Fluorescence behavior of powders and high-pressure compacts of silica containing silyl-functionalized benzazole dyes

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Abstract

Four silyl-functionalized benzazole dyes were covalently bonded in the silica network by sol–gel technique using tetramethyl orthosilicate (TMOS) as inorganic precursor. High-pressure technique was used to produce fluorescent and transparent compacts of grafted silica at 6.0 GPa and room temperature. The excited state intramolecular proton transfer (ESIPT) mechanism of the benzazole dyes in the grafted silica powders and compacts was investigated by steady-state fluorescence spectroscopy.
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1. Introduction

Organic molecules that present a photophysical process known as ESIPT have generated a lot of interest in many fields. ESIPT structural changes may be the driving mechanism for optical sensing [1], non-linear optical materials [2], dye laser [3,4], scintillation detectors [5], fluorescent probes to labeling proteins [6] and probing nanocavities [7]. 2-(2′-Hydroxyphenyl)benzazole (HPB) molecules are important dyes that exhibit ESIPT mechanism and it is well known that in solution, more than one molecular species are found in the ground state, related to tautomerism. In Scheme 1 are showed the tautomeric forms I and II involved on the ESIPT mechanism, which causes a fluorescence emission with large Stokes shift, called F_2. The tautomeric forms (III), (IV) and (V) present the primary emission, called F_1, so these solutions can present dual emission [8–15]. The proton transfer of HPB dyes is influenced by different hosts or media and it has been clearly demonstrated in some works like: the rigid-rod or main-chain [16,17], PMMA [18,19] and silica [20–24]. The photophysical behavior of these dyes in a solid media reveals many useful excited state properties and leads to several different assignments in fluorescence spectroscopy for HPB [16–19]. Additionally, the covalent binding of the triethoxysilylated HPB dye within a silica matrix is interesting since an improvement in photostability can be achieved.

In this work, in order to acquire a better understanding of the excited state behavior of HPB dyes in solid media, the grafting of these dyes was accomplished in a silica matrix by the sol–gel method. To obtain grafted silica, triethoxysilane group was bound directly on 2-(2′-hydroxyphenyl)benzoxazole and 2-(2′-hydroxyphenyl)benzothiazole dyes, previously synthesized [22,23], allowing its covalent anchoring during the inorganic polymerization. In order to obtain dense, transparent, chemically and mechanically resistant optical materials, it was used the high-pressure technique to compact the grafted silica powders at 6.0 GPa and room temperature. The high-pressure promotes a cold sintering process that results in a very efficient and alternative method to produce stiff compacts with closed pores without dye destruction and highly resistant to leaching [25].
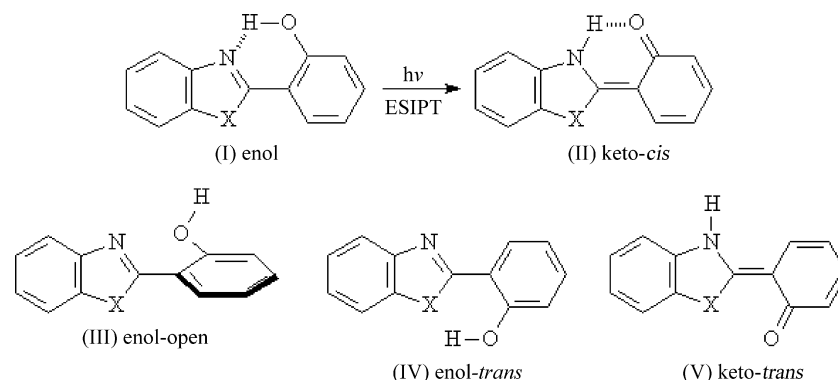
2. Experimental

The triethoxysilylated HPB dyes were synthesized starting from amino benzazoles (Fig. 1) and 3-(triethoxysilyl)propyl iso-

(I) enol $\xrightarrow[\text{ESIPT}]{h\nu}$ (II) keto-*cis*

(III) enol-open   (IV) enol-*trans*   (V) keto-*trans*

Scheme 1. Structures of HPB dyes and its tautomer (X = O, S, NH). Keto-*cis* tautomer exists only in the excited state.

