Photochromism of cationic spiropyran-doped silica gels

Anne Léaustic,* Agnès Dupont, Pei Yu and René Clément

Laboratoire de Chimie Inorganique (CNRS UMR 8613), Université Paris-Sud, Bat 420, 91405 Orsay cedex, France. E-mail: leaustic@icmo.u-psud.fr

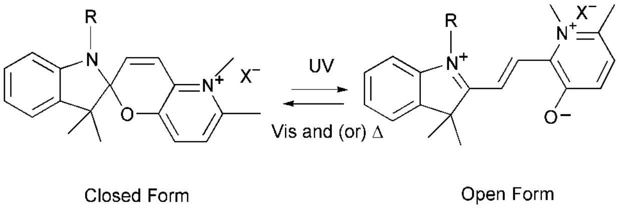
Received (in Montpellier, France) 21st May 2001, Accepted 13th July 2001
First published as an Advance Article on the web 3rd September 2001

New cationic spiropyrans $(SP–R)^+X^-$ (R = Me, Ph, Hex, C_2H_4OH; X = I, Cl, NO_3) have been synthesised and embedded in a silica gel prepared from the gelation of TMOS (tetramethyloxysilane). The influence of the substituent R and of the anion on the gelation time has been studied. Spectroscopic studies of these new spiropyran-doped gels provide evidence for negative solvatochromism and for a competition between normal and reverse photochromism.

Spiropyrans, spirooxazines and other photochromic organic molecules have been the subject of intensive research over several decades and the chemistry and potential uses of these compounds have been extensively reviewed.[1–3] Photochromism in spiropyrans involves photocleavage of the C–O bond, which allows reversible switching between a colourless closed form and a strongly coloured merocyanine opened form (Scheme 1). The process takes place when the photoactive species are either in solution or embedded in various matrices or polymers, but usually does not occur when the species are in the crystalline state. In spite of the large number of species already known, our group has recently synthesised new cationic spiropyrans and spirooxazines bearing a pyridinium nucleus that are the first to exhibit photochromic properties in the pure, crystalline state, in contrast to other spiropyrans previously synthezised.[4–6]

This unusual behavior was suggested[4] to be related to the presence of the electron-withdrawing *N*-methyl pyridinium ring, which increases the stability of the merocyanine form, and to the lowering of kinetic barriers due to the presence of a counter-ion, which probably provides sufficient free volume around the spiropyran to allow intra-molecular rearrangement. It is therefore of interest to know whether these new ionic spiropyrans would behave differently from the neutral spiropyrans, once dispersed in a matrix. The purpose of this work is thus to study the photochromic response of these cationic dyes embedded in a gel derived from the tetramethoxysilane precursor (TMOS).

The sol–gel process offers the possibility of preparing materials in which organic molecules are introduced on a nanometric scale in an inorganic network.[7–14] Influence of the network on the photochromism of neutral spiropyrans (and spirooxazines) is now well documented.[12,15–18] A general trend is that hydrophilic polar networks favour reverse photochromism, whereas hydrophobic ones favour normal photochromism. In the present case, a prerequisite was to study the feasability of preparing gels with these cationic spiropyrans, and to determine the influence of both the anion and the substituent group of the indoline heterocycle on the polymerisation of TMOS.



Scheme 1

Experimental

All chemicals and solvents were used as received unless otherwise stated. Elemental analyses were performed by the Service de Microanalyse du CNRS, Gif sur Yvette, France.

