Supporting Information

Efficient Deep Blue Fluorescent Polymer Light-Emitting Diodes (PLEDs)

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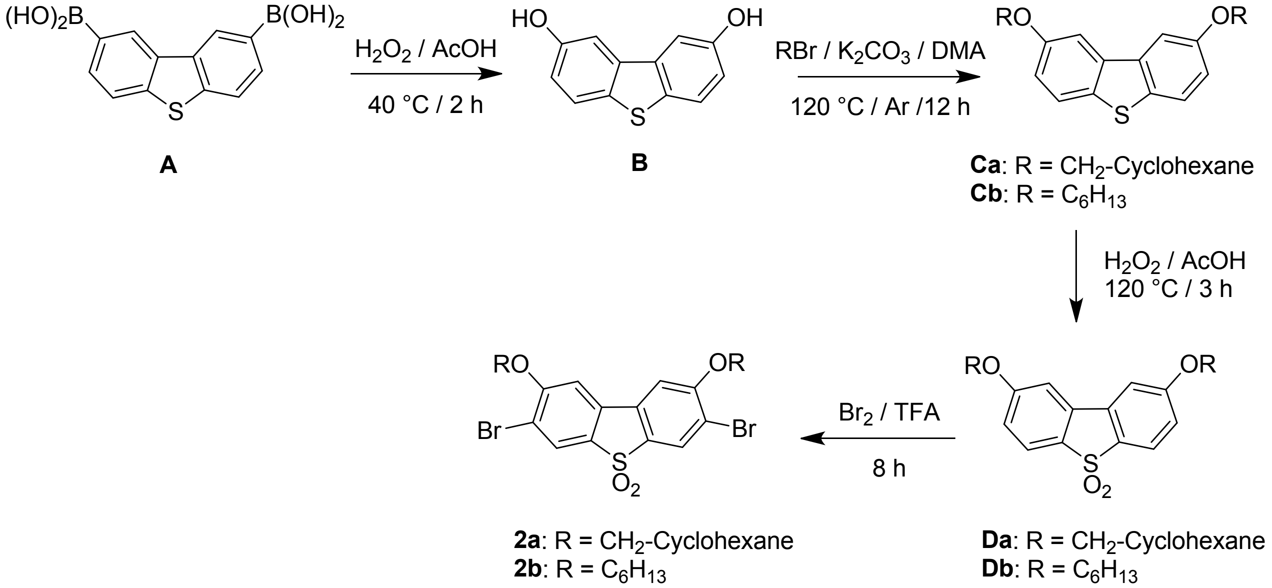
Monomer Synthesis

Monomers **1** and **3** were synthesised following literature routes.[1] Monomers **2a** and **2b** were synthesised as shown in Scheme S1.[2]



Scheme S1. Synthesis of the dibenzothiophene-*S,S*-dioxide monomers **2a** and **2b**.

Material Synthesis and Characterisation

Materials obtained from commercial suppliers were used without further purification. Solvents were dried and degassed following standard procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. ASAP-TOF and HR mass spectra were measured either on a Xevo QToF mass spectrometer (Waters Ltd, UK) equipped with an Agilent 7890 GC (Agilent Technologies UK Ltd, UK) or a LCT Premier XE mass spectrometer and an Acquity UPLC (Waters Ltd, UK). Elemental analysis was performed on a CE-400 elemental analyser.

2,8-Dihydroxydibenzothiophene (B): To a solution of dibenzothiophene-2,8-diboronic acid **A**[3] (2.19 g, 8.05 mmol) in AcOH (80 mL), hydrogen peroxide was added (1.8 mL, 35% v/v) and the resulting mixture was stirred at 40 °C for 3 h, then cooled to room temperature and water (130 mL) was added. A white precipitate of **B** was isolated by filtration and dried at low pressure (1.47 g, 85%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 10.43 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 2H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 2H). MS (ASAP$^+$): *m/z* = 216.0 (100%, M$^+$).

