

**Supporting Information for**

**Poly(3,6-dibenzosilole) – a High Energy Gap Host for Phosphorescent Light  
Emitting Devices\*\***

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**General Methods** :  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Bruker DRX-400 (400 MHz) or Bruker DRX-500 (500 MHz) instruments using  $\text{CDCl}_3$  as an internal deuterium lock. IR spectra were recorded on a Nicolet 510 Fourier transform infrared spectrometer. UV-Vis spectra were recorded using a HP 8452A Spectrophotometer. Photoluminescence spectra were recorded on Aminco-Bowman Series 2 Fluorescence Spectrometer. Melting points were determined using a Gallenkamp melting point apparatus or a Büchi 510 melting point apparatus, and are uncorrected. Mass Spectra were recorded by the EPSRC National Mass Spectrometry Service Centre, University of Swansea. Electron Impact (EI) and Chemical Ionisation (CI) low resolution spectra were carried out on a VG model 12-253 under ACE conditions and a Quattro II low resolution triple quadrupole MS. Accurate measurements for EIO and CI were performed on a +VG ZAB-E and Finnigan MAT 900 XLT instruments. All CI measurements were performed with  $\text{NH}_3$  as the carrier gas. Gel Permeation Chromatography measurements were done with HPLC grade chloroform as eluent on a PL gel Mixed B column. Readings were taken with a differential refractometer at a flow rate of  $1 \text{ cm}^3 \text{ min}^{-1}$ , and were calibrated with standard monodispersed polystyrene. Thermogravimetric analysis was carried out on a Perkin Elmer Pyris 1 Thermogravimetric Analyzer.

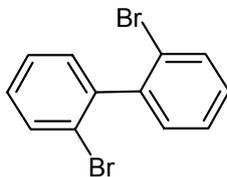
**Materials** : *fac*-tris[2-(2-pyridyl- $\kappa\text{N}$ )-5-methylphenyl]iridium(III) (American Dye Source), *n*-butyllithium (Arcos), *t*-butyllithium (Aldrich), *n*-hexyllithium (Aldrich), 1,2-dibromobenzene (Aldrich), iodine (Aldrich), bromine (Aldrich), iron powder (Aldrich), dichlorodioctylsilane (Fluorochem), dichlorodimethylsilane (Aldrich), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (Aldrich), sodium periodate (Aldrich), acetic anhydride (Aldrich), concentrated sulfuric acid (Fischer), acetic acid (Fison), chlorotrimethylsilane (Aldrich), iodine monochloride (Aldrich), palladium acetate (Lancaster), tricyclohexylphosphine (Aldrich), tetraethylammonium hydroxide (Aldrich), bromobenzene (Aldrich) and phenylboronic acid (Aldrich) were used as obtained.

Column chromatography was carried out on silica gel [Merck Kieselgel 60 (230-400 mesh)] or florisil [BDH Laboratory Supplies (200 mesh)]. Reagents and solvents were used as obtained from commercial suppliers except where indicated otherwise. Dry

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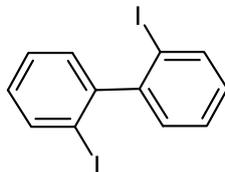
tetrahydrofuran (THF) was distilled from potassium in a recycling still using benzophenone ketyl as indicator. Other solvents were purified by standard techniques. Ether, DCM and PET refers to diethyl ether, dichloromethane and petrol ether 40-60 respectively. Procedures using air/moisture sensitive materials were carried out in a nitrogen filled glove box and/or by the use of a nitrogen filled dual manifold using standard Schlenk line techniques.

**2,2'-Dibromobiphenyl (1)**



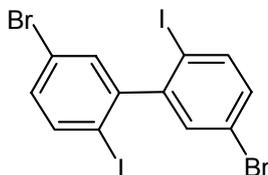
*n*-Butyllithium (20.9 cm<sup>3</sup>, 33.4 mmol) was added dropwise over 1 h into a magnetically stirred solution of 1,2-dibromobenzene (15.0 g, 63.6 mmol) in dry THF (150 cm<sup>3</sup>) at -78 °C under nitrogen atmosphere over. The mixture was stirred at room temperature overnight and the reaction was quenched by water. The crude product was extracted into ether, dried over magnesium sulfate and evaporated to dryness. Purification by crystallization with hexane afforded the title compound (10.0 g, 87 %) as colourless crystals (Found: C, 46.2; H, 2.5. C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub> requires C, 46.2; H, 2.6 %); mp. 79-80 °C (lit.,<sup>[1]</sup> 79-80 °C);  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 761, 1002, 1025, 1422, 1455;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 7.24 (1H, m, ArH), 7.28 (1H, m, ArH), 7.37 (1H, dd, *J* 7.8 1.2 ArH), 7.67 (1H, dd, *J* 7.5 0.8 ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 125.5, 127.1, 129.3, 129.8, 135.8, 141.6; *m/z* (EI) 309.8984 (M<sup>+</sup>. C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub> requires 309.8987), 232.9 (32 %), 152.2 (100), 74.1 (47), 63.2 (39), 50.2 (75).

