



Short communication

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

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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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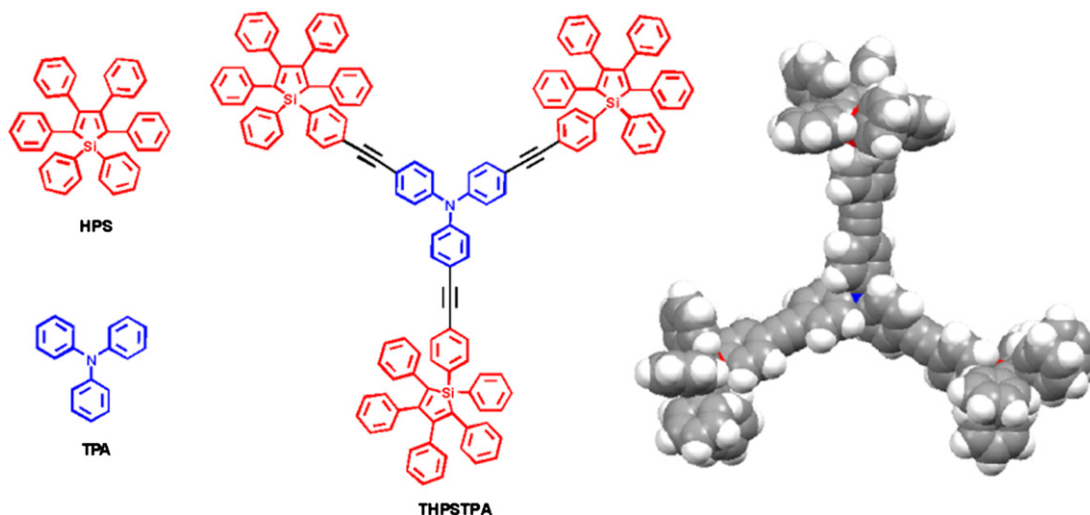


Fig. 1. Molecular structures of HPS, TPA and their adduct THPSTPA, and molecular model of THPSTPA optimized by the MM⁺ method in Hyperchem7.5 program.

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-pentaphenylsilyloxy)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.

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