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Short note

Dispersion and photoluminescence of free-metal phtalocyanine doped in sol–gel polyphenylsiloxane glass films

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Abstract

The optical absorption and photoluminescence of metal-free phtalocyanine (H_2Pc) in a glassy matrix were discussed regarding the preparation method used. We show that fluorescent monodisperse free metal phtalocyanine can be doped in polyphenylsiloxane glass films using a non-aqueous sol–gel derived method. No fluorescence study of metal-free phtalocyanine doped in polysiloxane sol–gel materials has been reported so far due to the miscibility problem of the dye and its aggregation behavior in aqueous sols.

Keywords: Phtalocyanine; Fluorescence; Polyphenylsiloxane; Non-aqueous sol–gel coating

1. Introduction

There is a great interest in incorporating phtalocyanines dyes in a host solid matrix. Phtalocyanines are one of the organic molecules that have received considerable attention because of their potential applications in a variety of fields [1] due to their semi-conductivity, photoconductivity, stability and optical absorption in the UV–vis region. Some of the most important applications of these organic molecules are in the fabrication of the solar cells, electronic displays [2], chemical sensors and biosensing [3] but also as efficient laser dyes with an increasing interest for application in non-linear optics (including optical limitation) [4]. It is well-known that porphyrins are representative of photofunctional organics, and they show remarkable photo-, electro- and biochemical properties and that contributes to light harvesting by their strong absorption in photosynthesis.

Here, we focused on organic–inorganic hybrid polysiloxane-based glass as a host matrix for the development of new metal-free phtalocyanine-doped glass films. Metal-free phtalocyanine is only soluble in chloronaphtalene, therefore, no study on the photoluminescence and more generally on the optical properties of such metal-free phtalocyanine-doped sol–gel glasses films materials were reported. In fact, the conventional sol–gel coating route involving coating sols composed of a mixture of alkoxysilanes in an aqueous media with ethanol, water, and acid catalyst, do not permit the miscibility and homogeneous dispersion of the dye. The sols generally led to extra complexities arising from accelerated chemical reaction caused by solvent evaporation and viscosity changes being driven by the hydrolysis and condensation reactions occurring during coating [5].

It was then important to find a simple and easy way matching with these miscibility conditions in order to obtain well-dispersed dye doped materials and study in detail these new materials with the aim to know better about the optical properties and the aggregation states of the dye in such glass system. This study is therefore of practical consequence as well as scientific interest.

Recently, we successfully derived the sol–gel route by the so-called gel-melting method [6] to obtain phenylsilsesquioxane–diphenylsiloxane-based glass $(1-x)\mathrm{PhSiO}_{3/2}$–$(x)\mathrm{Ph}_2\mathrm{SiO}_{2/2}$. This glass system exhibits low-softening temperature (<200 °C) and high stability in organic solvents (such as acetone, acetonitrile, alcohols, dichloromethane, tetrahydrofuran, cyclohexane, chloronaphtalene). Neither phase separation nor decomposition of the glass occurred when the polysiloxane-based glass was dissolved in these solvents. We used this property to obtain highly

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transparent and homogeneous coating sols by solubilizing the polyphenylsiloxane with the solvent and obtain polyphenylsiloxane films via spin-coating technique at room temperature [7]. In this process, the phenyl/diphenyl hybrid low-melting glass matrix is already formed and when a dye solution in the appropriate solvent is added to the host matrix, in contrast with the conventional sol–gel coating method, the coatings are not affected by any miscibility problem during hydrolysis and polycondensation.

From this tremendous possibility, we are eager to characterize the optical properties of metal-free phtalocyanine doped in such solid host matrices. Here we discuss the dispersion and the photoluminescence of the metal-free phtalocyanine dye in the polyphenylsiloxane hybrid system owing to the method used.