**2,2'-Diiodobiphenyl (2)**



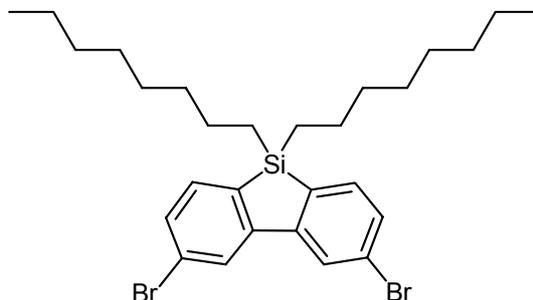
*n*-Butyllithium (154 cm<sup>3</sup>, 0.25 mol) was added over 1 h to a solution of 2,2'-dibromobiphenyl **2** (35 g, 0.11 mol) in dry ether (175 cm<sup>3</sup>) at -78 °C under nitrogen atmosphere. The mixture was stirred at room temperature overnight. A solution of iodine (63 g, 0.25 mol) in ether (260 cm<sup>3</sup>) was added dropwise into the mixture at 0 °C and the resulting purple solution raised to room temperature and stirred for 2 h. The reaction was quenched with sodium thiosulfate solution (5 g in 300 cm<sup>3</sup> H<sub>2</sub>O). The crude product was extracted into ether, dried with anhydrous MgSO<sub>4</sub> and evaporated to dryness. Purification by filtering through a silica plug (10 cm) with hexane as the eluant, and recrystallization with hexane afforded the title compound (39.0 g, 85 %) as colourless crystals (Found: C, 35.7; H, 1.9. C<sub>12</sub>H<sub>8</sub>I<sub>2</sub> requires C, 35.5; H, 2.0 %); mp. 108-109 °C (lit.,<sup>[1]</sup> 109-110 °C);  $\nu_{\max}$  / cm<sup>-1</sup> (Neat solid) 720, 755, 998, 1016, 1418, 1429, 1450, 1557, 1577;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 7.10 (2H, ddd, *J* 8.0 7.6 1.7, *ArH*), 7.20 (2H, dd, *J* 7.6 1.7, *ArH*), 7.44 (2H, ddd, *J* 7.6 7.6 1.1, *ArH*), 7.96 (2H, dd, *J* 8.0 1.1, *ArH*);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 99.6, 128.0, 129.4, 129.9, 138.9, 148.9; *m/z* (EI) 405.8716 (M<sup>+</sup>. C<sub>12</sub>H<sub>8</sub>I<sub>2</sub> requires 405.8710), 279.1 (44 %), 152.1 (100), 126.8 (80), 98.1 (16), 87.1 (18), 74.1 (42), 63.2 (31), 50.2 (52).

**5,5'-Dibromo-2,2'-diiodobiphenyl (3)**



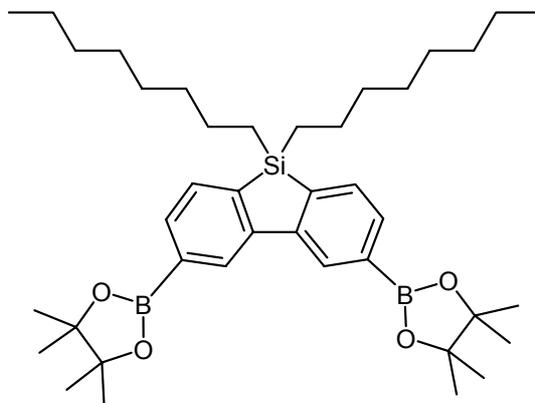
Iron powder (0.1 g, 1.79 mmol) and bromine (2.52 cm<sup>3</sup>, 49.3 mmol) was added to a solution of 2,2'-diiodobiphenyl (5.0 g, 12.3 mmol) in chloroform (100 cm<sup>3</sup>) in nitrogen atmosphere and the mixture was stirred at 50 °C overnight. The reaction was quenched with sodium thiosulfate solution (2 g in 100 cm<sup>3</sup> H<sub>2</sub>O). The crude product was extracted into DCM, dried with anhydrous MgSO<sub>4</sub> and evaporated to dryness. The crude material was vigorously washed with DCM (10 cm<sup>3</sup>), filtered off and dried to afford the *title compound* (3.5 g, 50 %) as a white powder (Found: C, 25.4; H, 1.0. C<sub>12</sub>H<sub>6</sub>Br<sub>2</sub>I<sub>2</sub> requires C, 25.6; H, 1.1 %); mp. 198-200 °C;  $\nu_{\max}$  / cm<sup>-1</sup> (Neat solid) 722, 806, 880, 999, 1017, 1087, 1355, 1387, 1440;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 7.24 (2H, dd, *J* 8.4 2.3, *ArH*), 7.32 (2H, d, *J* 2.3, *ArH*), 7.78 (2H, d, *J* 8.4, *ArH*);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 97.3, 122.3, 132.6, 132.9, 140.3, 149.3; *m/z* (EI) 561.6915 (M<sup>+</sup>. C<sub>63</sub>H<sub>72</sub>O requires 561.6920), 436.9 (26 %), 150.0 (100), 126.9 (48), 98.0 (37), 74.1 (52).

