Supporting Information

Fabrication and Characterization of Multilayer Films from Amphiphilic Poly(*p*-phenylene)s

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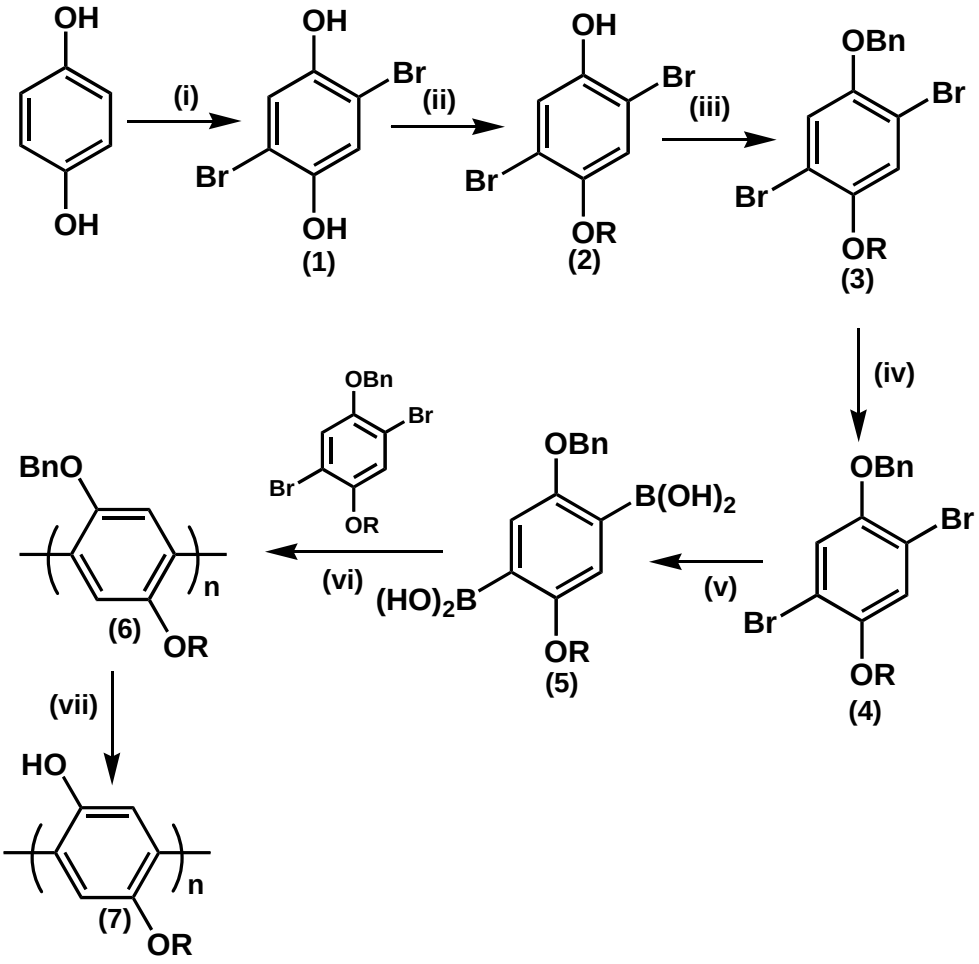
SI 1. Experimental details of the polymer synthesis



Scheme 1. General synthetic scheme for **C_nPPPOH**. (i) Br_2 in gl. AcOH, 85%; (ii) NaOH in abs EtOH, RBr (1 equiv.), 60 °C for 10 h, 60%; (iii) anhydrous K_2CO_3 in abs EtOH, BnBr, 40-50 °C for 10 h, 95%; (iv) BuLi in hexanes (1.6 M soln), THF/Et_2O at -78 °C, B(O*i*Pr)$_3$, water stirred at RT for 10 h, 80%, acidic work-up, (v) 1,3-propanediol, toluene, reflux, 3 h, 80%. (vi) 2 M Na_2CO_3 solution, toluene, 1-1.5 mol % $Pd(PPh_3)_4$, reflux for 3 days, (vii) H_2, 10% Pd/C, EtOH/THF.