2. Experimental

The preparation of H_2Pc doped films using the hybrid polyphenylsiloxane glass system $(1-x)PhSiO_{3/2}$–$(x)Ph_2SiO_{2/2}$ ($x = 0.2$) has been carried out *via* a non-aqueous sol–gel derived method that can be described as follow: the preformed non-doped polyphenylsiloxane glass was obtained following the gel-melting method procedure. Typically, phenyltriethoxysilane (19.22 g, 80 mmol, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) is added dropwisely at room temperature in the aqueous solution composed of distilled water (5.04 g, 280 mmol), ethanol (23.02 g, 500 mmol, Nacalai Tesque, Ltd., Japan, 99.5%) and hydrochloric acid (0.036 g, 1 mmol) used as acid catalyst. The reaction mixture was left under stirring at room temperature for 3 h prior to add dropwisely diphenyldiethoxysilane (5.44 g, 20 mmol, Shin-Etsu Chemical Co., Ltd.). The solution mixture was left under stirring until complete evaporation of the solvent. The gel formed was heat-treated during 2 h under vacuum at 125 °C, and transparent doped-glass was obtained. To obtain the coating sol, the polyphenylsiloxane glass (4 g) was dissolved homogeneously under an ultrasonic bath for 10 min by addition of the dye solution of concentration (0.06 g H_2Pc/10 ml chloronaphtalene). The films were prepared via the spin-coating technique at room temperature at different rotational speed step. First, a thick layer solution (0.35 ml) is applied on the substrate covering its surface area and during rotation, the sol flows radially outward. Prior to spinning, latency times of 1 min were necessary to consistent and uniform the gel layer. The second stage is characterised by the low-speed (100 rpm for 900 s) as the fluid thin enough that the viscous shear drag exactly balances the rotational accelerations. The following stages consist of spinning successively at 300, 500 and 800 rpm for 30 s with a latency time of 1 min between each step. Prior to coating, silica substrates were cleaned in a sequence of solvents (water, methanol and acetone) and heat-treated at 600 °C for 30 min. The doped low-melting glass thick-films were obtained after heat-treatment of the gel-films at 125 °C under vacuum for 30 min to remove chloronaphtalene from the films. The concentration of phtalocyanine in the films was further determined using the Beer–Lambert relation from UV–vis spectra.

For a comparative study, we tried to prepare the coating sol via the conventional sol–gel method, the dye is added in a solution mixture containing phenyltriethoxysilane, diphenyldiethoxysilane and the aqueous media composed of water, ethanol and hydrochloric acid using the same molar ratio as for the non-aqueous sol–gel route. The reaction mixtures were then stirred for 3 h at room temperature in order to obtain the coating sol. However, only a partial miscibility of the dye occurred. To remove any residual dust and potential non-dissolved H_2Pc, the coating sol obtained were filtered using a using a 0.2 μm PTFE membrane (Millex, Millipore Corp.) mounted on a plastic syringe.

The films obtained were characterized using the Atomic Force Microscopy for the roughness measurements recorded on a WITec Scanning Near-field Optical Microscope Alpha*SNOM* capable of AFM measurements. The optical absorption spectra of the films were recorded using UV–vis–NIR U 3500 Hitachi spectrometer. The fluorescence emission and excitation spectra were measured on a Hitachi U-850 spectrofluorometer.

3. Results and discussion

Coatings from phtalocyanine-containing sol are not so easy taking in account the solubility problems of the dye in the most common solvents. When phtalocyanine with chloronaphtalene (0.06/10 ml) was added through the aqueous media containing EtOH, H_2O, and HCl, in presence of $PhSi(OEt)_3$ and $Ph_2Si(OEt)_2$ for the preparation of the coating sol from the conventional sol–gel coating method, a blue precipitate forms quite readily suggesting a partial miscibility of the dye through the aqueous media (Fig. 1(a)). Phenyl–diphenyl hybrid glass system presents the advantage to dissolve in the most common organic solvent and to remain stable. These properties represent an important issue to the miscibility problem. The homogeneous sol (Fig. 1(b)) composed therefore of the low-melting glass and phtalocyanine in chloronaphtalene can be used for coating.

The phtalocyanine doped-films obtained were homogeneous and stable against the ambient atmosphere. The coating surface measured by atomic force microscopy for a film of 61 μm thick showed a very smooth surface with an average roughness estimated to 3.47×10^{-3} μm within 50 μm × 50 μm area.

The optical absorption (Fig. 2(a)) for the doped-films obtained from the conventional sol–gel method shows the low and broad absorption band with a peak centred at 625 nm (that differs from the 662 nm absorption of the dye in the pure chloronaphtalene solution) and a shoulder at 700 nm associated, respectively, to the vibronic structure and the main transition. This broad and low absorption band suggests the high aggregation state of phtalocyanine molecules in the film that can be explained by the intermolecular interactions between the phtalocyanine macrocycles leading consequently to the low miscibility of the dye when added through the aqueous media. These interactions are typical for peripherally unsubstituted phtalocyanines and their solubility in aqueous solvents can be improved by introducing substituents (carboxylic acid and sulphonic groups) in the periphery which increases the distance between the planar macrocycle rings carrying the π-electron and making