Synthesis of the cationic spiropyrans

The cationic spiropyrans $(SP–R)^+I^-$ used in this work are abbreviated as $(SP–Me)^+I^-$, $(SP–Ph)^+I^-$, $(SP–Hex)^+I^-$ and $(SP–C_2H_4OH)^+I^-$ for respectively R = methyl, phenyl, hexyl and 2-hydroxyethyl (see Scheme 1). Synthesis of $(SP–Me)^+I^-$ was reported previously.[4] $(SP–Ph)^+I^-$ was prepared similarly by reacting 3-hydroxy-6-methyl-2-pyridinecarboxaldehyde[19] in EtOH with 1-phenyl-3,3-dimethyl-2-methyleneindoline,[20] followed by N-methylation of the pyridine ring with iodomethane in THF. For the syntheses of $(SP–C_2H_4OH)^+I^-$ and $(SP–Hex)^+I^-$, 1-(2-hydroxyethyl)-3,3-dimethyl-2-methyleneindoline and 1-hexyl-3,3-dimethyl-2-methyleneindoline were generated *in situ* by addition of equimolar triethylamine into an ethanol solution of 1-(2-hydroxyethyl)-2,3,3-trimethylindoleninium bromide or 1-hexyl-2,3,3-trimethylindoleninium iodide, prepared by reacting 2,3,3-trimethylindolenine with 2-bromoethanol or 1-iodohexane.[21] $(SP–Ph)^+I^-$, $(SP–Hex)^+I^-$ and $(SP–C_2H_4OH)^+I^-$ were characterised by ^1H NMR and elemental analysis. $(SP–Ph)^+I^-$ (from CH_2Cl_2): Calc. (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%). $(SP–Hex)^+I^-$: Calc. (found) for $C_{25}H_{33}IN_2O$: C 59.50 (59.31), H 6.60 (6.46), N 5.55% (5.42%). $(SP–C_2H_4OH)^+I^-$: Calc. (found) for $C_{21}H_{25}N_2O_2I$: C 54.30 (54.01), H 5.43 (5.39), N 6.03 (5.81), O 6.89% (6.96%). The iodide ions in the above spiropyrans were readily replaced with chloride or nitrate by metathesis in MeOH with AgCl or $AgNO_3$, respectively.

Gel sample preparations

Silicate gels containing spiropyrans were prepared by adding 2 ml of a solution of spiropyran in methanol (conc. from 0.006 to 0.106 mol l^{-1}) to 3 ml of a 4.4 M solution of TMOS and water in methanol. The pH of the water was previously

DOI: 10.1039/b104456g

adjusted to 2 with hydrochlohydric acid. For all samples the initial molar ratio Si : H_2O was the same and equal to 1 : 2. Bulk samples were prepared by pouring the sol into covered flasks and allowing gelification to proceed over a few days. After gelation, the bottle covers were removed and replaced by plastic films pierced with a few needle holes to allow solvent evaporation. Monolithic transparent yellow xerogels were obtained. However, most measurements have been carried out on thin films of a few μm thick cast on glass slides from the viscous colloidal solution using the spin-coating technique. Such very thin films appeared colourless; however, thicker films deposited by spreading a few drops of solution appeared slightly yellow-coloured.

Irradiation

Irradiation by visible light was carried out using a 200 W Hg (Xe) lamp (Oriel) with standard bandpass filters 450 FS80-25 and 500 FS80-25 (LOT-Oriel). Irradiations in the UV region were effected at 365 nm with a 100 W high pressure Hg lamp.

UV-visible absorption spectra and kinetic studies

UV-visible spectra were recorded on thin films of the gels using a Varian Cary 5E spectrophotometer operating between 800 and 300 nm.

Normal (direct) photochromism was studied by irradiating the sample at 365 nm to generate the merocyanine form, and then monitoring the colour fading in the dark. In the case of "reverse" photochromism, the film was first completely decolourized by visible light irradiation. The colouration that subsequently reappeared in the dark was monitored at the wavelength of the maximal absorption of the open form.

Results and discussion

The gelation process

The influence of several factors relative to the spiropyran salt (concentration of the spiropyran salt, nature of the anion, change of substituent on the indoline part) on the gelation process has been investigated.

Firstly, the gelation of solutions of TMOS without any spiropyran or containing various $(SP\text{–}Me)^+X^-$ salts ($X^- = I^-$, Cl^-, NO_3^-) has been studied in a series of experiments where the initial molar ratio Si : H_2O was the same (1 : 2). The initial molar ratio Si : $SP\text{–}Me^+X^-$ was taken as 1 : 0.006. Results are shown in Table 1. Gelation proceeds faster in the presence of spiropyran salts, particularly when the anion is iodide.

Secondly, the influence of the molar ratio of chromophore to silicon on the gelation time has been studied in the case of the iodides $(SP\text{–}Me)^+I^-$ over a range of Si : H_2O : $(SP\text{–}Me)^+I^-$ extending from 1 : 2 : 0.001 to 1 : 2 : 0.016. It is clear from Fig. 1 that the gelation time decreases as the concentration of the spiropyran salt increases.

