

Supporting information for

**First disubstituted dibenzothiophene-5,5-dioxide monodispersed
molecular materials for efficient blue-electroluminescence**

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Experimental and computational details

All reactions were carried out under inert nitrogen atmosphere using Schlenk techniques. All solvents were carefully dried and freshly distilled prior to use. 2-Bromofluorene (**1**) and all other reactants were purchased from Aldrich, Acros or Fluka, and were used without further purifications. 3-Bromocarbazole (**4**),¹ 3,7-dibromo-dibenzothiophene-5,5-dioxide (**7**),² 2,8-dibromo-dibenzothiophene-5,5-dioxide³ (**8**) were synthesized according to literature procedures. ¹H and ¹³C{¹H}NMR spectra were recorded at 295 K on a Bruker Avance 400 MHz. UV-Vis and fluorescence spectra were measured on a Kontron Uvikon 942 instrument and a Varian Cary Eclipse spectrofluorimeter respectively. Quantum yields were measured by the dilute solution method, using a 9,10-diphenylanthracene solution in cyclohexane ($\Phi = 0.90$) as standard.⁴ GCMS data (EI, 70 eV) were acquired on a HP 6890 instrument equipped with a HP-5MS 5% phenyl methyl siloxane (30.0 m \times 250 μ m \times 0.25 μ m) coupled with a HP 5973 mass spectrometer. Mass analyses were performed by direct injection on an Agilent HPLC system equipped with a MS systems (Agilent 1200/6320 LC-MS) and an APCI interface. Melting points have been measured with a Büchi B-545 and are uncorrected. Cyclic voltammetry scans were carried out under inert

nitrogen atmosphere using an Autolab potentiostat PGSTAT 10 and a three-electrode cell (a glassy carbon, platinum or ITO as working electrode, an Ag wire as reference electrode, and a platinum counter electrode), a rate scan of 200 mV/s and n-Bu₄NClO₄ (0.1 M) as a supporting electrolyte. The CV measurements were carried out in CH₂Cl₂ solutions and calibrated with respect to the Fc/Fc⁺ couple. Thermogravimetric analyses (TGA) were carried out under nitrogen on a TA Instruments 2590 thermobalance using a heating ramp of 10 °C/min. Differential scanning calorimetry (DSC) was measured on a TA Instruments Q200 calorimeter. All samples were typically subjected to a heating scan to 250 °C, a cooling scan to room temperature and a re-heating scan (all carried out at 10 °C/min under inert atmosphere).

Density functional theory (DFT) and time dependent (TD-DFT) calculations for molecular geometries, absorption and emission energies of the emitting materials were performed using the TURBOMOLE quantum chemistry package.⁵ The B3-LYP⁶ functional and the TZVP⁷ basis set were used to calculate the lowest excitation energies at the optimized ground-state geometry and at the optimized geometry of the lowest optically active state.⁸ The calculations were restricted to the molecules in the gas phase; test calculations of absorption energies explicitly including the CHCl₃ solvent molecules, showed effects on the computed excitation energies of the order of 0.1 eV, comparable with the global accuracy of the B3-LYP/TZVP calculations.

The p and n layers were commercial. All compounds were deposited by evaporation in a UHV cluster tool at a base pressure of $\sim 10^{-8}$ mbar. The deposition rate ranged from 0.5 to 1.0 Å/s. The deposition rates and layer thickness were controlled by a quartz sensor. The ITO substrates were cleaned in acetone, deionized water and i-propanol for 10 min at 60 °C in an ultrasonic bath. The active area of the OLED (15 mm²) was defined by the overlap between the ITO anode and the device cathode; 8 pixels could be defined on each substrate. The electrical-optical characteristics of the devices were measured under vacuum with an Optronics OL770 spectrometer, coupled with a OL610 telescope unit through an optical fiber for the luminance measurements. The whole system

was NIST calibrated using a standard lamp. The current-voltage measurements were carried out by a Keithley 2420 source meter.

