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Supplementary Material

Synthesis of Discotic Columnar Side-Chain Liquid Crystalline Polymers by Ring-Opening Metathesis Polymerization (ROMP)

Marcus Weck, Bernhard Mohr, Bob R. Maughon, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Preparation of 1,2-didecyloxybenzene 4: 1-Bromodecane (100 g, 0.45 mol) was added dropwise under argon to a mixture of catechol (20 g, 0.182 mol) and potassium carbonate (82 g) in 200 mL dimethylformamide and the mixture was stirred under reflux for 24 hours. The mixture was filtered and the product precipitated as a white solid at 0°C. The crystalline solid was dried *in vacuo* to yield 49.5 g (70%). ¹H-NMR (CDCl₃) δ 6.93 (s, 4H), 4.03 (t, 4H, *J* = 6.6 Hz), 1.87 (q, 4H, *J* = 6.9 Hz), 1.53 (m, 4H), 1.33 (m, 26H), 0.94 (t, 6H, *J* = 6.3 Hz); ¹³C-NMR (CDCl₃) δ 149.3, 121.1, 114.0, 69.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3; IR (thin film on a NaCl plate) 3014, 2922, 2851, 1593, 1506, 1467, 1454, 1389, 1331, 1257, 1224, 1122, 1047, 1022, 988, 938, 896, 757, 737, 669, 599 cm⁻¹; Anal. calcd. for C₂₆H₄₆O₂: C, 79.94; H, 11.87, found: C, 80.40; H, 11.78; HRMS (FAB) calcd. for C₂₆H₄₆O₂ (MH)⁺ 390.3498, found 390.3495.

Preparation of 1,2-dipentoxybenzene 5: 5 was synthesized according to the procedure described above using 1-bromopentane (55 g, 0.36 mol) and catechol (15 g, 0.14 mol) in 150 mL dimethylformamide to give 33.8 g (99%) of a colorless oil. ¹H-NMR (CDCl₃) δ 6.95 (s, 4H), 4.05 (t, 4H, *J* = 6.6 Hz), 1.89 (q, 4H, *J* = 1.2 Hz), 1.50 (m, 8H), 1.02 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (CDCl₃) δ 149.0, 120.8, 113.9, 69.0, 28.8,

28.0, 22.3, 13.8; IR (thin film on a NaCl plate) 3063, 2955, 2869, 1593, 1503, 1469, 1453, 1387, 1329, 1256, 1223, 1157, 1125, 1074, 1050, 1024, 1006, 991, 918, 832, 805, 738, 597 cm^{-1} ; Anal. calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$: C, 76.74; H, 10.47, found: C, 76.20; H, 10.04; HRMS (FAB) calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$ (MH)⁺ 250.3844, found 250.1931.

Preparation of 1-bromo-3,4-didecyloxybenzene 6: A solution of **4** (20 g, 0.051 mol) in 100 mL dichloromethane was cooled to -20°C and treated sequentially with a catalytic amount of iron powder and bromine (8.4 g, 0.053 mol) in 40 mL dichloromethane. The solution was stirred at -20°C for three hours and then at room temperature for 12 hours. The reaction was washed with saturated aqueous solutions of sodium dithionate and sodium carbonate. The organic phase was dried over magnesium sulfate and the solvent was evaporated under reduced pressure to yield a light brown oil which was dissolved in methanol. The product precipitated as a white solid after two days in the refrigerator. Final purification was achieved by repeated recrystallization from methanol to yield 18.4 g (77%) of a white crystalline solid. $^1\text{H-NMR}$ (CDCl_3) δ 6.97 (d, 1H, $J = 2.4$ Hz), 6.95 (d, 1H, $J = 1.8$ Hz), 6.71 (d of d, 1H, $J = 3.3$ Hz), 3.94 (t, 2H, $J = 6.6$ Hz), 3.93 (t, 2H, $J = 6.6$ Hz), 1.77 (m, 4H), 1.41 (m, 4H), 1.25 (m, 26H), 0.86 (t, 6H, $J = 6$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 149.8, 148.1, 123.2, 116.7, 114.9, 112.5, 69.3, 69.1, 31.7, 29.4, 29.2, 29.0, 28.9, 25.7, 22.5, 13.9; IR (thin film on a NaCl plate) 3422, 2953, 2919, 2848, 1637, 1585, 1504, 1465, 1432, 1400, 1392, 1324, 1295, 1252, 1220, 1134, 1070, 1046, 1023, 987, 938, 909, 890, 856, 832, 792, 722, 643, 577 cm^{-1} ; Anal. calcd. for $\text{C}_{26}\text{H}_{45}\text{O}_2\text{Br}$: C, 66.51; H, 9.66, found: C, 66.82; H, 9.45; HRMS (FAB) calcd. for $\text{C}_{26}\text{H}_{45}\text{O}_2\text{Br}$ (MH)⁺ 468.2603, found 468.2587.

