Electronic Supplementary Information for Dalton Transactions

Hybrid Organic-Inorganic Nanomaterials Based on Polythiophene Dendronized Nanoparticles

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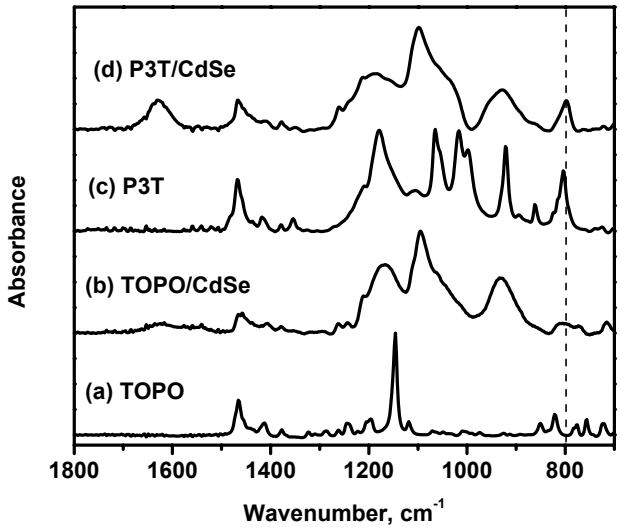
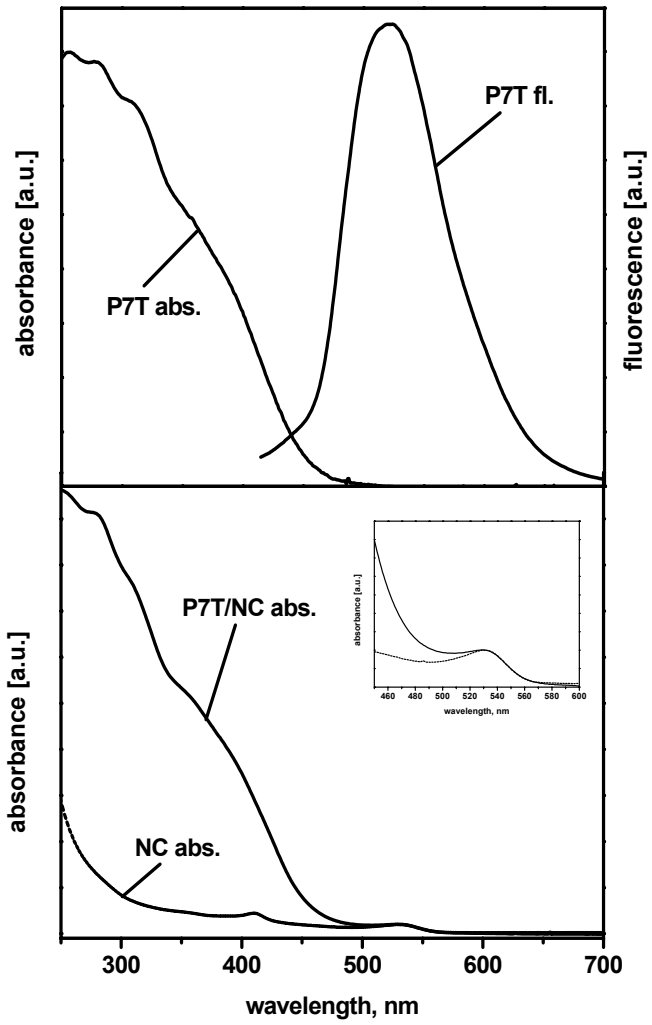
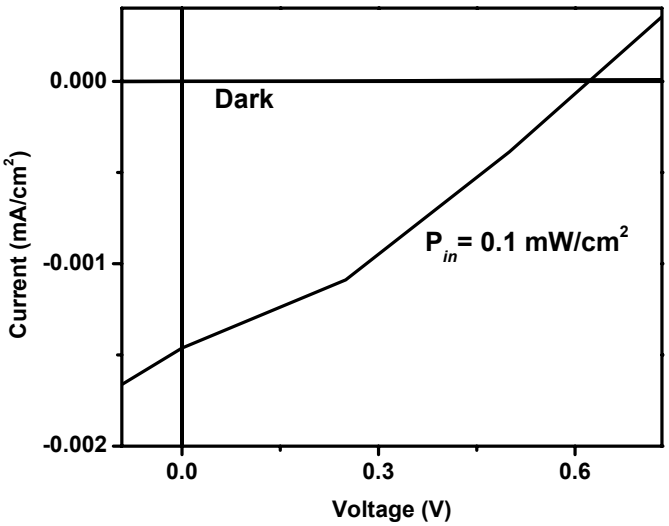
Electronic Supplementary Information (ESI)



