

Modified mesoporous MCM-41 as hosts for photochromic spirobenzopyrans

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The influence of the chemical composition and silylation of mesoporous MCM-41 materials on the photochromic behaviour of adsorbed spirocyan (BIPS) and 6-nitrospirocyan was studied. Upon incorporation, the spirocyans underwent ring opening to form either zwitterionic merocyanine or its corresponding *O*-protonated form. In all silica MCM-41 or in the MCM-41 containing aluminium, the *O*-protonated merocyanine was predominantly formed. In the case of MCM-41 modified by silylation of the OH groups, a mixture of zwitterionic merocyanine and spirocyan was present. The photochromic response was studied by means of steady-state irradiation and by laser flash photolysis. Steady-state irradiation ($\lambda > 450$ nm) of the solid samples gives rise in all cases to an intensity decrease of the absorption bands corresponding to either the protonated or the unprotonated merocyanine form (reverse photochromism). In contrast, laser flash photolysis at 308 nm of spirocyans supported on silylated MCM-41 allows observation of the photochemical ring opening of residual spirocyan to the corresponding zwitterionic form (normal photochromism).

Introduction

Spirocyans are one of the best studied photochromic molecules.¹⁻³ Their photochromic reaction generally involves interconversion of a colourless spirobenzopyran to a coloured merocyanine form initiated by light.⁴⁻¹² Not all spirocyans are stable in the pyran form and polar substituents may stabilise the zwitterionic merocyanine either in solution or in the crystalline state. In these cases photoinduced decolouration of the merocyanine form to the colourless spirocyan is termed reverse photochromism.⁴⁻⁷ The nature of the medium also plays an important role in determining the relative stability of the spirocyan and merocyanine forms. The merocyanine form has also been found to be relatively stable in non-hydrogen bonding polar solvents in which a slow rate for the thermal ring closing isomerisation is frequently observed.¹³ In solution this interconversion reaction occurs in the subnanosecond time domain, thus, making spirocyans ideal molecules to be used in the development of fast optical switches, memories and logic gates.⁷⁻¹⁵

When developing devices based on photochromism of spirocyans one of the crucial issues is to choose a solid host that allows the photochromic reactions to occur at the same rate and efficiency as those found in solution. Generally, the fast response to light exposure is no longer achievable when spirocyans are adsorbed on solid matrices or supports. The response time varies depending on the type of materials used.^{7,15-23} An ideal support should be inert, not alter the course of the photochromic reaction and permit the remarkable conformational changes induced during the photochromic reaction. In addition, the adsorption of the photochromic molecule should not compromise the mechanical properties of the material support. Glasses, sol-gel derived materials and polymers have been the preferred solids to study the photodynamic of spirocyans. Reports on the use of spirocyans as a probe for monitoring the gelation process in silicas indicated formation of the merocyanine species upon dehydration of the gel.²³ Lewis acidic sites which are formed during the dehydration catalyse the ring opening reaction to give rise

the zwitterionic merocyanine. This zwitterionic species establishes hydrogen bonds with the silanol groups of the silica, becoming the stable form present in the solid. Similarly other organosilica hybrid materials provoked this ring opening reaction.^{15,20}

Recently, there has been a surge in the use of synthetic MCM mesoporous materials as hosts to adsorb organic guests mainly for their application in catalysis. Mesoporous aluminosilicates of MCM type are host materials whose structure is formed by an array of parallel hexagonal channels. This interest in using MCM solids as hosts derives from the extremely high surface area of these materials (~ 800 m² g⁻¹), the periodic ordering of their void space and the large size (>20 Å) of their pores.²⁴⁻³⁰ Interestingly, a study on the possible use of mesoporous materials as a support for spirocyans is lacking. The possibility of suitable structural modifications without altering the ordering of their mesoporous nature could be a tool to tune the polarity and hydrogen bonding ability of the internal surface. The most attractive feature of MCM-like materials compared to conventional microporous zeolites is the large size of the pores that permits freedom in loading of the guest molecule without affecting the structural and mechanical properties of the support. In this report we have studied the influence of the adsorption on the photochemistry of spirocyan (BIPS) and 6-nitrospirocyan (6-NO₂-BIPS). For our study we have used three different porous MCM-41: all silica MCM-41 (MCM-41), an MCM-41 containing 15% aluminium (Al/MCM-41) and a trimethylsilyl modified sample (MCM-41Si). It was expected that adsorption on these three different mesoporous supports would produce remarkable changes in the chemical and photochromic behaviour of the spirocyans due to the presence of weak acid sites (in the case of MCM-41 and Al/MCM-41) or changes in the relative hydrophilicity/hydrophobicity of the surface (MCM-41Si is much more hydrophobic compared to MCM-41). Information about the chemistry of a spirocyan molecule on these supports will give us a lead towards the design of optimum MCM-41 materials for use in the fabrication of optical switching devices. In an earlier communication related to this work we have demonstrated the ship-in-a-bottle

