

The role of organic groups in ormosil matrices in the photochromism of naphthopyrans in sol–gel thin films

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Photochromic 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran molecules were embedded in sol–gel prepared thin organically modified silica films. The introduction of organic functional groups into a silica matrix allows the surfaces of its pores to be tailored and thus the polarity of the pores to be modified. The photochromic properties of the naphthopyran molecules, such as the spectral properties of the colored forms and the kinetics of thermal bleaching, were found to depend strongly on the polarity of the pores in which the molecules are located and hence, on the nature and loading of the organic groups (Me, Ph or *i*Bu) in the ormosil matrix. The large isobutyl substituents showed the largest reduction in the polarity of the pore, due to the effective screening of the polar OH groups at the surfaces of the pores. Hence, the absorption band of the open colored form of the photochromic dye could be adjusted by as much as 35 nm in the yellow-to-orange range by changing the composition of the embedding matrix. Reducing the polarity of the pore walls in the ormosil matrix resulted in a substantial acceleration of the bleaching kinetics of the photochromic effect.

Introduction

Naphthopyran (NP) compounds have been known to exhibit photochromism since the first report of Becker and Michl in the early 1960's.¹ The industrial interest in these materials started in the early 1990's, and was directed towards the preparation of photochromic ophthalmic lenses.² Most of the scientific research done on photochromic NP compounds has been devoted to the optimization of the spectrokinetic properties of NP by substitution of functional groups in the photochromic molecule. From this work more than 40 industrial patents have been published in which the photochromic properties of the new substituted naphthopyrans in solution or imbibed in polymer matrices are presented.^{3,4} The most remarkable properties of these materials are the absorption spectra, particularly the position of the absorption maxima, the intensity of color obtained upon irradiation with UV light and the kinetics of the bleaching process (*i.e.* recovery of the original transparency). All these properties were successfully controlled by chemical substitution of the NP molecules.⁵

In order to obtain photochromic materials for optical applications, the dye molecules should be dispersed in a solid, transparent and stable matrix to allow the performance of the doped photochromic molecules.

In a similar way to solvatochromic compounds in liquids,⁶ the properties of the photochromic molecules dispersed in solid matrices will depend strongly on the polarity of the environment in which the molecules are located. Moreover, in solids, the size and shape of the pores containing the dye molecules will also have an important effect on the spectrokinetic properties of the photochromic system, as it may provoke steric inhibitions during molecule opening–closing processes.

The sol–gel method is a very useful tool for preparing porous inorganic matrices at a low temperature, in which organic materials can be incorporated.⁷ Moreover, it allows thorough control over the polarity and size of the resulting porosity. The method involves hydrolysis and condensation of silicon alkoxides to form a tri-dimensional silica network. The introduction of organically modified silicon alkoxides to the initial sol, leads to the formation of a hybrid organic–inorganic

matrix with non-hydrolysable organic groups attached to the surface of the pores. These organic groups have a very important effect on the polarity of ormosil matrices, as studied recently by Rottman and Avnir and their co-workers.^{8,9} In early the work the importance of the dye–matrix interaction on the photochromic response of spiropyran in sol–gel matrices was raised.^{10,11} In recent work we demonstrated the feasibility of introducing different naphthopyran derivatives into sol–gel ormosil matrices.¹²

The aim of this work was to induce changes in the spectral and dynamic behavior of the photochromic naphthopyran dye by adjusting the composition of the embedded ormosil matrix. This would allow us to tailor the properties of the resulting photochromic materials by changing the environment of the molecule rather than the photochromic molecule itself. The R groups to be used for the preparation of the different matrices were selected from size and polarity considerations and interaction/affinity with the photochromic dye. The ability to control the photochromic properties by adjusting the chemical formulation of the ormosil matrix will be of great interest from the point of view of future applications.

Experimental

Materials

Tetracetoxysilane (TAS) and (isobutyl)triethoxysilane (*i*Bu-TES) were purchased from ABCR. (Methyl)triethoxysilane (MeTES), (phenyl)triethoxysilane (PhTES), and tetrahydrofuran (THF) were purchased from Aldrich Chemicals and ethanol from Merck. For all preparations doubly-distilled water was used. The photochromic dye used for sample preparation (3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran) was generously donated by PPG Industries Inc. The chemical structures of the closed and open forms of the dye⁵ are given in Fig. 1.