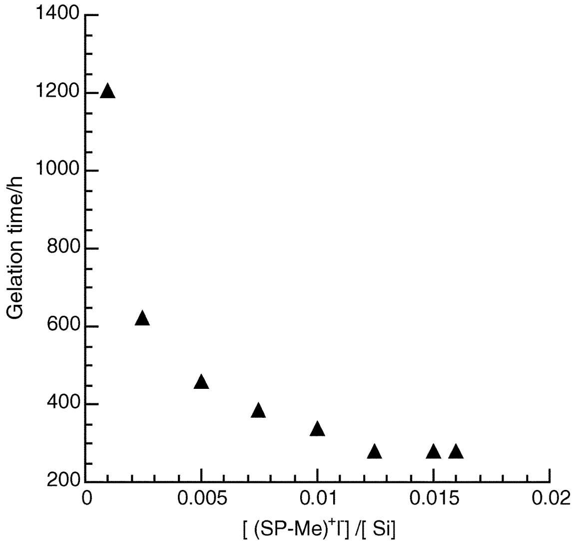


Fig. 1 Influence of the molar ratio of spiropyran to silicon on the gelation time of TMOS.

Finally, the gelation time has also been determined in the case of spiropyran iodides bearing various substituents. The initial molar ratio Si : H_2O : $(SP\text{–}R)^+I^-$ was the same (1 : 2 : 0.006) throughout the series. Results show that whereas the size of the substituent does not cause any significant changes (R = Me, Ph, Hex), the introduction of O–H functions does (Table 2).

The most striking feature shown by these data is the spectacular increase (by two orders of magnitude) of the gelation rate on changing the spiropyran counter-ion from nitrate to iodide, other factors being kept constant (*cf.* Table 1). The gelation process involves hydrolysis and condensation steps that are sensitive to the pH (acid and basic catalysis) and to the presence of nucleophilic catalysts.[22–24] Nucleophilic catalysts coordinate to the alkoxysilane species, giving rise to pentacoordinate silicon atoms that are more reactive toward subsequent nucleophilic substitutions (by water or silanol). The iodide ion is usually considered as having a stronger nucleophilic character than chloride and therefore I^- might be thought of as a being a better catalyst than Cl^-, a conclusion apparently consistent with the experimental data in Table 1. However, I^- is a soft Lewis base that has little affinity towards the hard Si(IV) centres, in contrast to the hard F^- ion, which is known to form complexes with Si(IV) and whose catalytic role has been clearly recognised.[24] Indeed, to our knowledge, no publication mentions a possible catalytic role of the iodide ion. Therefore, the influence of other factors, such as the dissociation of the ion pair (SP^+I^-) should also be considered, but we lack appropriate data to discuss this problem. The weak dependance of the gelation time on the nature of the indoline substituent (R) suggests that the latter does not play a prominent role except when the substituent brings about a specific interaction. Thus, hydroxylated substituents cause gelation to slow down, an effect probably related to

Table 1 Gelation time of spiropyran $(SP\text{–}Me)^+X^-$ doped silica gels

$(SP\text{–}Me)^+X^-$	Gelation time/h
$(SP\text{–}Me)^+I^-$	15
$(SP\text{–}Me)^+Cl^-$	306
$(SP\text{–}Me)^+NO_3^-$	1176
No spiropyran	1872

Table 2 Gelation time of spiropyran $(SP\text{–}R)^+I^-$ doped silica gels

$(SP\text{–}R)^+I^-$	Gelation time/h
$(SP\text{–}Me)^+I^-$	234
$(SP\text{–}Ph)^+I^-$	<234
$(SP\text{–}Hex)^+I^-$	304
$(SP\text{–}C_2H_4OH)^+I^-$	720

hydrogen bonding between the hydroxyl group of the spiropyran and the silanol groups that hinders polymerisation.

Photochromic properties

$(SP–Ph)^+I^-$, $(SP–C_2H_4OH)^+I^-$ and $(SP–Hex)^+I^-$ were found to show (direct) photochromism in both solution and the pure crystalline state qualitatively similar to that reported for $(SP–Me)^+I^-$.[4]

Spiropyran solutions. UV-visible spectra of solutions of the various spiropyran salts (0.04 M in MeOH) were recorded between 300 and 800 nm. Prior to any irradiation, the solutions were colourless and their spectra showed only one band centred around 350 nm, characteristic of the closed form of the spiropyrans. Upon irradiation at 365 nm, the solutions rapidly turned pink to violet. The spectra after irradiation are presented in Fig. 2 and the wavelengths of the maxima of the absorption bands are reported in Table 3.

