JOURNAL OF Materials CHEMISTRY

Fluorescence properties of benzoxazole type dyes entrapped in a silica matrix by the sol–gel method

Tania M. H. Costa,[a] **Valter Stefani,**[a] **Márcia R. Gallas,***[b] **Naira M. Balzaretti**[b] **and João A. H. da Jornada**[b,c]

[a]*Instituto de Química, UFRGS, CP 15003, 91501-970 Porto Alegre (RS), Brazil. Fax: (55) 51 3316-7304; Tel: (55) 51 3316-6279; E-mail: taniaha@ iq.ufrgs.br*
[b]*Instituto de Física, UFRGS, CP 15051, 91501-970 Porto Alegre (RS), Brazil. Fax: (55) 51 3316-7286; Tel: (55) 51 3316-6542; E-mail: marcia@ if.ufrgs.br*
[c]*INMETRO, Av. Nosa Senhora das Graças 50, CEP, 25250-020 Xerém (RJ), Brazil*

Received 20th March 2001, Accepted 26th June 2001
First published as an Advance Article on the web 1st October 2001

For the first time, the incorporation of 2,5-bis(benzoxazol-2′-yl)-4-methoxyphenol (BM) in a silica matrix by the sol–gel method has been accomplished, producing transparent and translucent monoliths with fluorescence properties. The intensity and wavelength range of the fluorescence bands F_1 (primary structures) and F_2 (proton-transferred forms) were extremely sensitive to the presence of solvents and to the dye concentration in the silica pores. The F_2 band was observed when the silica pores contained solvent; however, after the solvent evaporation, the interactions of the dye with the silica host hindered the proton-transfer reaction, eliminating the F_2 band and indicating the polar and acidic character of this host. Nevertheless, it was observed that the proton-transfer could be recovered after insertion of suitable solvents inside the matrix, like water, ethanol or DMF. Changes in the fluorescence spectra due to the use of different dye concentrations were observed when the monoliths were prepared with ethanol as solvent. During the aging process, the F_2 band persists at high dye concentrations, but it disappears for low dye concentrations. The high sensitivity of the proton-transfer reaction of this dye in a particular environment, where the solvent and the host play important roles, suggests the possible application of this dye as a photoprobe for this kind of system.

Introduction

2-(Hydroxyphen-2′-yl)benzoxazole and its derivatives have been studied due to their interesting spectroscopic and photophysical properties.[1–4] This kind of molecule shows fluorescent emission with a large Stokes shift that originates from an intramolecular proton-transfer reaction in the electronic excited state (ESIPT).[1,2] This phenomenon has widespread implications in the action of many lasing dyes, photostabilizers and in biology.[5] The basic process of ESIPT is shown in Fig. 1, where S_0 is the fundamental hydrogen bonded enol form.[6] The proton-transfer occurs from the lowest excited singlet state molecule S_1 to a phototautomer S'_1 in a subpicosecond time scale, even in a rigid medium and at temperatures as low as 4 K.[5] After the conversion to the ground state S'_0 the proton falls back to its original place, regenerating the fundamental form S_0. The difference between these absorbing and emitting molecular structures originates the large Stokes shift (near 200 nm).

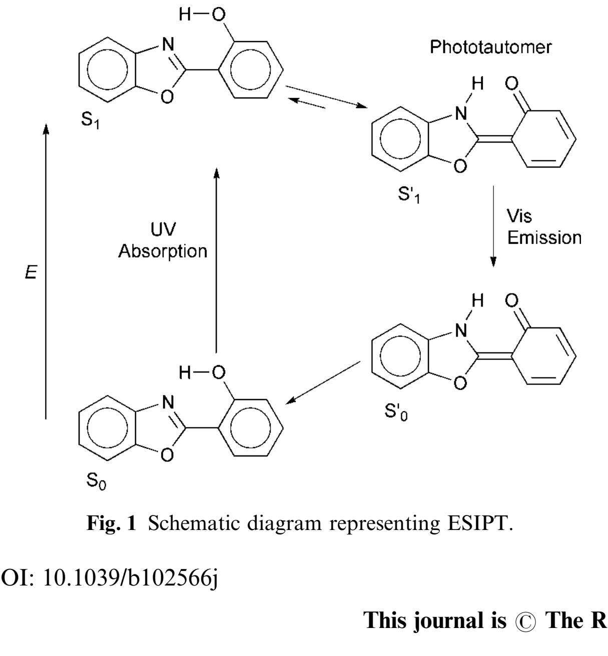

Fig. 1 Schematic diagram representing ESIPT.