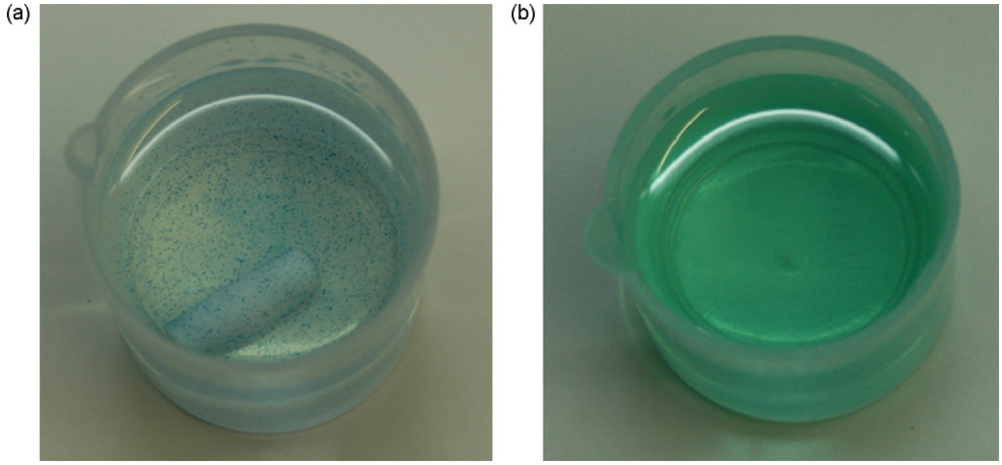

Fig. 1. Photographs of the coating sols obtained: (a) from the conventional sol–gel method and (b) from the method ascribed as non-aqueous with polyphenylsiloxane hybrid directly dissolved in the dye solution of pure chloronaphtalene.

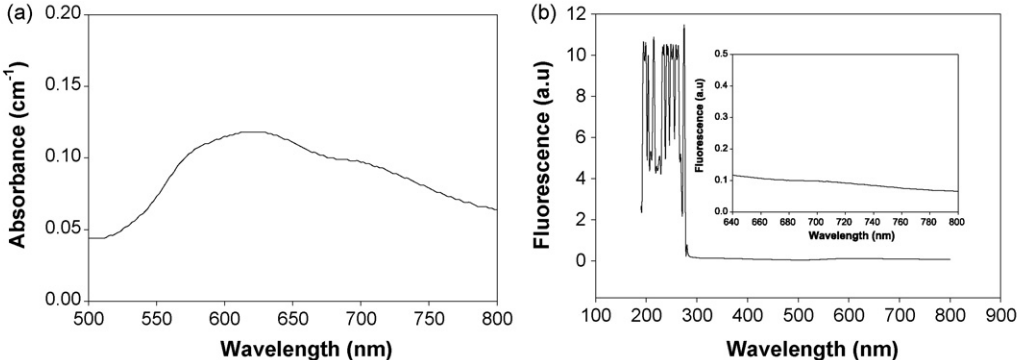

Fig. 2. (a) Optical absorption spectrum and (b) fluorescence spectrum for the film obtained via the conventional sol–gel method. The inset shows that no emissions peaks in the range of 600–800 nm are observed.

the solubilization easier [1]. In fact, the incorporation of the unsubstituted metal-free phtalocyanine in the solution composed of the aqueous media and alkoxysilane precursors led to its aggregation.

The aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and is driven by enhanced van der Waals' attractive forces between phtalocyanine rings. In the aggregated state, the electronic structure of the complexed phtalocyanine rings is perturbed resulting in an alteration of the ground state and excited state properties. Consequently, the high aggregation state is often characterized by a broadening and diminishing of the red absorption band and a blue-shift of the band by 30–50 nm (from 666 to 625 nm). The aggregation (especially in aqueous media) is a very common phenomenon in this family of compounds due to their large π-conjugated systems, which reduces their optical properties such as their photosensitizing efficiency. According to the exciton coupling theory, the dimer conformation causes the individual monomeric singlet levels to split into pairs of new states. In this geometry, the HOMO–LUMO optical transition is allowed only to the upper dimmer level (accounting for the blue-shift of the Q-band for most phtalocyanine dimers), whereas the transition from the lowest excited singlet level to the ground state is optically forbidden, so that most phtalocyanine dimers