Synthesis of Polymers: Synthesis and characterization of dibromohydroquinone, 2,5-dibromo-4-dodecyloxyphenol, and polymers C_{12}PPPOBZn, C_{12}PPPOH, C_{18}PPPOBZn, and C_{18}PPPOH have been reported earlier.[17a] The details of the synthesis all the three polymers C_6PPPOH, C_{12}PPPOH and C_{18}PPPOH and the monomers are summarized below. Characterization details of the derivatives of all the three polymers C_6PPPOH, C_{12}PPPOH and C_{18}PPPOH are denoted as (a) for $–C_6H_{13}$, (b) for $-C_{12}H_{25}$, and (c) for $-C_{18}H_{37}$ respectively.

2,5-Dibromo-hydroquinone (2). 2,5-Dibromo-hydroquinone was synthesized using the procedure reported in the literature.[17b]

2,5-Dibromo-4-alkoxyphenol (3). 2,5-Dibromohydroquinone (25g, 0.093 mol) was dissolved in absolute alcohol under nitrogen atmosphere. Sodium hydroxide (5.59g, 0.139 mol) was added to the reaction mixture and warmed to 55 °C. Hexyl bromide (10.5 ml, 0.074 mol) was added dropwise to the above reaction mixture. After 16 hours, the reaction mixture was cooled to room temperature, filtered and concentrated under reduced pressure. Distilled water (1.5 L) was added along with a few drops of concentrated hydrochloric acid until the mixture was acidic. It was stirred for 2 hours, filtered, washed with water and dried in vacuum. The crude product was purified using column chromatography with a mixture of hexane : dichloromethane (6:4). The yield = 55%.

2,5-Dibromo-4-hexyloxyphenol (3a) 7.23(s, 1H, aromatic C-H), 6.98(s, 1H, , aromatic C-H), 5.19(s, 1H, O-H), 3.93(t, 2H, OCH_2), 1.80(q, 2H, OCH_2CH_2), 1.48(m, 6H, CH_2), 0.91(t, 3H, CH_3); ^{13}C NMR ($CDCl_3$ δ ppm): 150, 146.7, 120.20, 116.6, 112.40, 108.2, 70.31, 31.3, 28.9, 25.5, 22.4, 13.90. MS-ESI: m/z, 351.2. Elemental analysis calculated

(%) for $C_{12}H_{16}Br_2O_2$: C, 40.94; H, 4.58. Found: C, 40.63; H, 4.84. FT-IR (KBr, cm^{-1}): 3253, 2916, 2852, 1498, 1435, 1388, 1219, 1064, 854, 790, 719.

2,5-Dibromo-4-dodecyloxyphenol (3b) ^{1}H NMR ($CDCl_3$ δ ppm): 7.25 (s, 1H, aromatic C-H), 6.97 (s, 1H, aromatic C-H), 5.16 (s, 1H, O-H), 3.92 (t, 2H, OCH_2), 1.62 (q, 2H, OCH_2CH_2), 1.4 (m, 18H, CH_2); 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 150.01, 146.7, 120.2 116.6, 112.4, 108.2, 70.3, 31.8, 29.5, 29.5, 29.2, 29.2, 28.01, 25.8, 22.6, 14. MS-ESI: m/z, 437. Elemental analysis calcd. for $C_{18}H_{28}Br_2O_2$: C, 49.56; H, 6.47; Found: C, 49.87; H, 6.73. FT-IR (KBr, cm^{-1}): 3241, 2911, 2853, 2384, 2337, 1498, 1434, 1386, 1211, 1062, 855, 792, 718.

2,5-Dibromo-4-octadecyloxyphenol (3c) ^{1}H NMR ($CDCl_3$ δ ppm): 7.25 (s, 1H, aromatic C-H), 6.90 (s, 1H, aromatic C-H), 5.11 (s, 1H, O-H), 3.85 (t, 2H, OCH_2), 1.75 (q, 2H, OCH_2CH_2), 1.4 (m, 30H, CH_2); 0.83 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$ δ ppm): 150.01, 146.7, 120.2, 116.2, 112.4, 108.2, 70.3, 31.8, 29.6, 29.5, 29.01, 25.8, 22.6, 14.03. MS-ESI: m/z, 520.1. Elemental analysis calcd for $C_{24}H_{40}Br_2O_2$: C, 55.39; H, 7.75. Found: C, 55.66; H, 8.16. FT-IR (KBr, cm-1): 3225, 2917, 2848, 2359, 1498, 1466, 1434, 1386, 1211, 1062, 855, 722.

