Electronic supplementary information (ESI) for

"Bisindoles Containing 2,1,3-Benzothiadiazole Unit: Novel Non-Doping Red Organic Light-Emitting Diodes with Excellent Color Purity"

Qiang Fang,* Bing Xu, Biao Jiang,* Haitao Fu, Xiaoyao Chen and Amin Cao,

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China

1. Synthesis procedure for the new compounds

1.1 Synthesis of 4,7-bis(3-indolyl)-2,1,3-benzothiadiazole

A mixture of TBS protected indolylboronic acid (30 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (2.205 g, 7.5 mmol), tetrakis(triphenylphosphine) palladium (867 mg, 0.75 mmol), aqueous sodium carbonate (2 M, 30 mL), toluene (100 mL) was refluxed for 24 hours under argon atmosphere. The resulting solution was added water (100 mL) and then extracted twice with EtOAc (50 mL×2). The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent, the crude product was dissolved in THF (50 mL). TBAF (1 M in THF, 30 mL) was added and the resulting mixture was stirred at room temperature for 8 hours. Water (100 mL) was added and the mixture was extracted twice with EtOAc (50 mL×2). The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent, the crude product was recrystallized from a mixture of toluene and methanol to give product (2.7 g, 98%). m.p. 296-297 ^{o}C; IR (KBr) ν_{max} 3395, 1592, 1458, 1102, 749, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ8.47 (s, 2H), 8.26 (s, 2H), 8.13-8.19 (m, 2H), 7.54-7.62 (m, 2H), 7.17-7.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 75MHz): δ 158.6, 141.3, 131.7, 130.4, 130.2, 126.2, 124.4, 124.3, 116.3; EIMS m/z (%) 366 (M^{+}, 100); HRMS Calcd. for $C_{22}H_{14}N_4SNa^{+1}$: 389.0831. Found: 389.0843.

1.2 Synthesis of 1a-1c.

To a solution of 4,7-bis(3-indolyl)-2,1,3-benzothiodiazole (2.5 mmol) in DMF (20 mL) was added NaH (10 mmol). The suspended mixture was stirred for 15 minutes at room temperature, then, 10 mmol of iodo-methane (for **1a**) or iodo-ethane (for **1b**) or benzyl bromide (for **1c**) was added to the mixture. After stirring for 2 hours at r. t., the reactant mixture was quenched by the addition of water

(200 mL) and extracted twice with EtOAc (50 mL×2). The organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude product was recrystallized a mixture of THF and hexane to give **1a-1c.** **1a**, yield of 77 %. m.p. 245-246 °C; IR (KBr) ν_{max} 1591, 1478, 1372, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.95 (s, 6H), 7.26-7.37 (m, 4H), 7.43-7.45(m, 2H), 8.12-8.14 (m, 2H) 8.18 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.5, 137.5, 131.0, 126.6, 126.4, 125.7, 122.3, 120.5, 120.4, 111.8, 109.9, 33.3; MALDI-MS m/z (%) 394 (M^+, 100); HRMS Calcd. for $C_{24}H_{18}N_4S$: 394.1247. Found: 394.1246. **1b**, yield of 57 %. m.p. 124-125 °C; IR (KBr) ν_{max} 1588, 1522, 1218, 875, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.57 (t, 7.2 Hz, 6H), 4.33(q, 7.2Hz, 4H), 7.24-7.53 (m, 4H), 7.47 (d, 8.1 Hz), 8.12-8.15 (m, 2H), 8.26(s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.4, 136.4, 129.4, 126.7, 126.2, 125.6, 122.0, 120.6, 120.3, 111.8, 109.9, 41.3, 15.5; MALDI-MS m/z (%) 422 (M^+, 100); Anal. Calcd. for $C_{26}H_{22}N_4S$: C, 73.90; H, 5.25; N, 13.26. Found: C, 73.83; H, 4.91; N, 13.12. **1c,** yield of 71 %. m.p. 199-200 °C; IR (KBr) ν_{max} 1590, 1516, 1468, 1391, 1183, 873, 737, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.50 (s, 4H), 7.24-7.42 (m, 16H), 8.14-8.19 (m, 4H), 8.32 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.2, 137.1, 136.8, 130.4, 128.8, 127.6, 126.73, 126.69, 126.2, 125.5, 122.3, 120.4, 112.2, 120.4, 50.3; MALDI-MS m/z (%) 546 (M^+, 100); Anal. Calcd. for $C_{26}H_{22}N_4S$: C, 79.09; H, 4.79; N, 10.25. Found: C, 78.76; H, 4.84; N, 10.19.

2. Measurement

FT-IR spectra were recorded on a Nicolet spectrometer with KBr pellets. ^1H NMR spectra were carried out on a Bruker DRX 400 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. Elemental analysis was taken with a Carlo Erba 1106 elemental analyzer. UV-visible absorption spectra were obtained with a Hitachi 2800 spectrophotometer. Photoluminescence was measured with a Hitachi F-4500 fluorescence spectrophotometer. DSC was determined with a Du Pont 2100 analyzer at a heating rate of 10 ºC min^{-1} in nitrogen. Cyclic voltammetry of the compounds was performed in an dichloromethane solution containing $[Bu_4N]ClO_4$ (0.10 M, Bu = butyl)) under argon using (0.10 M $AgNO_3$)/Ag and platinum wire as reference and counter electrodes, respectively. A CHI 600B analyzer (Shanghai Chen Hua Company) was used for the cyclic voltammetry.