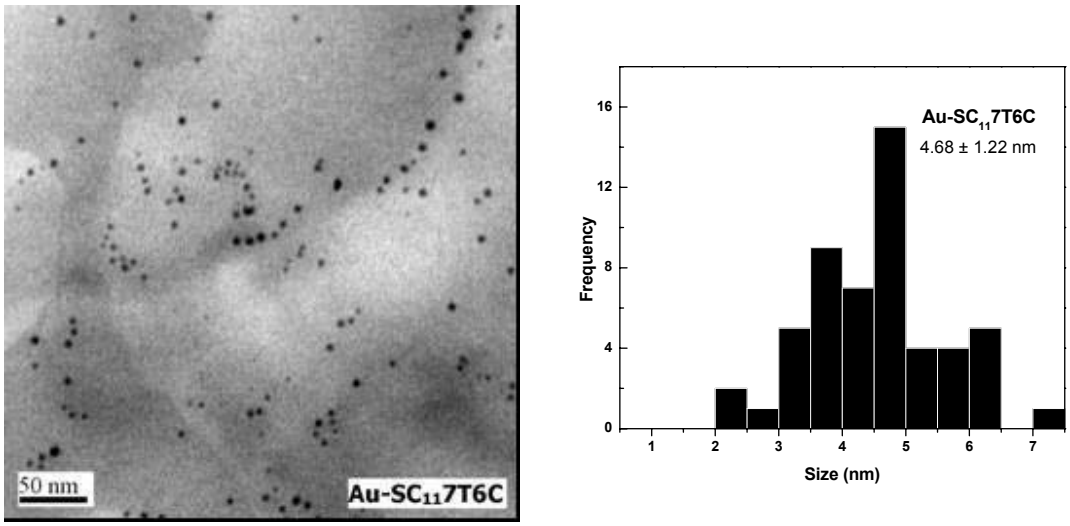
ESI Figure 1. FT-IR spectra of TOPO, P3T, and CdSe nanocrystals before and after exchange with the dendrons in the P=O stretching region. Reference 16.



ESI Figure 2. Absorption and Fluorescence spectra of P7T in $CHCl_3$. The bottom graph is of the P7T/NC complex. The fluorescence for both P7T and NC is completely quenched in the complex. Deconvolution yields about 34 P7T molecules per NC. For more details, see the text. Reference 16.



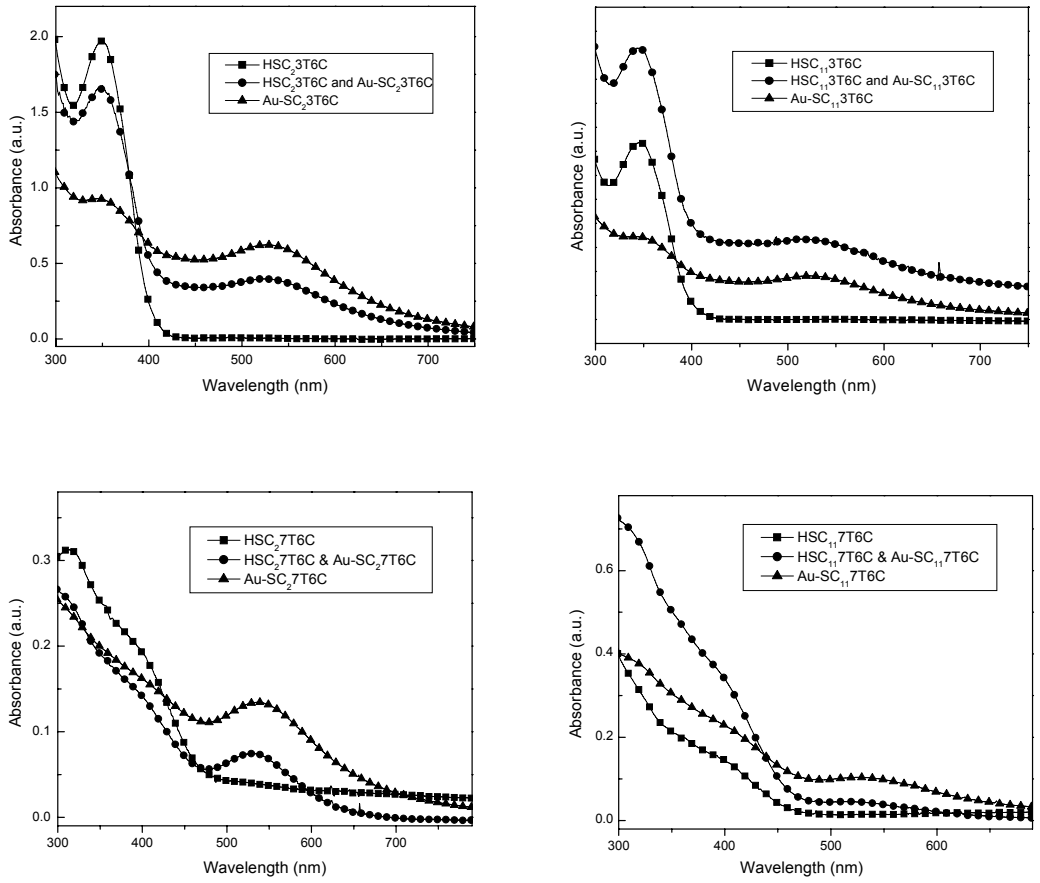
ESI Figure 3. Current density vs voltage for a P7T/CdSe device in the dark and under 0.1 mW/cm^2 illumination. Reference 16.