synthesis of spiropyrans in Y zeolites.¹⁸ A large contrast in the properties of spiropyrans was observed upon adsorption on mesoporous MCM-41 materials compared to Y zeolite.

Experimental

MCM-41 and Al/MCM-41 were prepared by hydrothermal crystallisation of gels of appropriate composition using cetyltrimethylammonium bromide as the structure directing agent in combination with tetramethylammonium hydroxide. More detailed experimental procedures have been reported elsewhere.³¹ MCM-41Si functionalized with trimethylsilyl groups was prepared by the reaction between dehydrated (250 °C, under vacuum for 3 h) MCM-41 and hexamethyldisilazane in THF under reflux conditions. The progress of the reaction was monitored by gas chromatography of the supernatant liquid and the suspension filtered after 90% of the initial hexamethyldisilazane had been used up. The residue obtained was washed several times with THF and then with CH₂Cl₂ and dried under vacuum. The degree of silylation achieved for MCM-41Si was determined by comparing the IR spectra in the region of the silanol groups at 3650 cm⁻¹ before and after treatment. From these measurements it was estimated that the maximum degree of silylation was 70% and only 30% of the residual silanol groups (probably located in "hidden", inaccessible nests) survives this treatment. The spiropyran derivatives were prepared by condensation of 2-methylene-1,3,3-trimethylindoline and benzaldehyde or *p*-nitrobenzaldehyde in ethanol at room temperature.³² The spiropyrans thus prepared were recrystallized twice from ethanol.

Incorporation of the spiropyrans was carried out by stirring a suspension of corresponding dehydrated mesoporous support (1 g) in a solution of the spiropyran (10 ml, 1 × 10⁻⁴ M) in dichloromethane under reflux for 3 hours. On completion, the suspension was filtered and the residue was washed with 10 ml of dichloromethane and dried under vacuum. All the samples were analysed by combustion chemical analysis using a Fisons EA 1108 CHNS combustion chemical analyser, and by thermogravimetry and differential scanning calorimetry using a Netzsch STA 409 thermobalance and kaolin as inert standard. From these measurements, the amount of spiropyrans loaded was estimated to be 3% by weight. Diffuse reflectance UV-Vis spectra were recorded using a Shimadzu Model UV 2101 PC spectrophotometer fitted with a Praying Mantis accessory for solid samples and BaSO₄ as standard. FT Raman spectra were obtained by using Bio-Rad Model II FT Raman spectrophotometer with a Nd-YAG laser as the excitation source and a liquid nitrogen cooled detector. The power of the laser at the sample was 100 mW and the spectral resolution was 1 cm⁻¹. Steady-state irradiations of the zeolite powders were carried out using the 200 W output of a high pressure mercury or Xenon lamps with a 450 nm band pass filter. The fluorescence spectra were recorded using an Edinburgh FL900 fluorescence spectrophotometer. Laser flash photolysis studies were carried out using the 308 nm output of an excimer laser and an Oriol kinetic spectrometer which has been described elsewhere.³³

Results and discussion

Influence of incorporation on the spiropyran-merocyanine equilibrium

Diffuse reflectance spectra. The absorption spectra of spiropyran can be rationalized as the result of the sum of two spectra arising from the independent trimethylindole ring and phenolic chromophores. No conjugation exists between these two moieties because of the orthogonality maintained by the spiro linkage. In contrast, the optical spectrum of the merocyanine form corresponds to that of a conjugated π -system involving the phenolate and the quaternary nitrogen of the

indole ring. Samples obtained upon incorporation of BIPS and 6-NO₂-BIPS to MCM-41, MCM-41Si or Al/MCM-41 were initially colourless but on storage for one day became coloured. Samples did not undergo further changes with time. This time evolution indicates that after adsorption a slower intraparticle diffusion/relocation of spiropyrans is taking place until a stationary distribution is reached. This slow diffusional relocation is common for processes in the solid state. The diffuse reflectance spectra recorded for these samples exhibited a different feature to those of the spiropyran or its open merocyanine form.

