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Photochromic organic–inorganic hybrid materials†

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Photochromic organic–inorganic hybrid materials have attracted considerable attention owing to their potential application in photoactive devices, such as optical memories, windows, photochromic decorations, optical switches, filters or non-linear optics materials. The growing interest in this field has largely expanded the use of photochromic materials for the purpose of improving existing materials and exploring new photochromic hybrid systems. This *tutorial review* summarizes the design and preparation of photochromic hybrid materials, and particularly those based on the incorporation of organic molecules in organic–inorganic matrices by the sol–gel method. This is the most commonly used method for the preparation of these materials as it allows vitreous hybrid materials to be obtained at low temperatures, and controls the interaction between the organic molecule and its embedding matrix, and hence allows tailoring of the performance of the resulting devices.

1. Photochromism

Photochromism is the reversible transformation of a chemical specie between two forms, A and B, having different absorption spectra, induced in one or both directions by the absorption of electromagnetic radiation (Fig. 1).^{1–3} The inter-conversion between the states is usually accompanied by changes in the physical properties of the chemical specie, such as the refractive index, solubility, viscosity, surface wettability or dielectric constants. The thermodynamically stable form A

is transformed by irradiation into the less stable form B, having a different absorption spectra, which can be reverted to form A, both thermally or photochemically³ (Fig. 1). Usually, the stable form in most photochromic compounds is colourless or pale yellow, and acquires colouration when irradiated (positive photochromism). Less common photochromic compounds show a coloured form A and a colourless form B (negative or inverse photochromism), or exhibit a reversible change between different colours.

Photochromism can take place in both inorganic and organic compounds, and is also observed in biological systems (for example the retina in the vision process^{3,4}). Among the inorganic or organometallic compounds showing photochromism we can find some metal oxides, alkaline earth

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Marcos Zayat

Marcos Zayat obtained his PhD degree in Chemistry from the Hebrew University of Jerusalem, Israel, in 1997 under the supervision of Prof. Renata Reisfeld. Since 1998 he has been based in the Materials Science Institute in Madrid, Spain (ICMM-CSIC), first as a post-doctoral fellow and subsequently (2008) as a tenured Scientist. He has authored over 50 papers centered on the design, preparation and characterization of new sol–gel materials for optical and electrooptical applications: thin films, protective coatings, smart windows, mixed oxides nanoparticles, etc.

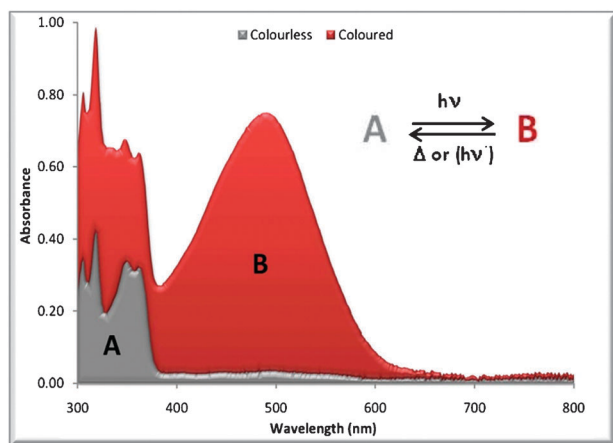


Fig. 1 Absorption spectra of the A (colourless) and B (coloured) forms.

sulfides, titanates, metal halides and some transition metal compounds such as the carbonyls.¹ There are also certain minerals in nature that show photochromic properties such as hackmanite, shown in Fig. 2. This mineral is a well-known variety of sodalite which is initially violet and fades quickly to colourless when exposed to visible light. The original colour is restored slowly in the dark or more quickly by exposure to ultraviolet light (inverse photochromism).

There are many organic compounds that show photochromism, such as some anilines, disulfoxides, hydrazones, osazones, semicarbazones, stilbene derivatives, succinic anhydride, camphor derivatives, *o*-nitrobenzyl derivatives and spiro compounds.^{1,2} Some of the most common processes involved in the photochromism of these compounds are pericyclic reactions, *cis-trans* isomerizations, intramolecular hydrogen



Fig. 2 Photochromic mineral (Hackmanite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$) made by nature.

transfer, intramolecular group transfers, dissociation processes and electron transfers (oxidation–reduction). Organic photochromic compounds are almost exclusively activated by ultraviolet light in the range of 200–400 nm. For some organic compounds this range can be extended to 430 nm, however very few organic photochromic compounds can be activated by visible light. On the other hand, even though most inorganic photochromic materials can be driven by ultraviolet light, some of these compounds can be activated by other wavelengths from infrared to X-rays or gamma.¹

Among the photochromic inorganic compounds, it is well known that silver halide particles in borosilicate or aluminoborosilicate glass exhibit reversible photochromism upon exposure to sunlight.⁵ The silver compounds are added to the melt of an aluminoborosilicate glass together with copper halides, with the silver halide content between 0.5–1 wt%. The glass is heat-treated at 500–800 °C in order to allow precipitation and subsequent crystallization of the AgCl crystallites. Upon irradiation, the silver ions are reduced to metallic silver particles, which are responsible for the colouration of the glass. Fig. 3 shows the different steps in the formation of the metallic silver particles.

In the absence of light, the silver halide glasses may be transparent colourless or opaque white depending on the particles size and the concentration of the dispersed particles. Fig. 3 shows different colours obtained in sol–gel films doped with silver halide particles having different particle size, after irradiation with UV light. The size of the metallic Ag precipitates determines the colour of the resulting films, showing a shift to the red in the absorption spectra as the size of the Ag particles is increased from 8 nm (clear yellow) to 30 nm (purple).⁶ Silver chloride is being used extensively for the manufacture of photochromic lenses that are very sensitive to sunlight; although these glasses show a fast response they offer a limited colour range.⁷

Organic photochromic compounds have been studied extensively owing to the possibility of obtaining a photochromic



David Levy

David Levy started his research activities in 1982 at The Hebrew University of Jerusalem, with the pioneering application of the Sol–Gel process to the preparation of “organically doped silica gel-glasses”. He was awarded the “First Ulrich Prize” in 1991. He was nominated by the CSIC for the “Juan Carlos I Rey” research award. He has authored or co-authored over 110 papers, reviews, book chapters and patents related to optical Sol–Gel materials and

their applications, and was Principal Investigator for 23 R&D Industry Projects. He is member of the International Advisory Board of the “International Sol–Gel Conferences” and Chair of the 2013 Sol–Gel Conference, and is a member of “Sol–Gel Optics” and “Optoelectronics and Optical Science and Technology” of the SPIE, and of the Experts Panel of the Materials Research Program of the EU. He is heading the Sol–Gel Group (SGG) at ICMM, and is currently Research Professor at ICMM-CSIC, and also headed for 10 years the LINES of the National Institute of Aerospace Technology, INTA.

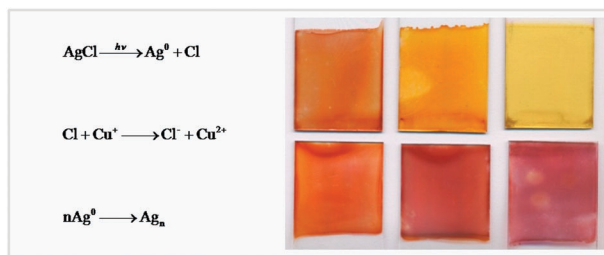


Fig. 3 Steps of the formation of the metallic silver particles upon irradiation and sol–gel photochromic coatings based on AgCl, after irradiation with UV light. Particle size ranging from 8 nm (yellow) to 30 nm (purple).

response in a wide range of wavelengths in the visible spectrum. More than one hundred organic photochromic molecules have been developed, the most commonly known being diarylethenes, fulgides, azobenzenes, spiropyrans, spirooxazines and naphthopyrans.^{1,2} The structures and processes involved in the photochromism of these compounds are shown in Fig. 4. Only diarylethenes and fulgide derivatives exhibit thermally irreversible photochromism (their acquired colouration does not fade in the dark), which make them suitable for applications such as optical memories, optical switching devices and displays.⁸ In the case of the diarylethenes, the stability depends on the aryl group type.² When the aryl groups are furan or thiophene rings, which have low aromatic stabilization energies, the photogenerated closed-ring forms are thermally stable and do not return to the open-ring form in the dark. On the other hand, the closed-ring forms of diarylethenes bearing phenyl or indole rings,

which have rather high aromatic stabilization energies, are thermally unstable. Stilbene, for instance, is well known to undergo a colour change by a *trans-cis* photoisomerization upon irradiation with UV light and exhibits a thermally reversible photochromism.¹⁻³

