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Supporting Information

Porphyrin, Phthalocyanine and Porphyrazine Derivatives with Multi-Fluorenyl Substituents as Efficient Deep-Red Emitters

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General Details. All reactions were performed in an argon atmosphere, which was dried by passage through a column of phosphorus pentoxide. All reagents were of standard reagent grade and purchased from Aldrich, Lancaster and Fluorochem and used as supplied. All solvents were used without prior purification. Column chromatography was carried out on silica gel (40-60 μm). ^{1}H NMR spectra were recorded on a Varian VXR 400s at 400 MHz or a Varian Inova 500 spectrometer at 500 MHz using deuteriated solvent as the lock and tetramethylsilane as the internal reference. ^{13}C NMR spectra were recorded using broad-band decoupling on the above spectrometers at 100 and 125 MHz, respectively. Electron Ionisation (EI+) mass spectra were recorded using a Micromass Autospec spectrometer operating at 70 eV. Matrix assisted laser desorption ionization time of flight (MALDI-ToF) mass spectra were recorded using a Voyager-DE STR BioSpectrometry Workstation (Applied Biosystems). Melting points were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser.

Hyperchem V6.03 was used for all modelling calculations with the following general procedures. The macrocyclic core was first minimized using the molecular mechanics function with the Polak-Ribiere method to an RMS gradient of 0.001. The peripheral substituents were then added and the molecule again energy minimized using the same method, with between 1000 and 10000 cycles, depending on the size of the molecule and number of fluorene units added. The hexyl chains were then added, and the fluorene units manually rotated so as to orient the hexyl chains away from the plane of the macrocycle in an alternating fashion. The calculation was then run again using the same method. For compound **2** an RMS gradient of 0.001 was achieved after 1000 cycles; for the other structures ca. 0.01 was achieved after ca. 30,000 cycles.)

For modelling of compound **9**, the structure of **18** was first minimized using the above method to give a structure essentially identical to that of the X-ray molecular structure obtained experimentally (Figure S1). This molecule was then tetramerized and the calculation rerun to produce a structure to which the peripheral fluorenes and then the hexyl chains were added as before and the structure was again minimized.

Synthetic Details

9,9-Dihexyl-9*H*-fluorene-2-carbaldehyde 11 was synthesized by a modification of the literature methods.[1] A 2.5 M solution of n-butyllithium in hexane (5.32 mL, 13.3 mmol) was added dropwise to a stirred solution of 2-bromo-9,9-dihexylfluorene (5.0 g, 12.09 mmol) in degassed anhydrous diethyl ether (150 mL) at –78 ^{o}C, maintaining a temperature of <–70 ^{o}C. The solution

was stirred at this temperature for 30 min before being allowed to warm to room temperature and stirred for a further 30 min. The solution was then cooled to –78 ^{o}C and degassed anhydrous dimethylformamide (2.5 mL, 32.29 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 20 h before the addition of 2 M aq. HCl (200 mL). After a further 2 h stirring, the layers were separated and the aqueous layer extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (50 mL), dried over anhydrous magnesium sulphate and the solvent removed *in vacuo* to give a colourless oil. Purification by column chromatography (eluent 50% DCM in hexane) gave **11** as a colourless oil (3.21 g, 73%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.56-0.58 (4H, m), 0.74 (6H, t, ^{3}J = 6.9 Hz), 1.01-1.15 (12H, m), 1.95-2.02 (4H, m), 7.38-7.39 (3H, m), 7.77-7.80 (2H, m), 7.85-7.87 (2H, d, ^{3}J = 6.6 Hz), 10.06 (1H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.01, 22.34, 23.98, 29.97, 31.98, 40.05, 55.96, 120.02, 121.01, 123.87, 123.97, 127.89, 129.45, 130.88, 135.98, 139.99, 148.23, 151.92, 152.37, 192.28; IR (Nujol): 3047, 2954, 2925, 2854, 2726, 1700, 1607, 1574, 1466, 1425, 1378, 1344, 1304, 1242, 1227, 1178, 1157, 1100, 1004, 933, 906, 886, 827, 780, 739, 641, 574, 498; MS (ES^{+}): *m/z* 363.3, 364.3 ([M+H]$^{+}$, 385.5, 386.5, 387.5 ([M+Na]$^{+}$), 417.3 ([M+Na+CH_3OH]$^{+}$), 747.6, 748.6 ([2M+Na]$^{+}$); elemental analysis calcd (%) for $C_{26}H_{34}O$: C 86.13, H 9.45; found: C 85.77, H 9.43.

9,9-Dihexyl-9*H*-fluorenyl-2-boronic acid 13 was synthesized by a modification of the literature route.[2] A 2.5 M solution of n-butyllithium in hexane (5.9 mL, 14.75 mmol) was added dropwise to a solution of 2-bromo-9,9-dihexylfluorene (5.58 g, 13.50 mmol) in degassed anhydrous diethyl ether (100 mL) at -78 ^{o}C, maintaining a temperature of <-70 ^{o}C. The solution was stirred at this temperature for 30 min before being allowed to warm to room temperature and stirred for a further 1 h. The solution was then cooled to -78 ^{o}C and a solution of triisopropylborate (9.32 mL, 40.4 mmol) in degassed anhydrous diethyl ether (50 mL) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred for 20 h. A solution of 2 M aq. HCl (50 mL) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with diethyl ether (50 mL) and the combined organic layers were washed with water (100 mL), dried over magnesium sulfate and evaporated to give a crude white solid (3.62 g). Purification of this solid by column chromatography over silica gel (eluent 30% ethyl acetate in hexane) and subsequent recrystallization from hexane gave **13** as a white solid (3.22 g, 63%): mp 92-98 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.64-0.66 (4H, m), 0.73-0.75 (6H, m), 1.03-1.07 (12H, m), 1.28-1.29 (4H, m), 7.37-7.40 (3H, m), 7.75-7.77 (1H, m), 7.90 (1H, d, ^{3}J = 7.8 Hz), 8.21 (1H, s), 8.35 (1H, d, ^{3}J = 7.7 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.49, 22.63, 24.09, 29.66, 31.63, 40.80, 55.08, 119.49, 120.77, 123.56, 127.50, 128.13, 129.03, 133.65, 141.24, 143.06, 149.57, 151.27; IR

