

Supporting information

A First Synthesis of Thiophene Dendrimers

Chuanjun Xia, Xiaowu Fan, Jason Locklin, and Rigoberto C. Advincula*

*Department of Chemistry, University of Alabama at Birmingham,
Birmingham, Alabama, 35294
gobet@uab.edu*

Synthesis.

Synthesis of 2-hexylthiophene (1) n-butyl lithium (2.5M in hexane) (60ml, 0.15mol) was added dropwise to a solution of thiophene (15g, 0.18mol) in 150ml of THF at -78°C. After 45 minutes upon addition, 27g of 1-bromohexane (0.11mol) were added to the solution. The reaction mixture was then warmed to room temperature, stirred for another 3 hours and poured into water. The mixture was extracted with ether, dried over magnesium sulfate, and the solvent evaporated. The compound was purified by vacuum distillation. 24.2g of pure product (colorless liquid) were obtained. (Yield: 96%) ¹H NMR (in CDCl₃ δ ppm) 7.09(dd, 1H, J=5.1Hz, 1.2Hz), 6.90(dd, 1H, J=5.1Hz, 3.4Hz), 6.77(dd, 1H, J=3.4Hz, 1.1Hz), 2.82(t, 2H, J=7.7Hz), 1.67(p, 2H, J=7.7Hz), 1.34(m, 6H), 0.89(t, 3H, J=6.6Hz)

Synthesis of 2-Bromo-5-hexylthiophene (2) 25.6g of NBS in 50ml of DMF was added dropwise under darkness to a solution of 24g of 2-hexylthiophene in DMF at 0°C.

The reaction mixture was stirred at room temperature for another 10 hours before being poured into water. After extraction with methylene chloride, the organic phase was separated, dried over magnesium sulfate. The pure product (colorless liquid) was obtained through vacuum distillation. (28g, Yield: 80%) ^1H NMR (in CDCl_3 δ ppm) 6.85(d, 1H, $J=3.6\text{Hz}$), 6.54(dt, 1H, $J=3.6\text{Hz}$, 0.9Hz), 2.74(td, $J=7.6\text{Hz}$, 0.9Hz), 1.63(p, 2H, $J=8.1\text{Hz}$), 1.31(m, 6H), 0.90(t, 3H, $J=6.7\text{Hz}$). ^{13}C NMR (in CDCl_3 δ ppm) 147.65, 129.37, 124.33, 108.55, 31.53, 31.44, 30.35, 28.67, 22.58, 14.09.

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene (3) (3T) The Grignard reagent formed from 23.5g of 2-Bromo-5-hexyl-thiophene (95mmol) and magnesium was slowly added to a mixture of 2,3-dibromothiophene (40mmol), Ni(dppp)Cl_2 (0.4mmol), and 100ml ether at 0°C , then warmed to room temperature. The reaction was quenched by dilute HCl after 20 hours. The organic phase was separated, and combined with the ether extraction from the aqueous phase. The solvent was evaporated after drying over magnesium sulfate. The residue was then run through a flash column using hexanes as eluent. Pale yellow viscous liquid was obtained. (15g, Yield: 90%) ^1H NMR (in CDCl_3 δ ppm) 7.20(d, 1H, $J=5.3\text{Hz}$), 7.11(d, 2H, $J=5.3\text{Hz}$), 6.93(d, 1H, $J=3.5\text{Hz}$), 6.86(d, 1H, $J=3.5\text{Hz}$), 6.67(d, 1H, $J=3.5\text{Hz}$), 6.64(d, 1H, $J=3.5\text{Hz}$), 2.77(t, 4H), 1.65(m, 4H), 1.34(m, 12H), 0.88(t, 6H, 6.5Hz). ^{13}C NMR (in CDCl_3 δ ppm) 147.53, 146.03, 134.99, 132.30, 132.12, 131.35, 129.62, 127.64, 125.94, 124.15, 124.01, 123.98, 31.59, 31.55, 30.18, 30.12, 28.79, 28.77, 22.68, 22.61, 14.11. Elemental Analysis Calculated for $\text{C}_{24}\text{H}_{32}\text{S}_3$ C, 69.17; H, 7.74; S, 23.09. Found: C, 69.42; H, 7.61; S, 22.98