Within the ensemble of benzoxazole type dyes, one important molecule is 2,5-bis(benzoxazol-2′-yl)-4-methoxyphenol (Fig. 2), due to its great photostability and very high quantum yield in fluorescence emission. This molecule exhibits dual luminescence, even in aprotic solvents. The first fluorescence band F_1 arises from the primary excited forms, which are related to a fraction of solvated molecules that is not able to undergo the proton-transfer reaction. The second band F_2 arises from the tautomeric forms, which are the proton-transferred forms.[1,2]

This molecule presents infrared spectroscopy evidence for very strong intramolecular H bond formation in the ground state and it is known that ESIPT occurs effectively along this H bond.[7,8] In general, the intramolecular reaction is influenced by specific H bonding solvation, which could create distinct conformers having different H bonded sites.[4] Therefore, apolar solvents do not influence the proton-transfer reaction, while polar (dimethylformamide, DMF) and mainly protic (ethanol)

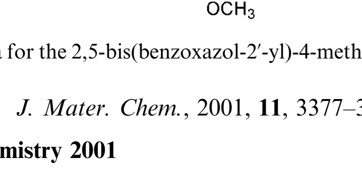

Fig. 2 Formula for the 2,5-bis(benzoxazol-2′-yl)-4-methoxyphenol dye.

solvents cause hindrance of intramolecular H bonding. Consequently the substitution of these bonds for intermolecular H bonds causes the increase of the intensity of the F_1 band and the reduction of the intensity of the F_2 band. Corrêa observed that the intensity of the F_1 emission increases with the increasing of the water content in water–dioxane (apolar) mixtures.[9] This behavior enables the use of this kind of molecule as a photoprobe of solvent polarity, of pore environment and of molecule matrix interactions in sol–gel and polymeric materials.[10]

Many spectroscopic techniques, such as NMR, FTIR and Raman, have been used to study the state of the bulk sol–gel material, however these methods are not able to provide detailed information about the local conditions around low-concentration dopants. Hence, methods of monitoring the microenvironments on the molecular scale that are sensitive to the low dopant concentrations used in these materials are needed. Fluorescence spectroscopy offers sensitive methods of reporting the local environment of the probe molecule.[10] Although the fluorescence of benzazole type dyes has been studied in matrices like polyethylene, polymethyl methacrylate, and polyvinylchloride, the fluorescence of these dyes in inorganic media has not yet been studied.[4,9,11]

The behavior of benzoxazole type dyes in the silica-gel matrix is not unexpected, but *a priori* knowledge of this behavior is difficult due to the very large number of variables.[2,6,9] Apart from the pure scientific interest, inorganic matrices are attractive also as a possible source of new optical materials, especially for lasing media. Therefore, there is great interest in the incorporation of these dyes in solid matrices like silica, which is transparent, mechanically resistant and can be prepared at room temperature using the sol–gel method.[12]

In this work is reported for the first time the incorporation of 2,5-bis(benzoxazol-2′-yl)-4-methoxyphenol in a silica-gel matrix, using the sol–gel method with ethanol and DMF solvents, using different dye concentrations. The effect of the silica matrix on the fluorescence of this dye was studied in order to verify the potential use of this kind of molecule as a probe for sol–gel materials and, furthermore, to develop novel materials for optics and photonics applications. In a subsequent paper, we will report the fluorescence properties of this system submitted to high pressure (4.5 GPa).

