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Supplementary Information

Blue Thermally Activated Delayed Fluorescence Materials Based upon Bis(phenylsulfonyl)benzene Derivatives

Ming Liu¹, Yuki Seino², Dongcheng Chen¹, Susumu Inomata², Shi-Jian Su^{*1}, Hisahiro Sasabe^{*2}, and Junji Kido^{*2}

¹State Key Laboratory of Luminescent Materials and Devices
Institute of Polymer Optoelectronic Materials and Devices
South China University of Technology
Guangzhou, 510640, P. R. China
E-mail: mssjsu@scut.edu.cn
²Department of Organic Device Engineering
Research Center for Organic Electronics (ROEL)
Yamagata University
Yonezawa, 992-8510, Japan
E-mail: h-sasabe@yz.yamagata-u.ac.jp; kid@yz.yamagata-u.ac.jp

General Methods

The NMR data were collected on a Bruker AVANCE Digital 600 MHz NMR workstation at room temperature. Matrix-assisted laser desorption ionization time-offlight (MALDI-TOF) mass spectra were recorded on a Bruker Autoflex III Smartbean. Mass spectrometry (MS) data were obtained on a Waters TQD. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under a N₂ flow at a heating rate of 10 $^{\circ}$ min⁻¹. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. Photoluminescence (PL) spectra were measured by using a Jobin-Yvon spectrofluorometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a Pt working electrode and a Pt wire counter electrode at a scanning rate of 100 mV s⁻¹ against a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile and solution of 0.1 mol L^{-1} tetrabutylammonium dichloromethane (DCM) hexafluorophosphate. The potential of the reference electrode was calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc⁺), using an energy level of -4.8 eV. PL quantum yields (PLQY) of the solution and film were measured by using an integrating sphere on a HAMAMATSU absolute PL quantum yield spectrometer C11347. Transient PL was measured with an Edinburgh FL920 fluorescence spectrophotometer. All reagents for synthesis were obtained from Alfa Aesar or Sigma-Aldrich and were used without further purification.

1. Synthesis

1,4-bis((*4-bromophenyl*)*thio*)*benzene* (*1*): 1,2-Bis(4-bromophenyl)disulfane (7.5 g, 20 mmol), 1,4-diiodobenzene (6.6 g, 20 mmol), anhydrous potassium carbonate (6.9 g, 50 mmol) were added into 100 mL of dimethyl sulfoxide. The mixture was heated to 120 \mathbb{C} and stirred for 24 h. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was recrystallized from ethanol to yield a white product (5.8 g, yield 64%). Mp: 151.8 °C. MS (ESI⁺, *m*/z): calcd for C₁₈H₁₂Br₂S₂, 449.9; found, 449.9. ¹H NMR (600 MHz, CDCl₃, δ): 7.46 (d, *J* = 8.1 Hz, 4H), 7.25 (s, 4H), 7.23 (d, *J* = 8.1 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃, δ): 134.68, 134.35, 132.80, 132.43, 131.48, 121.55.

1,3-bis((*4-bromophenyl*)*thio*)*benzene* (**2**): **2** was synthesized according to the procedure as described above for the synthesis of **1** by combining 1,3-diiodobenzene and 1,2-bis(4-bromophenyl)disulfane, giving a white solid in 60% yield. Mp: 123.6 °C. MS (ESI⁺, *m*/z): calcd for C₁₈H₁₂Br₂S₂, 449.9; found, 449.9. ¹H NMR (600 MHz, CDCl₃, δ): 7.42 (d, *J* = 8.5 Hz, 4H), 7.24-7.20 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 4H), 7.14 (m, 3H). ¹³C NMR (150 MHz, CDCl₃, δ): 137.22, 133.75, 133.25, 132.41, 131.49, 129.87, 128.76, 121.80.

1,4-bis((*4-bromophenyl*)*sulfonyl*)*benzene* (**3**): A combination of **1** (4.5 g, 10 mmol) and 150 mL of acetic acid was heated to 100 °C. Then 10 mL of 30% hydrogen peroxide was added. After stirred for 18 h, the reaction mixture was poured into 1 L of water. The precipitate was collected by filtration, washed with ethanol and further recrystallized from ethanol to yield a white solid (4.0 g, yield 78%). Mp: 275.4 °C. MS (ESI⁺, *m*/z): calcd for C₁₈H₁₂Br₂O₄S₂, 513.9; found, 513.8. ¹H NMR (600 MHz, CDCl₃, δ): 8.04 (s, 4H), 7.78 (d, *J* = 8.7 Hz, 4H), 7.67 (d, *J* = 8.7 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃, δ): 145.95, 143.47, 139.20, 133.00, 129.55, 128.72.

1,3-bis((4-bromophenyl)sulfonyl)benzene (4): **4** was synthesized according to the procedure as described above for the synthesis of **3** by oxidizing **2**, giving a white solid in 68% yield. Mp: 189.3 °C. MS (ESI⁺, m/z): calcd for C₁₈H₁₂Br₂O₄S₂, 513.9; found,

513.8. ¹H NMR (600 MHz, CDCl₃, δ): 8.49 (t, *J* = 1.6 Hz, 1H), 8.10 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 4H), 7.69-7.66 (m, 5H). ¹³C NMR (150 MHz, CDCl₃, δ): 143.28, 139.29, 133.04, 132.18, 130.89, 129.51, 129.43, 126.77.