The spectra show two absorption bands: a first one, around 350 nm, insensitive to the substituent R, and a second one strongly dependent on the substituent, centred at a wavelength varying between 530 and 570 nm; this band in the visible region is characteristic of the merocyanine form. The thermally unstable merocyanine forms return to the initial closed forms both thermally and photochemically upon visible light irradiation. In polar and protic solvent such as MeOH, the open forms of $(SP–Ph)^+I^-$ and $(SP–C_2H_4OH)^+I^-$ were found to revert back to the corresponding closed forms much faster than $(SP–Me)^+I^-$ and $(SP–Hex)^+I^-$, leading to the weak optical densities observed for the former two compounds.

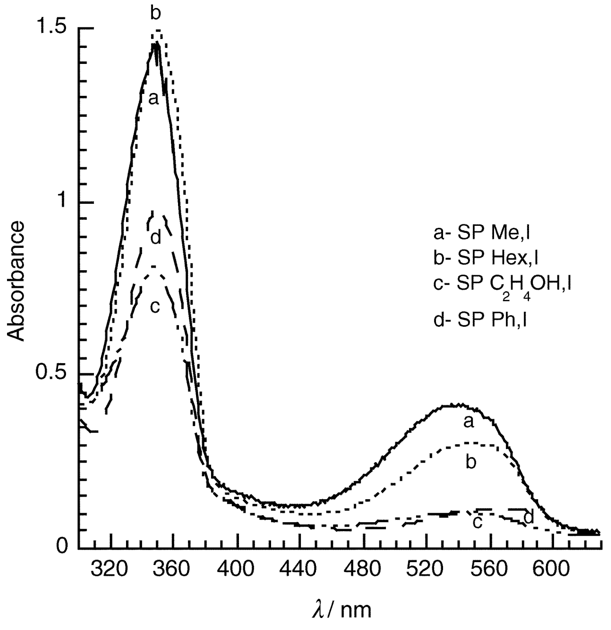


Fig. 2 UV-visible absorption spectra of the cationic spiropyrans in methanolic solution (0.04 M). Spectra are recorded after UV irradiation at 365 nm.

Table 3 Absorption maxima of spiropyrans $(SP–R)^+I^-$ in two media after irradiation at 365 nm

$(SP–R)^+I^-$	In MeOH λ_{max}/nm	In silica gels λ_{max}/nm
$(SP–Me)^+I^-$	350, 531	347, 502
$(SP–Ph)^+I^-$	348, 572	349, 529
$(SP–Hex)^+I^-$	351, 550	—
$(SP–C_2H_4OH)^+I^-$	348, 540	349, 469

Spiropyran-TMOS films. Thin films of spiropyran-doped silicate gels, stored under normal laboratory lighting conditions, were also found to be colourless. Their UV-vis spectra presented a unique band centred around 350 nm, indicating the presence of the closed form of the spiropyrans. Upon UV irradiation (365 nm), the films turned to orange–red or red, depending on the nature of R, and their spectra showed an intense absorption band centred at a wavelength that depended on the particular SP (between 470 and 530 nm). Results are summarised in Table 3.

These data reveal that the absorption band at 350 nm (closed form) remains unaffected when the spiropyrans change from the MeOH environment to the silica matrix, whereas the absorption band of the merocyanine form is strongly blue-shifted (by 30 nm for R = Me to 70 nm for $R = C_2H_4OH$). $(SP–Me)^+I^-$ and similar cationic spiropyrans are reported to exhibit negative solvatochromism in solution, similar to that of neutral spiropyran molecules.[4] Therefore, the blue shift observed when these species are included in the gel can be confidently ascribed to the strongly polar character of the gel as compared to the methanol solution. The very large value of the shift in the case of $(SP–C_2H_4OH)^+I^-$ is probably due to the strong stabilisation of the zwitterionic structure of the corresponding merocyanine form caused by hydrogen bonding of the $–CH_2CH_2OH$ substituent with the oxygen or silanol groups of the gel.

