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Synthesis and optical properties of naphthopyran dyes conjugated with fluorescent stilbazolium moieties†

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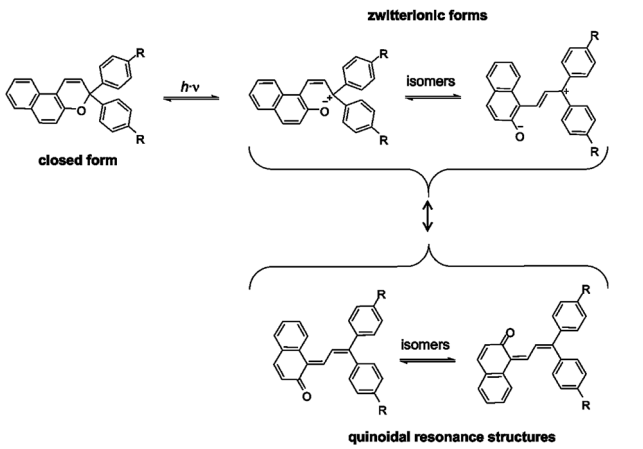
The synthesis of new 3*H*-naphtho[2,1-*b*]pyran dyes substituted at position 8 of the naphthalene ring by either a stilbazolium or an 4-ethenyl-quinolinium group and their photochemical properties are described. In non-polar media the naphthopyran–stilbazolium conjugates do not show any photochromic response while the formation of the ring opened species is promoted in strong polar media. Additional investigations of the new dyes within the pores of mesoporous MCM 41 particles showed a significant enhancement of the photochromism compared with that in solution. The generation of the ring-opened species upon irradiation with UV-light is accompanied by a decrease of the fluorescence intensity, which could be recovered by illumination with visible light.

Introduction

In recent years, photochromic materials have attracted much attention in various fields of science due to their great potential for applications such as ophthalmic lenses,[1] optical storage,[2] optical switching,[3–5] nonlinear devices,[6] and especially for decorative purposes, *e.g.* textiles and cosmetics.[7,8] Among various photochromic systems including spiropyrans, spirooxazines, fulgides, diarylethenes and azo compounds, naphthopyrans are of current interest because of the large spectral range of their light induced open coloured forms. The photochromism of naphthopyrans was first reported in the year 1965 and involves a ring-opening reaction *via* photochemical cleavage of the C(sp^3)–O bond.[9] This process is associated with the generation of coloured ring-opened isomers, which can be either zwitterionic or more likely quinoidal depending on the substituent R (Scheme 1).

While the transoid-*cis* isomer is cyclised thermally over a period of time, the transoid-*trans* species is more stable and its ring-closing takes place upon irradiation with visible light.[10,11] Besides these interesting properties in colour switching, recent investigations were made on fluorescence modulation and fluorescence switching.[12] Therefore, a combination of photochromic and fluorescent dyes is the focus of current studies of different working groups. Some attempts were made for bonding a highly fluorescent boradiazaindacene core covalently or through hydrogen bonding to diarylethenes, spiropyrans, oxazines and recently even naphthopyrans.[13–17] There has also been a report on a photochromic naphthopyran bearing a fluorescent naphthalimide chromophore.[18]

In this work, we report our results on the synthesis, characterization and optical properties of some new 3*H*-naphtho[2,1-*b*]pyran dyes in conjugation with stilbazolium moieties. Especially styrylpyridinium and styrylquinolinium merocyanines have been known not only for their fluorescence or solvatochromic properties and structure–colour relationships, but also for their



Scheme 1 Structure of naphthopyran dyes and their photo-induced stereoisomers of the coloured ring-opened form.

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potential applicability in non-linear optics, such as optical sensors, and in physiology and biochemistry areas.[19–23]

In several cases, it is necessary to incorporate photochromic compounds into a rigid host material for practical applications.[4,24–26] Therefore, the polarity of the surrounding medium is of great importance for the photochromic response of such materials. Accordingly, the investigation of the naphthopyran-conjugates was performed once in solution as well as within surface-modified and non-functionalized MCM 41 particles in order to make comparative statements about the influence of the surrounding medium with regard to polarity and rigidity.

Experimental

Materials

Unless otherwise stated, reagents were used as supplied by the major chemical catalogue companies. All used solvents were redistilled over appropriate drying agents prior to use.

Instrumentation

^{1}H NMR (250 MHz) and ^{13}C NMR (69.9 MHz) spectra were recorded on a Bruker Avance 250 NMR spectrometer. The residue signals of the solvents were used as internal standards. UV/Vis absorption measurements in solution were performed using a MCS 400 diode array UV/Vis spectrometer from Carl Zeiss, connected *via* glass-fibre optics. UV/Vis investigation of reflectance was carried out on a Zeiss multi channel spectrometer system MCS 601/CLD using a deuterium lamp (215–620 nm) and a CLX 75 W/Sch xenon lamp (290–900 nm) as light sources. Fluorescence spectra were recorded on a FluoroMax®-4 from Horiba.

