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A New ESIPT Fluorescent Dye-Doped Silica Aerogel

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Summary: A silyl-functionalized benzazole dye, fluorescent by excited state intramolecular proton transfer (ESIPT) mechanism, was synthesized by reacting 2-(2′-hydroxyphenyl)benzoxazole with 3-(triethoxysilyl)propyl isocyanate. The fluorescent silica gel was prepared by the addition of a solution of 2-propanol and the fluorescent dye after the gelation time. The monolithic aerogel was obtained via supercritical CO_2 drying of the fluorescent gel. The resulting aerogel is transparent in the visible light and fluorescent in the blue-green region under UV radiation.

Keywords: benzazole dyes; fluorescence; photophysics; supramolecular structures

Introduction

Aerogels are interesting materials originated from inorganic and/or organic wet gels dried under supercritical conditions,[1] which result in a material with very low apparent densities and very high relative pore volumes.[2] The research and application of silica aerogels as host dyes has increased over the last few years,[3] once they also consist of a network of fractal aggregates[4] implying in a wide distribution of pore sizes.[5] They have also been investigated as host for different kinds of molecules.[6,7] The research and application of photoactive molecules confined or covalently bound in an inorganic network has increased over the last few years,[8–10] since they present many interests in fluorescent sensors fields and for new materials preparation.[11–16]

ESIPT-exhibiting molecules, such as 2-(2′-hydroxyphenyl)benzazoles, are particularly interesting since they are highly fluorescent, with a large Stokes shift due to an fototautomerism in the excited state (ESIPT)[17] (Figure 1), presenting many applications, such as scintillation detectors.[18] When one combines the properties of aerogels and ESIPT dyes, new photoluminescent materials can be expected.[19] In this work we describe the covalent bound of a fluorescent benzazole derivative dye in a silica matrix by a specific sol-gel route followed by supercritical drying of the fluorescent wet gel.

Experimental Part

Analytical grade 2-propanol, hydrofluoric acid (48% wt) and 3-(triethoxysilyl)propyl isocyanate were obtained from Sigma-Aldrich and used as received. Prepolymerized tetraethoxysilane precursor (P750) came from PCAS. Carbon dioxide (standard grade) used for supercritical drying was provided by Air Liquide. Elemental analyses were performed by Perkin-Elmer model 2400 CHN. Spectroscopic infrared characterization of the benzazole dye was carried out using a Nicolet XR60 in KBr pellets. ^1H spectra were performed on a Varian XL (300 MHz) using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ (Merck) as the solvent at room temperature. UV-Vis absorption spectra were performed on a Shimadzu

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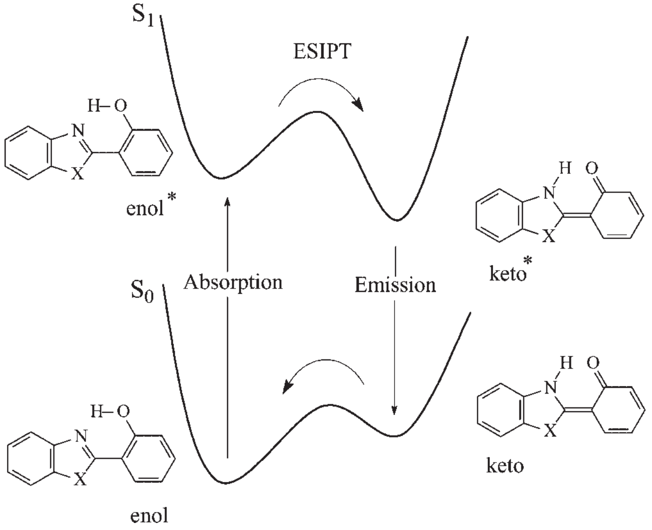


Figure 1.
ESIPT mechanism of 2-(2′-hydroxyphenyl)benzazole dyes (X = O, S, or NH).

UV-1601PC spectrophotometer. Steady-state fluorescence spectra in solution and in solid-state were measured on a Hitachi spectrofluorometer model F-4500. All experiments were performed at room temperature. Spectroscopic grade solvents (Merck) were used to UV-Vis and fluorescence emission measurements.

The silyl-functionalized benzazole dye was prepared as presented in Figure 2.[16] The reaction consists in the addition of the 3-(triethoxysilyl)propyl isocyanate into the solution of the benzoxazole **1** in ethyl acetate and stirred under reflux yielding the silyl-functionalized benzazole dye **2**.