Preparation of 1-boronic acid-3,4-didecyloxybenzene 7: 25 mL 1.6 M n-Butyllithium in hexane (40 mmol) was slowly added to a solution of **6** (14 g, 30 mmol) in diethylether (300 mL) at 0°C . The reaction mixture was then stirred for two hours at room temperature, transferred to an addition funnel and carefully added to a solution of trimethyl borate (10.4 g, 100 mmol) in 100 mL dimethylether at -60°C . The reaction

mixture was slowly warmed to room temperature after complete addition and stirring was continued for 20 hours under argon. The solution was hydrolyzed with 150 mL 2N hydrochloric acid and extracted several times with ether. The combined organic phases were washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo*. Final purification was achieved by a silica column chromatography. All starting materials and side products were removed using dichloromethane as eluent. The product was obtained in high purity using *t*-butyl-methyl-ether as eluent to yield 2.14 g (17%) of a white crystalline solid. $^1\text{H-NMR}$ (CDCl_3) δ 7.79 (d, 1H, $J = 9$ Hz), 7.67 (s, 1H), 6.98 (d, 1H, $J = 8.1$ Hz), 4.11 (t, 2H, $J = 6.6$ Hz), 4.06 (t, 2H, $J = 6.6$ Hz), 1.85 (m, 4H), 1.48 (m, 4H), 1.25 (m, 26H), 0.86 (t, 6H, $J = 6$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 153.0, 148.2, 129.7, 122.1, 120.3, 112.3, 69.3, 68.6, 31.7, 29.4, 29.3, 29.2, 29.0, 28.9, 25.9, 25.8, 22.5, 13.9; IR (thin film on NaCl plate) 2921, 2850, 1599, 1514, 1467, 1418, 1352, 1329, 1259, 1213, 1139, 1071, 1021, 987, 876, 813, 741, 712, 595 cm^{-1} .

Preparation of 3,4,3',4'-tetradecyloxybiphenyl 8: Solvents used in this reaction were dried and degassed. **6** (0.9 g, 1.9 mmol), **7** (0.9 g, 2.1 mmol) and palladium(0) tetra-kis-(triphenyl)phosphine (24 mg) were added to the heterogeneous system 7.5 mL toluene, 5 mL tetrahydrofuran and 14 mL 2M potassium carbonate under vigorous stirring and heated to 100°C for 24 hours under argon. After 24 hours the same amount of catalyst was added and stirring was continued for 24 hours. Upon cooling to room temperature the organic phase was separated and the aqueous phase repeatedly extracted with ether. The combined organic phases were washed with water and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the product was purified by column chromatography (SiO_2 /dichloromethane) to obtain a white crystalline solid in 96% (1.43 g) yield. $^1\text{H-NMR}$ (CDCl_3) δ 7.04-6.88 (m, 6H), 4.12 (m, 8H), 1.81 (q, 8H, $J = 6.6$ Hz), 1.46 (m, 8H), 1.25 (m, 55H), 0.86 (t, 12H, $J = 6$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ 149.0, 148.3, 134.1, 119.1, 114.0, 113.0, 69.3, 69.2, 31.7, 29.4, 29.3, 29.2, 29.1, 25.8, 22.5, 13.9; IR (thin film on NaCl plate) 3076, 2916, 2850, 1640, 1465, 1368,

1352, 1264, 995, 911, 743, 707, 640, 555 cm^{-1} ; Anal. calcd. for $\text{C}_{52}\text{H}_{90}\text{O}_4$: C, 80.21; H, 11.57, found: C, 79.98; H, 11.49; HRMS (FAB) calcd. for $\text{C}_{52}\text{H}_{90}\text{O}_4$ (MH)⁺ 778.6839, found 778.6826.

