

# Vapochromism and Crystallization-Enhanced Emission of 1,1-Disubstituted 2,3,4,5-Tetraphenylsiloles

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**Abstract** Effects of solvent vapor on the photoluminescence (PL) of 2,3,4,5-tetraphenylsiloles carrying different 1,1-substituents [(PhC)<sub>4</sub>SiRR', R = Ph, R' = CH<sub>3</sub> (**2**); R = Ph, R' = C≡CH (**3**); R = R' = C≡CH (**4**)] were investigated. The emission of the silole spots on the TLC plates can be turned “off” and “on” continuously and reversibly by wetting by, and de-wetting from, vapors of organic solvents, respectively. After fumigation by solvent vapor, the thin film of **4** coated on the quartz substrate emits stronger and bluer PL owing to the transformation of film morphology from the amorphous to the crystalline phase. Analysis by X-ray diffraction reveals that the molecular conformations of the crystals of **2–4** are locked and stabilized by multiple C–H⋯π hydrogen bonds. This structural rigidification has made the silole crystals stronger emitters.

**Keywords** Amorphous · Crystal · Light emission · Silole · Vapochromism · Aggregation-induced emission · Crystallization-enhanced emission

## 1 Introduction

Development of new methodologies for the detection of chemicals and biomolecules is a hot area of research [1–3].

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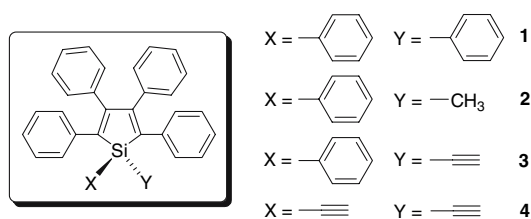
Chemical sensors based on luminescent materials are of particular interest because they enjoy high sensitivity, selectively, rapidity, and portability [4–6]. Whereas many chromophoric molecules are highly emissive when molecularly dissolved in solutions, they become weak emitters when dispersed in the aqueous phase or fabricated into thin films due to aggregate formation [7–9].

We have recently discovered an exactly opposite effect of “aggregation-induced emission (AIE)”: a large variety of nonemissive, propeller-shaped molecules are induced to emit intensely by aggregation formation [10–19]. The AIE effect greatly boosts their fluorescence quantum yields (up to 300-fold), turning them from faint emitters to strong fluorophors. Utilizing the AIE effect, we have fabricated light-emitting diodes based on the AIE-active molecules, which show outstanding device performances [20]. Though the dye molecules are excellent light-emitting materials, their utilization as luminescent sensory materials has rarely been explored.

During our study on the AIE phenomenon, we have found that the emission of hexaphenylsilole (**1**; Chart 1) on the TLC plate can be turned “off” and “on” by exposure to, and removal from, organic solvent vapors. Its film coated on a quartz substrate exhibits novel chromic effect and becomes highly emissive after solvent-fuming [19]. To test whether the phenomena are general characteristics for all silole molecules, in this work we investigated the chromism of 2,3,4,5-tetraphenylsiloles with different 1,1-substituents.

## 2 Experimental

Siloles **2–4** were prepared according to our published methods [15]. PL spectra were recorded on a Perkin-Elmer



**Chart 1** Structures of siloles

LS 55 spectrofluorometer. UV spectra were measured in THF solutions (concentration:  $10^{-5}$  M) on a Milton Roy Spectronic 3000. X-ray diffraction patterns were recorded on a PW1830 powder X-ray diffractometer with a graphite monochromator using  $1.5418 \text{ \AA}$   $\text{CuK}\alpha$  wavelength at room temperature (scanning rate:  $0.025^\circ/\text{s}$ ; scan range:  $2\text{--}55^\circ$ ). Morphologies of the silole 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 ( $\sim 99 \text{ \AA}$  in thickness) onto the samples using a Denton Sputtering utility. The packing patterns of the silole crystals were taken from our previous publications [15, 21].

Spots of siloles were formed by dropping their THF solutions with a concentration of  $\sim 10^{-3}$  M onto TLC plates. Thin films of siloles were prepared by dropping their diethyl ether solutions (concentration:  $\sim 10^{-3}$  M) onto inner walls of quartz cells. Crystals of siloles and their amorphous powders were obtained by recrystallization from ethanol/THF mixtures and rapid quenching of their melts by liquid nitrogen, respectively. All measurements were carried out at room temperature.