The photogenerated isomers of photochromic azobenzenes, spiropyrans, spirooxazines and naphthopyrans are thermally unstable and return to the initial isomers, even in the dark, by reversible photochromic reactions. Among the different photochromic dyes, spirooxazines (SO) have been the most extensively investigated due to their high fatigue resistance, as reported by Kawauchi *et al.*⁹ and Chu.¹⁰ The photochromism of these molecules involves a photoinduced heterolytic cleavage of the C(sp³)-O bond of the oxazine ring that leads to the formation of coloured merocyanine structures, shown in Fig. 5. The system reverts thermally or by irradiation with visible light to its original colourless form.¹⁻³

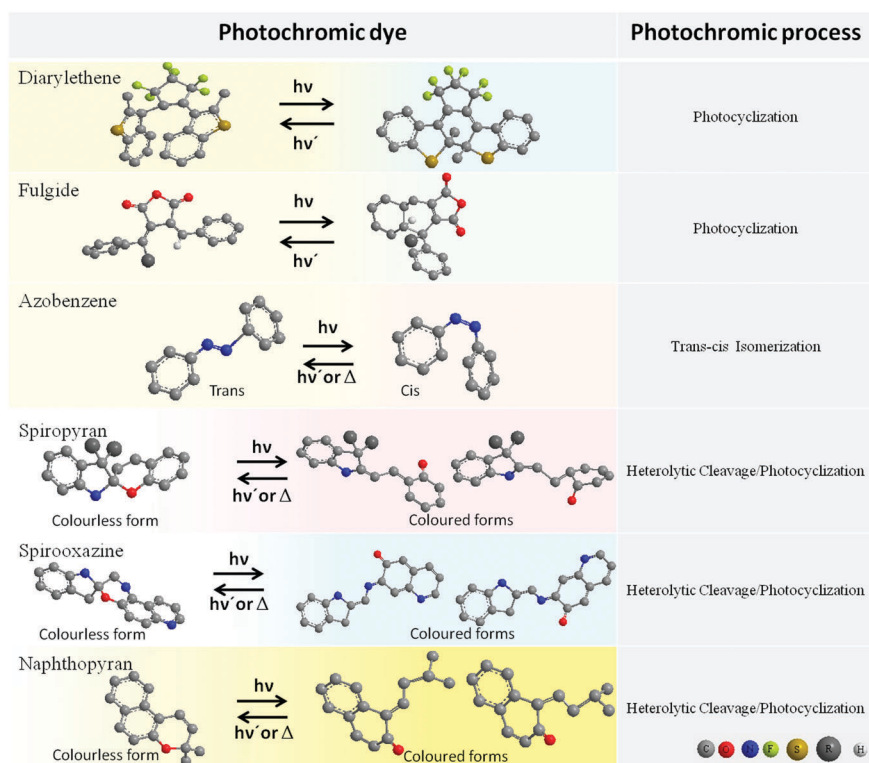


Fig. 4 Structures and processes involved in the photochromism of the different photochromic dyes (diarylethenes, fulgides, azobenzenes, spiropyrans, spirooxazines and naphthopyrans). The colours of the different states of the photochromic dyes are shown.

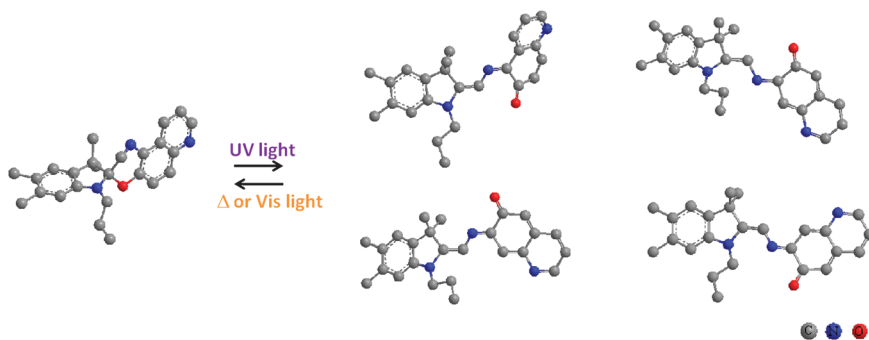


Fig. 5 Colourless form (left) and coloured forms (right) of photochromic spirooxazines.

Considerable efforts have been devoted to improving the properties of the photochromic compounds to fulfil the requirements of the different applications. The most remarkable properties of these compounds are their absorption spectra, particularly the position of the absorption maxima, the intensity of colour obtained upon irradiation with UV light and the kinetics of the bleaching process. Most of the scientific research done on photochromic compounds has been devoted to the optimization of their spectrokinetic properties by substitution of functional groups in the photochromic molecules. More than one hundred patents have been published dealing with the properties of the new substituted photochromic molecules in solution or imbedded in polymer matrices.^{2,3} The photochromic behaviour of these molecules depends strongly on the environment properties in which they are dissolved or allocated, such as the polarity, pH, solubility or temperature.¹⁻³ Many scientists pay more attention to exploring new photoresponsive multicomponent systems, which can be obtained by embedding the photochromophores (molecules, nanoparticles...) into a variety of polymeric matrices or anchoring a photochromophore in a functional monomer/oligomer that will be used to prepare the matrix.¹¹

Photochromic organic-inorganic hybrid materials are one of the most studied systems. It has been believed that the synergy of organic and inorganic compounds in hybrid materials can preserve or even improve the features of the components. Nowadays it has been demonstrated that hybrid systems can also confer new properties upon the material, different from those of the single components.¹² Generally, inorganic compounds have thermal stability, high strength and diverse coordination chemistry. On the other hand, there is a large variety of organic compounds which are easy to modify or process. The extremely versatile physical and chemical properties, compositions and processing techniques of organic-inorganic hybrids offer a wide range of possibilities to fabricate tailor-made photochromic materials.

2. Photochromic organic-inorganic hybrid materials

The ability to combine, in a single material, organic and inorganic components at molecular or nanometric level represents a great step in material science with extraordinary implications for developing novel multifunctional materials. Organic-inorganic hybrids have the advantages of both organic (light weight, flexibility, versatility, *etc.*) and inorganic materials (high thermal and mechanical resistance), which make them suitable for applications in many fields, such as optics, solid electrolytes, catalysis, biomaterials and biomedical applications.¹² Furthermore, some photoactive molecules, either organic or inorganic, can be introduced into organic, inorganic or hybrid matrices in order to exhibit properties such as photochromism.¹³

The uses of such a hybrid approach to obtain photochromic materials with greatly improved properties, from the point of view of potential applications, are now being widely studied in many research groups.¹⁴ He *et al.*¹⁵ studied the photochromism of composites and hybrid materials based on transition-metal oxides and polyoxometalates, and found that

an improvement in the photochromism is obtained, due to the charge transfer between inorganic and organic moieties. The design of these hybrid systems (appropriate inorganic and organic molecules) is of great importance so the charges (electrons and/or protons) can be reversibly transferred between the two constituents upon photoirradiation. Other authors¹⁶ have studied different photochromic hybrid materials based on metal halides and metal cyanides, polyoxometalates and metal chalcogenides, and metal-organic complexes. The mechanism of the photochromism in these materials involves photoinduced charge transfer between the inorganic and organic components. Among these photochromic materials, the polyoxometalates have received considerable attention in recent years due to their potential applications in optical switching or optical storage media.¹⁷ Polyoxometalates are also incorporated in organic-inorganic matrices as their porous structure offers enough free spaces for the reversible structural changes of the photochromic components during photochromic transformations.¹⁸

Photochromic molecules have been embedded into a wide range of solid matrices¹⁹ including polymers like PMMA, inorganic materials like sol-gel derived silicates and aluminosilicates, and also in hybrid organic-inorganic composites like ormosils and surfactant templated mesostructured materials. The photochromic molecules can be incorporated into a matrix in two ways, either by covalent bonding or by doping. Andersson and co-workers²⁰ reported the synthesis of photochromic pigments that can be added to various matrices using traditional coating or paint-based technology. The photochromic spiropyran and spirooxazine dyes were introduced into surfactant templated mesostructured particles using a simple one-pot spray synthesis technique and these dye-loaded materials are referred to as photochromic organic-inorganic hybrid pigments. This material combines the mechanically and chemically rigid silica matrix with an organic phase where the dyes have a high conformational degree of freedom. The versatility of these photochromic pigments was demonstrated by the preparation of latex-based films with good optical quality, opening new possibilities to produce photochromic objects of different shapes and materials.²⁰

To move towards realistic technological implementations of photochromic devices, the materials selected should be shaped as thin films, coatings, monoliths, or other suitable forms, as required from engineering considerations. However, it seems difficult to prepare photochromic hybrid materials by the standard methods of vacuum evaporation or sputtering, as most of the photochromic compounds have the tendency to decompose when heated. These methods are limited to preparation of hybrid materials with inorganic photochromic compounds such as MoO₃ or WO₃.¹⁵

The sol-gel process²¹ is the most commonly used method for the preparation of photochromic hybrid materials. This process, being a low temperature method, allows the preparation of transparent, solid and porous inorganic matrices and the incorporation of optically active organic molecules in its porosity.²² The method involves reactions of hydrolysis and condensation of alkoxides (Fig. 6) to produce 3D, amorphous, porous and stable networks. The most widely used alkoxides are those of silicon, titanium, zirconium or aluminium.²³

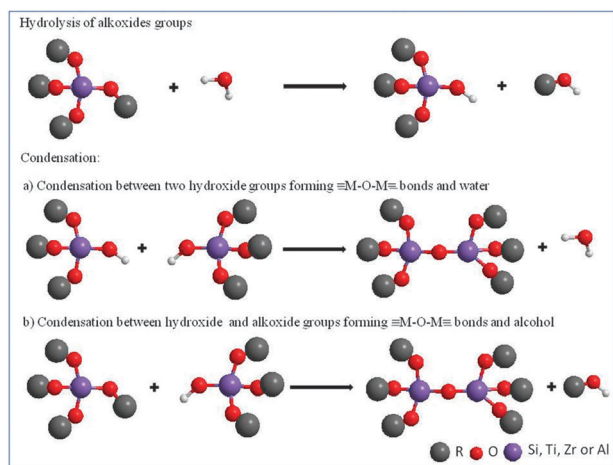


Fig. 6 Sol-gel reactions to amorphous matrices.

