Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 178 (2006) 26–32

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Spectral properties of amorphous silica (SiO_2) and mesoporous structured silicates (MCM-41 and ITQ-6) functionalized with ESIPT chromophores

Leandra Franciscato Campo [a], Félix Sánchez [b,**], Valter Stefani [a,*]

[a] *Universidade Federal do Rio Grande do Sul, Laboratório de Novos Materiais Orgânicos (LNMO), Av. Bento Gonçalves, 9500 CP 15003, CEP 91501-970 Porto Alegre-RS, Brazil*

[b] *Instituto de Química Orgánica (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain*

Received 10 March 2005; received in revised form 22 June 2005; accepted 22 June 2005

Available online 1 August 2005

Abstract

2-(2′-Hydroxyphenyl)benzazole (HPB) derivatives, fluorescent by an intramolecular proton-transfer mechanism in the electronically excited state (ESIPT), were synthesized and incorporated by physisorption and covalently bound into amorphous silica (SiO_2) and mesoporous structured silicates (MCM-41) and delaminated zeolite (ITQ-6). The new fluorescent hybrid-materials were prepared by one-step implantation of the dyes into the inorganic framework. The photophysical behaviour of the triethoxysilylated benzazoles, which are covalently bounded into inorganic matrices, is quite different from the non-silylated benzazoles, which are physisorped into inorganic matrices. The fluorescence emission spectra of the bounded dyes were found to be dependent on the heteroatom, since the ESIPT emission was more affected for the benzothiazole and benzimidazole derivatives. The mechanism associated with the ESIPT process was not significantly modified for non-silylated benzazoles, except for a benzimidazole derivative which the fluorescence emission spectra in the inorganic matrices are similar to that observed in MeOH, suggesting that the molecules are surrounded by the SiOH groups.

Keywords: ESIPT; Benzazole dyes; MCM-41; ITQ-6; Fluorescent hybrid-materials

1. Introduction

The encapsulation of organic dyes in porous silica leads to composite materials with attractive optical properties [1,2]. Since the first attempt to incorporate organic dyes within a sol–gel matrix [3], hybrid materials have attracted much interest in the field of materials science due to its useful applications, such as laser materials [4], nonlinear optical materials [2], sensors [5] and artificial antenna systems [6,7]. Over the last years, several methods have been reported inserting organic dyes into inorganic networks [1,2,9,10]. These methods include physical entrapment of a component, usually the organic portion, covalent binding, electrostatic binding, and physical sorption [1,2,5,10]. Nowadays, the covalent binding of the dye within a silica matrix is more useful since an improvement in photostability can be achieved.

A large variety of organic chromophores featuring different structures have been used for hybrid organic–inorganic composites [1–4,7–15]. On the other hand, chromophores like 2-(2′-hydroxyphenyl)benzazoles (HPBs) are important dyes, which emit fluorescence with large Stokes shift ascribed to an intramolecular proton-transfer process in the excited-state (ESIPT) [16–18]. Dyes which present ESIPT are useful as laser dyes [4], fluorescent silica aerogels [11], UV-light stabilizer [19], and fluorescent probes to labelling proteins [20].

In this work, we describe the inclusion of HPBs derivatives into amorphous silica (SiO_2) and mesoporous struc-

---

[*] Corresponding author. Tel.: +55 51 3316 6285; fax: +55 51 3316 7304.

[**] Co-corresponding author. Tel.: +34 91 5622900; fax: +34 91 5644853.

E-mail addresses: vstefani@iq.ufrgs.br (V. Stefani), felix-iqo@iqog.csic.es (F. Sánchez).

URL: http://www.iq.ufrgs.br/lnmo.

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.