General method for the synthesis of 3,3-diaryl-8-formyl-[3*H*]-naphtho[2,1-*b*]pyrans

The synthesis of the formyl-substituted naphthopyrans was performed in analogy to published procedures.[27] Therefore, a solution of 10 mmol of 6-hydroxy-2-naphthaldehyde, 10 mmol of 1,1-diphenylpropyn-l-ol (for compound **1**) or 1,1-bis-(4-methoxyphenyl)-propyn-1-ol (for compound **2**) and a catalytic amount of *p*-toluenesulfonic acid, in 40 mL of methylene chloride was stirred at ambient temperature overnight. The solution was washed with a solution of $NaHCO_3$ (5% in water) and then with water. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude product was recrystallized from ethyl acetate–hexane (1/20 v/v).

3,3-Diphenyl-8-formyl-[3*H*]-naphtho[2,1-*b*]pyran (1). White solid (71% yield), M_p. 134 °C, ^{1}H NMR ($CDCl_3$): 6.32 (1H, d, J = 10.0 Hz); 7.26–7.39 (8H, m); 7.49 (4H, dd, J = 8.0 Hz and 1.6 Hz); 7.80 (1H, d, J = 9.1 Hz); 7.91 (1H, dd, J = 8.6 Hz and 1.5 Hz); 8.02 (1H, d, J = 8.6 Hz); 8.17 (1H, d, J = 1.5 Hz); 10.07 (1H, s). ^{13}C NMR ($CDCI_3$): 83.2; 114.4; 119.0; 119.6; 122.5; 123.8; 127.1; 127.9; 128.3; 128.4; 128.5; 131.7; 132.3; 133.2; 135.2; 144.5; 153.4; 192.1. Found: m/z 363.1368 calculated for $C_{26}H_{18}O_2$ + H: m/z 363.1380.

3,3-Bis-(4-methoxyphenyl)-8-formyl-[3*H*]-naphtho[2,1-*b*]pyran (2). Pale yellow solid (67% yield), M_p. 176 °C, ^{1}H NMR ($CDCl_3$): 3.78 (6H, s); 6.26 (1H, d, J = 10.0 Hz); 6.86 (4H, d, J = 8.8 Hz); 7.24 (1H, d, J = 4.9 Hz); 7.28 (1H, d, J = 4.9 Hz); 7.37 (4H, d, J = 8.8 Hz); 7.80 (1H, d, J = 9.0 Hz); 7.92 (1H, dd, J = 8.8 Hz and 1.4 Hz); 8.03 (1H, d, J = 8.8 Hz); 8.19 (1H, d, J = 1.4 Hz); 10.07 (1H, s). ^{13}C NMR ($CDCl_3$): 55.4; 82.9; 113.6; 114.4; 118.7; 119.7; 122.5; 123.8; 128.4; 128.9; 131.6; 132.2; 133.2; 135.2; 136.9; 153.5; 159.2; 192.1. Found: m/z 423.1603 calculated for $C_{28}H_{22}O_4$ + H: m/z 423.1591.

General method for the synthesis of 1-methyl-(4-(3′,3′-diaryl-[3*H*]-naphtho[2,1-*b*]pyran-8′-yl)vinyl)pyridinium or quinolinium iodides

1.05 mmol of the required formyl-substituted naphthopyran (compound **1** or **2**) and 1.15 mmol of 1,4-dimethylpyridinium or, respectively, quinolinium iodide were dissolved in 15 mL of methanol. After the addition of one drop of piperidine as a catalyst, the mixture was stirred under reflux for 3 h. Subsequently, the mixture was cooled to room temperature and the precipitate was filtered, washed with methanol and diethyl ether and dried under ambient conditions.