Experimental

Two dyes of the benzoxazole family were entrapped in the silica matrix: 2,5-bis(benzoxazol-2′-yl)-4-methoxyphenol (BM), which exhibits the proton-transfer reaction and, for comparison, 2,5-bis(benzoxazol-2′-yl)-1,4-dimethoxybenzene (BD), which does not undergo this kind of reaction. The synthesis and purification of these dyes were carried out according to procedures detailed elsewhere.[13] The silica gel samples were prepared by hydrolyses and polycondensation of tetraethyl orthosilicate (TEOS) in water and ethanol solutions under acidic (HF 40% by wt.) conditions.[14,15] The doped silica-gel monoliths were prepared with different dye concentrations (mol dye/mol TEOS) and with ethanol and DMF, as described in Table 1. The organic dyes were previously dissolved in ethanol. Separate solutions of hydrofluoric acid (0.1 ml) in distilled water and TEOS (5 ml) in ethanol were prepared and the acid solution was dropped with stirring (5 minutes) into the solution of TEOS plus the organic dyes. This mixture (with a maximum volume of 14 ml) was divided between three small plastic dishes with diameters of 3.5 cm, which were placed in a large covered (but not sealed) Petri dish. These solutions were then left to gelify and to evaporate slowly, in air, at room temperature. The obtained gel monoliths were of regular cylindrical form. The dye concentration in the monoliths was estimated also in weight % (Table 2), considering the initial weight of the dyes and the final weight of the monoliths, approximately 60 days after the synthesis. The bulk density was estimated from the weight and size of the dried gel discs.[14]

Table 1 Synthesis conditions for dyes BM and BD

Synthesis conditions	Dye concentration (mol dye/mol TEOS) ($\times 10^{-3}$)	Dye type	Solvent	
			Ethanol/ml	DMF/ml
1	13.7	BM	5	3
2	6.2	BM	5	3
3	3.1	BM	5	3
4	13.7	BM	5	—
5	6.2	BM	5	—
6	3.1	BM	5	—
7	6.2	BD	5	—
8	3.1	BD	5	—

Water adsorption measurements were carried out during the drying and aging period. The gel monoliths obtained from the different syntheses were immersed in distilled water at room temperature and at 50 °C. Every 5 minutes they were removed from water, dried with wet paper and weighted. This procedure was repeated until the sample weight became constant. The relative water adsorption was calculated by the ratio of the difference between the dry and the wet weight, and the dry weight.

Fluorescence spectra were obtained in line transmission, in the range of 400 to 700 nm, excited by a high pressure xenon lamp (100 W) with a UV filter ($\approx$350 nm) and detected by a CCD system coupled to a monochromator. The first spectrum of each sample was obtained after 6 days from the synthesis, and the last spectrum after several months.

Surface area measurements were obtained by the conventional nitrogen adsorption technique on a vacuum system, using a multipoint BET method.

Results

Table 2 shows the characteristics of the samples obtained from different synthesis conditions. The samples prepared with ethanol as a solvent for both dyes (synthesis 4–8) were broken,

Table 2 Characteristics of the samples obtained under different synthesis conditions

Synthesis conditions	Dye condition	Dye concentration (% by weight)	Sample aspect	Density/g cm^{-3}	Water adsorption (%)	Sample weight/g	
						30 d	60 d
1	agglomerated	0.022	transparent intact	1.00	9.1	5.08	3.20
2	agglomerated	0.013	transparent intact	1.05	1.6	4.86	3.34
3	dispersed	0.007	transparent intact	1.02	2.3	5.35	2.32
4	dispersed	0.069	translucent broken	0.30	66.6	1.49	1.44
5	dispersed	0.032	translucent intact	0.19	74.6	1.46	1.44
6	dispersed	0.017	translucent broken	0.30	76.8	1.41	1.40
7	dispersed	0.032	transparent broken	0.30	69.2	1.45	1.45
8	dispersed	0.017	transparent intact	0.31	68.5	1.46	1.44

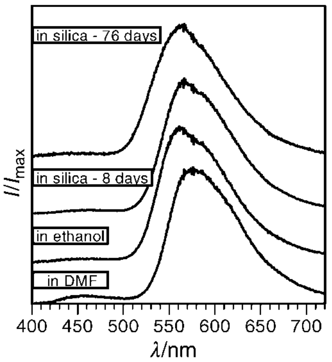

Fig. 3 Normalized fluorescence spectra, in the range of 400 to 700 nm, for BM dye incorporated into silica under synthesis conditions 1 (13.7×10^{-3} mol dye/mol TEOS, with ethanol and DMF), after different times of gelation. For comparison, the fluorescence spectra of the dye in ethanolic and DMF solution are shown.