2,5-Dibromo-1-benzyloxy-4-alkoxybenzene (4). The monoalkylated 2,5-dibromohydroquinone (15g, 0.042 mol) was dissolved in 200 ml methylethyl ketone, potassium carbonate (20.61g, 0.149 mol) was added and the temperature was raised to 80°C. To this solution, benzyl bromide (10.13 ml, 0.085 mol) was added dropwise. After 24 hours, the mixture was filtered and the filtrate was concentrated to obtain the crude product. The crude product was recrystallized from a mixture of chloroform and methanol (1:4) to get a white precipitate after stirring the mixture in an ice bath for 1 hour

and filtered. The precipitate was washed thoroughly with deionised water. Yield = 95% (17.89 g). **(4)**

2,5-Dibromo-1-benzyloxy-4-hexyloxybenzene (4a) ^{1}H NMR ($CDCl_3$ δ ppm): 7.40 (m, 5H, aromatic C-H) 7.17(s, 1H, aromatic C-H), 7.11(s, 1H, aromatic C-H), 5.07(s, 2H, benzylic –CH_2), 3.96(t, 2H, OCH_2), 1.81(q, 2H, OCH_2CH_2) 1.48(m, 6H, CH_2), 0.92(t, 3H, CH_3) ^{13}C NMR ($CDCl_3$ δ ppm): 150.5, 149.4, 136.1, 128.5, 128, 127.1, 119.3, 118.3, 111.5, 111.01, 71.9, 70.2, 31.4, 28.9, 25.51, 22.5, 13.9. MS-ESI: m/z, 442. Elemental analysis calcd for $C_{19}H_{22}Br_2O_2$: C, 51.61; H, 5.01. Found: C, 51.49; H, 5.00. FT-IR (KBr, cm^{-1}): 3225, 2917, 2848, 2359, 1498, 1466, 1434, 1386, 1211, 1062, 855, 722.

2,5-Dibromo-1-benzyloxy-4-dodecyloxybenzene (4b) ^{1}H NMR ($CDCl_3$ δ ppm): 7.46 (m, 5H, aromatic C-H), 7.21 (s, 1H, aromatic C-H), 7.15 (s, 1H, aromatic C-H), 5.11 (s, 2H, benzylic –CH_2), 3.99 (t, 2H, OCH_2), 1.85 (q, 2H, OCH_2CH_2), 1.32 (m, 18H, CH_2), 0.95 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$ δ ppm): 150.5, 149.5, 136.16, 128.5, 128.1, 127.2, 119.3, 118.3, 111.5, 111.01, 71.9, 70.1, 31.8, 29.6, 25.84, 22.6, 14.02. MS-ESI: m/z, 526.2. Elemental analysis calcd for $C_{25}H_{34}Br_2O_2$: C, 57.05; H, 6.51. Found: C, 57.16; H, 6.85. FT-IR (KBr, cm^{-1}): 2922, 2848, 2359, 1493, 1466, 1355, 1200, 1073, 1004, 855, 802, 754.

2,5-Dibromo-1-benzyloxy-4-octadecyloxybenzene (4c) ^{1}H NMR ($CDCl_3$ δ ppm): 7.39 (m, 5H, aromatic C-H), 7.15 (s, 1H, aromatic C-H), 7.10 (s, 1H, aromatic C-H), 5.06 (s, 2H, benzylic –CH_2), 3.95 (t, 2H, OCH_2), 1.82 (q, 2H, OCH_2CH_2), 1.50 (m, 30H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$ δ ppm): 150.5, 149.4, 136.1, 128.5, 128, 119.3, 118.3, 111.5, 110.03, 72, 70.2, 31.8, 29.01, 25.8, 22.6, 14.03. MS (ESI): *m*/*z*: 610.3

Elemental analysis calcd for $C_{31}H_{46}Br_2O_2$: C, 60.99; H, 7.59. Found: C, 60.49; H, 7.22. FT-IR (KBr, cm^{-1}): 2918, 2854, 1503, 1465, 1365, 1268, 1217, 1058, 1016, 843, 738.

