

Photochromism of spiropyran in molecular sieve voids: effects of host–guest interaction on isomer status, switching stability and reversibility

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Spiropyran or its preferred configurational isomers, respectively, are incorporated in faujasite (NaY, HY and DAY) cages by *in situ* synthesis, and in Si-MCM-41 channels by wetness impregnation. Luminescence spectra of the colored isomers indicate the non-aggregated incorporation of merocyanine forms. High quantum yields for the photochromism (~75%) demonstrate the ready access of the chromophores for the photons of the laser pulses, used for the photoinduced switching between the different configurational isomers. The strong retardation of the thermal relaxation rate from the photoproduct *cis*-merocyanine to the thermodynamically preferred *trans*-merocyanine in the faujasite hosts (HY, DAY) in comparison to spiropyrans in SiO₂ or Al₂O₃ is attributed to an increase of the rotation barriers by the imposed spatial restrictions. Among the different faujasites the dealuminated Y-zeolite (DAY) exhibits the lowest relaxation rates of the photoproduct and the highest switching reversibilities between the *trans*- and the *cis*-merocyanine.

1. Introduction

The peculiar characteristics of photochromic molecules, *i.e.*, the light-induced shifts of their absorption maxima, the resulting strong changes of the extinction coefficients as well as high quantum yields for the corresponding photochemical reactions, are the reasons for continued consideration of their potential practical applications. Up to now applications are realised only in a few cases, like polymer-based photochromic eyewear or security printing ink. However, there is potential for various items, like fluid-flow visualization, optical switching and information storage or reversible holographic systems.^{1–4} A broader application of organic photochromic compounds is mainly restricted by their limited lightfastness (fatigue) due to photodegradation processes and to quick relaxation of the energy-rich photoinduced state. Photochromic molecules, accommodated in porous silicas, are repeatedly studied with respect to the influence of host–guest interactions on the photoprocesses, giving indications for strongly increased lightfastness.^{5–8} Also, enhanced stabilities against thermal relaxation and improved photoswitching reversibility are observed for spiropyran derivatives in porous silica,⁹ or for azobenzene in the regular pore system of the zeolite ZSM-5 and of its structure analogue aluminium phosphate AlPO₄-5.¹⁰ Since the regular void system of molecular sieves has a crystallographically defined structure, which can be prepared reproducibly with respect to its structural and chemical properties, the study of photochromism in such host materials should give insight into various influences of host–guest interactions, like spatial constraints, polarities or acidities, on photochemical processes. In contrast, fast response of thermal relaxation was observed when embedding photochromic molecules in hydrophobic parts of Si-MCM-41.¹¹

In the following, the photochromism of spiropyran, the most widely studied photochromic dye,^{1,3} incorporated in the void structure of molecular sieves like NaY, HY and DAY is reported. Inclusion of coloured metal complexes in the voids of molecular sieves, which are stable towards intensive extraction procedures with solvents, could be achieved either *via in situ* (ship-in-the-bottle) synthesis procedures or *via* crystallisation inclusion.^{12,13} The incorporation of organic dyes *via in situ* synthesis, where a stable inclusion can be attributed either to sterical constraints or to strong coulomb interactions, is described only in a few cases.^{14–16}

A photochromic molecule of the spiropyran family is chosen, since the spiropyrans can be synthesised in the supercages of faujasites by a one-step reaction of a salicylaldehyde with a previously adsorbed indoline compound. This simple reaction is of great advantage, since especially for reactions in host materials the obtained yields decrease drastically with the complexity of the reactions. Further, spiropyrans were observed to exhibit especially strong matrix effects, *e.g.*, in porous silicas,^{9,17–22} which might be attributed to the zwitterionic mesomeric form of the *trans*-photomerocyanine, *i.e.*, with a partial positive charge at the spiro carbon in the heterocycle and a partial negative charge on the phenolic oxygen. This polar structure could peculiarly interact with a polar mineral host. The molecular sieve zeolite Y was selected not only with respect to its spatial constraints (cage diameter: 1.3 nm), but also due to its polar ionic lattice structure. To simulate the situation in the porous amorphous silicas, spiropyrans have been impregnated onto the inner pore walls of the mesoporous molecular sieve Si-MCM-41, providing wider but also regular pores (channels with diameters of about 3.5 nm). These samples and poly(vinyl acetate) (PV)-hosted spiropyran have been used for comparison.

2. Experimental

2.1 Materials

The applied Y-faujasites (Si:Al ratio: 2.9, crystal size: 1–2 μm , BET value: $985\text{ m}^2\text{ g}^{-1}$) are based on hydrothermally synthesised NaY.²³ The faujasite HY was obtained from the NaY *via* NH_4^+ ion exchange and subsequent calcination, using a heating rate of 40 K h^{-1} and keeping the final temperature of 835 K for 24 h. A DAY prepared from HY *via* isomorphous substitution of Al by Si (Si:Al ratio: 100, BET value: $964\text{ m}^2\text{ g}^{-1}$) was kindly provided by the DEGUSSA Company. Mesoporous silica material Si-MCM-41 was prepared using recipes described previously.²⁴ Commercial poly(vinyl acetate) (Hoechst) was used as an organic polymeric host material.

The photochromic dye 2*H*-spiro[[6]nitrochromene-2,2'-[1,3,3]trimethylindoline] (acronym: NBIPS) (Fig. 1, 3), which was used for impregnation procedures, was synthesised following standard procedures.²⁵ Mass, IR and UV-vis spectra were in agreement with reported analytical data for NBIPS.²⁶ An impregnation of Si-MCM-41 with NBIPS used concentrated solutions of 3 in ethanol (2×10^{-5} mol dye in 40 ml solvent). The slurry was shaken at room temperature for 4 d. Subsequently, the solvent was slowly removed using a vacuum rotation evaporator at 323 K.