The stationary diffuse reflectance UV-Vis spectra recorded for BIPS and 6-NO₂-BIPS on MCM-41 and Al/MCM-41 showed bands at 415–440 nm, whereas that of hydrophobic MCM-41Si showed an additional band at 545 nm, which was comparatively much more intense. The absorption bands with λ_{\max} centred around 440 nm (Figs. 1 and 2) are indicative of a

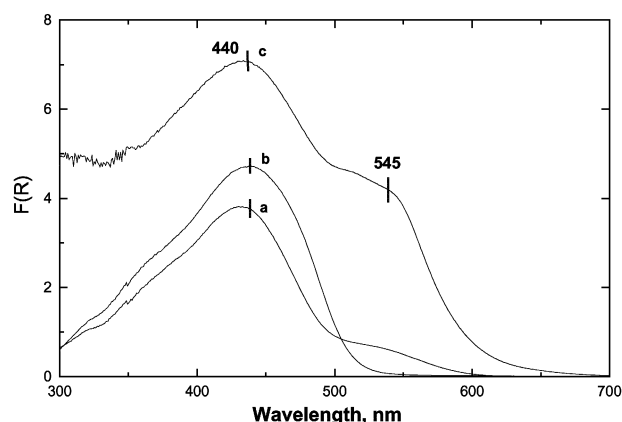


Fig. 1 UV-Vis diffuse reflectance spectra [plotted as the Kubelka-Munk function $F(R)$] recorded 24 h after the adsorption of BIPS on a) MCM-41; b) Al/MCM-41 and c) MCM-41Si. The bands at 440 and 545 nm are attributed to the protonated merocyanine form and the merocyanine form, respectively.

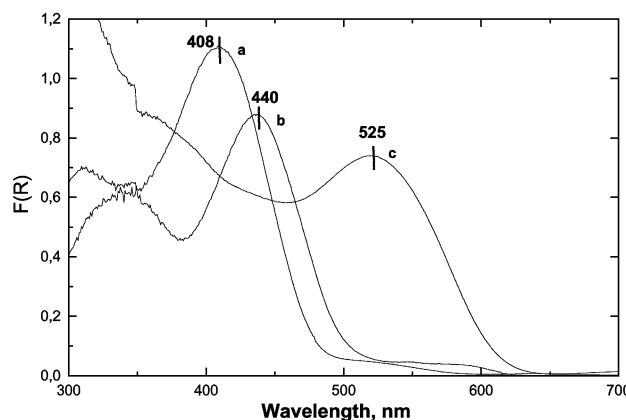
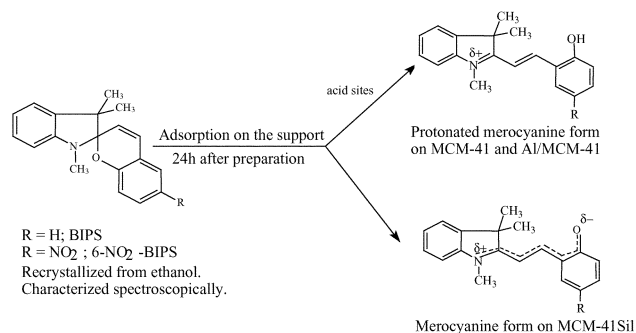


Fig. 2 UV-Vis diffuse reflectance spectra [plotted as the Kubelka-Munk function $F(R)$] recorded 24 h after the adsorption of 6-NO₂-BIPS on a) MCM-41; b) Al/MCM-41 and c) MCM-41Si. The bands at 408, 440 and 525 nm correspond to the protonated merocyanine form adsorbed on MCM-41 and Al/MCM-41 and the merocyanine on MCM-41Si, respectively.