2-[5′-N-(3-triethoxysilyl)propylurea-2′-hydroxyphenyl]benzoxazole 2

To a solution of 200 mg (0.85 mmol) of 2-(5′-amino-2′-hydroxyphenyl)benzoxazole **1** in ethyl acetate (20 ml) was added 0.25 ml (0.85 mmol) of 3-(triethoxysilyl)propyl isocyanate and heated in reflux for 2 d. The dye **2**, which precipitates in the reaction mixture, was filtered, dried at room temperature, and washed with ethyl acetate. Yield: 85%. Anal. Calcd. for $C_{23}H_{31}N_3O_6Si$: C 58.33%, H 6.66%, N 8.87%. Found: C 58.44%, H 6.62%, N 8.81%. Literature[16] IR (cm^{-1}): 3 320 (ν NH), 2 974 (ν_{alif} C–H), 1 628 (ν C=O), 1 581 and 1 549 (ν_{arom} C=C), 1249 (ν Si-CH$_2$), 1 079 (ν Si-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, OC*H*$_2$); 3.26 (2H, m, C*H*$_2$NH); 1.65 (2H, m, C*H*$_2$); 1.19 (9H, t, OCH$_2$C*H*$_3$); 0.65 (2H, t, C*H*$_2$Si).

In a solution of P750/2-propanol (50% v/v) (8 ml) was added hydrofluoric acid (2% in vol.) and homogenized under stirring for 2 min and the final solution was placed into a polyethylene container. After the gelation, which take place after 15 min, an excess of 2-propanol was added to cover the gel in order to prevent internal solvent evaporation. After 60 min, a solution of the fluorescent dye in 2-propanol ($0.70\ g \cdot l^{-1}$) was added into the container. The molar ratio dye/Si was 4.76×10^{-5} for the gel. The container was closed and placed in an oven at 50 °C (±1 °C) for 3 d. After aging, the doped gel was washed several times with 2-propanol in order to keep out the non-bound dyes and by-products (essentially

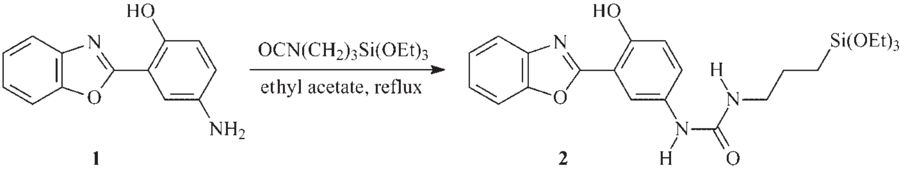


Figure 2.
Scheme of the synthesis of the silyl-functionalized benzazole dye **2**.

ethanol and water). The aerogel was obtained by supercritical CO_2 drying of the wet doped gel.[20]

Results and Discussion

In Figure 3, the UV-Vis absorption and fluorescence emission spectra of the benzazole dye in two different protic-polar solvents (10^{-5} M) are presented in order to rationalize some interactions of the dyes with the silanol groups present in the inorganic matrix. All maximum molar extinction coefficients values are in order of 10^4 $l \cdot mol^{-1} \cdot cm^{-1}$, as expected for π-π^* transitions. The typical UV-Vis absorption spectrum of the dye shows two main bands. A broad band around 355 nm assigned to a π-π^* transition and other around 300 nm, attributed to charge transfer mechanism due to the azole chromophore.[21]

It is well known that the 2-(2′-hydroxyphenyl)benzazole dyes can present a conformational equilibrium in solution in the ground state, where different conformers (E_I-E_{III}) can coexist (Scheme 1). In these species, when excited with UV radiation, only the enol-cis conformer (E_I) is converted to an excited keto tautomer by the ESIPT mechanism which decays emitting fluorescence with a large Stokes shift $(\Delta\lambda_{ST})_{keto}$. In this way, the enol-cis open (E_{II}) and enol-trans (E_{III}) conformers can compete with the keto tautomer responsible to the ESIPT mechanism. When this conformational equilibrium is present, a dual fluorescence emission can be observed, with a band at higher wavelengths ascribed to the ESIPT mechanism and a blue shifted one attributed to the other conformational forms which present a normal relaxation.

A dual fluorescence emission can be observed in octanol to the fluorescent dye,

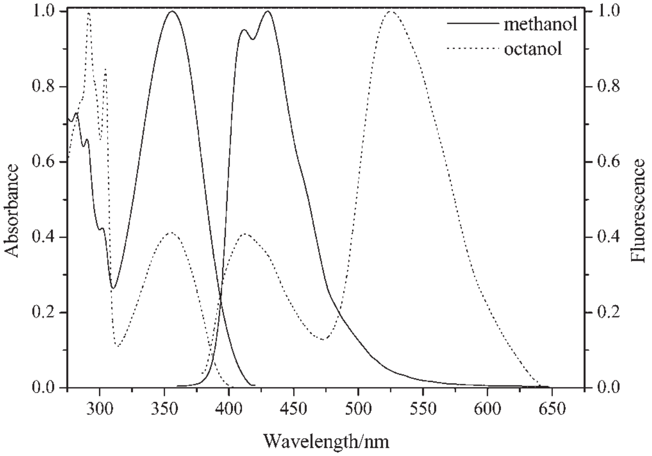
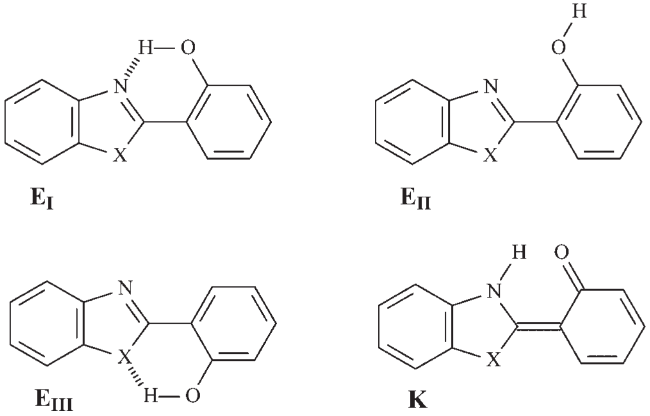


Figure 3.
Normalized UV-Vis absorption and fluorescence emission spectrum of dye **2**.