### 3 Results and Discussion

To see whether vapochromism is a unique phenomenon observed only in **1**, we checked the response of its structural congeners **2–4** to solvent vapor. We first investigated how the PL of **2** would change upon solvent fumigation. We dropped its solution onto TLC plates and put them in the Petri dishes saturated with different solvent vapors. To avoid direct contact of the samples with the solvents, plastic spacers were put in between the samples on the TLC plates and the solvents on the bottoms of the dishes. As can be seen in Fig. 1, the emission from the silole spots is quenched when they are exposed to acetone and chloroform vapors. 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 turned “off” their light emission. When the solvent vapors are evaporated, the molecules aggregate and emit (“on”) again. This “off/on” process is completely

reversible and can be repeated many times because of the nondestructive nature of the process. Such fluorescence switching behavior is also observed in **3** and **4**, confirming that the vapochromism is a general phenomenon observable in all the silole systems and suggesting that the silole molecules are promising candidates for fluorescence sensing of volatile organic compounds [22, 23].

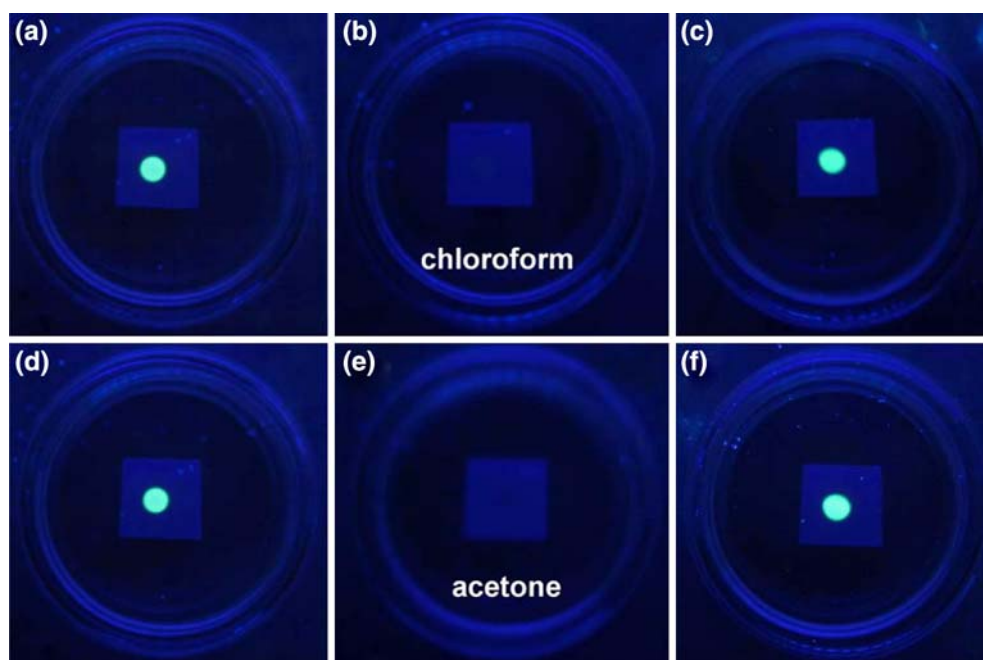
To have a spectroscopic picture, we followed the change in the PL of **2** in the atmosphere saturated with organic vapors using a spectrofluorometer. A thin solid film of **2** was coated on the inner wall of a quartz cell and several drops of acetone were added in a small container placed on the bottom of the cell. The emission of the silole film was then recorded at different time. Similar to the observation on the TLC plates, the PL of **2** becomes weaker and is almost completely quenched after exposure to the vapor for  $\sim 2$  min. Silole **3** behaves similarly. However, the fumed film of **4** shows stronger and bluer emission than the untreated one, offering an opportunity to tune vapochromism of siloles by changing their molecular structures (Fig 2).

But why do siloles **2–4** show different responses to the solvent vapor? It is known that solvent vapors can activate the dynamic recrystallization processes of many dyes [24, 25]. We have previously found that films of silole **1** on the quartz plate can change from the amorphous to the crystalline state under a solvent vapor atmosphere, leading to an enhanced emission at shorter wavelengths [19]. We thus investigated the morphologies of **2–4** by SEM before and after solvent exposure. The images are shown in Fig. 3. The untreated films of **2–4** are amorphous. After solvent fumigation, the films of **2** and **3** become smoother. Regularly shaped crystals are, however, formed in the fumed film of **4**. These results indicate that the acetone vapor has dissolved the molecules in the films of **2** and **3** on the quartz cells and hence decreased their PL. On the contrary, the solvent vapor has helped the molecules of **4** to crystallize in the supersaturated silole “solution” and thus shifted its PL spectrum to the bluer region with a higher intensity. The molecules of **4** on the TLC plate are, however, well segregated by the fine silica gel particles, making them impossible to crystallize. This accounts for the different behaviors of **4** on the TLC plate and the quartz cell.