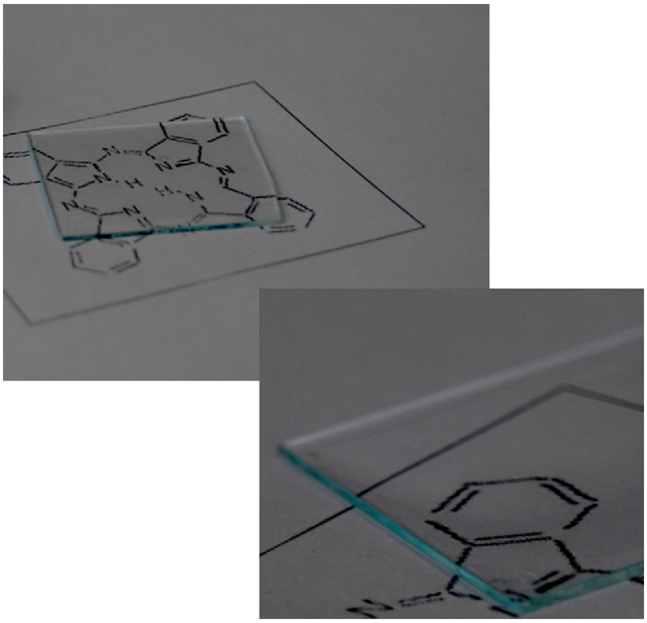

Fig. 3. Photograph of the H_2Pc-doped polyphenylsiloxane glass film obtained via the non-aqueous coating sol composed of polyphenylsiloxane glass dissolved in the dye solution of pure chloronaphtalene as solvent. We can notice the fluorescent blue-greenish at the edge of the silica substrate.

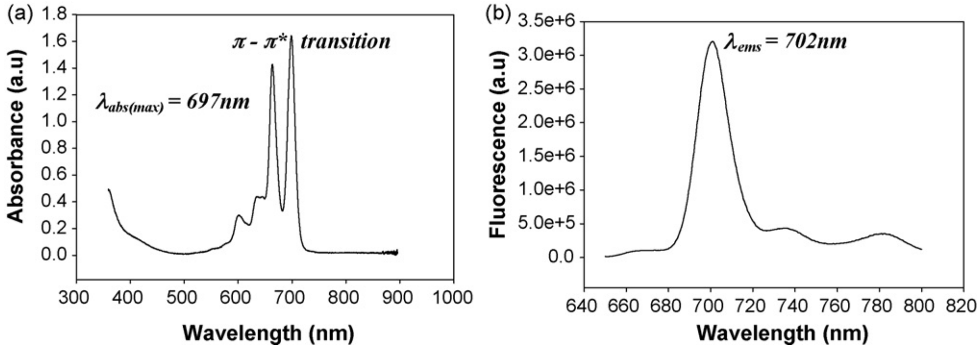

Fig. 4. (a) Optical absorption spectrum and (b) fluorescence spectrum for the phtalalocyanine solution in pure chloronaphtalene.

show no detectable fluorescence [8]. This is confirmed by the photoluminescence spectrum (Fig. 2(b)) for the film obtained via the conventional aqueous sol–gel method and that shows no emission.

In contrast, the non-aqueous route involving the dissolution and solubilization of the preformed hybrid glass with the dye solution in the pure chloronaphtalene solvent, permit us to have fluorescent doped-films. The films were transparent and show a fluorescent bluish-green colour (Fig. 3) at the edges of the substrates. It has been possible for us then to discuss the different intermolecular interactions between the individual phtalocyanine molecules within the solid host matrix compared to the phtalocyanine molecules in pure chloronaphtalene solutions.

Indeed, the absorption spectra (Fig. 4(a)) of phtalocyanine solutions in the pure chloronaphtalene exhibit the more intense absorption band at $\lambda_{\mathrm{abs_{max}}} = 697$ nm accompanied to lower intense bands at 596, 631 with a shoulder at 638 nm and 662 nm. Fluorescence spectrum (Fig. 4(b)), shows emission bands at 668, 740, 785 nm with a maximum intensity at 702 nm $(\Delta\lambda)_{1/2} = 18$–19 nm. The free-metal phthalocyanine (H_2Pc) shows two absorptions in solution (at 662 nm $(\Delta\lambda)_{1/2} = 20$ nm and at 697 nm $(\Delta\lambda)_{1/2} = 19$ nm) owing to the lower symmetry of the compound and the splitting in the π–π^* transition that this induces. The small peaks observed at shorter wavelengths than the main Q-band are additional components of the Q-band resulting from vibronic fine structure. It is known that vibronic structure in phthalocyanines is sensitive to the deviation of the phthalocyanine ring from planarity [9].

