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Sol–gel silicate thin films bearing attached pyrene fluorescing probes hidden from oxygen but still accessible to organic electron transfer quenchers

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Abstract

Acid or base catalysts were used to prepare sol–gel thin films of silica (AF and BF respectively) doped with a pyrene fluorescent probe covalently attached to the silica network. The polarity of the matrix was found to change according to the catalyst used. Fluorescence quenching of the excited states of the pyrene monomer by electron donors and acceptors enabled us to evaluate the accessibility of the probing dopant. A model considering the possibility of two different dopant sites is proposed for the understanding of the fluorescence quenching data. A fraction of the fluorophore is freely accessible and may be quenched, while the rest remains unquenched due, for instance, to a too deep entrapment in the silica network. The pyrene dopant was found to be almost insensitive to oxygen quenching. A tentative explanation of this peculiar protection versus oxygen is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electron transfer; Fluorescence spectroscopy; Sol–gel processes; Thin films; Oxygen

1. Introduction

In recent years, the photophysics and photochemistry of organic molecules adsorbed on the surface of silica gel has been investigated in depth [1–5]. More recently, photosensitizers grafted on silica beads were used [6–8] and this method was used to open a way to heterogeneous and solar photosensitized dechlorination of chloroaromatics [9]. A grafted sensitizer is possibly more efficient than the corresponding molecule used in homogeneous phase and its efficiency was found to be modulated by the derivatization or by the organization of the silica surface [9,10].

Silica supports synthesized by the sol–gel technique are now finding numerous potential applications and doped inorganic glasses [11] in various shapes like monoliths, films, fibers or powders [12] may be prepared using this technique. Various metal oxide precursors may be used but silica offers, among other advantages good chemical properties, rigidity and negligible swelling in liquids, a sufficient chemical inertness, a high photochemical and thermal stability and good optical properties like transparency in the visible and near UV regions. Entrapment of dopants in the sol–gel glasses has been widely used essentially in order to probe the sol–gel medium itself [13–15]. Other interests involve the design of sensors, luminescent and photochromic materials [16], supported catalysts for thermal reactions [17–19], etc.

There are relatively few examples of grafted compounds in sol–gel glasses. These ones have been prepared namely to obtain materials with non-linear optical properties [20,21] or to characterise sol–gel glasses. The rigidity of the matrix has been studied by Ueda et al. [22,23] with sol–gel silica thin films containing trapped and grafted azobenzene derivatives. One example of a covalently linked pyrene derivative was reported by M.A. Fox et al. [24] in a study of sol–gel films and glasses. The mobility of the covalently attached chromophore was shown to be very similar to one of the trapped molecule. The emission anisotropies for glassy films containing trapped or grafted pyrene derivatives are virtually identical.

To our knowledge, the photochemical reactivity of sensitizers in a sol–gel matrix was only reported by two groups [25–27]. In both cases, transition metal complexes of ruthenium and iridium trapped in the matrix were concerned and electron transfers were observed between adsorbed solute molecules and a photosensitizer embedded in the glass. Our present paper is devoted to the study of the properties of a

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photoactive molecule covalently grafted in sol–gel matrix. The chosen probe is a pyrene derivative (Pyr2, see Scheme 1) examined as a molecule playing the role of a potential sensitizer or of a sensor: the photochemical behaviour of the films is studied by fluorescence quenching experiments with electron donors and acceptors. The influence of the catalysis used in the sol–gel preparation of the films on the photophysical and photochemical properties of the grafted molecules is discussed.

2. Experimental details

2.1. Synthesis

Reagents were obtained from Aldrich and used without further purification. A magnetically stirred mixture of 1-pyrenemethanol (2.9 g, 1 eq.) and isocyanate (1.3 ml for Pyr1 or 3.4 ml for Pyr2, 1.1 eq.) dissolved in dry pyridine (25 ml), was heated at 50–60°C during 18 h. After reaction, the solvent was evaporated under vacuum and the crude product was recrystallized in hexane-dichloromethane to afford the desired compound. Yields were 90% (Pyr1) and 82% (Pyr2).

Characterizations: *Pyr1*: m.p.: 140°C. Mass spectrum (EI 70 eV, *m/z*): 317.1 ($M^{\circ+}$), 232.1, 215.1 ($pyrCH_2^{\circ+}$). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ(ppm) 0.9 (t, 3H, CH_3), 1.5 (m, 2H, CH_2), 3.2 (m, 2H, CH_2), 4.8 (broad s, 1H, NH), 5.8 (s, 2H, CH_2), 8.0–8.4 (m, 9H, Ar). IR (cm^{-1}): 1684 (C=O), 3325 (NH).