Scheme 1.

indicating the conformational equilibrium in solution in the ground state. The corresponding ESIPT band is located around 526 nm, with a large Stokes shift (171 nm). The blue shifted band is observed at 413 nm, which is attributed to the E_{II}-E_{III} conformers (Scheme 1). However, in methanol, only one structured band, with a vibrational character, can be observed around 420 nm.

The fluorescent monolithic silica aerogel could be obtained after supercritical CO_2 drying of the wet gel. A representative structure of the derivative covalently bound to the silica matrix is presented in Figure 4. The density (d) of the aerogel was determined by mercury densitometry and presented a value of 0.137 g cm^{-3}. The normalized fluorescence emission spectra in the solid-state of the silyl-functionalized

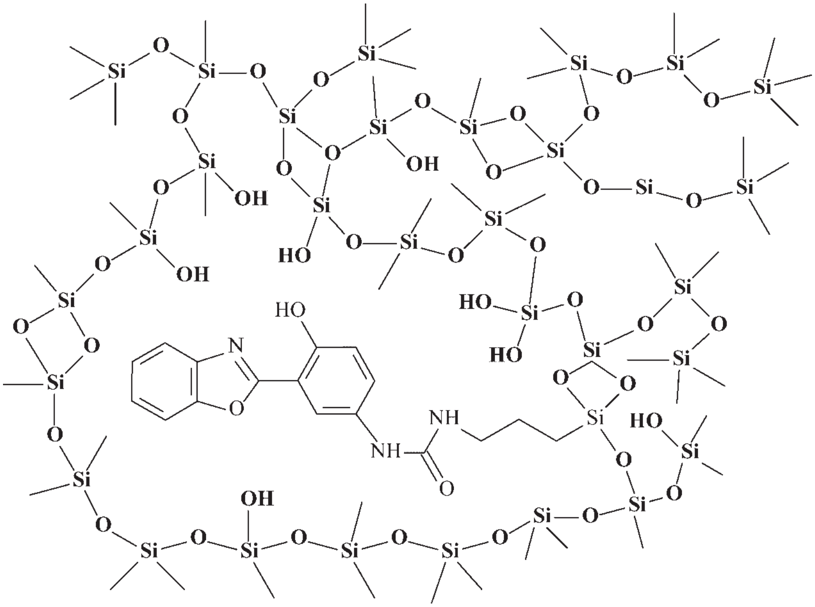


Figure 4.
Benzazole silyl-functionalized dye covalently bound in the silica matrix.

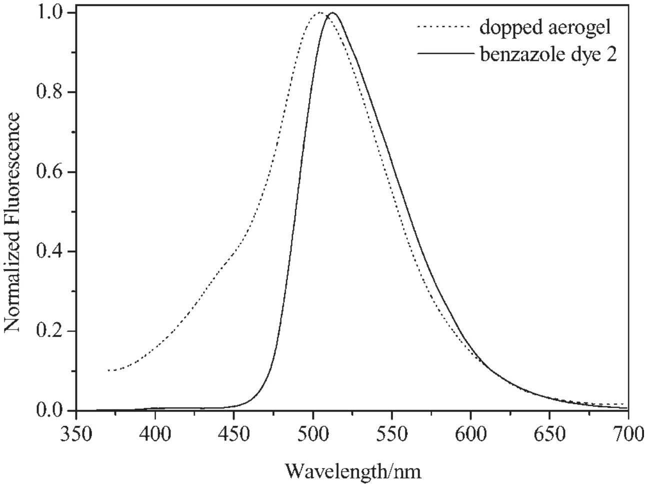


Figure 5.
Normalized solid-state fluorescence of the dye and the doped aerogel.

benzazole dye (solid line) and the aerogel containing this dye covalently bound in the silica matrix (dash line) are shown in Figure 5.

In the solid state, the dye presents a main emission band, described as the ESIPT band, at 514 nm. The corresponding aerogel presents the ESIPT band at 504 nm blue shifted in relation to the dye. The shift of the maximum emission due to dye incorporation in the aerogel indicates an interaction between the dye and silanol groups present in the inorganic matrix, as already observed in similar host/guest materials.[16]

Conclusion

A fluorescent silyl-functionalized benzazole dye and a prepolymerized tetraethoxysilane precursor were used to produce a fluorescent hybrid gel obtained via a specific sol-gel route. Supercritical CO_2 drying was performed in the wet gel to produce the aerogel, highly fluorescent in the blue-green region.

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