### 3,6-Dibromo-9,9-dioctyldibenzosilole (4)



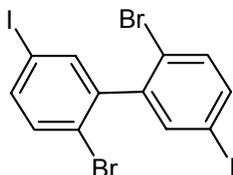
*t*-Butyllithium (13.1 cm<sup>3</sup>, 22.3 mmol, 1.7 M in Pentane) was added over 1 h to a solution of 5,5'-dibromo-2,2'-diiodobiphenyl (3.0 g, 5.32 mmol) in dry THF (100 cm<sup>3</sup>) at -90 °C under nitrogen atmosphere. The mixture was stirred for a further 1 h at -90 °C. Dichlorodioctylsilane (2.2 cm<sup>3</sup>, 6.39 mmol) was subsequently added and the mixture was raised to room temperature and stirred overnight. The reaction was quenched with distilled water, and the THF was removed by vacuum. The product was then extracted into diethyl ether and the organic layer washed with brine, dried with anhydrous MgSO<sub>4</sub> and evaporated. Purification by column chromatography (hexane) yielded the *title compound* (1.92 g, 64 %) as a colourless oil (Found: C, 59.7; H, 7.3. C<sub>28</sub>H<sub>40</sub>Br<sub>2</sub>Si requires C, 59.6; H, 7.1 %);  $\nu_{\max}$  / cm<sup>-1</sup> (Neat liquid) 725, 817, 870, 1023, 1062, 1373, 1455, 1538, 1577, 2852, 2921, 2955;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 0.87 (6H, t, *J* 7.9, CH<sub>3</sub>), 0.91 (4H, m, CH<sub>2</sub>), 1.18-1.30 (24H, m, CH<sub>2</sub>), 7.41 (2H, dd, *J* 7.5 1.5, ArH), 7.46 (2H, d, *J* 7.5, ArH), 7.90 (2H, d, *J* 1.5, ArH);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>) 12.0, 14.1, 22.6, 23.8, 29.0, 29.1, 29.3, 31.8, 33.2, 124.4, 125.2, 130.6, 134.5, 136.8, 149.1; *m/z* (EI) 562.1263 (M<sup>+</sup>. C<sub>28</sub>H<sub>40</sub>Br<sub>2</sub>Si requires 562.1261), 451.1 (39 %), 339.0 (100), 259.1 (24), 179.1 (12), 57.3 (69).

**9,9-Dioctyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)dibenzosilole (5a)**



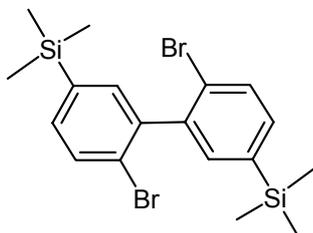
3,6-Dibromo-9,9-dioctyl-9H-9-dibenzosilole **5** (2.0 g, 3.54 mmol) was dissolved in dry THF (20 cm<sup>3</sup>) at -78 °C. *t*-Butyllithium (8.55 cm<sup>3</sup>, 14.5 mmol, 1.7 M in pentane) was then added dropwise over 1 h. The solution was stirred for 30 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (1.81 cm<sup>3</sup>, 8.86 mmol) was then added dropwise and stirring continued overnight at room temperature. Water was carefully added to destroy any excess *t*-butyllithium. The product was extracted into ether, dried with magnesium sulfate and evaporated to give a pale yellow oil. The crude product was purified by column chromatography (hexane) on florisil and recrystallised in ethanol to give the *title compound* (1.8 g, 75 %) as colourless crystals (Found: C, 72.8; H, 9.7. C<sub>40</sub>H<sub>64</sub>Br<sub>2</sub>O<sub>4</sub>Si requires C, 73.0; H, 9.8 %); mp. 87-89 °C;  $\nu_{\max}$  / cm<sup>-1</sup> (Neat solid) 673, 711, 852, 964, 1069, 1096, 1145, 1261, 1315, 1354, 1381, 1418, 1540, 2854, 2923, 2977;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 0.85 (6H, t, *J* 7.0, CH<sub>3</sub>), 0.91-0.95 (4H, m, CH<sub>2</sub>), 1.18-1.35 (24H, m, CH<sub>2</sub>), 1.40 (24H, s, CH<sub>3</sub>), 7.64 (2H, d, *J* 7.0, ArH), 7.73 (2H, d, *J* 7.0, ArH), 8.38 (2H, s, ArH);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>) 12.2, 14.1, 22.6, 23.8, 24.9, 29.0, 29.1, 31.8, 33.3, 83.8, 127.0, 132.5, 133.4, 141.5, 147.7; *m/z* (EI) 676.5104 (M<sup>+</sup>. C<sub>40</sub>H<sub>64</sub>Br<sub>2</sub>O<sub>4</sub>Si requires 676.5098), 658.6 (8 %), 433.3 (25), 83.2 (64), 69.2 (36), 57.3 (100).