cyanate in ethyl acetate under reflux temperature, as previously described [22,23]. The grafted silica powders were prepared by hydrolysis and polycondensation of TMOS in water and ethanol solution under acidic conditions, with 2.0×10^{-4} M of the dyes. This concentration is low because the poor solubility of the dyes in ethanol. The silylated dyes were previously dissolved in ethanol (5 ml) and added to TMOS (5 ml). A separate solution of hydrofluoric acid (HF 40 wt.%, 0.1 ml) in distilled water (1.6 ml) was dropped in the solution of TMOS together with the dye, in a continuous mixing for about 5 min. This mixture was divided among three small plastic dishes with diameter of about 3 cm and covered without sealing. Polycondensation, drying and aging was accomplished in air, at room temperature for about 20 days. The monoliths were washed exhaustively with various solvents (chloroform, ethanol and *N,N*-dimethylformamide) up to no dye were detected in the washing solution by UV–vis absorption. Finally, the monoliths were dried for 30 min in an oven at 100 °C. The resulting monoliths were comminuted in an agate mortar to obtain grafted silica powders. In order to obtain compacts, these powders were first pre-compacted in a piston-cylinder type apparatus to approximately 0.1 GPa, and then placed inside a lead container with internal diameter of 8 mm, which acts as a quasi-hydrostatic pressure transmitting medium. The compaction was accomplished in a toroidal-type high-pressure chamber at 6.0 GPa and room temperature, during 10 min to promote the cold sintering process. In Fig. 1 is showed the preparation scheme of the grafted silica powders and compacts.
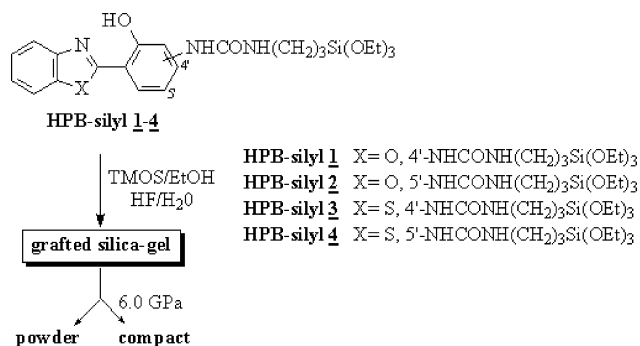
HPB-silyl 1–4

TMOS/EtOH
HF/H$_2$0

grafted silica-gel

HPB-silyl **1**   X= O, 4'-NHCONH(CH$_2$)$_3$Si(OEt)$_3$
HPB-silyl **2**   X= O, 5'-NHCONH(CH$_2$)$_3$Si(OEt)$_3$
HPB-silyl **3**   X= S, 4'-NHCONH(CH$_2$)$_3$Si(OEt)$_3$
HPB-silyl **4**   X= S, 5'-NHCONH(CH$_2$)$_3$Si(OEt)$_3$

6.0 GPa

powder   compact

Fig. 1. Grafted silica prepared by sol–gel synthesis with HPB-silyl dyes.

Steady-state excitation and fluorescence spectra were measured with a Hitachi spectrofluorometer model F-4500. The fluorescence spectra for both liquid and solid samples were obtained with an excitation wavelength of 355 nm and the excitation spectra were obtained using the corresponding maximum wavelength for the emission spectra of each sample. The front face illumination was the geometry used for solid samples to reduce inner filter effects. The spectra of the powders and the compacts were acquired at the same day. In order to detect possible leaching of the dye on the washing solution of the monoliths, UV–vis absorption spectra were performed on a Perkin-Elmer Lambda 16 spectrophotometer.

The specific surface area of the powders and compacts were determined from the BET multipoint method using N$_2$ adsorption isotherms in a home-made volumetric apparatus. The SEM (scanning electron microscopy) images were obtained using a JEOL model JSM 5800 microscope, with 20 kV and a magnification of 23,000× and 33,000×.

3. Results and discussion

The dyes were chemically bound to Si–O–Si network through silyl-functionalization obtaining grafted silica named HPB-silyl **1–4**, as shown in Fig. 1. The grafted silica powders have a surface area of 305 ± 15 m^2/g almost the same value obtained for the silica powder without dye. Fluorescent grafted silica compacts containing a triethoxysilylated HPB dyes were obtained combining sol–gel synthesis and high-pressure technique at room temperature. A surface area of 35 ± 2 m^2/g was measured for these compacts, showing a significant reduction when compared to the powder, indicating an effective compaction. Additionally, the SEM image of the grafted silica materials showed homogeneous pore dispersion, with the network structure being drastically reduced after the compaction. Fig. 2 shows the electron micrography of the HPB-silyl **3** in a silica matrix before and after compaction.