For the *in situ* synthesis of the photochromic dye in faujasites (zeolite Y) the precursor molecules 1,3,3-trimethyl-2-methyleneindoline (Aldrich M 4,620-9) (Fig. 1, 1) and 5-nitrosalicylaldehyde (Merck 820904) (Fig. 1, 2) were used.

1 g Faujasite (HY, DAY or NaY) was suspended in a solution of 5×10^{-4} mol of 1,3,3-trimethyl-2-methyleneindoline in 15 ml ethanol. The slurry was shaken for 3 d to achieve a high degree of adsorption, filtered and thoroughly washed with ethanol. Subsequently, a solution of 4×10^{-3} mol of 5-nitrosalicylaldehyde in 15 ml ethanol was added, and the suspension was stirred at room temperature (RT) for 3 h and heated under reflux for 70 h. Since the nitrosalicylaldehyde diffuses slowly through the pores and reacts with adsorbed indoline molecules, the colour of the suspension changes gradually from red–orange to red–violet. Finally, the slurry was filtrated hot and, subsequently, extracted in a Soxhlet with ethanol for 70 h.

2.2 Characterisation

The qualities of the parent host materials and of the obtained composite materials were checked by X-ray diffraction in the high-angle (zeolites) and low-angle (Si-MCM-41) range, scanning electron microscopy and adsorption measurements.²⁴

Chromophore syntheses were examined by UV-vis spectroscopy, and mass spectrometry. The host–guest interactions of

the composites were determined by diffuse reflectance (DR) UV-vis spectroscopy and fluorescence spectroscopy.

2.3 Photochromism

Photochromism experiments were carried out using laser pulses of high irradiation power or quantum density, respectively, enabling reduction of the irradiation time for complete switching by one or two orders of magnitude compared to conventional UV-vis light sources.²⁶ The irradiation was generated with dye lasers (Radiant Dyes RDP-1-NA) filled with either Coumarin 307 (465–550 nm) or RDC 360-NEU dye (340–370 nm). The dye laser was pumped with an excimer laser (Radiant Dyes RD-EXC-100) filled with a Xe–HCl–BCl₃ mixture (308 nm), which provided an average power of 500 mW cm^{-2} at a pulse frequency of 5 Hz and a pulse duration of 100 ns. The laser beam, which was widened by means of a lens, was directed to the sample ($\sim 50\text{ mg}$) which was fixed in a sample holder (diameter: $\sim 1\text{ cm}$).

For the photochromism experiments the dye-loaded zeolite and Si-MCM-41 samples have been diluted with parent matrix material to an overall dye concentration of 1×10^{-5} mole g^{-1} , *i.e.* 50 mg of irradiated sample in all cases contain 3.0×10^{17} dye molecules.

Since a direct measurement of the diffuse reflectance of the samples under laser irradiation was impossible with our system, the sample was transferred into the dedicated chamber (Harrick) of an UV-vis spectrometer (Varian, Cary 4, Praying Mantis light collector) immediately after laser irradiation. Since the time required for the sample transfer and for recording a DR-UV-vis spectrum ($\sim 1\text{ min}$) was two ($t_{1/2} = 100\text{ min}$, poly(vinyl acetate) host) to four ($t_{1/2} = 10000\text{ min}$, DAY host) orders of magnitude smaller than the half-lifetimes measured for the thermal relaxation processes, the study of the kinetics of the switching stability was not significantly affected by this procedure.

3. Results

3.1 Synthesis of spirocyan dyes in the host materials

The *in situ* synthesis of NBIPS into the faujasite structures NaY, HY or DAY, as schematically shown in Fig. 1, yielded loadings which can be expressed as a percentage of filled supercages (Table 1), *i.e.*, NaY (0.2%) < DAY (4%) < HY (30%). The degrees of loading from *in situ* synthesis were estimated from calibrations, using (i) series of dye-impregnated faujasites, and (ii) dilution with the parent zeolite material to keep the Kubelka–Munk function in a range of 0.1–3, where linear correlation with the dye concentration is valid. All the zeolite samples were extracted in a Soxhlet apparatus with ethanol until the solution was clear, which indicates that the

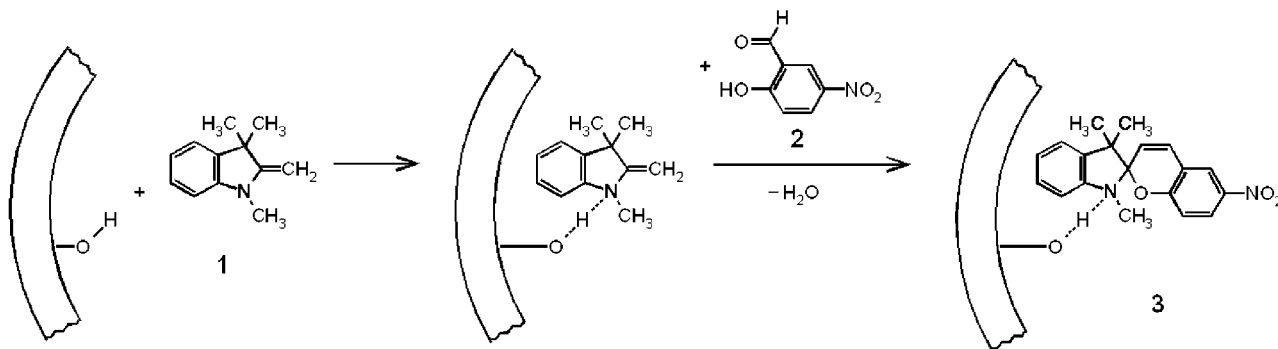


Fig. 1 Synthesis scheme of the formation of 2*H*-spiro[[6]nitrochromene-2,2'-[1,3,3]trimethylindoline] (3) from the precursors 1,3,3-trimethyl-2-methyleneindoline (1) and 5-nitrosalicylaldehyde (2). All components are attached to the matrix *via* hydrogen bonding to silanol groups in the different matrices.