less conjugated system than merocyanine. Previously Shimizu *et al.* and later Raymo *et al.* studied the effect of acids on the properties of the spiropyrans and found similar absorption spectra for the spiropyrans in acidic media to those shown in Figs. 1 and 2. These authors assigned these unique UV-Vis spectra to the protonated form of merocyanine.⁵⁻⁷ A similar absorption was observed for spiropyran in acidified fluorinated alcohols and in ethanolic solutions.¹³ Taking these precedents into account, the band observed at 440 nm can be attributed to

a protonated merocyanine form. Therefore, the slow colouration of the materials on standing indicates that adsorption of spiropyrans on MCM-41 and Al/MCM-41 produces a slow ring opening reaction leading to the formation of the protonated form of the merocyanine by interaction with the acidic silanol groups present in the mesoporous material as illustrated in Scheme 1. Further evidence for the nature of the species present can be obtained from Raman spectroscopic studies.



Scheme 1 Processes observed upon adsorption of spiropyrans on MCM-41 aluminosilicates.

Raman spectral studies. To confirm the rationalisation of the results obtained in the diffuse reflectance UV–Vis measurements, the Raman spectra of these materials were also recorded.

Fig. 3 shows the Raman spectra obtained for BIPS adsorbed

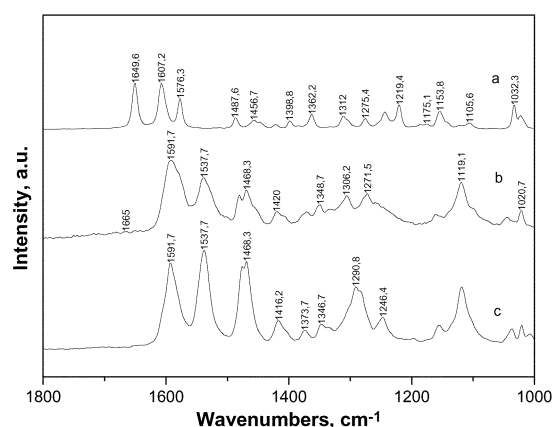


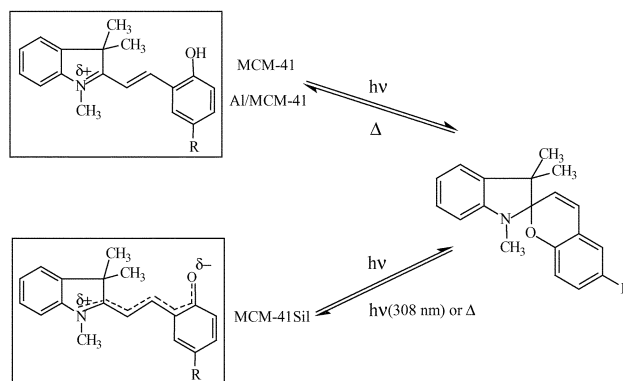
Fig. 3 Raman spectrum of pure BIPS crystals (a) and those recorded 24 h after adsorbing BIPS on MCM-41 (b) and Al/MCM-41 (c).

on MCM-41 and Al/MCM-41. For the sake of comparison, Fig. 3 also includes the Raman spectrum for a crystalline BIPS sample corresponding to the closed spiropyran form. Since the Raman spectrum of the closed spiropyran form is totally different to that recorded for the MCM-41 and Al/MCM-41 solids it can be concluded that a complete transformation of BIPS has spontaneously occurred upon adsorption. Furthermore, the Raman spectra of the adsorbed guests show a one to one correspondence with the Raman absorptions reported by Yoda *et al.* for the protonated form of BIPS with prominent bands at 1592, 1537, 1468, 1290, 1246, 1156, 1119, 932 and 631 cm⁻¹.³⁴ These authors assigned the structure to the protonated form on the basis of the Raman spectra of BIPS obtained for acidified solutions as well as from NMR data of the protonated merocyanine form. The coincidence of the Raman spectra firmly demonstrates that the stable form obtained after incorporation into the mesoporous MCM-41 as well as Al/MCM-41 is the protonated merocyanine in good agreement with the diffuse reflectance UV–Vis spectra. In contrast, the Raman spectra obtained for BIPS and 6-NO₂-BIPS incorporated on modified MCM-41SiI appeared to arise from a