1-Methyl-(4-(3′,3′-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran-8′-yl)-vinyl)-pyridinium iodide (3). Yellow solid (67% yield), M_p. 226 °C, ^{1}H NMR (DMSO d_6): 4.25 (3H, s); 6.67 (1H, d, J = 10.0 Hz); 7.24–7.41 (7H, m); 7.50 (4H, dd, J = 8.2 Hz and 1.3 Hz); 7.54 (1H, d, J = 9.9 Hz); 7.60 (1H, d, J = 16.9 Hz); 7.89 (1H, d, J = 9.0 Hz); 7.94 (1H, dd, J = 9.0 Hz and 1.4 Hz); 8.11 (1H, s); 8.12 (1H, d, J = 16.1 Hz); 8.23 (2H, d, J = 6.7 Hz); 8.23 (1H, d, J = 9.0 Hz); 8.85 (2H, d, J = 6.7 Hz). ^{13}C NMR (DMSO d_6): 46.9; 82.0; 114.3; 119.1; 119.2; 122.8; 122.9; 123.4; 124.7; 126.3; 127.6; 128.2; 128.8; 130.0; 130.4; 130.8; 140.5; 144.5; 145.0; 151.3; 152.5. Found: m/z 452.2010 calculated for $C_{33}H_{26}NO^+$: m/z 452.2009; $\varepsilon_{(MeOH)}$ = 23 300 L mol^{-1} cm^{-1}.

1-Methyl-(4-(3′,3′-bis-(4-methoxyphenyl)-[3*H*]-naphtho[2,1-*b*]-pyran-8′-yl)vinyl)pyridinium iodide (4). Yellow solid (61% yield), M_p. 230 °C, ^{1}H NMR (DMSO d_6): 3.71 (6H, s); 4.25 (3H, s); 6.54 (1H, d, J = 10.0 Hz); 6.91 (4H, d, J = 8.8 Hz); 7.32 (1H, d, J = 9.0 Hz); 7.36 (4H, d, J = 8.8 Hz); 7.49 (1H, d, J = 10.1 Hz); 7.60 (1H, d, J = 15.3 Hz); 7.86 (1H, d, J = 9.0 Hz); 7.94 (1H, dd, J = 9.0 Hz and 1.1 Hz); 8.10 (1H, d, J = 1.1 Hz); 8.12 (1H, d, J = 16.1 Hz); 8.20 (1H, d, J = 9.0 Hz); 8.22 (2H, d, J = 6.7 Hz); 8.85 (2H, d, J = 6.7 Hz). ^{13}C NMR (DMSO d_6): 46.9; 55.1; 81.8; 113.5; 114.2; 118.7; 119.1; 122.8; 123.4; 124.6; 127.7; 128.7; 129.2; 130.0; 130.7; 136.7; 140.5; 145.0; 151.4; 152.5; 158.5. Found: m/z 512.2210 calculated for $C_{35}H_{30}NO_3^+$: m/z 512.2220; $\varepsilon_{(MeOH)}$ = 20 800 L mol^{-1} cm^{-1}.

1-Methyl-(4-(3′,3′-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran-8′-yl)-vinyl)-quinolinium iodide (5). Red solid (72% yield), M_p. 278 °C, ^{1}H NMR (DMSO d_6): 4.54 (3H, s); 6.68 (1H, d, J = 10.0 Hz); 7.25–7.3 (8H, m); 7.52 (4H, d, J = 8.3 Hz); 7.58 (1H, d, J = 9.9 Hz); 7.91 (1H, d, J = 8.9 Hz); 8.06 (1H, t, J = 7.6 Hz); 8.21–8.30 (4H, m); 8.42 (1H, d, J = 15.1 Hz); 8.43 (1H, d, J = 9.0 Hz); 8.53 (1H, d, J = 6.5 Hz); 9.11 (1H, d, J = 8.5 Hz); 9.35 (1H, d, J = 6.5 Hz). ^{13}C NMR (DMSO d_6): 44.6; 82.1; 114.3; 116.0; 119.0; 119.2; 119.3; 122.5; 125.5; 126.2; 126.3; 126.5; 127.6; 128.3; 128.8; 129.1; 130.1; 130.9; 131.1; 131.2; 134.9; 138.6; 142.8; 144.6; 147.9; 151.4; 152.5. Found: m/z 502.2154 calculated for $C_{37}H_{28}NO^+$: m/z 452.2165; $\varepsilon_{(MeOH)}$ = 28 000 L mol^{-1} cm^{-1}.

1-Methyl-(4-(3′,3′-bis-(4-methoxyphenyl)-[3*H*]-naphtho[2,1-b]-pyran-8′-yl)vinyl)quinolinium iodide (6). Red solid (82% yield), M_p. 237 °C, ^{1}H NMR (DMSO d_6): 3.72 (6H, s); 4.54 (3H, s); 6.55 (1H, d, J = 10.0 Hz); 6.91 (4H, d, J = 8.9 Hz); 7.33 (1H, d, J = 8.9 Hz); 7.37 (4H, d, J = 8.9 Hz); 7.53 (1H, d, J = 10.1 Hz); 7.88