**2,2'-Dibromo-5,5'-diiodobiphenyl (6)**



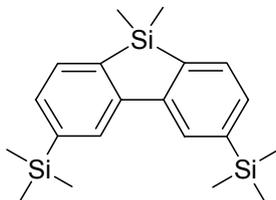
Finely ground iodine (12.0 g, 35.1 mmol) and sodium periodate (11.3g, 52.7 mmol) was added into a stirring mixture of acetic anhydride (30.0 cm<sup>3</sup>) and glacial acetic acid (60.0 cm<sup>3</sup>). Concentrated sulfuric acid (18.8 cm<sup>3</sup>) was added dropwise at 0 °C over 1 h. A separate solution of 2,2'-dibromobiphenyl (12.0 g, 38.5 mmol) in acetic anhydride (10.0 cm<sup>3</sup>) and glacial acetic acid (20.0 cm<sup>3</sup>) was prepared and added quickly to this mixture at 0 °C. The resulting mixture was stirred at room temperature overnight, and quenched by adding it dropwise into a saturated aqueous solution of sodium sulfite (ca. 50 cm<sup>3</sup>) kept at 0 °C. The solid pink precipitate was filtered, allowed to air-dry overnight, and recrystallised in hexane (ca. 500 cm<sup>3</sup>) to afford 2,2'-dibromo-5,5'-diiodobiphenyl (8.7 g, 40 %) as colourless crystals (Found: C, 25.6; H, 1.1. C<sub>12</sub>H<sub>6</sub>Br<sub>2</sub>I<sub>2</sub> requires C, 25.6; H, 1.1 %); mp. 160-161 °C;  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 1278, 1447, 1566, 2986, 3046;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 7.38 (2H, d, *J* 8.4, Ar*H*), 7.56 (2H, d, *J* 2.0, Ar*H*), 7.58 (2H, dd, *J* 8.4 2.0, Ar*H*);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 91.9, 123.2, 134.2, 138.7, 139.3, 142.5; *m/z* (EI) 561.6925 (M<sup>+</sup>. C<sub>12</sub>H<sub>6</sub>Br<sub>2</sub>I<sub>2</sub> requires 561.6920), 482.8 (31 %), 355.9 (18), 149.9 (100), 126.9 (52), 74.1 (85).

**2,2'-Dibromo-5,5'-bis(trimethylsilyl)biphenyl (7)**



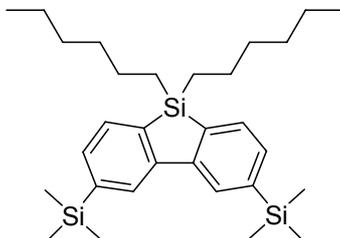
2,2'-Dibromo-5,5'-diiodo-biphenyl (3.0 g, 5.32 mmol) was dissolved in dry ether (200 cm<sup>3</sup>) under nitrogen atmosphere. *n*-Butyllithium (6.98 cm<sup>3</sup>, 1.6 M in hexane) was added dropwise over 3 h at -78 °C and the mixture allowed to raise to room temperature overnight. The mixture was returned to -78 °C and chlorotrimethylsilane (1.42 cm<sup>3</sup>, 1.12 mmol) was added dropwise over 45 min. Stirring continued at room temperature for a further 8 h before water was carefully added to destroy any excess *n*-butyllithium. The solvent was removed under vacuum and the product extracted into DCM, dried with magnesium sulfate and evaporated to give a brown oil. The crude product was purified by column chromatography (hexane) to give the *title compound* (2.05 g, 84 %) as colourless crystals (Found: C, 47.5; H, 5.3. C<sub>18</sub>H<sub>24</sub>Br<sub>2</sub>Si<sub>2</sub> requires C, 47.4; H, 5.3 %); mp. 46-47 °C;  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 1349, 1452, 1468, 1550, 2896, 2955, 3027;  $\delta_{\text{H}}$ (500 MHz, CDCl<sub>3</sub>) 0.30 (18 H, s, SiCH<sub>3</sub>), 7.40 (2H, d, *J* 7.4, ArH), 7.41 (2H, s, ArH), 7.67 (2H, d, *J* 7.4, ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) -1.17, 124.49, 131.89, 134.09, 136.03, 139.56, 141.37; *m/z* (EI) 453.9778 (M<sup>+</sup>. C<sub>18</sub>H<sub>24</sub>Br<sub>2</sub>Si<sub>2</sub> requires 453.9778), 441.0 (85 %), 289.1 (18), 213.0 (23), 165.0 (38), 138.9 (49), 73.1 (100).

