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Supporting Information

Well-Defined Triblock Hybrid Dendrimers Based on Lengthy Oligothiophene Cores and Poly(benzylether) Dendrons

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Materials All reagents were purchased from Aldrich and used without further purification unless otherwise noted. 2,2'-Bithiophene was filtered through silica gel using petroleum ether as the eluent. NBS was recrystallized from a 1:1 acetic acid/water mixture. Potassium carbonate was pulverized and dried at 120 °C overnight prior to use. 3-Octylthiophene was prepared according to a method described by Zimmer and coworkers.[8a] 2-(Trimethylstannyl)-4-octylthiophene was prepared via a lithiation protocol described by Yu and coworkers followed by quenching with trimethylstannyl chloride.[3b] 5-(Trimethylstannyl)-2,2'-bithiophene was prepared using a method described by Groenendaal et al.[8b] 2,5-Bis(trimethylstannyl)thiophene was prepared according to a literature procedure.[9] THF was distilled over sodium/benzophenone. Dichloromethane was distilled over CaH_2. N,N-Dimethylformamide (Fisher) was used as received. *n*-Butyllithium in hexanes (2.65 M) was purchased from Alfa. Third generation bromide ([G-3]-OH) poly(benzylether) dendron was prepared according to a literature procedure described by Hawker et al.[5a] All reactions were performed under Argon. Nitrosonium tetrafluoroborate was purchased from Lancaster.

Characterization Thin layer chromatography was performed on Merck Kieselgel 60 F_{254}. Silica used for flash chromatography was Merck Kieselgel 60 (230-400 mesh). Compound purities and reactions were monitored by HPLC (Waters 501 pump, 486 UV detector, $\lambda = 254$ nm); Microsorb-MV reverse phase column (Rainin 86-200-5, 5 mm particle size, 100Å pore size, 25 cm length; Millennium 2.0 software; acetonitrile/tetrahydrofuran mobile phase (Fisher). Melting points (mp) and glass transition temperatures (T_g) were measured on a Seiko II (DSC 6200) differential scanning calorimeter and taken upon the second heating (10 °C/min). Infrared spectra were collected on a Mattson Genesis II FT-IR using potassium bromide with a diffuse reflectance accessory (Pike). UV-Vis-NIR spectra were collected on a Bruker IFS 66v/s and HP-8453 spectrophotometer. UV-Vis spectra and extinction coefficients were taken on a Hewlett-Packard HP 8452A spectrophotometer. Solid state absorption data was taken on a quartz disk after spin casting the substrate from a chloroform solution. Emission spectra were recorded on a ISA/SPEX Fluorolog 3.22 equipped with double excitation and double emission monochromators and a digital photon-counting photomultiplier. ^{1}H-NMR and ^{13}C-NMR were recorded on Bruker AM-400 and DRX-500 instruments. MALDI-TOF data was collected on a Perseptive Biosystems Voyager-DE instrument in positive ion mode. The instrument was calibrated using Bovine Insulin and the matrix system was α-cyano-4-hydroxycinnamic acid. Electron Impact MS (low and high resolution) were taken on a Micromass ProSpec, double focusing mass spectrometer (EBE geometry) at 70 eV electrons. FAB MS (low resolution) was done on a Micromass 70-SE double focusing mass spectrometer (EB geometry) with a nitro benzyl alcohol matrix (NBA). FAB MS (high resolution) was done on a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Size exclusion chromatography was carried out on a Waters chromatograph (Waters 150-EV plus) equipped with a M486 tunable absorbance detector ($\lambda = 254$ nm) and a DRI detector. Polystyrene standards (18) were used for calibration and the mobile phase was tetrahydrofuran (1 mL/minute, 45 °C). A bank of 4 PL Gel columns from Polymer Laboratories was used: 100Å, 100 Å, 500 Å and a Mixed C. Elemental analyses were performed at M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85060 or at the UC Berkeley microanalysis laboratory.