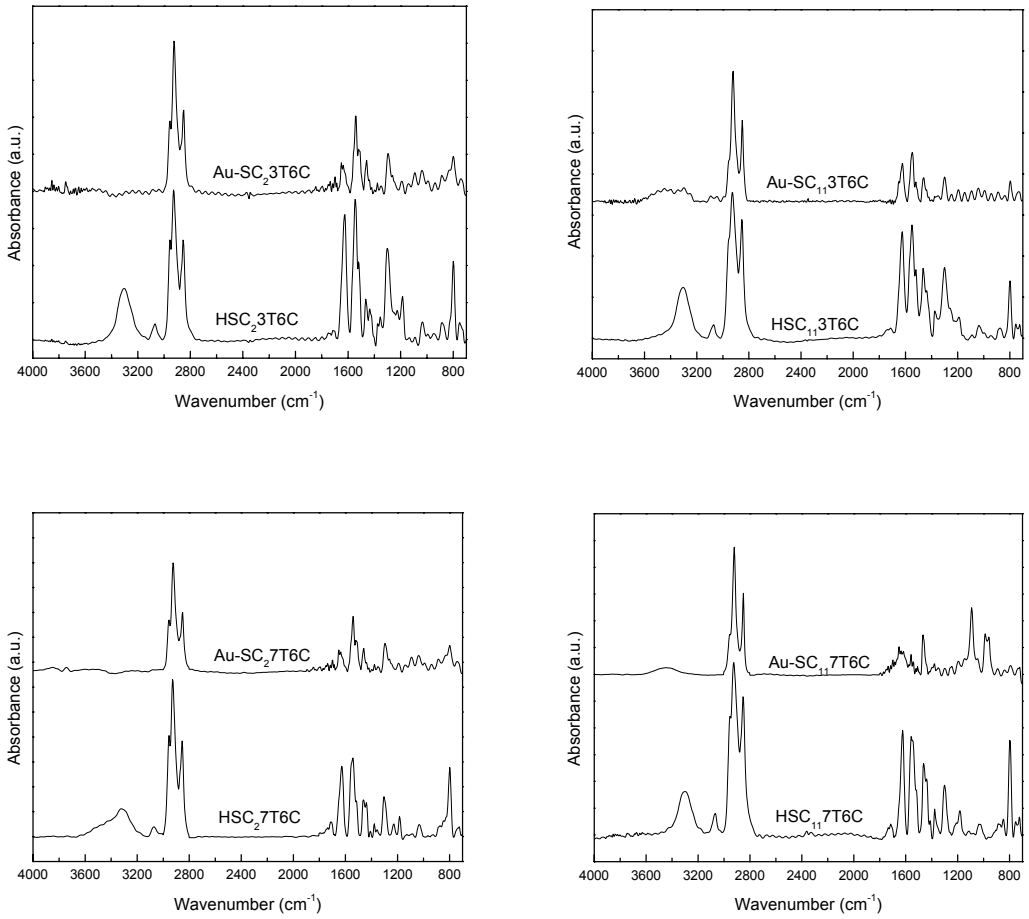
ESIFigure 4. HRTEM micrographs and size-distribution histograms for Au-$SC_2$3T6C and Au-SC_{11}7T6C.

Table 1. Summary of TEM, Absorption and Fluorescence Spectra Data

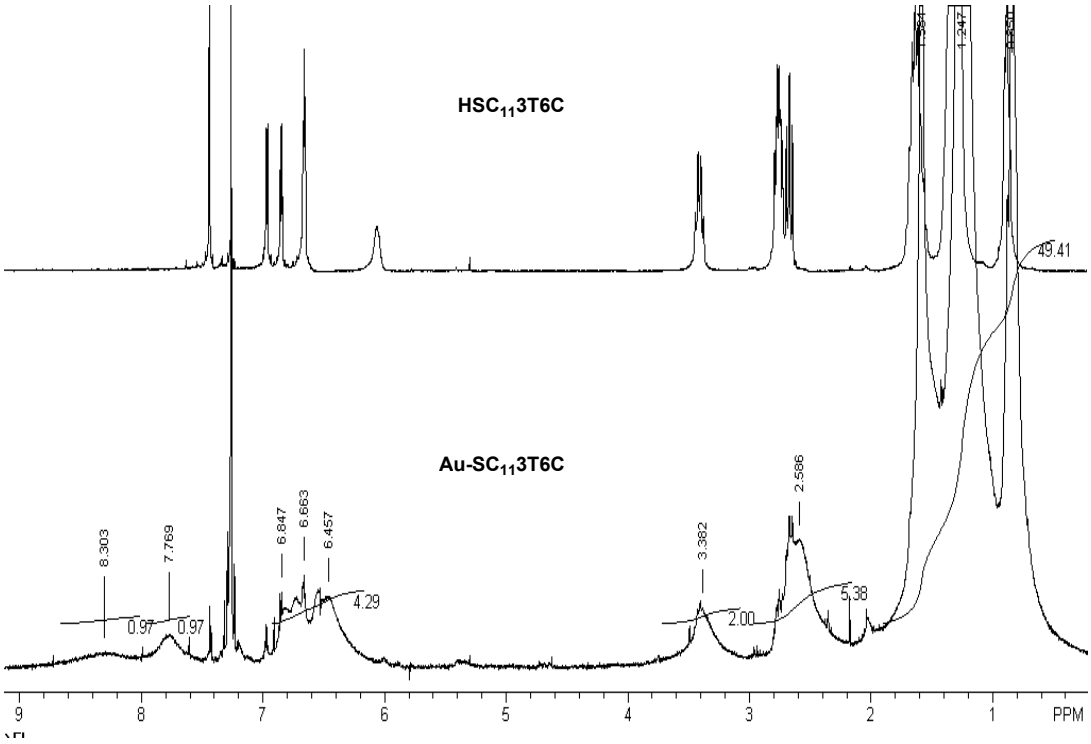
	core diameter (nm)	λ^{abs}_{max}(nm)	surface plasmon λ_{max}(nm)	λ^{fl}_{max}(nm)
$HSC_2$3T		349		456
Au NPs + $HSC_2$3T		350	523	455
Au-$SC_2$3T	2.88 ± 0.69	349	526	457
HSC_{11}3T		349		455
Au NPs + HSC_{11}3T		344	522	453
Au-SC_{11}3T	4.09 ± 1.03	342	527	454
$HSC_2$7T		311		536
Au NPs + $HSC_2$7T			531	533
Au-$SC_2$7T	3.84 ± 0.97		534	536
HSC_{11}7T				534
Au NPs + HSC_{11}7T			524	535
Au-SC_{11}7T	4.68 ± 1.22		535	540