The sol-gel method allows also the preparation of hybrid organic-inorganic matrices, by using organically modified alkoxide precursors [RM(OR)₃, where R is an organic functional group and OR are the alkoxy groups] (Fig. 7). The non-hydrolysable organic groups of the alkoxide remain attached to the matrix porosity. Fig. 8 shows a scheme of the pore structure in the hybrid silica matrix where the organic molecules are located. The usage of these precursors allows controlling the polarity and size of the pores according to the nature and amount of the non-hydrolysable organic groups used.²⁴ Difunctional alkoxides [RR'M(OR)₂] have also been used for the preparation of hybrid organic-inorganic matrices, with methyl (-CH₃) and phenyl (-C₆H₅) the most commonly used functional groups (R and R').²³

Since the pioneering work of Avnir, Levy and Reisfeld in 1984,²² the sol-gel process has been a powerful method for the

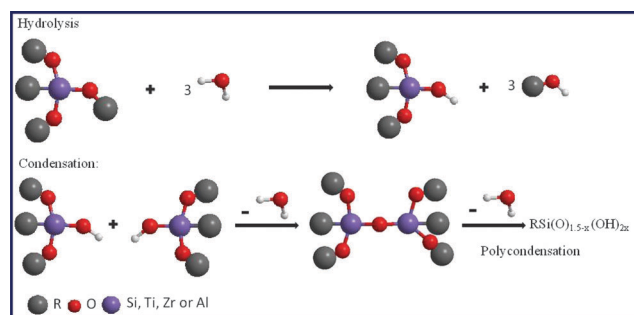


Fig. 7 Sol-gel reactions of organically modified alkoxide precursors

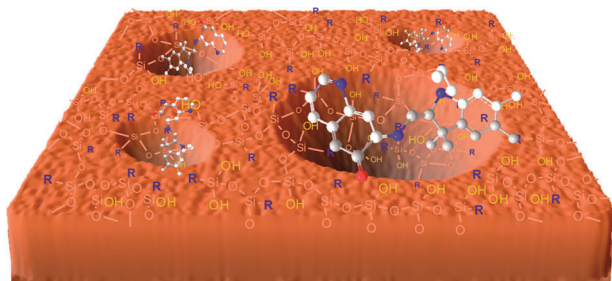


Fig. 8 Schematic representation of the pore structure in the hybrid silica matrix.

preparation of porous gel-glasses doped with organic molecules, as the relatively low temperatures (<150 °C) used for preparation do not produce damage to the organic molecular structures. These molecules are incorporated in the starting solution used for the gel-glass preparation and remain trapped in the porosity of the resulting matrix (Fig. 8). The great versatility of the sol-gel method allows the preparation of different glasses or ceramics in the form of particles, thin films, fibers, monolithic bulk and extremely porous materials such as aerogels.²¹ The final products exhibit good optical quality (high transmission in the visible region) and the mechanical strength required for most applications.²⁵ Moreover, the porous structure of these materials offers enough free room for the reversible structural changes of the dye molecules during photochromic transformations. In the early stages of the research on hybrid photochromic materials, attention has been focused on embedding organic or organo-metallic chromophores in transparent matrices or networks (SiO₂, Al₂O₃), ormocers (organically modified ceramics) and ormosils (organically modified silica) *etc.* made mainly by the sol-gel method.

3. Sol-gel prepared photochromic hybrid materials

In order to take advantage of the photochromic effect in different applications, the active molecules must be isolated in a solid matrix, since the photochromic compound in its crystalline form is totally inactive. The usage of polymer matrices is a good choice for the entrapment of photochromic molecules; however it is limited by the low stability of the matrix upon UV irradiation.²⁶ On the other hand, the traditional method for the preparation of glass does not allow the incorporation of organic matter into the glass due to the high temperature of the processing. The sol-gel procedure,²¹ being a low temperature method, provides a versatile solution for hosting the photochromic dyes. The first incorporation of photochromic molecules into sol-gel glasses was reported in the late 1980's,²⁷ consisting of molecules of aberchrome 670 or molecules of the spiropyran family embedded in organically modified silica glasses. The intense research work done in this field was mainly devoted to dispersions of molecules of the spiropyran and spirooxazine families in sol-gel matrices,²⁸ mainly prepared as thin film coatings on glass substrates.²⁹ Sanchez *et al.*³⁰ reported on the preparation of photochromic hybrid materials based on spirooxazine and spiropyran dyes in different hybrid matrices, showing the very high sensitivity of the photochromism to dye-matrix interactions. In previous work, we have demonstrated the feasibility of introducing photochromic naphthopyran derivatives into sol-gel hybrid matrices and the effect of different organic functional substituents in the matrix on the photochromic properties of the embedded molecules.³¹ Naphthopyran compounds are known to exhibit photochromism since the first report of Becker and Michl in the early 1960's.³² These molecules undergo a strong change in colouration when irradiated with UV light (360–365 nm) due to the reversible heterolytic scission of the C(sp³)-O bond of the pyranic ring, leading to the formation of coloured merocyanine structures² as shown in Fig. 9. The

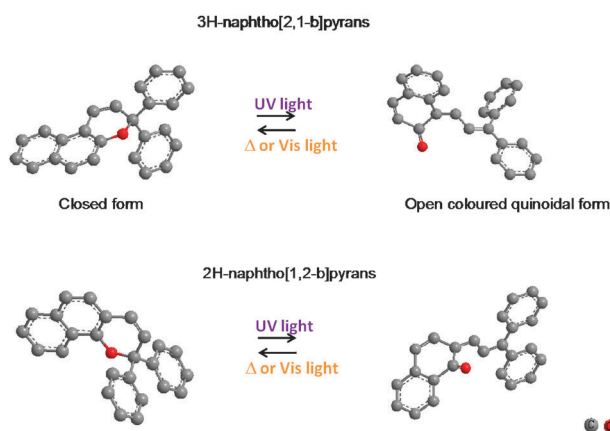


Fig. 9 Colourless (left) and coloured (right) forms of photochromic naphthopyrans.

system reverts through a thermal pathway to its original closed form.

The photochromic molecules of the naphthopyran family have been studied extensively owing to the high fatigue resistance and the possibility of obtaining a photochromic response in a wide range of wavelengths in the visible spectrum.³³ Photochromic naphthopyrans can be divided into two sub groups: the 3*H*-naphtho[2,1-*b*]pyran (3*H*-NP) and the 2*H*-naphtho[1,2-*b*]pyran (2*H*-NP) families (Fig. 9). Many naphthopyran derivatives were synthesized in order to obtain photochromic molecules with modified spectral and kinetic properties.³⁴ In general, molecules from the 2*H*-NP families have more stable coloured forms than the corresponding 3*H*-NP molecule, due to the strong steric interaction between the hydrogen atoms in the open quinoidal form of the 3*H*-NP (Fig. 9) affecting its stability. In general 3*H*-NP's have much faster thermal bleaching than 2*H*-NP's together with a much lower ΔOD (difference in absorption between dark and bleached states, measured at λ_{max}). The photochromic properties of these molecules have been measured in different solvents or as dispersions in polymers.³⁵ In solid matrices, such as the polymeric matrices, the photochromic properties of the embedded molecules are strongly influenced by the polarity of the environment where the molecules are located.²⁴ Moreover, the size and shape of the pores containing the dye molecules (Fig. 8) have also an important effect on the spectral and kinetic properties of the photochromic system, as it may provoke steric inhibitions during the molecule opening–closing process.