1-Benzyloxy-4-alkoxyphenyl-2,5-bis(boronic acid) (5). The benzylated monomer (14.5g, 0.032 mol) was dissolved in 100 ml of freshly distilled tetrahydrofuran (THF) under nitrogen atmosphere at -78 °C, followed by the dropwise addition of 1.6 molar butyllithium (100 ml, 0.147 mol). The reaction mixture was stirred for another 2 hours at -78 °C. The mixture was stirred at room temperature for 15 minutes. The temperature was again decreased to -78 °C and triisopropylborate (80 ml, 0.328 mol) was added dropwise into the reaction mixture. After stirring at -78 °C for 2 hours, the reaction mixture was warmed to RT and stirred overnight. 1 L deionized water and 100 ml THF was added to the reaction mixture and stirred overnight. The THF layer was collected and concentrated to get crude product. The product was recrystallised from acetone and dried. Yield = 60% (7.30g).

1-Benzyloxy-4-hexyloxyphenyl-2,5-bis(boronic acid) (5a) ^{1}H NMR (DMSO-d_6, δ ppm): 7.83 (s, 2H, B-OH), 7.79 (s, 2H, B-OH), 7.48 (m,5H, aromatic C-H), 7.31 (s,1H, aromatic C-H), 7.19 (s,1H, aromatic C-H), 5.12 (s, 2H, benzylic –CH_2), 4.01(t, 2H, OCH_2), 1.74(q, 2H, OCH_2CH_2), 1.31(m, 6H, CH_2), 0.89(t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 157.05, 156.3, 137.2, 128.4, 127.5, 118.3, 117.8, 70.06, 68.4, 30.8, 28.6, 25.04, 21.9, 13.7. MS (ESI): *m*/*z*: 372. Elemental analysis calcd for $C_{19}H_{26}B_2O_6$: C, 61.34; H, 7.04. Found: C, 61.81; H, 7.30. FT-IR (KBr, cm-1): 3494, 3352, 2920, 2848, 1498, 1413, 1392, 1296, 1200, 1052, 796, 727.

1-Benzyloxy-4-dodecyloxyphenyl-2,5-bis(boronic acid) (5b) ^{1}H NMR (DMSO-d_6, δ ppm): 7.81 (s, 2H, B-OH), 7.76 (s, 2H, B-OH), 7.42 (m, 5H, aromatic C-H), 7.29 (s, 1H,

aromatic C-H), 7.16 (s, 1H, aromatic C-H), 5.10 (s, 2H, benzylic –CH_2), 3.99 (t, 2H, OCH_2), 1.72 (q, 2H, OCH_2CH_2), 1.24 (m, 18H, CH_2), 0.85 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 157.4, 156.7, 137.6, 128.8, 128.2, 127.9, 118.7, 118.1, 70.4, 68.7, 31.6, 29.06, 25.8, 22.4, 14.3. MS (ESI): *m*/*z*: 456. Elemental analysis calcd for $C_{25}H_{38}B_2O_6$: C, 65.82; H, 8.40. Found: C, 65.87; H, 8.86. FT-IR (KBr, cm-1): 3493, 3350, 2920, 2848, 2359, 1496, 1411, 1392, 1296, 1200, 1052, 796, 727.

1-Benzyloxy-4-octadecyloxyphenyl-2,5-bis(boronic acid) (5c) ^{1}H NMR (DMSO-d_6, δ ppm): 7.81 (s, 2H, B-OH), 7.76 (s, 2H, B-OH), 7.46 (m, 5H, aromatic C-H), 7.37 (s, 1H, aromatic C-H), 7.17 (s, 1H, aromatic C-H), 5.10 (s, 2H, benzylic –CH_2), 3.99 (t, 2H, OCH_2), 1.73 (q, 2H, OCH_2CH_2), 1.23 (m, 30H, CH_2), 0.83 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 157.4, 156.7, 137.6, 128.8, 127.9, 118.7, 118.2, 70.4, 68.7, 31.6, 29.06, 25.8, 22.4, 14.2. MS (ESI): *m*/*z*: 540. Elemental analysis calcd for $C_{31}H_{50}B_2O_6$: C, 68.91%; H, 9.33. Found: C, 68.41; H, 8.84. FT-IR (KBr, cm-1): 3448, 3363, 2917, 2853, 2359, 1498, 1429, 1392, 1296, 1195, 1057, 781, 722.

Poly(1-benzyloxy-4-alkoxy-*p*-phenylene) (6). Boronic acid **(5a)** (6g, 0.016 mol) and benzylated monomer **(4a)** (7.148g, 0.016 mol) were mixed with 200 ml toluene under inert atmosphere. 400 ml 2M K_2CO_3 was added to this mixture followed by $Pd(PPh_3)_4$ (5 mol% of monomer.) The temperature was raised to 80 °C, stirred for 72 hours and precipitated from methanol to yield the crude polymer.