Table 1 Loading of matrices with NBIPS by *in situ* synthesis or impregnation. The errors for the estimation of the loadings are about $\pm 10\%$

Host	Kind of loading	Loading/ moles dye per g matrix	Supercages occupied by dye molecules (%)
Poly(vinyl acetate)	Impregnation	$\sim 5 \times 10^{-6}$	—
Si-MCM-41(1)	Impregnation	$\sim 1 \times 10^{-5}$	—
Si-MCM-41(2)	Impregnation	$\sim 5 \times 10^{-5}$	—
HY	<i>In situ</i> synthesis	$\sim 1 \times 10^{-4}$	~ 30
DAY	<i>In situ</i> synthesis	$\sim 2 \times 10^{-5}$	~ 4
NaY	<i>In situ</i> synthesis	$\sim 1 \times 10^{-6}$	~ 0.2

dye molecules attached to the external surface have been quantitatively removed. In the case of NBIPS which was impregnated into the open pore system of the Si-MCM-41 reference samples, the materials became completely colourless after this procedure. Together with the high loading of non-aggregated dye molecules (see below) which cannot be hosted on the external surface of a HY zeolite (about $50 \text{ m}^2 \text{ g}^{-1}$) this strongly indicates that the NBIPS molecules are really hosted in the faujasite pores. The obtained loadings for the faujasite samples after extraction demonstrate that the acidic centers of the faujasite HY are important for the interaction with the basic indoline compound leading to its adsorption. Although in solution the indoline compound reacts in a molar ratio of 1 : 1 with the salicylaldehyde, much higher molar ratios of salicylaldehyde to indoline must be offered to the faujasite system to obtain complete reaction to the NBIPS product. Fig. 2 shows that with a molar ratio of 5-nitrosalicylaldehyde to 1,3,3-methyl-2-methyleneindoline of 2 : 1 a large amount of unreacted indoline is present. In contrast, with a molar ratio of 8 : 1 no indication of non-reacted 1,3,3-methyl-2-methyleneindoline is seen in the UV-vis spectra. A high amount of salicylaldehyde seems to be necessary to overcome the blocking of the external zeolite pores by NBIPS formed at first. The large NBIPS molecules ($1.4 \times 0.74 \times 0.7 \text{ nm}^3$) fill the faujasite cage (diameter: 1.2 nm) to a high extent. Since most of the encapsulated dye molecules are probably formed in supercages of the outer shell of the zeolite crystals, the adsorption properties of the starting material species used are of high importance for the degree of reaction in the zeolite pores. Comparable results have also been observed for the *in situ* synthesis of azo dyes in the supercages of faujasites.¹⁶

The structure of the applied faujasite host was maintained during all steps of treatment: (i) NH_4^+ ion exchange, (ii) calcination and (iii) dye incorporation with subsequent oxidative removal of the dye in a stream of air at 673 K, *i.e.*,

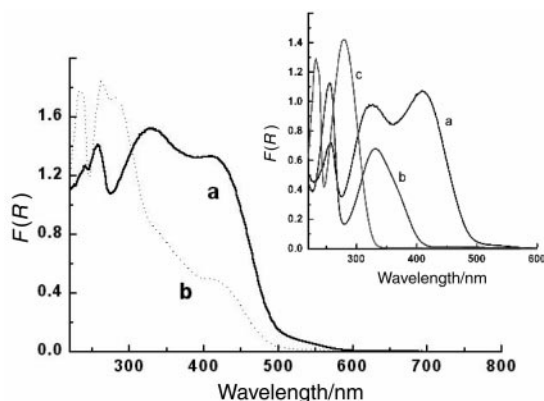


Fig. 2 Diffuse reflectance UV-vis spectra of NBIPS/HY samples after *in situ* synthesis with different molar ratios of 5-nitrosalicylaldehyde to 1,3,3-methyl-2-methyleneindoline: (a) 8 : 1 and (b) 2 : 1. The inset shows the spectra of NBIPS (a) 5-nitrosalicylaldehyde (b) and 1,3,3-methyl-2-methyleneindoline (c) each adsorbed on the zeolite HY.

after all these three process steps the BET values (*ca.* $960\text{--}980 \text{ m}^2 \text{ g}^{-1}$) varied in the range of a standard deviation of 5% only. A BET determination of the zeolites with incorporated dye molecules, *i.e.* prior to their oxidative removal, did not lead to reliable values, since the dye molecules are more or less destroyed during the heat treatment (at least $\sim 473 \text{ K}$), which is necessary to remove the residual organic solvent and water molecules also adsorbed in the zeolite pores.

The X-ray diffractograms of the highly loaded HY exhibited significant changes in the intensity ratios of the reflections [200] and [311] from 1 : 0.67 to 1 : 1.11, which disappeared after dye removal. This points to an incorporation of dye molecules at crystallographically defined positions with specific host–guest interactions in the supercages of the faujasite structure, which has been observed earlier for encapsulated thionine.²⁷

From the dye loadings (Table 1) the average distance l of the dye molecules in the host material can be estimated using eqn. (1), *i.e.*, the geometric model of a cube for the face-centered cubic faujasite structure (n is the number of unit cells hosting the dye molecule and 2.5 the size (nanometre) of the unit cell):

$$l = 2.5 \sqrt[3]{n} \quad (1)$$

The calculated average distances l are in the order: NaY ($\sim 9 \text{ nm}$) > DAY ($\sim 3.6 \text{ nm}$) > HY ($< 2.5 \text{ nm}$).