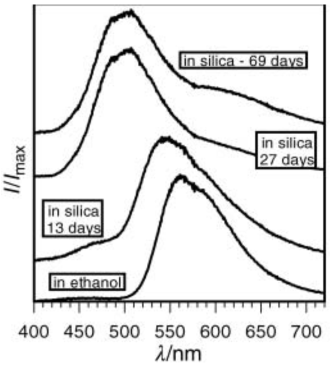

Fig. 5 Normalized fluorescence spectra, in the range of 400 to 700 nm, for BM dye incorporated into silica under synthesis conditions 5 (6.2×10^{-3} mol dye/mol TEOS, with ethanol), after different times of gelation. For comparison, the fluorescence spectrum of the dye in ethanolic solution is shown.

transparent or translucent, and presented very high water adsorption, near 70%. These samples also showed constant weight 30 days after the synthesis and density values near 0.3 g cm^{-3}. The average value for the surface area of these samples was 240 ± 12 m^2 g^{-1}. The samples prepared with a mixture of ethanol and DMF were intact (homogeneous and crack free), transparent, presented regular cylindrical form, with a diameter of approximately 2 cm and thickness of 3.5 mm. These samples showed low water adsorption, below 10%, density near 1.00 g cm^{-3}, and their weight continued to decrease even after 60 days. The average value for the surface area of these samples was 180 ± 9 m^2 g^{-1}.

Fig. 3 shows the normalized fluorescence spectra for the gel discs obtained under synthesis conditions 1 (Table 1) together with the spectra of the dye in ethanolic and DMF solutions. Similar spectra were observed for synthesis conditions 2 and 3, which contained different BM concentrations. As a general feature, the fluorescence of the dye incorporated in the silica-gel matrix was in the same wavelength range observed for the dye in ethanolic solution, with a maximum wavelength at 565 nm corresponding to F_2. There was almost no shift of the fluorescence band during the period between 8 and 76 days after the synthesis, however a decrease in the intensity of approximately 70% was observed for all three syntheses conditions.

Fig. 4 shows the normalized fluorescence spectra for the gel discs obtained under synthesis conditions 4 (Table 1). The spectrum for the monolith which was 6 days old had only one maximum at 565 nm, which was also observed for the dye in ethanolic solution. An important change was observed for the monolith at 27 days old. The F_2 band presented a shift to 540 nm, *i.e.* shorter wavelength compared to the dye in ethanol. Another band appeared at 480 nm, which is related to fluorescence from the primary structure (F_1). The relative intensity for these two maxima was $I_{540}/I_{480} \cong 1.6$ and this decreased to 1.2 after 69 days. At this point we assumed that the fluorescence emission became stable.

Fig. 5 shows the normalized fluorescence spectra for the gel discs obtained under synthesis conditions 5 (Table 1). The spectrum for the 6 days old monolith was the same as that observed for the dye in the ethanolic solution. For the 13 days old monolith there was a hypsochromic shift of the F_2 band to 545 nm, and after 27 days a high intensity band at 500 nm appeared, with a shoulder at about 545 nm, that was attributed to F_2. This same spectrum was observed up to 69 days after the synthesis.

Fig. 6 shows the normalized fluorescence spectra of the transparent gel discs obtained under synthesis conditions 6 (Table 1). The spectrum for the 7 days old monolith had a band at approximately 550 nm which is slightly hypsochromic shifted compared to the dye in ethanolic solution (570 nm). However, the spectra of the monolith obtained after 49 and 240 days show maxima at 480 nm, attributed to primary species F_1, with a small shoulder at about 545 nm.