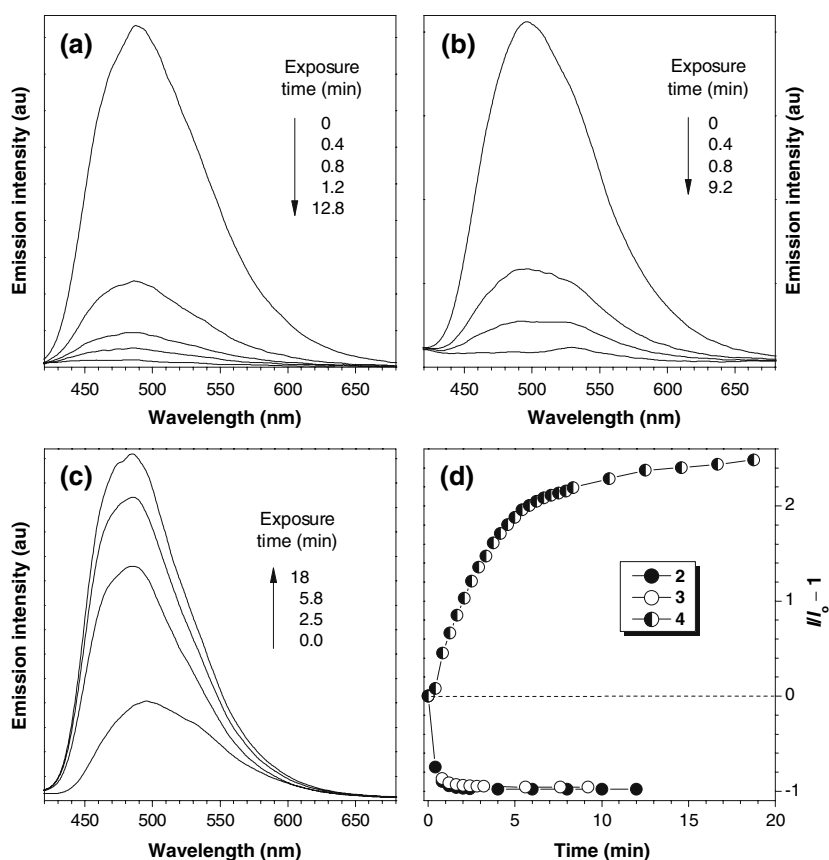
As can be seen in Chart 1, **4** is similar to **1** and possesses a symmetric molecular structure, which may pack well during the fuming process. Siloles **2** and **3** are, however, asymmetric in shape, which may have prevented their packing into crystalline forms under the solvent vapor atmosphere.

To check whether crystals of **2** and **3**, like those of **1** and **4**, are also stronger and bluer emitters than their amorphous counterparts, we prepared their crystals by recrystallization from their ethanol/THF solutions. We also prepared their

**Fig. 1** Photos of the spots of silole **2** on the TLC plates in the Petri dish sets (a and d) in the absence of and (b and e) after exposure to vapors of organic solvents for about 1 min. Photos in (c and f) were taken in about 2 min after the solvents were evaporated. All the photos were taken under UV illumination at room temperature



**Fig. 2** Effect of acetone vapor on the photoluminescence spectra of films of siloles (a) **2**, (b) **3**, and (c) **4** coated on quartz cells at different exposure time. (d) Changes in the emission intensities of **2–4** with the time of exposure to the solvent vapor. Excitation wavelength (nm): 370 (**2** and **3**), 374 (**4**)



amorphous powders by rapid quenching of their melts using liquid nitrogen. We investigated their structures by X-ray diffraction, an example of which is shown in Fig. 4. The crystal of **2** gives many sharp diffraction peaks at the

low angles. Upon photoexcitation, the crystal emits a blue light with a fluorescence peak at 460 nm. In contrast, its amorphous counterpart shows broad halos of low intensities and behaves as a green emitter.