(1H, d, J = 8.9 Hz); 8.06 (1H, t, J = 8.1 Hz); 8.20–8.30 (5H, m); 8.42 (1H, d, J = 15.6 Hz); 8.44 (1H, d, J = 9.0 Hz); 8.52 (1H, d, J = 6.8 Hz); 9.11 (1H, d, J = 8.4 Hz); 9.35 (1H, d, J = 6.5 Hz). ^{13}C NMR (DMSO d_6): 44.7; 55.1; 81.9; 113.5; 114.2; 116.1; 118.8; 119.1; 119.3; 122.6; 125.5; 126.3; 126.6; 127.7; 128.8; 129.2; 130.2; 130.8; 131.1; 133.3; 135.0; 136.7; 138.7; 142.9; 148.0; 151.5; 152.6; 158.5. Found: m/z 562.2375 calculated for $C_{39}H_{32}NO_3^+$: m/z 562.2377; $\varepsilon_{(MeOH)}$ = 24 000 L mol^{-1} cm^{-1}.

Synthesis of MCM 41 particles

The MCM-41 was synthesized according to the literature.[28] 2.4 g of *n*-cetyltrimethylammonium bromide was dissolved in 120 g of deionised water and stirred until the solution was homogeneous and clear. Then 8 mL of ammonium hydroxide was added and stirred for 5 min after which 10 mL of tetraethoxysilane (TEOS) was added to the solution. The mixture was stirred overnight at room temperature, and the products were collected by filtration, dried and calcined in air. Calcination was performed at 823 K for 5 h. The gel molar composition was 1 M TEOS : 1.64 M NH_4OH : 0.15 M CTAB : 126 M H_2O.

Surface modification of MCM 41 particles

1,1,1,3,3,3-Hexamethyldisilazane (HMDS) was used for the silylation of the mesoporous materials. For this purpose 1 g of the calcined sample was heated at 120 °C for 2 h under vacuum to remove water adsorbed in the pores of the material. 15 mL of toluene was added to the powder under a nitrogen atmosphere. 4 mmol of HMDS was then added and the mixture was gently refluxed for 4 h. The powder was filtered off, washed with abs. ethanol, and dried at room temperature under vacuum (5 mbar) for 8 h. The amount of trimethylsilyl groups on MCM materials was 2.14 mmol g^{-1} which was calculated from C-content measured by elemental analysis.

Impregnation of MCM 41 particles with photochromic dyes

The MCM 41 particles were dried at 120 °C under vacuum for 3 h. Afterwards the host material was impregnated with the synthesized photochromic dyes from solution by the incipient wetness technique.

5 wt% naphthopyran with respect to the amount of used MCM 41 was dissolved in a small amount of dichloromethane and added to the mesoporous powder under vacuum. This mixture was shaken for 3 h. Capillary forces draw the solution into the pores. The loaded materials were filtered and dried under ambient conditions.

Results and discussion

Synthesis

Photochromic naphthopyrans are readily accessible by the acid-catalysed condensation of naphthol and 1,1-diarylprop-2-yn-1-ol. Styrylpyridinium or styrylquinolinium merocyanines are commonly obtained by Knoevenagel condensation: alkylated 4-methylpyridinium or 4-methylquinolinium salts are condensed with an aromatic aldehyde in methanol or absolute ethanol with piperidine as the catalyst.

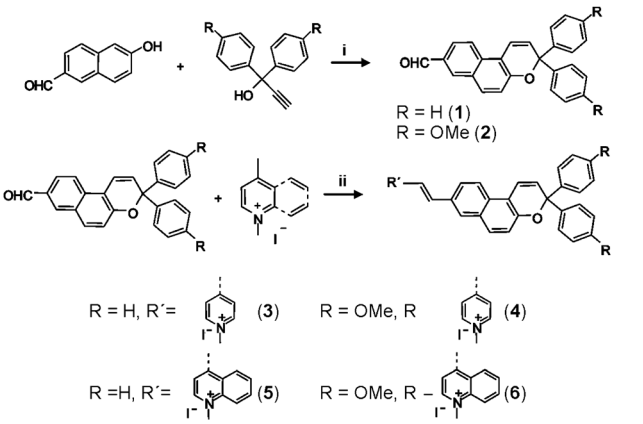
Considering these two reaction types, 6-hydroxy-2-naphthaldehyde was the initial starting material which was converted to the respective formyl-substituted naphthopyran dye in the first step, followed by the condensation with either 1,4-dimethylpyridinium iodide or 1,4-dimethylquinolinium iodide in the second step (Scheme 2).

The molecular structure of the products was clearly evidenced by electrospray ionization time-of-flight mass spectrometry and NMR spectroscopic measurements (see ESI†). The ^{1}H-NMR spectra of all naphthopyran compounds showed the typical 2-H pyran ring doublet in the region between δ 6.24 ppm and 6.68 ppm (J = 10 Hz). All observed signals for the vinylic hydrogens of the conjugated vinylpyridinium or vinylquinolinium units showed typical coupling constants for the *trans*-conformation (J = 15–16 Hz).

