



Short communication

Luminescent aggregates of a starburst silole-triphenylamine adduct for sensitive explosive detection

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ARTICLE INFO

Article history:

Received 24 January 2011

Received in revised form

28 February 2011

Accepted 4 March 2011

Available online 15 March 2011

Keywords:

Aggregation-induced emission

Silole

Tripheylamine

Aggregates

Explosive detection

Picric acid

ABSTRACT

A starburst luminogen (THPSTPA) consisting of a triphenylamine core and 1,1,2,3,4,5-hexaphenylsilole peripheries is designed and synthesized. Whereas it is weakly luminescent when molecularly dissolved in good solvent, it becomes highly emissive when aggregated in poor solvent, exhibiting a novel phenomenon of aggregation-induced emission (AIE). THPSTPA is morphologically and thermally stable, showing high glass transition and thermal degradation temperatures at 150 and 303 °C, respectively. The emission of its aggregates can be quenched exponentially by picric acid with a quenching constant up to $\sim 7.0 \times 10^4 \text{ L mol}^{-1}$, suggesting that it can work as a sensitive chemosensor for explosive detection.

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1. Introduction

Explosive detection has attracted great attention due to the unprecedented severe terrorism menace in the globe range. Nitroaromatic compounds such as 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, and picric acid (PA) are warfare explosives, sensitive detection of which is of antiterrorism implications. Sensing of these explosives in groundwater or seawater is very important in the detection and location of buried unexploded ordnance and underwater mines as well as in the monitoring of groundwater and soil for assessing contamination levels [1–4]. However, most methods for the detection of explosives are only applicable to air samples as a consequence of interference problems encountered in complex aqueous media.

Siloles (silacyclopentadienes) have been studied extensively due to their unique electronic properties and potential high-technological applications. They are considered as novel $\sigma^*-\pi^*$ conjugated materials with a low-lying lowest unoccupied molecular orbital energy level [5–7], and thus exhibiting high electron affinity and fast electron mobility [8,9]. Recently, a novel phenomenon of “aggregation-induced emission (AIE)” has been observed in silole

and its derivatives [10–12]. Whereas they are practically non-luminescent when molecularly dissolved in the solutions, they are induced to emit intensely when aggregated as nanoparticles in poor solvents or fabricated as thin films in solid state. Restriction of intramolecular rotations (IMR) is rationalized to be the main cause for the AIE effect [13,14]. Thanks to such effect, silole-containing small molecules [15], oligomers [16], and linear and hyperbranched polymers [17–19] have been utilized for the construction of efficient chemosensors for explosive detection. The AIE aggregate-based sensors exhibit strong light emissions, showing high sensitivity and suffering no false-positive effect. They also contain many cavities for the explosive molecules to enter and to interact with the chromophores. All these advantageous structural features endow them with a high sensing performance, making them more applicable to real-world detection of trace explosives dissolved in water. To further enhance the sensitivity of the detection requires the synthesis of new materials. In this letter, we designed and synthesized a novel starburst fluorophore by decorating triphenylamine (TPA) with multiple 1,1,2,3,4,5-hexaphenylsilole (HPS) [13,14] units as peripheries (Fig. 1). HPS is a typical AIE luminogen, showing strong emission in the aggregate state and high electron affinity. TPA, on the other hand, is electron rich but it, similar to most conventional chromophores, suffers from aggregation-caused emission quenching (ACQ) in the condensed phase. Adduct generated from these two units is anticipated to possess novel optical

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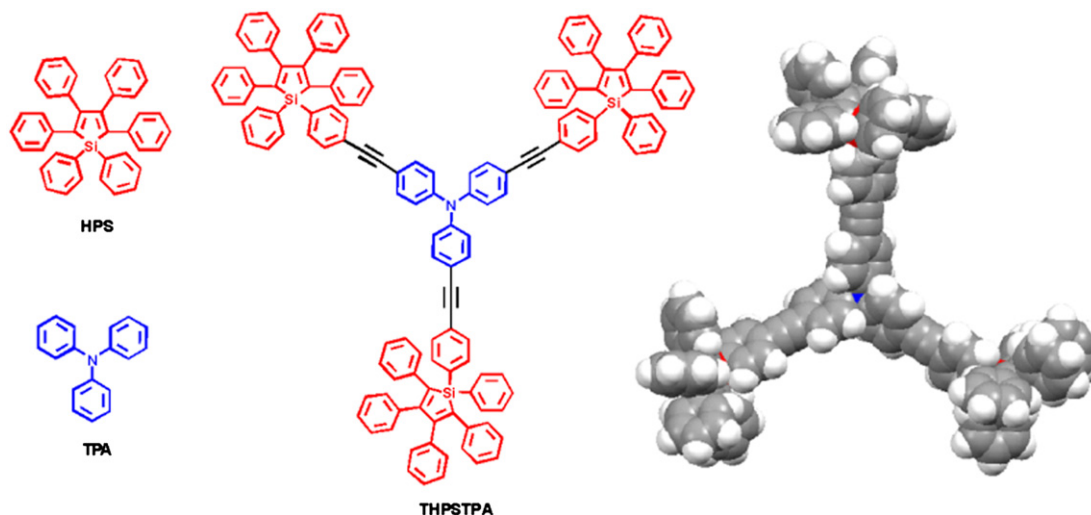