Preparation of films

The introduction of photochromic dyes into a sol is limited by the low stability of the dyes to the acidic medium of acid catalyzed sols. For this reason, acetoxy precursors were chosen,

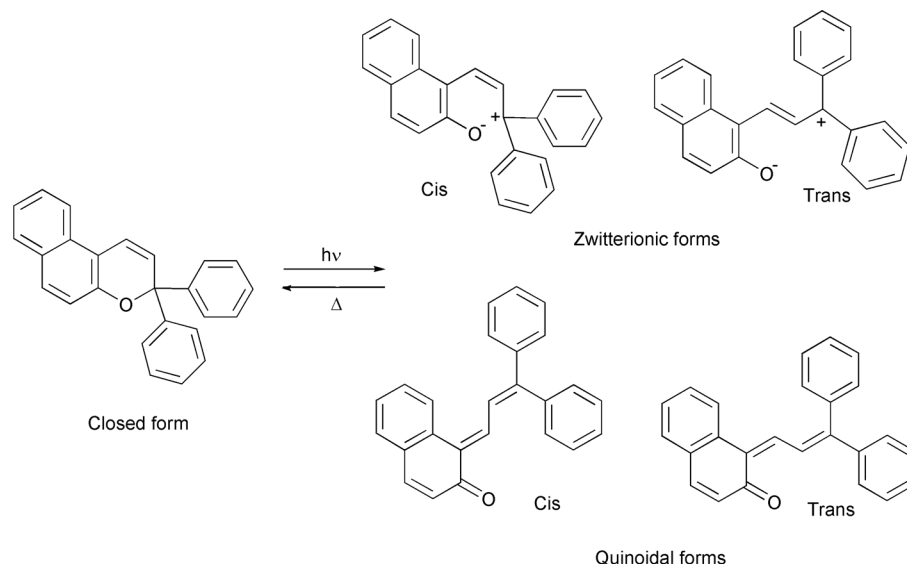


Fig. 1 Chemical structure of the naphthopyran dye used for sample preparation and the possible open colored forms.

which release acetic acid slowly during hydrolysis, leading to a gentle catalysis of the sol.¹² Samples were prepared from mixtures of TAS and the organically modified alkoxides in the appropriate ratio ($\text{TAS}_x : \text{RTES}_y : \text{H}_2\text{O}_{2+4x+3y}$), where R is the organofunctional substituent in the ormosil precursor, namely Me (methyl), iBu (isobutyl) or Ph (phenyl). The amount of acid released by the TAS and responsible for the catalysis of the reaction, is somewhat higher in samples with low R contents. The amount of catalyst, however, could not be unified for the different samples by adding acid, since the acid is released slowly and progressively during the hydrolysis and gelation of the sol, even after the deposition of the film. The amount of water to hydrolyzing group was kept at 1 : 1 for all samples. The sols were allowed to hydrolyze for 24 hours under stirring. The dyes were dissolved in THF to obtain the highest dye concentration with the minimum modification of the gelling and layer formation process. A THF solution of the photochromic dye was added to the sol to give a Si : photochromic dye molar ratio of 100 : 1. The spin-coating technique was chosen for the deposition of the films due to the large amount of sol needed to prepare samples using the dip-coating technique. A sample volume of 0.1 ml was used for the preparation of each film with the sample holder spinning at 2000 rpm. The films were dried for 24 hours at 100 °C. The samples were named after the organic substituents used for preparation followed by the atomic percentage of R (RTES) in the silica matrix. Table 1 summarizes the composition of the sols used for film preparation.

Table 1 Chemical composition of the sols used for film deposition. R represents Me, Bu or Ph

Sample name	Molar composition				R : Si ratio
	TAS	RTES	H ₂ O	Dye	
R90	0.20	1.80	6.20	0.01	0.90
R70	0.60	1.40	6.60	0.01	0.70
R50	1.00	1.00	7.00	0.01	0.50
R30	1.40	0.60	7.40	0.01	0.30
R20	1.60	0.40	7.60	0.01	0.20
R10	1.80	0.20	7.80	0.01	0.10
R8	1.84	0.16	7.84	0.01	0.08
R6	1.88	0.12	7.88	0.01	0.06
R4	1.92	0.08	7.92	0.01	0.04
R2	1.96	0.04	7.96	0.01	0.02
R0	2.00	0	8.00	0.01	0