doi:10.1016/j.jphotochem.2005.06.016

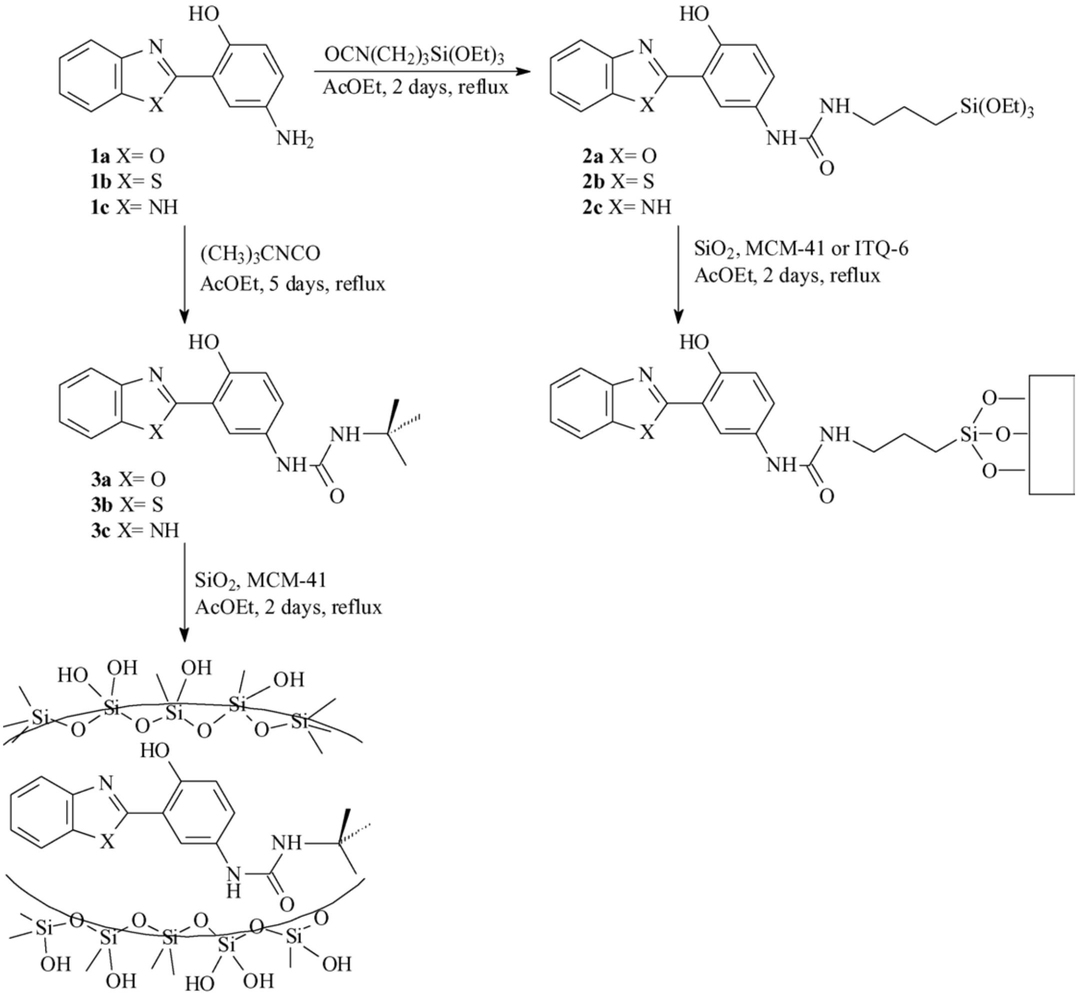

Fig. 1. Preparation of fluorescent hybrid organic–inorganic materials covalently bonded with the triethoxysilylated benzazoles **2a–c** and encapsulated with the non-silylated benzazoles **3a–c**.

tured silicates (MCM-41 and ITQ-6) by covalent bonding and physical sorption (Fig. 1). The preparation of the new fluorescent hybrid organic–inorganic materials by covalent bonding was performed by the reaction between triethoxysilylated benzazoles and the external silanol groups of the inorganic matrices. Additionally, it was synthesized corresponding non-silylated benzazoles and physisorped then into the silicates to compare the fluorescence behaviour of such host–guest systems with the triethoxysilylated dyes.

2. Experimental

2.1. Materials and instruments

Silica gel (Merck, average pore diameter 40 Å), MCM-41 and delaminated zeolite ITQ-6 were used as inorganic supports. MCM-41 and ITQ-6 were synthesized according to literature [21,22]. Infrared spectroscopic was made using a Nicolet XR60 and a Galaxy Series FT-IR3000 in KBr pellets. ^{1}H NMR spectra were performed on a Varian model INOVA-300 using tetramethylsilane (TMS) as the internal standard; CDCl$_3$ and DMSO-d_6 were used as the solvents. Elemental analyses were performed on a Perkin-Elmer 240C. UV–vis absorption spectra of the dyes in solution were performed on a Shimadzu UV-1601 PC spectrophotometer. Diffuse reflectance UV–vis spectra of the fluorescent inorganic matrices were recorded on a Shimadzu UV-2401 PC spectrophotometer and the data have been subject to Kubelka Munk transformation. Steady-state fluorescence emission spectra were measured with a Perkin-Elmer LS 50B. Different excitation wavelengths were used to obtain the fluorescence spectra and the 355 nm was chosen for all matrices. All experiments were performed at room temperature. Spectroscopic grade solvents were used to UV–vis and fluorescence emission measurements.

2-(5′-Amino-2′-hydroxyphenyl)benzazoles **1a–c** were synthesized and purified according to the methodology previously described [23]. 3-(Triethoxysilyl)propyl isocyanate and *tert*-butyl isocyanate (Aldrich) were used as received.

2.2. Synthesis of the dyes

2.2.1. General procedure for the synthesis of the triethoxysilylated benzazoles **2a–c**

The reaction consists in the addition of the 3-(triethoxysilyl)propyl isocyanate (0.25 ml) into the solution of the corresponding 2-(5′-amino-2′-hydroxyphenyl)benzazoles **1a–c** (200 mg) in ethyl acetate (20 ml) (Fig. 1). The reaction mixtures were stirred under reflux temperature for 2 days and the 2-[5′-*N*-(3-triethoxysilyl)propylurea-2′-hydroxyphenyl] benzazoles **2a–c**, which precipitates into the reaction mixture, were filtered, washed with ethyl acetate and dried at room temperature. No additional purification was needed.