Fig. 1. Molecular structures of HPS, TPA and their adduct THPSTPA, and molecular model of THPSTPA optimized by the MM⁺ method in Hyperchem7.5 program.

properties and hence find potential high-technological applications. We herein describe how such hybrid is synthesized and present its optical and sensory properties.

2. Experimental

2.1. General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from Aldrich (USA) and used as received without further purification. ¹H and ¹³C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. PL spectra were recorded on a Perkin–Elmer LS 55 spectrofluorometer. The high resolution mass spectra were recorded on a GCT premier CAB048 mass spectrometer. Thermogravimetric analysis (TGA) was carried on a TA TGA Q5000 under dry nitrogen at a heating rate of 10 °C/min. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min.

2.2. Synthesis

2.2.1. Synthesis of 1-(4-ethynylphenyl)-1,2,3,4,5-pentaphenylsilole (HPSA)

Under dry nitrogen, freshly cut lithium shavings (0.07 g, 10 mmol) were added to a solution of tolan **4** (2 g, 11 mmol) in dry THF (20 mL). After stirring for 3 h at room temperature, a solution of trichlorophenylsilane (0.64 mL, 4 mmol) in dry THF (20 mL) was added dropwise into the reaction mixture. The mixture was refluxed for 6 h to yield intermediate **6** and was then cooled to room temperature. In the second experiment, *n*-butyllithium solution (5.5 mmol, 2.5 M in hexane) was added dropwise to a solution of **2** (1.3 g, 5 mmol) in dry THF (30 mL) under nitrogen at –78 °C. The mixture was stirred for 1 h to generate intermediate **3**, which was then transferred to the previous reaction mixture containing **6** by a syringe. After heating under reflux for 8 h, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over magnesium sulphate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by

silica-gel column chromatography using hexane as eluent. Without characterization, the product was transferred to a flask containing 40 mL THF, 60 mL methanol, and 0.5 g potassium carbonate. After stirring for 8 h at room temperature, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over magnesium sulphate. After filtration and solvent evaporation under reduced pressure, the residue was purified by silica-gel column chromatography using hexane as eluent. Green solid of HPSA was obtained in 45% (0.51 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.65–7.62 (m, 4H), 7.50–7.35 (m, 5H), 7.04–6.96 (m, 12H), 6.89–6.83 (m, 8H), 3.13 (s, 1H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 157.7, 140.0, 139.8, 139.3, 136.8, 136.6, 133.7, 132.4, 131.7, 131.0, 130.6, 129.9, 129.0, 128.5, 128.2, 127.2, 126.5, 124.5, 84.2, 79.1. HRMS (MALDI-TOF): m/z 562.2134 (M⁺, calcd 562.2117).

2.2.2. Synthesis of tris(4-[(1,2,3,4,5-pentaphenylsilolyl)phenyl]ethynyl)phenylamine (THPSTPA)

A mixture of HPSA (0.56 g, 1.0 mmol), tris(4-iodophenyl)amine (0.18 g, 0.3 mmol), Pd(PPh₃)₄ (0.012 g, 0.01 mmol), CuI (3.8 mg, 0.02 mmol), and PPh₃ (5.0 mg, 0.02 mmol) in 100 mL triethylamine was refluxed for 24 h under nitrogen. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane mixture as eluent. Yellow solid was obtained in 71% (0.42 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.67–7.28 (m, 63H), 7.09–6.98 (m, 24H), 6.90–6.85 (m, 12H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 157.6, 147.4, 140.0, 139.9, 139.3, 136.8, 136.6, 135.0, 134.9, 133.6, 131.8, 130.9, 130.6, 130.2, 129.9, 129.1, 129.0, 128.5, 128.1, 127.1, 126.4, 124.7, 118.5, 91.3, 89.9. HRMS (MALDI-TOF): m/z 1926.7118 (M⁺, calcd 1926.7119).