Pyr2: m.p.: 116°C. Mass spectrum (EI 70 eV, *m/z*): 479.2 ($M^{\circ+}$), 433.1, 232.1, 215.0 ($pyrCH_2^{\circ+}$). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ(ppm) 0.7 (t, 2H, CH_2-Si-), 1.2 (t, 3H, CH_3), 1.6 (m, 2H, CH_2), 3.3 (m, 2H, N-CH_2-), 3.9 (q, 6H, O-CH_2-), 5.0 (broad s, 1H, NH), 5.8 (s, 2H, Ar-CH_2-O-), 8.0–8.4 (m, 9H, Ar). IR (cm^{-1}): 1080 (Si–O), 1684 (C=O), 3302 (NH).

2.2. Glass support preparation

Standard microscope glass slides (Vel) were used and quartz plates were chosen in the case of fluorescence lifetime measurements. A good homogeneous wetting of the surface was obtained after careful cleaning: a 15 min sonication in 1% RBS-X20 detergent solution was followed by rinsing with demineralized water. The slides were then kept 24 h in 6 N NaOH or in the so-called ‘piranha’ solution ($H_2O_2 : H_2SO_4$, 1:5) [28]. After a new thoroughly rinsing with demineralized water, the plates were dried in an oven at 110°C and stored in a desiccator.

2.3. Thin film preparations

The following starting solution was used: Triton-X100 (Aldrich, 1.5 g), Pyr2 (0.026 or 0.131 g), ethanol (Fluka abs, 42.5 ml) tetramethyl orthosilicate (TMOS) (Aldrich 99+%, 5 ml) and 0.01 N hydrochloric acid or sodium hydroxide (2.5 ml). According to the initial high or low concentration of Pyr2 and to the acidic or basic catalysis used the silica films will be denoted as AF_{high}, AF_{low}, or BF_{low}, respectively. The solution was allowed to stand several hours at room temperature under magnetic stirring and the slides were coated. The solution filtered over 0.5 µm Millipore filter was poured onto the support and spin-coated for 90 s at 1000 rpm. The coated slides were kept 1 h at room temperature and then overnight at 110°C in an oven under nitrogen atmosphere. After drying, the coated slides were stored in a desiccator. The film thickness has been estimated to a mean value of 0.55 and 0.40 ± 0.05 µm for AF and BF respectively by measurement with a DEKTAK profilometer.

2.4. Spectroscopic measurements

SLM Aminco DW2000 or a Varian Cary 5E spectrophotometer was used for the absorbance spectra and the SLM Aminco 48000S spectrofluorimeter equipped with a front-face system was used for the fluorescence measurements performed on films in open air. Solutions in milliQ water or HPLC grade (Rathburn) acetonitrile and methanol were used in the fluorescence quenching experiments performed on films dipped in these solutions. Fluorescence lifetime were measured by phase-fluorimetry in the laboratory of B. Valeur [29] using a CW He/Cd laser (325 nm) as excitation source and a POPOP solution as reference.

2.5. Grafting of silica beads

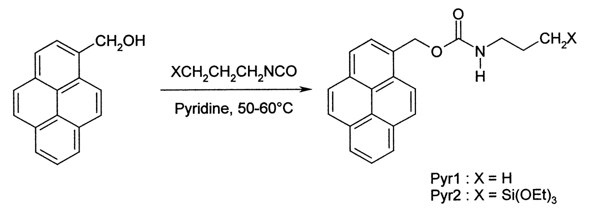
Silica gel (Aldrich 40,360-1) dried under vacuum at 60°C for 12H00 was suspended in anhydrous dimethylformamide with Pyr2. After stirring at 110°C during 24H00, the grafted silica is separated, washed in a Soxhlet with dichlorometane, methanol, diethyl ether and dried under vacuum at 80°C.

3. Results and discussion

3.1. Synthesis and film preparation

A Pyr2 compound which can be covalently grafted in silica film has been obtained by reacting 1-pyrenemethanol with 3-(triethoxysilyl)propyl isocyanate in dry pyridine. This way to get a graftable dopant is attractive: no by-product is formed during the carbamate synthesis and this functional group is not expected to interfere with the sol–gel process. A model compound, Pyr1, has also been synthesized by the same way, using propyl isocyanate (Scheme 1).