combination of two species which were assigned as the spiropyran and the zwitterionic merocyanine forms. Again this agrees with the information provided by diffuse reflectance UV–Vis spectra in which significant absorption bands at 290 and 540 nm corresponding to the closed spiropyran and the zwitterionic merocyanine can be observed (see plot c in Figs. 1 and 2). Silylation reduces the number of OH groups, thus transforming the original hydrophilic MCM-41 into a hydrophobic, non-hydrogen bonding MCM-41SiI solid. Although the degree of silylation of MCM-41SiI is not complete (see Experimental section) it can be estimated that silylation masks 70% of the initial silanol groups. It is very likely that the unaffected OH groups are those located in inaccessible nests of MCM-41. In any case, the increase in the hydrophobicity of MCM-41SiI is immediately reflected in the absence of the *O*-protonated form present in the solid and also in the photochemical behaviour of the organic guests (see following section).

Study of the photochromism in mesoporous supports

The photochromic behaviour upon immobilization of BIPS and 6-NO₂-BIPS on the three mesoporous supports was studied carrying out steady-state irradiations, monitoring the diffuse reflectance spectra as a function of time. Since merocyanine (in the case of MCM-41SiI) or its protonated form (in the case of MCM-41 and Al/MCM-41) are initially the species present in the materials, irradiations were carried out using a cut-off filter of $\lambda > 450$ nm, thus, ensuring the selective irradiation of the protonated or unprotonated merocyanine forms. As expected, this produced in all cases the decolouration of the solids. This decolouration can be interpreted as the result of the photo-induced ring closure back to the colourless spiropyran form (Scheme 2). This behaviour corresponds to what is known as “reverse” photochromism.^{4–7}



Scheme 2 Photochromic behaviour observed for BIPS and 6-NO₂-BIPS adsorbed on the mesoporous supports.

Precedents showing that the *O*-protonated merocyanine in acid solutions exhibits “reverse” photochromism, as we claim here, are sufficiently well documented.^{4–7}

Upon standing for several minutes the colour is regained and the characteristic absorption band above 400 nm reappears. Fig. 4 shows two representative examples for BIPS and 6-NO₂-BIPS of consecutive irradiation ($\lambda > 450$ nm)–dark storage cycling that gives an idea of the extent of decolouration, response time, completeness of recovery and fatigue of the systems.

The results shown in Fig. 4 deserve some comments. Firstly, the photochromic response on Al/MCM-41 is more complete for BIPS [80% relative decrease of $F(R)$ measured at 460 nm] than for 6-NO₂-BIPS [10% of relative $F(R)$ variation]. The influence of substituents on the photochromism of spiropyrans is well established in the literature.⁴ Secondly, a certain fatigue in the recovery of the initial $F(R)$ value after irradiation–dark storage cycling is observed. This fatigue is again more pronounced in the case of BIPS (33% of the total response after 4

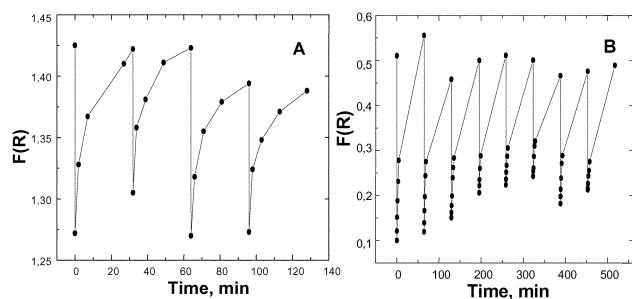


Fig. 4 Changes in the absorbance [measured as the Kubelka-Munk function $F(R)$] at 460 nm for consecutive cycles of irradiation ($\lambda > 450$ nm)-dark storage for the samples BIPS on Al/MCM-41 (A) and 6-NO₂-BIPS on Al/MCM-41 (B).

cycles) as compared with 6-NO₂-BIPS (7% fatigue of the total response after 8 cycles).

