Supporting Information

Porphyrin-Based Hole Conducting Electropolymer

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Synthesis

5-(4-Acetamidophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4). To a flask was added 157 mg (0.250 mmol) of 5-bromo-10,20-bis(2,4,6-trimethylphenyl)porphyrin,^{S1} 1.06 g (5.0 mmol) of tribasic potassium phosphate, 314 mg (1.76 mmol) of 4-acetamidophenylboronic acid and 70 mL of tetrahydrofuran (THF). The suspension was flushed with argon for 10 min, 39 mg (0.025 mmol) of tetrakis(triphenylphosphine)palladium(0) was added, and the argon flushing procedure was continued for an additional 10 min. The reaction mixture was then warmed to reflux under an argon atmosphere for 48 h. The solvent was evaporated at reduced pressure, the residue was redissolved in dichloromethane and washed with water, the organic phase was dried over sodium sulfate, and the solvent was once again evaporated at reduced pressure. The crude product was chromatographed on silica gel (dichloromethane/1% acetone) to give 124 mg (73% yield) of porphyrin **4**. ¹H NMR (300 MHz) δ -2.89 (2H, s, N-H), 1.84 (12H, s, Ar-CH₃), 2.33 (3H, s, acetyl-CH₃), 2.67 (6H, s, Ar-CH₃), 7.29 (4H, s,

Ar-H), 7.47 (1H, s, N-H), 7.85 (2H, d, $J=8$ Hz, Ar-H), 8.15 (2H, d, $J=8$ Hz, Ar-H), 8.72 (2H, d, $J=5$ Hz, β -H), 8.82 (4H, d, $J=5$ Hz, β -H), 9.26 (2H, d, $J=5$ Hz, β -H), 10.11 (1H, s, *meso*-H); MALDI-TOF-MS m/z calcd. for $C_{46}H_{41}N_5O_1$ 679.33, obsd. 679.33; UV/vis (CH_2Cl_2) 413, 509, 541, 586, 637 nm.

5-(4-Aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (1) – preparation 1.

A flask containing 100 mg (0.147 mmol) of **4**, 50 mL of trifluoroacetic acid and 100 mL of concentrated hydrochloric acid was warmed to 80 °C. After 18 h the acid was neutralized with concentrated aqueous ammonia, the purple porphyrin was extracted into dichloromethane, and the solvent was evaporated. The residue was then chromatographed on silica gel (dichloromethane/15-5% hexanes) to give 89 mg (95% yield) of porphyrin **1**. 1H NMR (300 MHz) δ -2.87 (2H, s, N-H), 1.84 (12H, s, Ar-CH₃), 2.64 (6H, s, Ar-CH₃), 3.99 (2H, s, N-H), 7.04 (2H, d, $J=8$ Hz, Ar-H), 7.29 (4H, s, Ar-H), 7.99 (2H, d, $J=8$ Hz, Ar-H), 8.71 (2H, d, $J=5$ Hz, β -H), 8.81 (2H, d, $J=5$ Hz, β -H), 8.91 (2H, d, $J=5$ Hz, β -H), 9.24 (2H, d, $J=5$ Hz, β -H), 10.08 (1H, s, *meso*-H); MALDI-TOF-MS m/z calcd. for $C_{44}H_{39}N_5$ 637.32, obsd. 637.32; UV/vis (CH_2Cl_2) 414, 510, 545, 585, 642 nm.

5-(4-*tert*-Butylphenylcarbamate)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (5).

To a glass tube was added 250 mg (0.40 mmol) of 5-bromo-10,20-bis(2,4,6-trimethylphenyl)porphyrin, 1.28 g (4.00 mmol) of 4-(Boc-amino)benzeneboronic acid pinacol, 1.70 g (8.00 mmol) of tribasic potassium phosphate and 75 mL of THF. The suspension was flushed with a stream of argon for 10 min, 46 mg (0.04 mmol) of tetrakis(triphenylphosphine)palladium(0) was added, and the argon flushing was continued for an additional 10 min. The tube was sealed with a Teflon[®] screw plug and the reaction mixture was warmed to 68 °C with vigorous stirring. After 20 h the reaction

mixture was cooled and filtered through celite, the residue was washed with dichloromethane, and the filtrate was concentrated by distillation at reduced pressure. The residue was chromatographed on silica gel (dichloromethane/hexanes 2:1) to give 268 mg (91% yield) of the desired porphyrin. ¹H NMR (300 MHz) δ -2.90 (2H, s, N-H), 1.64 (9H, s, CH₃), 1.84 (12H, s, Ar-CH₃), 2.64 (6H, s, Ar-CH₃), 6.82 (1H, s, N-H), 7.29 (4H, s, Ar-H), 7.73 (2H, d, *J*=9 Hz, Ar-H), 8.13 (2H, d, *J*=9 Hz, Ar-H), 8.72 (2H, d, *J*=5 Hz, β-H), 8.82 (2H, d, *J*=4 Hz, β-H), 8.84 (2H, d, *J*=5 Hz, β-H), 9.26 (2H, d, *J*=4 Hz, β-H), 10.10 (1H, s, *meso*-H); MALDI-TOF-MS *m/z* calcd. for C₄₉H₄₇N₅O₂ 737.37, obsd. 737.37; UV/vis (CH₂Cl₂) 413, 509, 542, 585, 638 nm.

