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Synthesis of transparent and ordered mesoporous silica monolithic films embedded with monomeric zinc phthalocyanine dye

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Monolithic transparent mesoporous silica films embedded with zinc phthalocyanine (ZnPc) have been synthesized and it is shown that the encapsulated ZnPc dye molecules exist predominantly in monomeric form.

Phthalocyanines are a family of aromatic macrocycles based on an extensive delocalized two-dimensional conjugated π electron system, which exhibit a larger number of unique properties.[1] Due to their extensive delocalized π-system and their centrosymmetric structure, phthalocyanines are key targets to study nonlinear optical processes and are found to be very promising candidates for optical switching and optical limiting devices.[2] An ideal optical limiter exhibits linear transmission below a fluence threshold and above this threshold the transmission becomes highly nonlinear, a phenomenon commonly known as reverse saturable absorption. In order to exhibit reverse saturable absorption, a single molecular species is required to possess weak ground state absorption, strong excited state absorption, and a very high intersystem-crossing yield.[3] Many of the dyes used as nonlinear absorbers tend to aggregate at high concentration. The intermolecular interactions caused by aggregation considerably decrease the optical limiting capability of the dye molecules. Maintaining molecular symmetry without any aggregation in order to have a better optical limiting material is a significant challenge. Optical limiting experiments have traditionally been performed on phthalocyanines in solution.[4] However, from a practical point of view, phthalocyanine based solid-state optical limiters are more ideal. Such optical limiters may be achieved by immobilization of phthalocyanines in a solid matrix. Incorporation of dye molecules in the micellar phase of surfactant–silica mesophase has been reported.[5] The encapsulation of transition metal phthalocyanine complexes inside micro and mesoporous molecular sieves or glasses *via* sol–gel routes has also been well studied.[6–9] However, there has not been any detailed study on the state of the encapsulated phthalocyanines. Such information is crucial because the interaction between neighbouring phthalocyanine molecules (dimerisation or agglomeration), largely determines the optical properties. Maintaining the monomeric form of phthalocyanine is a vital consideration in optimizing the optical properties of the dye-doped sol–gel materials. We have studied the dispersion of zinc phthalocyanine within the pores of silica mesoporous molecular sieves (MMS) and here describe the encapsulation of predominantly monomeric phthalocyanine molecules in transparent monolithic (or thin film) composite materials.

The MMS silica thin film–monoliths were prepared by using tetraethyl orthosilicate (TEOS) as a silica source and hexadecyltrimethylammonium bromide (CTAB) as a template. In a typical synthesis, 1 g of CTAB was added to 20 ml of a ethanol–toluene (68 : 32 wt ratio) mixture. (For dye containing films–monoliths, the required amount of ZnPc was added with the toluene.) The resulting mixture was added to a 3 g TEOS solution containing 0.74 g of distilled water and 0.74 g of 0.1 N HCl and subjected to refluxing at 80 °C. After refluxing (at 80 °C) for 5 h, the reaction mixture was concentrated by evaporation using a rotary evaporator in a vacuum at 50 °C. The resulting liquid was then transferred onto a Petri dish, dried slowly and subsequently heated at 125 °C for 2 h. The final mesophase (designated ZnPc–MMS) was a transparent greenish thin film or monolith whose colour varied from pale green to dark green depending on the amount of ZnPc added. We also prepared ZnPc/MMS composites *via* a post-synthesis adsorption route, *i.e.*, calcined (550 °C for 5 h) transparent monoliths–films of MMS were immersed in a ZnPc–toluene solution for 2 h and subsequently dried to remove the solvent.

Fig. 1A shows the typical XRD patterns of the MMS films. The patterns indicate that the silica films possess ordered pore channels as evidenced by the *d*-spacing peak at low 2θ values. As-synthesized ZnPc–MMS films had XRD patterns similar to those of ZnPc free MMS films. On calcination, the films maintained their transparency but were subject to a reduction in the *d*-spacing (typically 3.6 nm) of *ca.* 0.6 nm. Post-synthesis adsorption of ZnPc onto the calcined MMS films (to generate ZnPc/MMS composites) had little influence on their XRD patterns. Fig. 1B shows typical nitrogen sorption isotherms of the (calcined) films before and after impregnation with ZnPc. The isotherms indicate that the films have ordered pore channels in the lower mesopore range. The calcined films typically had a surface area of 1400 $m^2\ g^{-1}$ and pore volume of *ca.* 0.65 $cm^3\ g^{-1}$. As expected, both surface area and pore volume reduced after (post-synthesis) adsorption of ZnPc to *ca.* 1120 $m^2\ g^{-1}$ and 0.60 $cm^3\ g^{-1}$ respectively.