Films incorporating the Pyr2 compound were prepared by the copolymerization of Pyr2 with a tetramethoxysilane monomer. Films were prepared with a high or low concentration of incorporated Pyr2 and with an acid or a base as catalyst since it is known that the nature of the catalyst influences the porosity of the matrix [30,31]. The following



Scheme 1.

acronyms will be used: AF_{high} of AF_{low} for acid catalyzed films with high or low Pyr2 concentrations respectively. Base catalyzed films (BF_{low}) were prepared at low concentration only.

3.2. Spectral characterization

The model compound Pyr1 derivative was used to characterize the fluorophore in homogeneous solution. The absorbance spectra of Pyr1 in methanol solution and of dry AF_{low} and AF_{high} containing Pyr2 are reported in Fig. 1. The absorbance of the doped films are low (≤ 0.06 for AF_{low} and 0.3 for AF_{high}). In the accessible wavelength domain (≥ 300 nm, the glass supports absorb light at higher energy), a slight red shift (ca. 5 nm) is observed when comparing the Pyr2 grafted films with Pyr1 in methanol homogeneous solutions. On the basis of the absorption spectra, film thickness and extinction coefficients measured in methanol, the concentration of the pyrenic dopant in the film can be roughly estimated at ca. 0.03 and 0.15 M for AF_{low} and AF_{high} respectively and this corresponds quite well to the ratio of the Pyr2 concentrations used in the film preparations. In a similar way, BF_{low} films gave absorbances in the expected range.

The excitation and emission spectra of Pyr1 in methanol solution and of an AF_{low} grafted film are shown in Figs. 2 and 3. No difference is found in AF_{high}. At low concentration in methanol, the emission spectrum of Pyr1 only shows the monomeric vibronically structured emission, showing maxima at 376, 387, 395 and a shoulder at 413 nm. Within the experimental errors (±1 nm) similar maxima are observed for the films. Comparing to pyrene itself, substitution induces a decrease of symmetry accompanied by a loss of fine structure in the emission. For Pyr1 and the film only three bands and a red shoulder can be distinguished, as compared to five bands and the shoulder for unsubstituted pyrene. For the ease of comparison, the three bands will be labelled I_1, I_3 and I_5 as in pyrene. It has been shown that the relative intensities of the vibronic bands are very sensitive to the polarity of the pyrene local surrounding [32,33]. The intensities of these bands for Pyr1 in protic solvents and for the films are reported in Table 1.

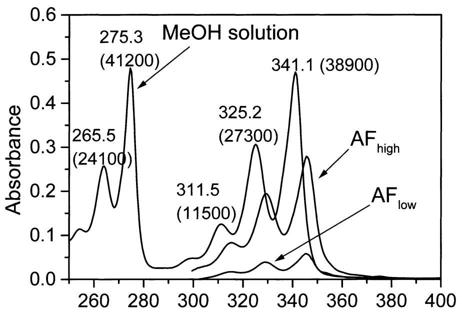


Fig. 1. Absorption spectra of Pyr1 in methanol solution and AF. Extinction coefficients are given between brackets in $M^{-1}\,cm^{-1}$.

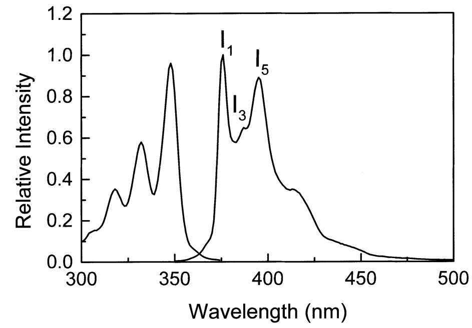


Fig. 2. Normalized excitation ($\lambda_{em} = 376$ nm) and emission ($\lambda_{exc} = 325$ nm) spectra of Pyr1 in methanol.

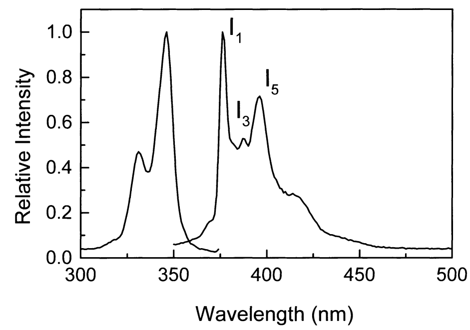


Fig. 3. Normalized excitation ($\lambda_{em} = 376$ nm) and emission ($\lambda_{exc} = 325$ nm) spectra of dry AF_{low}.