Fig. 7 shows the spectrum for the 240 days old monolith obtained under synthesis conditions 6, however in this case the monolith was translucent. The spectrum exhibits two bands, one with a maximum at 540 nm and another band with a maximum at 480 nm. The relative intensity of these two maxima was $I_{540}/I_{480} \cong 1.8$. For the same monolith a sequence of heat treatment at 60 °C, 100 °C and 200 °C showed that the relative intensity of these two maxima decreased to

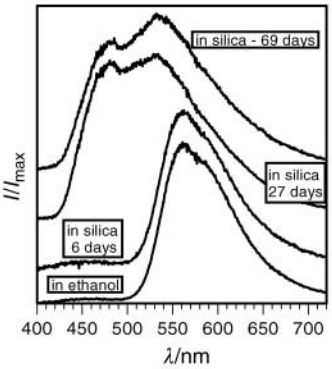

Fig. 4 Normalized fluorescence spectra, in the range of 400 to 700 nm, for BM dye incorporated into silica under synthesis conditions 4 (13.7×10^{-3} mol dye/mol TEOS, with ethanol), after different times of gelation. For comparison, the fluorescence spectrum of the dye in ethanolic solution is shown.

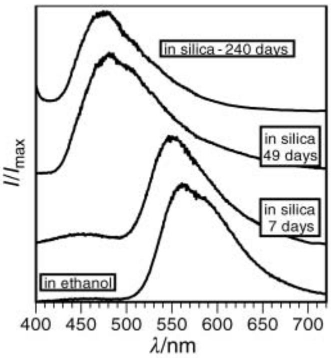

Fig. 6 Normalized fluorescence spectra, in the range of 400 to 700 nm, for BM dye incorporated into silica under synthesis conditions 6 (3.1×10^{-3} mol dye/mol TEOS, with ethanol), after different times of gelation. For comparison, the fluorescence spectrum of the dye in ethanolic solution is shown.

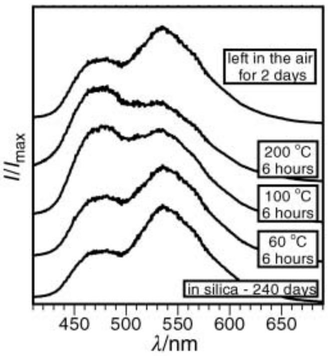

Fig. 7 Normalized fluorescence spectra, in the range of 400 to 700 nm, for a 240 days old sample (synthesis conditions 6), after heat treatment at different temperatures. For comparison, the fluorescence spectrum of this sample left in the air is shown.

approximately 1.4, 1.0 and 0.8, respectively. After the last heat treatment, the monolith was then left in the air for two days and the relative intensity returned to approximately 1.5.

Fig. 8 shows the normalized fluorescence spectra of the gel discs obtained under synthesis conditions 7 (Table 1). The spectrum of this dye in ethanolic solution had only one maximum at 460 nm, corresponding to normal fluorescence F_1. The spectra for the 7 and 15 days old monoliths had maxima at approximately 480 nm and 470 nm, respectively, which were slightly shifted to longer wavelength compared to the dye in ethanolic solution. However, the spectra of the 21 and 42 days old monoliths showed a maximum at 455 nm, approximately the same spectrum observed for ethanolic solution. Similar behavior was observed for the monolith prepared with lower dye concentration (synthesis conditions 8).

Discussion

Fluorescent silica monoliths doped with BM dye were obtained with satisfactory optical and mechanical properties, which depend on the synthesis conditions (solvent and dye concentration). According to Table 2, intact and transparent monoliths were obtained when DMF was used as a solvent. It is well known that DMF is a drying agent in sol–gel synthesis, increasing the mechanical resistance and reducing the crack formation in the monoliths.[15] On the other side, the density of these samples was high, the water adsorption was very low, and the weight of the monoliths did not become constant even after 60 days, which indicates that the pores were full of solvent, evaporating slowly during this period. It could be explained by the high boiling point of DMF (152 °C), which makes it difficult for solvents to evaporate from the silica matrix at room temperature.