*2.2.1.1. 2-[5′-N-(3-Triethoxysilyl)propylurea-2′-hydroxyphenyl]benzoxazole (**2a**).* Yield: 83%. Anal. Calcd. for $C_{23}H_{31}N_3O_6Si$: C 58.35%, H 6.76%, N 8.88%. Found: C 58.44%, H 6.62%, N 8.81%. IR (cm^{-1}): 3320 (νNH), 2974 (ν_{alif}C–H), 1628 (νC=O), 1581 and 1549 (ν_{arom}C=C), 1249 (νSi–CH$_2$), 1079 (νSi–O). ^{1}H NMR (CDCl$_3$, δ ppm): 11.35 (1H, s, OH); 8.06 (1H, d, $H_{6'}$, $J_{meta} = 2.7$ Hz); 7.73–7.69 (1H, m, H_5 or H_6); 7.60–7.40 (1H, m, H_5 or H_6); 7.39–7.34 (2H, m, H_4 and H_7); 7.27 (1H, dd, $H_{4'}$, $J_{meta} = 2.7$ Hz and $J_{ortho} = 8.7$ Hz); 7.06 (1H, d, $H_{3'}$, $J_{ortho} = 8.7$ Hz); 6.22 (1H, s, 5′-N*H*); 4.85 (1H, t, N*H*CH$_2$); 3.79 (6H, q, OCH_2); 3.26 (2H, m, CH_2NH); 1.65 (2H, m, CH_2); 1.19 (9H, t, OCH$_2$CH_3); 0.65 (2H, t, CH_2Si).

*2.2.1.2. 2-[5′-N-(3-Triethoxysilyl)propylurea-2′-hydroxyphenyl]benzothiazole (**2b**).* Yield: 74%. Anal. Calcd. for $C_{23}H_{31}N_3O_5SSi$: C 56.42%, H 6.38%, N 8.58%. Found: C 56.24%, H 6.32%, N 8.45%. IR (cm^{-1}): 3318 (νNH), 2973 (ν_{alif}C–H), 1638 (νC=O), 1587 (ν_{arom}C=C), 1244 (νSi–CH$_2$), 1079 (νSi–O). ^{1}H NMR (CDCl$_3$, δ ppm): 12.27 (1H, s, OH); 7.85–7.73 (2H, m, H_5 and H_6); 7.61 (1H, d, $H_{6'}$, $J_{meta} = 2.5$ Hz); 7.46–7.24 (2H, m, H_4 and H_7); 7.08 (1H, dd, $H_{4'}$, $J_{meta} = 2.5$ Hz and $J_{ortho} = 8.7$ Hz); 6.91 (1H, d, $H_{3'}$, $J_{ortho} = 8.7$ Hz); 6.19 (1H, s, 5′-N*H*); 4.78 (1H, t, N*H*CH$_2$); 3.65 (6H, q, OCH_2); 3.13 (2H, m, CH_2NH); 1.53 (2H, m, CH_2); 1.05 (9H, t, OCH$_2$CH_3); 0.45 (2H, t, CH_2Si).

*2.2.1.3. 2-[5′-N-(3-Triethoxysilyl)propylurea-2′-hydroxyphenyl]benzimidazole (**2c**).* Yield: 89%. Anal. Calcd. for $C_{23}H_{32}N_4O_5Si$: C 58.47%, H 6.77%, N 11.86%. Found: C 58.50%, H 6.58%, N 11.88%. IR (cm^{-1}): 3307 (νNH), 2973 (ν_{alif}C–H), 1632 (νC=O), 1579 (ν_{arom}C=C), 1257 (νSi–CH$_2$), 1078 (νSi–O). ^{1}H NMR (CDCl$_3$, δ ppm): 12.24 (1H, s, OH); 7.60–7.55 (2H, m, H_4 and H_7); 7.49–6.87 (10H, m, H_4–H_7, $H_{3'}$, $H_{4'}$ and $H_{6'}$); 6.20 (1H, s, 5′-N*H*); 5.62 (1H, t, N*H*CH$_2$); 3.75 (6H, q, OCH_2); 3.25 (2H, m, CH_2NH); 1.73 (2H, m, CH_2); 1.05 (9H, t, OCH$_2$CH_3); 0.75 (2H, t, CH_2Si).

2.2.2. General procedure for the synthesis of the non-silylated benzazoles **3a–c**

The reaction consists in the addition of the *tert*-butyl isocyanate (0.25 ml) into the solution of the corresponding 2-(5′-amino-2′-hydroxyphenyl)benzazoles **1a–c** (200 mg) in ethyl acetate (20 ml) (Fig. 1). The reaction mixtures were stirred under reflux temperature for five days and the 2-[5′-*N*-(3-*tert*-butylurea)-2′-hydroxyphenyl]benzazoles **3a–c**, which precipitates into the reaction mixture, were filtered, washed with ethyl acetate and dried at room temperature. No additional purification was needed.

*2.2.2.1. 2-[5′-N-(3-Tert-butylurea)-2′-hydroxyphenyl]benzoxazole (**3a**).* Yield: 45%. Anal. Calcd. for $C_{18}H_{19}N_3O_3$: C 66.45%, H 5.89%, N 12.91%. Found: 66.71%, H 6.04%, N 13.08%. IR (cm^{-1}): 3302 (νNH), 2964 (ν_{alif}C–H), 1644 (νC=O), 1567 and 1547 (ν_{arom}C=C). ^{1}H NMR (DMSO-d_6, δ ppm): 10.40 (1H, s, OH); 8.37 (1H, d, $H_{6'}$, $J_{meta} = 2.7$ Hz); 8.32 (1H, s, 5′-N*H*); 7.91–7.84 (2H, m, H_5 and H_6); 7.51–7.43 (2H, m, H_4 and H_7); 7.20 (1H, dd, $H_{4'}$, $J_{meta} = 2.7$ Hz and $J_{ortho} = 8.9$ Hz); 7.00 (1H, d, $H_{3'}$, $J_{ortho} = 8.8$ Hz); 5.96 (1H, s, N*H*C(CH$_3$)$_3$); 1.30 (9H, s, CH_3).