Naphthopyrans and spirooxazines in hybrid organic–inorganic matrices

Several hybrid matrices were prepared from mixtures of tetraacetoxysilane, TAS = $\text{Si}(\text{OCOCH}_3)_4$, with silicon alkoxides modified with organic groups, R–triethoxysilanes (RTES). These organic groups (R = $-\text{CH}_3$ (Me), $-\text{C}_2\text{H}_5$ (Et), $-\text{C}_3\text{H}_7$ (Pr), $-\text{C}_4\text{H}_9$ (iBu), $-\text{C}_6\text{H}_5$ (Ph) and $-\text{C}_6\text{F}_5$ (pFPh)) incorporated in the matrix network affect the chemical composition of the inner pore surface (R/OH groups ratio) and are, therefore, responsible for the properties of the pore environment where the photochromic molecules are located. The R groups used

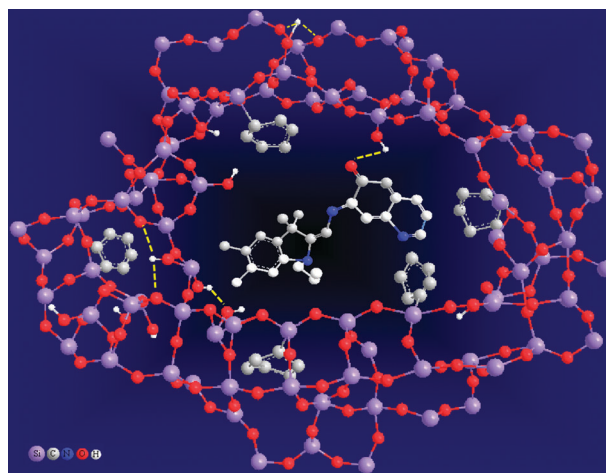


Fig. 10 Schematic representation of the pore structure in the phenyl modified silica matrix (SiO–Ph).

for the preparation of the different matrices were selected from size and polarity considerations and interaction/affinity with the photochromic dye. Fig. 10 shows a scheme of the pore structure in a phenyl modified silica matrix where the dye molecules are located.

The preparation of the photochromic hybrid coatings on glass slides is described in Fig. 11. In all preparations, water was added to allow the hydrolysis of the alkoxide precursors; the reaction was self-catalyzed by the slow release of acetic acid from the TAS. The sols were allowed to hydrolyze for 24 h under stirring at 25 °C. The photochromic dye was added as a THF solution, after the hydrolysis of the sol, to obtain the required photochromic-dye/Si molar ratios. THF was used as solvent due to its good miscibility with the coating sol. The deposition of the films was carried out after the addition of the photochromic dye using the spin-coating technique with the sample holder spinning at 2000 rpm. Finally, the films were further dried for 24 h at 100 °C.

Different photochromic naphthopyran derivatives have been incorporated in sol–gel prepared hybrid matrices to characterize their photochromic properties. Table 1 shows the chemical structures of the different photochromic dyes. Mixtures of

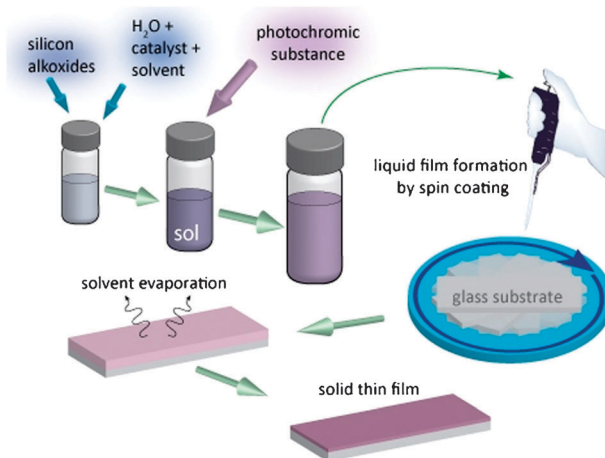
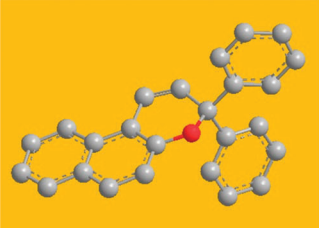
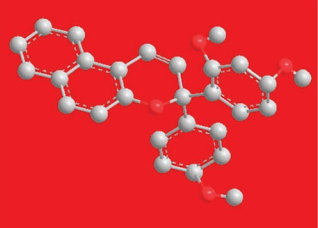
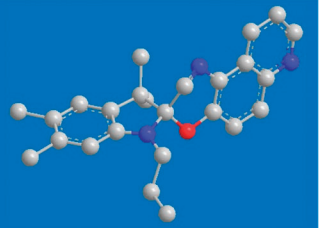


Fig. 11 Scheme of the coatings preparation process.

Table 1 Structures of the photochromic molecules incorporated in sol-gel prepared hybrid matrix

Yellow	Red	Blue
3,3-diphenyl-3H-naphtho[2,1-b]pyran	3-(2,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-3H-naphtho[2,1-b]pyran	1,3,3,5,6-pentamethyl-spiro [indoline-2-3'-[quinolino]oxazine]
		

photochromic dyes of different families such as naphthopyrans and spirooxazines can be incorporated in the hybrid matrices, expanding the colour range of the resulting films.^{31f}

The resulting coatings are transparent, colourless and show a rapid colouration upon exposure to UV light (365 nm),

acquiring blue, yellow, red and green colours. The green colour is obtained by the mixture of the yellow dye and blue dye. The picture in Fig. 12 shows the colouration of the films prepared with the different photochromic dyes, before and after irradiation with UV light.

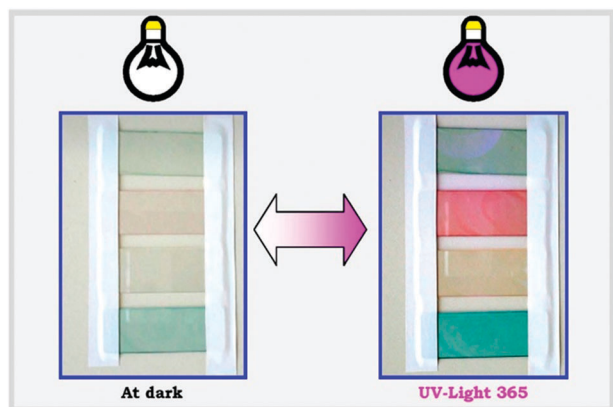


Fig. 12 Picture of the thin films prepared with different photochromic dyes, before and after irradiation with UV light.

3.1 Effect of the host matrix on the photochromism of naphthopyrans

In order to study the effect of the host matrix on the photochromism of the naphthopyrans, photochromic 3,3-diphenyl-3H-naphtho[2,1-b]pyran molecules were embedded in sol-gel prepared organically modified thin films.^{31a} The chemical structures of the colourless and coloured forms of the photochromic dye are given in Fig. 13. The most remarkable properties of these molecules, namely the absorption spectra upon irradiation with UV light and the kinetics of the bleaching process (recovery of original whiteness) have been measured in different organically functionalized matrices as a function of the composition of the hybrid matrix. These properties of the naphthopyran molecules depend strongly on the polarity of the pores where the molecules are located and hence, on the functionalization of the matrix.

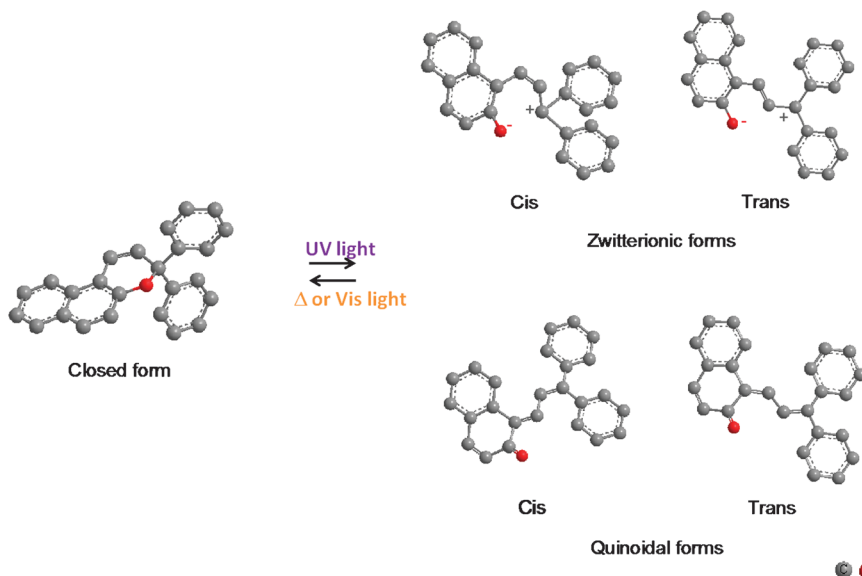


Fig. 13 Chemical structure of the naphthopyran dye used for sample preparation and the possible open coloured forms.

