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Communication

Vapochromism of Hexaphenylsilole

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The photoluminescence (PL) of the thin layer of hexaphenylsilole (HPS) on thin-layer chromatograph (TLC) or quartz plate is investigated. The PL of the HPS layer absorbed on the TLC plate can be turned "off" and "on" continuously and reversibly by solvent exposure and evaporation. On the other hand, the PL of the HPS film coated on the quartz plate becomes stronger with a blue-shift in its emission color after fumigation by solvent vapor. After solvent removal, the film does not return to its original blue-green emission. Analyses by SEM, TEM and XRD indicate that the transformation from amorphous to crystalline state is responsible for the vapor-induced stronger and bluer PL.

KEY WORDS: Silole; vapochromism; crystal; amorphous; blue-shift.

1. INTRODUCTION

The increasing demands for faster, simpler and less expensive detection methods for chemical and biochemical agents have stimulated dynamic research on the synthesis of new fluorescent materials. Siloles are a group of organometallic molecules that possess novel electronic and optical properties. The five-membered silacyclics exhibit, for example, high electron acceptability and fast electron mobility. Thanks to their fast electron mobility, siloles have been used as electron-transporting and light-emitting materials in the construction of electroluminescence devices, which are found to show outstanding performances [1–4].

We have recently observed a novel aggregation-induced emission (AIE) phenomenon in siloles: the molecules are practically nonemissive when molecularly dissolved in good solvents but become highly emissive when aggregated into nanoclusters or fabricated into thin films. The AIE effect greatly boosts the quantum yields of siloles by more than 300-fold, turning them from faint fluorophores into strong emitters [5, 6]. Although siloles are excellent light-emitting materials, their utilization as luminescent sensory materials has, however, rarely been studied [7, 8]. In this work, we studied the PL of the thin layers of HPS, whose molecular structure is shown in Chart 1,

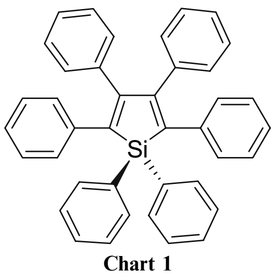

Chart 1

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on different substrates. In this paper, we show that the molecule shows interesting vapochromism.

2. EXPERIMENTAL

HPS was prepared according to a literature method [9]. PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. XRD patterns were recorded on a PW1830 Powder X-ray diffractometer with a graphite monochromator and 1.5418 Å Cu K_α radiation at room temperature (scanning rate: 0.025°/s; scan range: 2–55°). Morphologies of the HPS layers were investigated on a JEOL-6300 scanning electronic microscope (SEM) operating at an accelerating voltage of 10 kV after sputtering thin layers of gold (~99 Å in thickness) onto the samples using a Denton Sputtering utility. Transmission electron micrographs and electron diffraction patterns were obtained on a Philips CM-20 TEM. The packing pattern of HPS crystal was taken from our previous publication [5].

3. RESULTS AND DISCUSSION

We first tested how the PL of HPS would respond to solvent vapor on TLC plates. We dropped silole solutions onto TLC plates and put them in the Petri dishes saturated with different solvents. To avoid direct contact of the plates with the solvents, we put some plastic ‘‘spacers’’ in between the samples and the solvents. As shown in Fig. 1, the emission from the silole spot is turned ‘‘off’’ when put into a dish saturated with acetone or chloroform vapor. The emission, however, becomes visible again (‘‘on’’) when the solvent is removed (column c). The solvent vapors may have condensed and hence formed thin liquid layers on the surfaces of the TLC plates, which have dissolved the absorbed silole molecules and thus quenched their light emission. After solvent evaporation, the silole molecules aggregate and emit again. This off/on process is fully reversible and can be repeated for many times because the involved is a nondestructive physical cycle of dissolution-aggregation.

In addition to the visual observations, we studied the solvent effect on the silole emission using a PL spectrofluoremeter. We coated a thin film of HPS on the inner wall of a quartz cell and added several drops of acetone in a small container placed at the bottom of the cell. The change in the PL of the HPS film was then investigated.

Unlike the situation on the TLC plate, the PL of the HPS film on the quartz cell becomes stronger with time (Fig. 2). Meanwhile, the emission color progressively shifts from green (494 nm) to blue (462 nm). When the solvent is removed, interestingly, a blue light-emitting film is formed, which cannot return to its original blue-green color even after storage.

