

*Electronic Supplementary Information (ESI)*

**Full emission color tuning in luminogens constructed from tetraphenylethene, benzo-2,1,3-thiadiazole, and thiophene building blocks**

Zujin Zhao,<sup>ab</sup> Chunmei Deng,<sup>a</sup> Shuming Chen,<sup>c</sup> Jacky W. Y. Lam,<sup>a</sup> Wei Qin,<sup>a</sup> Ping Lu,<sup>d</sup> Zhiming Wang,<sup>d</sup> Hoi Sing Kwok,<sup>c</sup> Yuguang Ma,<sup>d</sup> Huayu Qiu<sup>b</sup> and Ben Zhong Tang<sup>\*a</sup>

<sup>a</sup> *Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China*

<sup>b</sup> *College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China*

<sup>c</sup> *Center for Display Research, HKUST*

<sup>d</sup> *State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China*

**Experimental**

*General*

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compound **1**<sup>1</sup>, **2**<sup>1</sup>, **3**<sup>2</sup>, **5**<sup>2</sup>, **7**<sup>2</sup>, and **8**<sup>2</sup> were prepared according to the literature methods. All other chemicals and reagents were purchased from Aldrich and used as received without further purification. <sup>1</sup>H and <sup>13</sup>C 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. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer. High resolution mass spectra were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Thermogravimetric analysis 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 using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min. The ground-state geometries were optimized using the density functional (DFT) with B3LYP

hybrid functional at the basis set level of 6-31G (d). All the calculations were performed using Gaussian 03 package.

### *Device fabrication*

The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of  $25\Omega/\square$ . Prior to load into the pretreatment chamber, the ITO-coated glasses were 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 ( $\text{CF}_4$ ) 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 *N,N*-bis(1-naphthyl)-*N,N*-diphenylbenzidine (NPB), emitter, 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi), and tris(8-hydroxyquinolinolato)aluminum ( $\text{Alq}_3$ ), which served as hole-transporting, light-emitting, hole-blocking, and electron-transporting 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.

### *Synthesis*

Compound **6**<sup>2</sup> and **8**<sup>2</sup> were prepared according to the literature methods. Their characterization data are given below.

**4,7-Bis(5-bromo-2-thienyl)benzo-2,1,3-thiadiazole (6):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.81 (d, 2H,  $J = 3.9$  Hz), 7.80 (s, 2H), 7.16 (d, 2H,  $J = 4.2$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 152.5, 140.9, 131.1, 127.7, 125.8, 125.4, 115.1. HRMS:  $m/z$  457.8054 ( $\text{M}^+$ , calcd 457.8039).

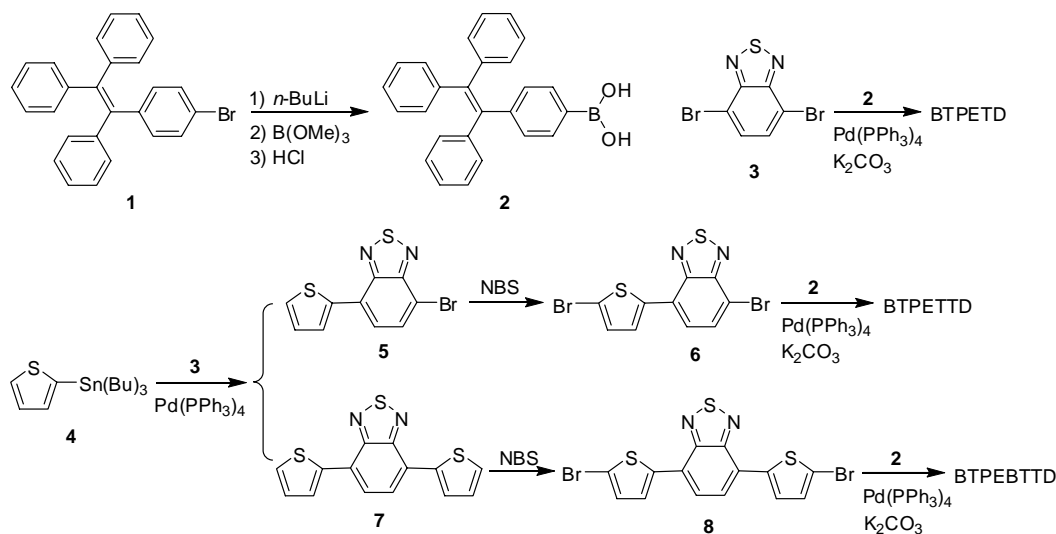
**4-Bromo-7-(5-bromo-2-thienyl)benzo-2,1,3-thiadiazole (8):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.85 (d, 1H,  $J = 7.5$  Hz), 7.79 (d, 1H,  $J = 3.9$  Hz), 7.65 (d, 1H,  $J = 7.8$  Hz), 7.15 (d, 1H,  $J = 3.9$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 154.4, 152.2, 140.5, 132.9, 131.5, 128.4, 126.9, 126.0, 115.8, 113.5. HRMS:  $m/z$  375.8160 ( $\text{M}^+$ , calcd 375.8162).