DTC-pBPSB: 3,6-Bis(*tert*-butyl)-9H-carbazole (1.22 g, 4.4 mmol), compound **3** (1.03 g, 2 mmol), iodide copper (0.04 g, 0.2 mmol), 18-Crown-6 (0.11 g, 0.4 mmol), anhydrous potassium carbonate (1.38 g, 10 mmol) were added into 15 mL of DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) and heated to 120 °C for 24 h with stirring. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic phase was combined and dried over magnesium sulfate. After the solvent was removed, the product was purified by column chromatography on silica gel to afford the target compound. The product was further sublimed at 300-320 °C and 4×10^{-2} Pa to give a white solid (1.19 g, yield 65%). MALDI-TOF (*m*/z): calcd for C₅₈H₆₀N₂O₄S₂, 912.40; found, 912.36. Anal. calcd for C₅₈H₆₀N₂O₄S₂: C 76.28, H 6.62, N 3.07, O 7.01, S 7.02 ; found: C 76.09, H 6.73, N 3.01, S 7.13. ¹H NMR (600 MHz, CDCl₃, δ): 8.21 (s, 4H), 8.16 (d, *J* = 8.6 Hz, 4H), 8.11 (d, *J* = 1.7 Hz, 4H), 7.79 (d, *J* = 8.6 Hz, 4H), 7.45 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.40 (d, *J* = 8.6 Hz, 4H), 1.45 (s, 36H). ¹³C NMR (150 MHz, CDCl₃, δ): 146.22, 144.31, 143.89, 138.12, 137.21, 129.91, 128.86, 126.59, 124.22, 124.05, 116.56, 109.13, 34.79, 31.92.

DTC-mBPSB: DTC-mBPSB was synthesized according to the procedure as described above for the synthesis of DTC-pBPSB by combining 3,6-bis(*tert*-butyl)-9H-carbazole and **4**, giving a white solid in 60% yield. MALDI-TOF (*m*/z): calcd for C₅₈H₆₀N₂O₄S₂, 912.40; found, 912.36. Anal. calcd for C₅₈H₆₀N₂O₄S₂: C 76.28, H 6.62, N 3.07, O 7.01, S 7.02; found: C 76.02, H 6.77, N 3.03, S 6.94. ¹H NMR (600 MHz, CDCl₃, δ): 8.71 (t, J = 1.6 Hz, 1H), 8.25 (dd, J = 7.9, 1.8 Hz, 2H), 8.21-8.16 (m, 4H), 8.11 (d, J = 1.5 Hz, 4H), 7.83-7.76 (m, 5H), 7.45 (dd, J = 8.7, 1.9 Hz, 4H), 7.41 (d, J = 8.6 Hz, 4H), 1.45 (s, 36H). ¹³C NMR (150 MHz, CDCl₃, δ): 144.24, 143.83, 143.60, 138.14, 137.36, 132.26, 130.94, 129.85, 126.97, 126.64, 124.19, 124.04, 116.53, 109.15, 34.78, 31.91.

2. Thermal analysis



Fig. S1 Thermogravimetric analysis (TGA) curves of the BPSB compounds DTCpBPSB and DTC-mBPSB.

3. Electrochemical cyclic voltammetry (CV)



Fig. S2 Cyclic voltammograms of DTC-mBPSB and DTC-pBPSB.

4. Low temperature PL spectra



Fig. S3 PL spectra of DTC-mBPSB and DTC-pBPSB in dichloromethane solution at 77 K.

5. Transient PL decays of solutions



Fig. S4 Transient PL decay curves of DTC-pBPSB (*top*) and DTC-mBPSB (*bottom*) in chloroform at room temperature.

6. PL spectra of doped films



Fig. S5 PL spectra of DTC-pBPSB and DTC-mBPSB co-deposited with DPEPO in a concentration of 10 wt%.

7. Comparison of the performance of the devices based on DPS and BPSB compounds



Fig. S6 EQE and current efficiency versus current density characteristics of the electroluminescence devices with an EML of 10 wt% DTC-pBPSB (\blacktriangle), DTC-mBPSB (\blacksquare), and DTC-DPS (\bigcirc) doped into DPEPO.

8. ¹H and ¹³C NMR spectra



¹H-NMR spectrum of 1,4-bis((4-bromophenyl)thio)benzene (1) in CDCl₃



 13 C-NMR spectrum of 1,4-bis((4-bromophenyl)thio)benzene (1) in CDCl₃



¹H-NMR spectrum of 1,3-bis((4-bromophenyl)thio)benzene (2) in $CDCl_3$



¹³C-NMR spectrum of 1,3-bis((4-bromophenyl)thio)benzene (2)



¹H-NMR spectrum of 1,4-bis((4-bromophenyl)sulfonyl)benzene (**3**) in CDCl₃



¹³C-NMR spectrum of 1,4-bis((4-bromophenyl)sulfonyl)benzene (**3**) in CDCl₃



¹H-NMR spectrum of 1,3-bis((4-bromophenyl)sulfonyl)benzene (4) in CDCl₃



¹³C-NMR spectrum of 1,3-bis((4-bromophenyl)sulfonyl)benzene (4) in CDCl₃



¹H-NMR spectrum of **DTC-pBPSB** in CDCl₃







¹H-NMR spectrum of **DTC-mBPSB** in CDCl₃



¹³C-NMR spectrum of **DTC-mBPSB** in CDCl₃