2,2′-Bithiophene-5-carboxylic acid (1) A 5.051 g (30.4 mmol) sample of 2,2'-bithiophene in 75 mL of dry THF was treated dropwise with 11.47 mL (30.4 mmol) of *n*-butyllithium and stirred for 1.5 h at –78 °C under an argon atmosphere. Carbon dioxide was bubbled through the solution via a drying tube for 3 h. After allowing the heterogeneous solution to stir overnight at room temperature, the solvent was evaporated and the white powder was set to reflux for 2 h in 200 mL of a 5 % KOH aqueous solution. The homogeneous solution was filtered hot through a fritted glass filter, allowed to cool to room temperature and then acidified to pH 2 with concentrated HCl. The precipitate was filtered and dried *in vacuo* overnight to yield a white powder (5.11 g, 24.3 mmol, 80%). mp (DSC) 178 °C. IR (KBr) 1678 cm^{-1}. UV-Vis (MeOH) $\lambda_{max} = 330$ nm, $\varepsilon_{330} = 18,000\ M^{-1}cm^{-1}$. ^{1}H-NMR ($CD_3OD$): δ 7.66 (d, $J = 3.9$ Hz, 1H), 7.42 (dd, $J = 5.1$ and 1.1 Hz, 1H), 7.34 (dd, $J = 3.6$ and 1.1 Hz, 1H), 7.21 (d, $J = 3.9$ Hz, 1H), 7.07 (dd, $J = 5.1$ and 3.6 Hz, 1H) ppm; ^{13}C-NMR (CD_3OD): δ 165.4, 145.5, 137.6, 135.5, 134.1, 129.4, 127.5, 126.5, 125.2 ppm. MS (EI) *m/z* calcd for ($C_9H_6O_2S_2$) 210, found 210. Anal. Calcd for $C_9H_6O_2S_2$: C, 51.41; H, 2.88; S, 30.50. Found; C, 51.19; H, 2.78; S, 30.39.

Benzyl 2,2′-bithiophene-5-carboxylate (2) A round bottom flask was charged with 4.500 g (21.4 mmol) of **1**, 5.923 g (42.9 mmol) of K_2CO_3, 3.477 g (20.3 mmol) of benzyl bromide and 0.3278 g (1.24 mmol) of 18-crown-6. To this mixture was added 103 mL of dry THF and the resulting solution was set to reflux overnight. The solvent was evaporated and the resulting solid was filtered through silica in a 1:1 hexanes/dichloromethane mixture. The solvent was removed and the off-white solid was dried *in vacuo* overnight (6.10 g, 20.3 mmol, 95%). mp (DSC) 59 °C. IR (KBr) 3107, 3079, 3047, 3030, 2965, 1693, 977, 937, 912, 841, 826, 796, 778, 756, 746, 700 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 338 nm, ε_{338} = 20,000 $M^{-1}cm^{-1}$, λ_{emi} = 400 nm. ^{1}H-NMR ($CDCl_3$): δ 7.69 (d, *J* = 3.9 Hz, 1H), 7.43 - 7.30 (m, 5H), 7.23 (m, 2H), 7.09 (d, *J* = 3.9 Hz, 1H), 6.99 (dd, *J* = 4.9 and 3.7 Hz, 1H), 5.31 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 144.3, 136.2, 135.7, 134.3, 131.2, 128.50, 128.19, 128.05, 128.02, 126.0, 125.2, 123.8, 66.6 ppm. HRMS (EI) *m/z* calcd for ($C_{16}H_{12}O_2S_2$) 300.0279, found 300.0285.

Benzyl 5′-bromo-2,2′-bithiophene-5-carboxylate (3) A 5.0447 g (16.8 mmol) sample of **2** was dissolved in 93 mL of DMF and 3.053 g (17.1 mmol) of NBS was subsequently added. After allowing the solution to stir at room temperature, overnight, under argon, the reaction mixture was diluted in diethyl ether and extracted three times with water to remove the DMF. The ether layer was dried over $MgSO_4$, filtered and evaporated. The obtained powder was dissolved in dichloromethane and eluted through silica in 1:4 ethyl acetate/hexanes. The solvent was evaporated and the off-white powder was dried *in vacuo* overnight (6.31 g, 16.6 mmol, 99%). mp (DSC) 93 °C. IR (KBr) 3080, 3059, 3022, 2911, 2851, 1704, 971, 907, 877, 821, 793, 753, 698 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 344 nm, ε_{344} = 20,000 $M^{-1}cm^{-1}$. ^{1}H-NMR ($CDCl_3$): δ 7.72 (d, *J* = 3.9 Hz, 1H), 7.47 - 7.36 (m, 5H), 7.07 (d, *J* = 3.9 Hz, 1H), 7.01 (2 x d, *J* = 3.9 Hz, 2H), 5.35 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 143.1, 137.7, 135.7, 134.4, 131.7, 130.9, 128.59, 128.32, 128.15, 125.3, 124.1, 113.0, 66.8 ppm. HRMS (EI) *m/z* calcd for ($C_{16}H_{11}BrO_2S_2$) 379.9363; found 379.9364.