3.1.1 Spectral behaviour of the naphthopyran dye embedded in hybrid coatings. The absorption spectra of the photochromic dye in the hybrid matrices prepared with different R groups, in their bleached or colourless state, show an absorption band in the 350–365 nm range (Fig. 1). Upon irradiation with UV light, the samples acquire a deep colouration showing a broad band centred around 450 nm. The position of the absorption band of the NP's was found to depend on the amount and nature of the organic groups (R) used for functionalizing the embedding hybrid matrix. A progressive shift to the UV is observed as the R/Si ratio in the matrix is increased

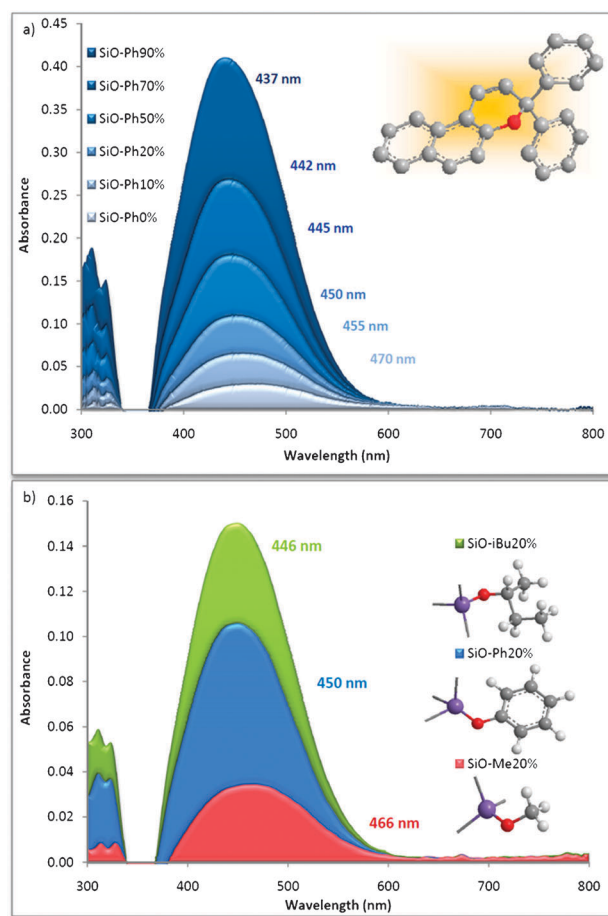


Fig. 14 UV-Vis absorption spectra of samples prepared: (a) different amounts of Ph groups in the matrix, (b) different modifying groups in the matrix.

from 0 to 90%. Fig. 14a shows this effect in matrices prepared with different relative amounts of phenyl groups (Ph).

The position of the absorption band of the NP after irradiation was also found to depend on the nature of the organic substituents used in the hybrid matrix. In this sense, samples prepared with isobutyl and phenyl groups (samples SiO-iBu and SiO-Ph) showed more important shifts to the UV as compared with those shown in samples prepared with methyl modified matrices (SiO-Me) with the same R/Si ratio (Fig. 14b). Table 2 summarizes the position of the absorption band of the NP as a function of the percentage of Si atoms modified with R groups in the matrix.

The nature and amount of the organic groups (R) in the hybrid matrix determine the polarity of the inner surface of the pores, where the photochromic molecules will be located, and therefore their spectral and kinetic properties. In samples prepared without organic substituents (R/Si = 0), the surface of the pores in the resulting matrix consists mainly of uncondensed silanol groups (Si-OH), which confers a very polar environment upon the pore (57.9 kcal mol⁻¹ in the Reichardt $E_T(30)$ scale).²⁴ 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.²⁴ This effect is due to the lower polarity of the R groups that remain attached to the pore surface and the fact that large organic groups may hinder the influence of the OH groups of the surface, reducing further the polarity of the environment in which the dye molecules are embedded (Fig. 8).³¹ From the data given in Fig. 15, a progressive blue shift in the absorption maxima is observed as the polarity of the matrix is reduced (the amount of R is increased). This effect is also observed in samples prepared with the same amount of R (Fig. 15), due to the difference in polarity of the different organic groups.³¹ An interesting behaviour was observed regarding this shift: samples prepared with Me groups (SiO-Me) showed a rather linear behaviour. Samples prepared with Ph (SiO-Ph) or iBu groups (SiO-iBu) showed two different linear behaviours 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 low amount of R groups, which have a strong influence over the polarity of the pore. Increasing the amount of R groups above 10% results in a screening of the small OH groups at the surface of the pore. Once this screening is effective, the changes in the R/OH ratio at the pore surface have a much lower effect on the polarity. In samples prepared

Table 2 Spectral position of the absorption band of the irradiated naphthopyran dye in the different hybrid matrices

Sample name R = Me, iBu or Ph	R/Si molar ratio	SiO-Me λ_{\max} (nm)	SiO-iBu λ_{\max} (nm)	SiO-Ph λ_{\max} (nm)
SiO-R _{90%}	0.90	—	439	437
SiO-R _{70%}	0.70	449	440	442
SiO-R _{50%}	0.50	457	444	445
SiO-R _{30%}	0.30	462	446	449
SiO-R _{20%}	0.20	466	446	450
SiO-R _{10%}	0.10	468	459	455
SiO-R _{8%}	0.08	467	463	459
SiO-R _{6%}	0.06	468	467	460
SiO-R _{4%}	0.04	470	468	462
SiO-R _{2%}	0.02	467	463	463
SiO-R _{0%}	0	470	470	470

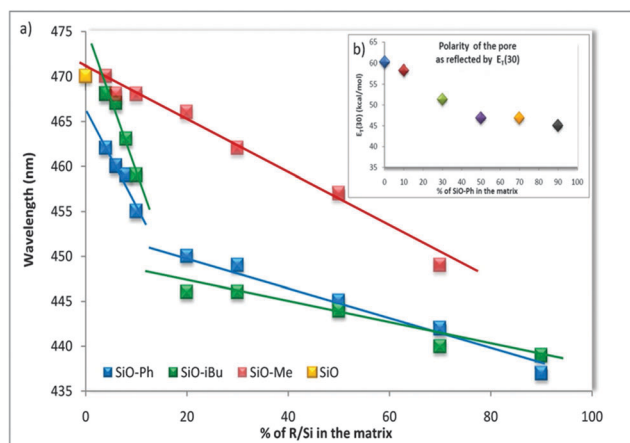


Fig. 15 (a) Position of the absorption band of coloured photochromic films as a function of the R groups/Si ratio in the matrix; (b) polarity of the pore as reflected by $E_T(30)$ as a function of % of SiO-Ph in the matrix.

with Me groups this effect is not observed due to the smaller size of the group, which is not able to effectively screen the OH groups.

3.1.2 Dynamic behaviour of the photochromic dye embedded in hybrid coatings. Upon cessation of the UV irradiation, the photochromic films undergo a thermal bleaching, recovering their original whiteness. The bleaching kinetics were measured by monitoring the light absorption at the peak maxima of the coloured films of the different samples in the dark. In most cases bi-exponential decay kinetics were observed, with kinetic constants strongly dependent on the matrix used for the encapsulation of the photochromic molecules. Only samples prepared with very low functionalizations (R loadings $\leq 4\%$) showed first order exponential decays. Fig. 16a shows the kinetics of the thermal bleaching of the photochromic dye in phenyl modified matrices (SiO-Ph).

The nature of the organic substituents in the matrix also plays an important role in the kinetics of the thermal