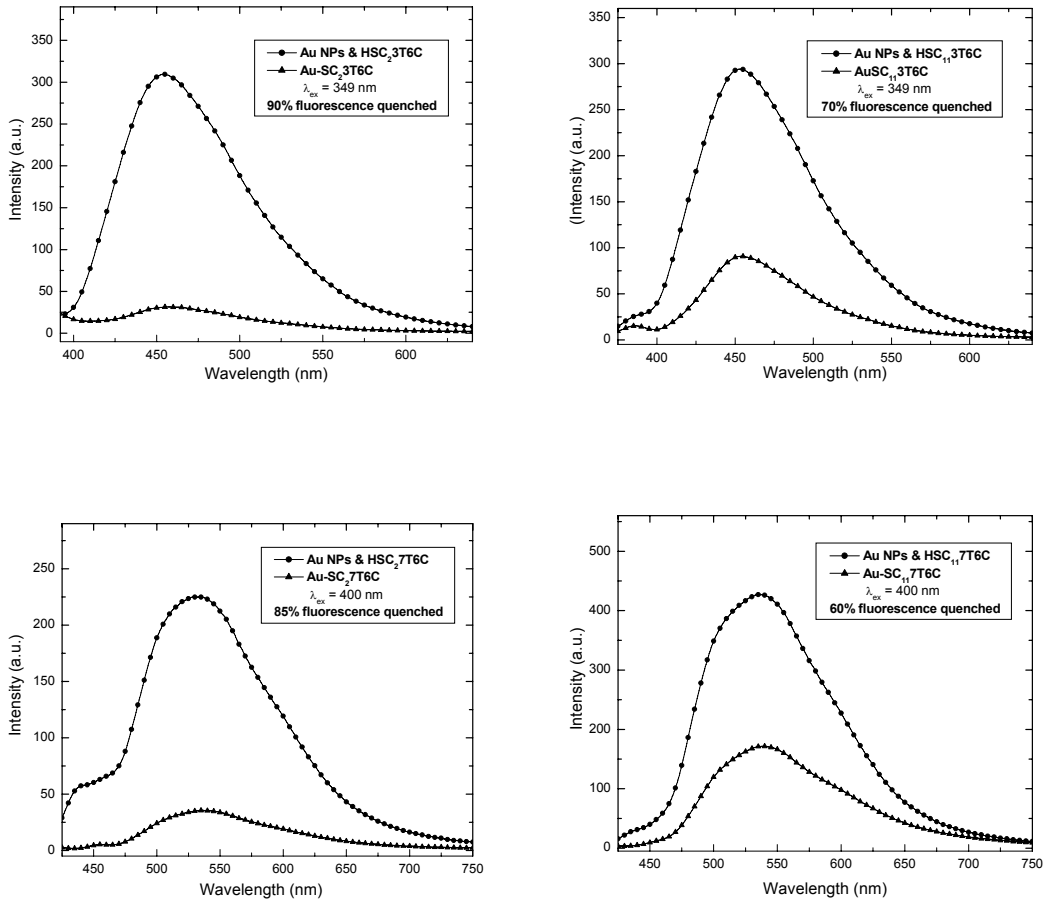
ESI Figure 5. UV-vis absorption spectra for dendritic thiol ligands, the reaction mixtures right before work-up and NCTDs after work-up. Solvent: toluene.



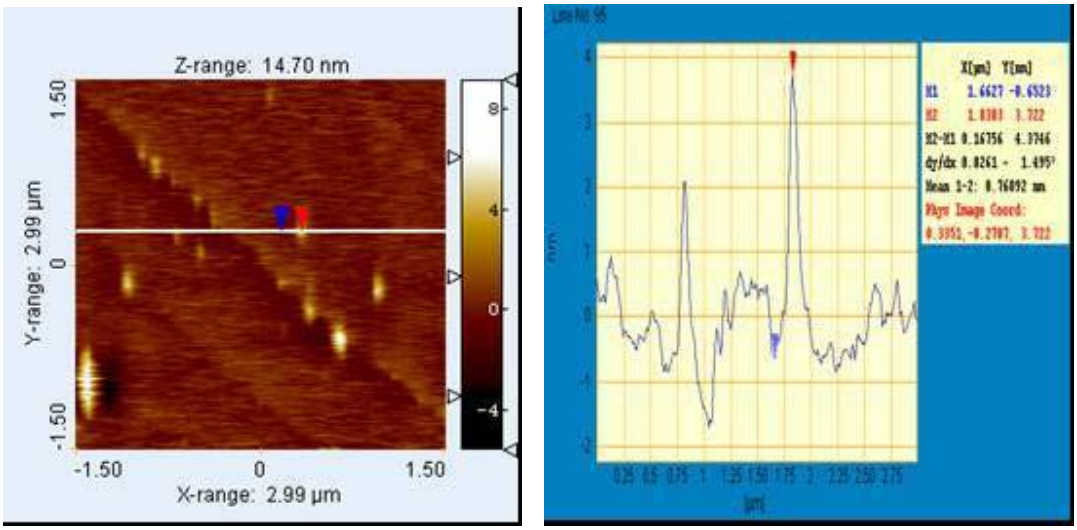
ESI Figure 6. FT-IR spectra for dendritic thiol ligands and NCTDs.