Benzyl 4″-octyl-2,2′:5′,2″-terthiophene-5-carboxylate (4) A 0.1900 g (0.501 mmol) sample of **3** and 0.2370 g (0.650 mmol) of 2-(trimethylstannyl)-4-octylthiophene was charged into a round bottom flask with 4 mL of DMF. The solution was deareated under vacuum and backfilled with argon ten times prior to the addition of $Pd(PPh_3)_2Cl_2$ catalyst (2-5 mol%). The resulting solution was heated to 40 °C over the course of 15 minutes at which point the solution turned black and the reaction looked finished as assessed by thin layer chromatography. The reaction was allowed to stir overnight at room temperature. The reaction was quenched in water and extracted with diethyl ether. The ether layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was chromatographed on silica using a 1:1 hexanes/dichloromethane mixture as the eluant. The solvent was evaporated and the yellow product was dried overnight *in vacuo* (0.2352 g, 0.476 mmol, 95%). mp (DSC) 63 °C. IR (KBr) 3097, 3069, 3038, 2972, 2953, 2916, 2845, 1708, 930, 906, 897, 870, 860, 827, 811, 793, 781, 743, 732, 722, 696 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 388 nm, ε_{388} = 29,000 $M^{-1}cm^{-1}$, $\lambda_{emi.}$= 472 nm. ^{1}H-NMR ($CDCl_3$): δ 7.74 (d, *J* = 4.0 Hz, 1H), 7.47 - 7.35 (m, 5H), 7.17 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 3.9 Hz, 1H), 7.07 (d, *J* = 3.8 Hz, 1H), 7.06 (d, *J* = 1.4 Hz, 1H), 6.85 (d, *J* = 1.3 Hz, 1H), 5.37 (s, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.65 (m, 2H), 1.4 - 1.25 (m, 10H), 0.93 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.8, 144.29, 144.18, 138.5, 136.1, 135.8, 134.5, 131.1, 128.58, 128.27, 128.12, 125.87, 125.55, 124.1, 123.6, 119.7, 66.7, 31.9, 30.44, 30.35, 29.39, 29.28, 29.23, 22.6, 14.1 ppm. HRMS (EI) *m/z* calcd for ($C_{28}H_{30}O_2S_3$) 494.1408, found 494.1401.

Benzyl 5″-bromo-4″-octyl-2,2′:5′,2″-terthiophene-5-carboxylate (5) A 1.6170 g (3.27 mmol) sample of **4** was dissolved in 40 mL of DMF and 0.5800 g (3.27 mmol) of NBS was subsequently added. After allowing the solution to stir at room temperature overnight, the reaction mixture was diluted in diethyl ether and extracted three times with water to remove the DMF. The ether layer was dried over $MgSO_4$, filtered and evaporated. The obtained powder was dissolved in dichloromethane and eluted through silica in 1:4 ethyl acetate/hexanes. The solvent was evaporated and the yellow solid was dried *in vacuo* overnight (1.8584 g, 3.24 mmol, 99%).

mp (DSC) 77 °C. IR (KBr) 3067, 3035, 2952, 2920, 2853, 1698, 949, 904, 898, 887, 845, 800, 783, 742, 695 cm^{-1}. UV-Vis ($CHCl_3$) $\lambda_{max} = 390$ nm, $\varepsilon_{390} = 31{,}000$ $M^{-1}cm^{-1}$. ^{1}H-NMR ($CDCl_3$): δ 7.73 (d, *J* = 4.0 Hz, 1H), 7.47 - 7.35 (m, 5H), 7.16 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 3.8 Hz, 1H), 6.89 (s, 1H), 5.36 (s, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 1.61 (m, 2H), 1.40 - 1.23 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 143.85, 143.14, 137.4, 135.95, 135.73, 134.96, 134.47, 131.3, 128.58, 128.29, 128.13, 125.9, 124.88, 124.35, 123.8, 108.5, 66.8, 31.8, 29.59, 29.53, 29.33, 29.20, 22.6, 14.1 ppm. HRMS (EI) *m/z* calcd for ($C_{28}H_{29}BrO_2S_3$) 574.0493;, found 574.0487.