In the case of HY more than one dye molecule is hosted per unit cell (number of unit cells: $\sim 8 \times 10^{-5} \text{ moles g}^{-1}$), *i.e.*, neighboring supercages can be filled with a chromophore molecule. Although distances of $< 2.5 \text{ nm}$ are much smaller than the distances of $\sim 6 \text{ nm}$ obtained for Förster quenching in solvents or $\text{AlPO}_4\text{-5}$ molecular sieves,²⁸ high fluorescence intensities are seen.²⁹ Presumably, the steep Coulomb field gradients in the faujasite structure affect the Förster mechanism, *i.e.*, the long-range resonance coupling between excited chromophores and non-excited ones.

Si-MCM-41 samples having dye loadings with NBIPS of 1×10^{-5} and $5 \times 10^{-5} \text{ mol g}^{-1}$ were obtained from wetness impregnation procedures. The dye is predominately spread on an internal surface of $\sim 1000 \text{ m}^2$, yielding average distances for the dye molecules of around 5–10 nm. The X-ray diffractogram of the Si-MCM-41 material exhibited at least four reflections in the 2θ range of $2\text{--}7^\circ$. The evaluation of the N_2 adsorption isotherms yielded total BET surfaces in the range $1000\text{--}1100 \text{ m}^2 \text{ g}^{-1}$, pore diameters around 3.5 nm, and pore volumes around $0.7 \text{ cm}^3 \text{ g}^{-1}$. These data point to a perfect structure of the host material.²⁴ The intensities of the X-ray reflections decreased after dye incorporation due to increasing scattering of the filled pore voids.

3.2 Stable constitutional isomers

The nature of the thermodynamically stable constitutional isomer of a spiropyran incorporated in a host matrix depends on the host–guest interaction, as elucidated for various mineral matrices.^{9,17–22} If the host exhibits significant Brønsted acidity, like in the case of molecular sieves, the protonated isomers^{30,31} of encaged spiropyrans have to be considered, too (Figs. 3,4). The different spectral patterns obtained for zeolite-encaged spiropyran isomers (Fig. 5) can be assigned to the following species, which can exist in acidic environments. For NaY-encaged dye the pattern of a mixture contains predominately the neutral closed spiropyran (SP) and the protonated open form (BH^+), gleaned from the maxima around 230, 270, 350 and 400 nm. In the more acidic DAY host the protonated *trans* form (BH^+), with maxima around 300 and 420 nm, exists predominantly. For the most acidic HY matrix, the superposition of the BH^+ form and the protonated *cis* form Y dominates the spectral patterns, leading to a maximum of $\sim 320 \text{ nm}$ (Fig. 5).

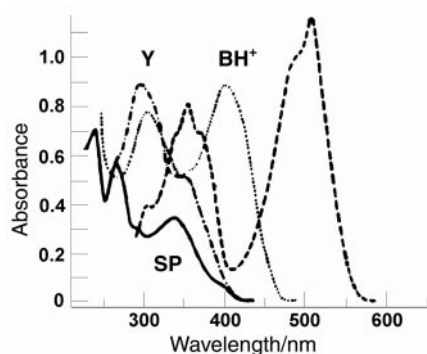


Fig. 3 Absorption spectra of the constitutional isomers of NBIPS (Fig. 1, formula 3) (i) unprotonated spiropyran SP, (ii) unprotonated *trans*-merocyanine B, (iii) protonated *trans*-merocyanine BH⁺ and (iv) protonated *cis*-merocyanine Y (cf. Fig. 4).³¹

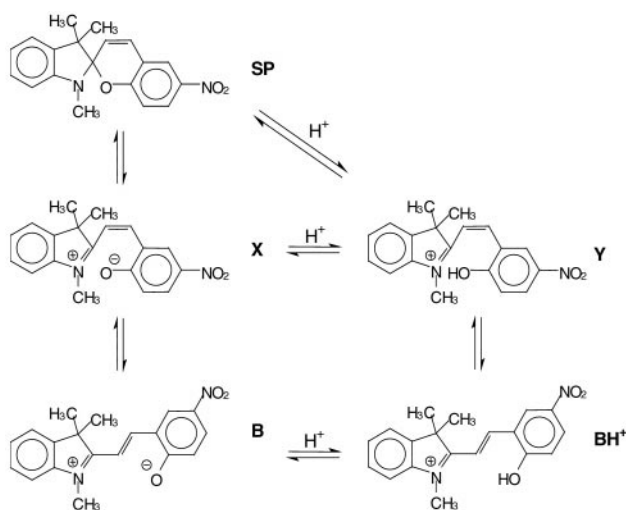


Fig. 4 Proposed constitutional isomers for zwitterionic (X,B) and protonated (Y, BH⁺) merocyanine forms of NBIPS.³¹

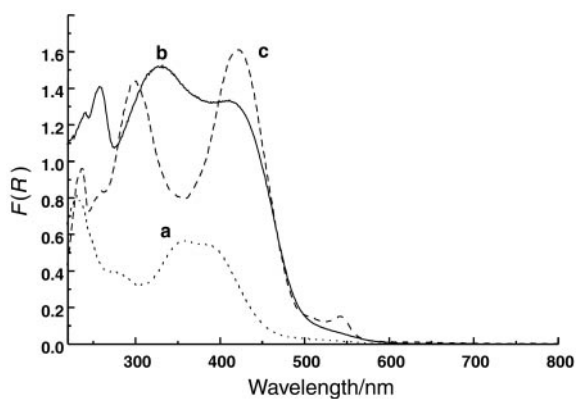


Fig. 5 DR UV-vis spectra of constitutional isomers of NBIPS (Fig. 4) incorporated in the zeolites NaY (a), HY (b) and DAY (c) *via in situ* synthesis.