**Fig. 3** SEM images of films of siloles (**a** and **b**) **2**, (**c** and **d**) **3**, and (**e** and **f**) **4** (**a**, **c**, and **e**) before and (**b**, **d**, and **f**) after exposure to acetone vapor for 10 h

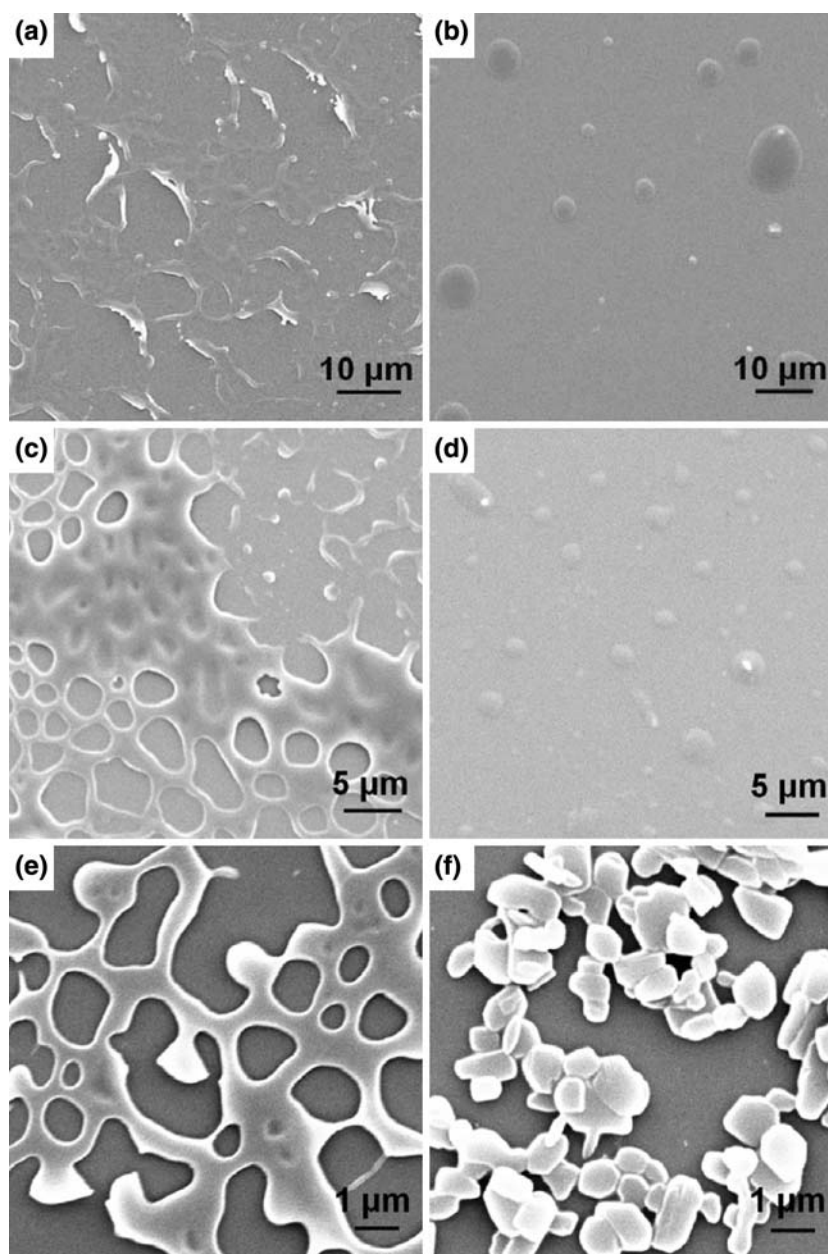
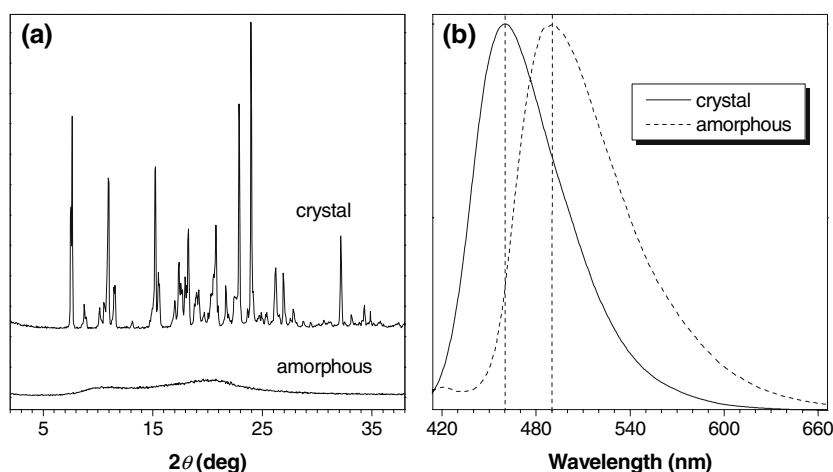


Table 1 summarizes the optical properties of **2–4** along with those of **1**. The emissions of all the silole crystals are blue-shifted, in comparison to those of their amorphous cousins. It is noteworthy that when the methyl group of **2** is replaced by phenyl (**1**) and ethynyl (**3**) groups, both the absorption and emission peaks are shifted to the longer wavelengths. This is probably due to the increase in the electronegativity of the groups, which changes in the order of Me (2.3) < Ph (3.0) < C≡CH (3.3) [26]. Clearly, the optical properties of siloles are affected by, the inductive effects of their 1,1-substituents.