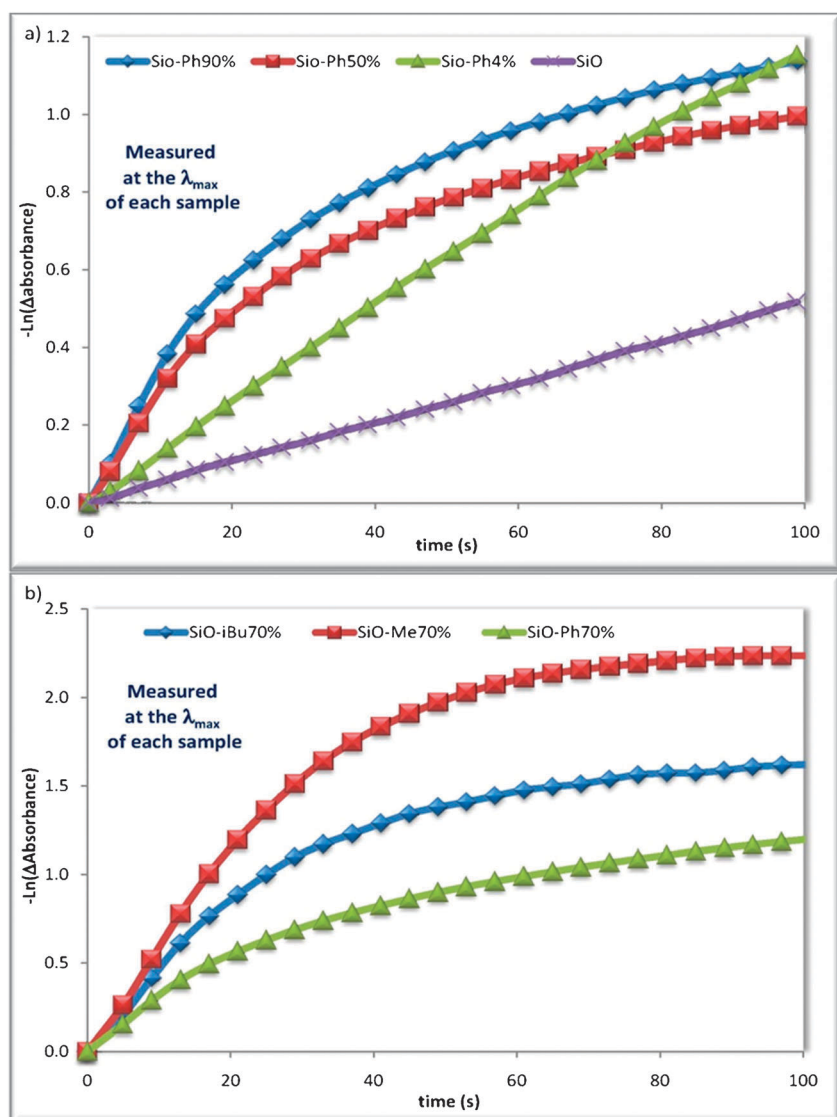


Fig. 16 Thermal bleaching kinetics of the photochromic molecules (a) in phenyl modified matrices (SiO-Ph); (b) in samples SiO-R_{70%}, where R is iBu, Ph and Me.

bleaching. Matrices modified with iBu groups showed faster kinetics as compared with matrices modified with the same amount of Me or Ph groups. The bleaching kinetics of samples SiO-iBu_{70%}, SiO-Me_{70%} and SiO-Ph_{70%} are given in Fig. 16b to illustrate this observation. As mentioned before, the kinetics of the thermal bleaching follows a bi-exponential decay. The kinetic measurements revealed the existence of two different decay processes in matrices with R loadings above 4%, which can be explained by the co-existence of two different sites in the matrix allocating photochromic molecules.³¹ The first site, rich in R groups and responsible for the fast kinetic constant (k_1), was found to increase with the amount of R in the matrix. The second site, rich in uncondensed OH groups, exists in all samples (including those with high functionalization) and gives rise to the slower kinetic constant (k_2) that remained nearly constant and very close to the value obtained in unmodified matrices ($R/Si = 0$). An exception was found in matrices modified with isobutyl (iBu) groups: in contradiction with samples SiO-Me_{90%} and SiO-Ph_{90%}, sample SiO-iBu_{90%} shows single exponential decay kinetics. Moreover, samples SiO-iBu_{70%} and SiO-iBu_{50%} show higher k_2 -values than the corresponding SiO-Me or SiO-Ph samples. The kinetic constants k_1 and k_2 of the different samples are represented in Fig. 17.

The shape and the larger size of the iBu groups are probably responsible for the more effective screening of the OH groups of the pore surface even in pores with relatively high amounts of OH groups, resulting in a lower polarity of the pore cage. This observation can also be explained by the formation of micelle like structures in matrices with high iBu loadings,³⁶ able to accommodate the organic dye. In this case the photochromic molecules will be 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 movement of the photochromic molecules inside the pore resulting in faster isomerization kinetics.³¹

Another possible explanation for the fast and slow bleaching kinetics found in these samples is the stronger stabilization of the zwitterionic open coloured forms (Fig. 13) of the photochromic dye as compared to the other coloured forms of the dye in environments with higher polarity.²

3.2 Effect of the chemical environment on the degradation of photochromic dyes in hybrid coatings

The loss of photochromic properties upon prolonged exposure to UV light, commonly referred to as fatigue, limits the use of photochromic molecules in outdoors applications or in environments with strong UV radiation. The first studies on the photodegradation of photochromic compounds with UV light were carried out by Gautron in the 1960's on spiropyran derivatives.³⁷ Salemi-Delvaux *et al.*³⁸ and Balliet³⁹ investigated the stability of photochromic naphthopyran derivatives in solvents and polymer networks, respectively. The photodegradation of some photochromic molecules in the indolinospiropyran and indolinospirioxazine series was studied, in solvent solutions⁴⁰ and in the solid state.⁴¹ In recent work, we have studied the photostability of a photochromic naphthopyran dye (3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran) in different sol-gel prepared

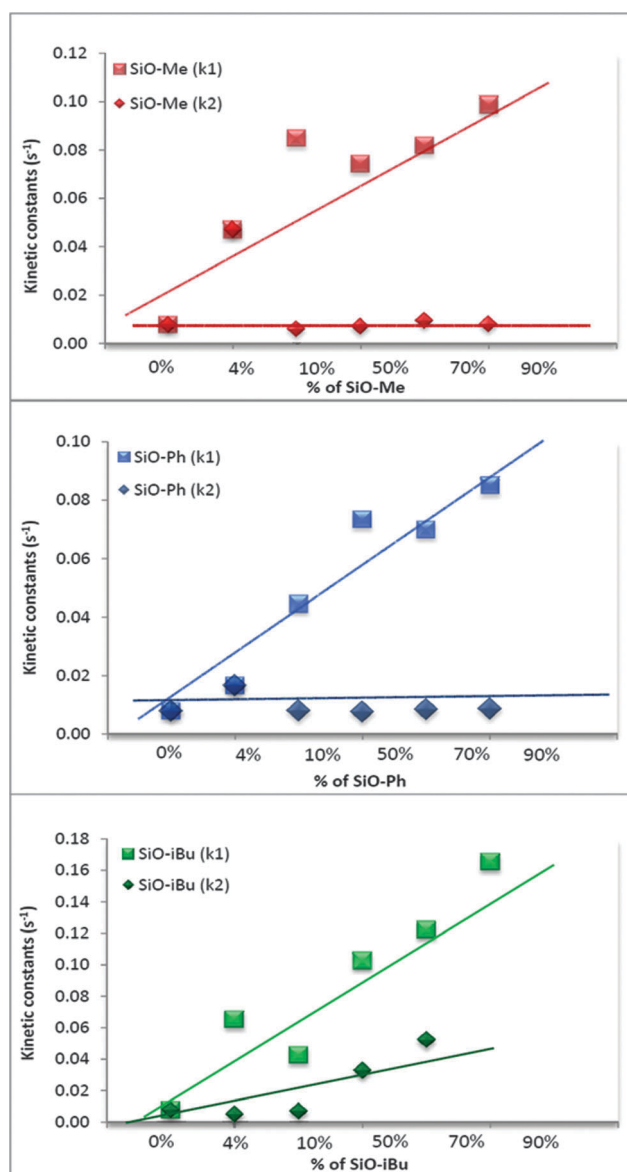


Fig. 17 Kinetic constants of the bleaching process of the photochromic naphthopyran molecules in different hybrid matrices.

hybrid coatings upon prolonged exposition to UV light.⁴² The photostability of these molecules embedded in hybrid matrices was found to depend strongly on the nature of the embedding matrix. The introduction of organic functional groups into the inner pore surface of the matrices affects the stability of the molecules, in terms of the effectiveness of the interaction between the photochromic molecules and the surface of the pores. The photostability of the photochromic molecules upon prolonged irradiation with UV light depends also on the temperature at which the photodegradation of the films is carried out. Temperature favours the side-reactions between the coloured open form of the photochromic dye and the matrix pore surface, responsible for the degradation of the dye.⁴² The photodegradation or fatigue of the photochromic dye embedded in hybrid matrices was measured as a function of the composition of the matrix (amount of the phenyl groups) and the dye loading. The photodegradation of the

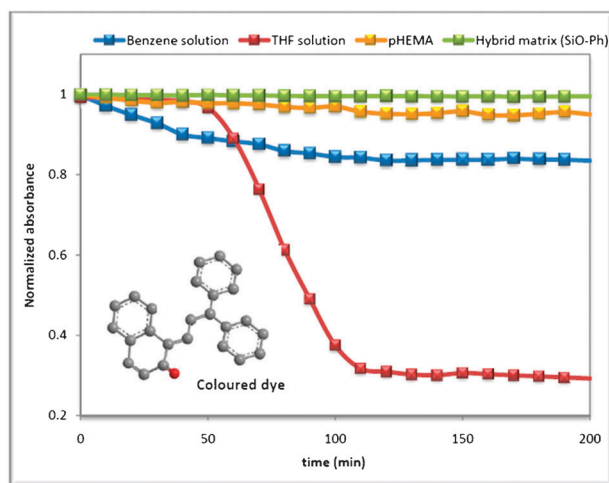


Fig. 18 Photodegradation of a naphthopyran molecule in THF and benzene solutions, and embedded in pHEMA and phenyl modified hybrid matrices (SiO-Ph).

photochromic molecules was also measured in solvents (THF or benzene) and dispersed in a polymeric matrix (pHEMA) for comparison with the organic-inorganic hybrid matrices. The absorbance of the photochromic samples was monitored *vs.* time, while irradiating the samples with a UV lamp, to follow the photodegradation of the photochromic molecules.