*2.2.2.2. 2-[5′-N-(3-Tert-butylurea)-2′-hydroxyphenyl]benzothiazole (**3b**).* Yield: 47%. Anal. Calcd. for $C_{18}H_{19}N_3O_2S$: C 63.32%, H 5.61%, N 12.31%. Found: C 63.60%, H 5.68%, N 12.38%. IR (cm^{-1}): 3289 (νNH), 2965 (ν_{alif}C–H), 1642 (νC=O), 1565 (ν_{arom}C=C). ^{1}H NMR (CDCl$_3$, δ ppm): 12.41 (1H, s, OH); 8.01–7.90 (2H, m, H_5 and H_6); 7.60 (1H, d, $H_{6'}$, $J_{meta} = 2.6$ Hz); 7.55–7.40 (2H, m, H_4 and H_7); 7.22 (1H, dd, $H_{4'}$, $J_{meta} = 2.6$ Hz and $J_{ortho} = 8.8$ Hz); 7.07 (1H, d, $H_{3'}$, $J_{ortho} = 8.8$ Hz); 5.98 (1H, s, 5′-N*H*); 4.49 (1H, s, N*H*C(CH$_3$)$_3$); 1.38 (9H, s, CH$_3$).

*2.2.2.3. 2-[5′-N-(3-tert-Butylurea)-2′-hydroxyphenyl]benzimidazole (**3c**).* Yield: 48%. Anal. Calcd. for $C_{18}H_{20}N_4O_2$: C 66.65%, H 6.21%, N 17.27%. Found: C 66.85%, H 6.50%, N 17.48%. IR (cm^{-1}): 3301 (νNH), 2964 (ν_{alif}C–H), 1647 (νC=O), 1556 (ν_{arom}C=C). ^{1}H NMR (DMSO-d_6, δ ppm): 12.00 (1H, s, OH); 7.88 (1H, d, $H_{6'}$, $J_{meta} = 2.6$ Hz); 7.80 (1H, s, 5′-N*H*); 7.68–7.62 (2H, m, H_5 and H_6); 7.27–7.25 (2H, m, H_4 and H_7); 7.15 (1H, dd, $H_{4'}$, $J_{meta} = 2.6$ Hz and $J_{ortho} = 8.8$ Hz); 6.93 (1H, d, $H_{3'}$, $J_{ortho} = 8.8$ Hz); 6.00 (1H, s, N*H*C(CH$_3$)$_3$); 1.80 (9H, s, CH_3).

2.3. Insertion of benzazole dyes into the inorganic framework

2.3.1. By covalently bonding of the **2a–c** on SiO$_2$, MCM-41 and ITQ-6

A solution of **2a–c** (50 mg) in ethyl acetate (20 ml) was added to an ethyl acetate (30 ml) suspension of either amorphous silica (SiO$_2$) or MCM-41 or ITQ-6 (700 mg) and the mixture was stirred at reflux temperature for 24 h (Fig. 1). The solid was filtered and washed several times with ethanol to remove the remaining non-bounded benzazole. The silica supports containing the triethoxysilylated benzazoles **2a–c** were dried in vacuum and characterized by UV–vis diffuse reflectance and fluorescence emission.

*2.3.2. By physisorption of **3a–c** on SiO_2 and MCM-41*

A solution of **3a–c** (50 mg) in ethyl acetate (20 ml) was added to an ethyl acetate (30 ml) suspension of either amorphous silica (SiO_2) or MCM-41 (700 mg) and the mixture was stirred at reflux temperature for 24 h (Fig. 1). The solid was filtered and washed twice with CH_2Cl_2. The inorganic supports containing the non-silylated benzazole **3a–c** were dried in vacuum and characterized by UV–vis diffuse reflectance and fluorescence emission.

3. Results and discussion

3.1. Spectroscopic properties of the dyes

The absorption spectra of **2a–c** and **3a–c** in chloroform (10^{-5} M) are showed in Fig. 2 and the relevant photophysical data are summarized in Table 1. The UV–vis spectra of the dyes show two main bands. The absorption bands in the 320–400 nm range are intense and can be assigned to the (π, π^*) transition from S_0 to S_1 states. Below 320 nm, the spectra are structured, with an intense absorption around 290 nm due to the azole chromophore [24,25]. The strong intramolecular hydrogen bond (IHB) existing in these dyes is reflected in the significant differences between its electronic absorption spectra and those where the IHB is absent [26].

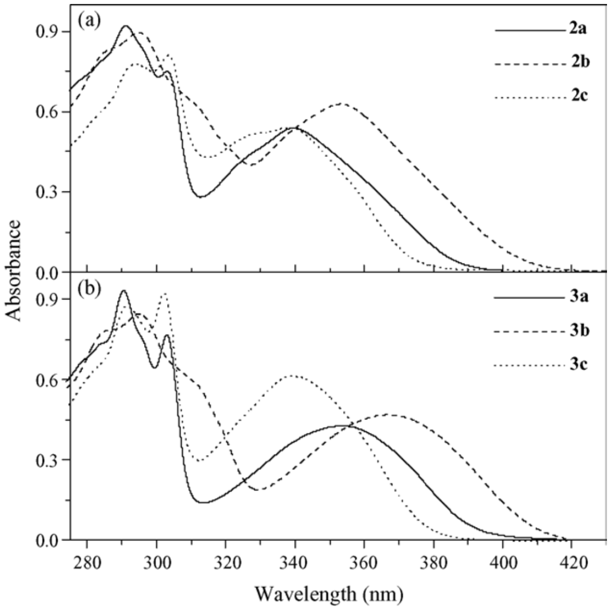

Fig. 2. UV–vis absorption of triethoxysilylated benzazoles **2a–c** (a) and non-silylated benzazoles **3a–c** (b) in chloroform.