Crystallization usually red shifts the emission spectra and decreases the emission intensity. Why is the PL of **2–4** enhanced, and blue-shifted upon crystallization?

Thanks to the steric hindrance between the peripheral phenyl rings, the silole molecules take propeller-like, instead of planar, conformations, which prevent them from suffering emission quenching due to  $\pi$ - $\pi$  stacking in the solid state. The amorphous silole molecules may adopt more planar conformations and hence exhibit redder emissions than those in the crystalline state. As can be seen in Fig. 5, the molecular conformations of the silole crystals are locked and stabilized by multiple C-H $\cdots$  $\pi$  hydrogen bonds, which hamper the aromatic rings from undergoing conformational changes caused by such movements as intramolecular rotations. This structural rigidification may have made the crystals stronger emitters.

**Fig. 4** (a) Powder X-ray diffractograms and (b) photoluminescence spectra of crystalline and amorphous solids of silole **2**. Excitation wavelength: 371 nm



**Table 1** Absorption and emission characteristics of Siloles<sup>a</sup>

Silole	$\lambda_{ab}^b$ (nm)	$\lambda_{em}$ (nm)		
		Solution <sup>b</sup>	Crystal	Amorphous
<b>1</b>	364.4	500	465	500
<b>2</b>	364.0	490	460	490
<b>3</b>	372.0	502	481	502
<b>4</b>	375.5	505	485	499

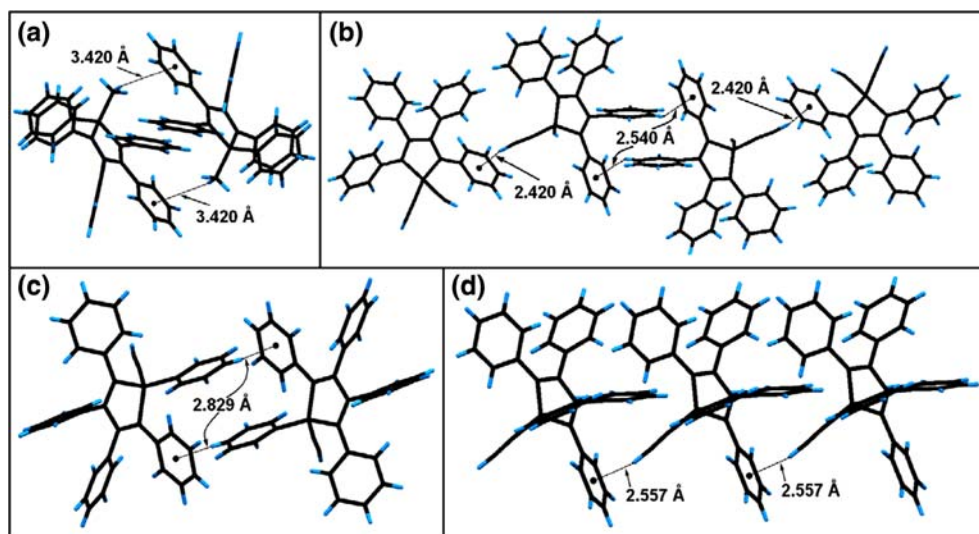
<sup>a</sup> Abbreviations:

$\lambda_{ab}$  = absorption maximum,

$\lambda_{em}$  = emission maximum

<sup>b</sup> Measured in THF

**Fig. 5** Perspective view of the packing arrangements in crystals of siloles (a) **2**, (b) **4**, (c) and (d) **3**. The aromatic C-H $\cdots$  $\pi$  hydrogen bonds are denoted by dotted lines



## 4 Conclusions

In this work, we studied the solvent vapor effect on the PL of siloles with different 1,1-substituents. The emission of the silole spots on the TLC plates can be turned “off” and “on” by wetting and de-wetting processes, respectively. After solvent fuming, the film of **4** coated on the quartz substrate emits stronger light owing to its transformation from amorphous to crystal state. The more twisted peripheral phenyl rings and the locking of the molecular conformation in the crystals of **2–4** by multiple C-H $\cdots$  $\pi$

hydrogen bonds may account for their stronger and bluer PL. The AIE molecules with the vapochromism and crystallization-enhanced emission characteristics may find an array of technological applications in chemosensory systems and light-emitting diodes.

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