The photodegradation, leading to the formation of benzophenones, β -phenylcinnamaldehydes and other minor photoproducts,^{38,43} is much faster in solution than in solid matrices (Fig. 18), due to the higher mobility of the dye molecules.⁴⁴ Photochromic dye in a THF solution undergoes a faster photodegradation than in a benzene solution, due to the higher polarity of THF,⁴⁵ that results in a stabilization of the open coloured form of the dye molecules, promoting the photodegradation of the naphthopyran dye.⁴⁴ No important differences were observed in the photostability of the dye molecules in polymeric and organic-inorganic hybrid matrices. However, in polymeric matrices, the photostability of the naphthopyrans is limited by the low stability of the matrix itself upon UV irradiation.²⁶ The usage of hybrid matrices is, therefore, the best choice for the entrapment of photochromic molecules due to the improved photostability of both the photochromic molecules and the matrices.

Organic functional groups in hybrid matrices

The nature and amount of the organic functional groups in the matrix have an important effect on the photodegradation of the naphthopyran dye.⁴² The introduction of organic groups (R) into the sol-gel matrix results in a decrease in the relative amount of the silanol groups in the inner pore surface where the photochromic molecules are located and therefore, in a decrease in the pore surface polarity.³¹ In order to correlate the photodegradation of the dye with the composition of the matrix, the time required to produce a photodegradation with UV light of 20% of the molecules embedded in the film (20% drop in the intensity of the absorbance peak) was measured as a function of the amount of organic groups incorporated in the silica matrix. Increasing the R/Si molar ratio in the matrix

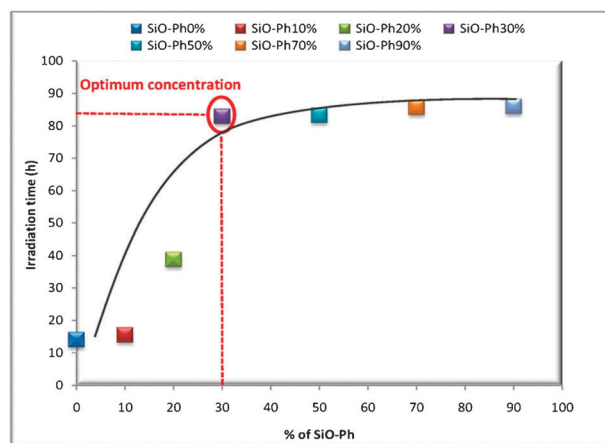


Fig. 19 Time of UV irradiation that causes the degradation of 20% of the photochromic molecules embedded in phenyl modified matrices (SiO-Ph) with different Ph/Si molar ratio.

results in a progressive increase in the time required for the degradation, reaching a saturation value around R/Si = 0.3 (SiO-R_{30%}), as shown in Fig. 19 for phenyl modified hybrid matrices. This effect is due to the fact that the zwitterionic forms of the open coloured merocyanine molecules (Fig. 13) are stabilized in more polar environments, favouring its interaction with the OH groups in the pore surface *via* hydrogen bonding or ionic interactions⁴⁶ that promote the degradation of the photochromic molecules.⁴²

The photodegradation of the dye molecules in the hybrid matrices was reduced by a factor of 9 in phenyl modified matrices as compared to that in an unmodified silica matrix, with $t_{1/2}$ (deg) values (the time required for half of the molecules to be degraded by irradiation with UV light) of 181 and 21 h, respectively. The degradation half-times have been calculated taking into account the intensity of the absorption band of the samples during irradiation with UV light.

Photochromic dye loading in the matrix

The dye loading in the matrix also has an important effect on photodegradation of the photochromic films. Fig. 20 shows the photodegradation of the naphthopyran dye embedded in phenyl modified matrices as a function of the dye/Si molar ratio (from 0.005 to 0.035). An increase in the relative amount of dye in the hybrid matrix enhances the photostability of the photochromic molecules, as it diminishes the interaction of the dye with the pore surface (hydrogen bonding or ionic interactions). Large amounts of dye in the pores can also lead to the screening of the UV light, responsible for its degradation, by the dye molecules themselves.⁴⁷

The ability to obtain photochromic films with high dye loadings is of great importance from the point of view of possible applications, as it allows the obtainment of films that develop a deep colouration upon irradiation with UV light, enhancing at the same time the photostability of the dye.

4. Applications of photochromic hybrid materials

In 1956, Hirshberg⁴⁸ demonstrated that photochromic dyes can be applied to optical information storage. This initiated

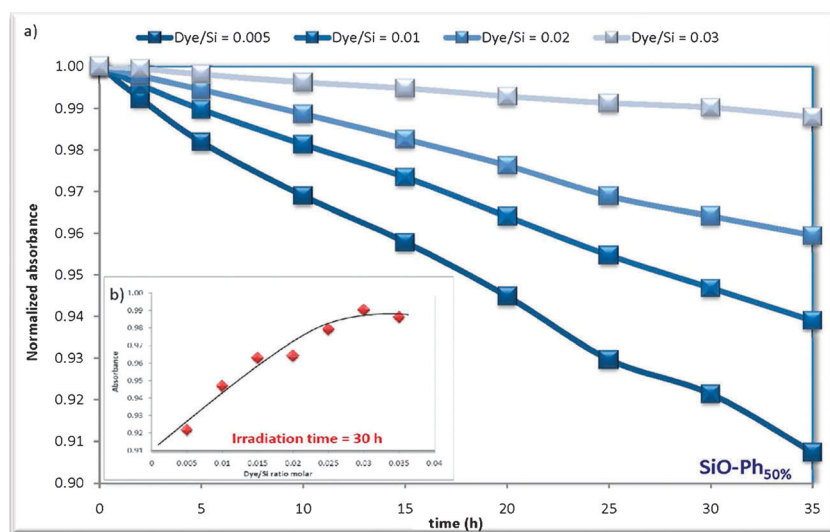


Fig. 20 (a) Effect of the dye loading on the photodegradation of the photochromic naphthopyran molecules embedded in a phenyl modified matrix (SiO-Ph_{50%}); (b) absorbance of the dye molecules as a function of dye/Si molar ratio after 30 h of UV irradiation.

widespread research on photochromic dyes, extending their applications from optical memory media to coatings for windows, photochromic decorations, optical switches, filters, *etc.* In this section different examples of applications of photochromic hybrid materials will be illustrated.

The interest in photochromic materials arises from the many potential applications a scientist can imagine for a reversible photosensitive material. Photochromic hybrid materials can find application as photochromic decorations,¹³ variable optical transmission materials,⁴⁹ UV sensors, waveguide/fibre-optics optical delay generators,⁵⁰ optical memory devices,⁵¹ holographic recording media,⁵² non-linear optics,^{53a} *etc.* The applications of photochromic materials extend from simple changes in colour to more sophisticated applications involving changes in refractive index, solubility, viscosity, surface wettability or dielectric constants of the materials, which occur simultaneously with the colour change.

Variable optical transmission materials such as photochromic camera filters⁴⁹ or photochromic lenses used in sun protection glasses were, initially, made by impregnation of glass with inorganic compounds, mainly silver salts. In recent years organic photochromic lenses, being lighter and therefore, more comfortable, were also used.⁵⁴ When these lenses are exposed to UV light, they acquire a deep colour as shown in Fig. 21.

The change in colour of the photochromic materials upon irradiation with UV light can be used as a UV-radiation

sensor. This type of sensor can be incorporated in any item *e.g.* watches, credit cards or sunscreen bottle caps.⁵⁵ Spiropyran and spirooxazine dyes embedded in polymer matrices have been extensively used in the fabrication of UV sensors. Fig. 22 shows a photochromic solar card that can check the intensity of solar UV radiation. Sol-gel derived photochromic coatings⁵⁶ are a better choice as matrices for UV sensors, due to the higher stability of the matrix upon UV irradiation.²⁶ Less attention has been paid to the thermochromic properties of these hybrid materials, although they can be used as temperature sensors.^{57a} Some photochromic compounds such as naphthopyrans and spirooxazines show thermochromic properties, with the naphthopyrans as better photochromic but worse thermochromic compounds than spirooxazines.^{57b} Inorganic thermochromic compounds such as those based on copper and tungsten embedded in sol-gel matrices are being widely studied as temperature sensors.^{57c}

Photochromic hybrid materials have been applied to optical delay generators and waveguide/fibre-optics, allowing the control of the propagation times of the light signal. Fig. 23 shows a simple device consisting of two fibres connected by an adapter in which the photochromic material is deposited.⁵⁰ An Ar⁺ laser is connected to the fibre, however, the light is not transmitted to the second fibre until the photochromic

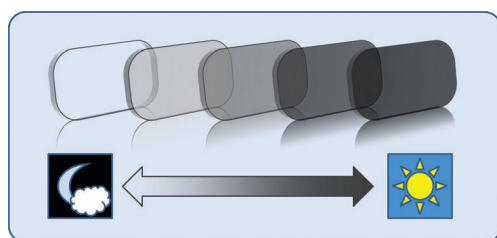


Fig. 21 The color of the lens changes from clear, when indoors or at night, to dark when exposed to sunlight.