2-Bromo-9,9-dimethylfluorene (2). Potassium *t*-butoxide (7.18 g, 64.0 mmol) was added portionwise to a solution of **1** (3.92 g, 16.0 mmol), potassium iodide (0.27 g, 1.6 mmol), and methyl iodide (5.11 g, 36.0 mmol) in DMSO (30 mL). The addition was performed in 1 hour at room temperature. The obtained mixture was vigorously stirred overnight. Then the reaction was quenched with water (30 mL) for extraction with diethyl ether (3 × 60 mL) and the resulting organic layer was dried over Na₂SO₄. After solvent removal, the crude product was purified by flash chromatography (SiO₂, petroleum ether 40-60 °C) to afford **2** (3.20 g, 73%) as a white solid. m.p. = 56.7-57.9 °C. MS (EI, 70 eV): *m/z* 274 (46), 272 (M⁺, 48), 259 (55), 257 (57), 193 (29), 178 (100). ¹H-NMR (400 MHz, CDCl₃): δ 7.76-7.71 (m, 1H), 7.64-7.60 (m, 2H), 7.52-7.45 (m, 2H), 7.40-7.36 (m, 2H), 1.52 (s, 6H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 155.7, 153.2, 138.2, 138.1, 130.1, 127.7, 127.2, 126.2, 122.7, 121.4, 121.1, 120.1, 47.1, 27.0.

2-(9,9-Dimethylfluoren-2-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3). To a solution of **2** (3.00 g, 10.98 mmol) in THF (40 mL) kept at -80 °C, a solution of *n*-BuLi (1.6 M in hexanes, 7.2 mL, 11.50 mmol) was added dropwise. The obtained mixture was vigorously stirred for 1 hour at -80 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (2.23 g, 12.00 mmol) in one portion. The resulting solution was then allowed to reach room temperature and stirred for further 4 hours. After solvent removal, the obtained solid was dissolved in CH₂Cl₂ (50 mL) and the solution washed with water (3 × 50 mL). The organic phase was dried over Na₂SO₄ and the solvent removed in vacuo. The obtained crude product was purified by flash chromatography (SiO₂, petroleum ether 40-60 °C/ CH₂Cl₂ = 1/1) to give **3** (2.87 g, 80%) as a white solid. m.p. = 131.8-132.7 °C. MS (EI, 70 eV): *m/z* 320 (M⁺, 68), 305 (100), 221 (20), 205 (47), 178 (19). ¹H-NMR (400 MHz, CDCl₃): δ 7.91 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.80-7.74 (m, 2H), 7.49-

7.44 (m, 1H), 7.39-7.34 (m, 2H), 1.52 (s, 6H), 1.40 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 154.3, 152.7, 142.2, 138.9, 133.9, 128.8, 127.0, 122.7, 120.5, 119.4, 83.8, 46.9, 27.1, 24.9.

3-Bromo-N-methylcarbazole (5). Potassium *t*-butoxide (3.59 g, 32.0 mmol) was added portionwise to a DMSO solution (30 mL) of **4** (3.94 g, 16.0 mmol), potassium iodide (0.27 g, 1.6 mmol), and methyl iodide (2.55 g, 18.0 mmol) kept at room temperature. The addition was performed in 1 hour and the obtained mixture was vigorously stirred overnight. Then, the reaction was quenched with water (30 mL) for extraction with diethyl ether (3×60 mL) and the resulting organic layer was dried over Na_2SO_4 . After solvent removal, the crude product was purified by flash chromatography (SiO_2 , petroleum ether 40-60 °C) to afford **5** (1.40 g, 34%) as a white solid. m.p. = 74.5-75.6 °C. GC-MS (EI, 70 eV): m/z 261 (94), 259 (M^+ , 100), 246 (7), 244 (8), 179 (24), 164 (15). ^1H -NMR (400 MHz, CDCl_3): δ 8.21 (d, $J = 2.0$ Hz, 1H), 8.06 (d, $J = 7.7$ Hz, 1H), 7.58-7.50 (m, 2H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.26-7.24 (m, 2H), 3.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 141.2, 139.6, 128.3, 126.4, 124.4, 123.0, 121.7, 120.5, 119.3, 111.6, 109.0, 108.7, 29.2.

2-(N-methylcarbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (6). To a solution of **5** (1.24 g, 4.78 mmol) in THF (20 mL) kept at -80 °C, *n*-BuLi (1.6 M in hexanes, 3.1 mL, 4.90 mmol) was added dropwise. The obtained mixture was vigorously stirred for 1 hour at -80 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (0.95 g, 5.10 mmol) in one pot. Subsequently, the resulting solution was allowed to reach room temperature and stirred for further 4 hours. After solvent removal, the obtained solid was dissolved in CH_2Cl_2 (50 mL) washed with water (3×50 mL) and the organic phase was dried over Na_2SO_4 . After solvent removal, the crude product was purified by flash chromatography (SiO_2 , petroleum ether 40-60 °C/ $\text{CH}_2\text{Cl}_2 = 1/2$) to give **6** (1.13 g, 77%) as white solid. m.p. = 150.6-151.8 °C. GC-MS (EI, 70 eV): m/z 307 (M^+ , 100), 292 (5), 234 (20), 207 (52), 193 (11). ^1H -NMR (400 MHz, CDCl_3): δ 8.62 (s, 1H), 8.15 (d, $J = 7.4$ Hz, 1H), 7.95 (d, $J = 7.4$ Hz, 1H), 7.53, 7.47 (m, 1H), 7.45-7.40 (m, 2H), 7.30-7.24 (m, 1H), 3.88 (s,