What is the cause of such a novel chromism? Some molecular semiconductors have been found to undergo crystallization upon solvent fumigation [10, 11] and we thus checked the morphology of HPS before and after solvent exposure. As shown in Fig. 3a, the untreated silole film is amorphous. Silole

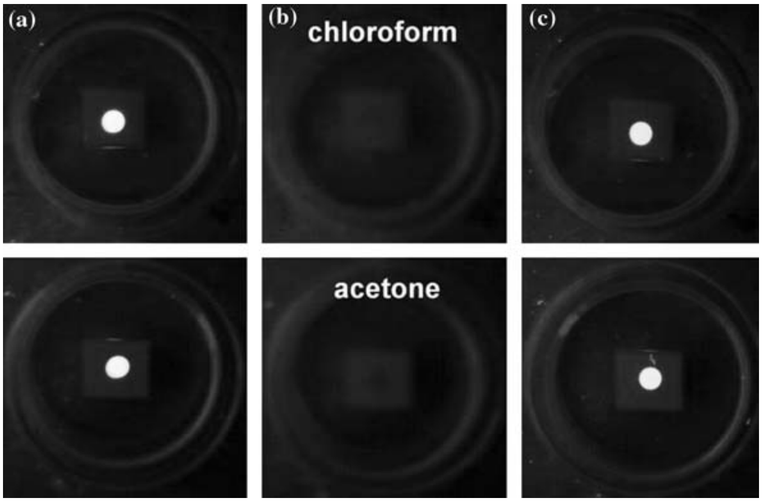

Fig. 1. Photos of the HPS spots on the TLC plates placed in the Petri dishes in the (a) absence and (b) presence of organic vapors. Photos in column c were taken after the solvent had evaporated. All the photos were taken under UV illumination.

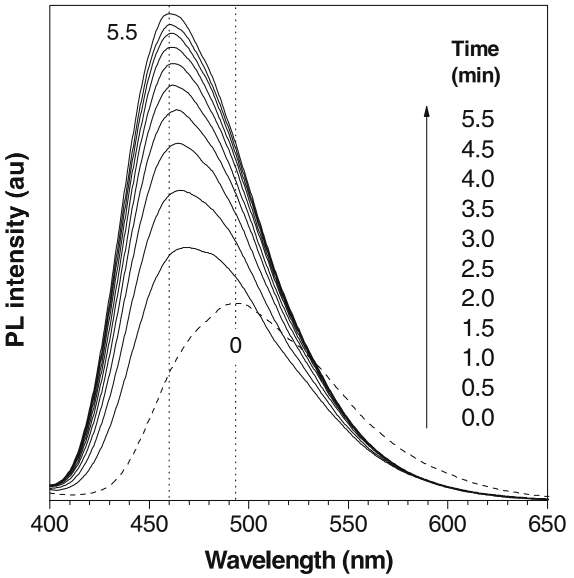

Fig. 2. Effect of acetone vapor on the photoluminescence spectrum of a HPS film coated on a quartz cell at different time interval. Excitation wavelength: 370 nm.

crystals are, however, formed after fumigated by the solvent vapor. Similar results are obtained from the TEM analysis. The ED pattern of untreated film shows only a diffuse halo (Fig. 3c). On the contrary, diffraction spots are clearly seen in the fumed film, suggestive of its crystalline nature. These results indicate that the solvent vapor does not dissolve all the molecules in the "pure" silole films on the quartz cells but helps them crystallize into stable crystal forms in the supersaturated silole "solution". The silole molecules on TLC plate are, however, well dispersed in the silica gels or segregated by the fine gel particles, which make it impossible for the silole molecules to crystallize. This accounts for the different PL behaviors of the silole molecules on the TLC plate and quartz cell.

To further confirm the results shown in Fig. 3, we prepared crystals of HPS by recrystallization from an ethanol/THF mixture and its amorphous powders by rapidly quenching its melt by liquid nitrogen. The PL of the two samples was then investigated. As can be seen from Fig. 4a, the silole molecules are well-ordered, exhibiting many sharp diffraction peaks at low angles. Upon photoexitation, the crystal emits a blue light, with a peak maximum at 462 nm. In sharp contrast, the amorphous powder shows broad halos of low intensities. Unlike its crystalline cousin, the amorphous powder is a green emitter, clearly