Table 1
UV–vis absorption and fluorescence emission data of **2a–c** and **3a–c** in solution and into inorganic matrices

Dye	Solvent/ matrix	λ_{max}^{abs} (nm)	$(\lambda_{max}^{em})_{enol}$ (nm)	$(\lambda_{max}^{em})_{keto}$ (nm)	$(\Delta\lambda_{ST})_{keto}$ (nm)
2a	$CHCl_3$	340	405	521	181
	MeOH	355	412	–	–
	MCM-41	356	466	519	163
	ITQ-6	356	464	519	163
	SiO_2	345	422	512	167
2b	$CHCl_3$	353	436	538	185
	MeOH	353	442	–	–
	MCM-41	373	435	516	143
	ITQ-6	369	–	480	111
	SiO_2	352	426	528	176
2c	$CHCl_3$	338	387	496	158
	MeOH	336	398	494	158
	MCM-41	335	–	458	123
	SiO_2	335	–	475	140
3a	$CHCl_3$	352	435	508	156
	MeOH	349	416	505	156
	MCM-41	362	–	507	145
	SiO_2	363	–	509	146
3b	$CHCl_3$	365	–	547	182
	MeOH	358	420	505	147
	MCM-41	364	–	532	168
	SiO_2	365	423	532	167
3c	$CHCl_3$	338	–	497	159
	MeOH	344	440	527	183
	MCM-41	331	430	–	–
	SiO_2	338	432	–	–

It is well known that the HPBs can present a conformational equilibrium in solution in the ground state, where different enol conformers can coexist (Fig. 3). In this species, when excited with UV radiation, only the enol-*cis* conformer (I) is converted to an excited keto-*cis* phototautomer (IV) by the ESIPT mechanism which decays emitting fluorescence with a large Stokes shift. In this way, the enol-*trans*

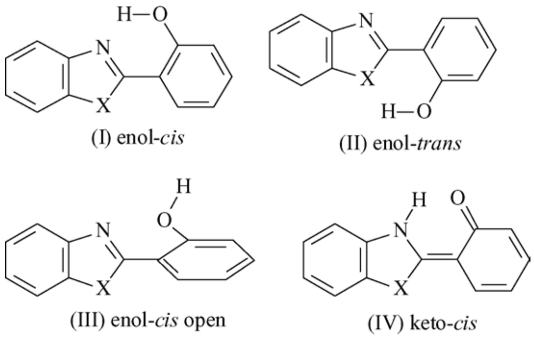

Fig. 3. The normal (I–III) and tautomeric (IV) species of 2-(2′-hydroxyphenyl)benzazole dyes (X = O, benzoxazole; X = S, benzothiazole; X = NH, benzimidazole).

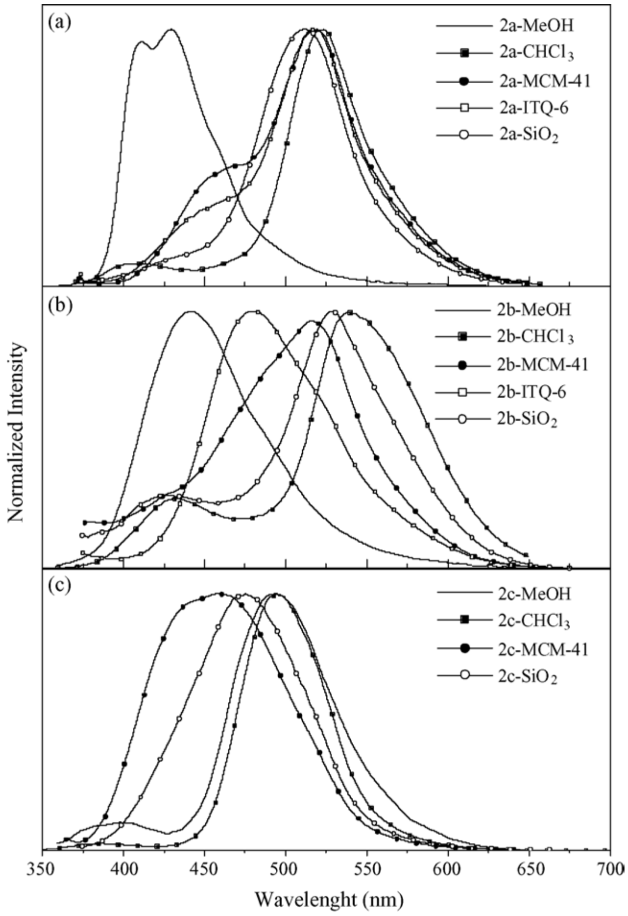

Fig. 4. Fluorescence spectra of (a) dye **2a** in methanol, chloroform and into inorganic matrices, (b) dye **2b** in methanol, chloroform and into inorganic matrices, (c) dye **2c** in methanol, chloroform and into inorganic matrices.