Benzyl 4″-octyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-5-carboxylate (6) A 0.1205 g (0.210 mmol) sample of **5** and 0.1690 g (0.510 mmol) of 5-(trimethylstannyl)-2,2'-bithiophene was charged into a round bottom flask with 2.5 mL of DMF. The solution was deaerated under vacuum and backfilled with argon ten times prior to the addition of the $Pd(PPh_3)_2Cl_2$ catalyst (2-5 mol%). The reaction was stirred at room temperature for 15 minutes before increasing the temperature to 70 °C. The reaction was stopped after 6 h, when all the solvent had evaporated. The reaction was quenched in water and extracted with diethyl ether. The ether layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was chromatographed on silica using a 1:1 hexanes/dichloromethane mixture as the eluant. The solvent was removed and the orange product was dried *in vacuo* overnight (0.1244 g, 0.189 mmol, 90%). mp (DSC) 120 °C. IR (KBr) 3107, 3088, 3058, 3033, 2954, 2925, 2852, 1704, 949, 938, 912,848,836, 819, 803, 796, 745, 698 cm^{-1}. UV-Vis ($CHCl_3$) $\lambda_{max} = 424$ nm, $\varepsilon_{424} = 41{,}000$ $M^{-1}cm^{-1}$, $\lambda_{emi.} = 555$ nm. ^{1}H-NMR ($CDCl_3$): δ 7.69 (d, *J* = 4.0 Hz, 1H), 7.44 - 7.31 (m, 5H), 7.19 (dd, *J* = 4.9 and 1.0 Hz, 1H), 7.16 (dd, *J* = 3.6 and 1.0 Hz, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.07 (2 x d, *J* = 3.9 Hz, 2H), 7.03 - 6.98 (m, 4H), 5.32 (s, 2H), 2.71 (t, *J* = 7.9 Hz, 2H), 1.64 (m, 2H), 1.40 - 1.23 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 144.0, 140.5, 137.76, 137.22, 136.9, 135.7, 134.71, 134.51, 134.46, 134.13, 131.1, 130.2, 128.55, 128.25, 128.08, 127.84, 127.01, 126.4, 125.9, 124.50, 124.24, 123.95, 123.65, 123.62, 66.7, 31.8, 30.4, 29.52, 29.43, 29.37, 29.23, 22.6, 14.1 ppm. HRMS (EI) *m/z* calcd for ($C_{36}H_{34}O_2S_5$) 658.1162, found 658.1173.

Benzyl 5''''-bromo-4''-octyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene-5-carboxylate (7) A 1.2660 g (1.9211 mmol) sample of **6** was dissolved in 80 mL of DMF upon heating and 0.3510 g (1.9720 mmol) of NBS was subsequently added. After the NBS addition, the reaction cooled to room temperature while stirring under argon. After 15 minutes, the product precipitates from the solution. After 1 hour of stirring, the product is filtered and washed with cold DMF and water. The filtrate is re-filtered and washed and the collected solids are combined and dried *in vacuo* overnight (1.3715 g, 1.863 mmol, 97%). mp (DSC) 126 °C. IR (KBr) 3086, 3059, 3030, 2950, 2925, 2852, 1700, 981, 966, 932, 909, 847, 820, 805, 796, 791, 744, 697 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 424 nm, ε_{424} = 43,000 M^{-1}cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.69 (d, J = 3.9 Hz, 1H), 7.45 - 7.31 (m, 5H), 7.12 (d, J = 3.8 Hz, 1H), 7.07 (d, J = 3.9 Hz, 1H), 7.01 - 6.96 (m, 4H), 6.94 (d, J = 3.9 Hz, 1H), 6.88 (d, J = 3.8 Hz, 1H), 5.32 (s, 2H), 2.70 (t, J = 7.9 Hz, 2H), 1.64 (m, 2H), 1.45 - 1.23 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 144.0, 140.7, 138.4, 137.7, 136.1, 135.76, 135.04, 134.84, 134.46, 134.37, 131.2, 130.6, 129.9, 128.57, 128.26, 128.10, 127.0, 126.3, 125.9, 124.32, 124.18, 123.7, 111.1, 66.7, 31.9, 30.4, 29.53, 29.46, 29.37, 29.24, 22.7, 14.1 ppm. HRMS (FAB) *m/z* calcd for ($C_{36}H_{33}BrO_2S_5$) 736.0268, found 736.0278.