**9,9-Dimethyl-3,6-bis(trimethylsilyl)dibenzosilole (8)**



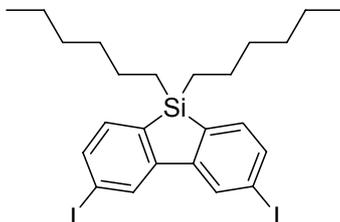
A solution of 2,2'-dibromo-5,5'-bis(trimethylsilyl)biphenyl (1.79 g, 3.92 mmol) in dry ether (35.0 cm<sup>3</sup>) was cooled to -78 °C under nitrogen atmosphere, and *t*-butyllithium (9.30 cm<sup>3</sup>, 15.81 mmol, 1.7 M in pentane) was added dropwise over 1 h. The reaction was stirred at -78 °C for a further 1 h and dichlorodimethylsilane (0.98 cm<sup>3</sup>, 8.08 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight. A pale yellow solution and a white precipitate were obtained. The white precipitate was removed by filtration under nitrogen, and solvent was evacuated to give a yellow oil. Purification of the crude product by filtration through a florisil plug (2 cm) with hexane as the eluant, and subsequent recrystallisation in hexane yielded the *title compound* (1.12 g, 81 %) as colourless crystals (Found: C, 67.8; H, 8.6. C<sub>20</sub>H<sub>30</sub>Si<sub>3</sub> requires C, 67.7; H, 8.5 %); mp. 136 °C;  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 1108, 1151, 1248 (Si-C), 1369, 2955;  $\delta_{\text{H}}$ (500 MHz, CDCl<sub>3</sub>) 0.33 (18 H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.40 (6H, s, SiCH<sub>3</sub>), 7.43 (2H, d, *J* 7.4, ArH), 7.61 (2H, d, *J* 7.4, ArH), 8.00 (2H, s, ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) -3.37, -1.13, 125.07, 131.98, 132.25, 139.56, 142.36, 146.90; *m/z* (EI) 372.1993 (M<sup>+</sup>. C<sub>20</sub>H<sub>30</sub>Si<sub>3</sub> requires 372.1994), 354.2 (42 %), 339.2 (70), 162.3 (29), 73.1 (100).

**9,9-Dihexyl-2,7-bis(trimethylsilanyl)dibenzosilole (9)**



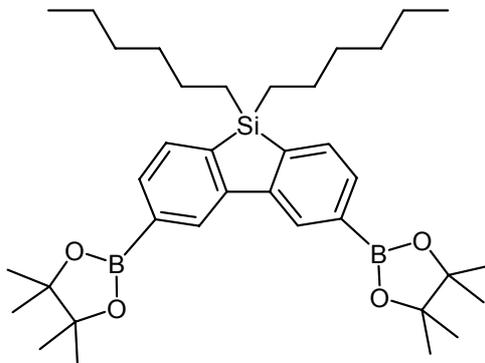
A solution of 9,9-dimethyl-2,7-bis(trimethylsilanyl)dibenzosilole (0.80 g, 2.26 mmol) in dry THF (20 cm<sup>3</sup>) was cooled to -78 °C under nitrogen atmosphere, and *n*-hexyllithium (2.26 cm<sup>3</sup>, 5.19 mmol, 2.3 M in hexane) was added over 30 min. The reaction was raised to room temperature and quenched with water. The crude product was extracted into ether, dried over magnesium sulfate and evaporated to dryness. Purification by filtration through a neutral alumina plug (10 cm) with hexane as the eluant afforded the *title compound* (1.06 g, 95 %) as a colourless oil (Found: C, 73.1; H, 10.2. C<sub>30</sub>H<sub>50</sub>Si<sub>3</sub> requires C, 72.8; H, 10.2 %);  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 1249 (Si-C), 1368, 1406, 1456, 1466, 1529, 1591, 2923, 2955;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 0.33 (18H, s, SiCH<sub>3</sub>), 0.79-0.84 (4H, m), 0.87 (6H, m), 1.15-1.29 (12H, m), 1.31-1.37 (4H, m), 7.41 (2H, d, *J* 7.4, ArH), 7.59 (2H, d, *J* 7.4, ArH), 7.99 (2H, s, ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) -1.12, 12.24, 14.00, 22.49, 23.89, 31.32, 33.08, 125.04, 132.02, 132.51, 138.57, 142.00, 147.39; *m/z* (EI) 494.3217 (M<sup>+</sup>. C<sub>20</sub>H<sub>30</sub>Si<sub>3</sub> requires 494.3215), 494.4 (43 %), 409.3 (16), 325.2 (87), 73.1 (100).