(Nujol): 2854, 2852, 2725, 2661, 1608, 1561, 1461, 1377, 1307, 1209, 1155, 1064, 997, 967, 915, 885, 833, 757, 740, 722, 618, 572; MS (EI): *m/z* 165, 166 ([M-B(OH)$_2$-2hexyl]$^+$), 178, 179,180 ([M-B(OH)$_2$-2hexyl+CH$_2$}$^+$), 249, 250, 251 ([M-B(OH)$_2$-hexyl]$^+$), 334, 335, 336 ([M-B(OH)$_2$]$^+$); elemental analysis calcd (%) for $C_{75}H_{99}B_3O_3$ (i.e. the boroxine structure) C 83.33, H 9.23; found: C 82.98, H 9.34.

5,10,15,20-Tetrakis-[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]-porphyrin zinc(II) 5

Compound **3** (38.9 mg, 0.02 mmol) and zinc acetate (20 mg, 0.11 mmol) were stirred together in degassed anhydrous chloroform (10 mL) at 62 ^{o}C for 4 h. Removal of the solvent *in vacuo* followed by purification via column chromatography (eluent DCM) gave **5** as a dark red powder (38 mg, 95%): mp 302-303 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88-0.70 (40H, m), 1.24-1.05 (48H, m), 2.21-2.04 (16H, m), 7.43-7.34 (12H, m), 7.79 (4H, dd, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 7.93-7.86 (12H, m), 8.09 (8H, d, ^3J = 8.0 Hz), 8.35 (8H, d, ^3J = 8.0 Hz), 9.12 (8H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.00, 21.60, 22.85, 28.77, 30.53, 39.54, 54.30, 118.82, 119.99, 120.49, 121.94, 124.26, 125.18, 125.83, 126.11, 131.11, 134.00, 138.67, 139.62, 139.77, 139.81, 140.66, 149.31, 150.05, 150.67; MS (MALDI-ToF): *m/z* 2007.1 ([M]$^+$); elemental analysis calcd (%) for $C_{144}H_{156}N_4Zn•H_2O$: C 85.36, H 7.86, N 2.77; found: C 85.30, H 7.90, N 2.74.

5,10,15,20-Tetrakis-{[9,9-bis(6-carbazol-9-yl-hexyl)-9*H*-fluoren-2-yl]phenyl}-porphyrin 4

Compound **12**[3] (140 mg, 0.15 mmol), compound **14**[4] (463 mg, 0.63 mmol), tetrakis(triphenylphosphine)palladium (20.7 mg, 0.018 mmol) and sodium carbonate (79 mg, 0.75 mmol) were stirred together in a degassed solution of THF (12 mL), toluene (12 mL) and water (0.75 mL) at 105 ^{o}C for 24 h. The residue was redissolved in DCM (20 mL) and washed with water (30 mL) before being dried over anhydrous magnesium sulphate. After removal of the solvent *in vacuo* and purification by column chromatography (eluent 50% DCM in hexane) **4** was obtained as a dark red powder (252 mg, 52%): mp 140-141 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.55 (2H, s, NH), 0.85-0.71 (16H, m), 1.27-1.11 (32H, m), 1.79-1.67 (16H, m), 2.16-2.01 (16H, m), 4.15 (16H, t, ^3J = 7.2 Hz), 7.18 (16H, ddd, ^3J = 7.6 Hz, ^3J = 7.4 Hz, ^4J = 0.4 Hz), 7.30 (16H, d, ^3J = 8.0 Hz), 7.44-7.33 (28H, m), 7.81 (4H, d, ^3J = 7.2 Hz), 7.96-7.90 (12H, m), 8.06 (16H, d, ^3J = 7.6 Hz), 8.10 (8H, d, ^3J = 8.0 Hz), 8.37 (8H, d, ^3J = 8.0 Hz), 9.02 (8H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.78, 26.91, 28.81, 29.81, 40.48, 42.91, 55.20, 108.66, 118.71, 120.03, 120.34, 121.45, 140.90, 141.19, 150.76, 151.40; MS (MALDI-ToF): *m/z* 3266.6 ([M]$^+$); elemental analysis calcd (%) for $C_{240}H_{214}N_{12}•4H_2O$: C 86.35 H 6.70, N 5.03; found: C 86.49, H 6.59, N 5.04.

5,10,15,20-Tetrakis-{[9,9-bis(6-carbazol-9-yl-hexyl)-9*H*-fluoren-2-yl]phenyl}-porphyrin zinc(II) 6

