to MPS_3 intercalation chemistry, insertion in clays usually takes place at room temperature and permits monitoring of the concentration of inserted species.

The synthesis of the 4-[4-(dimethylamino)-α-styryl]-1-methylpyridinium (DAMS$^+$) iodide, and of the other derivatives (DAZOP$^+$, DAES$^+$, DEMS$^+$) used in this work, has already been reported.[6,7]

DAMS$^+$

DAZOP$^+$

DAES$^+$

DEMS$^+$

The last three of these present only slight modifications from the DAMS$^+$ skeleton to ensure a similar molecular quadratic hyperpolarisability β.[8,9] Bentonite SPV (Comptoir de Minéraux et de Matières Premières) with a cation exchange capacity (CEC) of 90 mequiv. per 100 g of the clay was used after equilibration with a sodium chloride solution. Aqueous suspensions with bentonite concentrations from 0.4 to 4 g l^{-1} and dye concentrations from 10^{-5} to 10^{-3} mol l^{-1} were allowed to stand overnight at room temperature. The strongly coloured solids were collected by centrifugation, thoroughly washed with water and dried.

Intercalation of the dyes was ascertained by powder X-ray diffraction, using a Siemens diffractometer with a Cu-Kα anode. The diffractograms of the four compounds show a relatively narrow 001 reflection (width ca. $2\theta = 0.5°$) indicating a basal spacing of ca. 16 Å. Assuming a van der Waals thickness of a clay layer around 9 Å,[10] a value of ca. 7 Å can be derived for the thickness of the dye layer, which is consistent with the value found in the MPS_3 intercalates. This suggests that the chromophores lie edge-on within the galleries. The amount of inserted dye also compares with the MPS_3 analogues [from elemental analysis, C 11.8%, N 1.5% (by mass) for the bentonite–DAMS intercalate at maximum loading].

Fig. 1 shows the evolution of the UV–VIS absorption spectra of the DAMS$^+$ and DAES$^+$ intercalates with increasing chromophore concentrations. At low concentrations, both materials present a broad and slightly asymmetrical band with a maximum absorption around 460 nm, this wavelength being very close to the charge transfer band of the organic molecules in aqueous solution. As the amount of inserted cations
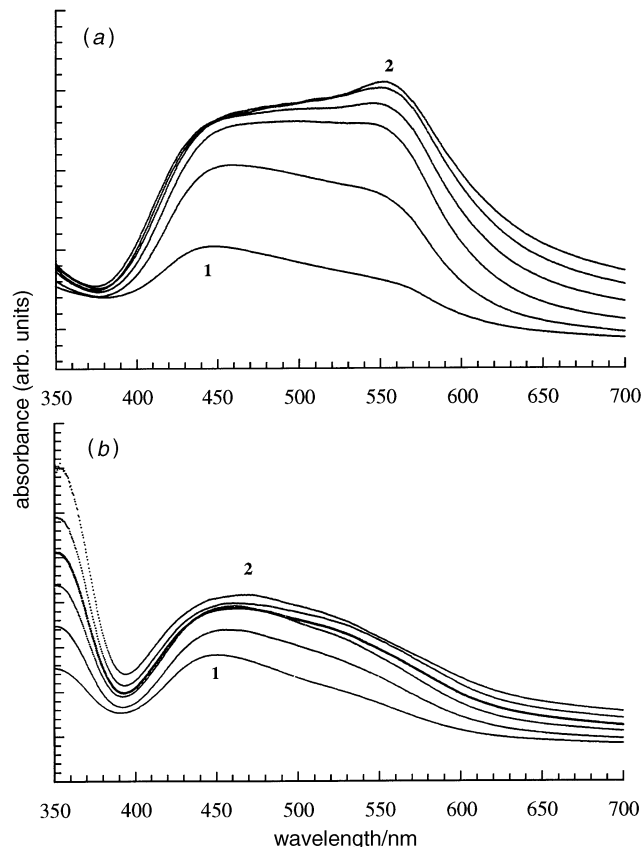