3H), 1.43 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 143.1, 141.1, 132.2, 127.7, 125.7, 123.0, 122.5, 120.5, 119.3, 108.5, 107.9, 83.6, 29.1, 25.0.

3,7-Bis-(9,9-dimethylfluoren-2-yl)-dibenzothiophene-5,5-dioxide (3,7-DBTOF). A mixture of **3** (0.87 g, 2.72 mmol), **7** (0.51 g, 1.35 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.02 mmol) in toluene (16 mL) and a 2.0 M K_2CO_3 aqueous solution (8 mL) was refluxed overnight. After cooling the mixture down to room temperature, CH_2Cl_2 (40 mL) was added and the obtained mixture was washed with water (3×40 mL). After solvent removal, the crude product was purified by flash chromatography (SiO_2 , petroleum ether 40-60 °C/ $\text{CH}_2\text{Cl}_2 = 1/2$) to afford **3,7-DBTOF** (0.66 g, 81%) as a pale yellow solid. APCI (m/z): calcd. 600.2; found 601.7 ($\text{M}^+ + 1$). ^1H -NMR (400 MHz, CDCl_3): δ 8.17 (s, 2H), 7.93 (d, $J = 8.2$ Hz, 2H), 7.87 (d, $J = 7.7$ Hz, 2H), 7.83 (d, $J = 7.7$ Hz, 2H), 7.80-7.76 (m, 2H), 7.73 (s, 2H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.52-7.48 (m, 2H), 7.42-7.36 (m, 4H), 1.58 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 154.7, 154.0, 144.0, 139.8, 138.6, 138.4, 137.7, 132.5, 130.0, 127.8, 127.2, 126.1, 122.8, 122.0, 121.3, 120.7, 120.6, 120.3, 47.1, 27.2.

3,7-Bis-(N-methylcarbazol-3-yl)-dibenzothiophene-5,5-dioxide (3,7-DBTOC). A mixture of **6** (0.22 g, 0.72 mmol), **7** (0.13 g, 0.35 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (12 mg, 0.01 mmol) in toluene (6 mL) and a 2.0 M K_2CO_3 aqueous solution (3 mL) was refluxed overnight. After cooling the mixture down to room temperature, CH_2Cl_2 (30 mL) was added and the obtained mixture was washed with water (3×30 mL). After solvent removal, the crude product was purified by flash chromatography (SiO_2 , CH_2Cl_2) to afford **3,7-DBTOC** (0.16 g, 79%) as a yellow solid. APCI (m/z): calcd. 574.2; found 575.5 ($\text{M}^+ + 1$). ^1H -NMR (400 MHz, CDCl_3): δ 8.40 (s, 2H), 8.23-8.17 (m, 4H), 8.05-7.97 (m, 2H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.80 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.59-7.45 (m, 6H), 7.35-7.29 (m, 2H), 3.93 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 144.4, 141.6, 141.1, 138.6, 132.5, 129.8, 129.5, 126.3, 124.8, 123.5, 122.8, 121.9, 120.5, 119.4, 119.0, 109.1, 108.8, 29.7.