Optical properties

The optical properties of the new naphthopyran-conjugates **3–6** have been investigated in several organic liquids to study the influence of solvent polarity of the surrounding medium. For this reason, UV/Vis spectra have been measured once during UV-irradiation (at 350 nm) and also without illumination with UV-light to observe the photochromic behaviour. In addition, fluorescence measurements were also made for each solution. The results are summarized in Table 1. Generally, the naphthopyran-conjugates did not show any solvatochromism, but a significant hypsochromic shift was observed for the emission maxima in acidic media. This means that Brønsted acidic sites strongly interact with the dye molecules in their excited states. But only the methoxy-substituted naphthopyran-conjugates **4** and **6** showed a ring opening process in stronger acidic media, *e.g.* formic acid, as could be seen in Fig. 1, while no ring-cleavage was observed in weaker acids, like acetic acid.

The observed ring-cleavage of dyes **4** and **6** in formic acid was solely forced by the interaction with Brønsted acidic sites. Therefore, several UV/Vis absorption bands appeared in the visible region. The simple ring-opened form is assigned to the absorption band at longer wavelengths of about 630 nm.



Scheme 2 Synthesis of naphthopyrans substituted in the 8-position with a vinylpyridinium or vinylquinolinium unit. Reaction conditions: (i) CH_2Cl_2, cat. *p*-toluenesulfonic acid, RT, 12 h; (ii) CH_3OH, cat. piperidine, 3 h reflux.

Table 1 UV/Vis absorption maxima/emission maxima (values in nm) of conjugates **3–6** in several organic solvents (for recording the emission spectra, the samples were excited at 450 nm)

Solvent	3	4	5	6
THF	417/614	416/620	463/666	469/668
Acetone	418/615	419/622	453/660	455/665
DMF	416/613	419/621	454/670	456/672
Formamide	416/612	419/619	453/662	456/669
DMSO	417; 650[a]/615	417; 650[a]/618	453/669	456/677
MeOH	420/616	424/618	458/666	462/672
Tetramethyl-urea	417; 650[a]/613	420; 650[a]/619	456/670	459/669
Acetic acid	417/607	420/610	458/646	465/658
Formic acid	417/585	400; 478[b]; 629/562; 667[b]	457/627	430; 480[b]; 630/613; 648[b]

[a] Increasing UV/Vis absorption band upon UV-irradiation. [b] UV/Vis absorption bands or emission of the protonated species.

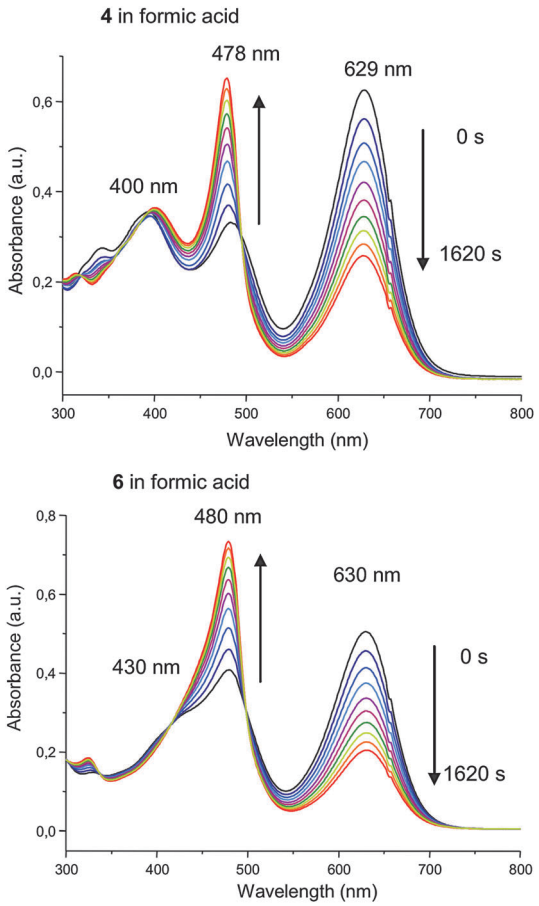
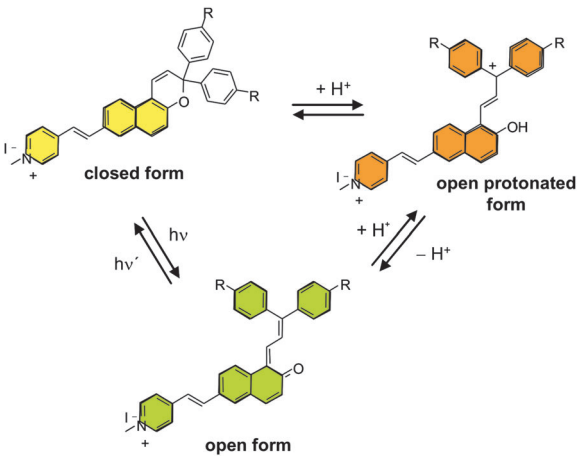