Compound **4** (65.3 mg, 0.02 mmol) and zinc acetate (20 mg, 0.11 mmol) were stirred together in degassed anhydrous chloroform (10 mL) at 62 ^{o}C for 4 h. Removal of the solvent *in vacuo* followed by purification via column chromatography (eluent DCM) gave **6** as a dark red powder (63 mg, 95%): mp 143-144 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.65 (16H, m), 1.21-1.09 (32H, m), 1.73-1.62 (16H, m), 2.12-1.97 (16H, m), 4.13 (16H, t, ^{3}J = 7.2 Hz), 7.14 (16H, ddd, ^{3}J = 7.6 Hz, ^{3}J = 7.4 Hz, ^{4}J = 0.8 Hz), 7.27 (16H, d, ^{3}J = 8.0 Hz), 7.40-7.29 (28H, m), 7.78 (4H, d, ^{3}J = 7.2 Hz), 7.94-7.86 (12H, m), 8.01 (16H, d, ^{3}J = 7.6 Hz), 8.07 (8H, d, ^{3}J = 8.0 Hz), 8.33 (8H, d, ^{3}J = 8.0 Hz), 9.07 (8H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.67, 25.81, 27.70, 28.70, 39.38, 41.79, 54.09, 107.54, 117.59, 118.91, 119.21, 119.91, 120.32, 121.69, 121.79, 124.24, 124.45, 125.32, 125.98, 126.22, 131.09, 134.02, 138.62, 139.28, 139.44, 139.74, 140.75, 149.25, 149.64, 150.29; MS (MALDI-ToF): *m/z* 3329.3 ($[M]^{+}$); elemental analysis calcd (%) for $C_{240}H_{212}N_{12}Zn•7H_2O$: C 83.41, H 6.59, N 4.86; found: C 83.49, H 6.51, N 4.71.

3,5-Diphenylbenzaldehyde 15

Phenylboronic acid (1.0 g, 8.20 mmol), 3,5-dibromobenzaldehye (1.03 g, 3.90 mmol), tetrakis(triphenylphosphine)palladium(0) (0.18 g, 0.164 mmol) and sodium carbonate (1.09 g, 10.3 mmol) were stirred together in a degassed solution of THF (60 mL), toluene (75 mL) and water (9 mL) at 105 ^{o}C for 120 h. The solution was then allowed to cool to room temperature, the solvents were removed *in vacuo* and the residue was redissolved in DCM (150 mL) and water (100 mL). The layers were separated, the aqueous phase extracted with DCM (2 × 75 mL) and the combined organic layers were then dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and subsequent purification via column chromatography (eluent 50% DCM in hexane) gave **15** as a white solid (994 mg, 98%); mp 96-97.5 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.54 (6H, m), 7.67 (4H, d, ^{3}J = 7.95 Hz), 8.04-8.05 (3H, m), 10.10 (1H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 127.53, 127.84, 128.65, 129.82, 137.88, 140.04, 143.17, 192.23; IR (Nujol): 2944, 2842, 2728, 2665, 1952, 1887, 1806, 1709, 1698, 1591, 1460, 1377, 1335, 1301, 1183, 1165, 1077, 1027, 1002, 972, 941, 910, 883, 851, 758, 722, 697, 642, 613, 551, 539, 499; MS (ES^{+}): *m/z* 257.2 ($[M-H]^{+}$; calcd for $C_{19}H_{14}O$ 258.1045; found: 258.1046; elemental analysis calcd (%) for $C_{19}H_{14}O$: C 88.34, H 5.46; found: C 88.15 H, 5.46.

5,10,15,20-Tetrakis[(3,5-diphenyl)phenyl]-porphyrin 7

Trifluoroacetic acid (0.11 mL, 1.5 mmol) was added dropwise to a stirred solution of pyrrole (0.07

mL, 1.0 mmol) and **15** (0.26 g, 1.0 mmol) in degassed anhydrous chloroform and the solution was stirred at 50 ^{o}C for 2 h. After allowing the solution to cool to room temperature, DDQ (0.23 g, 1.0 mmol) was added and stirring was then continued for a further 2.5 h. Triethylamine (0.21 mL, 1.5 mmol) was added dropwise and the reaction mixture was filtered through a short column (initial eluent DCM followed by ethyl acetate) giving a crude product after the removal of solvents *in vacuo*. Purification via column chromatography (eluent 0.01% methanol in DCM) gave **7** as a purple solid (42 mg, 14%); mp >400 ^{o}C. ^{1}H-NMR (300 Mz, $CDCl_3$) δ -2.50 (2H, s, NH), 7.41 (8H, t, ^{3}J = 6.9 Hz), 7.50 (16H, q, ^{3}J = 7.2 Hz), 8.50 (8H, d, ^{4}J = 1.8 Hz), 9.07 (8H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 127.67, 127.80, 127.86, 129.19, 129.24, 140.30, 141.09; MS (MALDI-ToF): *m/z* 1222.5, 1223.5, 1224.5 ($[M]^+$), 1223.5, 1224.5, 1225,5, 1226.5 ($[M+H]^+$.

4,5-Bis(9,9-dihexyl-9*H*-fluoren-2-yl)benzene-1,2-dicarbonitrile 17

Compound **16** (0.38 g, 1.33 mmol), compound **13** (1.00 g, 2.64 mmol), tetrakis(triphenylphosphine)palladium(0) (0.06 g, 51.9 μmol) and sodium carbonate (0.46 g, 4.34 mmol) were stirred together in a degassed solution of THF (70 mL), toluene (85 mL) and water (10 mL) at 110 ^{o}C for 96 h. The reaction mixture was then allowed to cool to room temperature and the solvents removed *in vacuo*. The residue was redissolved in dichloromethane and water and the layers separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL) and the combined organic layers were then washed with water (1 × 50 mL) before being dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and subsequent purification by column chromatography (eluent 50% DCM in hexane) gave **17** as a yellow powder (916 mg, 87%): mp 128-130 ^{o}C. (Found: C, 87.54, H, 8.65, N, 3.26%; $C_{58}H_{68}N_2$ requires C, 87.83, H, 8.64, N, 3.53%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.58 (8H, m), 0.74 (12H, t, ^{3}J = 6.75 Hz), 0.99 (24H, m), 1.82 (8H, m), 7.15-7.20 (10H, m), 7.56-7.62 (4H, m), 7.93 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.43, 22.86, 23.99, 29.97, 32.01, 40.05, 55.78, 114.03, 116.02, 120.03, 120.09, 123.78, 124.23, 127.83, 128.02, 128.82, 136.22, 136.88, 140.49, 142.04, 146.67, 151.85, 151.99; IR (Nujol): 2925, 2855, 2715, 2660, 1734, 1459, 1376, 1296, 1210, 1201, 1142, 1070, 951, 909, 873, 837, 765, 721, 516; MS (ES^+): *m/z* 794, 795, 796 ($[M]^+$), 815.5, 816.5, 817.5 ($[M+Na]^+$, 824.5, 825.5, 826.5 ($[M+MeOH]^+$; elemental analysis calcd (%) for $C_{58}H_{68}N_2$: C 87.83, H 8.64, N 3.53; found: C 87.54, H 8.65, N 3.26.