2.3. Preparation of aggregates

Stock THF solution of THPSTPA with a concentration of 10^{–5} M was prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{–6} M solutions with different water contents (0–90 vol%). The PL measurements of the resultant solutions were then performed immediately.

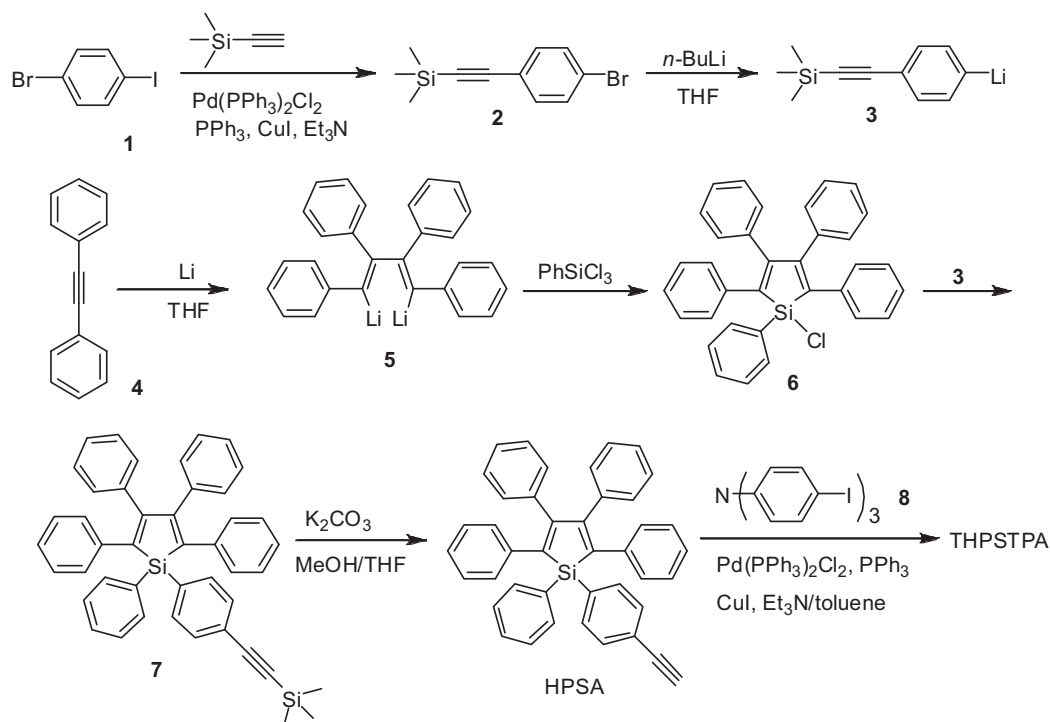
3. Results and discussion

THPSTPA was synthesized according to the multi-step reaction route depicted in Scheme 1. HPSA was the key intermediate and was prepared by the reaction of **3** with **6** followed by base-catalyzed hydrolysis of the resultant product **7**. The acetylene unit in HPSA underwent Sonogashira coupling with **8** in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , and PPh_3 under nitrogen, furnishing the desirable luminogen THPSTPA in satisfactory yield after column chromatography. The molecular structure of THPSTPA was fully characterized by spectroscopic methods with satisfactory results. The adduct is soluble in common organic solvents, such as THF, dichloromethane, chloroform, and toluene but insoluble in methanol and water. The thermal properties of THPSTPA are investigated by differential scanning calorimetry and thermogravimetric analysis. The glass transition and thermal decomposition temperatures of THPSTPA are observed at 150 and 303 °C, respectively, suggesting that it enjoys high thermal and morphological stabilities. The structure of THPSTPA was optimized by the MM^+ method in the Hyperchem7.5 program package. The molecule shows a starburst 3D conformation, in which the silole peripheries arrange in a “propeller-like” shape (Fig. 1). This hampers the close π – π stacking of the molecules and lengthens the intermolecular distance, which creates many cavities in the aggregate state capable of capturing small molecules.