Characterization

The samples were irradiated with radiation of 365 nm using a 100 W B-100AP UV lamp from UVP. The absorption spectra of the resulting films as well as the kinetics of the bleaching process were measured using a Varian Cary 50 Bio UV-Visible spectrophotometer. The spectra are given as DAs ($A_{\text{ai}} - A_{\text{bi}}$), where A_{ai} and A_{bi} are the absorptions after and before irradiation, respectively. The decay of the photochromic effect was monitored *vs.* time at the wavelength of the maximum absorption of each sample (visible) at 25 °C. The kinetic constants were calculated from the decay curves using a bi-exponential decay equation. $t_{1/2}$ is defined as the time required by the sample to achieve $DA_{\text{max}}/2$ during the thermal bleaching process. The thickness of the Ph containing films was measured with a Taylor-Hobson Form Talysurf-50 profile analyzer, and showed a progressive increment in thickness (from 0.2 mm for 0% R to 3 mm for 90% R) as the Ph loading in the sample was increased.

Results

The absorption spectra of the films obtained were measured between 300 and 800 nm. All samples showed an absorption band in the 350–365 nm range. Upon irradiation with UV light, the samples acquired a deep coloration with a broad band centered around 450 nm. The position of the band was found to depend on the matrix used for film preparation. A progressive shift to the UV was observed as the R : Si ratio in the matrix was increased. The spectra of the samples prepared with a Ph-modified matrix are given in Fig. 2 to illustrate this effect. The position of the band was also found to depend on the nature of the organic substituents used in the matrix. In this sense, samples prepared with iBu and Ph groups showed more significant shifts to the UV compared with samples prepared with the same relative amount of Me groups (see Fig. 3).

The positions of the absorption bands of the different samples prepared in this work are summarized in Table 2 and given as a function of the percentage of R in the matrix in Fig. 4. A rather linear change is observed in Me samples over the 0–70% range, while iBu and Ph samples show two different linear behaviors: a very steep slope in the 0–10% range and a much flatter slope in the 20–90% range.

Upon cessation of UV irradiation, the photochromic films undergo thermal bleaching (in the dark), recovering their original whiteness. Bleaching kinetics were measured by monitoring the light absorption at the peak maxima of the colored films of the

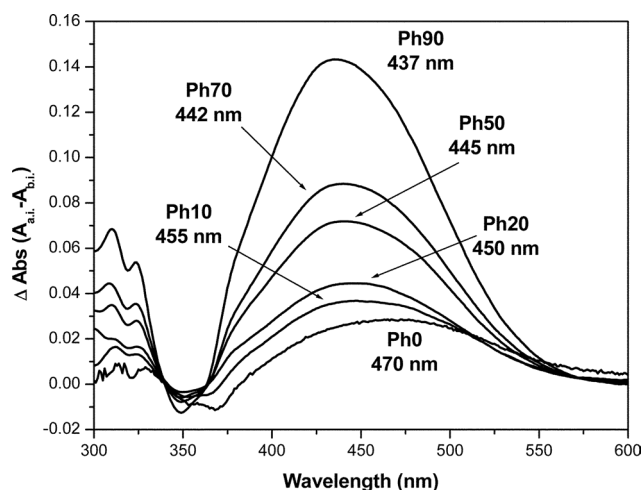


Fig. 2 UV-Vis absorption spectra of samples prepared with different amounts of Ph groups in the matrix.

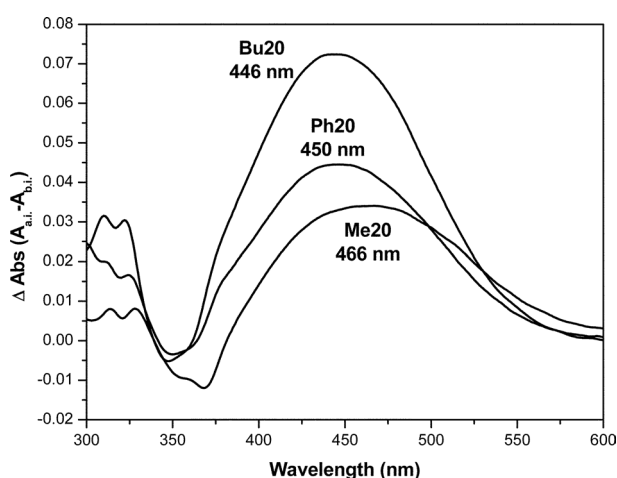


Fig. 3 UV-Vis spectra of photochromic naphthopyran molecules embedded in ormocers with different modifying groups.

different samples with time. The kinetics of this bleaching process were found to follow a bi-exponential decay in most cases and was strongly dependent on the matrix used for the encapsulation of the photochromic molecules; increasing the amount of R groups in the matrix resulted in a faster bleaching of the samples. In samples prepared with very low R loadings ($\leq 4\%$), the curves followed a first order exponential decay. Fig. 5 shows the kinetics of the thermal bleaching of the photochromic effect in Ph-modified silica matrices.