As far as ratios of intensities are considered, Table 1 clearly reveals a very high polarity of the sol–gel silica surface for AF: this may be explained by the interactions of Pyr2 with the surface made of silanol groups with chemisorbed water molecules. Such interactions between the silica surface and a dopant have been previously reported for pyrene and pyrenecarboxaldehyde trapped in TEOS (tetraethyl orthosilicate) sol–gel matrix [34]. Depending on the matrix preparation conditions they have estimated a dielectric constant between 65 and 87 for the dry matrix. In the case reported here, a still higher value may be estimated since the ratio I_3/I_1 is 0.57 for formamide ($\varepsilon = 109.5$) and 0.50 for the dry AF. We believe that it is more realistic to consider this very high value of the surface polarity as the result of specific interactions between the silanols and the grafted Pyr2 instead to discuss it in terms of a bulk dielectric constant. A silanol-rich silica surface is expected in our films since, with a drying process which was done at only 110°C,

Table 1
Pyrenic probe monomer vibronically structured fluorescence: relative peak intensities[a]

Solvent or medium	I_1	I_3	I_5
Pyr1 in solvents[b]			
1-Butanol (17.1)	1.0	0.74	0.97
Ethanol (24.3)	1.0	0.68	0.91
Methanol (32.6)	1.0	0.70	0.90
Formamide (109.5)	1.0	0.57	0.82
Pyr2 in dry films[c]			
AF_{low}	1.0	0.50	0.70
AF_{high}	1.0	0.50	0.70
BF_{low}	1.0	0.77	1.05
Pyr2 in films dipped in solvents			
AF_{low} in water	1.0	0.57	0.79
AF_{low} in acetonitrile	1.0	0.60	0.85
BF_{low} in water	1.0	0.66	0.94
BF_{low} in acetonitrile	1.0	0.61	0.82

[a] Excitation wavelength 325 nm.
[b] Solvent dielectric constant in brackets.
[c] Dry films in open air.

the dehydration of silanols giving siloxanes is not supposed to take place. Upon dipping the films in water or in acetonitrile, the ratio of the observed relative intensities of the vibronic bands changes indicating a decrease in the number of Pyr2–silanols interactions due to the presence of solvent in the pore network.

Surprisingly, BF_{low} display a vibronic bands ratio corresponding to a lower polarity medium (less polar than 1-butanol). It is known that a basic catalysis produces a more open matrix with larger pores [30,31]. In our BF_{low}, the structure of the matrix must be different since the bound pyrene molecules seem to have almost no interaction with silanol groups. It is possible that the difference between BF_{low} and AF is not only porosity but also silanol density or the presence of residual alkoxy silyl groups (in BF_{low}). Residual protonated silanols in AF or silanolates in BF_{low} may also change the surface properties. This last hypothesis has been checked by dipping the films in demineralized water in order to dilute at least partially the possible residual acidity or basicity. After drying at 110°C, the fluorescence spectra of both kind of films remained unchanged when compared to spectra recorded before the water rinsing.

No excimer emission was shown in the films in spite of a high pyrene derivative concentration. On the other hand, Pyr1 presents a strong broad excimeric band centered around 483 nm when the concentration is high (5 mM for instance in methanol). As indicated previously the dopant concentration in the films is significantly higher than 5 mM. This means that in the film the dopant molecules are well immobilized and separated by the matrix network even at these relatively high concentrations.

3.3. Fluorescence lifetime and oxygen effect

Fluorescence lifetime of Pyr1 has been measured by phase fluorometry in two solvents. The results are presented in Table 2.

The strong oxygen effect observed on the τ_1 fluorescence decay time has been confirmed by steady-state measurements: a ratio of 14.5 has been observed between the fluorescence quantum yield of Pyr1 in CH_3CN and in degassed CH_3CN after argon bubbling for 25 min.