ESI Figure 7. ^{1}H NMR spectra for dendritic thiol ligands and hybrid nanoparticles.



ESI Figure 8. Fluorescence spectra for the NCTDs and their optically matched mixtures.



ESI Figure 9. AFM topographic images and height profiles of **Au-SC$_2$3T6C** (top).

DETAILS OF THE SYNTHESIS:

Phosphonic Acid-terminated Dendron Synthesis

The synthetic protocol for some of the dendron precursors is shown in Scheme 1. A detailed synthetic procedure for some of these materials has been published previously.[Error! Bookmark not defined.]

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene (3) (3T). The Grignard reagent formed from 7.51 g of 2-Bromo-5-hexyl-thiophene (7.51 g, 30.3 mmol) and magnesium (0.78 g, 32 mmol) was slowly added to a mixture of 2,3-dibromothiophene (3.09 g, 12.76 mmol), $NidpppCl_2$ (7 mg, 0.13mmol), and 100ml ether at 0 ^oC. After 20 hours, the reaction was quenched with dilute HCl and 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 though a flash column using hexanes as eluent. Pale yellow viscous liquid was obtained (4.62 g, Yield: 87%). ^1H NMR (in CDCl3) 7.20(d, 1H, J=5.3Hz), 7.11(d, 2H, J=5.3Hz), 6.93(d, 1H, J=3.5Hz), 6.86(d, 1H, J=3.5Hz), 6.67(d, 1H, J=3.5Hz), 6.64(d, 1H, J=3.5Hz), 2.77(t, 4H), 1.65(m, 4H), 1.34(m, 12H), 0.88(t, 6H, 6.5Hz). ^{13}C NMR (in $CDCl_3$) 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 $C_{24}H_{32}S_3$ C, 69.17; H, 7.74; S, 23.09. Found: C, 69.42; H, 7.61; S, 22.98.

Synthesis of 5'-Bromo-5,5''-dihexyl-[2,2';3',2'']terthiophene. In the absence of light, 1.96 g of N-Bromosuccinimide (NBS., 11.0 mmol) in 15 mL dimethylformamide (DMF) was added dropwise to a solution of 4.16 g of 5,5''-dihexyl-[2,2';3',2'']terthiophene (3T, 10.0 mmol) in 5 mL DMF at 0ºC. The reaction mixture was stirred overnight and then poured into water. After extraction with hexane, the organic layer was dried over $MgSO_4$ and concentrated. Pale yellow viscous liquid was obtained by chromatography on silica gel using hexane as eluent (4.32 g, Yield: 87.1%). ^1H NMR (in CDCl3) 7.08(s, 1H), 6.90(d, 1H, J=3.6Hz), 6.83(d, 1H, J=3.3Hz), 6.67(d, 1H, J=3.6Hz), 6.63(d, 1H, J=3.3Hz), 2.76(m, 4H), 1.64(m, 4H), 1.31(m, 12H), 0.88(t, 6H, 6.6Hz). ^{13}C NMR (in $CDCl_3$) 148.08, 146.44, 133.54, 132.48, 132.27, 131.85, 130.89, 128.00, 126.21, 124.09, 123.89, 110.646, 31.41, 30.03, 29.94, 28.62, 22.47, 13.98.

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophenyl phosphonic acid diethyl ester.[1] A mixture of 2.48 g of 5'-bromo-5,5''-dihexyl-[2,2';3',2'']terthiophene (5.0 mmol), 2.5 g of triethyl phosphite and 0.25 g of $NiBr_2$ was heated up to 135ºC overnight under N_2. The reaction mixture was first cool to r.t. and triethyl phosphite was removed by vacuum distillation. The residue was purified by flash column on silica gel using hexane/dichloromethane/ethyl acetate (5:1:2) as eluent (yellow liquid, 1.67 g, Yield: 60.4%). ^1H NMR (in CDCl3) 7.61(d, 1H, J=8.7Hz), 6.98(d, 1H, J=3.0Hz), 6.88(d, 1H, J=3.0Hz), 6.68(d, 1H, J=3.3Hz), 6.66(d, 1H, J=3.3Hz), 4.17(m, 4H), 2.77(t, 4H, J=8.0Hz), 1.64(p, 4H, J=7.2Hz), 1.31(m, 18H), 0.88(t, 6H, 6.6Hz). ^{13}C NMR (in $CDCl_3$) 148.59, 146.74, 138.94, 138.80, 133.35, 132.69, 132.48, 130.79, 128.12, 126.61, 124.30, 124.04, 62.73, 62.65, 31.43, 31.40, 31.37, 30.02, 29.97, 28.61, 22.46, 16.24, 16.16, 13.97. ^{31}P NMR (in $CDCl_3$): 11.72 (s).