2,8-Di(cyclohexylmethyloxy)dibenzothiophene (Ca): B (2.80 g, 13 mmol) was dissolved in *N,N*-dimethylacetamide (DMA) (20 mL) under argon, then K_2CO_3 (8.3 g, 60 mmol) and bromomethylcyclohexane (5.6 g, 40 mmol) were sequentially added. The resulting yellow suspension was stirred for 12 h at 120 °C, cooled to room temperature, filtered and the filtrate was evaporated. The residue was redissolved in DCM, washed with water, dried with Na_2SO_4, filtered and the solvent evaporated. Purification by column chromatography (silica gel, DCM/hexane 2:1 v/v) gave **Ca** as a white solid (72%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 2H), 7.06 (dd, *J* = 8.4, 2.4 Hz, 2H), 3.94 (d, *J* = 6.0 Hz, 4H), 1.88-1.62 (m, 12H), 1.35-1.02 (m, 10H). MS (ASAP$^+$): *m/z* = 408.2 (100%, M$^+$).

2,8-Dihexyloxydibenzothiophene (Cb): Following the same procedure as for **Ca**, using 1-bromohexane, compound **Cb** was obtained as a white solid (72%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 2H), 7.30 (dd, *J* = 8.0, 2.4 Hz, 2H), 4.13 (t, *J* = 6.8 Hz, 4H), 1.80-1.74 (m, 4H), 1.50-1.40 (m, 4H), 1.36-1.30 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 6H). MS (ASAP$^+$): *m/z* = 384.2 (100%, M$^+$).

2,8-Di(cyclohexylmethyloxy)dibenzothiophene-*S,S*-dioxide (Da): Compound **Ca** (2.0 g, 4.9 mmol) was dissolved in AcOH (20 mL), then H_2O_2 (3 mL, 35% v/v) was added and the reaction mixture was stirred and heated at 125 °C for 12 h. When cooled to room temperature, the mixture was added to water (100 mL) and extracted with AcOEt. The organic layers were dried with Na_2SO_4, filtered and vacuum evaporated. The residue was purified by column chromatography (silica gel, DCM/hexane 2:1 v/v). to give **Da** as a white solid (80%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.83 (d, *J* = 2.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 8.4, 2.4 Hz, 2H), 3.97 (d, *J* = 6.4 Hz, 4H), 1.88-1.62 (m, 12H), 1.36-1.02 (m, 10H). HRMS (ASAP): *m/z* calculated for $C_{26}H_{32}O_4S$: 440.2021; found 440.2020.

2,8-Dihexyloxydibenzothiophene-*S,S*-dioxide (Db): Following the same procedure as for **Da**, **Cb** gave **Db** as a white solid (84%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.82 (d, *J* = 2.0 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 2H), 4.15 (t, *J* = 6.8 Hz, 4H), 1.80-1.72 (m, 4H), 1.50-1.40 (m, 4H), 1.36-1.28 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 6H). HRMS (ASAP): *m/z* calculated for $C_{26}H_{32}O_4S$: 416.2021; found 416.2022.

3,7-Dibromo-2,8-di(cyclohexylmethoxy)dibenzothiophene-*S,S*-dioxide (2a): To a solution of **Da** (1.40 g, 3.18 mmol) in trifluoroacetic acid (20 mL), Br_2 (0.32 mL, 6.36 mmol) was added and stirred overnight. The mixture was quenched with water (50 mL) and extracted with DCM. The organic layers were dried with $NaSO_4$, filtered and vacuum evaporated. The residue was purified by column chromatography (silica gel, DCM/hexane 2:1 v/v) to give **2a** as a white solid (1.76 g, 93%) which was recrystallised from a mixture of methylcyclohexane and THF. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.87 (s, 2H), 7.04 (s, 2H), 3.98 (d, *J* = 5.5 Hz, 4H), 1.98-1.75 (m, 12H), 1.43-1.18 (m, 10H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.3, 132.2, 130.9, 127.0, 114.9, 104.8, 75.5, 38.0, 30.0, 26.6, 26.0. MS (ASAP): *m/z* = 597.0 (M+1$^+$). HRMS (ASAP): *m/z* calculated for $C_{26}H_{30}Br_2O_4S$: 596.0232; found: 596.0234. Elemental analysis: calculated: C, 52.19; H, 5.05; found: C, 52.04; H, 5.11%.