Evidence for reverse photochromism of the films. A photochromic cycle was performed on a thick film of a $(SP–Me)^+I^-$ doped gel stored under normal laboratory lighting conditions. The initial absorption spectrum of the film only displayed a band at 350 nm, as shown in Fig. 3(a). After UV irradiation, the film rapidly took on a red colouration characterised by a strong band at 502 nm [Fig. 3(b), (c)]. Bleaching of the film was achieved by irradiation with visible light at 500 nm; the visible absorption band at this stage had completely disap-

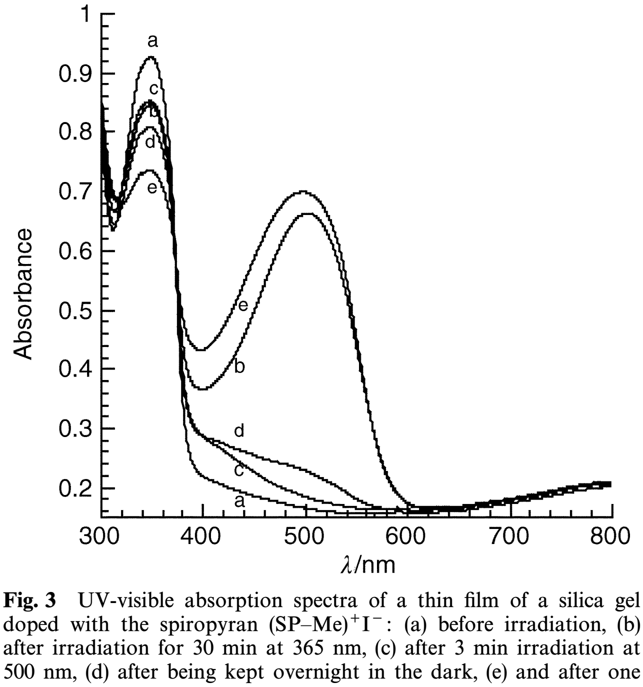


Fig. 3 UV-visible absorption spectra of a thin film of a silica gel doped with the spiropyran $(SP–Me)^+I^-$: (a) before irradiation, (b) after irradiation for 30 min at 365 nm, (c) after 3 min irradiation at 500 nm, (d) after being kept overnight in the dark, (e) and after one month in the dark.

peared [Fig. 3(c)]. The film was then kept in the dark and the absorption band at 502 nm slowly reappeared [Fig. 3(d),(e)]. After one month, this visible absorption band had become even more intense than it was just after the UV irradiation, while the 350 nm band had become very weak. Hence at this stage, a majority of the spiropyran species are present under their open merocyanine form, which is thermodynamically more stable.

Kinetics studies

The competition between normal and reverse photochromism has been studied on thin films of the four spiropyran iodide doped TMOS gels. In each case, the film was irradiated at 365 nm, then the decay of the absorption band of the film maintained in the dark was monitored at λ_{max}. A representative result is shown in Fig. 4 in the case of a film containing (SP–Ph)$^{+}$I^{-}.

Two of the four "thermal bleaching" curves, those obtained for (SP–Ph)$^{+}$I^{-} and (SP–hex)$^{+}$I^{-} could be fitted by a monoexponential equation $[A = B\ \exp(-kt) + C)$, and the extracted values of the k parameter are gathered in Table 4. The "closure rate" is always small and in all cases not all of the merocyanine reverts to the closed form. This is particularly marked in the case of (SP–Me)$^{+}$I^{-} and (SP–C$_2$H$_4$OH)$^{+}$I^{-} where the merocyanine form remains perfectly stable on the time scale of our studies (5×10^4 s). As a comparison, the time constant for the decay of the merocyanine form of (SP–Me)$^{+}$I^{-} in its pure crystalline state is $k = 2.6 \times 10^{-6}\ \mathrm{s}^{-1}$.[4] These data again strongly suggest that the zwitterionic form of the merocyanine is stabilised in the gels through interactions with the polar matrix, to such an extent that the "closure" process can even be blocked.[12]

Even though the UV-irradiated films did not spontaneously return to a totally decolourised state thermally, they were completely decolourised by visible light irradiation (450–500 nm). However, the bleached films, when left in the dark, progressively regained some colouration. This process, called reverse photochromism, was monitored by recording the recolouration at λ_{max} of the open form. Kinetic data and fit for the (SP–Ph)$^{+}$I^{-} doped gel are shown in Fig. 5.