**9,9-Dihexyl-2,7-diiodo-dibenzosilole (10)**



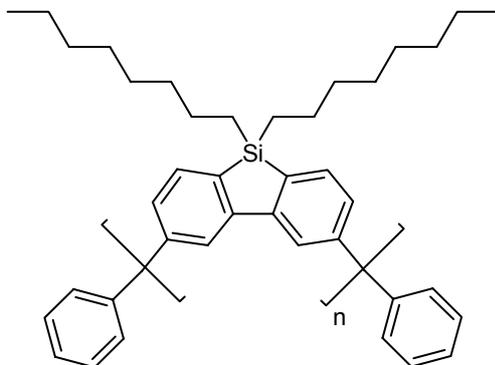
Iodine monochloride (1.0 M in DCM, 4.0 cm<sup>3</sup>, 4.00 mmol) was added to a mixture of 9,9-dihexyl-2,7-bis(trimethylsilyl)dibenzosilole (0.99 g, 2.00 mmol) in DCM (40 cm<sup>3</sup>) at -20 °C over 2.5 h. The mixture was then brought to room temperature and stirred for a further 10 min. The reaction was quenched with saturated sodium thiosulfate (2 cm<sup>3</sup>). The crude product was extracted with DCM and the combined organic layers washed with brine, dried over magnesium sulfate and evaporated to give a light brown oil. Purification by filtration through a neutral alumina plug (10 cm) with hexane as the eluant afforded the *title compound* (0.93 g, 77 %) as a pale yellow oil (Found: C, 48.0; H, 5.6. C<sub>24</sub>H<sub>32</sub>SiI<sub>2</sub> requires C, 47.9; H, 5.4 %);  $\nu_{\max}$  / cm<sup>-1</sup> (NaCl window) 1368, 1452, 1532, 1573, 2853, 2922;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 0.80-0.92 (10H, m, CH<sub>2</sub>+CH<sub>3</sub>), 1.15-1.30 (16H, m, CH<sub>2</sub>), 7.31 (2H, d, *J* 7.5, ArH), 7.61 (2H, d, *J* 7.5, ArH), 8.10 (2H, s, ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 11.96, 14.02, 22.47, 23.74, 31.28, 32.93, 97.32, 130.30, 134.57, 136.49, 137.14, 148.96; *m/z* (EI) 602.0347 (M<sup>+</sup>. C<sub>24</sub>H<sub>32</sub>SiI<sub>2</sub> requires 602.0357), 602.1 (28 %), 517.0 (42), 432.9 (100), 305.9 (41), 179.1 (40).

**9,9-Dihexyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)dibenzosilole (5b)**



9,9-Dihexyl-2,7-diiododibenzosilole (0.40 g, 0.66 mmol) was dissolved in dry THF (8 cm<sup>3</sup>) at -78 °C. *t*-Butyllithium (1.60 cm<sup>3</sup>, 2.82 mmol, 1.7 M in pentane) was then added dropwise over 2 h. The resulting murky yellow solution was stirred for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (0.34 cm<sup>3</sup>, 1.66 mmol) was then added dropwise and stirring continued overnight at room temperature. Water was carefully added to destroy any excess *t*-butyllithium. The solvent was removed under vacuum and the product extracted into ether, dried with magnesium sulfate and evaporated to give a pale yellow oil. The crude product was purified by column chromatography (hexane) on silica gel to give the *title compound* (170 mg, 42 %) as a colourless oil;  $\delta_{\text{H}}$ (125 MHz, CDCl<sub>3</sub>) 0.82-0.95 (10H, m, CH<sub>2</sub>+CH<sub>3</sub>), 1.17-1.39 (16H, m, CH<sub>2</sub>), 1.41 (12H, m, OCCH<sub>3</sub>), 1.41 (12H, s, OCH<sub>2</sub>CH<sub>3</sub>), 7.64 (2H, d, *J* 7.0, ArH), 7.73 (2H, d, *J* 7.0, ArH), 8.37 (2H, s, ArH);  $\delta_{\text{C}}$ (125 MHz, CDCl<sub>3</sub>) 12.15, 13.98, 22.44, 23.78, 24.84, 31.27, 32.98, 83.78, 126.94, 132.46, 133.40, 141.49, 147.72;  $\delta_{\text{Si}}$ (100 MHz, CDCl<sub>3</sub>) 3.07; *m/z* (EI) 620.4474 ([M+NH<sub>4</sub>]<sup>+</sup>. C<sub>36</sub>H<sub>56</sub>B<sub>2</sub>O<sub>4</sub>Si requires 620.4472), 602.4 (67 %), 517.3 (30), 433.3 (100), 333.2 (33), 233.0 (19), 83.1 (63).

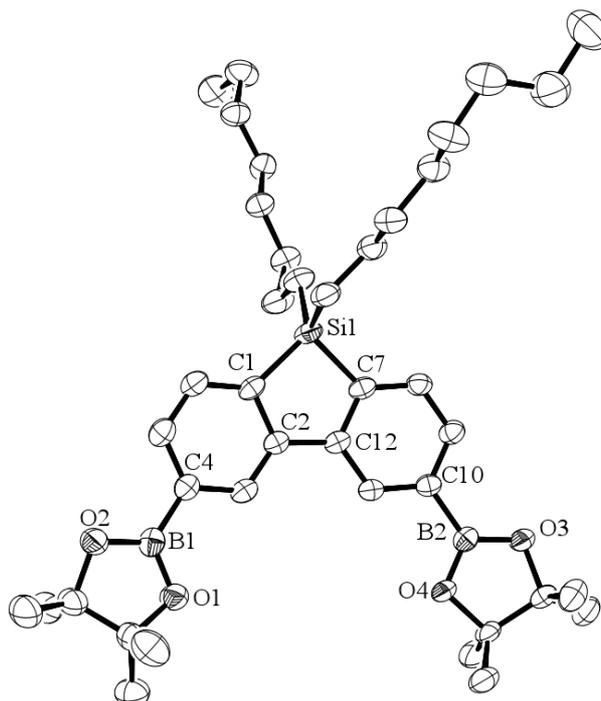
**Poly(9,9-dioctyl-3,6-dibenzosilole) (11)**



