



## Piezochromic luminescent and electroluminescent materials comprised of tetraphenylethene plus spirobifluorene or 9,9-diphenylfluorene



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### ABSTRACT

In this work, a series of luminogens comprised of tetraphenylethene plus spirobifluorene or 9,9-diphenylfluorene are synthesized and characterized. Whereas these luminogens are weakly fluorescent in solutions, they are highly emissive in the aggregated state, with high fluorescence quantum yields up to 99% in solid films, demonstrating aggregation-induced emission characteristics. Reversible piezochromic luminescence is observed from the solids of the luminogens. A notable emission color change from blue (445 nm) to green (503 nm) is readily realized by grinding the pristine powder of the luminogen. The blue emission is recovered by fuming the ground powder with dichloromethane vapor. The undoped electroluminescence devices using the luminogens as light-emitting layers are fabricated, affording high current efficiencies up to 7.2 cd/A.

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### 1. Introduction

Organic solids with efficient photoluminescence (PL) are highly desired because of their practical applications in organic light-emitting diodes (OLEDs), organic lasers, non-linear optics, fluorescent sensors, etc [1]. Recently, intense research activities are attracted by the piezochromic luminescent organic solids that respond to external stimulus, such as mechanical stress, organic vapor, temperature, etc [2]. The piezochromic luminescence is mainly caused by the morphology transition between crystalline and amorphous states, or between different crystalline states, without provoking structural damage of the molecule [3–5]. This interesting emission property allows the organic solids to be used

in mechano-sensors, optical data storage, security papers, etc [6]. The high emission efficiency of the solid is of particular importance to generate vivid emission color change under external stimulation. However, many chromophores that show good emissions in solutions suffer from emission-quenching in the solid state, which limits their practical utility. To address this issue, creation of luminogens by adopting building blocks that possess aggregation-induced emission (AIE) [7] characteristics is a facile and effective approach. The integration of AIE-active units with various conventional chromophores or diverse functional groups can generate efficient solid-state luminescent materials with specific property, and thus, great potential in environmental, scientific and technological aspects [8].

Tetraphenylethene (TPE) is a typical AIE-active molecule. Currently, it becomes the subject of numerous investigations because of not only its remarkable AIE attribute, but also its simple molecular structure that allows facile preparation and chemical modification [9]. The propeller-like conformation of TPE avoids tight packing of the molecules in the aggregated state, which

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alleviates intermolecular  $\pi$ – $\pi$  interaction and thus emission quenching. Therefore, solids of TPE derivatives can fluoresce strongly, enabling them to serve as efficient host light emitters for OLEDs [10,11]. In addition, the loose packing also offers opportunity for the molecules to form metastable morphology, which induces stimuli-responsive emission behavior [12]. To enrich efficient solid-state emitters for piezochromic study as well as for the application in OLEDs, in this work, a series of luminogens with AIE characteristics are prepared based on TPE and fluorene derivatives. Highly luminescent solids of the adducts of TPE and fluorene derivatives are obtained. The piezochromic luminescent and electroluminescent properties of the adducts are investigated and delineated.

## 2. Experimental

### 2.1. General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compounds **2** and **4** were prepared by the methods in the literature [13]. All other chemicals and reagents were purchased from Aldrich or J&K Scientific Ltd. and used as received without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AV 400 spectrometer in deuterated chloroform using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Elementary analysis was performed on Vario EL III. UV spectra were measured on a Shimadzu UV-2450 spectrophotometer. PL spectra were recorded on a Perkin–Elmer LS 55 spectrofluorometer.

### 2.2. Device fabrication and measurements

The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of  $25 \Omega/\square$ . Prior to loading into the pretreatment chamber, the ITO-coated glass was soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned samples were treated by perfluoromethane plasma with a power of 100 W, gas flow of 50 sccm, and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of  $7 \times 10^{-7}$  Torr for the deposition of NPB, emitter, and TPBi, which served as hole-transport, light-emitting, and electron-transport layers, respectively. The samples were then transferred to the metal chamber for cathode deposition which composed of lithium fluoride (LiF) capped with aluminum (Al). The light-emitting area was  $4 \text{ mm}^2$ . The current density-voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence spectra were obtained by a PR650 spectrophotometer. All measurements were carried out under air at room temperature without device encapsulation.