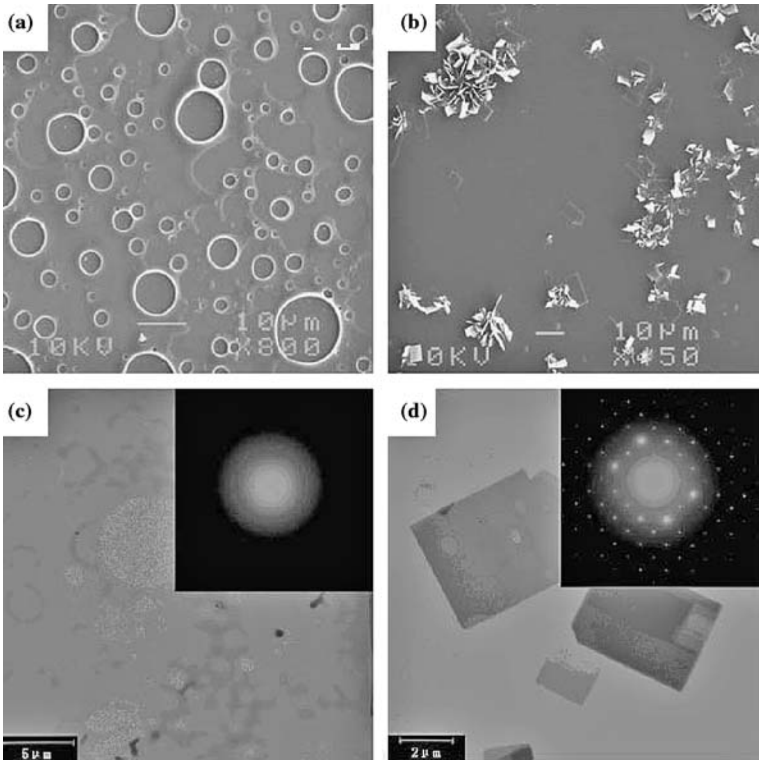

Fig. 3. (a and b) SEM and (c and d) TEM images of HPS films (a and c) before and (b and d) after exposure to acetone vapor for 10 h. The insets in Fig. 3c and d are the ED patterns.

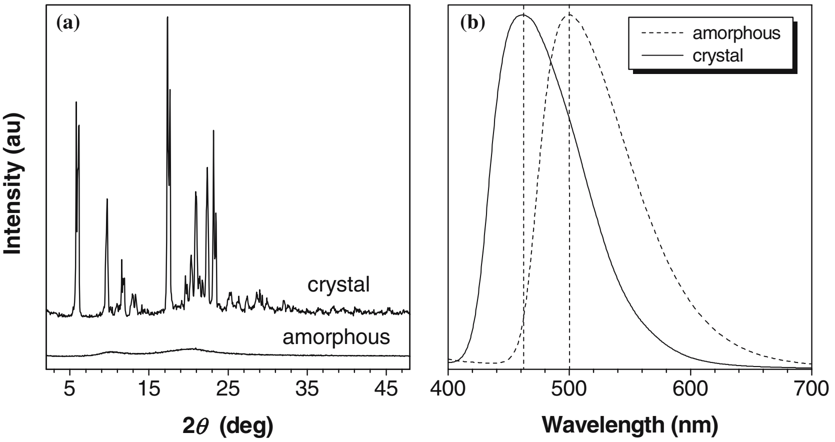

Fig. 4. (a) X-ray diffractograms of crystalline and amorphous samples of HPS and (b) their photoluminescence spectra. Excitation wavelength: 370 nm.

demonstrating that the PL of HPS can be tuned by changing its morphology.

Packing of most organic molecules always results in emission at longer wavelengths with low efficiencies due to the formation of delocalized excitons or excimers [12–17]. Why does HPS crystal show the opposite phenomenon? To answer this question, we checked its packing pattern.

As shown in Fig. 5, the silole molecules are nonplanar due to the steric hindrance between the peripheral phenyl rings [5]. The interplane molecular distance is ~ 10Å, suggestive of the lack of strong molecular interactions that tends to induce nonradiative recombination or red-shifts as seen in the "normal" crystals with strong π–π interactions. Thus, the PL from the silole crystals should originate from discrete silole molecules and this explains why we observed no PL at longer wavelengths. However, we are still uncertain why the crystalline form emits PL with shorter wavelength or bluer color. It will be helpful to interpret this uncommon process if we know the conformation of, and packing in, the amorphous solid. Such information is, unfortunately, difficult to obtain experimentally. We suspect that the silole molecules in the amorphous powder may adopt a more planar conformation and hence exhibit redder PL than those in the crystal form.

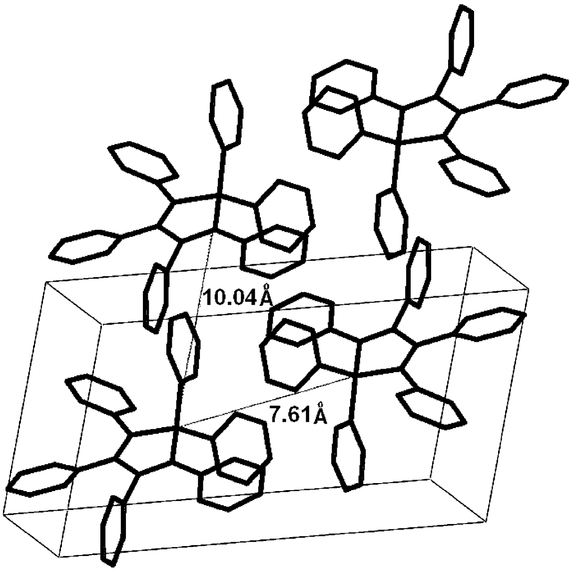

Fig. 5. Packing diagram of the crystal of HPS molecules, where the interplane distance is 10.04 Å and the intermolecular distance within the unit cell is 7.61 Å.

4. CONCLUSIONS

In this work, we studied the PL of HPS on different substrates. The emission of the silole layer on the TLC plate can be turned "off" and "on" by solvent exposure and evaporation. The film coated on the quartz cell is transformed from a green fluorophore to a blue emitter after solvent fumigation, which does not return back to its original color even after solvent evaporation. Transformation from an amorphous phase to a crystalline structure is responsible for this novel phenomenon of fumigation-induced blue shift.

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