**4,7-Bis[4-(1,2,2-triphenylvinyl)phenyl]benzo-2,1,3-thiadiazole (BTPETD):** A mixture of **3** (0.29 g, 1 mmol), **2** (0.82 g, 2.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.11 g, 0.1 mmol), and potassium carbonate (1.1 g, 8 mmol) in 100 mL of toluene/ethanol/water mixture (8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane mixture as eluent. Greenish yellow solid of BTPETD was obtained in 86% yield (0.68 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.77 (d, 4H,  $J = 8.4$  Hz), 7.72 (s, 2H), 7.20–7.04 (m, 34H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 154.7, 144.5, 144.4, 144.3, 142.2, 141.2, 135.9, 133.3, 132.3, 132.2, 132.1, 129.0, 128.6, 128.5, 128.4, 128.3, 127.3, 127.2. HRMS:  $m/z$  796.2905 ( $\text{M}^+$ , calcd 796.2912).

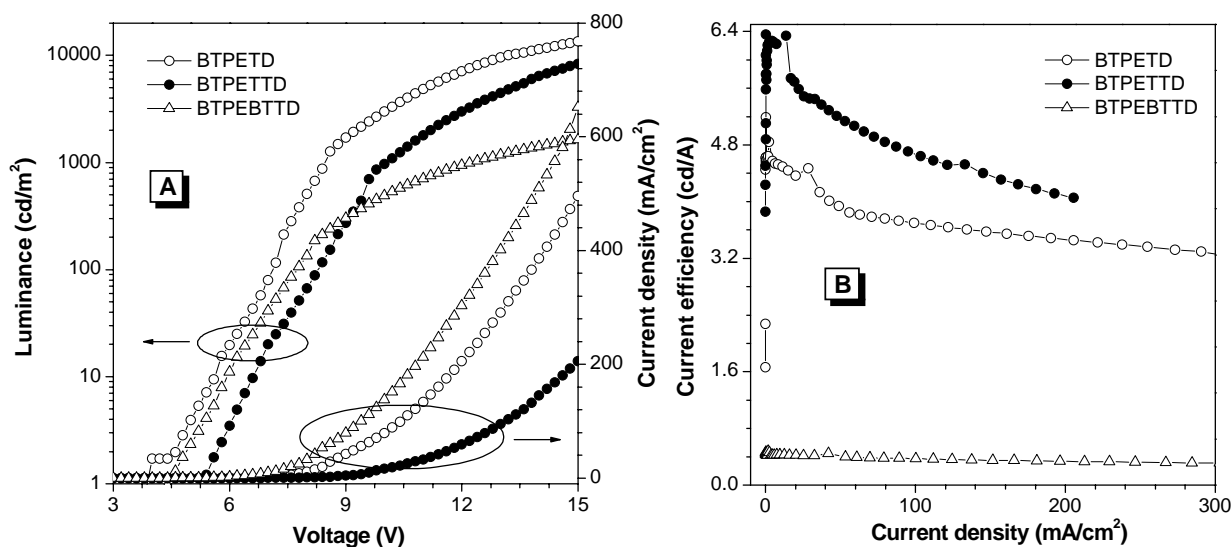
Compound BTPETTD and BTPEBTTD are prepared by an analogous method as described for BTPETD.

**4-[4-(1,2,2-Triphenylvinyl)phenyl]-7-[5-[4-(1,2,2-triphenylvinyl)phenyl]-2-thienyl]benzo-2,1,3-thiadiazole (BTPETTD):** Orange-red solid; yield 75%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.08 (d, 1H,  $J = 3.6$  Hz), 7.89 (d, 1H,  $J = 7.2$  Hz), 7.77 (d, 2H,  $J = 8.7$  Hz), 7.70 (d, 1H,  $J = 7.8$  Hz), 7.45 (d, 2H,  $J = 8.1$  Hz), 7.36 (d, 1H,  $J = 3.9$  Hz), 7.20–7.04 (m, 34H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 153.4, 146.1, 144.5, 144.4, 144.3, 144.2, 144.1, 142.2, 142.0, 141.2, 141.0, 139.1, 135.8, 132.9, 132.6, 132.3, 132.2, 132.0, 129.3, 129.0, 128.5, 128.4, 128.3, 127.2, 126.8, 126.0, 125.6, 124.5. HRMS:  $m/z$  878.2714 ( $\text{M}^+$ , calcd 878.2789).

**4,7-Bis{5-(4-[1,2,2-triphenylvinyl]phenyl)-2-thienyl}benzo-2,1,3-thiadiazole (BTPEBTTD):** Red solid; yield 72%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.08 (d, 2H,  $J = 3.9$  Hz), 7.86 (s, 2H), 7.45 (d, 4H,  $J = 8.1$  Hz), 7.35 (d, 2H,  $J = 3.6$  Hz), 7.13–7.05 (m, 34H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 153.3, 146.1, 144.3, 144.2, 144.1, 142.1, 141.0, 139.1, 132.7, 132.6, 132.0, 129.3, 128.5, 128.4, 127.2, 126.4, 125.9, 125.6, 124.7, 124.6. HRMS:  $m/z$  960.2673 ( $\text{M}^+$ , calcd 960.2667).



**Scheme S1.** Synthetic routes to the TPE-substituted heterocyclics.



**Fig. S1.** (A) Change in luminance and current density with voltage and (B) current efficiency versus current density curves of multilayer EL devices of BTPETD, BTPETTD, and BTPEBTTD.

## References

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2. Y. Zhou, Q. He, Y. Yang, H. Zhong, C. He, G. Sang, W. Liu, C. Yang, F. Bai and Y. Li, *Adv. Funct. Mater.*, 2008, **18**, 3299.