

Electronic Supplementary Information

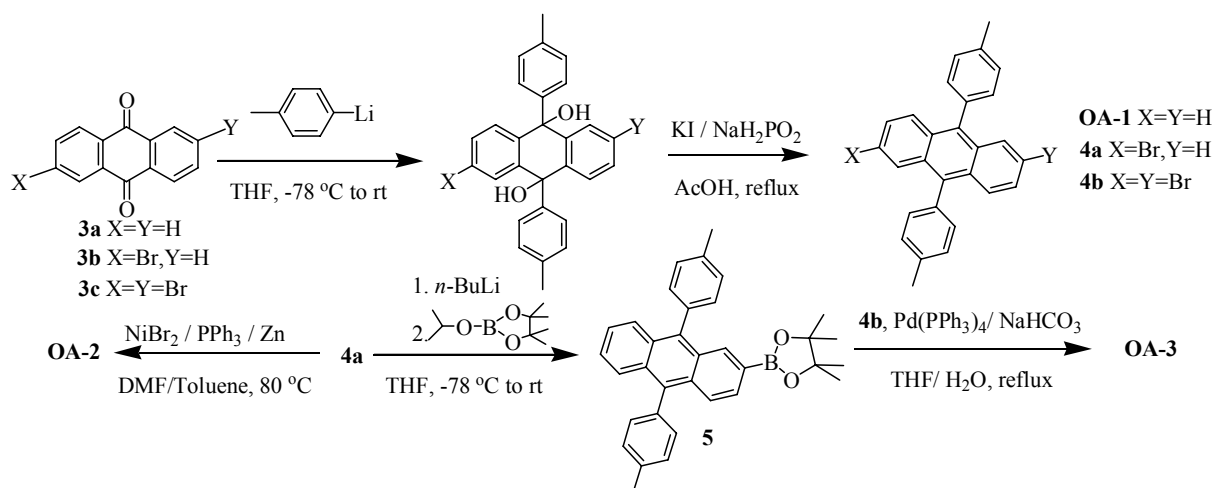
Materials. Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone. Other reagents were obtained from commercial sources and used without further purification unless otherwise stated. The compounds 2-bromoanthraquinone (**3b**), 2,6-dibromoanthraquinone (**3c**) and *p*-bromododecylbenzene were prepared following the reference procedures.¹⁻²

2,6-Dibromo-9,10-di(*p*-dodecylphenyl)-anthracene-9,10-diol (1**).** To a solution of *p*-bromododecylbenzene (2.04 g, 6.27 mmol) in THF (50 mL) was added *n*-BuLi (2.4 mL, 5.9 mmol, 2.5 M in hexane) at -78 °C. After 1 h, 2,6-dibromoanthraquinone (**3c**, 0.979 g, 2.67 mmol) was added. The resulting mixture was allowed to warm to room temperature slowly. After stirred overnight, the mixture was poured into water, extracted with petroleum ether (PE). The organic layer was washed with brine, dried over anhydrous MgSO₄. After solvent removal, the residue was further purified by column chromatography on silica gel with PE: ethyl ether= 8:1 to afford **1** (1.3 g, 57 %) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 0.85-0.90 (m, 6 H), 1.18-1.24 (m, 36 H), 1.45 (m, 4 H), 2.40 (t, *J*= 7.75 Hz, 4 H), 2.77 (s, 2 H), 6.68-6.74 (m, 8 H), 7.55 (dd, *J*₁= 8.38 Hz, *J*₂= 2.05 Hz, 2 H), 7.71 (d, *J*= 8.37 Hz, 2H), 8.00 (d, *J*= 2.04 Hz, 2 H).

2,6-Dibromo-9,10-di(*p*-dodecylphenyl)anthracene (2**).** A mixture of **1** (0.60 g, 0.70 mmol), KI (1.04 g, 6.06 mmol), Na₂H₂PO₂·H₂O (1.04g, 8.06 mmol) and acetic acid (7 mL) was heated at reflux for 40 min. The precipitate was collected and dissolved in dichloromethane (DCM). The organic solution was washed with brine, dried over anhydrous MgSO₄. After solvent removal, the residue was purified by column chromatography on silica gel with PE:DCM=4:1 and then recrystallization from acetone to afford **2** (0.40 g, 69 %) as a light yellow solid. ¹H NMR (400 MHz, C₂D₂Cl₄) δ 0.81-0.84 (m, 6 H), 1.22-1.40 (m, 36 H), 1.70-1.74 (m, 4 H), 2.72 (t, *J*=5.85 Hz, 4 H), 7.27 (d, *J*= 8.00 Hz, 4 H), 7.32 (dd, *J*₁= 9.60 Hz, *J*₂= 2.00 Hz, 2 H), 7.37 (d, *J*= 8.00 Hz, 4 H), 7.52 (d, *J*= 9.60 Hz, 2 H), 7.79 (d, *J*= 2.00 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ 14.07, 22.69, 29.38, 29.58, 29.71, 31.43, 31.94, 35.93, 120.04, 128.68, 128.80, 128.97, 130.99, 134.82, 136.91, 142.78. Anal. Calcd for C₅₀H₆₄Br₂:

C, 72.81; H, 7.82. Found: C, 72.63; H, 8.08.