### 2.3. Synthesis

#### 2.3.1. 9,9-Diphenyl-2,7-bis(4-(1,2,2-triphenylvinyl)phenyl)fluorene ((TPE)<sub>2</sub>PF)

A mixture of **2** (0.83 g, 2.2 mmol), **5** (0.48 g, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.11 g, 0.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.1 g, 8.0 mmol) in toluene/ethanol/water (100 mL, 8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. Then the reaction mixture was cooled to room

temperature and poured into water. The organic layer was extracted with dichloromethane, and the combined organic layers were washed with a saturated brine solution and water, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of (TPE)<sub>2</sub>PF was obtained in 56% yield.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.67 (d, 2H,  $J = 7.2$  Hz), 7.49–7.45 (m, 4H), 7.22–6.95 (m, 48H).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 152.2, 145.9, 143.8, 143.7, 142.8, 141.1, 140.5, 140.1, 139.0, 138.8, 131.8, 131.5, 131.4, 128.3, 127.8, 127.7, 126.7, 126.6, 126.5, 126.2, 124.5, 120.5, 65.7. HRMS (MALDI-TOF):  $m/z$  978.4228 (M<sup>+</sup>, calcd 978.4226). Anal. Calcd for C<sub>77</sub>H<sub>54</sub>: C, 94.44; H, 5.56. Found: C, 94.33 H, 5.52.

#### 2.3.2. 1,2-Bis(4-(9,9-diphenyl-9H-fluoren-2-yl)phenyl)-1,2-diphenylethene (TPE(PF)<sub>2</sub>)

Pale green solid; yield 55%.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.78–7.75 (m, 4H), 7.59–7.54 (m, 4H), 7.40–7.21 (m, 30H), 7.12–7.03 (m, 14H).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 151.8, 151.5, 145.9, 143.8, 142.9, 140.6, 140.1, 139.8, 139.3, 138.9, 131.8, 131.4, 128.3, 128.2, 127.9, 127.7, 127.6, 126.7, 126.6, 126.5, 126.2, 125.6, 124.5, 120.4, 120.2, 68.0, 65.6. HRMS (MALDI-TOF):  $m/z$  964.5 (M<sup>+</sup>, calcd 964.4069). Anal. Calcd for C<sub>76</sub>H<sub>52</sub>: C, 94.57; H, 5.43. Found: C, 94.26; H, 5.35.

#### 2.3.3. 2,7-Bis[4-(1,2,2-triphenylvinyl)phenyl]-9,9'-spirobifluorene ((TPE)<sub>2</sub>SF)

Green solid; yield 41%. The NMR signals are too weak due to the poor solubility of (TPE)<sub>2</sub>SF. HRMS (MALDI-TOF):  $m/z$  976.4080 (M<sup>+</sup>, calcd 976.4069). Anal. Calcd for C<sub>77</sub>H<sub>52</sub>: C, 94.64; H, 5.36. Found: C, 94.46; H, 5.28.

#### 2.3.4. 1,2-Bis[4-(9,9'-spirobifluorene-7-yl)phenyl]-1,2-diphenylethene (TPE(SF)<sub>2</sub>)

Green solid; yield 45%.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.83 (d, 8H,  $J = 7.6$  Hz), 7.56–7.53 (m, 2H), 7.37–7.33 (m, 6H), 7.15–7.02 (m, 16H), 6.96–6.88 (m, 10H), 6.74–6.69 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 149.3, 149.2, 148.7, 143.8, 142.7, 141.8, 141.4, 141.0, 140.4, 140.3, 138.6, 131.7, 131.6, 131.4, 131.3, 127.9, 127.7, 127.6, 126.7, 126.5, 126.4, 126.2, 126.0, 124.1, 124.0, 122.3, 120.2, 120.0, 68.0, 66.0. HRMS (MALDI-TOF):  $m/z$  960.3771 (M<sup>+</sup>, calcd 960.3756). Anal. Calcd for C<sub>76</sub>H<sub>48</sub>: C, 94.97; H, 5.03. Found: C, 94.78; H, 5.01.

## 3. Results and discussion

### 3.1. Synthesis

Scheme 1 illustrates the synthetic routes to the luminogens comprised of TPE plus spirobifluorene or 9,9-diphenylfluorene. The detailed procedures and characterization data are given in Experimental section. Suzuki couplings of commercially available fluorene derivatives **5**–**8** with **2** or **4** generated target products in moderate yields. The structures of the final products are characterized by NMR, mass spectrometry, and elementary analysis. The solubility of (TPE)<sub>2</sub>PF, TPE(PF)<sub>2</sub> and TPE(SF)<sub>2</sub> is good in common organic solvents, such as THF, dichloromethane, chloroform, etc., but (TPE)<sub>2</sub>SF shows poor solubility in these solvents. All the luminogens are insoluble in water and methanol.

### 3.2. Optical properties

Fig. 1 shows the absorption spectra of the adducts of TPE and fluorene derivatives. The spectral profiles are varied as different fluorene derivatives incorporated. (TPE)<sub>2</sub>PF and (TPE)<sub>2</sub>SF show

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