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophenyl phosphonic acid.[2] To 1.07 g of 5,5''-dihexyl-[2,2';3',2'']terthiophenyl phosphonic acid diethyl ester (1.94 mmol), 2.0 g of bromotrimethylsilane was added dropwise with a needle under N_2. The reaction mixture was stirred for 2 hrs. Bromotrimethylsilane was removed by house vacuum and then 30 mL of methanol was added. The reaction mixture was refluxing for 4 hrs. and concentrated to give grayish solid (0.94 g, Yield: 97.7%). ^{1}H NMR (in CDCl3) 7.63(d, 1H, J=9.6Hz), 6.92(d, 1H, J=3.0Hz), 6.82(d, 1H, J=3.3Hz), 6.62(d, 1H, J=3.0Hz), 6.56(d, 1H, J=3.3Hz), 3.74(br, 2H), 2.73(m, 4H), 1.61(m, 4H), 1.29(m, 12H), 0.87(m, 6H). ^{13}C NMR (in $CDCl_3$) 148.06, 146.27, 138.99, 138.02, 133.43, 132.59, 132.38, 130.97, 128.21, 126.72, 124.02, 123.79, 31.44, 31.39, 31.34, 30.02, 29.94, 28.69, 22.49, 13.99. ^{31}P NMR (in $CDCl_3$): 14.32 (s). FTIR (KBr): 3300-2400 (v, br, OH), 3068 (C-H_{aro}), 2957,2927,2871,2853 (C-H), 1467, 1180 (P=O), 1063 (Ar-P-O), 1014 (P-O-H_{sy}), 998 (P-O-H_{asy}), 920(Ar-P-O), 859, 802.

Synthesis of Tributyl-(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)stannane (4). BuLi (2.5M in hexane) (2.43ml, 6.06mmol) was added to a solution of (5,5''-Dihexyl-[2,2';3',2'']terthiophene (2.3 g, 5.5 mmol) in THF at -78 ^{o}C. After 45 minutes, tributyltin chloride (1.99g, 6.1 mmol) 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 further without other purifications (estimated yield from NMR, 80%). ^{1}H NMR (in CDCl3) 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). ^{13}C NMR (in $CDCl_3$) 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 3.72 g of (4), 0.425 g of 2,3-dibromothiophene (1.75 mmol), 0.01g of $Pd(PPh_3)_4$, and 30ml of DMF. After three freeze-thaw cycles, the mixture was heated to 100 ^{o}C. After 24 hours, the 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/methylene chloride (10:1) as eluent. (viscous orange liquid) (1.31 g, yield=82%) ^{1}H NMR (in CDCl3) 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), 2.79(t, 8H, J=7.0Hz), 1.67(p, 8H, J=7.0Hz), 1.34(m, 24H), 0.91(t, 12H, J=6.4Hz). ^{13}C NMR (in $CDCl_3$) 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 $C_{52}H_{64}S_7$ C, 68.37; H, 7.06; S, 24.57. Found: C, 68.57; H, 7.10; S, 24.28.

Synthesis of 2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophene phosphonic acid diethyl ester (6). BuLi (2.5M in hexane) (0.242 ml, 0.55mmol) was added to a solution of 2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophene (0.5 g, 0.55mmol) in THF at -78 ^{o}C. After 45 minutes, diethylchlorophosphate (0.189 g, 1mmol) was added through an addition funnel. The reaction was allowed to warm to room temperature for 24 hours. After extraction with methylene chloride, the organic layer was dried over magnesium sulfate and solvent removed by evaporation. The residue was purified using hexanes/methylene chloride (8:2) as eluent. ^{1}H NMR (in CDCl3)

7.68(d, 1H, J=8.7Hz), 7.24(s, 1H), 7.19(s, 1H), 6.95(m, 2H), 6.85(t, 2H, J=3.6Hz), 6.66(m, 4H), 4.20(m, 4H), 2.76(t, 8H), 1.63(m, 8H), 1.41-1.25(m, 30H), 0.88(t, 12H, J=6.4Hz)

Synthesis of 2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophene phosphonic acid (P7T). Bromotrimethylsilane (0.38g, 2.48mmol) was added to a solution of 2,3-di(5,5''-dihexyl-[2,2';3',2'']terthiophen-5'-yl)thiophene phosphonic acid diethyl ester (0.325g, 0.31mmol) in THF and the solution was stirred overnight. The solvent was removed by rotovap and bromotrimethylsilane was removed by house vacuum. Then 30 mL of methanol and 5 ml of THF was added. The reaction mixture was refluxing for 4 hrs. and concentrated to give dark brown viscous oil (0.29 g, Yield: 95%) ^{1}H NMR (in $CDCl_3$) 8.32(br, 2H), 7.73(d, 1H, J=9.2Hz), 7.20(s, 1H), 7.14(s, 1H), 6.88(m, 2H), 6.81(d, 2H, J=3.1Hz), 6.60(m, 4H), 2.73(m, 8H), 1.62(m, 8H), 1.29(m, 24H), 0.88(t, 6H). ^{13}C NMR (in $CDCl_3$) 147.95, 147.61, 146.51, 146.26, 134.67, 134.21, 134.18, 133.61, 132.49, 132.15, 132.09, 132.04, 131.75, 131.27, 131.08, 130.15, 127.97, 127.76, 126.67, 126.45, 124.31, 124.25, 124.13, 124.09, 31.72, 31.68, 31.63, 30.30, 30.27, 29.85, 28.93, 22.74, 14.23. FT-IR (KBr): 3200-2509(v, br, OH), 3067(C-H), 2955, 2928, 2855 (C-H), 1627, 1466(C=C), 1437(CH_3), 1374(C-C), 1184(P=O), 1053(Ar-P), 1011(P-O-H), 927(Ar-P), 796(C-H_{def}).