5,6-Bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile 18 was synthesized by a modification of the literature route.[5] Dibromobenzil (2.5 g, 6.79 mmol) and diaminomaleonitrile (0.88 g, 8.15 mmol) were stirred together in a solution of acetic acid (30 mL) at 120 ^{o}C for 4 h. The solution was

allowed to cool to room temperature and the solvents were removed *in vacuo*. The residue was dissolved in methanol (15 mL) and placed in an ice bath for 2 h. Precipitation gave a crude brown solid (2.96 g) which after purification by column chromatography (eluent DCM) gave **18** as a pale yellow solid (2.30 g, 77%); mp 209-211 ^{o}C (lit. mp 208 ^{o}C).[5] ^{1}H-NMR (200 MHz, DMSO-d_6) δ 7.48 (4H, d, ^{3}J = 8.4 Hz), 7.71 (4H, d, ^{3}J = 8.2 Hz); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 115.23, 125.72, 131.01, 132.84, 135.79, 154.31; IR (Nujol): 2934, 2909, 2854, 2715, 2655, 2227, 1897, 1583, 1508, 1463, 1377, 1298, 1272, 1216, 1186, 1125, 1106, 1068, 1065, 1005, 931, 825, 722, 672, 629, 570, 547, 528, 499; MS (MALDI-ToF): *m/z* 305.0 ([M-2Br+Na]$^{+}$), 438.1, 440.2, 442.2 ([M]$^{+}$); calcd for $C_{18}H_8N_4Br_2$–2H: 437.8939; found: 437.9142; elemental analysis calcd (%) for $C_{18}H_8N_4Br_2$: C 49.13, H 1.83, N 12.73; found: C 49.15, H 1.80, N 12.79.

Crystals were grown by a slow diffusion of hexane into a solution of **18** in DCM.

5,6-Bis[4-(9,9-dihexyl-9*H*-fluoren-2-yl)phenyl]pyrazine-2,3-dicarbonitrile 19

Compound **13** (0.25 g, 0.66 mmol), compound **18** (0.15 g, 0.33 mmol), tetrakis(triphenyl-phosphine)-palladium(0) (15 mg, 13.2 μmol) and sodium carbonate (87 mg, 0.825 mmol) were stirred together in a degassed solution of THF (20 mL), toluene (25 mL) and water (3 mL) at 105 ^{o}C for 72 h. The solution was then allowed to cool to room temperature, the solvents were removed *in vacuo* and the residue was then redissolved in DCM (100 mL) and water (100 mL). The layers were separated, the aqueous phase was extracted with DCM (75 mL) and the combined organic layers were then washed with water (50 mL) and dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and purification via column chromatography (eluent 50% DCM in hexane) gave a crude yellow solid which after a second purification by column chromatography (eluent 33% hexane in chloroform) gave **19** as a bright yellow solid (191 mg, 59%); mp 96-98 ^{o}C. (Found: C, 85.80, H, 7.89, N, 5.69%; $C_{68}H_{74}N_4$ requires C, 86.21, H, 7.87, N, 5.91%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.64.070 (8H, m), 0.75 (12H, t, ^{3}J = 6.9 Hz), 1.05-1.12 (24H, m), 1.99-2.04 (8H, m), 7.34-7.37 (6H, m), 7.62 (4H, d, ^{3}J = 9.75 Hz), 7.76 (12H, dd, ^{3}J = 8.1 Hz, ^{4}J = 4.8 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.05, 22.76, 24.01, 29.65, 31.89, 40.84, 55.93, 113.75, 120.02, 120.04, 121.72, 123.64, 126.05, 127.12, 127.95, 129.86, 130.84, 134.44, 138.45, 140.56, 141.94, 144.89, 151.67, 151.68, 151.99, 155.43, IR (Nujol): 2905, 2857, 2725, 2658, 2022, 1603, 1492, 1463, 1377, 1300, 1219, 1187, 1153, 1067, 1013, 962, 937, 889, 847, 824, 762, 727, 722, 677, 653, 628, 574, 529 MS (MALDI-ToF): *m/z* 946.5, 947.5, 948.5 ([M]$^{+}$); calcd for $C_{68}H_{74}N_4$: 946.5913; found: 946.5915.

X-Ray crystal structure of 18

The X-ray diffraction experiment was carried out on a Bruker 3-circle diffractometer with a

SMART 6K CCD area detector, using graphite-monochromated Mo-K_α radiation ($\overline{\lambda}$=0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. *Crystal data*: $C_{18}H_8Br_2N_4$, M= 440.10, T=120 K, monoclinic, space group $P2_1/n$ (No. 14, non-standard setting), a=7.260(1), b=18.487(2), c=12.260(1) Å, β=93.48(1)º, U=1642.4(3) Å^3, Z=4, D_c=1.780 g cm^{-3}, μ=4.94 mm^{-1}, 22486 reflections with 2θ≤60º. Absorption correction by numerical integration based on crystal face-indexing (transmission factors 0.4293 to 0.7642) reduced R_{int} from 0.126 to 0.036. Using SHELXTL software (version 6.14, Bruker AXS, Madison WI, USA, 2003), the structure was solved by direct methods and refined against F^2 of all reflections, refinement converging at $R(F)$=0.024 for 3889 reflections with $F^2 \geq 2\sigma(F^2)$ and w$R(F^2)$=0.056 for all 4792 unique reflections. Full structural data in cif format have been deposited with the Cambridge Crystallographic Data centre, CCDC-628573. The molecular structure is shown in Figure S1.