Figs. 3a–6a show the excitation and fluorescence spectra of the HPB-silyl **1–4** dyes in the solid state, in chloroform (CHCl$_3$) and ethanol (EtOH) solutions and Figs. 3b–6b show the excitation and fluorescence spectra of grafted silica powders and compacts. The photophysical behavior observed for the powder and compact samples after washing assure that the dyes
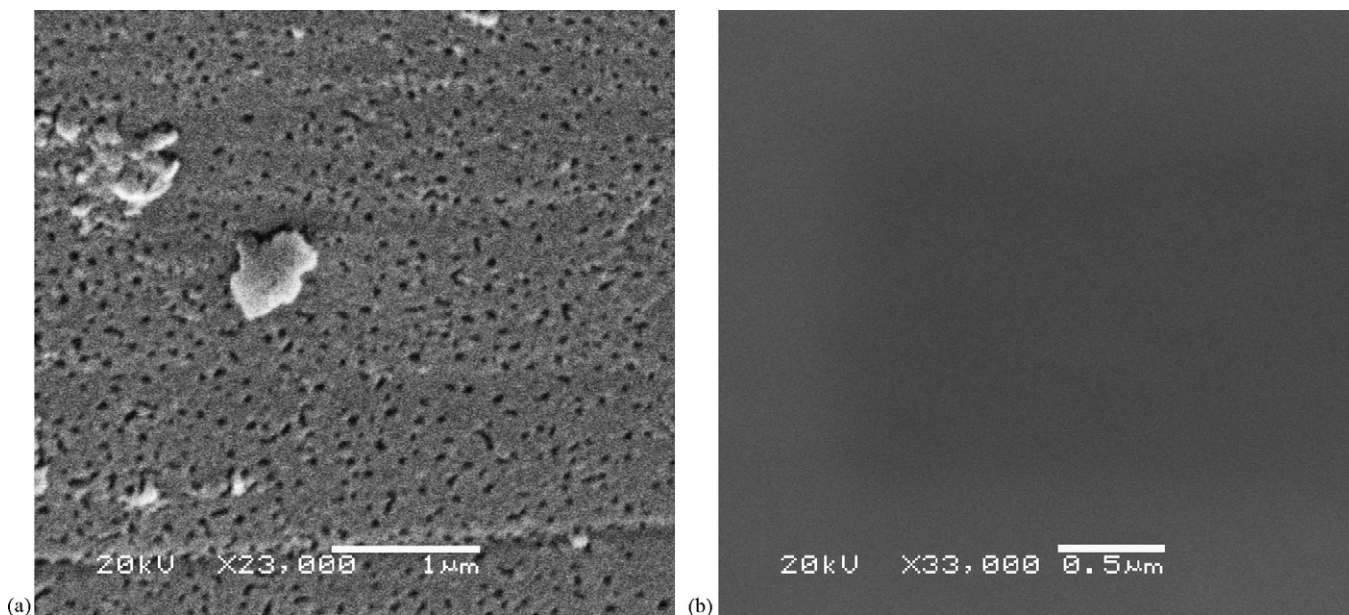
Fig. 2. SEM micrograph of HPB-silyl **3** in a sol–gel matrix (a) before and (b) after high-pressure compaction.

were really grafted in the silica network. This behavior indicates that the molecular structure of the chromophores is maintained after polycondensation and the high-pressure compaction did not destroy the dye molecules.

The excitation spectra for the grafted silica with HPB-silyl **1**–**2** are similar to the excitation spectra of the dyes in solid state, whereas for the HPB-silyl **3**–**4**, there are some differences, as can be observed in Figs. 3–6. However, in all cases the excitation spectra of grafted silica are broadened and redshifted (about 30 nm) compared to those HPB-silyl **1**–**4** dyes in chloroform, indicating strong interactions in the solid environment. It could be interpreted by strengthening of π conjugation in the rigid system, since neither dimers nor aggregates of the dyes were observed [23]. Furthermore, the excitation spectra monitored at different wavelength (not shown here) remained unchanged.