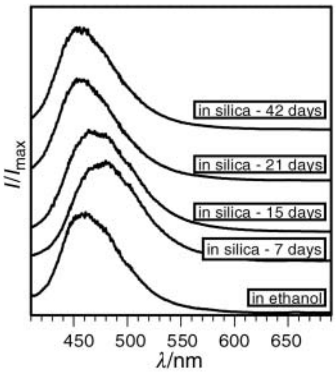

Fig. 8 Normalized fluorescence spectra, in the range of 400 to 700 nm, for BD dye incorporated into silica under synthesis conditions 7 (6.2×10^{-3} mol dye/mol TEOS, with ethanol), after different times of gelation. For comparison, the fluorescence spectrum of the dye in ethanolic solution is shown.

The monoliths prepared only with ethanol as a solvent were mostly broken, translucent and in some cases, transparent. The low density (see Table 2), high water adsorption, and a constant weight after 30 days indicated that the solvent evaporated very rapidly and almost completely, causing cracks and broken samples.

The high BET values found were expected for this kind of system. The changes in the surface area measurements were due to the different solvents used (ethanol and DMF) and not due to the changes in dye concentrations for all synthesis conditions. These results were predicted due to the very low dye concentration in the sol–gel synthesis (Table 1).

The fluorescence properties of the silica monoliths were significantly affected by the characteristics described above, mainly regarding the solvents retained in the pores during the gelation and aging processes, and the dye concentration. The behavior observed in Fig. 3 could be explained by the fact that the dye molecules were solvated in ethanol and DMF, where ethanol could be segregated to near the dye molecules.[9] As is well known, DMF is an aprotic and polar solvent and ethanol is a protic and polar solvent, however their interactions with the dye molecules are not as strong as they could be to hinder the proton-transfer reactions and the F_2 band was maintained.[9]

According to Fig. 4, 5 and 6, the fluorescence spectra changed drastically with the aging time for all the dye concentrations studied, when only ethanol was used as the solvent. For the 6 days old monolith, the dye molecules were totally solvated in ethanol and it was observed that the monoliths were completely wet. After 13 days the monoliths were very opaque and the fluorescence emission was very low. This temporary opacity during the drying process was due to different solvent evaporation rates from the open and closed pores.[16] After 27 days, the monoliths became translucent and the fluorescence emission increased, presenting changes for the different dye concentrations. In Fig. 4 (the highest dye concentration), both bands, F_1 and F_2, were observed. The hypsochromic shift observed in the F_2 band was due to the interaction between the dye molecules and adsorbed water that covers the silica surface.[9] At this time, the ethanol evaporation was almost complete and the dye molecules started to interact with the silica matrix. It is well known that this matrix is rich in isolated OH groups that can form H-bridges with the OH groups and/or N of the dye molecule.[17,18] This interaction hindered the proton-transfer process and lowered the intensity of the F_2 band, creating molecular species that generated the fluorescence band F_1. For long drying periods, the interaction of the dye molecule with the matrix increased, and the intensity of both bands, F_1 and F_2, was almost the same for this concentration. It was observed that the intensity of the F_2 band was still observable, indicating that the dye molecules could be agglomerated or interacting with the residual ethanol or water, which would enable the proton-transfer reaction to take place. It has been observed that this kind of dye agglomerates at concentrations between 10^{-4}–10^{-3} mol l^{-1} in $CHCl_3$.[4] The same agglomeration could also occur in the pores of the silica matrix, being responsible for the remaining F_2 band.

For Fig. 5 and 6 (lower dye concentrations), the abrupt reduction of the intensity of the F_2 band indicated a strong interaction of the dye molecule with the matrix, eliminating almost completely the proton-transfer reactions. The existence of a main band near 500 nm in Fig. 5 has been attributed to fluorescence emitted by ionic species created by the protonation of the nitrogen atoms, which hindered the intramolecular proton-transfer reaction.[9] In acidic systems a great reduction in the intensity of the original bands (F_1 and F_2) and an increasing of the intensity of a band near 500 nm were observed. In our case, the dye would be protonated by OH groups of the silica matrix. In Fig. 6, there is a main band at 480 nm, favouring the molecular species that generated the F_1 band.