Synthesis of Tributyl-(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)stannane (4)

BuLi (2.5M in hexane) (6.4ml, 16mmol) was added to a solution of (5,5''-Dihexyl-[2,2';3',2'']terthiophene (6.0g, 14.5mmol) in THF at -78°C. After lithiation, tributyltin chloride (5.2g, 16mmol) was added to the mixture. The reaction was allowed to warm to room temperature for 3 hours. After normal workup, the product (pale yellow liquid) was used for another reaction without further purifications. ¹H NMR (in CDCl₃ δ ppm) 7.11(s, 1H), 6.91(d, 1H, J=3.5Hz), 6.87(d, 1H, J=3.5Hz), 6.66(d, 2H, J=3.5Hz), 2.78(m, 4H), 1.65(m, 4H), 1.57(m, 6H), 1.36(t, 6H, J=7.3Hz), 1.30(m, 12H), 1.12(t, 6H, J=8.3Hz), 0.92(m, 15H). ¹³C NMR (in CDCl₃ δ ppm) 146.97, 145.78, 138.03, 137.40, 135.92, 135.36, 133.05, 132.92, 126.82, 125.78, 124.11, 124.00, 31.63, 31.61, 31.59, 31.56, 30.19, 30.17, 28.96, 28.82, 28.79, 27.30, 22.61, 14.11, 13.70, 10.86.

Synthesis of 2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophene (5) (7T)

In a one-neck flask was charged 9g of (4), 1.0g of 2,3-dibromothiophene (4mmol), 0.1g of Pd(PPh₃)₄, and 30ml of DMF. After three freeze-thaw cycles, the mixture was heated up to 100°C for 20 hours under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with methylene chloride, and washed thoroughly with KF solution to remove tributyltin chloride. The organic layer was then dried over magnesium sulfate, and the solvent evaporated. The residue was purified by flash column using hexanes/ethyl acetate (10:1) as eluent. (orange liquid) (3.3g, yield=90%) ¹H NMR (in CDCl₃ δ ppm) 7.28(d, 1H, J=5.3Hz), 7.21(s, 1H), 7.18(s, 1H), 7.17(d, 1H, J=5.3Hz), 6.94(d, 1H, J=1.7Hz), 6.93(d, 1H, J=1.7Hz), 6.88(d, 1H, J=3.5Hz), 6.86(d, 1H, J=3.5Hz), 6.51(m, 4H), 2.76(t, 8H), 1.66(m, 8H), 1.34(m, 24H), 0.88(t, 6H,

6.7Hz). ^{13}C NMR (in CDCl_3 δ ppm) 147.66, 147.45, 146.28, 146.12, 135.08, 134.81, 134.50, 132.94, 132.58, 132.22, 131.95, 131.90, 131.85, 131.69, 131.45, 131.13, 130.47, 129.68, 129.32, 127.59, 127.44, 126.34, 126.15, 124.87, 124.17, 124.14, 124.01, 124.00, 31.58, 31.56, 30.17, 30.13, 28.79, 28.76, 22.60, 22.59, 14.10. Elemental Analysis Calculated for $\text{C}_{52}\text{H}_{64}\text{S}_7$ C, 68.37; H, 7.06; S, 24.57. Found: C, 68.57; H, 7.10; S, 24.28.

Synthesis of Tributyl-{2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophen-5-yl}stannane (6) The procedure is the same as with compound (4). This compound was used without further purification. (Yield=90%) ^1H NMR (in CDCl_3 δ ppm) 7.20(s, 1H), 7.19(s, 1H), 7.16(s, 1H), 6.94(d, 1H, $J=3.2\text{Hz}$), 6.93(d, 1H, $J=3.4\text{Hz}$), 6.87(d, 2H, $J=3.5\text{Hz}$), 6.65(m, 4H), 2.76(m, 8H), 1.65(m, 8H), 1.58(m, 6H), 1.36(t, 6H, $J=7.3\text{Hz}$), 1.30(m, 24H), 1.12(t, 6H, $J=8.3\text{Hz}$), 0.92(m, 21H).