The nature of the organic substituents in the matrix also plays

Table 2 Spectral positions of the absorbance bands of naphthopyrans in ormocer matrices. R represents Me, Bu or Ph

Sample	λ_{\max}/nm		
	Me	Bu	Ph
R90	— ^a	439	437
R70	449	440	442
R50	457	444	445
R30	462	446	449
R20	466	446	450
R10	468	459	455
R8	467	463	459
R6	468	467	460
R4	470	468	462
R2	467	463	463
R0	470	470	470

^aNot possible to measure.

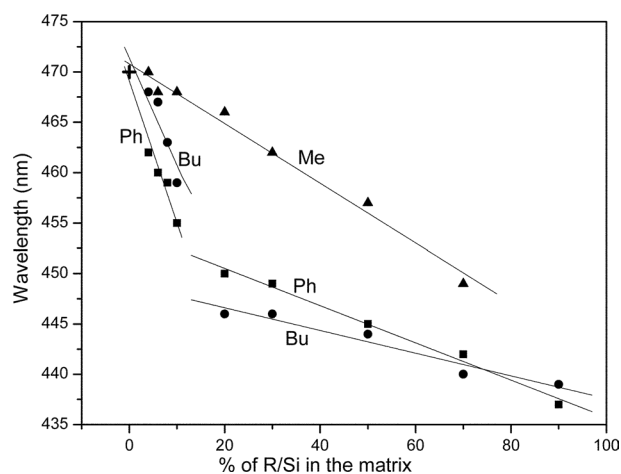


Fig. 4 Position of the spectral band of photochromic films as a function of the atomic percentage of R groups in the matrix.

an important role in the kinetics of thermal bleaching. iBu-modified matrices showed faster kinetics as compared with Me or Ph modified matrices with the same amount of R. The bleaching kinetics of samples Bu70, Me70 and Ph70 are given in Fig. 6 to illustrate this observation. As mentioned before, the kinetics of the thermal bleaching follows bi-exponential decay. The kinetic data of representative samples measured are summarized in Table 3. Two kinetic constants k_1 and k_2 were observed for each of the different samples (see later) and are represented in Fig. 7.

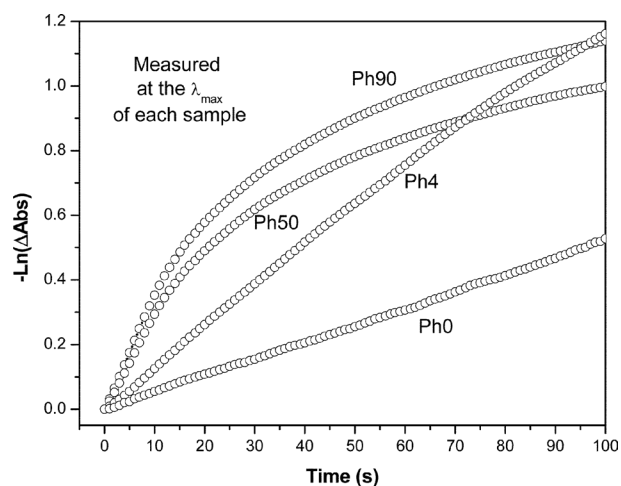


Fig. 5 Thermal bleaching kinetics of the photochromic effect in Ph modified silica samples.

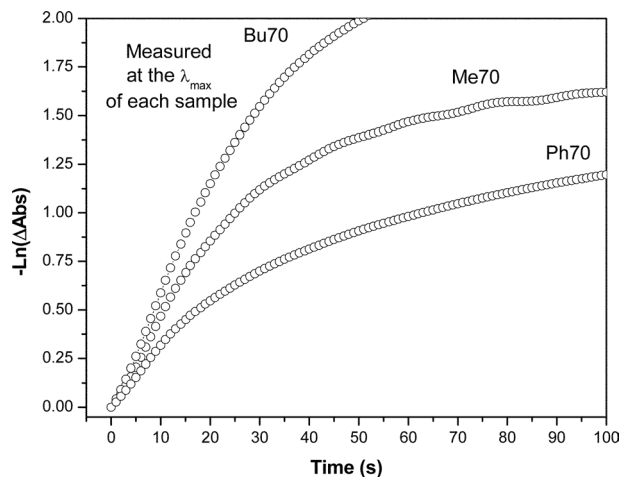


Fig. 6 Thermal bleaching kinetics of the photochromic effect in R70 samples.