Benzyl 4'',4'''''-dioctyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene-5-carboxylate (8) A 1.0960 g (1.485 mmol) sample of **7** and 0.6780 g (1.888 mmol) of 2-(trimethylstannyl)-4-octylthiophene was charged into a round bottom flask with 60 mL of DMF. The solution was deaerated under vacuum and backfilled with argon ten times prior to the addition of $Pd(PPh_3)_2Cl_2$ catalyst (2-5 mol%). The resulting solution was heated to 60 °C, at which point **7** dissolved. The reaction was allowed to continue for 75 minutes. The reaction was quenched in water and extracted with dichloromethane. The dichloromethane layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was chromatographed on silica using a step gradient starting with a 2:1 hexanes/dichloromethane mixture as the eluant followed by a 3:2 hexanes/dichloromethane. The solvent was removed and the orange solid was dried *in vacuo* overnight (1.1517 g, 1.351 mmol, 91%). mp (DSC) 101 °C. IR (KBr) 3087, 3063, 2957, 2921, 2852, 1701, 914, 848, 801, 746, 698 cm^{-1}. UV-Vis ($CHCl_3$) $\lambda_{max} = 436$ nm, $\varepsilon_{436} = 51{,}000\ M^{-1}cm^{-1}$, $\lambda_{emi.}$= 565 nm. ^{1}H-NMR ($CDCl_3$): δ 7.69 (d, J = 3.9 Hz, 1H), 7.45 - 7.31 (m, 5H), 7.12 (d, J = 3.8 Hz, 1H), 7.07 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.8 Hz, 1H), 7.03 - 6.98 (m, 6H), 6.78 (s, 1H), 5.32 (s, 2H), 2.72 (t, J = 7.8 Hz, 2H), 2.56 (t, J = 7.9 Hz, 2H), 1.65 - 1.54 (m, 4H), 1.47 - 1.24 (m, 20H), 0.88 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 144.18, 144.05, 140.5, 137.78, 137.00, 136.82, 136.57, 135.78, 135.38, 134.76, 134.56, 134.47, 134.17, 131.1, 130.2, 128.57, 128.26, 128.10, 127.1, 126.4, 125.95, 125.06, 124.27. 124.19, 123.97, 123.76, 123.64, 119.2, 66.7, 31.9, 30.48, 30.36, 29.56, 29.50, 29.42, 29.32, 29.26, 22.7, 14.1 ppm. HRMS (FAB) *m/z* calcd for ($C_{48}H_{52}O_2S_6$) 852.2292, found 852.2282.

Benzyl 5′′′′′-bromo-4″,4′′′′′-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene-5-carboxylate (9) A 0.6050 g (0.7090 mmol) sample of **8** was dissolved in 40 mL of DMF upon heating and 0.1290 g (0.725 mmol) of NBS was subsequently added. After the NBS addition, the reaction cooled down to room temperature while stirring under argon. After 16 h, the product is filtered and washed with cold DMF and water. The filtered solid was dried *in vacuo* overnight (0.6463 g, 0.6948 mmol, 98%). mp (DSC) 110 °C. IR (KBr) 3062, 2921, 2853, 1701, 907, 840, 829, 802, 796, 788, 756, 744, 728, 693 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 438 nm, ε_{438} = 61,000 M^{-1} cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.69 (d, *J* = 3.9 Hz, 1H), 7.45 - 7.31 (m, 5H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.07 (d, *J* = 3.9 Hz, 1H), 7.04 - 6.92 (m, 6H), 6.82 (s, 1H), 5.32 (s, 2H), 2.72 (broad s, 2H), 2.50 (t, *J* = 7.7 Hz, 2H), 1.67 - 1.55 (m, 4H), 1.45 - 23 (m, 20 H), 0.88 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.7, 144.0, 143.0, 140.5, 137.7, 136.63, 136.40, 135.84, 135.77, 135.59, 134.82, 134.76, 134.43, 134.19, 131.1, 130.1, 128.55, 128.24, 128.07, 127.0, 126.3, 125.9, 124.29, 124.25, 124.19, 124.11, 123.91, 123.60, 107.82, 66.7, 31.9, 30.3, 29.61, 29.56, 29.54, 29.39, 29.35, 29.25, 29.23, 22.7, 14.1 ppm. HRMS (FAB) *m/z* calcd for ($C_{48}H_{51}BrO_2S_6$) 930.1398, found 930.1388.