To a dried Schlenk tube was added 3,6-dibromo-9,9-dioctyldibenzosilole (282 mg, 0.50 mmol, 1.0 equiv.), 9,9-dioctyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)dibenzosilole (329 mg, 0.50 mmol, 1.0 equiv.), palladium(II) acetate (2.2 mg, 1  $\mu$ mol, 2 %) and tricyclohexylphosphine (11 mg, 4  $\mu$ mol, 8 %) under nitrogen atmosphere. Dry toluene (0.9 cm<sup>3</sup>) was added and the mixture was stirred at 90 °C for 5 min. 20% w/w Tetraethylammonium hydroxide aqueous solution (1.0 cm<sup>3</sup>) was then added. The mixture was stirred for a further 2 h. During this period, the viscosity of the solution was reduced by adding dry toluene (0.5 cm<sup>3</sup>). To the mixture was then added bromobenzene (50 mm<sup>3</sup>, 0.50 mmol, 1.0 equiv.), and after stirring for 2 h, phenylboronic acid (122 mg, 1.0 mmol, 2.0 equiv.) was added. After stirring for a further 2 h, the mixture was cooled to room temperature and poured into stirring methanol (30 cm<sup>3</sup>). The precipitate was dissolved in chloroform (10 cm<sup>3</sup>), filtered through silica plug (10 cm), and the resulting polymer redissolved in chloroform (3 cm<sup>3</sup>) and reprecipitated in stirring methanol (30 cm<sup>3</sup>). The precipitated product was filtered and then dried in vacuo to yield the *title compound* (370 mg, 93 %) as an off-white solid (Found: C, 83.1; H, 10.0. Polymer requires C, 82.1; H, 10.0 %); GPC assay in THF vs. narrow polystyrene standards revealed  $M_w = 23\ 000$ ,  $M_n = 11\ 000$ ,  $M_p = 23\ 000$ , PDI = 2.0;  $\nu_{\max}$  / cm<sup>-1</sup> (Neat solid) 720, 820, 883, 1084, 1139, 1241, 1376, 1465, 1533, 1597, 2852, 2920, 2955;  $\delta_H$ (400 MHz, CDCl<sub>3</sub>) 0.81-0.84 (m, CH<sub>3</sub>), 0.97-1.01 (m, CH<sub>2</sub>), 1.19-1.43 (m, CH<sub>2</sub>), 7.60 (br d,  $J$  7.4, ArH), 7.73 (br d,  $J$  7.4, ArH), 8.17 (br s, ArH);  $\delta_C$ (100 MHz, CDCl<sub>3</sub>) 12.4, 14.1, 22.6, 23.9, 29.1, 29.2, 31.8, 33.4, 120.0, 126.6, 133.6, 137.2, 143.6, 148.8.

### Crystal structure determination

Crystallographic data were collected using the synchrotron radiation source at Station 9.8, Daresbury SRS, UK, on a Bruker SMART CCD diffractometer. The structures were solved by direct methods using the program SIR92. The refinement (on  $F$ ) and graphical calculations were performed using the CRYSTALS program suite. Crystal data for **5a**.  $C_{40}H_{64}B_2O_4Si$ ,  $M = 658.62$ ,  $Z = 4$ , monoclinic, space group  $P2_1/c$ ,  $a = 12.5372(7)$ ,  $b = 11.5468(6)$ ,  $c = 28.4282(15)$  Å,  $\alpha = 90$ ,  $\beta = 98.6880(10)$ ,  $\gamma = 90^\circ$ ,  $U = 4068.2(4)$  Å<sup>3</sup>,  $T = 150(2)$  K,  $\mu(\text{Mo-K}\alpha) = 0.094$  mm<sup>-1</sup>, synchrotron radiation  $\lambda = 0.6771$  Å. Of 31943 reflections measured, 6916 were independent ( $R_{\text{int}} = 0.04$ ). The structure was solved by direct methods and refined by full-matrix least-squares on  $F$ . Final  $R1 = 0.0427$  (3115 reflections with  $I > 3\sigma(I)$ ) and  $wR2(F) = 0.0487$  (all data). Programs: SIR92: A. Altomare, G. Carascano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343; CRYSTALS: a) D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, CRYSTALS, Issue. 10, **1996**, Chemical Crystallography Laboratory, University of Oxford, UK, 1996; b) P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Cryst.* **2003**, *36*, 1487. CCDC 272583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Fig. S1** Thermal ellipsoid diagram of structure **5a** (50 % probability) rendered with ORTEP. Hydrogen atoms have been omitted for clarity. Selected bond angles [°]: C(1)-Si(1)-C(7) = 91.4(1), C(1)-C(2)-C(12) = 114.5(3), O(1)-B(1)-O(2) and O(3)-B(2)-O(4) averaging 113.4.