Table 3 Kinetic data for the thermal bleaching of some of the photochromic samples prepared in this work

Sample	Me			Bu			Ph		
	$k_1/10^{23} \text{ s}^{-1}$	$k_2/10^{23} \text{ s}^{-1}$	$t_{1/2}/\text{s}$	$k_1/10^{23} \text{ s}^{-1}$	$k_2/10^{23} \text{ s}^{-1}$	$t_{1/2}/\text{s}$	$k_1/10^{23} \text{ s}^{-1}$	$k_2/10^{23} \text{ s}^{-1}$	$t_{1/2}/\text{s}$
R90	98.6	8.1	11.8	165.3	—	5.1	84.8	8.6	19.1
R70	81.5	9.6	12.6	122.1	52.3	9.2	69.8	8.4	22.5
R50	74.0	7.2	15.9	102.7	32.8	11.1	73.3	7.6	26.1
R10	84.5	6.1	10.6	42.7	7.0	19.2	44.5	8.0	22.6
R4	47.0	—	17.9	65.4	5.9	13.0	16.6	—	47.6
R0	7.8	—	116	7.8	—	116	7.8	—	116

Discussion

The nature and amount of organic groups (R) in the ormoser determine the polarity of the inner surfaces of the pores, where the photochromic molecules will be located, and therefore their

spectral and kinetic properties. In samples prepared without organic substituents (0% R), the surfaces of the pores in the resulting matrix consist mainly of uncondensed OH groups, which confer a very polar environment on the pore (57.9 kcal mol⁻¹ in the Reichardt $E_T(30)$ scale).⁸ The incorporation of R groups into the structure results in a decrease in the polarity of the matrix, which is a function of the R loading in the matrix.⁸ This effect is due to the lower polarity of the R groups attached to its surface and the fact that large organic chains may hinder the influence of the OH groups at the pores' surfaces, reducing further the polarity of the cage as sensed by the dye molecule. The representative spectra given in Fig. 2 and the data in Fig. 4 show a progressive blue shift in the absorption maxima as the polarity of the matrix is reduced (*i.e.* as the amount of R is increased). The difference in polarity of the different organic groups can be observed in the spectra of samples prepared with the same amount of R (Fig. 3). Interesting behavior was observed regarding this shift: samples prepared with R ~ Me showed a rather linear behavior. Samples with R ~ Ph or iBu showed two different linear behaviors for low and high R contents in the matrix. At very low concentrations of R (0–10%) the pore surface is mainly composed of OH groups with a small amount of R groups, which have a strong influence on the polarity of the pore. Increasing the amount of R groups above 10% results in screening of the small OH groups on the surfaces of the pores. Once this screening is effective, the changes in the R : OH ratio in the pore surface have a much lower effect on the polarity. In samples prepared with Me groups this effect is not observed due to the smaller size of the group, which prevents screening of the OH groups.

The kinetic measurements revealed the existence of two decay processes in the matrices having R loadings above 4%. The faster kinetic constant for all samples (k_1) was found to increase with the amount of R groups in the matrix, while the slower constant (k_2) remained nearly constant and very close to the value obtained in matrices with 0% R (Fig. 7). This can be explained by the co-existence of two different sites in which the photochromic molecules are located within the matrix. The first site, rich in OH groups, exists in all samples (including those with 90% R) and gives rise to the slower kinetic constant. The second site, rich in R groups and responsible for the fast kinetic constant, was found to increase with the amount of R in the sample. An exception was found for iBu-modified matrices: in contradiction with samples Me90 and Ph90, sample Bu90 shows single exponential decay kinetics (Fig. 7 and Table 3). Moreover, samples Bu70 and Bu50 show higher k_2 -values than the corresponding Me or Ph samples (Fig. 7).