Concerning the recovery time, after irradiation it takes the spiropyrans adsorbed on Al/MCM-41 about 30 min in the dark to evolve towards the pre-irradiation state. This time is much longer than that required for 6-NO₂-BIPS in ethanolic solution where it takes less than a minute. This reflects the influence of adsorption on a solid surface restricting the conformational mobility of the adsorbed guest.

As noted earlier, MCM-41SiI is the most hydrophobic material, being the only solid support in which the spiropyran and zwitterionic forms are present. For this sample irradiation with light of wavelength longer than 450 nm also produces decolouration of the solid accompanied by a concurrent increase of the absorption band at 290 nm corresponding to the spiropyran (Fig. 5), both intensity variations following the same

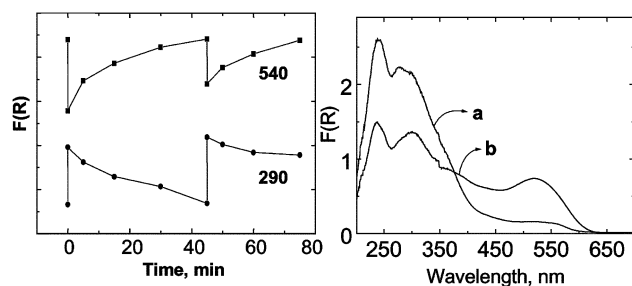


Fig. 5 Left: changes in absorbance during consecutive cycles of irradiation ($\lambda > 450$ nm)-dark reaction for 6-NO₂-BIPS on MCM-41SiI. Right: diffuse reflectance UV-Vis spectra of 6-NO₂-BIPS on MCM-41SiI recorded a) after 20 minutes of irradiation and b) before irradiation.

kinetics. Again upon standing for several minutes the colour and the initial concentration of merocyanine are recovered.

Furthermore, recovery of the merocyanine could be remarkably accelerated by irradiation in the absorption band of the spiropyran using 308 nm laser excitation, which indicates that the “normal” photochromism could also take place for this solid. In fact, distinctive of the silylated MCM-41SiI was the presence of a sufficient concentration of spiropyran that allowed observation (exclusively for this solid) of the occurrence of direct “normal” photochromism. This was demonstrated by performing diffuse reflectance laser flash photolysis of BIPS and 6-NO₂-BIPS on hydrophobic MCM-41SiI. Laser excitation at 308 nm of BIPS on MCM-41SiI and 6-NO₂-BIPS on MCM-41SiI resulted in an instantaneous build-up of absorption from 400 to 650 nm that did not fully decay on the longest time scale available to our nanosecond system that goes up to 1 ms. Numerous examples can be found in the literature for which the lifetime of the unstable intermediates undergoes a dramatic increase compared to solution upon adsorption on solid surfaces. The transient absorption spectrum shown in Fig. 6 matches the UV-Vis spectrum of the corresponding

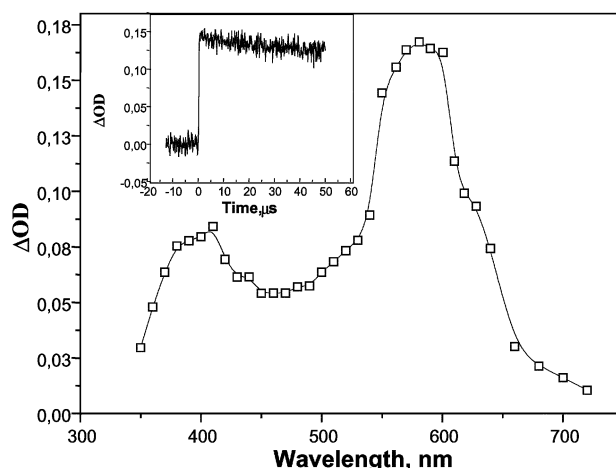


Fig. 6 Transient absorption spectrum of BIPS on MCM-41SiI recorded 2.5 μ s after 308 nm laser excitation. The insert shows the signal build-up and decay monitored at the maximum wavelength.

zwitterionic merocyanine form reported in the literature, firmly proving that direct photochromism is occurring in this case. Since the transient absorption spectrum does correspond to the UV-Vis difference spectrum before and after the laser pulse, it shows exclusively the species that is formed photochemically (only the zwitterion), even if other species are present before and after the laser flash. Noteworthy is the fact that this photochemical ring opening could not be observed for any of the four MCM-41 and Al/MCM-41 samples, probably reflecting the lack of a sufficient concentration of the spiropyranic forms on these two hydrophilic solids with acidic sites. This illustrates the influence of surface silylation on the photochemical behaviour of the adsorbed guest.