Benzyl 4″,4′′′′′-dioctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′-octithiophene-5-carboxylate (10) A 0.5100 g (0.547 mmol) sample of **9** and 0.3850 g (1.170 mmol) of 5-(trimethylstannyl)-2,2'-bithiophene was charged into a round bottom flask with 30 mL of DMF. The solution was deaerated under vacuum and backfilled with argon ten times. The resulting solution was heated to 70 °C, at which point **9** dissolved and $Pd(PPh_3)_2Cl_2$ catalyst (2-5 mol%) was added. The reaction was allowed to continue for 18 h. The reaction was quenched in water and extracted with dichloromethane. The dichloromethane layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was chromatographed on silica using a step gradient starting with a 2:1 hexanes/dichloromethane mixture as the eluant followed by a 3:2 hexanes/dichloromethane mixture. The solvent was revoved and the red solid was dried *in vacuo* overnight (0.4946 g, 0.4868 mmol, 89%). mp (DSC) 136 °C. IR (KBr) 3060, 2920, 2850, 1708, 907, 851, 827, 806, 796, 744, 726, 697 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 452 nm, ε_{452} = 69,000 M^{-1}cm^{-1}, λ_{emi}.= 565 nm ^{1}H-NMR ($CDCl_3$): δ 7.68 (d, *J* = 3.9 Hz, 1H), 7.44 - 7.32 (m, 5H), 7.19 (dd, *J* = 5.1 and 1.0 Hz, 1H), 7.15 (dd, *J* = 3.6 and 1.0 Hz, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 7.07 (2 x d, *J* = 5.0 Hz, 2H), 7.04 (d, *J* = 3.8 Hz, 1H), 7.02 - 6.95 (m, 8H), 5.31 (s, 2H), 2.71 (t, *J* = 7.8 Hz, 4H), 1.65 (m, 4H), 1.47 - 1.24 (m, 20 H), 0.88 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.8, 144.1, 140.48, 140.44, 137.79, 137.06, 136.87, 136.05, 135.80, 135.70, 134.77, 134.72, 134.67, 134.47, 134.19, 131.2, 130.2, 129.6, 128.58, 128.27, 128.10, 127.84, 127.07, 126.55, 126.36, 126.23, 125.95, 124.44, 124.27, 124.20, 123.97, 123.84, 123.62, 66.7, 31.9, 30.42, 30.36, 29.58, 29.54, 29.50, 29.42, 29.27, 22.7, 14.1 ppm. HRMS (FAB) *m/z* calcd for ($C_{56}H_{56}O_2S_8$) 1016.2046, found 1016.2032.

Benzyl 5′′′′′′′-bromo-4′′,4′′′′′-dioctyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′-octithiophene-5-carboxylate (11) A 0.4480 g (0.440 mmol) sample of **8** was dissolved in 100 mL of DMF upon heating and 0.0790 g (0.444 mmol) of NBS was subsequently added. After the NBS addition, the reaction cooled down to room temperature while stirring under argon. After 1 hour of stirring, the product was filtered and washed with cold DMF and water. The filtrate is re-filtered and washed and the collected solids are combined, recrystallized from a THF/ACN mixture and dried *in vacuo* overnight (0.4429 g, 0.4048 mmol, 92%). mp (DSC) 145 °C. IR (KBr) 3061, 2921, 2852, 1708, 909, 850, 806, 796, 790, 744, 726, 696 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 452 nm, ε_{452} = 66,000 $M^{-1}cm^{-1}$. ^{1}H-NMR ($CDCl_3$): δ 7.72 (d, *J* = 3.9 Hz, 1H), 7.45 - 7.31 (m, 5H), 7.18 (d, *J* = 3.8 Hz, 1H), 7.11 (2 x d, *J* = 3.8 Hz, 2H), 7.06 - 7.00 (m, 8H), 6.98 (d, *J* = 3.8 Hz, 1H), 6.92 (d, *J* = 3.8 Hz, 1H), 5.34 (s, 2H), 2.75 (m, 4H), 1.75 - 1.60 (m, 4H), 1.50 - 1.20 (m, 20H), 0.88 (m, 6H) ppm. HRMS (FAB) *m/z* calcd for ($C_{56}H_{55}BrO_2S_8$) 1094.1151, found 1094.1164.