**Table S1.** Crystallographic data of **12**

Empirical formula	C40 H64 B2 O4 Si
Formula weight	658.62
Temperature	150(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.5372(7) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 11.5468(6) \text{ \AA}$ $\beta = 98.6880(10)^\circ$ . $c = 28.4282(15) \text{ \AA}$ $\gamma = 90^\circ$ .
Volume	$4068.2(4) \text{ \AA}^3$
Z	4
Absorption coefficient	$0.094 \text{ mm}^{-1}$

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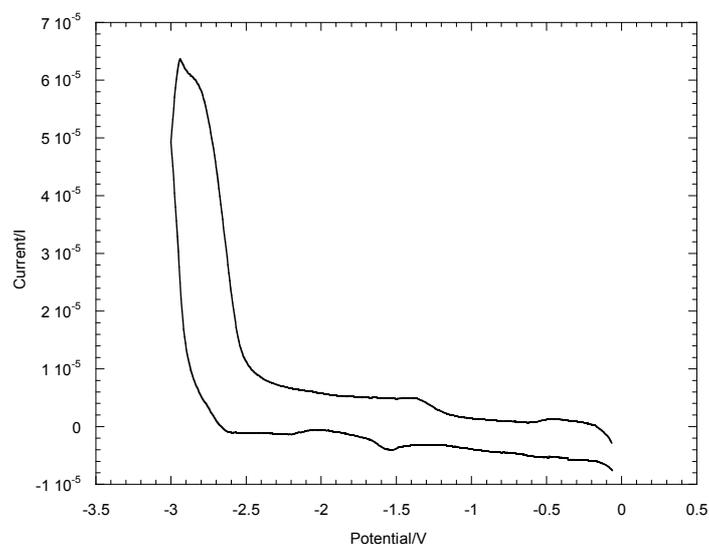
F(000)	1440
Crystal size	0.02 x 0.05 x 0.05 mm <sup>3</sup>
Theta range for data collection	1 to 24 °.
Reflections collected	31943
Independent reflections	6916 [R(int) = 0.04]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	1.1442
Final R indices [ $I > 3\sigma(I)$ ]	R1 = 0.0427 and wR2(F) = 0.0487
R indices (all data)	R1 = 0.0952, wR2(F) = 0.0622

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### **OLED fabrication procedure**

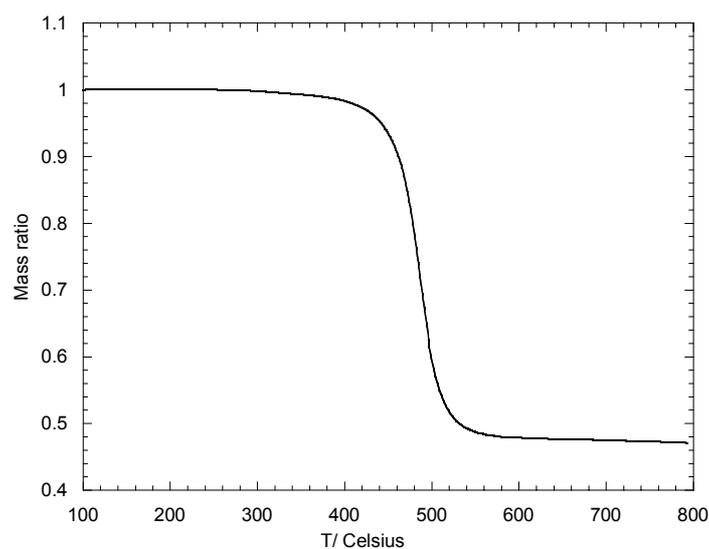
The light emitting diode was fabricated on indium-tin oxide (ITO) patterned glass substrate which was cleaned by successive 20-minute sonications in neutral detergent, 1:1 NH<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and then deionised water. A conventional spin-coater was used to deposit first a 50nm layer of filtered PEDOT:PSS [poly(2,4-ethylenedioxythiophene):poly(styrenesulfonic acid)]. The PEDOT:PSS layer was dried in a 140 °C oven for 2 h to remove any residual water prior to spinning on the emissive layer. A toluene solution consisting of 8 wt. % of Ir complex **12** in polymer **11** was prepared, filtered, and spin-coated over the PEDOT:PSS layer at 4000 r.p.m. in air. A 0.5 nm LiF layer was evaporated onto the device through a shadow mask, and capped with an evaporated aluminium layer (80 nm). Electroluminescence spectra were taken with Varian Cary Eclipse fluorescence spectrometer under ambient conditions.

### **Cyclic voltammogram**



**Fig. S2** The cyclic voltammogram of **11** was measured in a solution of  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  (0.10 M) in acetonitrile at a scan rate of  $1000 \text{ mV s}^{-1}$  at room temperature. A silver wire was used as the working electrode, a platinum wire as the counter electrode and a Ag/AgCl electrode as the reference electrode. All measurements were calibrated against ferrocene which has an ionization potential of 4.8 eV under vacuum. Reductions were measured and the redox processes were found to be irreversible.

### Thermogravimetric Analysis



**Fig. S3** Thermogravimetric Analysis measurement of **11**. Polymer reaches 5% decomposition at 442 °C.

### References

- [1] T. K. Dougherty, K. S. Y. Lau, F. L. Hedberg, *J. Org. Chem.* **1983**, *48*, 5273.
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