Incorporation of spiropyran in Si-MCM-41 *via* impregnation at lower loading (Fig. 6) yields spectra, which are characteristic of the BH⁺ form, *i.e.*, exhibiting maxima at 300 and 400 nm (cf. Fig. 3,4). At higher loadings (Fig. 7) broader maxima appear, which are shifted to 350 and 500 nm, indicating that the dye is also adsorbed on non-acidic sites in the zwitterionic open merocyanine form B, for which absorption maxima around 360 nm and 520 nm are valid (cf. Fig. 3,4).

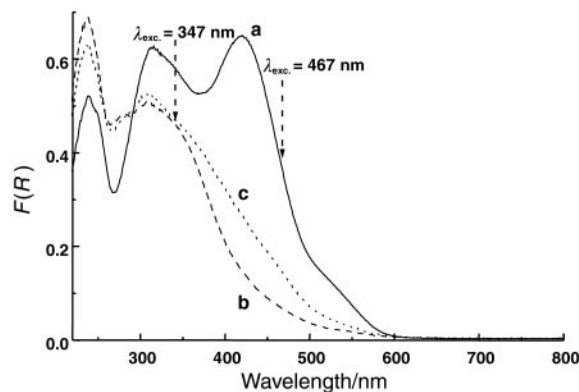


Fig. 6 DR UV-vis spectra of constitutional isomers of NBIPS in Si-MCM-41 (1×10^{-5} moles NBIPS per g molecular sieve) (i) after dye incorporation *via* impregnation (a), (ii) after irradiation at $\lambda_{exc} = 467$ nm (b), and (iii) after irradiation at $\lambda_{exc} = 347$ nm (c).

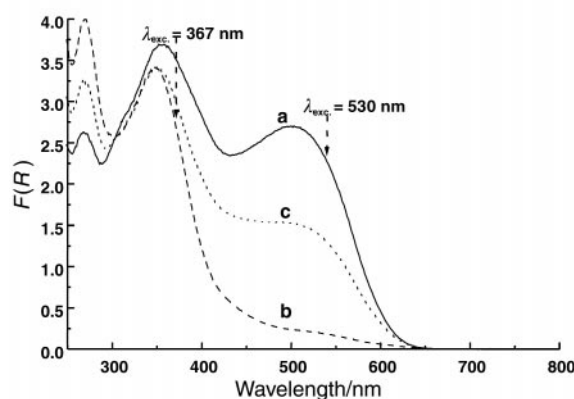


Fig. 7 DR UV-vis spectra of constitutional isomers of NBIPS in Si-MCM-41 (5×10^{-5} moles NBIPS per g molecular sieve) (i) after dye incorporation *via* impregnation (a), (ii) after irradiation at $\lambda_{exc} = 540$ nm (b), and (iii) after irradiation at $\lambda_{exc} = 367$ nm (c).

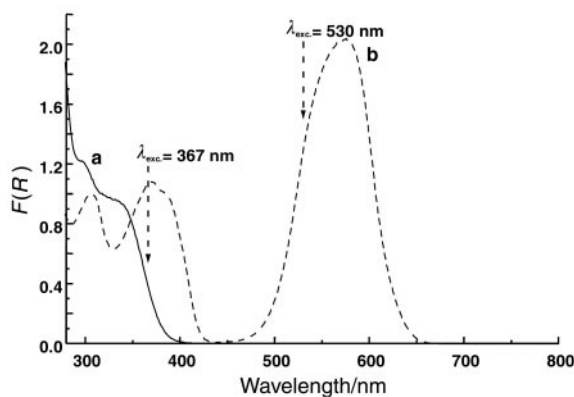


Fig. 8 DR UV-vis spectra of constitutional isomers of NBIPS in poly(vinyl acetate) exhibit the closed spiropyran form SP (a), and the merocyanine form B after irradiation at $\lambda_{exc} = 367$ nm (b). Irradiation at $\lambda_{exc} = 530$ nm restores the spiropyran form SP.

The reference sample, *i.e.*, poly(vinyl acetate) (PV)-hosted spiropyran, exhibits the spectrum of the closed form SP (Fig. 8 and cf. Fig. 3). All samples, even the highly loaded HY, exhibit a broad fluorescence peak centred around 510 nm. This indicates the presence of the merocyanines (i) in the open form, because the closed form SP is not fluorescent,^{25b} and (ii) in a non-aggregated state, since no self-quenching occurs.

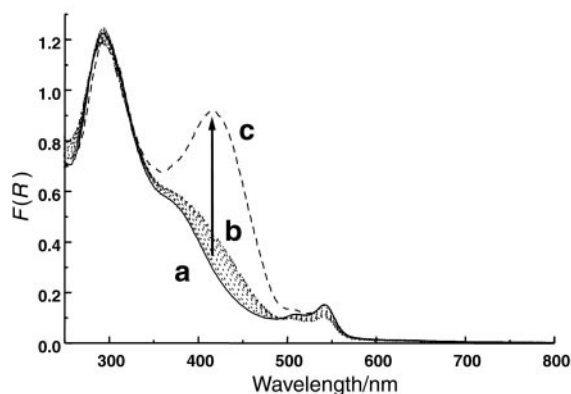


Fig. 9 DR UV-vis spectra: (a) of the protonated form Y (*cf.* Fig. 4) in DAY (1×10^{-5} moles NBIPS per g) after irradiation ($\lambda_{\text{exc}} = 467$ nm) of the incorporated BH^+ (*cf.* Fig. 4); (b) after thermal relaxation at RT for 65 h; (c) after irradiation ($\lambda_{\text{exc}} = 347$ nm).