Poly[9,10-di(*p*-dodecylphenyl)anthracen-2,6-diyl] (PBPA). Into the mixture of bis(cyclooctadiene)nickel ($\text{Ni}(\text{COD})_2$, 0.510 g, 1.87 mmol), cyclooctadiene (0.202 g, 1.87 mmol) and 2,2'-bipyridine (0.292 g, 1.87 mmol) was added anhydrous N,N-dimethylformamide (6 mL). The mixture was stirred at 80 °C under argon for 30 min. Then **2** (0.700 g, 0.848 mmol) in anhydrous toluene (18 mL) was added and the resulting mixture was stirred at the same temperature for 36 h. Then *p*-bromotoluene (20 mg) in anhydrous toluene (2 mL) was added for end-capping. After heated an additional 12 h, the mixture was poured into a mixture of methanol, acetone and concentrated HCl (1:1:1, 450 mL) and stirred for 2 h. The precipitated solid was collected, redissolved in chloroform (30 mL) and then reprecipitated in methanol (250 mL). The resulting solid was collected and subjected to a Soxhlet extraction with hexane. The polymer was precipitated again from chloroform into methanol to yield **PBPA** (0.34 g, 60 %) as a yellow fiber-like solid. ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 80 °C) δ 0.77-0.78 (m, 6 H), 1.20 (m, 36 H), 1.74 (broad, 4 H), 2.74 (broad, 4 H), 7.29-7.30 (m, 8 H), 7.44-7.45 (m, 2 H), 7.65 (m, 2 H), 7.83 (broad, 2 H). Anal. Calcd for $\text{C}_{50}\text{H}_{64}$: C, 90.30; H, 9.70. Found: C, 88.94; H, 9.57.



Scheme 1. Synthesis of the oligomers **OA-n**.

9,10-Di(*p*-tolyl) anthracene (OA-1). To a solution of *p*-bromotoluene (0.610 g, 3.56 mmol) in THF (20 mL) was added *n*-BuLi (1.4 mL, 3.4 mmol, 2.5 M in hexane) at -78 °C. After the

mixture was stirred for 1 h, anthraquinone (**3a**, 0.320 g, 1.54 mmol) was added, and the temperature was allowed to warm to room temperature slowly. After stirred overnight, the mixture was poured into water, extracted with PE. The organic layer was washed with brine, dried over anhydrous MgSO_4 . After solvent removal, the residue together with KI (2.30 g, 13.9 mmol), $\text{Na}_2\text{H}_2\text{PO}_2\cdot\text{H}_2\text{O}$ (2.30g, 17.8 mmol) and acetic acid (12 mL) were heated at reflux for 45 min. The precipitate was collected and dissolved in DCM. The organic solution was washed with brine, dried over anhydrous MgSO_4 . After solvent removal, the residue was purified by column chromatography on silica gel with PE:DCM=15:1 to afford **OA-1** (0.45 g, 82 %) as a white solid. ^1H NMR (300 MHz, CDCl_3): δ 2.54 (s, 6 H), 7.28-7.33 (m, 4 H), 7.34-7.43 (m, 8 H), 7.69-7.75 (m, 4 H). The ^1H NMR spectrum is identical to that reported in the reference.³ Mp: 299-300 °C.

2-Bromo-9,10-di(p-tolyl)anthracene (4a). The procedure for the synthesis of **OA-1** was followed to prepare **4a** from **3b** as a white solid in a yield of 70%. ^1H NMR (300 MHz, CDCl_3): δ 2.54-2.55 (m, 6 H), 7.32-7.36 (m, 7 H), 7.40-7.43 (m, 4 H), 7.59 (d, J = 9.30 Hz, 1 H), 7.68-7.72 (m, 2 H), 7.87 (d, J = 1.8 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.78, 120.02, 125.64, 125.88, 127.45, 128.70, 129.06, 129.39, 129.58, 129.69, 130.60, 131.06, 131.27, 131.50, 135.62, 135.83, 137.78. Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{Br}$: C, 76.89; H, 4.84. Found: C, 76.75; H, 4.60.

2,6-Dibromo-9,10-di(p-tolyl)anthracene (4b). The procedure for the synthesis of **OA-1** was followed to prepare **4b** from **3c** as a white solid in a yield of 50%. ^1H NMR (300 MHz, CDCl_3): δ 2.55 (s, 6 H), 7.30 (d, J = 7.92 Hz, 4 H), 7.36 (dd, J_1 = 9.35 Hz, J_2 = 1.97 Hz, 2 H), 7.42 (d, J = 7.80 Hz, 4 H), 7.56 (d, J = 9.27 Hz, 2 H), 7.84 (d, J = 1.92 Hz, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.78, 120.45, 129.16, 129.37, 129.80, 131.39, 135.03, 137.22, 138.10. Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{Br}_2$: C, 65.14; H, 3.90. Found: C, 65.00; H, 3.39.