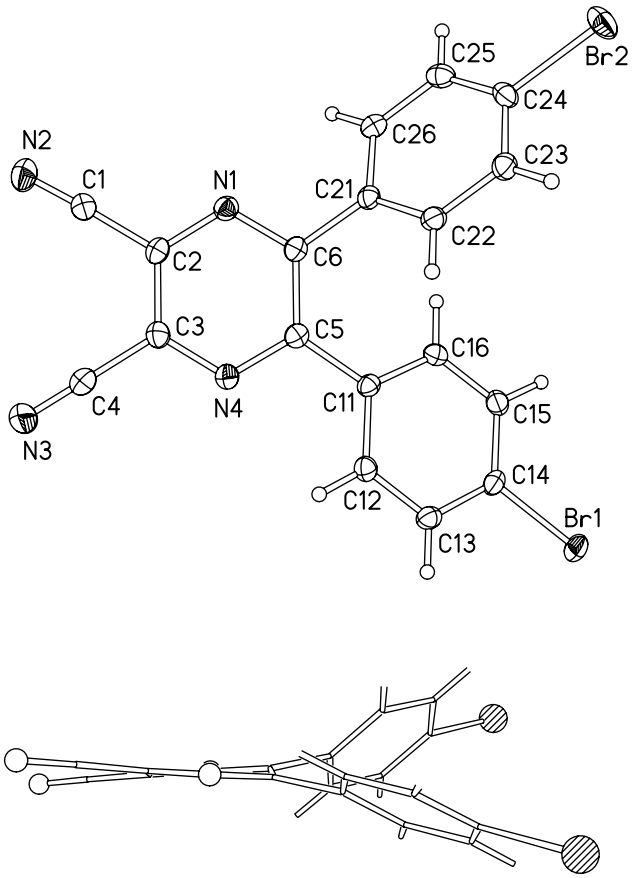

Figure S1. X-Ray molecular structure of **18**. Top: the ORTEP drawing (50% thermal ellipsoids), bottom: view along the N(1)…N(4) vector. Note the twist of the pyrazine ring. Torsion angles: Br(2)··N(1)··N(4)··Br(1) –21.4º, N(2)··N(1)··N(4)··N(3) –9.1º.

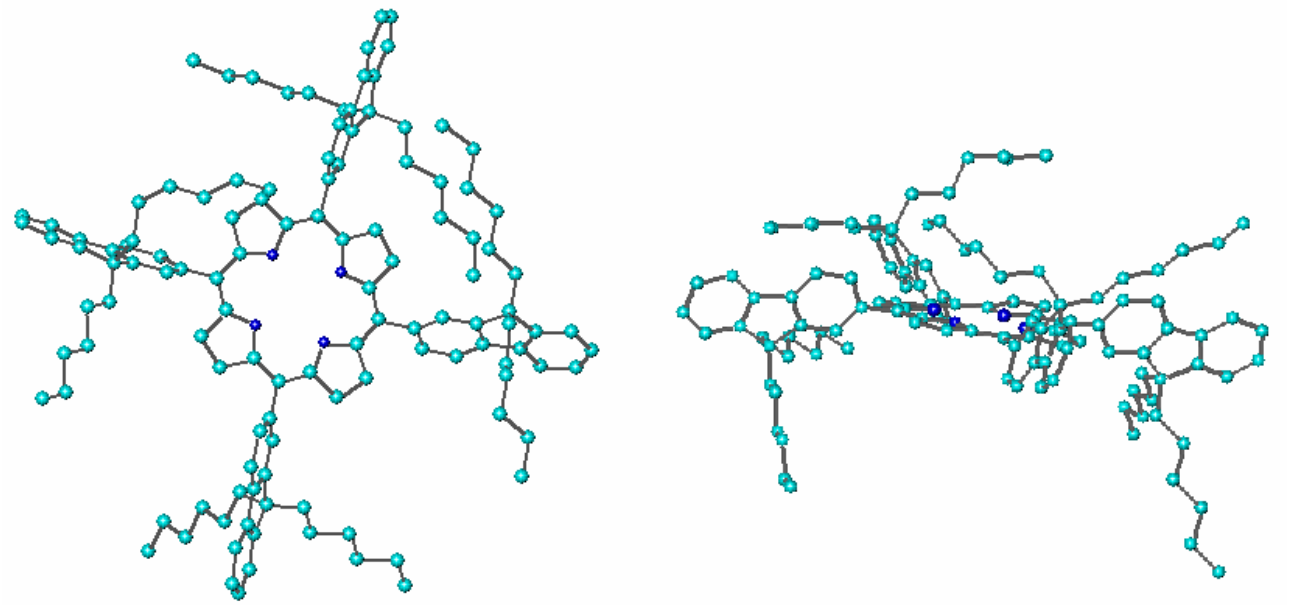

Figure S2. Face (left) and side-on (right) views of an optimized geometry of porphyrin derivative **2** (hydrogens omitted for clarity).