For synthesis conditions 6 (lowest dye concentration) some gel discs were opaque, showing different spectra compared to the transparent ones. This anomalous behavior was studied and the results are shown in Fig. 7. The existence of the F_2 band indicated the presence of some solvent retained in the matrix pores, like water, which acted on the dye molecules, replacing the interactions of the molecules with the OH of the silica pores and recovered partially the proton-transfer reactions. When the samples were heat treated, the water was gradually eliminated and the dye molecules interacted with the silica matrix again, losing the capability to undergo proton-transfer reactions. When the samples were left in the air, they adsorbed water, recovering the proton-transfer reactions.

The incorporation of the BD dye, which is known to be unable to undergo proton-transfer reactions, was performed and the fluorescence properties were compared to that of the BM dye. As expected, there is only the F_1 band in the fluorescence spectrum of the BD dye. The small shifts observed can be ascribed to solvent (bathochromic shift) or silica (hypsochromic shift) interactions with the dye molecule.[19] For this type of dye the fluorescence properties are not significantly influenced by the silica matrix, as is well known.[12,14,20]

It is interesting to point out that the behavior of the fluorescence properties of the BM dye incorporated in an inorganic system (silica) observed in this work followed the approach already discussed in the literature for organic solvents and polymeric hosts, contributing to the knowledge of these dyes, widening their potential applications.

Acknowledgements

This research was supported by CNPq, CAPES, FAPERGS, PRONEX/MCT and FINEP (Brazil). We would like to thank Dr Celso Camilo Moro for the BET measurements (IQ - UFRGS).

References

1 A. Mordzinski, A. Grabowska, W. Kühnle and A. Krówczynski, *Chem. Phys. Lett.*, 1983, **101**, 291.
2 A. Mordzinski and W. Kühnle, *J. Phys. Chem.*, 1986, **90**, 1455.
3 M. F. Rodríguez Prieto, B. Nickel, K. H. Grellmann and A. Mordzinski, *Chem. Phys. Lett.*, 1988, **146**, 387.
4 A. Mordzinski, *Chem. Phys. Lett.*, 1988, **150**, 254.
5 K. Das, N. Sarkar, A. K. Ghosh, D. Majumdar, N. D. Nath and K. Bhattacharyya, *J. Phys. Chem.*, 1994, **98**, 9126.
6 N. S. Domingues, C. Krug, P. R. Livotto and V. Stefani, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1861.
7 A. Grabowska, A. Mordzinski, N. Tamai and K. Yoshihara, *Chem. Phys. Lett.*, 1988, **153**, 389.
8 L. J. Bellamy, *Infrared Spectra of Complex Molecules, vol. 1*, Chapman and Hall, London, 1975.
9 D. S. Corrêa, PhD Thesis, IQ-UFRGS, Porto Alegre, Brazil, 1998 (in Portuguese).
10 B. Dunn and J. I. Zink, *Chem. Mater.*, 1997, **9**, 2280.
11 G. Yang, Z. A. Dreger, Y. Li and H. G. Drickamer, *J. Phys. Chem. A*, 1997, **101**, 7948.
12 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328.
13 V. Stefani, A. A. Souto, A. U. Acuña and F. Amat-Guerri, *Dyes Pigm.*, 1992, **20**, 97.
14 S. Sakka, K. Aoki, H. Kozuka and J. Yamaguchi, *J. Mater. Sci.*, 1993, **28**, 4607.
15 C. J. Brinker and G. W. Scherer, *Sol–Gel Science*, Academic Press, New York, 1990.
16 S. Sakka, K. Aoki and H. Kozuka, in *Sol–gel Science and Technology, Ceramic Transaction 55*, ed. E. J. A. Pope, S. Sakka and L.C Klein, The American Ceramic Society, Westerville, OH, 1995, p. 117.
17 J. Y. Ying, J. B. Benziger and A. Navrotsky, *J. Am. Ceram. Soc.*, 1993, **76**, 2571.
18 D. L. Wood and E. M. Rabinovich, *Appl. Spectrosc.*, 1989, **43**, 263.
19 C. N. R. Rao, *Ultra-violet and Visible Spectroscopy - Chemical Applications*, Butterworths, London, 1975.
20 T. M. H. Costa, V. Stefani, N. M. Balzaretti, L. T. S. T. Francisco, M. R. Gallas and J. A. H. Jornada, *J. Non-Cryst. Solids*, 1997, **221**, 157.