Fig. 1 Time-dependent spectral evolution of dyes **4** and **6** in formic acid, showing an equilibrium between protonated and unprotonated ring-opened species with isosbestic points at 494 nm (**4**) and 498 nm (**6**).



Scheme 3 Assumed interaction of stilbazolium-conjugated naphthopyrans with Brønsted acidic sites and the resulting equilibrium.

This strong bathochromic shift is explained by the increased conjugated π-electron system. This species undergoes an acid–base equilibrium with the protonated species showing a UV/Vis absoption maximum at 480 nm. This strong hypsochromic shift results from the two electron-withdrawing substituents at the naphthalene ring, namely the stilbazolium unit and the carbo cation. The UV/Vis absorption bands of the initial closed species were also observed at shorter wavelengths (400 nm for dye **4** and about 430 nm for dye **6**). As the two other dyes **3** and **5** did not show ring-cleavage in formic acid, we conclude that electron donating substituents at the C-3 aryl rings seem to promote the formation of the open species by stabilizing the carbocation. The isomerization and the resulting equilibrium is depicted in Scheme 3.

Besides these processes in acidic solution, the stilbazolium-conjugates **3** and **4** showed photochromism in strong polar, non acidic solvents, like tetramethylurea and dimethyl sulfoxide (DMSO), as exemplified in Fig. 2. Concerning these observations, a strong interaction between the dyes and strong polar media seems to be necessary for a photochromic response. By comparing the spectral evolution of the two compounds **3** and **4** in DMSO upon UV-irradiation, one can see that the methoxy substituted naphthopyran-conjugate **4** shows a much more pronounced photochromism. This observation supports the hypothesis that electron donating groups at the C-3 geminal aryl units promote the ring-opening reaction. But in contrast, the quinolinium dyes did not show any photochromic response in polar solution upon illumination with UV-light, whether electron donating groups are present or not. For this reason, the quinolinium group, as a strong electron withdrawing substituent, seems to impair the photochromic process in solution. The pyridinium unit, however, as a weaker electron-withdrawing group, allows photochromism in such polar environments.

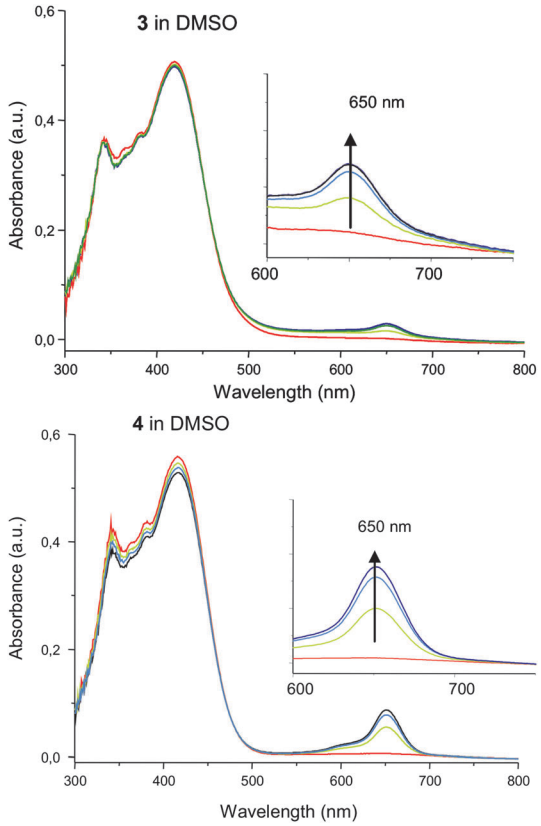


Fig. 2 Spectral evolution of dyes **3** and **4** in DMSO ($c \sim 3 \times 10^{-5}$ mol L^{-1}) upon irradiation with UV-light.