Comparatively to the films, it is clear that the nature of the phtalocyanine and its physical state has a significant bearing on the wavelength of the Q-band and even how many peaks are seen. The effects of applying the phtalocyanines as solid glass thick-films (the concentration of phtalocyanine in the film determined by the Beer–Lambert law is of 4.87×10^{-5} M) result in a sharp and intense absorption band at $\lambda_{\max} = 666$ nm $(\Delta\lambda)_{1/2} = 44$ nm, a less intense one at 702 nm $(\Delta\lambda)_{1/2} = 36$ nm. Additional peaks at shorter wavelengths 610 and 637 nm are much broader due to the extensive excitonic coupling (Fig. 5(a)). This phenomenon is often referred to as 'Davydov splitting'. A cofacial arrangement and interaction of molecules leads to a blue-shift in absorption, whereas an edge-to-edge configuration leads to a red-shift. The interaction of the transition moments (dimer interactions) of molecules at an angle to each other leads to the observation of both red-shifted and blue-shifted bands. This theory can be extended to describe the absorption of infinite stacks, but the interactions are often more complicated. Chau et al. [10] note that any significant disorder within such layers will lead to additional exciton splitting patterns. These spectra also suggest that there may be significant longer-range interaction between non-adjacent Pc molecules in the films. The shape of the absorption spectra for these films is consistent with literature examples [11].

From the fluorescence spectrum, it is worth noting that the doped-film from the coating sol obtained from the non-aqueous route (by direct dissolution of the glass in the dye solution of pure chloronaphtalene as solvent) exhibits a single intense emission band at $\lambda_{\mathrm{ems}} = 707$ nm with a half fluorescence

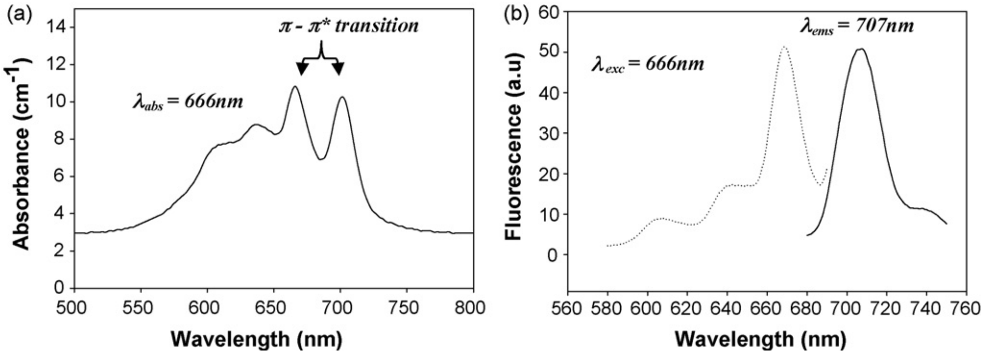

Fig. 5. (a) Optical absorption and (b) excitation (dotted curve) and fluorescence (solid curve) spectra for the phtalalocyanine-doped film (61 μm thick-film with 4.87×10^{-5} M of dye concentration) obtained via the non-aqueous coating sol composed of polyphenylsiloxane glass dissolved in the dye solution with pure chloronaphtalene as solvent.

bandwidth $(\Delta\lambda)_{1/2} = 26$ nm and the excitation band at 666 nm (Fig. 5(b)). The spectrum shows clearly a good dispersion of the dye in the glass films and a comparable wavelength emission peak at 702 nm to the fluorescence spectra of the dye in solution.

4. Conclusion

We have developed a new approach for incorporating dyes into polyphenylsiloxane hybrid glasses to generate functional thick-films. Due to the problem of miscibility of phtalocyanine in most common solvents and consequently the difficulties to obtain well-dispersed dyes in a solid state matrix, the survival of fracture-free doped-glass films makes this synthetic route more of an art. The attractive optical properties of phtalocyanine in the solid host, with particularly intensive absorption spectra and strong enhancement of their emission intensity, leads to promising applications to be investigated in the field of optics and photonics, such as NLO materials and biosensing. In addition, there is the potential to incorporate several dyes and consequently add various functionalities into the system owing to the solubility of the dye in the different solvents. The method can also be used for coating polysiloxane-based glass films on any substrate or support (titania, silica, PET, silicon and so on) which is unique.

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