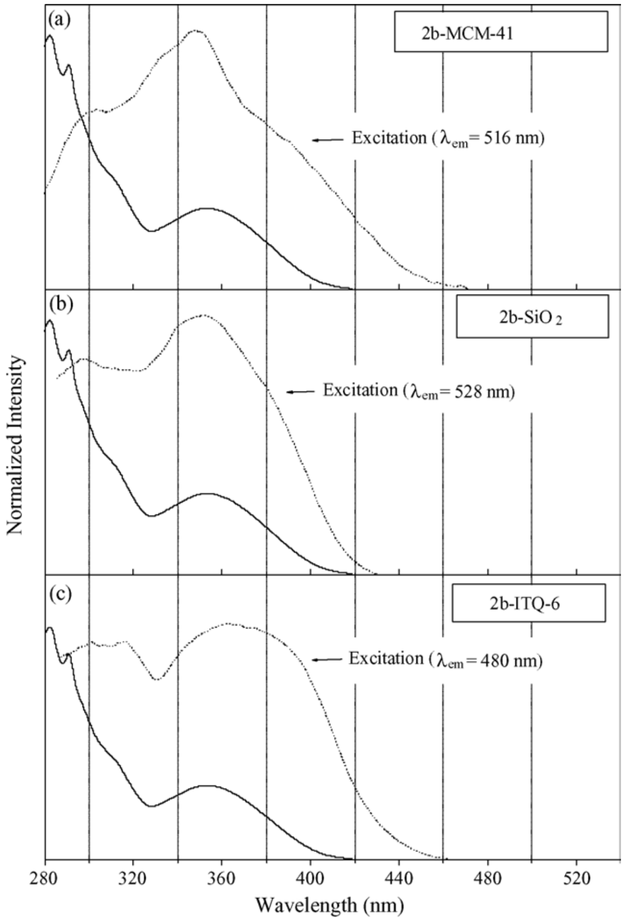

Fig. 5. Normalized excitation spectra of **2b** in methanol and into (a) MCM-41, (b) SiO_2 and (c) ITQ-6.

(II) and enol-*cis* open (III) conformers can compete with the keto-*cis* responsible to the ESIPT mechanism. The existence of these different species affects the absorption and emission spectra of the HPBs in solvents with different dielectric constants and hydrogen bonding ability. When the conformational equilibrium is present, a dual fluorescence emission can be observed, with a band at higher wavelengths ascribed to the ESIPT mechanism (tautomer IV) and a blue shifted one, attributed to the other conformational forms (conformers II–III) [16–18,24–26].

For the dyes synthesized in this work, only the benzimidazoles **2c** and **3c** present a single fluorescence ESIPT emission in polar-aprotic solvent (Figs. 4c and 5c). However, in hydrogen bonding media the enol-*cis* open (III) emission takes place and is the main band for **3c**. A dual fluorescence emission can be observed to the dyes **2a**–**b** (Fig. 4a and b) and **3a**–**b** (Fig. 5a and b) even in polar solvent, indicating that the conformational equilibrium in solution is sensitivity to the solvent polarity. As already related [24–26], in polar solvents there is the possibility of disruption of IHB leading to a decrease in the concentration of (I) and an increase in the concentration of (II). In MeOH as the solvent, the emission spectra of the dyes **3a**–**b** exhibit a second emission band of (III), and for the dyes **2a**–**b** this band overcomes of (IV) emission. This indicated that the triethoxysilylated benzazoles are more affected by the intermolecular hydrogen bond than the non-silylated benzazoles.

3.2. *Insertion of benzazoles into amorphous silica and mesostructured materials*

Although the behaviour of the HPBs has been studied in organic polymeric matrices [4,23,27], the fluorescence of these dyes in inorganic media host received little attention. To the best of our knowledge, Gallas et al. 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 [28,29] and later, the incorporation of 2-(2′-hydroxyphenyl)benzothiazole inside the supercages of nanosized FAU zeolite was reported by Mintova et al. [30].

In the following sections, it is presented ESIPT fluorescent silicate materials containing a covalently bounded dyes **2a**–**c** and a dispersed dyes **3a**–**c** into amorphous silica or a mesoporous structured silicates MCM-41 or a delaminated zeolite ITQ-6.

3.2.1. Insertion by covalently bonding

There are several methods for achieving the covalently bound of the organic molecules in inorganic materials. The obtention of these hybrid materials can be performed by the inorganic surface functionalization with alkoxysilane groups followed by a reaction of the organic molecule or by the organic moiety functionalization, which will react with the silanol groups in the inorganic surfaces [1–5,7–10].

A second approach employing the reaction of the amorphous silica or a structured MCM-41 and ITQ-6 silicates with triethoxysilylated benzazoles **2a–c** was performed. The insertion of **2a–c** in an inorganic support take place via covalent bonds between the solid (silanol groups −SiOH) and the dye, which present appropriate groups like the $-Si(OEt)_3$. These hybrid organic–inorganic materials are non-fluorescent when observed at the visible light and fluorescent when irradiated with UV-light. The fluorescence spectra of **2a–c** in solution (10^{-5} M) and attached to the SiO_2, MCM-41 and ITQ-6 are shown in Fig. 4a–c.