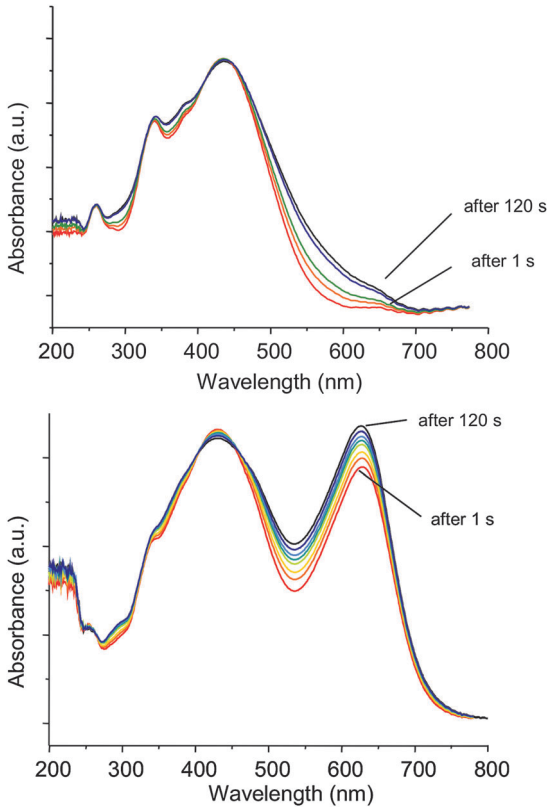


Fig. 3 Spectral evolution of dye **4** in the pores of surface-modified MCM 41 particles (above) and non-functionalized MCM 41 particles (below) upon irradiation with UV-light (at 350 nm).

Therefore, additional investigations were performed within the pores of MCM 41 particles, which are known for their strong polar surface. It was shown previously that the incorporation of photochromic molecules in micro- and mesoporous matrices leads to advanced optical materials with the advantage of being able to tune the optical properties by surface modification.[25,26]

But the open coloured forms of photochromic naphthopyrans or spiropyrans were often stabilized in the pores of porous silica matrices, leading to disturbance of photochromism. Also acidic sites at the surface of such aluminosilicate compounds may lead to ring-opening and simultaneous protonation reactions.[26–30]

For comparison purposes, optical measurements were performed within the pores of non-functionalized and also surface-modified MCM 41 particles, which were treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) to produce trimethylsilyl groups at the surface, lowering the acidity and polarity of the material. In this way, the influence of surface-polarity on the spectroscopic behaviour was studied within a rigid host material.

The UV/Vis absorption spectra of dyes **3–6** within the surface-modified MCM 41 particles showed no or only very weak photochromic response upon irradiation with UV-light, comparable with that in solution. But a significant enhancement of the photochromism was observed for all fluorophore-conjugates within the pores of non-functionalized MCM 41 particles, as exemplified in Fig. 3 for compound **4** (the spectra of all samples are presented in the ESI†). This result is a further confirmation for the requirement of a highly polar environment to promote a photochromic reaction. But mainly it was shown that a photochromic process is significantly enhanced within a solid matrix compared with the behaviour in solution. A very fast response was indicated by an increasing UV/Vis absorption band at 626 nm just immediately after irradiation with UV-light.

Since stilbazolium dyes are known to be highly fluorescent, the influence of the photoinduced ring-cleavage on their fluorescence properties was also the focus of this work.[22] The fluorescence of the naphthopyran-conjugates shows a kind of ''on–off switch'' mechanism caused by the photoinduced conversion between the closed and open forms. After UV-irradiation of the photochromic naphthopyran materials for several seconds, the emission band diminishes quickly. This may also be a result of a possible *cis–trans*-isomerization, for which stilbazolium dyes are generally known for.[31,32] But this effect is rather negligible, as could be seen in Fig. 3.

Here the fluorescence quenching of the stilbazolium moieties in the open form of the naphthopyran-conjugates may result from an intramolecular energy transfer mechanism. The emission of the respective stilbazolium or vinylquinolinium iodides overlaps significantly with the UV/Vis absorption bands of the photoinduced ring-opened merocyanines, thus allowing energy transfer leading to fluorescence quenching. This effect is reversible as shown by

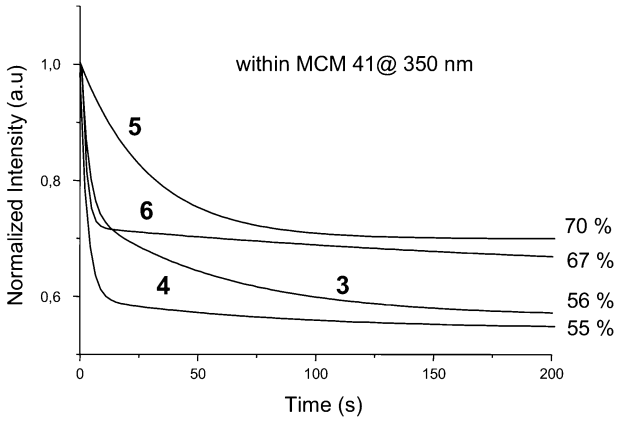


Fig. 4 Observed emission maxima of compounds **3–6** upon excitation with UV-light at 350 nm over a period of time.