Dibenzyl 4′′,4′′′′′,3′′′′′′′′′′,3′′′′′′′′′′′′′-tetraoctyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′:5′′′′′′′,2′′′′′′′′:5′′′′′′′′,2′′′′′′′′′:5′′′′′′′′′,2′′′′′′′′′′:5′′′′′′′′′′,2′′′′′′′′′′′:5′′′′′′′′′′′,2′′′′′′′′′′′′:5′′′′′′′′′′′′,2′′′′′′′′′′′′′:5′′′′′′′′′′′′′,2′′′′′′′′′′′′′′:5′′′′′′′′′′′′′′,2′′′′′′′′′′′′′′′-

hepdecithiophene-5,5′′′′′′′′′′′′′′′′-dicarboxylate (12) A 0.4170 g (0.380 mmol) sample of **11** and 0.0785 g (0.192 mmol) of 2,5-bis(trimethylstannyl)thiophene was charged into a round bottom flask with 120 mL of DMF. The solution was deaerated under vacuum and backfilled with argon ten times. The resulting solution was heated to 95 °C, at which point **11** dissolved and the $Pd(PPh_3)_2Cl_2$ catalyst (2-5 mol%) was added. The reaction became heterogeneous after 20 minutes and was allowed to continue for 18 h. The product was filtered and taken up in 250 ml of $CHCl_3$ and set to reflux for 2 h and filtered hot. The filtered, burgundy colored product was subsequently dried, recrystallized from CS_2 and dried overnight *in vacuo* (0.315 g, 0.149 mmol, 78%). mp (DSC) 210 °C. IR (KBr) 3060, 2952, 2925, 2851, 1713, 839, 829, 807, 786, 744, 729, 695 cm^{-1}. UV-Vis (CS_2) λ_{max} = 492, 590 nm, $\lambda_{emi.}$= 586, 635 nm. ^1H-NMR (CS_2, 45 °C): δ 7.52 (d, *J* = 3.7 Hz, 2H), 7.29 - 7.17(m, 10H), 7.02 (d, *J* = 4.0, 2H), 6.99 – 6.82 (m, 26H), 5.14 (s, 4H), 2.66 (t, *J* = 6.7 Hz, 8H), 1.60 (br, 8H), 1.40 – 1.18 (br, 40H), 0.83 (m, 12H) ppm. MS (MALDI-TOF) *m/z* calcd for ($C_{116}H_{112}O_4S_{17}$) 2115.18, found 2115.10. Anal. Calcd for $C_{116}H_{112}O_4S_{17}$: C, 65.81; H, 5.30; S, 25.75. Found; C, 65.59; H, 5.73; S, 25.12.

5′′′′-bromo-4′′-octyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene-5-carboxylic acid (13) A 0.1830 g (0.248 mmol) sample of **7** was dissolved 3 mL of THF and 2.0 mL of 5% KOH aqueous solution was added. The resulting homogeneous solution was stirred overnight at 70 °C. Conversion was monitored by thin layer chromatography. The reaction mixture becomes heterogeneous at room temperature. HCl (1M) was added until a pH of 2 was reached. The THF was evaporated and the product was suspended in water, filtered, washed with generous amounts of water, small amounts of methanol and redissolved in THF. The solvent was evaporated and the red product was dried overnight *in vacuo* (0.159 g, 0.246 mmol, 99%). ^1H-NMR shows the loss of the benzyl resonances.

[G-3]-5′′′′-bromo-4′′-octyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene-5-carboxylate (14) A 0.5067 g (0.783 mmol) sample of **13** was dissolved in 5 mL of dry THF and placed under argon. To the solution was added 0.1989 g (1.57 mmol) of oxalyl chloride followed by 2 drops of DMF. The resulting solution was set to reflux for 4 hours at which point the reaction looked complete as assessed by thin layer chromatography. The solvent was evaporated and the resulting burgundy solid was dried *in vacuo* overnight. To the flask containing the acid chloride was added 1.3300 g (0.834 mmol) [G-3]-OH and 0.3096 g (3.92 mmol) of pyridine. The solids were dissolved in 25 mL of dry dichloromethane and set to reflux for 3 days. The heterogeneous reaction mixture was diluted in dichloromethane and washed with a saturated solution of cupric sulfate to remove the pyridine. The dichloromethane layer was dried over MgSO$_4$, filtered, and the solvent was removed. The orange residue was taken up in minimal amounts of 2:3 petroleum ether/dichloromethane and was purified by column chromatography on silica using a 2:3 petroleum ether/dichloromethane mixture as the eluant. The solvent was removed and the orange foam was dried overnight *in vacuo* (1.40 g, 0.630 mmol, 80%). T$_g$ (DSC) 31.9 °C. IR (KBr) 3065, 3031, 2926, 2855, 1706, 1620, 1451, 1373, 1294, 1054 832, 737, 697 cm^{-1}. UV-Vis (CHCl$_3$) λ_{max} = 424 nm, ε_{424} = 45,000 M^{-1}cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.61 (d, *J* = 3.9 Hz, 1H), 7.37 - 7.25 (m, 40H), 7.05 (d, *J* = 3.8 Hz, 1H), 7.00 - 6.91 (m, 6H), 6.86 (d, *J* = 3.8 Hz, 1H), 6.65-6.52 (m, 21H), 5.20 (s, 2H), 4.99 (m, 28H), 2.68 (t, 2H), 1.63 - 1.59 (m, 2H), 1.37 - 1.26 (m, 10H), 0.88 (t, 3H) ppm; ^{13}C-NMR (CDCl$_3$): δ 161.63, 160.08, 160.01, 159.96, 143.99, 140.71, 139.13, 138.41, 138.08, 137.59, 136.70, 136.04, 135.01, 134.78, 134.53, 134.38, 131.03, 130.67, 129.80, 128.50, 127.92, 127.48, 127.03, 126.38, 126.04, 124.37, 124.22, 123.75, 123.70, 111.08, 106.92, 106.30, 101.81, 101.52, 70.00, 69.89, 66.49, 31.83, 30.36, 29.50, 29.42, 29.34, 29.21, 22.63, 14.10. MS (MALDI-TOF) *m/z* calcd for ($C_{134}H_{117}O_{16}S_5Br$) 2223.59, found