The emission spectra of **2a** bounded to all inorganic matrices are similar to those recorded for a dilute solution in chloroform, showing that the ESIPT emission band was not affected by the matrix surroundings. On the other hand, the band (shoulder-like) at 460 nm to MCM-41/ITQ-6 and at 420 nm in SiO_2, do not coincide with the normal emission band in the protic solvent. For **2c** the emission spectra in SiO_2 and MCM-41 are broad and blue-shifted with respect to the dye in solution. This behaviour indicates probably that more than one species are in equilibrium in both inorganic matrices. For dye **2b** in SiO_2 the emission spectrum is similar to that in chloroform, although blue-shifted (∼10 nm). However, in MCM-41 and ITQ-6 the emission spectra are significantly different from that chloroform and methanol solutions. The new band that appears in these matrices does not resemble the ESIPT and the normal emission bands. To find the origin of these bands, the fluorescence excitation spectra of **2b** in methanol, MCM-41, ITQ-6 and SiO_2 were recorded (Fig. 5). The fluorescence excitation spectrum of the dye in SiO_2 resembles one in methanol solution. Otherwise, for MCM-41 and ITQ-6 they are different from that in solution. This suggests that the respective emission is observed by exciting different species in the ground state. The photophysical properties of the three studied molecular systems, **2a–c**, reveals that: (a) the different nature of the heteroatom affect the photophysical properties of the benzazoles into the inorganic matrices; (b) the benzoxazole is less affected by the environment of the inorganic matrices than benzothiazole and benzimidazole and (c) the fluorescence emission spectra of the dyes into the different matrices do not seems that one in a protic solvent, suggesting that the molecules are not surrounded by SiOH groups.

3.2.2. Encapsulation by physisorption

To better understand the influence of the inorganic matrices in the ESIPT mechanism, it was performed a study doping the supports with non-bounded fluorescent dyes. The non-silylated benzazoles **3a–c** were synthesized and entrapped into SiO_2 and MCM-41. In this case, the molecules are physically adsorbed in the inorganic matrices and can therefore be extracted.

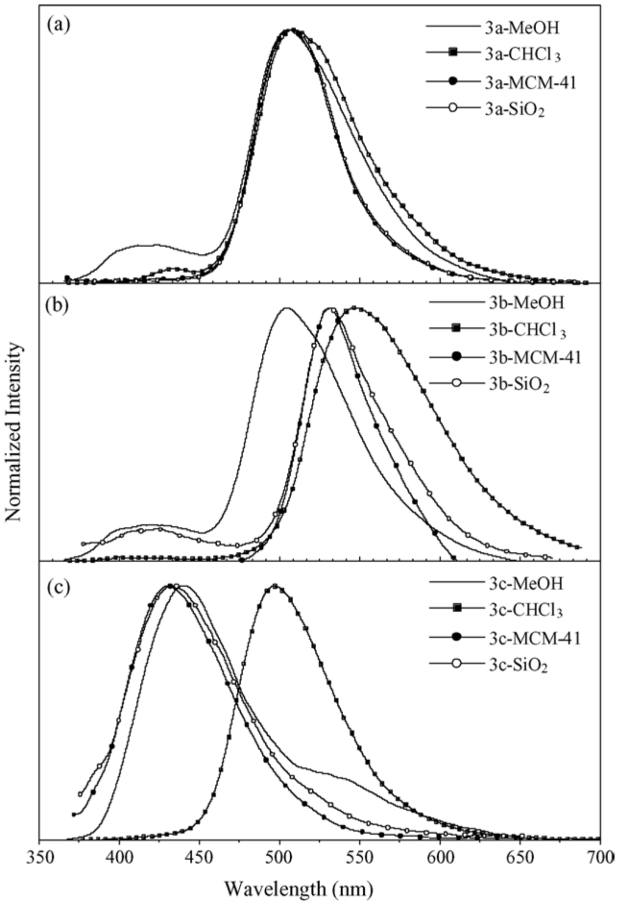

Fig. 6. Fluorescence spectra of (a) dye **3a** in methanol, chloroform and into inorganic matrices, (b) dye **3b** in methanol, chloroform and into inorganic matrices, (c) dye **3c** in methanol, chloroform and into inorganic matrices.

The emission spectra of **3a–c** in solution (10^{-5} M) and attached to the SiO_2 and MCM-41 are shown in Fig. 6a–c. Different excitation wavelengths were used to obtain the fluorescence spectra and the 355 nm was chosen for all matrices. The behaviour of these dyes is quite different from the dyes covalently bounded in the inorganic matrices. The mechanism associated with the ESIPT process was not significantly modified for **3a–b** adsorbed in the inorganic matrices. For **3c** the emission spectra in the inorganic matrices are similar that observed in MeOH, suggesting that the molecules are surrounded by SiOH groups.

4. Conclusions

New ESIPT benzazoles were synthesized and incorporated by physisorption and covalently bound into amorphous silica and mesoporous structured silicates. These hybrid organic–inorganic materials are non-fluorescent when observed at the visible light and fluorescent when irradiated with UV-light. The supports containing the dyes covalently bounded were prepared by reaction with a triethoxysilylated benzazoles. Additionally, we have synthesized corresponding non-silylated benzazoles and physisorped then into the silicates to compare the fluorescence behaviour of such host–guest systems with the triethoxysilylated dyes.

The photophysical behaviour of the triethoxysilylated dyes is quite different from the non-silylated. The fluorescence emission spectra of the bounded dyes into the silicates were found to be dependent on the heteroatom. The ESIPT process was less affected for the benzoxazole dye and more affected for the benzothiazole and benzimidazole derivatives. The mechanism associated with the ESIPT process was not significantly modified for non-silylated benzazoles, except for a benzimidazole derivative which the fluorescence emission spectra in the inorganic matrices are similar that observed in MeOH, suggesting that the molecules are surrounded by SiOH groups.