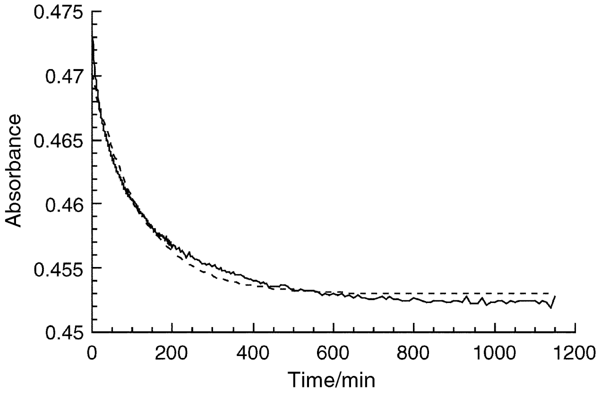


Fig. 4 Thermal fading of a (SP–Ph)$^{+}$I^{-} doped silica gel thin film left in the dark after irradiation at 365 nm. The thermal fading is observed at 500 nm.

Table 4 Photochromism kinetic data of (SP–R)$^{+}$I^{-} doped silica gels

(SP–R)$^{+}$I^{-}	Normal photochromism (closure in darkness $k/10^{-5}\ \mathrm{s}^{-1}$	Reverse photochromism (opening in darkness) $k/10^{-5}\ \mathrm{s}^{-1}$
(SP–Me)$^{+}$I^{-}	<0.01	5.16
(SP–Ph)$^{+}$I^{-}	13.6	4
(SP–C$_2$H$_4$OH)$^{+}$I^{-}	<0.01	3.5
(SP–Hex)$^{+}$I^{-}	10.8	4.5

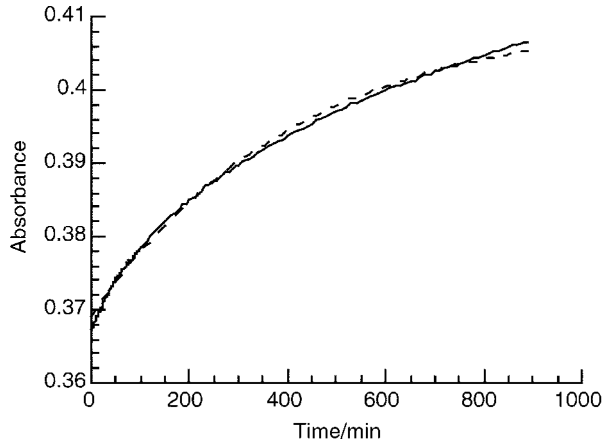


Fig. 5 Colouration of a (SP–Ph)$^{+}$I^{-} doped silica gel thin film left in the dark after irradiation at 500 nm. The colouration is observed at 540 nm.

The data characterising the thermal recolouration process could be fitted by a monoexponential equation $[A = B\ (1 - \exp(-kt) + C]$ and the extracted values of the k parameter are gathered in Table 4. The rate constants have nearly the same values for the four spiropyran-doped gels, whatever the nature of the substituent. The fact that only one rate constant is found is consistent with the chemical nature of the gel, where all cavities should be chemically identical. We are therefore led to the conclusion that a thermal equilibrium between the closed and open forms is reached in the dark, where normal and reverse photochromism are in competition. However, when the films of the doped gels are handled in normal laboratory lighting conditions, the incident visible radiation is sufficient to keep the films colourless.