Conclusion

The presence of aluminium in the chemical composition of MCM-41 plays a very marginal role in the distribution equilibrium between spiropyran and the *O*-protonated merocyanine form as well as in the photochemical behaviour of the guest. Both solids MCM-41 and Al/MCM-41 have been found to be sufficiently hydrophilic to favour ring opening and sufficiently acidic to protonate the zwitterionic form. Silylation of MCM-41 reduces considerably the hydrophilicity and acidity of the mesoporous solid. As a result, both the spiropyran and the unprotonated merocyanine simultaneously coexist, giving the opportunity to observe “normal” and “reverse” photochromism in the same system. Our results exemplify the influence that surface modifications of large surface area, mesoporous solids has on the hydrophilic/hydrophobic nature of the surface and on the control of the photochemical behaviour of photochromic guests.

References

- 1 R. C. Bertelson and G. H. Brown, in *Photochromism*, Wiley, New York, 1971.
- 2 E. Hadjoudis, *Photochromism. Molecules and Systems. In Studies in Organic Chemistry*, eds. H. Dürr and L. Bouas, Elsevier, Amsterdam, 1990, p. 685.
- 3 C. Reichardt, *Solvatochromic Dyes as Solvent Polarity Indicators*, *Chem. Rev.*, 1994, **94**, 2319–2358.
- 4 E. Berman, R. E. Fox and F. D. Thomson, Photochromic spiropyran. I. The effect of substituents on the rate of ring closure, *J. Am. Chem. Soc.*, 1959, **81**, 5605–5608.
- 5 I. Shimizu, H. Kokado and E. Inoue, Photoreversible photographic systems. VI. Reverse photochromism of 1,3,3-trimethylspiro[indoline-2,2'-benzopyran]-8'-carboxylic acid, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1730–1734.
- 6 I. Shimizu, H. Kokado and E. Inoue, Photoreversible photographic systems. V. Reverse photochromism of (photospiran/acid) system in acetone, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1726–1729.