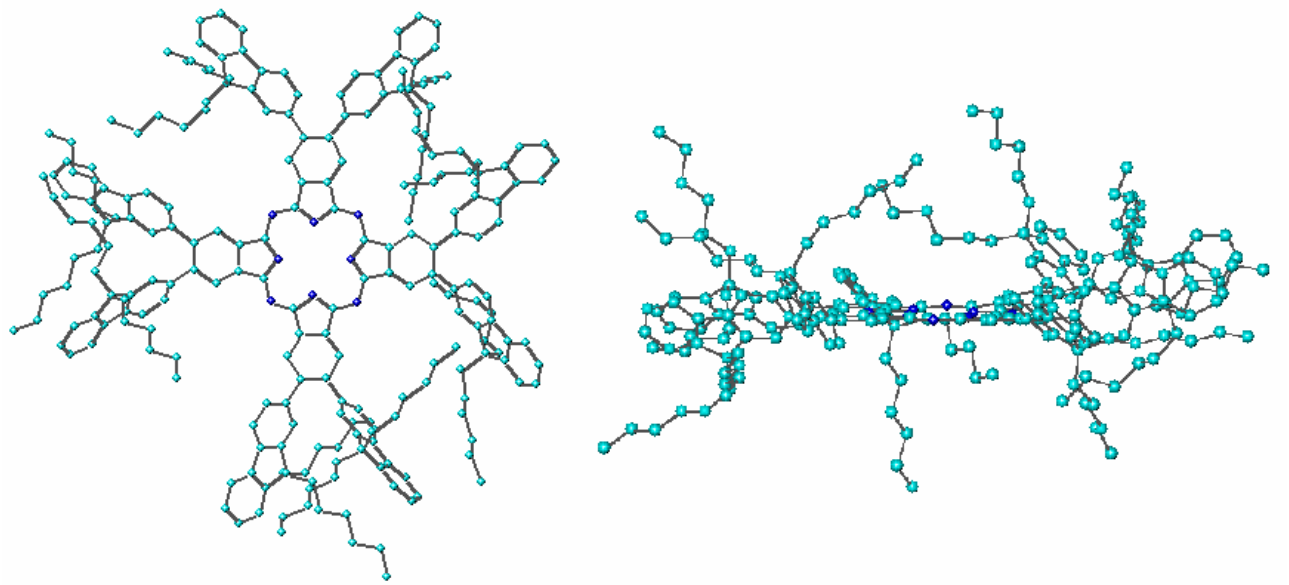

Figure S3. Face (left) and side-on (right) views of an optimized geometry of phthalocyanine derivative **8** (hydrogens omitted for clarity).

Photophysical Measurements.

Steady-State Spectra. Steady-state photophysical measurements were carried out using 10^{-6} M solutions of complexes **1d-f** and **2d-f** in toluene using an ATI Unicam UV/Vis UV2 spectrometer and Jobin Horiba Spex Fluorolog 3 spectrofluorimeter using quartz cuvettes with a pathlength of 1 cm. A right angle illumination method was used and appropriate optical filters were selected to

remove 2nd order peaks and Raman scatter.[6] Each spectrum obtained was corrected for the spectral response of the machine. All solutions were freshly prepared and degassed, by repeated freeze-pump-thaw cycles if required, prior to measurements.

Lifetimes. The luminescence decays of the complexes **1d-f** and **2d-f** in degassed toluene were measured using a home-built ns-laser pumped fluorimeter. The samples were excited by a 10 Hz train of 3rd harmonic (355 nm) radiation from a Q-switched Nd:YAG laser (Spectra Physics GCR-150-10). The energy of the laser was typically 1-2 mJ per pulse with a FWHM of approximately 6 ns. Stray light at 1064 nm (fundamental) and 532 nm (2nd harmonic) was removed by the use of optical filters. Luminescence was collected at 90° to the excitation beam and focused onto the entrance slits of a monochromator (Jobin Yvon Horiba, Triax 320) using a bandpass in the range of 0.1-2.0 nm. The intensity of light at a given wavelength was monitored by a photomultiplier (PMT) tube (Hamamatsu R928). The transient decays were digitized and averaged by a digital storage oscilloscope (Tetronix TDS-340) over at least 64 laser pulses. The data was transferred to a PC for analysis by Microsoft Excel. The luminescence lifetimes for aerated solutions are of the order of tens to hundreds of nanoseconds. The associated error with measured lifetimes is ± 10 %.

Quantum Yields. Photoluminescence quantum yields (PLQY) were recorded using the published method.[7] The associated error with these values is ± 10 %.

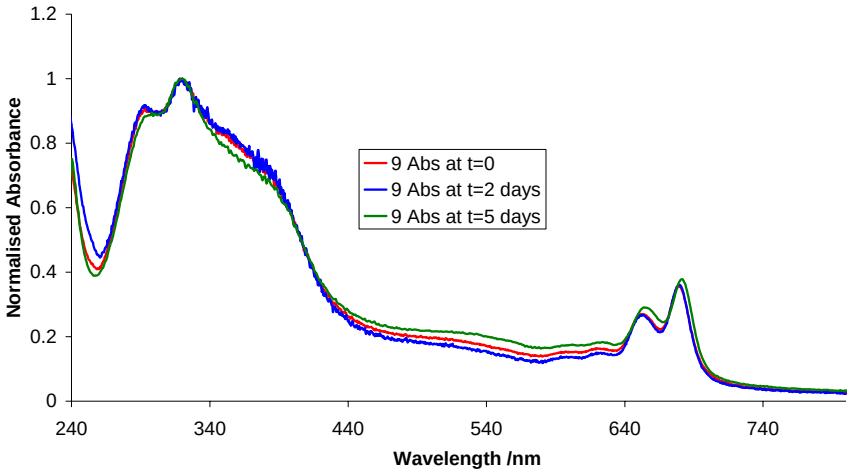

Figure S4: Absorption spectra of **9** after storage in DCM in the sunlight for 2 and 5 days at 298 K.