3. X-Ray structure of 1b

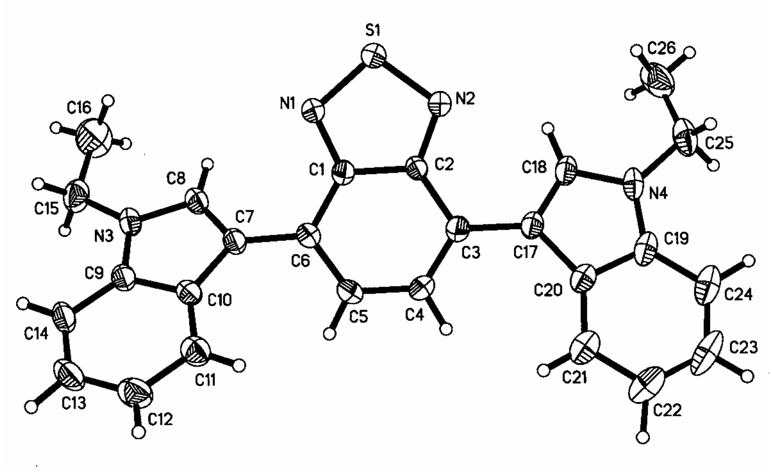

Fig. S1. Single crystal X-ray structure of **1b**.

4. Properties of the compounds

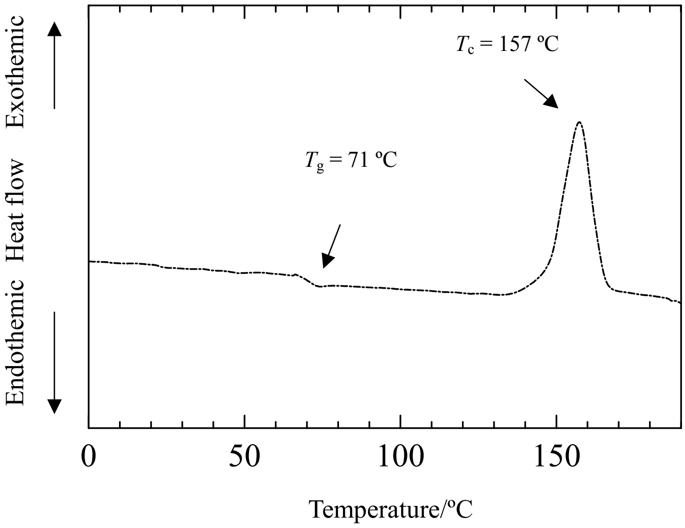

Fig. S2. DSC trace of **1c** (T_g and T_c are glass transition and crystallization temperature, respectively). The samples for measurement were pretreated by heating to melting point following to be cooled in liquid nitrogen quickly.

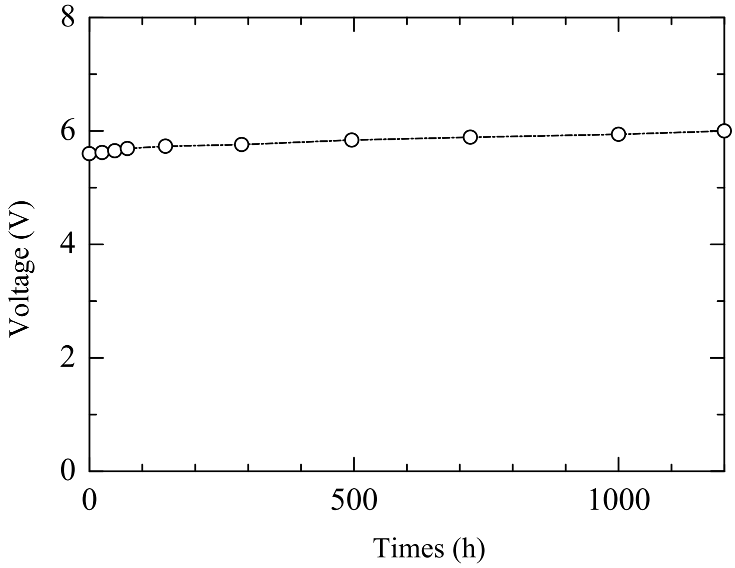

Fig. S3. Time-voltage curve of the device at 12 mA/cm^{-2}.

Table S1. UV-Vis spectra and optical band gaps of **1a-1c.**

Compounds	UV-vis (λ_{max}, nm) In solution [a] (log ε)[b]	E_g^{op} (eV)[c]
1a	309, 480 (4.14)	2.13
1b	309, 481 (4.13)	2.15
1c	307, 476 (4.20)	2.22
precursor[d]	358	

[a] In dichloromethane at room temperature. [b] Molar absorption coefficient. [c] Optical band gap estimated from the UV-vis absorption onset wavelength of the compounds. [d] 4,7-dibromo-2,1,3-benzothiadiazole