For HPB-silyl **1**–**4** the fluorescence spectra in chloroform consist of two emission bands, one named normal emission (F_1) and the other, which exhibits a large Stokes shift, named ESIPT emission (F_2). In the strongly hydrogen-bonding ethanolic medium, intermolecular hydrogen bonding (IHB), favoring the enol-open emission (structure III in Scheme 1), was observed. In the solid state, the dyes show only F_2 emission band, with exception of HPB-silyl **1**, which presents a dual emission.

The fluorescence spectra of the dyes covalently bond in silica powder and compact differ markedly from the dye in solution and in the solid state. These spectra are independent of the excita-
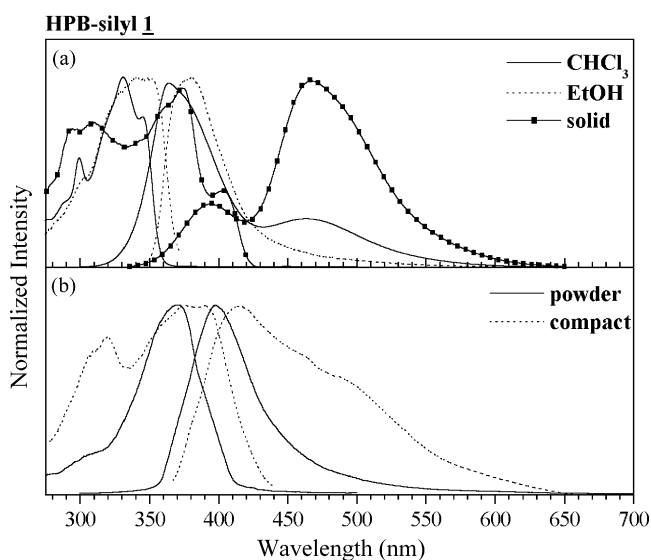

Fig. 3. (a) Excitation and fluorescence spectra of HPB-silyl **1** in the solid state and in solution (chloroform and ethanol). (b) Excitation and fluorescence spectra of HPB-silyl **1** grafted silica, powder and compact.
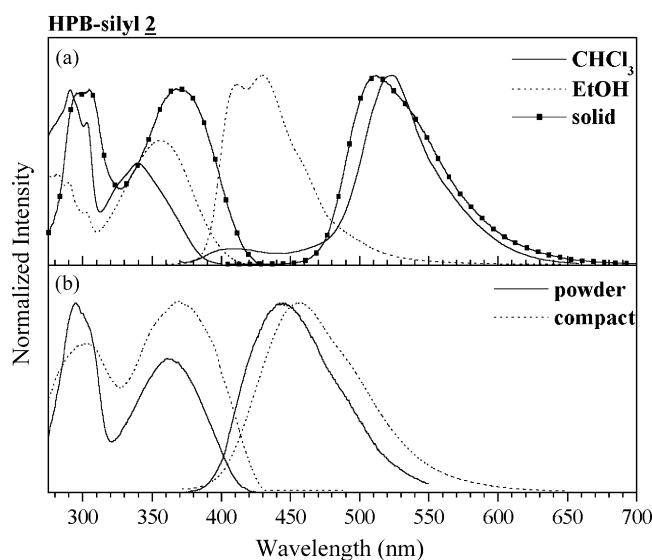

Fig. 4. (a) Excitation and fluorescence spectra of HPB-silyl **2** in the solid state and in solution (chloroform and ethanol). (b) Excitation and fluorescence spectra of HPB-silyl **2** grafted silica, powder and compact.
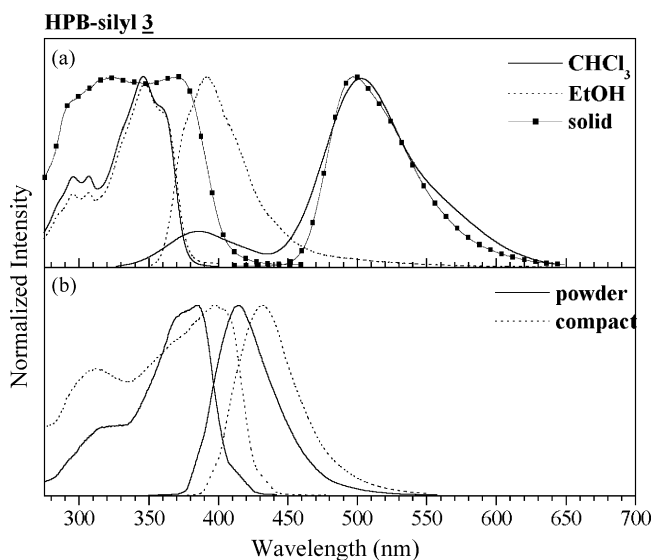
HPB-silyl 3