To further characterise the embedded ZnPc, we studied the state (monomer, dimer or aggregates) of the phthalocyanine in ZnPc–MMS films using diffuse reflectance spectroscopy. The linear optical spectra of phthalocyanine compounds are dominated by two bands; the Q-band in the visible region (600–800 nm) and the B-band in the near UV region (300–400 nm). The Q band is very sensitive to the environment of the phthalocyanine molecules, and to changes in the number and orientation of nearest neighbour phthalocyanine in the solid state.[10] The absorption spectra of ZnPc in toluene is shown in Fig. 2a. In solution, the monomer signal (M_{0-0}) of the Q band was found at

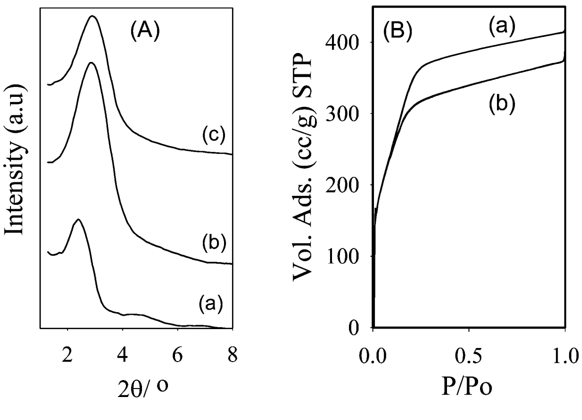

Fig. 1 (A) XRD patterns of (a) as–synthesized (sol-gel route) ZnPc–MMS (b) calcined (550 °C for 5 h) MMS film, (c) ZnPc/MMS (*i.e.*, ZnPc in calcined MMS prepared *via* post-synthesis adsorption of ZnPc) and (B) nitrogen sorption isotherms of (a) calcined MMS film and (b) ZnPc/MMS (0.45 μM ZnPc).

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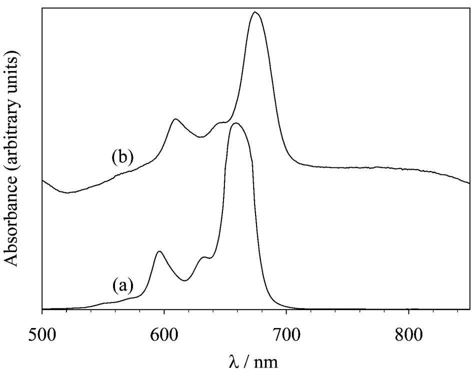

Fig. 2 (a) Absorption spectrum of ZnPc in toluene and (b) diffuse reflectance spectrum of ZnPc embedded in MMS mesophase (*i.e.*, as-synthesized ZnPc–MMS).

660 nm. This is the (0–0) transition from the HOMO to the LUMO.[11] A second characteristic band lies at *ca*. 600 nm; this is the (0–1) transition from HOMO to the first overtone of the LUMO.[11] The bands at *ca*. 600 and 660 nm are indicators of monomeric phthalocyanine. The shoulder at *ca*. 630 nm is usually attributed to dimers or aggregates. Fig. 2a is therefore consistent with the fact that, in solution, ZnPc exists predominantly in monomeric form. The diffuse reflectance spectrum of the as-synthesized ZnPc–MMS mesophase is shown in Fig. 2b. It is interesting to note the similarities (shape and number of peaks) of the two spectra in Fig. 2. This similarity indicates that the phthalocyanine in ZnPc–MMS exists in the same manner as ZnPc in toluene solution, *i.e.*, predominantly in monomeric form. Such monodispersion of the phthalocyanine may be attributed to the incorporation of the ZnPc in the hydrophobic region of the surfactant micelles. The ZnPc may also interact directly with the MMS mesostructure. For the ZnPc–MMS (Fig. 2b), the position of the Q band exhibits a 16 nm red shift (compared to ZnPc in toluene solution) to *ca*. 676 nm due to a change in the chemical environment. It is plausible that the MMS mesophase provides a favourable environment to accommodate the ZnPc molecules effectively trapping them in a manner that does not allow aggregation or intermolecular interaction. The homogeneity of ZnPc distribution in the MMS host can be verified from the sharpness of the Q-band.[6] By comparing the full width at half maximum (FWHM) of the Q bands of spectrums a and b in Fig. 2, it can be concluded that the ZnPc molecules are embedded uniformly into the MMS host.