3.3 Stability of photoinduced switching

For applications based on stable switching states, like information storage, a long-term stability of the switched state against thermal relaxation is required. To compare and to judge on different systems, data on the relaxation kinetics, *e.g.*, the time $t_{1/2}$, in which half of the molecules relax thermally into the original state, are necessary. Recently, it was shown that spiropyran, after incorporation into mesoporous molecular sieves of the SBA-15 type containing hydrophobic parts, exist in the SP form. After switching to the B form, rapid thermal relaxation to the SP form occurs with $t_{1/2} \sim 1.25$ h.¹¹

In the following, the switching procedure is presented exemplarily for NBIPS in DAY. The as-prepared state (Fig. 5, spectrum c), *i.e.*, the BH^+ form, is switched using the excitation wavelength $\lambda_{\text{exc}} = 467$ nm, provided by the dye laser with Coumarin 307 (465–550 nm). This excitation in the flank of the band is advantageous, since it prevents overheating or thermal degradation, respectively. The switched state (Fig. 9, spectrum a) is assigned to the protonated *cis* form Y (*cf.* Fig. 4). This switching process from the *trans* to the *cis* form is called “reverse photochromism”. The thermal relaxation of the *cis* form to the *trans* proceeds very slowly and results in Fig. 9 spectrum b after 65 h. The attainment of the final state would have required several weeks. However, the expected spectrum of this final state (*trans*-merocyanine BH^+) was produced by photoexcitation (re-switching), using $\lambda_{\text{exc}} = 347$ nm (laser dye: RDC-NEU-360). The extinction of the 420 nm band in this final state (Fig. 9, spectrum c) is strongly reduced compared to the initial state after the *in situ* preparation (*cf.* Fig. 5, spectrum c). This means that the initial states for the as-prepared samples are metastable and are converted into photostationary states after irradiation.

The photochromism experiments on the dye-loaded HY gave changes of the spectrum similar to that on DAY. However, faster thermal relaxation is observed (Fig. 10).

The patterns for the final states of the dye-loaded Si-MCM-41 composites exhibit significant differences compared to the faujasite system. The excitation wavelength $\lambda_{\text{exc}} = 467$ nm (low-loading) and $\lambda_{\text{exc}} = 540$ nm (high-loading) are used for the photoswitching (Figs. 6,7). Here, the band in the range 300–350 nm decreases markedly, and the band in the range 250–300 nm increases strongly. This behavior is assigned to the formation of a predominating fraction of spiropyran, *i.e.*, the closed form SP. Thermal relaxation appears in Si-MCM-41 much faster than in all the faujasites (Fig. 10). Here, the initial state is attained by thermal relaxation but not by photoexcited re-switching, since at the wavelength used, 347 nm, the photoproduct as well as the initial starting material absorb (Figs. 6,7).

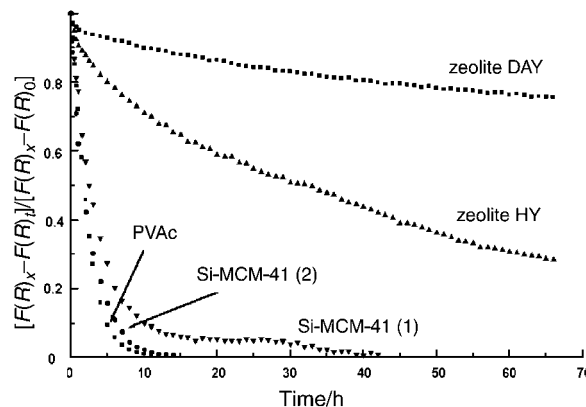


Fig. 10 Rates of absorption changes at a selected observation wavelength, monitoring thermal relaxation rates for the constitutional isomers of NBIPS after photoinduced switching in various host materials.

Spiropyran in poly(vinyl acetate) exhibits the “normal photochromism” behavior from the *cis* form SP to the *trans* form B (Fig. 8). The photoproduct relaxes thermally very rapidly (Fig. 10). The attainment of the initial state upon switching is nearly complete (90%).

The thermal relaxation kinetics could be largely fitted by a first-order rate equation [eqn. (2)]. Only in the case of the dye-DAY composite did a bi-exponential rate equation [eqn. (3)] give a better fit.

$$\ln \frac{dF(R)_t}{dF(R)_{t=0}} = -kt \quad (2)$$

$$dF(R)_t / dF(R)_{t=0} = ae^{-k_1 t} + (1-a)e^{-k_2 t} \quad (3)$$

$F(R)_{t=0}$ and $F(R)_t$ are the Kubelka–Munk values at a fixed wavelength in the absorption peak of the switched state prior to and after thermal relaxation, k , k_1' and k_2' are the rate constants and a is the fitting parameter. The evaluated data for the stability of photoinduced switching, *i.e.*, the half-lifetimes of thermal relaxation ($t_{1/2}$) for the studied host–guest systems, are summarised in Table 2.