Fig. 5. (a) Excitation and fluorescence spectra of HPB-silyl **3** in the solid state and in solution (chloroform and ethanol). (b) Excitation and fluorescence spectra of HPB-silyl **3** grafted silica, powder and compact.

tion wavelength. The grafted silica powders with dyes HPB-silyl **1–4** show emission bands located at 398, 442, 413 and 479 nm, respectively, and for the compacts, these bands are redshifted to 416, 455, 432 and 494 nm. This redshift observed for all samples could be attributed to the increasing in the conjugation of the π system [21]. Comparing the spectra, it is evident that the solvated tautomer (III-enol open), as well as, the ESIPT tautomer (II keto-*cis*) were not presented in the grafted silica samples. All-important, in the silica matrix the emission maximum exhibits a small Stokes shift (<100 nm) indicating that the ESIPT does not occur neither in the powders and nor in the compacts. The data observed here have implications for understanding our recent works concerning the study of optical
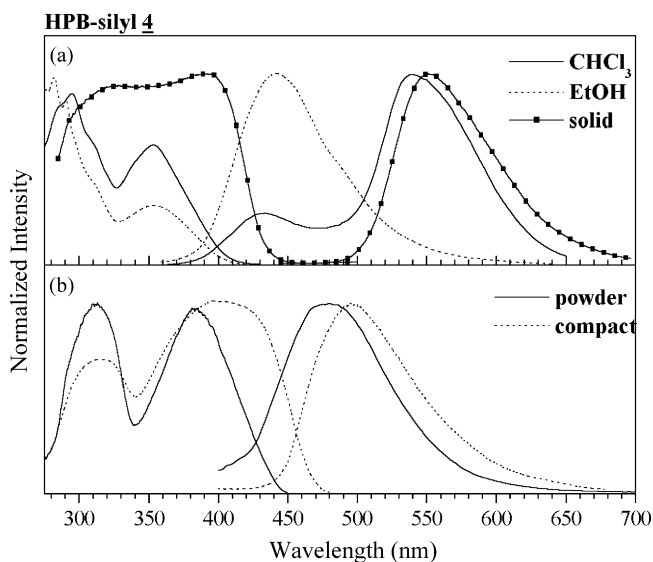
HPB-silyl 4

Fig. 6. (a) Excitation and fluorescence spectra of HPB-silyl **4** in the solid state and in solution (chloroform and ethanol). (b) Excitation and fluorescence spectra of HPB-silyl **4** grafted silica, powder and compact.

properties of HPB dyes entrapped and/or covalently bonded into silica matrices [20,23]. Costa et al. demonstrated that for another molecule, called BIS-HPB dye, only entrapped in silica matrix, the fluorescence spectra were very dependent on the aging and on the solvent content of the monoliths. These monoliths achieved stability after 1 month, however with a decrease of ESIPT band intensity [20,21]. The powders obtained from these monoliths were processed at high-pressure and an interesting result was observed: the ESIPT band intensity was restored. This effect was explained by the reduction in the interaction of the intermolecular hydrogen bonding of the dye with the silanol groups of the matrix, and in this case, even in an OH rich environment like silica, ESIPT was restored [21]. In the present work, the photophysical behavior of HPB dye is completely different, not only because the dye was covalently bonded in the silica network, but also because this molecule presents many tautomeric forms, differently from BIS-HPB. In the present case, where the covalent attachment of the dye with silica takes place, the ESIPT mechanism could be affected and more than one species could be in equilibrium in the inorganic matrices [22,23].