5-(4-Aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (1) – preparation 2.

To a flask containing 250 mg (0.34 mmol) of **5** was added 30 mL of trifluoroacetic acid. The green solution was stirred under a nitrogen atmosphere for 15 min. The reaction mixture was then poured into dichloromethane (200 mL) and the resulting solution was washed with water (×2) and then with aqueous sodium bicarbonate. After drying the organic phase over sodium sulfate, the solvent was evaporated and the residue was chromatographed on silica gel (dichloromethane/15-10% hexanes) to give 203 mg (94% yield) of **1**. ¹H NMR (300 MHz) δ -2.87 (2H, s, N-H), 1.84 (12H, s, Ar-H), 2.64 (6H, s, Ar-H), 4.00 (2H, s, N-H), 7.04 (2H, d, *J*=8 Hz, Ar-H), 7.29 (4H, s, Ar-H), 7.99 (2H, d, *J*=8 Hz, Ar-H), 8.71 (2H, d, *J*=5 Hz, β-H), 8.81 (2H, d, *J*=5 Hz, β-H), 8.91 (2H, d, *J*=5 Hz, β-H), 9.24 (2H, d, *J*=5 Hz, β-H), 10.08 (1H, s, *meso*-H); MALDI-TOF-MS *m/z* calcd. for C₄₄H₃₉N₅ 637.32, obsd. 637.32; UV/vis (CH₂Cl₂) 414, 510, 545, 585, 642 nm.

5-Phenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (6). To a tube was added 156 mg (0.250 mmol) of 5-bromo-10,20-bis(2,4,6-trimethylphenyl)porphyrin,¹ 304 mg (2.49

mmol) of phenylboronic acid, 1.06 g (5.00 mmol) of tribasic potassium phosphate and 60 mL of THF. The suspension was flushed with argon for 15 min, 29 mg (0.025 mmol) of tetrakis(triphenylphosphine)palladium (0) was added, and the argon flushing was continued for an additional 5 min. The tube was sealed with a Teflon[®] screw plug and then warmed to 68 °C for 17 h. The reaction mixture was filtered through celite and the filtrate was concentrated under vacuum. The residue obtained was chromatographed on silica gel (flash column, hexanes/dichloromethane 2:1 to 1:1) to give 146 mg (94% yield) of the desired porphyrin. ¹H NMR (300 MHz) δ -2.88 (2H, s, N-H), 1.84 (12H, s, Ar-CH₃), 2.64 (6H, s, Ar-CH₃), 7.30 (4H, s, Ar-H), 7.69-7.77 (3H, m, Ar-H), 8.21 (2H, dd, *J*=7Hz, 2Hz, Ar-H), 8.73 (2H, d, *J*=5Hz, β-H), 8.81-8.83 (4H, m, β-H), 9.26 (2H, d, *J*=5Hz, β-H), 10.11 (1H, s, *meso*-H); MALDI-TOF-MS *m/z* calcd. for C₄₄H₃₈N₄ 622.31, obsd. 622.32; Uv/vis (CH₂Cl₂) 413, 508, 539, 584, 638 nm.

5-Bromo-15-phenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (7). To a flask containing 120 mg (0.193 mmol) of **6** and 25 mL of chloroform was added 36 mg (0.202 mmol) of N-bromosuccinimide. The solution was stirred for 20 min, the solvent was evaporated at reduced pressure, and the residue was chromatographed on a silica gel column (hexanes/dichloromethane 2:1) to give 120 mg (89% yield) of the brominated porphyrin **7**. ¹H NMR (300 MHz) δ -2.58 (2H, s, N-H), 1.83 (12H, s, Ar-CH₃), 2.63 (6H, s, Ar-CH₃), 7.28 (4H, s, Ar-H), 7.71-7.75 (3H, m, Ar-H), 8.16-8.19 (2H, m, Ar-H), 8.65 (2H, d, *J*=5Hz, β-H), 8.73-8.75 (4H, m, β-H), 9.59 (2H, d, *J*=5Hz, β-H); MALDI-TOF-MS *m/z* calcd. for C₄₄H₃₇N₄Br₁ 702.22, obsd. 702.22; Uv/vis (CH₂Cl₂) 419, 518, 551, 597, 652 nm.

5-(4-Acetamidophenyl)-15-phenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (8).