2-[9,10-di(p-tolyl)anthracen-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5). To a solution of **4a** (1.45 g, 3.32 mmol) in THF (50 mL) was added *n*-BuLi (1.5 mL, 3.8 mmol, 2.5 M in hexane) at -78 °C. After 1 hour, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.82 mL, 3.98 mmol) was added dropwise. The mixture was stirred at room temperature overnight, poured into water, and then extracted with DCM. The organic layer

was washed with brine, dried over anhydrous MgSO_4 . After solvent removal, the residue was purified with column chromatography on silica (PE: ethyl acetate = 10:1) to afford **5** (1.0 g, 64 %) as a white solid. ^1H NMR (300 MHz, CDCl_3): δ 1.30 (s, 12 H), 2.51-2.56 (m, 6 H), 7.29-7.44 (m, 9 H), 7.60-7.73 (m, 4 H), 8.29 (s, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.80, 25.21, 84.12, 125.12, 125.62, 126.34, 127.36, 127.75, 129.32, 129.50, 131.14, 131.64, 131.77, 136.13, 136.44, 131.37. Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{BO}_2$: C, 84.30; H, 6.87. Found: C, 84.21; H, 6.27.

9,10,9',10'-Tetrakis(*p*-tolyl)-2,2'-bianthracenyl (OA-2): A mixture of NiBr_2 (0.0315 g, 0.144 mmol), PPh_3 (0.300 g, 1.15 mmol), Zn powder (0.420 g, 6.40 mmol) and 2,2'-bipyridine (2 mg) was added anhydrous N,N -dimethylformamide (6 mL). Then the mixture was heated at 80 °C with stirring under argon for 30 min to generate the catalyst. The compound **4a** (0.700 g, 1.60 mmol) in toluene (20 mL) was added. The resulting mixture was stirred for 3 days and then poured into 160 mL HCl /methanol (1:3). The precipitate was collected, washed with HCl , H_2O and methanol. The crude product was further purified by column chromatography on silica (PE: DCM= 8:1) to afford **OA-2** (0.28 g, 49 %) as a light-yellow solid. ^1H NMR (300 MHz, CDCl_3) δ 2.54-2.56 (m, 12 H), 7.29-7.43 (m, 18 H), 7.55 (dd, $J_1 = 9.14$ Hz, $J_2 = 1.79$ Hz, 2 H), 7.69-7.76 (m, 6 H), 7.94 (d, $J = 1.47$ Hz, 2 H). Anal. Calcd for $\text{C}_{56}\text{H}_{42}$: C, 94.08; H, 5.92. Found: C, 93.50; H, 5.31. m/z [MALDI-TOF]: 714.82 (M^+).

9,10,9',10',9'',10''-Hexakis(*p*-tolyl)-2,2';6',2''-teranthracene (OA-3): A mixture of **4b** (0.320, 0.619 mmol), **5** (0.660 g, 1.36 mmol), NaHCO_3 (0.570 g, 6.78 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg), and THF/ H_2O (30 mL/6 mL) was stirred at reflux for 24 h. The precipitate was collected, washed with water and ethanol. The solid was subjected to a Soxhlet extraction with chloroform and then recrystallization from chloroform to yield a light-yellow solid (0.44 g, 67 %). ^1H NMR (300 MHz, CDCl_3) δ 2.54-2.56 (m, 18 H), 7.29-7.42 (m, 28 H), 7.54 (d, $J = 9.21$ Hz, 4 H), 7.70-7.75 (m, 8 H), 7.92 (d, $J = 4.35$ Hz, 4 H). Anal. Calcd for $\text{C}_{84}\text{H}_{62}$: C, 94.17; H, 5.83. Found: C, 93.90; H, 5.17. m/z [MALDI-TOF]: 1070.58 (M^+).

Measurements. ^1H NMR and ^{13}C NMR were recorded on a Bruker 300 M Hz or a 400 MHz spectrometers in CDCl_3 with tetramethylsilane (TMS) as an internal standard or $\text{C}_2\text{D}_2\text{Cl}_4$ with

solvent residue as the standard. Elemental analysis was conducted on an Eager 300 elemental analyzer. MALDI-TOF mass spectra were recorded on a Voyager-DE STR mass spectrometer. GPC measurements were conducted on a Waters GPC system with chloroform as the solvent and polystyrene as the standard. Electronic absorption and PL spectra were recorded on a PerkinElmer Lambda35 UV/vis and a PerkinElmer LS50B Luminescence spectrometers, respectively. PL quantum yield of the polymer was measured in chloroform with quinine as a standard (0.546 in 1.0 N H₂SO₄). Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ under a nitrogen flow. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC7 at a heating/cooling rate of 10/-10 °C min⁻¹ under a nitrogen flow. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in DCM at a scan rate of 50 mV/s. A Pt disk, a Pt wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The potential was calibrated by the ferrocene/ferrocenium. The HOMO energy levels were estimated by the equation: HOMO = $-(4.8 + E_{onset}^{ox})$.⁴

References

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