Fig. 1 Selected UV–VIS spectra of (a) bentonite–DAMS$^+$ and (b) bentonite–DAES$^+$ intercalates in a concentration range of 10^{-4} (spectrum 1) to 10^{-2} mol (spectrum 2) of dye per 100 g of clay

increases, two different behaviours are observed. In the DAMS$^+$ case [Fig. 1(a)], a new band arises around 550 nm, which grows stronger and narrower than the previous one as the maximum dye concentration is reached. In contrast, the bentonite–DAES$^+$ spectra [Fig. 1(b)] show no equivalent feature, the bandshape remaining essentially the same when concentration is increased. Finally, the DAZOP$^+$ cation presents the same behaviour as DAMS$^+$ whereas DEMS$^+$ seems to resemble DAES$^+$. As already discussed,[6] the strong red-shift of the UV band of intercalated DAMS$^+$ and DAZOR$^+$ can be attributed to the formation of J-type aggregates.

Second harmonic generation (SHG) experiments were carried out on 100 µm sieved samples using the Kurtz–Perry powder technique[11] operating at variable fundamental intensity, the harmonic signal from the unknown powder being plotted with respect to the harmonic emission from a reference urea powder.[12] The laser source is a ns Nd–YAG pulsed laser operating at 1.34 µm. Pure bentonite, bentonite–DAES$^+$ and bentonite–DEMS$^+$ did not generate any significant signals. In contrast, bentonite–DAMS$^+$ and bentonite–DAZOP$^+$ compounds were found to exhibit SHG signals whose intensity increased with chromophore concentration to reach a maximum value of 0.25 times urea in the bentonite–DAMS$^+$ case.

Upon comparison of these results with the previously reported ones concerning MPS$_3$ intercalates,[7] the same discrimination in UV–VIS spectra and NLO properties was observed. More precisely, only the intercalates containing aggregated dyes gave rise to SHG. The lower efficiency, as compared to MPS$_3$–DAMS$^+$, of the bentonite–DAMS$^+$ compound may be attributed, at least in part, to the poor crystallinity of the clay samples.

In conclusion, this work provides another example of a host–guest system that exhibits SHG properties even though the host lattice is known to be centrosymmetrical. The negatively charged layers appear to favour the formation of highly positive J-aggregates leading to a non-centrosymmetric arrangement of the dyes.[13,14] Moreover, the strong concentration dependence and the striking sensitivity to the chromophore structure of the aggregation process suggest a very tight close packing of the organic molecules, consistent with the nearly 100 nm shift of the charge-transfer band observed for the intercalates. We are currently studying the photophysical properties of these materials to obtain more information concerning the size and structure of these aggregates.

References

1   S. Tomaru, S. Zembutsu, M. Kawachi and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1984, 1207.
2   V. Ramamurthy and D. F. Eaton, *Chem. Mater.*, 1994, **6**, 1128.
3   B. Lebeau, C. Sanchez, S. Brasselet, J. Zyss, G. Froc and M. Dumont, *New J. Chem.*, 1996, **20**, 13.
4   R. Hoss, O. König, V. Kramer-Hoss, U. Berger, P. Rogin and J. Hulliger, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1664.
5   P. G. Lacroix, R. Clément, K. Nakatani, J. Zyss and I. Ledoux, *Science*, 1994, **263**, 658.
6   T. Coradin, R. Clément, P. G. Lacroix and K. Nakatani, *Chem. Mater.*, 1996, **8**, 2153.
7   S. R. Marder, J. W. Perry and C. P. Yakymyshyn, *Chem. Mater.*, 1994, **6**, 1137.
8   *Non Linear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, New York, 1987.
9   *Molecular Non Linear Optics: Materials, Physics and Devices*, ed. J. Zyss, Academic Press, New York, 1994.
10 *Intercalation Chemistry*, ed. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982.
11 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **19**, 3798.
12 P. D. Maker, *Phys. Rev. A*, 1970, **1**, 923.
13 D. Möbius, *Adv. Mater.*, 1995, **7**, 437.
14 R. Cohen and S. Yariv, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1705.