- 7 F. Raymo and M. S. Giordani, Signal processing at the molecular level, *J. Am. Chem. Soc.*, 2001, **123**, 4651–4652.
- 8 C. Lenoble and R. S. Becker, Photophysics, photochemistry, kinetics, and mechanism of the photochromism of 6'-nitro-indolinospiropyran, *J. Phys. Chem.*, 1986, **90**, 62–65.
- 9 N. P. Ernstring and T. Arthen-Engeland, Photochemical ring-opening reaction of indolinospiropyran studied by subpicosecond transient absorption, *J. Phys. Chem.*, 1991, **95**, 5502–5509.
- 10 S. Aramaki and G. H. Atkinson, Spiroanthropyran photochromism: picosecond time-resolved spectroscopy, *J. Am. Chem. Soc.*, 1992, **114**, 438–444.
- 11 N. Tamai and H. Masuhara, Femtosecond transient absorption spectroscopy of a spirooxazine photochromic reaction, *Chem. Phys. Lett.*, 1992, **191**, 189–194.
- 12 V. S. Marevtsev and N. L. Zaichenko, Peculiarities of photochromic behavior of spiropyran and spirooxazines, *J. Photochem. Photobiol., A*, 1997, **104**, 197–202.
- 13 T. Suzuki, F.-T. Lin, S. Priyadashy and S. G. Weber, Stabilization of the merocyanine form of photochromic compounds in fluoro alcohols is due to a hydrogen bond, *Chem. Commun.*, 1998, 2685–2686.
- 14 S. Aramaki and G. H. Atkinson, Spirooxazine photochromism: picosecond time-resolved Raman and absorption spectroscopy, *Chem. Phys. Lett.*, 1990, **170**, 181–186.
- 15 G. Wirnsberger, B. J. Scott, B. F. Chmelka and G. D. Stucky, Fast response photochromic mesostructures, *Adv. Mater. (Weinheim, Ger.)*, 2000, **12**, 1450–1454.
- 16 A. Tork, F. Boudreault, M. Roberge, A. M. Ritcey, R. A. Lessard and T. V. Galstian, Photochromic behavior of spiropyran in polymer matrices, *Appl. Opt.*, 2001, **40**, 1180–1186.
- 17 R. Matsushima, M. Nishiyama and M. Doi, Improvements in the fatigue resistances of photochromic compounds, *J. Photochem. Photobiol., A*, 2001, **139**, 63–69.
- 18 I. Casades, S. Constantine, D. Cardin, H. Garcia, A. Gilbert and F. Marquez, 'Ship-in-a-Bottle' Synthesis and Photochromism of Spiropyran Encapsulated within Zeolite Y Supercages, *Tetrahedron*, 2000, **56**, 6951–6956.
- 19 M. Alonso, V. Reboto, L. Guiscardo, A. S. Martin and J. C. Rodriguez-Cabello, Spiropyran Derivative of an Elastin-like Bioelastic Polymer: Photoresponsive Molecular Machine to Convert Sunlight into Mechanical Work, *Macromolecules*, 2000, **33**, 9480–9482.
- 20 H. Tagaya, T. Nagaoka, T. Kuwahara, M. Karasu, J.-I. Kadokawa and K. Chiba, Preparation and photochromism of sulfonated spiropyran-silica nanocomposites, *Microporous Mesoporous Mater.*, 1998, **21**, 395–402.
- 21 G. Baillet, G. Giusti and R. Guglielmetti, Study of the fatigue process and the yellowing of polymeric films containing spirooxazine photochromic compounds, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1220–1225.
- 22 V. Weiss and V. Z. Krongauz, Photokinetics in photochromic polymers studied by holographic recording, *J. Phys. Chem.*, 1994, **98**, 7562–7565.
- 23 D. Preston, J. C. Pouxviel, T. Novinson, W. C. Kaska, B. Dunn and J. I. Zink, Photochromism of spiropyran in aluminosilicate gels, *J. Phys. Chem.*, 1990, **94**, 4167–4172.
- 24 A. Corma, From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis, *Chem. Rev.*, 1997, **97**, 2373–2419.
- 25 M. Hartmann and L. Kevan, Transition-Metal Ions in Aluminophosphate and Silicoaluminophosphate Molecular Sieves: Location, Interaction with Adsorbates and Catalytic Properties, *Chem. Rev.*, 1999, **99**, 635–663.
- 26 V. Ramamurthy, *Photochemistry in Organized and Constrained Media*, VCH, New York, 1991.
- 27 V. Ramamurthy, D. F. Eaton and J. V. Caspar, Photochemical and photophysical studies of organic molecules included within zeolites, *Acc. Chem. Res.*, 1992, **25**, 299–307.
- 28 R. G. Weiss, V. Ramamurthy and G. S. Hammond, Photochemistry in organized and confining media: a model, *Acc. Chem. Res.*, 1993, **26**, 530–536.
- 29 N. J. Turro, Supramolecular organic and inorganic photochemistry: radical pair recombination in micelles, electron transfer on starburst dendrimers, and the use of DNA as a molecular wire, *Pure Appl. Chem.*, 1995, **67**, 199–208.
- 30 J. C. Scaiano and H. Garcia, Intrazeolite Photochemistry: Towards the Control of Molecular Photochemistry, *Acc. Chem. Res.*, 1999, **32**, 783–793.
- 31 A. Corma, Preparation and catalytic properties of new mesoporous materials, *Top. Catal.*, 1998, **4**, 249–260.
- 32 K. Maeda, Photochromism in organized media, *Yuki Gosei Kagaku Kyokaiishi*, 1991, **49**, 554–565.
- 33 J. C. Scaiano, *CRC Handbook of Organic Photochemistry*, CRC Press, Boca Raton, 1989.
- 34 K. Yoda, T. Ohzeki, T. Yuzawa and H. Takahashi, Resonance Raman studies of the solvatochromism and acid-base equilibria of 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], *Spectrochim. Acta, Part A*, 1989, **45A**, 855–862.