2223.04; MS (SEC-UV) Mn=2,039 Daltons (PDI=1.01). Anal. Calcd for $C_{134}H_{117}O_{16}S_5Br$: C, 72.38; H, 5.30; S, 7.21. Found; C, 72.19; H, 5.08; S, 7.00.

Bis[G-3]-4'',3'''''''-dioctyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''' :5'''''',2''''''':5''''''',2'''''''':5'''''''',2'''''''''-undecithiophene-5,5'''''''''-dicarboxylate (15) A 1.2536 g (0.564 mmol) sample of **14** and 0.1155 g (0.282 mmol) of 2,5-bis(trimethylstannyl)thiophene was charged into a round bottom flask with 8.0 mL of DMF. The solution was deaerated under vacuum and backfilled with argon ten times. The resulting solution was heated to 80 °C and the $Pd(PPh_3)_2Cl_2$ catalyst (2 mol%) was added. The reaction was allowed to stir for 18 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica using chloroform as the eluant. The solvent was removed and the residue was dried overnight *in vacuo* to provide a red solid (1.03 g, 0.236 mmol, 84%). T_g (DSC) 38.9 °C IR (KBr) 3062, 3032, 2920, 2851, 1704, 1596, 1451, 1373, 1293, 1262, 1157, 1090, 1054, 830, 798, 739, 697 cm^{-1}. UV-Vis ($CHCl_3$) λ_{max} = 472 nm, ε_{472} = 105,000 $M^{-1}cm^{-1}$, $\lambda_{emi.}$= 565, 608 nm. ^{1}H-NMR ($CDCl_3$): δ 7.61 (d, *J* = 3.8 Hz, 2H), 7.38 - 7.23 (m, 80H), 7.03 - 6.94 (m, 18H), 6.68-6.52 (m, 42H), 5.20 (s, 4H), 4.99 (m, 56H), 2.71 (s, 4H), 1.70 - 1.60 (m, 4H), 1.43 - 1.27 (m, 20H), 0.88 (t, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 161.58, 160.06, 159.99, 159.95, 144.02, 140.38, 139.14, 138.13, 137.59, 136.70, 136.56, 135.85, 135.77, 134.74, 134.63, 134.50, 134.10, 130.93, 130.16, 128.49, 127.91, 127.48, 127.06, 126.28, 126.05, 124.34, 124.26, 124.20, 123.95, 123.67, 106.82, 106.29, 101.73, 101.50, 69.97, 69.86, 66.47, 31.87, 30.27, 29.58, 29.39, 29.26, 22.66, 14.14. MS (MALDI-TOF) *m/z* calcd for ($C_{272}H_{236}O_{32}S_{11}$) 4369.50, found 4287 (t10), 4371(t11), 4452 (t12). MS (SEC-UV) Mn = 5,064 Daltons (PDI=1.01). Anal. Calcd for $C_{272}H_{236}O_{32}S_{11}$: C, 74.78; H, 5.44; S, 8.07. Found; C, 74.60; H, 5.56; S, 7.80.