The fluorescence lifetime of the grafted films has also been measured by phase fluorometry. The results are reported in Table 3. The experimental data were treated by least-square analysis using only the phase data or by the entropy maximisation method [35] giving the same results

Table 2
Fluorescence lifetime of Pyr1[a]

Solvent	α_1	τ_1 (ns)	α_2	τ_2 (ns)	χ^2
CH_3OH	0.99 ± 0.001	17.6 ± 0.1	0.01	3.0 ± 0.3	1.22
CH_3CN	0.99 ± 0.001	16.2 ± 0.1	0.01	2.2 ± 0.3	0.98
CH_3CN-Ar[b]	0.99 ± 0.01	255.4 ± 4.3	0.01	(4)[c]	1.81

[a] Excitation at 325 nm, observation through a Schott cut-off filter (GG375).
[b] Solution degassed by argon bubbling.
[c] Poorly resolved.

Table 3
Fluorescence lifetime of the grafted films[a]

	α_1	τ_1 (ns)	α_2	τ_2 (ns)	χ^{2b}
AF_{low}	0.96 ± 0.003	217.5 ± 3.5	0.04	21.7 ± 1.8	1.36
AF_{low} in MeCN	0.93 ± 0.004	200.6 ± 3.2	0.07	20.0 ± 1.8	0.96
AF_{low} in H_2O	0.93 ± 0.002	204.9 ± 5.3	0.07	16.7 ± 1.0	1.42
BF_{low}	0.82 ± 0.004	117.0 ± 3.6	0.18	4.6 ± 0.3	1.88

[a] Excitation 325 nm, observation through a Schott cut-off filter (GG375).
[b] From least-square analysis.

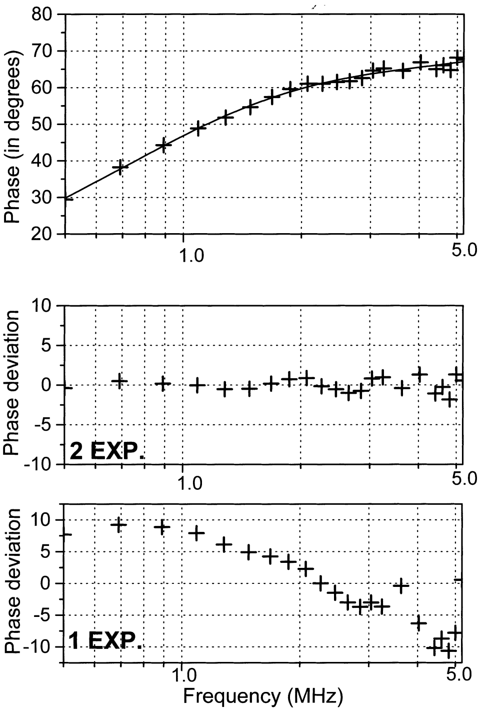


Fig. 4. Phase data for AF_{low} dipped in CH_3CN. Excitation at 325 nm. The solid line correspond to the best fit with a biexponential decay. Weighted residuals are shown for the best fit with one and two exponentials.

within experimental errors. An example of data treatment is given in Fig. 4. Some photobleaching has been observed during the measurements but control experiments showed that the modulation is more affected than the phase and that no fluorescent species is formed during the degradation. Narang et al. suggested to only use phase data for excited-state decay determinations since they are less affected than the modulation data by the 'spatial heterogeneity' between the sample, a thin film on quartz, and the reference used in the measurements, a solution in a fluorescence cell [15].

The observed decays are always biexponential with a major long component of ca. 200 ns for AF and 117 ns for BF_{low}. These values are on the same order of magnitude than the lifetime obtained for the Pyr1 model compound in *degassed* acetonitrile. The film measurements were done without any degassing and the bound pyrene thus seems to be protected against oxygen quenching by the silica sol–gel film. In the case of BF_{low}, the main lifetime (117 ns) is shorter than for AF and some sensitivity to the oxygen seems to be recovered in this case. The oxygen effect was also tested on the steady-state fluorescence of these films. The fluorescence intensity of a film dipped in acetonitrile increased by a factor of ca. 1.5 in the case of AF and ca. 2.6 for BF_{low} after degassing the surrounding solvent by N_2 bubbling for 30 min. These values have to be compared with the 14.5 ratio obtained for Pyr1 in MeCN.