Poly(1-benzyloxy-4-hexyloxy-*p*-phenylene) (6a) ^{1}H NMR ($CDCl_3$, δ ppm): 7.40 (b, aromatic C-H) 5.07 (b, benzylic –CH_2), 3.96 (b, OCH_2), 1.81(b, OCH_2CH_2) 1.48(b, CH_2), 0.92(b, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 150.5, 149.4, 136.1, 128.5, 128, 127.1, 119.3,

118.3, 111.5, 111.01, 71.8, 70, 31.3, 28.9, 22.4, 13.95. FT-IR (KBr, cm^{-1}): 2917, 2853, 2367, 1410, 1117, 1112, 727, 715.

Poly(1-benzyloxy-4-dodecyloxy-*p*-phenylene) (6b) ^{1}H NMR ($CDCl_3$, δ ppm): 7.27 (b, aromatic C-H), 4.97 (b, benzylic $–CH_2$), 3.92 (b, OCH_2), 1.60 (b, OCH_2CH_2), 1.27 (b, CH_2), 0.91 (b, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 150.5, 149.7, 137.7, 128.05, 127, 118.06, 116.8, 71.6, 69.4, 31.8, 29.5, 22.5, 14.02. FT-IR (KBr, cm^{-1}): 2916, 2853, 2367, 1413, 1116, 1114, 727, 715.

Poly(1-benzyloxy-4-octadecyloxy-*p*-phenylene) (6c) ^{1}H NMR ($CDCl_3$, δ ppm): 7.21 (b, aromatic C-H), 4.97 (b, benzylic $–CH_2$), 3.89 (b, OCH_2), 1.69 (b, OCH_2CH_2), 1.24 (b, CH_2), 0.88 (b, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 150.5, 149.6, 137.7, 128.07, 127, 118.06, 116.9, 71.6, 69.4, 31.8, 29.6, 22.59, 14. FT-IR (KBr, cm^{-1}): 2915, 2852, 2365, 1413, 1120, 1114, 727, 715.

Poly(1-hydroxy-4-alkoxy-*p*-phenylene) (7). Precursor polymer **(6a)** (1.32 g) was dissolved in an equal volume mixture of THF (50 ml) and absolute ethanol (50 ml) at RT. Pd/C (10%, 3 g) and 3 drops of concentrated HCl were added to the solution and the reaction flask was flushed with nitrogen gas three times to remove traces of oxygen. The debenzylation was carried out at RT under positive pressure of hydrogen (using a balloon) for 24 h with constant stirring. The reaction mixture was filtered through celite powder; the filtrate was evaporated and dried in vaccuo to yield the desired polymer (0.8 g).

Poly(1-hydroxy-4-hexyloxy-*p*-phenylene) (7a) ^{1}H NMR ($CDCl_3$, δ ppm): 7.09 (b, aromatic C-H), 6.82 (b, aromatic C-H), 3.94 (b, OCH_2), 1.69 (b, OCH_2CH_2), 1.29 (b,

CH_2), 0.87 (b, CH_3). FT-IR (KBr, cm^{-1}): 3420, 2922, 2844, 2360, 1650, 1466, 1201, 1025, 800.

Poly(1-hydroxy-4-dodecyloxy-*p*-phenylene) (7b) ^1H NMR ($CDCl_3$, δ ppm): 7.03 (b, aromatic C-H), 6.88 (b, aromatic C-H), 3.90 (b, OCH_2), 1.77 (b, OCH_2CH_2), 1.21 (b, CH_2), 0.85 (b, CH_3). FT-IR (KBr, cm^{-1}): 3415, 2920, 2845, 2362, 1643, 1466, 1205, 1025, 802.

Poly(1-hydroxy-4-octadecyloxy-*p*-phenylene) (7c) ^1H NMR ($CDCl_3$, δ ppm): 7.06 (b, aromatic C-H), 6.85 (b, aromatic C-H), 3.92 (b, OCH_2), 1.77 (b, OCH_2CH_2), 1.24 (b, CH_2), 0.85 (b, CH_3). FT-IR (KBr, cm^{-1}): 3340, 2917, 2845, 1625, 1470, 1406, 1201, 1054, 796, 720.