Synthesis of (7) (15T) The procedure is the same as with compound (5). (red viscous liquid) (Yield=77%) ^1H NMR (in CDCl_3 δ ppm) 7.33(d, 1H, $J=5.3\text{Hz}$), 7.28(s, 1H), 7.24(s, 1H), 7.237(s, 1H), 7.23(s, 1H), 7.21(s, 1H), 7.20(d, 1H, $J=5.3\text{Hz}$), 7.19(s, 1H), 6.93(m, 4H), 6.84(m, 4H), 6.62(m, 8H), 2.74(t, 16H, $J=7.4\text{Hz}$), 1.61(m, 16H), 1.29(m, 48H), 0.88(t, 24H, $J=5.4\text{Hz}$). ^{13}C NMR (in CDCl_3 δ ppm) 147.65, 147.61, 147.42, 147.36, 146.28, 146.25, 146.11, 146.08, 135.94, 134.84, 134.77, 134.55, 134.49, 134.41, 133.50, 133.16, 132.94, 132.61, 132.39, 132.22, 132.09, 131.95, 131.89, 131.42, 131.08, 130.51, 130.37, 129.71, 129.56, 129.36, 127.68, 127.63, 127.55, 126.45, 126.41, 126.27, 125.38, 124.14, 123.98, 31.58, 31.52, 30.18, 30.14, 28.80, 22.61, 14.11. Elemental Analysis

Calculated for $C_{108}H_{128}S_{15}$ C, 68.01; H, 6.76; S, 25.22. Found: C, 67.87; H, 6.75; S, 24.98. MALDI-TOF mass calcd for $C_{108}H_{128}S_{15}$ $[M+H]^+$ 1906.59 Found: 1906.27

Synthesis of (8) (6T) 0.9ml (2.3mmol) of BuLi (2.5M in hexane) was added dropwise to a solution of 0.8g (1.9mmol) of **3T** in THF at $-78^{\circ}C$. After stirring at this temperature for another 45 minutes, the mixture was transferred to another flask charged 0.77g (5.7mmol) of $CuCl_2$ in 10ml of THF at $-78^{\circ}C$. The solution was allowed to warm to room temperature and reacted overnight. After normal workup, the residue was purified by flash column using hexanes/ethyl acetate (10:1) as eluent. (yellow liquid) (0.43g, yield=54%) 1H NMR (in $CDCl_3$ δ ppm) 7.16(s, 2H), 6.95(d, 2H, $J=3.5Hz$), 6.90(d, 2H, $J=3.5Hz$), 6.67(d, 4H, $J=3.5Hz$), 2.77(m, 8H), 1.64(m, 8H), 1.32(m, 24H), 0.89(t, 12H, 6.5Hz). ^{13}C NMR (in $CDCl_3$ δ ppm) 147.67, 146.42, 134.39, 132.36, 132.08, 130.84, 127.45, 126.44, 126.34, 124.25, 124.10, 31.62, 31.60, 31.57, 30.19, 30.15, 28.78, 22.61, 14.12. Elemental Analysis Calculated for $C_{48}H_{62}S_6$ C, 69.34; H, 7.52; S, 23.14. Found: C, 69.08; H, 7.53; S, 22.91

Synthesis of (9) (14T-1) The procedure is the same as with compound (8). (red solid) (Yield=40%) 1H NMR (in $CDCl_3$ δ ppm) 7.25(s, 2H), 7.24(s, 2H), 7.23(s, 2H), 6.96(d, 2H, $J=3.3Hz$), 6.95(d, 2H, $J=3.5Hz$), 6.89(d, 2H, $J=3.5Hz$), 6.88(d, 2H, $J=3.5Hz$), 6.66(m, 8H), 2.77(m, 16H), 1.66(m, 16H), 1.30(m, 48H), 0.89(t, 24H, 7.3Hz). ^{13}C NMR (in $CDCl_3$ δ ppm) 147.78, 147.57, 146.40, 146.22, 134.93, 134.70, 134.40, 134.36, 133.15, 132.15, 131.95, 131.91, 130.74, 130.38, 129.85, 127.64, 127.53, 126.60, 126.43, 126.26, 124.18, 124.05, 31.59, 31.56, 31.52, 30.18, 30.15, 28.79, 28.77, 22.59, 14.10.