3.4 Reversibility

The analysis of the reversibility of the photoinduced switching is usually described *via* $N_{1/2}$, *i.e.*, the number of photoinduced switching cycles N , resulting in the reduction of the extinction difference ΔA , *i.e.* the difference between initial and final state extinctions at a selected observation wavelength, from ΔA to $\Delta A/2$. The results of the corresponding experiments are represented in Fig. 11.

The reversibility can be considered as a measure of the lightfastness, since thermal degradation mechanisms can be largely ruled out with respect to the applied short laser pulses

Table 2 Stability of photoexcited states of the constitutional isomers of NBIPS (Fig. 1, eqn. (3)) in various hosts ($t_{1/2}$: half-lifetime) and switching reversibilities at a selected observation wavelength ($N_{1/2}$: number of cycles for the reduction of the extinction difference from ΔA to $\Delta A/2$). In every case the irradiated samples contained about 3×10^{17} molecules of dye and the quantum yields were about 75%

Host	$t_{1/2}/\text{h}$	$N_{1/2}$
Poly(vinyl acetate)	1.5	7
Si-MCM-41(1)	2.7	25
Si-MCM-41(2)	1.8	16
HY	39	45
DAY	438	80

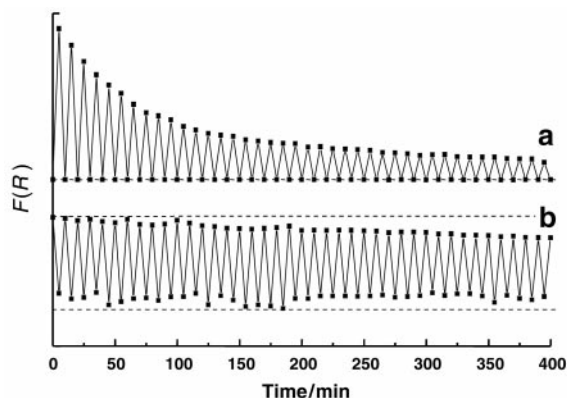


Fig. 11 Photoinduced switching cycles for (a) NBIPS in poly(vinyl acetate) as reference and (b) merocyanine conformers in the zeolite DAY at the observation wavelength 420 nm ($\lambda_{\text{exc}}=467$ nm and 347 nm).

(100 ns), and the irradiations in the flanks of the absorption signals, both avoiding significant local overheating or hot spots, respectively.

In all cases, where the dye was hosted in molecular sieves, the extinction changes after the first photoinduced switching cycle were used as initial ΔA , due to the metastable status of the isomers in the as-synthesised samples. All obtained $N_{1/2}$ values are summarised in Table 2.

4. Discussion

4.1 Nature of the dyes anchored in molecular sieves and photoexcited switching

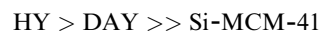
With the exception of azobenzene in $\text{AlPO}_4\text{-5}$ or ZSM-5 incorporated by sorption from the gas phase,^{10,32} or, very recently, of spiropyran in the mesoporous molecular sieve SBA-15 ¹¹ included by a wetness impregnation technique from solution, photochromism of dyes in molecular sieves have not yet been studied, up to now. In the hydrophobic parts of SBA-15 very rapid thermal relaxations were investigated.

More detailed knowledge about the photochromism of spiropyran has been elaborated in silicas.^{9,17–22} The incorporation of spiropyran in silica matrices, *i.e.*, in most cases *via* addition of the dissolved dye to the sol–gel batches and subsequent condensation, revealed the strong influence of the silica host material on the entrapped chromophore. As it can be deduced from the ready luminescence, the dye is accommodated preferentially in a non-aggregated state.^{19,21,22,29} In silica and aluminium silicate hosts the complex absorption patterns for the closed SP form as well as for the open merocyanine forms are observed.^{17,21,22} In contrast, for faujasites DAY or HY, and low-loaded Si-MCM-41 only the open forms are detected (Figs. 5 and 6). Due to their zwitterionic character the merocyanines are stabilised *via* strong interactions to the polar host structures which possess more or less acidic OH-groups. Upon irradiation at excitation wavelengths above 400 nm reverse photochromism occurs leading to a reduction of the absorption in the visible range (decoloration).^{1,2}

The various coloured isomers can range from the open *cis* to *trans* forms^{17,30} and can additionally comprise different protonated configurational isomers, *e.g.* in aqueous hydrochloric acid.³¹ The complex patterns of the absorption spectra of the merocyanine form entrapped in the molecular sieve host materials (Figs. 5–7) have to be considered on the basis (i) that the open isomers should dominate due to the strong host–guest interactions, and (ii) that various isomers could coexist, whose relative fractions depend on the nature and strength of

interaction as well as on the strength of acidity or degree of protonation, respectively. HY, DAY and Si-MCM-41 can accommodate the *trans*-merocyanine in the protonated form at their acidic sites. The protonation is deduced from absorption maxima in the range 400–500 nm, *i.e.*, up to *ca.* 100 nm blue-shifted compared to the unprotonated *trans*-merocyanine (Figs. 3, 5–7). In highly loaded Si-MCM-41 the number of acidic sites is too low to bind all the introduced dye molecules, and thus unprotonated merocyanine is additionally accommodated at non-acidic sites, as follows from the absorption maximum around 500 nm (Fig. 7). Upon irradiation with an excitation wavelength $\lambda_{\text{exc}}=467$ nm (only for highly loaded Si-MCM-41 $\lambda_{\text{exc}}=540$ nm was used) reverse photochromism proceeds, resulting in a fading of the colour, *i.e.*, the band above 400 nm is erased (Figs. 6 and 7). Presumably, the open *cis* isomer is formed, which can react further with the closed spiropyran.^{20,21}

The ring closure is impeded in a more acidic environment as provided by HY and DAY. Here, the band between 300 and 350 nm is not changed by the irradiation (Fig. 9), whereas a significant decrease appears in a Si-MCM-41 host (Figs. 6 and 7). This is in agreement with the order of acidity, *i.e.*,



The lower acidity or higher basicity, respectively, of the Si-MCM-41³³ explains the possibility of deprotonation of the dye, resulting in a significant fraction of ring closure to spiropyran, manifested in the decrease of the band at 300–350 nm. The higher Brønsted acidity of HY compared to DAY,³⁴ results in a higher fraction of stabilised *cis* isomers in the former zeolite type and explains the differences in the corresponding spectra (Fig. 5).