THPSTPA shows an absorption maximum at 376 nm associated with the π – π^* transitions of the silole units. From the onset absorption wavelength, an energy gap of 2.91 eV is determined. The dilute THF solution (10 μM) of THPSTPA is almost nonemissive and exhibits only a noisy photoluminescence (PL) spectrum without a discernable peak (Fig. 2A). The fluorescence quantum yield (Φ_F) determined using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard is 0.81%, revealing that THPSTPA is a genuinely weak emitter when molecularly dissolved in solutions. When a large

amount of water is added into its THF solution, intense PL is, however, recorded at 495 nm under the same experimental conditions. The higher the water fraction (f_w), the stronger is the PL intensity (Fig. 2B). Since water is a nonsolvent for THPSTPA, its molecules must have been aggregated in the solvent mixtures with high water contents, which restricts IMR process and blocks non-radiative pathways, thus making the silole aggregates highly luminescent. Clearly, THPSTPA, similar to HPS, is AIE-active. It should be pointed out that various chemical, physical, and engineering approaches have been taken to frustrate aggregation of conventional fluorophors but the attempts have met, in most cases, limited success [20–28]. The AIE feature of THPSTPA demonstrates that attachment of AIE units to ACQ dyes is a effective strategy for solving their thorny ACQ problem and generating efficient luminophors in the aggregate state [29–32].

THPSTPA has a 3D topological structure and its aggregates contain numerous molecular cavities for capturing analytes and have many pathways for exciton transport. Thus, it is expected that it may function as an efficient chemosensor. With this in mind, we chosen PA as a model explosive because of its commercial availability and monitored the PL change of THPSTPA aggregates in THF/water mixture ($f_w = 90\%$) upon PA addition. As shown in Fig. 3A, the emission of THPSTPA is quenched upon PA addition. The fluorescence quenching can be clearly discerned at a PA concentration ([PA]) as low as 1 ppm. At a [PA] of 78.5 μM , virtually no light is emitted from the solvent mixture. The Stern–Volmer plot of relative PL intensity (I_0/I) versus the PA concentration gives a curve bending upward, instead of a linear line (Fig. 3B). Similar PL quenching behaviours have been observed in our previous work [17–19]. A possible reason for the THPSTPA aggregates to give nonlinear Stern–Volmer plots is that the PL annihilation is caused by static quenching. Effective quenching sphere model [eqn. (1)] can be used to describe the quenching process by the static mechanism [17–19,33–35]



Scheme 1. Synthetic route to THPSTPA.

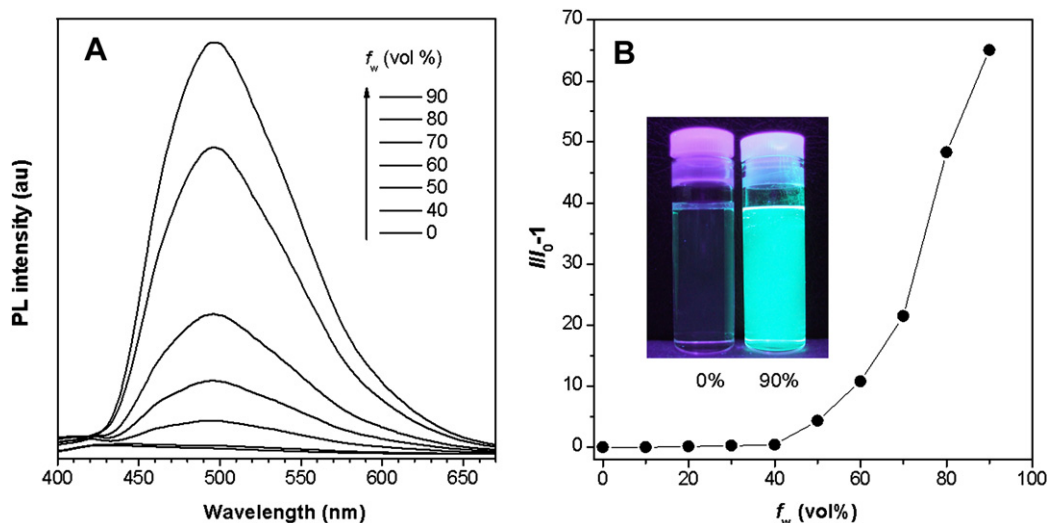


Fig. 2. (A) PL spectra of THPSTPA in THF/water mixtures with different water fractions (f_w). (B) Plots of $(I_0/I - 1)$ values versus water fractions in THF/water mixtures, where I_0 was the PL intensity in pure THF solution.