An oxygen shielding was already reported by Avnir et al. in the case of room temperature phosphorescence observed with various trapped aromatics and namely with pyrene helped by the presence of heavy atoms [36,37]. A matrix polarity effect on the luminescence quenching by oxygen has been recently observed by McCraith et al. in the case of an oxygen sensor based on Ruthenium complexes entrapped in sol–gel silica thin films [38,39]. A low sensitivity to oxygen dissolved in water has been observed for tetraethoxysilane (TEOS) films and a much larger sensitivity was obtained with methyltriethoxysilane (MTEOS) films having a lower polarity. In the case reported here, the films were prepared with TMOS giving in principle a more polar matrix than when using TEOS. Our results can be compared to the McCraith observations: AF display a very high polarity and seem to almost completely protect bound pyrene against oxygen. On the opposite, BF_{low} films seem less polar and somewhat less efficient in protecting the dopant against oxygen quenching.

As far as the dry films are concerned, the fluorescence intensity of AF and BF_{low} do not change when going from ambient air to N_2 atmosphere. The total lack of effect in this case compared to a weak effect when dipped in a solvent seems to show that gaseous exchange between outer atmosphere and inner pores is not efficient. All of these results clearly indicate that the bound pyrene molecules are isolated from oxygen, especially in the more polar matrix.

Photoinduced electron transfer from excited pyrene adsorbed on a silica gel surface has been observed [40] showing that the silica surface normally does not shield adsorbed molecules from oxygen quenching. Our observation in silica sol–gel films may well be somewhat particular: photooxidations of tethered dianthryl compounds embedded in sol–gel silica films was postulated by Ueda et al. If their interpretation is correct this shows that the sol–gel silica matrices do not provide significant protection against oxidation [41]. However, the presence of oxidized products cannot be demonstrated as in homogeneous solution, and their conditions to prepare the films (dip-coating, no added surfactant...) are different from our conditions. While remaining cautious in interpreting Ueda's results, we have also to take into account that the nature of the matrix surface might be rather different due to the preparation conditions: at this stage of the knowledge, general rules cannot be given.

3.4. Fluorescence quenching

Fluorescence quenching measurements with electron donors and acceptors have been performed in order to study the accessibility and the possible photochemical reactivity of a fluorophore grafted in a silica thin film. In comparison, similar measurements were done in homogeneous solution with Pyr1. The results are reported in Table 4.

In homogeneous solution, the classical Stern–Volmer relationship (Eq. (1)) is the standard way to treat fluorescence quenching

$$\frac{I^0}{I} = 1 + K_{SV}[Q] \qquad (1)$$

Table 4
Fluorescence quenching measurements of Pyr1 in homogeneous solution[a]

Quencher	K_{SV} (M^{-1})	K_q 10^{-9} M^{-1} s^{-1}[b]
MV^{++}	280.70 ± 13.4	16.0
Halothane	0.79 ± 0.02	0.05
o-Dicyanobenzene	192.04 ± 3.67	11.9
Tributylamine	131.12 ± 2.69	8.1
N-ethyldicyclohexylamine	198.54 ± 2.83	12.3
N,*N*-dimethylaniline	277.66 ± 10.54	17.2

[a] All experiments have been done in MeCN except for MV^{++} in MeOH.
[b] K_q calculated with $\tau = 17.6$ ns in MEOH and 16.2 ns in MECN.

I^0 and I are the fluorescence intensities in the absence and presence of quencher (Q) and K_{SV} is the so-called Stern–Volmer constant which is the product of the specific quenching rate constant (k_q) and of the fluorophore excited state lifetime, τ. In all cases presented in Table 4, the rate constants obtained using this equation are close to the diffusion (except when halothane is the quencher).

With the supported system, the quenching no longer follows the linear Stern–Volmer relationship: examples are reported in Fig. 5. A model has been proposed by Carraway et al. in 1991 [42,43] for the quenching of luminescent species adsorbed or bound to heterogeneous supports (silicas, inorganic, organic and biopolymers). This model assumes that the fluorophore is present under two forms as for instance a molecular and evenly distributed form on one hand and something like an aggregated form on the other hand. It may be reasonable to assume that the two forms have different decay times and or quenching constants. This model leads to Eq. (2). In this equation, f_1 and f_2 are relative weighting factors.

$$\frac{I}{I^0} = \frac{f_1}{1 + K_{SV1}[Q]} + \frac{f_2}{1 + K_{SV2}[Q]} \tag{2}$$

As can be seen in Fig. 5, the quenching seems to reach a plateau and fittings using this model leads to weak or close to zero K_{SV2} values. The quality of the fit is still better if this value is set at zero: this corresponds to a system in which two different location sites are considered for the dopant in the matrix with the first one easily accessible to the quencher while the second one, being for instance too deeply entrapped cannot be reached by the quencher. The results obtained when using this assumption are shown in Table 5 and Fig. 5 shows the fitted results obtained with an electron donating and an electron accepting quencher.