Elemental Analysis Calculated for $C_{104}H_{126}S_{14}$ C, 68.44; H, 6.96; S, 24.60. Found: C, 68.54; H, 7.03; S, 24.38. MALDI-TOF mass calcd for $C_{104}H_{126}S_{14}$ $[M+H]^+$ 1824.60 Found: 1824.98

Synthesis of 4,5,4',5'-Tetrabromo-[3,3']bithiophenyl (10) 2,3-dibromothiophene was lithiated by LDA using 1.65ml of BuLi (2.5M in hexane) and 0.64g of diisopropylamine, then coupled by $CuCl_2$. The crude product was run through a short column using hexanes as eluent, and then recrystallized from hexanes. 0.6g of yellow crystals were obtained. (Yield=60%) 1H NMR (in $CDCl_3$ δ ppm) 7.05(s, 2H). ^{13}C NMR (in $CDCl_3$ δ ppm) 132.98, 129.53, 114.83, 112.12. Elemental Analysis Calcd for $C_8H_2Br_4S_2$ C, 19.94; H, 0.42; Br, 66.33; S, 13.31 Found: C, 20.10; H, 0.35; S, 13.30; Br, 66.42

Synthesis of (11) (14T-2) The procedure is the same as with compound (5). (red viscous liquid) (Yield=63%) 1H NMR (in $CDCl_3$ δ ppm) 7.40(s, 2H), 7.24(s, 2H), 7.10(s, 2H), 6.98(d, 2H, $J=3.5$ Hz), 6.91(d, 2H, $J=3.5$ Hz), 6.84(d, 2H, $J=3.5$ Hz), 6.84(d, 2H, $J=3.5$ Hz), 6.78(d, 2H, $J=3.5$ Hz), 6.68(m, 4H), 6.60(m, 4H), 2.76(m, 16H), 1.63(m, 16H), 1.28(m, 48H), 0.87(m, 24H). Elemental Analysis Calculated for $C_{104}H_{126}S_{14}$ C, 68.44; H, 6.96; S, 24.60. Found: C, 68.44; H, 7.06; S, 24.82. MALDI-TOF mass calcd for $C_{104}H_{126}S_{14}$ $[M+H]^+$ 1824.60 Found: 1824.55

Synthesis of (12) (30T) The procedure is the same as with compound (5). (dark red solid) (Yield=58%) 1H NMR (in $THF-d_8$ δ ppm) 7.82(s, 2H), 7.53(s, 2H), 7.43(s, 2H),

7.28(s, 2H), 7.27(s, 2H), 7.15(s, 2H), 7.11(s, 2H), 6.87(d, 2H, J=3.5Hz), 6.85(d, 2H, J=3.5Hz), 6.83(d, 2H, J=3.5Hz), 6.80(d, 2H, J=3.5Hz), 6.76(d, 2H, J=3.5Hz), 6.75(d, 2H, J=3.5Hz), 6.71(d, 2H, J=3.5Hz), 6.70(d, 2H, J=3.5Hz), 6.60(d, 2H, J=3.5Hz), 6.59(d, 2H, J=3.5Hz), 6.58(d, 2H, J=3.5Hz), 6.57(d, 2H, J=3.5Hz), 6.52(d, 4H, J=3.5Hz), 6.49(d, 2H, J=3.5Hz), 6.48(d, 2H, J=3.5Hz), 2.66(m, 32H), 1.48(m, 32H), 1.21(b, 96H), 0.77(b, 48H). Elemental Analysis Calculated for $C_{216}H_{254}S_{30}$ C, 68.05; H, 6.72; S, 25.23. Found: C, 67.81; H, 6.79; S, 24.97. MALDI-TOF mass calcd for $C_{216}H_{254}S_{30}$ $[M+H]^+$ 3810.16 Found: 3810.49