$$\frac{I_0}{I} = Ae^{k[PA]} + B \quad (1)$$

where A and B are constants and k denotes the static quenching constant. By fitting the Stern–Volmer plot shown in Fig. 3B, eqn. (2) is obtained

$$\frac{I_0}{I} = 2.1e^{33333[PA]} - 1.1 \quad (2)$$

When the $[PA]$ is very low, eqn. (1) can be transformed to eqn. (3) using a mathematical treatment of Taylor expansion:

$$\frac{I_0}{I} = A(1 + k[PA]) + B = Ak[PA] + A + B = K[PA] + C \quad (3)$$

where $K = kA$ and $C = A + B = 1$. Therefore, the static quenching constant or the K value at the initial stage of the Stern–Volmer plot for THPSTPA aggregate in THF/water mixture ($f_w = 90\%$) is $\sim 7 \times 10^4 \text{ L mol}^{-1}$, which is about 3.5-fold higher than those of linear conjugated polysiloles and 3,4-bis(4-isopropylphenyl)-1,1,2,5-tetraphenylsilole ($< 20000 \text{ L mol}^{-1}$) [15,35]. By plotting the relative PL intensity (I_0/I) versus $e^{k[PA]}$, a linear line was obtained (Fig. 3C), which enables quantitative analysis.

THPSTPA is highly emissive not only in suspension but also in solid state. The powders of THPSTPA fluoresce intense greenish blue light and the emission is so strong that has made the powders look like white in the photo taken under 365 nm illumination from a UV lamp (Fig. 4B). Therefore, the explosive detection can also be carried out in the solid state using a THPSTPA-coated strip, thanks to the AIE characteristic of THPSTPA. A prototype of a solid-state chemosensor is prepared by simply dipping a filter paper into a THPSTPA solution. After solvent evaporation, a highly emissive test paper is obtained. The detection process is fast and the assay procedure is simple. When a PA solution is dropped onto the THPSTPA-coated filter paper, the PA-covered spot become non-emissive, which is vividly discernable even by the naked eye (Fig. 4C). These results encourage us to develop ultrasensitive and ultrafast chemosensor devices with portability for on-site detections of explosive vapours and particulates [17].

The fluorescence quenching is probably due to the energy transfer from the excited state of THPSTPA to the ground state of PA via the spectral overlap of the absorption of PA and emission of the THPSTPA as illustrated in Fig. 3D [1,36–38]. Moreover, instead of the 3D topological structure of THPSTPA, which promotes numerous internal voids to bind with quencher molecules and diffusion pathways for excitons to migrate, the dipole–dipole and/

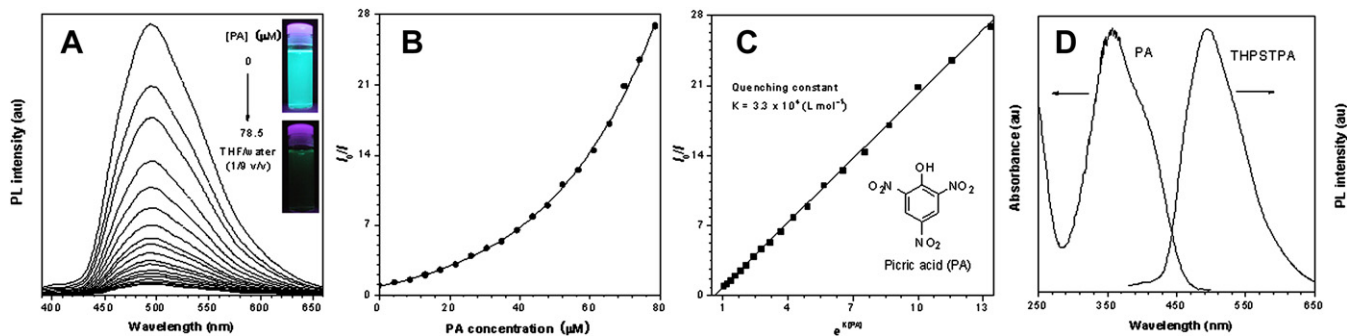


Fig. 3. (A) Change in the PL spectrum of THPSTPA with the addition of different amounts of PA in THF/water mixture ($f_w = 90\%$). Inset in panel A: fluorescent images of THPSTPA in THF/water mixture ($f_w = 90\%$) with $[PA]$ of 0 and 78.5 μM . Excitation wavelength = 350 nm; concentration of THPSTPA = 1 μM . (B) Stern–Volmer plots of I_0/I value versus $[PA]$ in THF/water mixture ($f_w = 90\%$). I_0 = PL intensity in the absence of PA. (C) Plots of I_0/I value versus $e^{k[PA]}$ in THF/water mixture ($f_w = 90\%$). (D) Normalized absorption spectrum of PA and PL spectrum of THPSTPA in THF/water ($f_w = 90\%$).