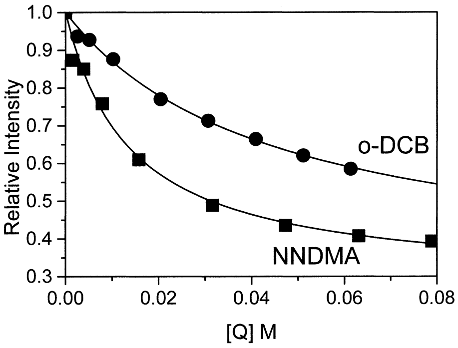


Fig. 5. Fluorescence quenching of ASF_{low} in CH_3CN by *N*,*N*-dimethylaniline (NDMA) and *o*-dicyanobenzene (*o*-DCB). The solid lines correspond to the best fit obtained with Eq. (2) and $K_{SV2} = 0$.

In a previous paper, we have presented results concerning a halogen anions sensor [44], *N*-dodecyl 6-methoxyquinolinium entrapped (and not covalently grafted) in sol–gel silica thin film. The leaching problem was solved in that case by an hydrophobic entrapment. The same model was tested and two sites were shown to be accessible, the Eq. (2) with K_{SV2} different from zero giving a significantly better fit of the results. The difference between both cases is probably related to the chosen fluorophores and to the nature of the quenchers. The quinolinium dopant with its polar charged heteroaromatic head and its long alkyl apolar tail favours aggregation if not micellization, which is not the case of our pyrene derivative. On the other hand, an halogen anion is expected to diffuse more freely in the silica matrix than the organic quenchers used in this study. Finally, the absence of excimeric emission for the films doped with bound pyrene derivative is an additional argument against a model with a distribution between evenly dispersed and aggregated molecules.

Since the fluorescence quenching experiments may be influenced by the catalyst used to prepare the films, measurements performed on BF_{low} are also shown in Table 5.

Table 5
Fitting results with Eq. (2)

Quencher[a]	Film	f_1[b]	K_{SV1}	χ^2
Methyl viologen	AF_{low}	0.62 ± 0.02	1642.03 ± 210.72	0.00046
Halothane	AF_{low}	0.70 ± 0.01	14.13 ± 0.72	0.00011
o-Dicyanobenzene	AF_{low}	0.71 ± 0.03	22.37 ± 1.86	0.00010
o-Dicyanobenzene	BF_{low}	0.92 ± 0.01	92.60 ± 2.40	0.00006
Tributylamine	AF_{low}	0.70 ± 0.07	23.96 ± 4.35	0.00073
N-Ethyldicyclohexylamine	AF_{low}	0.63 ± 0.02	64.55 ± 7.2	0.00039
N,*N*-Dimethylaniline	AF_{low}	0.72 ± 0.03	73.76 ± 9.0	0.00049
N,*N*-Dimethylaniline	BF_{low}	0.84 ± 0.01	145.19 ± 5.06	0.00005

[a] All experiments in MeCN except for MV^{++} in water.
[b] f_2 set as $(1 - f_1)$ and K_{SV2} fixed at zero.

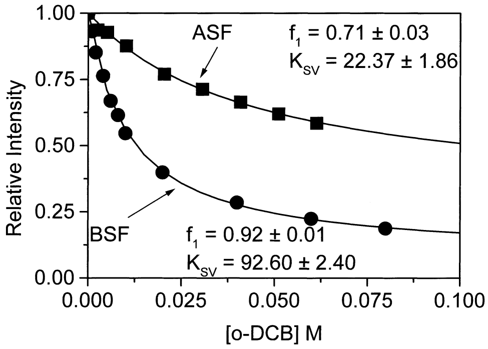


Fig. 6. Fluorescence quenching of ASF_{low} and BF_{low} by *o*-dicyanobenzene in MeCN. Solid lines correspond to the best fit obtained with Eq. (2) and $K_{SV2}=0$.