Typical diffuse reflectance spectra of ZnPc/MMS composites (at various ZnPc content) prepared *via* post-synthesis adsorption and a physical mixture of ZnPc and MMS are shown in Fig. 3. We first note that a typical spectrum for ZnPc/MMS composites (*e.g.* containing *ca*. 0.45 µM ZnPc) exhibits peaks characteristic of monomeric phthalocyanine. In Fig. 3 (spectrum a), the characteristic monomer peaks (observed at *ca*. 680 and 625 nm) are red shifted by *ca*. 20 nm compared to ZnPc in solution. We also note that the spectrum of a physical mixture of ZnPc and MMS (spectrum c, Fig. 3) indicates, as expected, that the phthalocyanine exists predominantly as dimers or aggregates; the monomer peak at 680 nm is much reduced while the dimer–aggregate peaks at *ca*. 640 and 720 nm are very prominent. We can therefore infer from the spectra that phthalocyanines in ZnPc/MMS composites are embedded within the calcined MMS pores predominantly in monomeric form. The strong red shift (*ca*. 20 nm) of the Q band observed for ZnPc/MMS is consistent with a change in chemical environment (compared to ZnPc in toluene solution); it is likely that the ZnPc molecules are adsorbed onto the pores of the MMS where their π electrons interact with the surface hydroxyl groups of the calcined MMS host.[12] Interestingly, an increase in the amount of ZnPc adsorbed on the MMS leads to aggregation of the embedded ZnPc, as shown in Fig. 3, spectrum b. At a ZnPc content of 0.9 µM, the resulting ZnPc/MMS composite exhibits a spectrum with reduced monomer peaks (at *ca*. 625 and 680 nm), an emerging dimer–aggregate peak at *ca*. 645 nm and broad bands at *ca*. 550 and 720 nm (similar to those observed for a physical mixture of ZnPc and MMS where the ZnPc exists as dimers or aggregates — see Fig. 3). This allows us to semi-quantitatively fit our spectra (and show a transformation from monomeric to dimeric–aggregated pthalocyanine as ZnPc content increases) which confirms that at certain ZnPc contents, the phthalocyanine in ZnPc/MMS composites exists predominantly in monomeric form.

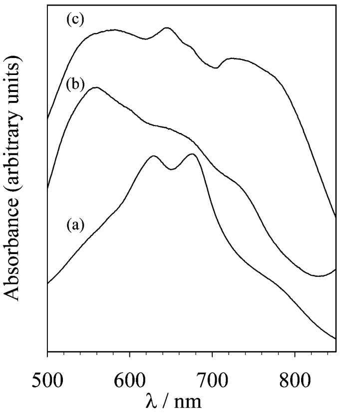

Fig. 3 Diffuse reflectance spectra of (a) ZnPc/MMS (0.45 µM ZnPc), (b) ZnPc/MMS (0.9 µM ZnPc) and (c) physical mixture of ZnPc and MMS.

We have shown that phthalocyanine in the directly prepared ZnPc/MMS mesophases or ZnPc–MMS composites prepared *via* a post-synthesis adsorption route exists predominantly in monomeric form. The *ordered* high surface area MMS provides an excellent host for monodispersion of phthalocyanines. This is important for optical applications because aggregation is known to damage the optical properties of such composites. Furthermore, when the dye is held rigidly in a solid matrix, many of the mechanisms that quench the triplet state are reduced by the dye–matrix interaction. Consequently, the optical nonlinearity of the material is increased.[13,14]

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