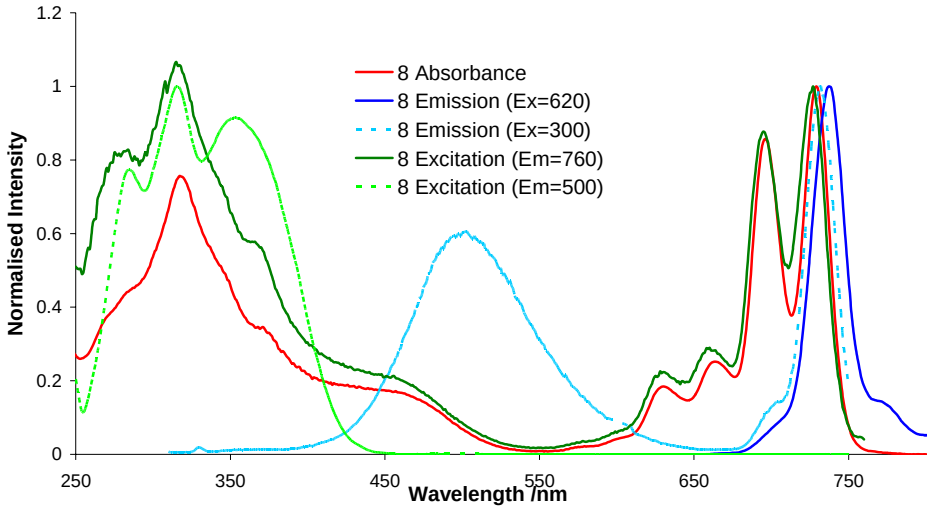

Figure S5. Absorption and fluorescence spectra of **8** in DCM at 298 K.

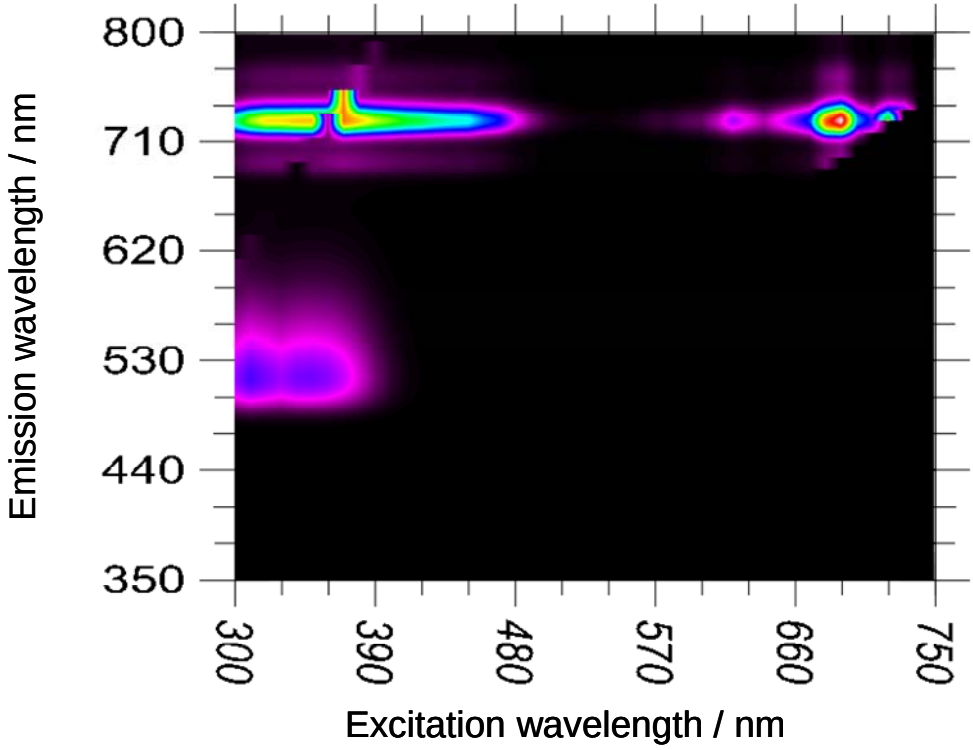

Figure S6. The excitation/emission matrix for compound **8** shows that the phthalocyanine centred emission at 725 nm is seen when the sample is excited in both the short and long wavelength regions, but that the fluorene centred emission, observed at ca. 480 nm is observed only upon excitation in the UV.

OLEDs. Devices were fabricated on indium tin oxide (ITO) coated glass substrates, of thickness 125 nm, with a sheet resistance of 13 Ω/square. The (ITO) coated substrate was cleaned with acetone and isopropanol and was treated with ozone for 3 min. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) obtained commercially from Bayer AG. Germany was spin-coated at 2500 rpm to produce a ~ 50 nm thick hole-transporting layer (HTL). The HTL coated substrates were baked under rotary pump vacuum at 50 ^{o}C overnight to extract residual water. Polyspirobifluorene copolymer[8] (Figure S7) was used as the host material and dissolved in chlorobenzene to form a solution of 10 mg/mL. The polymer-dopant solutions were spin-coated onto the HTL coated substrates at 2500 rpm to produce active layers of thickness ca. 60 nm as measured by ellipsometry. Each sample was shadow masked producing eight identical devices and the samples were then placed in a nitrogen glove box where 5 nm calcium cathodes were evaporated onto each device at a rate of < 1 Å s^{-1} at a pressure of ca. 8×10^{-6} mbar, followed by a 60 nm capping layer of aluminum under the same conditions. The electrical and luminance characteristics of the devices were tested under vacuum at a pressure of 2×10^{-2} mbar. The *I-V* characteristics and the light emission intensities were measured using a home written NI LabView program which controlled a Keithley 2000 voltmeter and Keithley 2400 current source meter, respectively. The electroluminescence (EL) spectra were measured using an Ocean Optics USB2000 spectrometer.