Preparation of 1-iodo-3,4-dipentoxybenzene 9: **5** (15 g, 0.06 mol), 30 mL acetic acid, 10 mL water, 10 mL chloroform, 0.5 mL sulfuric acid, iodine (5.1 g), and iodic acid (2.1 g, 0.01 mol) were mixed and then vigorously stirred at 40°C. After 24 hours 300 mL water was added and the organic phase was separated. The aqueous layer was extracted with dichloromethane several times. The combined organic phases were washed with NaHSO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and water, dried over magnesium sulfate and the solvent was removed *in vacuo*. Final purification was achieved by column chromatography (SiO_2 /dichloromethane) to obtain 19.8 g (88%) of a colorless liquid. $^1\text{H-NMR}$ (CDCl_3) δ 7.14 (m, 2H), 6.59 (d, 1H, $J = 8.4$ Hz), 3.92 (t, 4H, $J = 6.6$ Hz), 1.79 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ 149.9, 149.0, 129.6, 122.4, 115.4, 82.3, 69.2, 69.1, 28.7, 28.0, 22.2, 13.8; IR (thin film on NaCl plate) 3074, 2956, 2871, 1581, 1501, 1468, 1395, 1321, 1291, 1251, 1222, 1137, 1074, 1050, 1019, 989, 917, 854, 838, 796, 730, 631, 574 cm^{-1} ; Anal. calcd. for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{J}$: C, 51.07; H, 6.70, found: C, 50.61; H, 6.52; HRMS (FAB) calcd. for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{J}$ (MH)⁺ 376.0892, found 376,0722.

Preparation of 3,3',4,4'-tetrapentoxybiphenyl 10: **9** (10 g, 0.027 mol) was mixed with fine powdered copper (10 g) and heated to 250°C under argon and vigorous stirring. After four hours the temperature was lowered to 180°C and the hot solution was carefully poured into 200 mL of dichloromethane. The resulting mixture was filtered over celithe and the solvent was removed *in vacuo* to obtain a brown solid. Final purification was achieved by column chromatography (SiO_2 , hexane: dichloromethane 2:1 v/v) to obtain 5.7 g (86%) of a white crystalline solid. $^1\text{H-NMR}$ (CDCl_3) 7.05-6.89 (m, 6H), 4.02 (m, 8H), 1.83 (m, 8H), 1.41 (m, 16), 0.92 (t, 12H, $J = 6.9$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ 149.0, 148.2, 134.1, 119.1, 113.9, 112.9, 69.3, 69.2, 28.8, 28.0, 22.3,

13.8; IR (thin film on NaCl plate) 2956, 2931, 2858, 1604, 1576, 1513, 1466, 1388, 1319, 1293, 1259, 1222, 1147, 1074, 1028, 1001, 988, 914, 833, 788, 734, 619 cm^{-1} ; Anal. calcd. for $\text{C}_{32}\text{H}_{50}\text{O}_4$: C, 77.05; H, 10.11, found: C, 76.86; H, 10.41; HRMS (FAB) calcd. for $\text{C}_{32}\text{H}_{50}\text{O}_4$ (MH)⁺ 498.3697, found 498.3533.

Preparation of 1-decyloxy-2-hydroxybenzene 11: A solution of catechol (9 g, 0.082 mol) in 200 mL dimethylformamide was treated with sodiumhydride (3.36 g, 1.14 mol) under argon. After stirring under reflux for one hour the color changed to dark green. 1-Bromodecane (0.08 mol) was added dropwise and the reaction mixture was stirred under reflux for additional 16 hours. The hot reaction mixture was filtered and the product precipitated after two days in the refrigerator. The obtained solid was filtered and recrystallized several times from ether to yield 11.5 g (56%) of a white crystalline solid. ¹H-NMR (acetone d₆) δ 6.62 (m, 4H), 3.92 (t, 2H, $J = 7.2$ Hz), 1.70 (q, 2H, $J = 7.2$ Hz), 1.27 (m, 14H), 0.87 (t, 3H, $J = 5.7$ Hz). ¹³C-NMR (CDCl₃) δ 145.8, 121.1, 119.9, 114.4, 111.6, 68.5, 32.1, 29.8, 29.7, 29.6, 29.5, 28.8, 28.0, 22.8, 14.2; IR (thin film on a NaCl plate) 3549, 1051, 2926, 2854, 1614, 1598, 1501, 1468, 1393, 1367, 1302, 1258, 1223, 1198, 1108, 1035, 1019, 911, 786, 740 cm^{-1} ; Anal. calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$: C, 76.74; H, 10.47, found: C, 76.40; H, 9.94; HRMS (FAB) calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$ (MH)⁺ 250.3844, found 250.1606.