additional fluorescence measurements. For this purpose, the emission maxima of the samples were observed over a period of time during simultaneous irradiation with UV-light (excitation at 350 nm) and subsequent irradiation with visible light (excitation at 500 nm). The normalized bleaching curves, which were obtained during the irradiation at 350 nm, are shown in Fig. 4. It can be seen that the emission reaches a constant value, which is due to the resultant equilibrium between open and closed species. The stilbazolium-conjugated dyes **3** and **4** showed the strongest decrease of about 56% and 55% of their initial fluorescence intensity. The quinolinium-conjugated dyes **5** and **6** showed a less marked decrease in fluorescence (upto 70% and 67% of their initial fluorescence intensity) due to the hindered ring-opening process which was discussed before. Additionally, we observed that the fluorophore-conjugates **4** and **6** with substituted methoxy groups showed a much faster response compared with the non-substituted dyes **3** and **5**. This result further supports the hypothesis that electron donating substituents at the C-3 aryl rings seem to promote the formation of the ring-opened species.

Subsequently, the samples were excited at 500 nm and the emission maxima was observed again. The fluorescence intensity

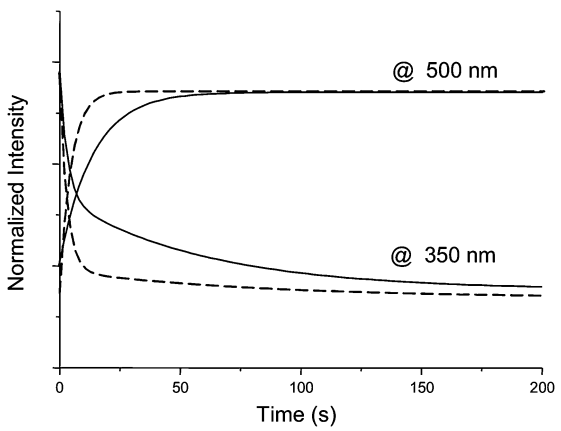


Fig. 5 Evolution of the emission intensity of compounds **3** (solid curves) and **4** (dotted curves) upon excitation at 350 nm and 500 nm.

Table 2 Half-lives $t_{\frac{1}{2}}$ of fading and recovery of the fluorescence intensity, UV/Vis absorption maxima of the closed and opened forms of dyes **3–6** in MCM 41 particles and their respective emission wavelengths

Dyes	$t_{1/2}$ (Fade) [s]	$t_{1/2}$ (Recover) [s]	Abs. λ_{max} [nm] closed form	Abs. λ_{max} [nm] open form	Emission λ_{max} [nm]
3	28.78	9.56	439	600	580
4	6.90	3.27	430	626	570
5	20.15	18.65	475	617	625
6	2.60	2.21	470	630	625

was recovered and a faster response was shown by the methoxy-substituted dyes again, as it is exemplefied for compounds **3** and **4** in Fig. 5 (all curves are shown in the ESI†).

The results of the optical investigation of naphthopyran–fluorophore conjugates **3–6** within the pores of MCM 41 particles are summerized in Table 2.

Conclusions

Some new photochromic naphthopyrans bearing either a stilbazolium or a vinylquinolinium moiety have been synthesized and investigated. The optical properties were studied in solution and within modified and non-modified MCM 41 particles to study the influence of the environmental polarity. The presence of the conjugated stilbazolium or rather vinylquinolinium units located at the 8-position of the naphthalene ring results in a minor photoactivity in less polar media compared with common chromene dyes. In contrast to this, the light-induced ring-opening reaction is promoted in strong polar media. Acidic media like formic acid facilitated the ring-opening reaction of the methoxy-substituted naphthopyran-conjugates and the ring-opened species underwent protonation, while no reaction was observed for dyes **3** and **5** without substituted aryl rings. Further investigations showed that only naphthopyran dyes in conjugation with stilbazolium moieties show a photochromic response in strong polar solvents, like DMSO. Only a very weak photochromism was observed within the surface-modified MCM 41 particles as well. In contrast, photochromism was significantly increased within the pores of non-modified MCM 41 particles for all compounds. The obtained results further showed that quinolinium units disturb the photochromism, while electron donating substituents at the C-3 aryl rings accelerate the photochromic process. Additionally, the photoinduced ring-opening of the naphthopyrans leads to a decrease of the fluorescence intensity, possibly caused by an energy transfer between closed and open species. This effect is reversible upon illumination with visible light. This leads to a kind of ''on–off''-fluorescence switch.

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