Alkyl-Thiol-terminated Dendron Synthesis

The synthetic protocol for some of the dendron precursors is shown in Scheme 1. A detailed synthetic procedure for some of these materials will be published in another paper.

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene-5'-carboxylic acid (HOOC3T6C). n-BuLi (2.5 M in hexane, 5.0 mL, 12.5 mmol) was added dropwise to a solution of 5,5''-dihexyl-[2,2';3',2'']ter-thiophene (3T6C, 4.17 g, 10.0 mmol) in 50 mL of THF at -78°C under N_2. After 30 minutes upon addition, about 5 g of dry ice was added and the reaction mixture was warmed up to room temperature very slowly overnight. After normal acidic workup, column chromatography with hexane/isopropanol (v/v, 10/1) as an eluent yielded 4.01 g (87%) of HOOC3T6C as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.83 (s, 1H), 7.03 (d, 1H, J= 3.9 Hz), 6.89 (d, 1H, J= 3.0 Hz), 6.68 (m, 2H), 2.79 (t, 2H, J= 7.8 Hz), 2.76 (t, 2H, J= 7.8 Hz), 1.64 (m, 4H), 1.30 (m, 12H), 0.89 (t, 6H, J= 6.3 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.08, 149.03, 147.08, 140.88, 137.49, 133.24, 132.24, 131.28, 129.00, 128.31, 127.05, 124.47, 124.18, 31.56, 31.54, 31.50, 31.42, 30.29, 30.12, 30.10, 28.71, 22.54, 14.06. FT-IR (KBr): O-H stretch 3450 ~ 2300 cm^{-1}, CH_2 asymmetric stretch 2928 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, C=O 1674 cm^{-1}, C-O 1296 cm^{-1}, C-H out of plane vibration of thiophene ring 798 cm^{-1}. UV-vis (toluene) λ_{max}, nm (log ε): 284 (4.14), 355 (4.01).

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene-5'-carboxylic acid 2,5-dioxo-pyrrolidin-1-yl ester (NHS3T6C). A solution of HOOC3T6C (460 mg, 1.0 mmol), *N*-hydroxysuccinimide (126.6 mg, 1.1 mmol) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (210.9 mg, 1.1 mmol) in 5 mL of anhydrous DMF was stirred at room temperature overnight. The mixture was filtered through a pad of silica gel with copious washing (Et_2O) and concentrated under reduced pressure. Purification by flash chromatography (hexane/isopropanol, v/v, 10/1) gave NHS3T6C (475 mg, 85%) as a yellow solid. ^{1}H NMR ($CDCl_3$): 7.95 (s, 1H), 7.05 (d, 1H, J= 3.9

Hz), 6.88 (d, 1H, J= 3.3 Hz), 6.69 (m, 2H), 2.89 (s, 4H), 2.77 (m, 4H), 1.64 (m, 4H), 1.31 (m, 12H), 0.88 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.10, 157.09, 149.67, 147.48, 143.06, 139.18, 132.50, 132.38, 130.75, 128.66, 127.46, 124.60, 124.25, 122.74, 31.54, 31.52, 31.46, 31.38, 30.10, 30.07, 28.67, 25.59, 22.55, 22.52, 14.05. FT-IR (KBr): CH_2 asymmetric stretch 2925 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, C=O 1741 cm^{-1}, C-O 1265 cm^{-1}, C-N 1200 cm^{-1}, C-H out of plane vibration of thiophene ring 802 cm^{-1}. UV-vis (toluene) λ_{max}, nm (log □): 284 (4.19), 370 (4.13).

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene-5'-carboxylic acid (2-mercapto-ethyl)-amide ($HSC_2$3T6C). A solution of NHS3T6C (200.8 mg, 0.36 mmol), cysteamine (30.9 mg, 0.40 mmol) and 1.0 mL of triethylamine in 15 mL of CH_2Cl_2 was stirred at room temperature overnight. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate, v/v, 50/1) to give $HSC_2$3T6C (46 mg, 23% recovery) and 121.5 mg of NHS3T6C in 65% yield as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.64 (s, 1H), 7.08 (t, 1H, J= 6.0 Hz), 6.95 (d, 1H, J= 3.6 Hz), 6.83 (d, 1H, J= 3.0 Hz), 6.65 (d, 1H, J= 3.0 Hz), 6.59 (d, 1H, J= 3.6 Hz), 3.77 (q, 2H, J= 6.0 Hz), 2.98 (t, 2H, J= 6.0 Hz), 2.74 (t, 2H, J= 7.8 Hz), 2.71 (t, 2H, J= 8.4 Hz), 1.60 (m, 4H), 1.28 (m, 12H), 0.87 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 162.16, 148.37, 146.64, 136.85, 135.35, 133.78, 131.99, 131.54, 130.96, 128.02, 126.80, 124.29, 124.05, 39.39, 37.86, 31.51, 31.45, 30.12, 30.04, 28.72, 22.55, 14.07. FT-IR (KBr): N-H 3304 cm^{-1}, CH_2 asymmetric stretch 2928 cm^{-1}, CH_2 symmetric stretch 2854 cm^{-1}, amide I 1626 cm^{-1}, amide II 1547 cm^{-1}, C-H out of plane vibration of thiophene ring 799 cm^{-1}. UV-vis (toluene) λ_{max}, nm (log □): 283 (4.22), 349 (4.09).