Conclusion

The main goal of this work was to establish whether a new class of cationic spiropyrans, capable of displaying photochromism in the pure crystalline state, would also behave in an unusual way if the active species were embedded in a silica gel. Satisfactory conditions have been found to prepare the cationic spiropyran-doped silica gels, either as homogeneous transparent monoliths or thin films. The spectroscopic study of the films provides evidence for a competition between normal and reverse photochromisms. Consideration of these effects in light of previous results makes it clear that the cationic spiropyrans embedded in the silica gel matrix behave pretty much in the same way as the neutral spiropyrans do. In particular, the polar character of the gels prepared by hydrolysis of TEOS favours the occurrence of reverse photochromism, because the local polarity strongly interacts with the zwitterionic structure of the merocyanine form.[7,12] The similar behaviour of cationic *vs.* neutral spiropyrans was not fully *predictable* for the following reason: in the case of neutral spiropyrans, there is a large difference between the interaction of the matrix and the closed form on the one hand and the interaction of the matrix and open form on the other hand. The large difference is due to the zwitterionic character of the open form, which gives rise to strong dipole–dipole interactions. In the case of cationic spiropyrans, a smaller difference might be expected as the close form is positively charged and hence already interacts with the matrix. Experimentally, it turns out that reverse photochromism is still favoured in polar gels even when the spiropyrans are cationic. This strongly suggests that the position of the charges in the closed spiropyran form is irrelevant to the photochromic process, whereas the dipole–dipole interaction, which is significant for the ring closure and responsible for the enhanced stability of merocyanine in silica gels, is probably similar to those occurring in the merocyanine form of the spiropyran. To favour normal photochromism, a strategy already applied to neutral spiropyrans has been to prepare less polar gels possessing organic groups grafted on the silicon atoms. In the case of cationic spiropyrans however, other strategies can be envisaged and are currently being sucessfully developed in our group, such as intercalation in transparent nonpolar layered MPS_3 compounds (M = Mn, Cd).[25]

References

1 J. C. Crano and R. J. Guglielmetti, *Organic Photochromic and Thermochromic Compounds*, Plenum, New York, 1999, vol. 1.

2 J. C. Crano and R. J. Guglielmetti, *Organic Photochromic and Thermochromic Compounds*, Plenum, New York, 1999, vol. 2.

3 B. L. Feringa, W. F. Jager and B. De Lange, *Tetrahedron*, 1993, **49**, 8267.

4 S. Bénard and P. Yu, *Adv. Mater.*, 2000, **12**, 48.

5 S. Bénard and P. Yu, *Chem. Commun.*, 2000, 65.

6 S. Yagi, K. Maeda and H. Nakazumi, *J. Mater. Chem.*, 1999, **9**, 2991.

7 D. Levy, *Chem. Mater.*, 1997, **9**, 2666.

8 J. Biteau, F. Chaput, Y. Yokoyama and J. P. Boilot, *Chem. Lett.*, 1998, 359.

9 J. Biteau, F. Chaput and J. P. Boilot, *J. Phys. Chem.*, 1996, **100**, 9024.

10 M. Nogami and Y. Abe, *J. Mater. Sci.*, 1995, **30**, 5789.

11 D. Preston, J. C. Pouxviel, T. Novinson, W. C. Kaska, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1990, **94**, 4167.

12 B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani and J. A. Delaire, *J. Mater. Chem.*, 1997, **7**, 61.

13 M. Nogami and T. Sugiura, *J. Mater. Sci. Lett.*, 1993, **12**, 1544.

14 R. Corriu, *C. R. Acad. Sci., Sér. IIc: Chim.*, 1998, **1**, 83.

15 D. Levy and D. Avnir, *J. Phys. Chem.*, 1988, **92**, 4734.

16 I. Cascades, S. Constantine, D. Cardin, H. Garcia, A. Gilbert and F. Marquez, *Tetrahedron*, 2000, **56**, 6951.

17 T. Seki and K. Ichimura, *J. Phys. Chem.*, 1990, **94**, 3769.

18 H. Tagaya, T. Kuwahara, S. Sato, J. Kadokawa, M. Karasu and K. Chiba, *J. Mater. Chem.*, 1993, **3**, 317.

19 C. D. Weis, *J. Heterocycl. Chem.*, 1978, **15**, 29.

20 E. Pottier, M. Sergent, R. Phan Tan Luu and R. Guglielmetti, *Bull. Soc. Chim. Belg.*, 1992, **101**, 719.

21 M. Inouye, M. Ueno, K. Tsuchiya, N. Nakayama, T. Konishi and T. Kitao, *J. Org. Chem.*, 1992, **57**, 5377.

22 E. J. A. Pope and J. D. Mackenzie, *J. Non-Cryst. Solids*, 1986, **87**, 185.

23 C. J. Brinker and W. S. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990.

24 J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420.

25 S. Bénard, A. Léaustic, E. Rivière, P. Yu and R. Clément, *Chem. Mater.*, 2001, in press.