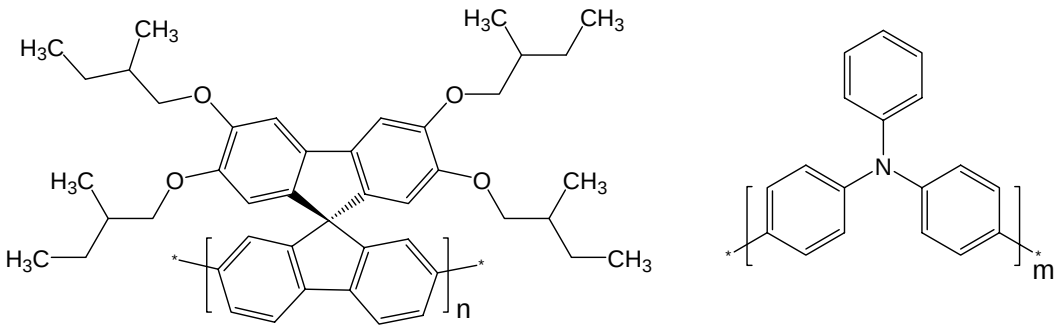

Figure S7. Chemical structure of the host copolymer used in the OLEDs: (left) repeat unit of polyspirobifluorene (PSBF) homopolymer and (right) the triarylamine hole transport moiety which is randomly incorporated in the PSBF backbone to give the copolymer.

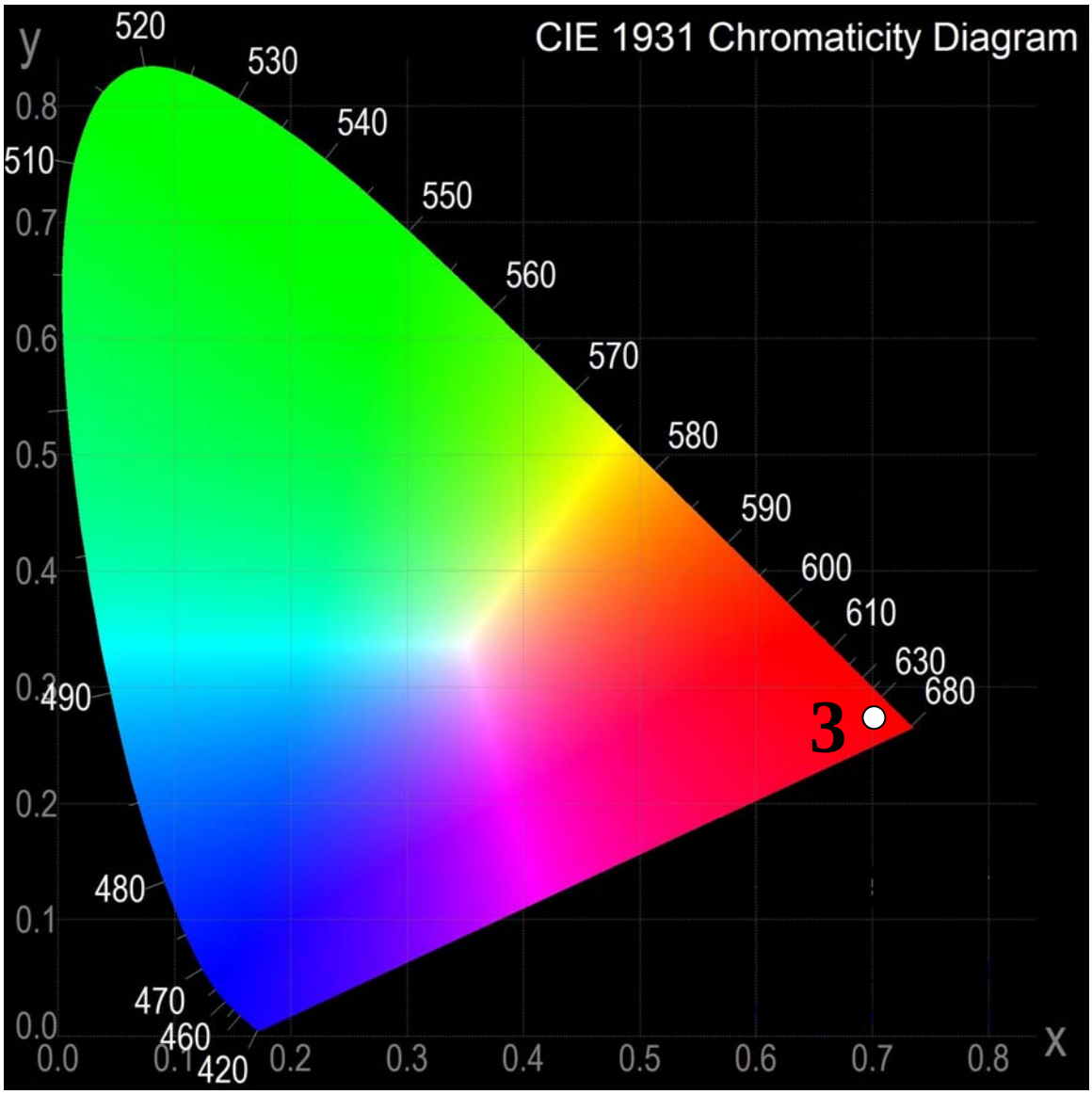

Figure S8. CIE 1931 chromaticity diagram for the device ITO/PEDOT:PSS/PSBFcopolymer:**3**/Ba/Al (5% by weight of **3** in the blend): $x = 0.70$; $y = 0.27$.

References for the Supporting Information

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