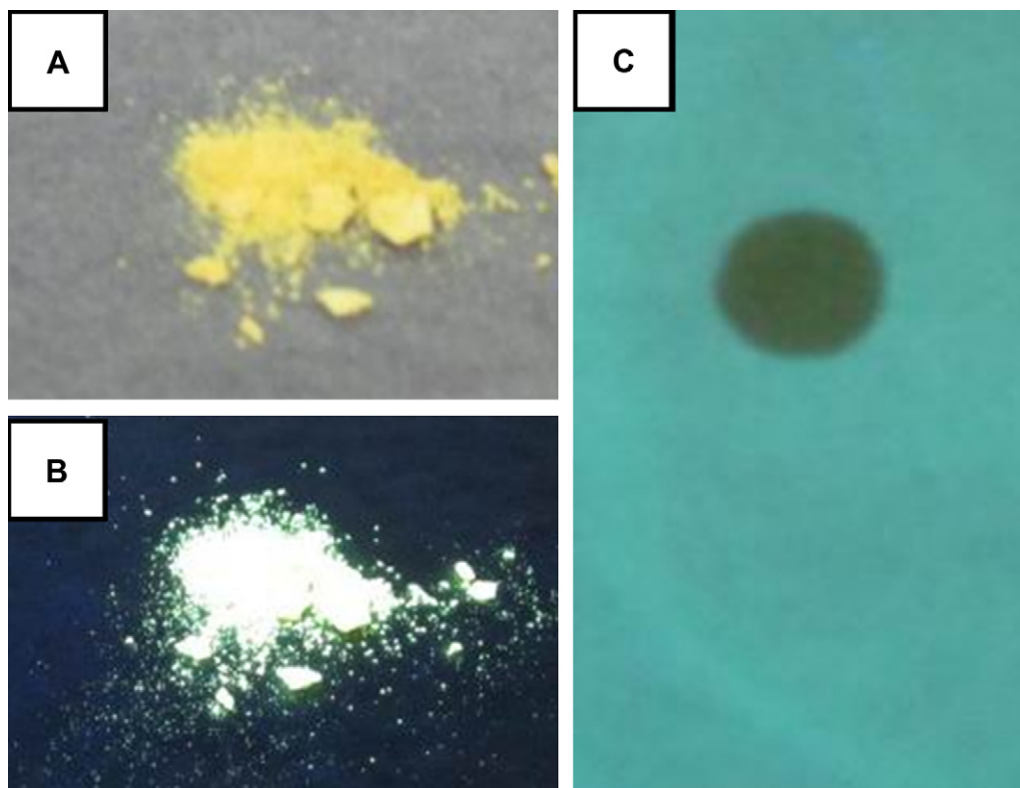


Fig. 4. Photos of THPSTPA powders taken under (A) daylight and (B) UV illumination. (C) Fluorescence image of THPSTPA deposited on a filter paper with a spot of PA solution.

or Lewis acid–base interactions between THPSTPA and the electron-deficient PA may also play as an assistant in the quenching process [4,20,39,40]. All these factors may have worked cooperatively to achieve high sensing performance. Thus, THPSTPA is a promising fluorescent chemosensor for explosive detection with high sensitivity and low detection limit.

4. Conclusions

In summary, a starburst HPS-TPA adduct (THPSTPA) was designed and synthesized. Whereas THPSTPA is practically non-emissive in the solution state, it is induced to emit intensely by aggregate formation, demonstrating a novel AIE phenomenon. The emission of THPSTPA aggregates can be quenched exponentially by picric acid with large quenching constant, revealing that it is a promising chemosensor for sensitive explosive sensing. Construction of efficient light-emitting diodes using THPSTPA as active layer is currently underway in our laboratory.

Acknowledgments

We thank the financial supports from the Innovation and Technology Commission (ITP/008/09NP), the University Grants Committee of Hong Kong (AoE/P-03/08), the Initial Funding of Hangzhou Normal University (HSQK0085), and National Natural Science Foundation of China (21074028 and 20974031).

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