Preparation of 1-pentoxy-2-hydroxybenzene 12: 12 was synthesized according to the above described procedure using 1-bromopentane (21 g, 0.14 mol) and catechol (20 g, 0.18 mol) in dimethylformamide to give 17.1 g (68%) of a colorless oil. ¹H-NMR (CDCl₃) δ 6.93 (m, 4H), 4.09 (t, 2H, $J = 6.3$ Hz), 1.89 (q, 2H, $J = 6.9$ Hz), 1.50 (m, 4H), 1.05 (t, 3H, $J = 6.6$ Hz). ¹³C-NMR (CDCl₃) δ 145.7, 121.1, 119.8, 114.4, 111.5, 68.7, 28.8, 28.0, 22.3, 13.8; IR (thin film on NaCl plate) 3544, 3054, 2957, 2934, 2873, 1613, 1598, 1503, 1469, 1394, 1365, 1302, 1259, 1224, 1155, 1107, 1073, 1035, 1019, 989, 913, 840, 788, 742 cm^{-1} ; Anal. calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30;

H, 8.95, found: C, 73.44; H, 9.09; HRMS (FAB) calcd. for $C_{11}H_{16}O_2$ (MH)⁺ 180.2490, found 180.1153.

Preparation of 2-(12'-hydroxydodecyloxy)-1-decyloxybenzene 13: **11** (4.8 g, 0.019 mol) was dissolved in 120 mL dimethylformamide. Sodiumhydride (0.49 g, 0.019 mol) was added and the mixture was allowed to stir under reflux for 30 min under argon. 12-Bromo-1-dodecanol (5g, 0.019 mol) was added dropwise and the mixture was allowed to stir for additional 24 hours during which a white solid precipitated. The mixture was filtered and the product precipitated after one day in the refrigerator. The obtained solid was recrystallized from ether and dried *in vacuo*. Final purification was achieved by column chromatography (SiO₂/dichloromethane) to obtain 3.14 g of a yellow crystalline solid in 38% yield. ¹H-NMR (CDCl₃) δ 6.86 (s, 4H), 3.97 (t, 4H, *J* = 6.6 Hz), 3.60 (t, 2H, *J* = 6.6 Hz), 1.82 (q, 4H, *J* = 6.9 Hz), 1.51 (m, 4H), 1.48 (m, 4H), 1.26 (m, 24H), 0.87 (t, 3H, *J* = 6.6 Hz); ¹³C-NMR (CDCl₃) δ 149.0, 120.8, 114.0, 69.1, 62.9, 32.6, 31.7, 29.4, 29.2, 29.1, 25.8, 25.5, 22.4, 13.9; IR (thin film on NaCl plate) 3422, 3058, 2932, 2857, 1641, 1593, 1501, 1468, 1457, 1390, 1327, 1255, 1222, 1155, 1124, 1051, 912, 788, 740, 599 cm⁻¹; Anal. calcd. for C₂₈H₅₀O₃: C, 77.36; H, 11.59, found: C, 77.07; H, 11.80; HRMS (FAB) calcd. for C₂₈H₅₀O₃ (MH)⁺ 434.7089, found 434.7077.

Preparation of 2-(12'-hydroxydodecyloxy)-1-pentoxybenzene 14: **14** was synthesized in analogy to **13** using **12** (3.6 g, 0.019 mol) and 12-bromo-1-dodecanol (5 g, 0.019 mol) to yield 5.5 g of **14** as a colorless liquid (80%). ¹H-NMR (CDCl₃) δ 6.86 (s, 4H), 3.97 (t, 4H, *J* = 6.6 Hz), 3.60 (t, 2H, *J* = 6.6 Hz), 1.79 (m, 2H), 1.59-1.26 (m, 24H), 0.90 (t, 3H, *J* = 7.5 Hz). ¹³C-NMR (CDCl₃) δ 149.0, 120.8, 113.9, 69.0, 62.8, 32.6, 29.4, 29.2, 29.1, 28.8, 25.8, 25.5, 22.3, 13.8; IR (thin film on NaCl plate) 3419, 3065, 2927, 2855, 1640, 1593, 1505, 1468, 1454, 1388, 1327, 1255, 1222, 1158, 1124, 1052, 912, 740, 597 cm⁻¹; Anal. calcd. for C₂₈H₅₀O₃: C, 75.78; H, 11.06, found: C, 74.60; H, 10.84; HRMS (FAB) calcd. for C₂₃H₄₀O₃ (MH)⁺ 364.2967, found 364.2969.