Acknowledgements

The authors thank the Brazilian agencies CNPq, CAPES and FAPERGS for financial support and scholarships. We also thank Dr. Marta Iglesias for UV–vis diffuse reflectance measurements and the Dirección General de Investigación Científica y Técnica of Spain (Project MAT2003-07945-C02-02).

References

[1] G. Schulz-Ekloff, D. Wöhrlr, B. van Duffel, R.A. Schoonheydt, Micropor. Mesopor. Mater. 51 (2002) 91.
[2] C. Sanchez, B. Lebeau, F. Chaput, J.-P. Boilot, Organic–Inorganic Materials, Wiley/VCH, Weinheim, 2004, pp. 122–171.
[3] D. Avnir, D. Levy, R. Reisfeld, J. Phys. Chem. 88 (1984) 5956.
[4] A. Costela, I. García-Moreno, R. Sastre, Handbook of Advanced Electronic and Photonic Materials and Devices: Liquid Crystals, Display and Laser Materials, vol. 7, Academic Press, 2001, pp. 161–208.
[5] B.D. MacCraith, C. McDonagh, J. Fluoresc. 12 (2002) 333.
[6] M.A. Villegas, L. Pascual, Thin Solid Films 351 (1999) 103.
[7] S. Huber, G. Calzaferri, Angew. Chem. Int. Ed. 43 (2004) 6738.
[8] G. Calzaferri, M. Pauchard, H. Maas, S. Huber, A. Khatyr, T. Schaafsma, J. Mater. Chem. 12 (2002) 1.
[9] D. Avnir, Acc. Chem. Res. 28 (1995) 329.
[10] D. Brühwiler, G. Calzaferri, Micropor. Mesopor. Mater. 72 (2004) 1.
[11] F.S. Rodembusch, L.F. Campo, A. Rigacci, V. Stefani, J. Mater. Chem. 15 (2005) 1537.
[12] P.N. Minoofar, R. Hernandez, S. Chia, B. Dunn, J.I. Zink, A.-C. Franville, J. Am. Chem. Soc. 124 (2002) 14388.
[13] F. Liu, L. Fu, J. Wang, Q. Meng, H. Li, J. Guo, H. Zhang, N. J. Chem. 27 (2003) 233.
[14] N.K. Mal, M. Fujiwara, Y. Tanaka, Nature 421 (2003) 350.
[15] T. Suratwala, Z. Gardlund, K. Davidson, D.R. Uhlmann, Chem. Mater. 10 (1998) 199.
[16] S.J. Formosinho, L.G. Arnaut, Photochem. Photobiol. A: Chem. 75 (1993) 21.
[17] M. Segala, N.S. Domingues, P.R. Livotto, V. Stefani, J. Chem. Soc., Perkin Trans. 2 (6) (1999) 1123.
[18] J. Elguero, A.R. Katritzky, O.V. Denisko, Adv. Heteroc. Chem. 76 (2000) 1.
[19] J. Catalán, J.C. Del Valle, J. Am. Chem. Soc. 115 (1993) 4321.
[20] (a) M.G. Holler, L.F. Campo, A. Brandeli, V. Stefani, J. Photochem. Photobiol. A 149 (2002) 217;
(b) F.S. Rodembusch, F.P. Leusin, L.F.C. Medina, A. Brandelli, V. Stefani, Photochem. Photobiol. Sci. 4 (2005) 254.
[21] (a) C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710;
(b) J.S. Beck, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, K.H. Olson, E. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenk, J. Am. Chem. Soc. 114 (1992) 10834.
[22] (a) A. Corma, U. Diaz, M.E. Domine, V. Fornes, Angew. Chem. Int. Ed. 39 (2000) 1499;
(b) A. Corma, U. Diaz, M.E. Domine, V. Fornes, J. Chem. Soc., Chem. Commun. 137 (2000).
[23] L.F. Campo, D.S. Correa, M.A. Araújo, V. Stefani, Macromol. Rapid Commun. 21 (2000) 832.
[24] D. LeGourriérec, V.A. Kharlanov, R.G. Brown, W. Rettig, J. Photochem. Photobiol. A: Chem. 130 (2000) 101.
[25] P. Purkayastha, N. Chattopadhyay, Phys. Chem. Chem. Phys. 2 (2000) 203.
[26] G.J. Woolfe, M. Melzig, S. Schneider, F. Dörr, Chem. Phys. 77 (1983) 213.
[27] F.S. Rodembusch, N.P. Silveira, D. Samios, L.F. Campo, V. Stefani, J. Polym. Sci., Part B: Polym. Phys. 41 (2003) 341.
[28] T.M.H. Costa, V. Stefani, M.R. Gallas, N.M. Balzaretti, J.A.H. Jornada, J. Mater. Chem. 11 (2001) 3377.
[29] T.M.H. Costa, V. Stefani, N.M. Balzaretti, M.R. Gallas, J.A.H. Jornada, Mol. Cryst. Liq. Cryst. Sci. Technol. 374 (2002) 201.
[30] S. Mintova, V.D. Waele, U. Schmidhammer, E. Riedle, T. Bein, Angew. Chem. Int. Ed. 42 (2003) 1611.