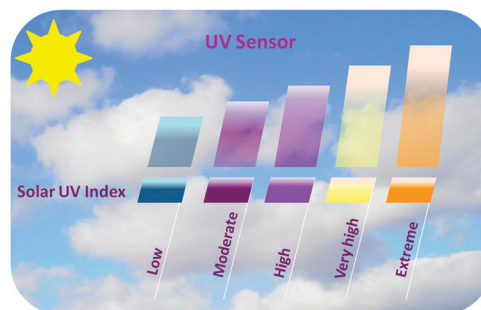


Fig. 22 Sensor of solar UV radiation.

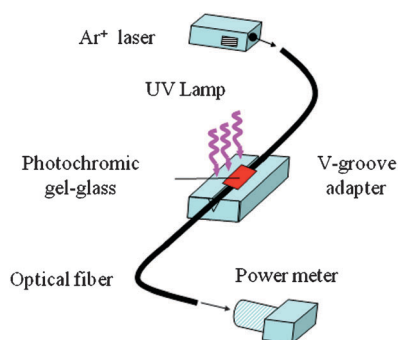


Fig. 23 Scheme of a device of photochromic optical fibres.

gel-glass is bleached by the laser light itself, producing a waveguide through the photochromic material.

The use of spiropyrans, diarylethenes, fulgides and azobenzenes has recently attracted significant attention from both the fundamental and practical points of view due to their potential applications as optical memory devices and switches.⁵⁸ Diarylethene derivatives are the most promising candidates because of their notable irreversible thermal photochromic behaviour, high photoisomerization quantum yields and outstanding fatigue resistance.⁵⁹ For practical applications in high density data storage systems, nondestructive readout capability is indispensable. Recently, we have reported a novel photochromic hybrid coating with a remarkable long-term stability of both the coloured and colourless states in the dark (bistability).⁶⁰ The coatings consist of a dispersion of a commercial spirooxazine in a functionalized sol-gel hybrid matrix that acquires a deep purple colouration upon irradiation

with UV light. The reversible colouration–bleaching process can only be achieved by irradiating the coatings with UV and visible light, respectively. This reversibility of the recording–erasing process of the photochromic coatings makes possible their use as optical data recording media as shown in Fig. 24a. In order to show the feasibility of recording optical data in the coating, a colourless photochromic sample was irradiated through a mask using UV light. The initials of the Instituto de Ciencia de Materiales de Madrid (ICMM) can be clearly seen in Fig. 24b. The recorded data can be erased by irradiation with either UV or Vis light, obtaining a fully coloured or fully bleached sample. The fatigue resistance of the coatings was tested by performing recording–erasing cycles showing no significant loss in colour for at least seven cycles (Fig. 24c).

The hybrid silica-based organic–inorganic materials functionalized by photochromic molecules showed encouraging perspectives for holographic application due to the high optical quality of the silica matrices and the photochromic properties of the dye. Materials based on photochromic azobenzene and spirooxazine dyes embedded in hybrids matrices were used as reversible holographic recording media. A diffraction grating was recorded by the light interference of two coherent laser beams converging on the photochromic film.⁵²

Photochromic non-linear optical materials have been widely used in optical limiters, which reduce the transmittance at high intensities above the threshold level.^{53b} The non-linear characteristics of these devices depend on the composition of the photochromic materials and intensity of irradiation.⁵³

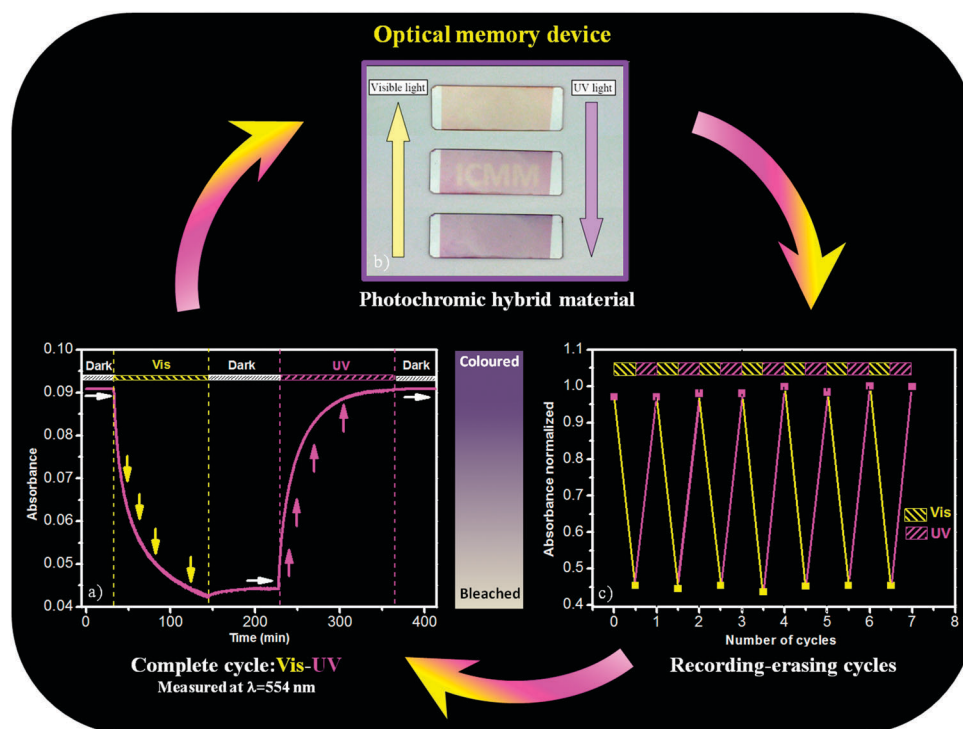


Fig. 24 (a) Full recording–erasing processes in a photochromic organic–inorganic hybrid coating by alternating UV and visible light irradiation, (b) recording–erasing processes through a mask and (c) fatigue resistance tested by performing recording–erasing cycles.

Photochromic hybrid materials can also have applications in the photo-modulation of properties, such as solubility, aggregation or optoelectronic properties.^{14,28} Among the different dyes, the azobenzene derivatives show a particular interest due to their ability to reversibly undergo a *trans-cis-trans* isomerization, which is accompanied with strong changes in the dielectric properties such as: molecular dipole moment, refractive index and permittivity, all being relevant to practical optoelectronic applications.⁶¹ A very interesting application is the use of these hybrid materials in textiles. A hybrid silica sol-gel doped with a photochromic dye can be applied to wool fabric to form a photochromic coating showing a very quick photochromic response.^{62a,b} The hybrid materials can be also used in cosmetics for hair colouration or make-up products, mainly as foundation.^{62c}

In recent years, the use of photochromic organic-inorganic materials in both science and industry has increased, due to their characteristic colour change and the high versatility of their physical and chemical properties, compositions and processing techniques, which offers a wide range of possibilities to fabricate tailor-made photochromic materials.

5. Conclusions

The possibility to combine organic and inorganic components in a single material represents a great advance in materials science, as it permits the design of materials with the advantages of both the organic and inorganic constituents and confers new properties upon the material, different from those of the single components. The extremely versatile properties and processing of organic-inorganic hybrids offer a wide range of possibilities for the design of materials with defined properties. There is a growing interest in these materials owing to their potential application in many areas, such as optics, electronics or mechanics.

The sol-gel method is a very useful tool for preparing organic-inorganic matrices at a low temperature, in which photochromic organic molecules can be incorporated. The properties of these photochromic molecules embedded in the porosity of the hybrid matrices can be controlled by the composition of the host matrix. The nature and amount of the organic functional groups incorporated in the network of the matrices, as well as the parameters of the sol-gel processing, affect the size and shape of the pores and the chemical composition of their surface, and determine the polarity of the inner surface of the pores, where the photochromic molecules will be located. Therefore, it provides a way of controlling the photochromic properties of the molecules in coatings and hence, their absorption spectra and the bleaching kinetics, which are greatly affected by the polarity of the environment.

The photostability of the photochromic molecules embedded in a hybrid matrix upon prolonged exposition to UV light depends strongly on the nature of the embedding matrix. The introduction of organic functional groups into the inner pore surface of the matrix affects the stability of the molecules, in terms of the effectiveness of the interaction between the photochromic molecules and the surface of the

pores and can be used as an important tool to increase the photostability of the photochromic dye in a device.

The usage of hybrid host matrices represents the most interesting alternative to prepare photochromic materials, as it allows the control of the photochromic properties and the photostability of the dye molecules by adjusting the chemical composition of the embedding matrix and the sol-gel preparation and processing parameters.

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