To a glass tube was added 150 mg (0.214 mmol) of **7**, 268 mg (1.50 mmol) of 4-acetamidophenylboronic acid, 0.91 g (4.28 mmol) of tribasic potassium phosphate and 50 mL of THF. The suspension was flushed with argon for 15 min, 25 mg (0.021 mmol) of tetrakis(triphenylphosphine)palladium (0) was added, and the argon flush procedure was continued for an additional 5 min. The tube was sealed with a Teflon[®] screw plug and the reaction mixture was warmed to 67 °C for 48 h. The solvent was then evaporated and the residue was chromatographed on silica gel (dichloromethane/0.5-4% acetone) to give 160 mg (87% yield) of porphyrin **8**. ¹H NMR (300 MHz) δ -2.62 (2H, s, N-H), 1.83 (12H, s, Ar-CH₃), 2.34 (3H, s, CH₃), 2.62 (6H, s, Ar-CH₃), 7.27 (4H, s, Ar-H), 7.48 (1H, s, N-H), 7.70-7.76 (3H, m, Ar-H), 7.87 (2H, d, *J*=8 Hz, Ar-H), 8.17 (2H, d, *J*=9 Hz, Ar-H), 8.20-8.23 (2H, m, Ar-H), 8.68 (4H, d, *J*=5 Hz, β-H), 8.78-8.81 (4H, m, β-H); MALDI-TOF-MS *m/z* calcd. for C₅₂H₄₅N₅O₁ 755.36, obsd. 755.37; Uv/vis (CH₂Cl₂) 419, 515, 549, 592, 648 nm.

5-(4-Aminophenyl)-15-phenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin (2). To a flask was added 110 mg (0.146 mmol) of **8**, 60 mL of trifluoroacetic acid and 120 mL of concentrated hydrochloric acid. The green solution was warmed to 80 °C for 20 h, cooled, and then brought to pH 8 by the dropwise addition of concentrated aqueous ammonia. The porphyrin was extracted into dichloromethane, dried over sodium sulfate and then concentrated to a purple solid by evaporation of the solvent at reduced pressure. This material was recrystallized from dichloromethane/methanol to give 98 mg (94% yield) of compound **2**. ¹H NMR (300 MHz) δ -2.60 (2H, s, N-H), 1.84 (12H, s, Ar-CH₃), 2.62 (6H, s, Ar-CH₃), 3.99 (2H, s, N-H), 7.05 (2H, d, *J*=8 Hz, Ar-H), 7.27 (4H, s, Ar-H), 7.70-7.75

(3H, m, Ar-H), 7.99 (2H, d, $J=8$ Hz, Ar-H), 8.20-8.23 (2H, m, Ar-H), 8.67 (4H, d, $J=5$ Hz, β -H), 8.77 (2H, d, $J=5$ Hz, β -H), 8.88 (2H, d, $J=5$ Hz, β -H); MALDI-TOF-MS m/z calcd. for $C_{50}H_{43}N_5$ 713.35, obsd. 713.35; Uv/vis (CH_2Cl_2) 421, 517, 553, 595, 649 nm.

5-[4-Methylphenylamino]-15-phenyl-10,20-bis(2,4,6-trimethylphenyl)porphyrin

(3). To a glass tube was added 100 mg (0.143 mmol) of **7**, 46 mg (0.428 mmol) of *p*-toluidine, 65 mg (0.20 mmol) of cesium carbonate, 12 mg (0.021 mmol) of bis(2-diphenylphosphinophenyl)ether (DPEphos) and 20 mL of THF. The suspension was flushed with argon for 15 min, 3.2 mg (0.014 mmol) of palladium acetate was added, and the flushing procedure was continued for an additional 5 min. The tube was sealed with a Teflon[®] screw plug and the reaction mixture was warmed to 65 °C for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel (flash column, hexanes/5% ethyl acetate) to give 93 mg (90% yield) of porphyrin **3**. 1H NMR (300 MHz) δ -2.30 (2H, s, N-H), 1.84 (12H, s, Ar-CH₃), 2.26 (3H, s, Ar-CH₃), 2.61 (6H, s, Ar-CH₃), 6.87 (2H, d, $J=9$ Hz, Ar-H), 6.99 (2H, d, $J=8$ Hz, Ar-H), 7.26 (4H, s, Ar-H), 7.63 (1H, s, N-H), 7.71-7.73 (3H, m, Ar-H), 8.16-8.18 (2H, m, Ar-H), 8.58-8.62 (4H, m, β -H), 8.70 (2H, d, $J=5$ Hz, β -H), 9.27 (2H, d, $J=5$ Hz, β -H); MALDI-TOF-MS m/z calcd. for $C_{51}H_{45}N_5$ 727.37, obsd. 727.37; Uv/vis (CH_2Cl_2) 421, 520, 563, 585, 664 nm.

References

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