The nature of the new emission band, in detriment of the ESIPT emission, is formed with the assistance of the silica matrix and after the grafting. As already mentioned, the rigidity of the silica network can play an important role in the photophysical behavior of molecules that exhibit ESIPT [26,27]. The fact that ESIPT emission does not occur in rigid-rod (organic) polymers have been studied and it was suggested that it could be due to an increase in the energy barrier on the excited state promoted by the extended conjugation [16]. On the other hand, effects of concentration quenching, molecular size and competition with excimer formation will lead to incomplete proton transfer and emission from another species [17]. Effects of concentration quenching are ruled out by us as the source of the energy barrier to ESIPT in powders and compacts because the concentration of the dye in the grafted silica is very low. The excimer pathway, that is known to be concentration-dependent, was not investigated because of the poor solubility of the dye in ethanol. We propose that the fluorescence emission of the dyes **1–4** in the silica matrix is similar to that observed by Mintova et al., in the work where they reported the incorporation of a HBT dye inside supercages of nanosized FAU zeolite [24]. These authors support the hypothesis that fluorescence of HBT-FAU is attributed to the presence of the keto-*trans* tautomer (V), showed in Scheme 1. The excitation and the fluorescence spectra showed in Figs. 3b–6b are very similar to that tautomer, which absorbs at longer wavelength than the enol (I) and the emission is redshifted respect to the enol-open tautomer (III) and blueshifted respect to the keto-*cis* tautomer (II). However, more experimental evidence is needed to elucidate the photophysics behavior of these hybrid organic–inorganic materials. It was observed in the present work, that the effect of high-pressure on the fluorescence is only a redshift of about 20 nm, which still allows violet–blue emission fluorescence. It is very interesting because the blue emission is an important wavelength for optical storage, solid state laser dyes and scintillation detectors.

Another interesting result is that the photophysical stability of these dyes in the high-pressure compacts remained for more
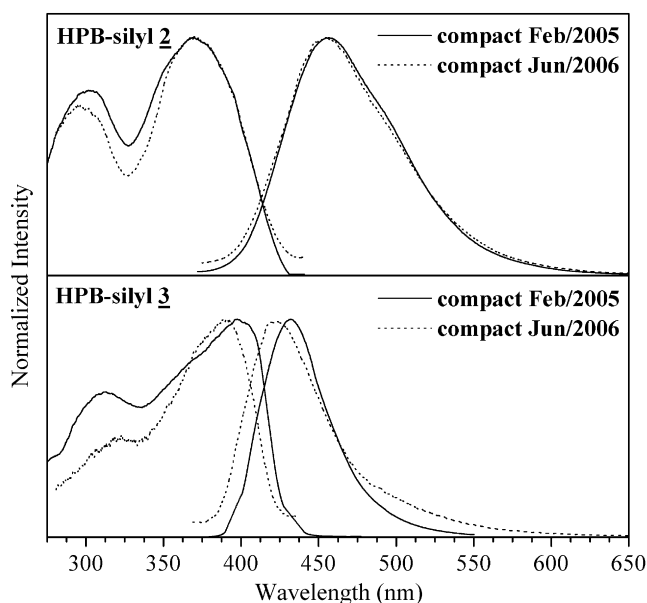
Fig. 7. Comparison of excitation and fluorescence spectra of compacts with HPB-silyl **2** and HPB-silyl **3**, performed with a time interval of 18 months, measured in the same samples.

than a year, as far as we could observe. Fig. 7 shows a comparison between excitation and fluorescence spectra of samples containing the HPB-silyl dyes **2** and **3**, obtained after 18 months. These samples were stored with no special care, which means, in an open box without controlled atmosphere, or temperature. It can be observed that for HPB-silyl dye **2**, the reproducibility of the fluorescence spectrum is excellent. For HPB-silyl dye **3**, we can observe a small shift to lower wavelength, but the fluorescence is still in the blue range, as it was measured more then a year later.

4. Conclusions

The fluorescence behavior of triethoxysilylated benzazole dyes covalently bonded in a silica matrix was investigated. The grafted silica powders were prepared by hydrolysis and polycondensation of TMOS in water and ethanol solution under acidic conditions. High-pressure technique was used to produce fluorescent, transparent and hard compacts of silica at 6.0 GPa and room temperature. The emission features of the dyes in solution were correlated to that grafted silica. The emission properties of the dyes in silica matrix are completely different from liquid solutions. For both, powder and compact samples, the ESIPT emission was not observed, however it was observed an intense blue emission for the compact samples and this emission remained for a time interval of 18 months, as long as we could monitor, showing a photophysical stability for these high-pressure compacts.

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