Here also the results support the model with two sites among which one is not accessible. The Fig. 6 display the difference of reactivity between AF_{low} and BF_{low} for the same *o*-dicyanobenzene quencher. Compared to AF_{low}, higher f_1 and K_{SV} are obtained. This is probably to be related to the lower density and larger pores of the matrix obtained with a basic catalyst. This known difference [30,31] confirms that our results are rather realistic and that this approach may be of great use in order to check the matrix properties.

The observed response rate for the fluorescence intensity decrease upon quencher addition was very rapid in all cases, lasting for a few seconds at maximum. An example of that response rate is given in Fig. 7. This means that the quenchers easily diffuse into the matrix to reach and to quench the fluorescence of the accessible dopant. As a bulky quencher like *N*-ethyldicyclo-hexylamine can also diffuse very rapidly, the porosity of the films must be high. We can, thus, suppose that the dopant molecules inaccessible to the quenchers are probably located in closed or ‘bottle-necked’ pores.

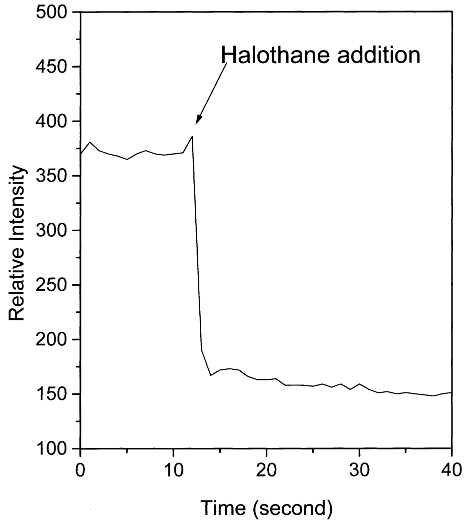


Fig. 7. Fluorescence response rate of ASF_{low} to a quencher addition.

3.5. *Pyrene accessibility to organic quenchers versus inaccessibility to oxygen*

Our results concerning the quenching of excited immobilized pyrene by organic donors or acceptors seem contradictory versus the insensitivity of the same excited pyrene to oxygen.

Hoping to find a reasonable hypothesis, other experiments were made on the fluorescence of excited pyrene covalently attached on the surface of silica beads. Grafted silica was prepared by reacting silica beads with the pyrene2 derivative in dimethylformamide and a weakly grafted silica (not more than 3 μmol/g of silica)[1] was used. Since grafting is in this case only at the surface we may expect an oxygen quenching behaviour closer to what is observed in homogeneous solution. When this modified silica powder was suspended in water solution (2 mg/3 ml) the fluorescence intensity ratio between degassed or not degassed water was 1.5. In an acetonitrile suspension, the ratio increases to 4 and this may well be the effect of oxygen higher solubility in the solvent. If a small amount of water (10 μl) is added to a 3 ml sample of the acetonitrile suspension, a significant decrease of the oxygen solubility in the solvent is not expected. However, the ratio decreases to 3.2 and this seems to confirm that water, adsorbing preferentially at the silica surface contributes heavily to the suppression of oxygen effect.

While recalling that the oxygen effect seems to be lower in the more polar films we may also remind that the oxygen solubility is almost ten times lower in water than in organic solvents. Knowing that perfect drying of silica is a difficult task, a residual film of chemisorbed water may expect to remain at the surface of sol–gel silica films. Such a film may be responsible for a drastic reduction of the oxygen concentration at the surface as well for a barrier slowing down the oxygen exchange between external air and the grafted molecules. This hypothesis will need further experiments.

4. Conclusion

The influence of the nature of the silica thin film matrix on the properties of a grafted photoactive compound is enlightend. The porosity of the matrix is affected by the catalyst of the polymerization, as already known. This is here correlated with a change in the quenching rate contants: the fluorescent grafted probe is more accessible in films prepared under base catalyzed conditions. The polarity of the film is also shown to be sensitive to the method of preparation.

The oxygen shielding of a dopant remaining widely accessible to external quenchers is, as far as we know, reported here at the first time. This peculiar behaviour may be explained by the thin water film adsorbed on the surface and reducing the oxygen local concentration as well

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[1] Detailed analysis of the grated silica will be published elsewhere

as by making a barrier to oxygen exchange between the surface and the exernal medium. This hypothesis merits great attention for future work since it may be of interest for the stability of photoprobes as well as for the intensity of their fluorescence and this may open the way for important developments in the field of supported photoactive molecules.

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