The shape and the larger size of the iBu groups are probably responsible for the more effective screening observed, even in pores with relatively high amounts of OH groups. This observation can also be explained by the formation of micelle like structures in matrices with high iBu loadings¹³ that are able to accommodate the organic dye. In this case the photochromic molecules are trapped in an environment with a much lower polarity. The increased flexibility of the iBu groups as compared with Me and Ph groups can also facilitate the

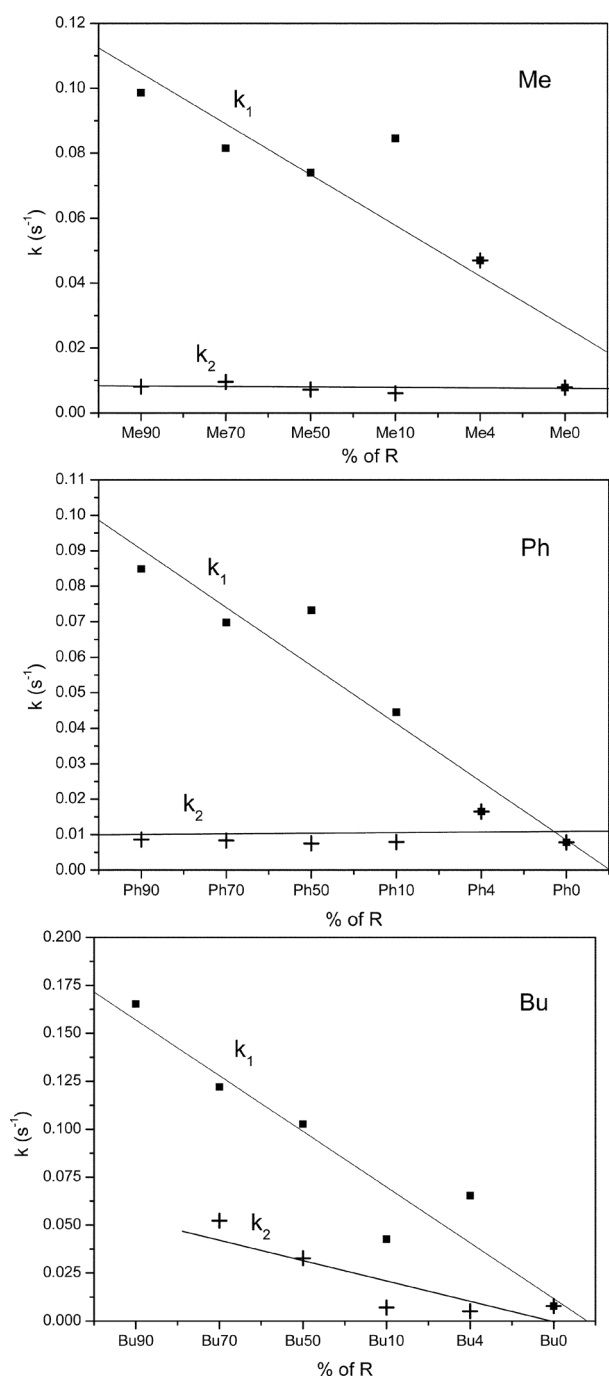


Fig. 7 Kinetic constants of the photochromic naphthopyran molecules in different ormosil matrices.

movement of the photochromic molecules inside the pore resulting in faster isomerization kinetics.

Another possible explanation for the fast and slow different bleaching kinetics found in these samples is the stabilization of the zwitterionic open colored forms (Fig. 1) of the photochromic dye in environments with higher polarity.⁴

Conclusions

The spectral and dynamic properties of a photochromic naphthopyran dye in a solid matrix were successfully controlled by the composition of the matrix in which the photochromic molecules are embedded. The introduction of organic groups covalently attached to the silica network has provided a way of controlling the polarity of the pore surface. In this way, organically modified matrices exhibited remarkably lower polarity compared with those prepared without organic substituents. This reduction in polarity is due to the lower polarities of the R groups as compared with the strongly polar silanol (Si-OH) groups on the surface. In addition, the introduction of iBu or Pr groups into the matrix results in screening of the OH groups at the pore surface, which is responsible for further reduction of the polarity as sensed by the photochromic molecules. Both the absorption spectra and the bleaching kinetics of the photochromic naphthopyrans are greatly affected by the polarity of its environment. As the polarity of the matrix is decreased a progressive blue shift is observed in the absorption maxima of the colored photochromic species. At the same time the bleaching kinetics are substantially accelerated. In general, for matrices with $\sim 4\%$ R, the bleaching kinetics follow a single exponential decay while matrices with $\sim 4\%$ R show bi-exponential behavior, suggesting the photochromic molecules are located in two different pore environments. The ability to control the spectrokinetic properties of the photochromic composites by varying the

chemical composition of the embedding matrix will be of great interest for the design of materials with defined properties.

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