The photoinduced fading of the merocyanines in molecular sieves proceeds readily to an equilibrium state, requiring an average irradiation energy of *ca.* 5×10^{-5} J or *ca.* 4×10^{17} photons. This means, for average dye contents ($\sim 3 \times 10^{17}$ molecules) of the irradiated samples (50 mg of diluted material spread on 1 cm^2) that quantum yields $\phi = n_m/n_p$ (n_m : number of dye molecules excited; n_p : number of photons) of 75% are valid, *i.e.*, that all dye molecules in the solid matrix are readily accessible to the imposing photons. High quantum yields are found usually for photoisomerization, if only open merocyanine isomers participate. Obviously, the photoinduced opening or closing of the sigma bond of the spiro form is kinetically impeded, resulting in much lower quantum yields of less than 20%.³¹

4.2 Stability of the photoproducts and switching reversibility

Photoinduced switching can be achieved with any constitutional isomer of a spiropyran compound, of which the direction depends on the excitation wavelength. Since the absorption spectra of the switched isomers overlap (*cf.* Figs. 6,7,9), an appearing absorption band under continuous or pulsed irradiation represents a photostationary state, deviating from the thermodynamically stable state. The kinetics of the thermal relaxation or decay rates for the photoproducts, respectively, to the stable states depend on various parameters, like temperature and concentration. But strongest retardations, expressed by long half-lifetimes of the photoproducts, are observed, if the dye undergoes strong interaction with a polar environment, *e.g.* in mineral matrices.^{1,9,10,17–22} The observed thermal relaxation kinetics for merocyanine dye in molecular sieve hosts (Fig. 9, Table 1) result in the following order of stabilities, *i.e.*, half-lifetimes, for the photoproducts of the spiropyran NBIPS in different hosts:

PV < Si-MCM-41 (high-loaded)
< Si-MCM-41 (low-loaded)
< HY < DAY

Due to the weak interactions and the absence of acidic sites in poly(vinyl acetate) (PV) the dye can readily undergo all rotational movements, which are necessary for the attainment of the thermodynamic equilibrium, *i.e.* the relaxation to the closed SP form (Fig. 3). For the molecular sieves the acidity of the host materials and the local polarities around the dye molecules in the cages and channels are decisive parameters to explain the order given above. The average local polarity of the environment for a dye-molecule in a high-loaded molecular sieve (HY) is lower compared to a low-loaded composite (DAY). The faster thermal relaxation rate (shorter $t_{1/2}$) in HY compared to DAY might be an effect of the different acidities. Indeed, an activation of the thermal relaxation process is observed in acids or acidified silica^{1,9,35–37} Since lower *pK* values are valid for the protonated, thermodynamically more stable *trans* forms,³⁸ the increase of the relaxation process rate points to a direct influence of the thermodynamic driving force ΔG on the kinetics, which is predicted by the theory of linear free energy relationship.³⁹

The switching reversibilities or $N_{1/2}$ values are largest for the faujasite samples (Fig. 11, Table 2). In the zeolite cages the merocyanines are by a factor of about 2 more stable than in silica films. For sulfonated spiropyran in silica films $N_{1/2}$ values between 9 and 33 have been measured.⁹ The high switching reversibilities observed in the faujasites, especially in DAY, can be attributed to the fact that in the photoinduced processes only a change of the configuration of the merocyanines from the *trans* to the *cis* form, but no bond breaking, is involved (Fig. 4). In contrast, when the closed spiropyran (SP) participates, as in poly(vinyl acetate), electrocyclic bond breaking to the merocyanine isomers occurs which may lead to side reactions. Another possibility is the photobleaching by oxygen. Because the diffusion of oxygen in the spiropyran filled pores is hindered, processes of photooxidations are impeded. For porphyrin dyes encapsulated in the molecular sieve AlPO₄-5 a strongly enhanced photooxidative stability was observed in comparison to that in solution.⁴⁰

5. Conclusions

The incorporation of photochromic spiropyran isomer compounds into molecular sieves *via in situ* synthesis results, especially in the dealuminated faujasite DAY, in the stabilisation of the open *trans*-merocyanine isomer. This is attributed to strong host–guest interactions between the dye and acid sites in the mineral host material. The stability of the open *cis* isomer of the dye, which is formed by photoswitching, towards thermal relaxation (expressed by high values of the half-lifetime $t_{1/2}$) is largest in the small faujasite supercages compared to the wide channel-structured Si-MCM-41 or to SiO₂ matrices formed by sol-gel processing. The spatial constraints in a zeolite cage slow down the thermal relaxation processes. An influence of strong host–guest interactions *via* dipole forces and spatial constraints is also observed for the switching reversibilities $N_{1/2}$, which are also largest in the faujasites, especially in DAY. Obviously, the photodegradation of the dyes is impeded, because (i) no bond breaking occurs, since the closed spiropyran takes no part in the processes and (ii) the spatial constraints hinder the diffusion of reactive oxygen species resulting in a reduced probability for a photooxidative attack.

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