2,8-Bis-(9,9-dimethylfluoren-2-yl)-dibenzothiophene-5,5-dioxide (2,8-DBTOF). A mixture of **3** (0.87 g, 2.72 mmol), **8** (0.51 g, 1.35 mmol) and Pd(PPh₃)₄ (23 mg, 0.02 mmol) in toluene (16 mL) and a 2.0 M K₂CO₃ aqueous solution (8 mL) was refluxed overnight. After cooling the mixture down to room temperature, methylene chloride (40 mL) was added and the obtained mixture was washed with water (3 × 40 mL). After solvent removal, the crude product was purified by flash chromatography (SiO₂, petroleum ether 40-60 °C/ CH₂Cl₂ = 1/3) to afford **2,8-DBTOF** (0.76 g, 94%) as a white solid. APCI (m/z): calcd. 600.2; found 601.7 (M⁺ + 1). ¹H-NMR (400 MHz, CDCl₃): δ 8.14 (s, 2H), 7.95 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.85-7.79 (m, 4H), 7.72 (s, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.53-7.48 (m, 2H), 7.44-7.36 (m, 4H), 1.60 (s, 12H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 154.6, 154.0, 147.9, 140.0, 138.4, 138.3, 136.6, 132.3, 129.5, 127.9, 127.2, 126.6, 122.8, 122.6, 121.7, 120.6, 120.4, 120.3, 47.1, 27.2.

2,8-Bis-(N-methylcarbazol-3-yl)-dibenzothiophene-5,5-dioxide (2,8-DBTOC). A mixture of **6** (0.22 g, 0.72 mmol), **8** (0.13 g, 0.35 mmol) and Pd(PPh₃)₄ (12 mg, 0.01 mmol) in toluene (6 mL) and a 2.0 M K₂CO₃ aqueous solution (3 mL) was refluxed overnight. After cooling the mixture down to room temperature, CH₂Cl₂ (30 mL) was added and the obtained solution was washed with water (3 × 30 mL). After solvent removal, the crude product was purified by flash chromatography (SiO₂, CH₂Cl₂) to afford **2,8-DBTOC** (0.11 g, 56%) as a pale yellow solid. APCI (m/z): calcd. 574.2; found 575.5 (M⁺ + 1). ¹H-NMR (400 MHz, CDCl₃): δ 8.43 (s, 2H), 8.25-8.20 (m, 4H), 7.95 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.82 (dd, J = 8.5, 1.8 Hz, 2H), 7.59-7.52 (m, 4H), 7.47 (d, J = 8.1 Hz, 2H), 7.34-7.29 (m, 2H), 3.94 (s, 6H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 148.3, 141.6, 141.2, 135.9, 132.5, 130.3, 129.2, 126.3, 125.2, 123.5, 122.7, 122.5, 120.5, 120.1, 119.4, 119.3, 109.1, 108.8, 29.7.

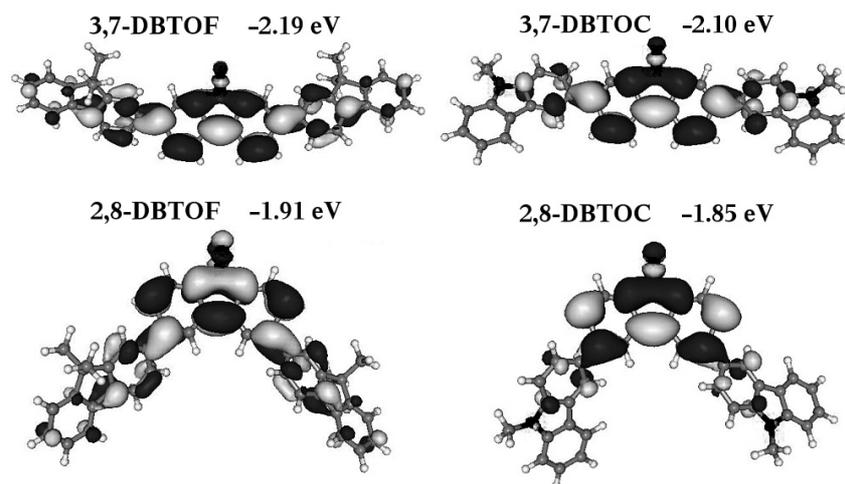


Figure S-1. LUMO molecular orbitals of the molecules in the ground-state configuration.

References

- [1] R. Grisorio, C. Piliago, P. Fini, P. Cosma, P. Mastrorilli, G. Gigli, G. P. Suranna and C. F. Nobile, *J. Phys. Chem. C*, 2008, **112**, 7005.
- [2] C. R. Newmoyer and E. D. Amstutz, *J. Am. Chem. Soc.*, 1947, **69**, 1920.
- [3] J. N. Demas, G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
- [4] (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Letters*, 1989, **162**, 165. (b) O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346. (c) M. V. Arnim and R. Ahlrichs, *J. Chem. Phys.*, 1999, **111**, 9183. (d) R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Letters*, 1996, **256**, 454. (e) F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2002, **117**, 7433. (f) F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2004, **121**, 12772.
- [5] (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785. (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- [6] A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.