3,7-Dibromo-2,8-dihexyloxydibenzothiophene-*S,S*-dioxide (2b): Following the same procedure as for **2a**, **Db** gave **2b** as a white solid (95%) which was recrystallised from an ethanol/ethyl acetate mixture. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (s, 2H), 6.95 (s, 2H), 4.08 (t, *J* = 6.4 Hz, 4H), 1.95-1.85 (m, 4H), 1.62-1.52 (m, 4H), 1.46-1.32 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.9, 131.8, 130.1, 126.5, 114.5, 104.4, 69.9, 31.5, 28.9, 25.7, 22.6, 14.0. MS (ASAP): *m/z* = 573.0 (M+1$^+$). HRMS (ASAP): *m/z* calculated for $C_{24}H_{30}Br_2O_4S$: 572.0232; found: 572.0237. Elemental analysis: calculated: C, 50.19; H, 5.26; found: C, 50.24; H, 5.21%.

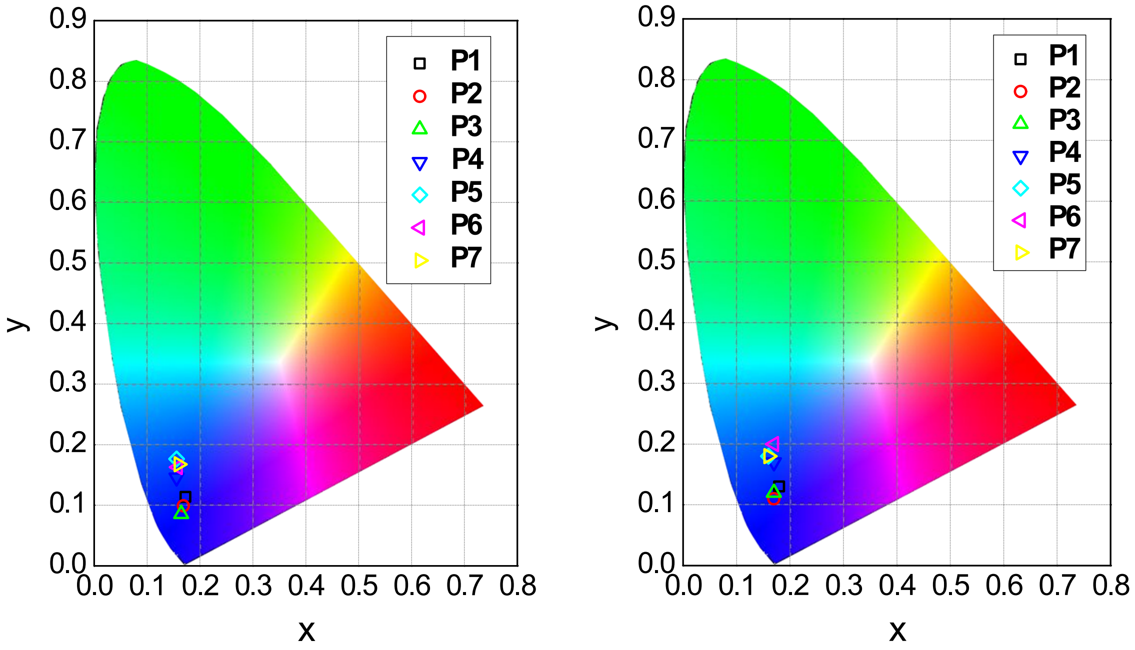


Fig. S1. CIE diagrams for **P1-P7** devices at turn-on voltage (10 cd m^{-2}) (left) and at maximum brightness (right).

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[1] Y. Song, W. Xu and D. Zhu, *Tetrahedron Lett.*, 2010, **51**, 4894-4897.

[2] H. Li, A. S. Batsanov, K. C. Moss, H. L. Vaughan, F. B. Dias, K. T. Kamtekar, M. R. Bryce and A. P Monkman, *Chem. Commun.*, 2010, **46**, 4812-4814.

[3] J. Ogura, T. Ueoka, Y. Tsubata, M. Kitano and C. Sekine, European Patent Application, 2003, EP 1344788A1.