Synthesis of 5,5''-Dihexyl-[2,2';3',2'']terthiophene-5'-carboxylic acid (11-mercapto-undecyl)-amide (HSC_{11}3T6C). A solution of NHS3T6C (200.8 mg, 0.36 mmol), 11-mercaptoundecylamine (81.4 mg, 0.40 mmol), and 1.0 mL of triethylamine in 15 mL of CH_2Cl_2 was stirred at room temperature overnight. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel (hexane/isopropanol, v/v, 20/1) to give 221.5 mg of HSC_{11}3T6C in 95% yield as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.44 (s, 1H), 6.97 (d, 1H, J= 3.9 Hz), 6.85 (d, 1H, J= 3.0 Hz), 6.66 (m, 2H), 6.06 (br, 1H), 3.41 (q, 2H, J= 6.6 Hz), 2.76 (m, 4H), 2.67 (t, 2H, J= 7.2 Hz), 1.64 (m, 8H), 1.30 (m, 26H), 0.88 (t, 6H, J= 6.3 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.62, 147.98, 146.28, 136.11, 135.97, 133.80, 131.70, 131.50, 130.17, 127.71, 126.45, 124.11, 123.89, 40.02, 38.97, 31.36, 31.31, 29.96, 29.91, 29.54, 29.39, 29.35, 29.24, 29.09, 29.03, 28.58, 28.36, 26.88, 22.44, 22.40, 13.93. FT-IR (KBr): N-H 3302 cm^{-1}, CH_2 asymmetric stretch 2928 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, amide I 1624 cm^{-1}, amide II 1551 cm^{-1}, C-H out of plane vibration of thiophene ring 798 cm^{-1}. UV-vis (toluene) λ_{max}, nm (log □): 284 (4.18), 349 (4.10).

Synthesis of 2,3-Di(5,5”-dihexyl-[2,2’;3’,2’’]terthiophene-5’-yl)thiophene-5-carboxylic acid (HOOC7T6C). n-BuLi (2.5 M in hexane, 1.2 mL, 3.0 mmol) was added dropwise to a solution of 2,3-di(5,5”-dihexyl-[2,2’;3’,2’’]terthiophene-5’-yl)thiophene (7T6C, 2.68 g, 2.93 mmol) in 30 mL of THF at -78°C under N_2. After 30 minutes upon addition, about 5 g of dry ice was added and the reaction mixture was warmed up to room temperature very slowly overnight. After normal acidic workup, column chromatography with $CHCl_3$/ethanol (v/v, 20/1) as an eluent yielded 2.40 g (86%) of HOOC7T6C as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.90 (s, 1H), 7.30 (s, 1H), 7.20 (s, 1H), 6.95 (d, 2H, J= 3.3 Hz), 6.87 (d, 2H, J= 3.0 Hz), 6.66 (br, 4H), 2.77 (t, 8H, J= 7.2 Hz), 1.65 (m, 8H), 1.31 (m, 24H), 0.88 (t, 12H, J= 6.0 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.46, 147.89, 147.50, 146.42, 146.13, 139.79, 137.07, 134.50, 134.25, 133.97, 133.49, 132.50, 131.97, 131.92, 131.88, 131.58, 131.55, 131.33, 131.10, 130.15, 127.76, 127.58, 126.54, 126.27, 124.18, 124.09, 124.00,

123.95, 31.52, 31.46, 30.12, 30.08, 28.77, 22.57, 14.08. FT-IR (KBr): O-H stretch 3300 ~ 2400 cm^{-1}, CH_2 asymmetric stretch 2925 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, C=O 1674 cm^{-1}, C-O 1300 cm^{-1}, C-H out of plane vibration of thiophene ring 800 cm^{-1}.

Synthesis of 2,3-Di(5,5”-dihexyl-[2,2’;3’,2’’]terthiophene-5’-yl)thiophene-5-carbo-xylic acid 2,5-dioxo-pyrrolidin-1-yl ester (NHS7T6C). A solution of HOOC7T6C (479 mg, 0.50 mmol), *N*-hydroxysuccinimide (63.3 mg, 0.55 mmol) and *N*-(3-dimethylamino-propyl)-*N’*-ethylcarbodiimide hydrochloride (105.4 mg, 0.55 mmol) in 30 mL of CH_2Cl_2 was stirred at room temperature overnight. The mixture was concentrated in vacuo and the residue was purified by flash chromatography (5% ethanol-$CHCl_3$) affording NHS7T6C (430 mg, 82%) as a yellow liquid. ^{1}H NMR ($CDCl_3$): 8.03 (s, 1H), 7.32 (s, 1H), 7.20 (s, 1H), 6.97 (d, 1H, J= 3.0 Hz), 6.96 (d, 1H, J= 3.9 Hz), 6.88 (d, 2H, J= 3.9 Hz), 6.67 (m, 4H), 2.91 (s, 4H), 2.76 (m, 8H), 1.64 (m, 8H), 1.31 (m, 24H), 0.89 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.96, 156. 87, 148.19, 147.74, 146.62, 146.30, 141.91, 138.72, 134.95, 134.28, 133.68, 132.92, 132.69, 132.06, 131.98, 131.79, 131.67, 131.49, 131.27, 130.58, 130.52, 127.87, 127.67, 126.62, 126.31, 124.26, 124.16, 124.07, 124.00, 123.90, 31.50, 31.38, 30.08, 30.04, 28.67, 25.56, 22.50, 14.03. FT-IR (KBr): CH_2 asymmetric stretch 2924 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, C=O 1741 cm^{-1}, C-O 1259 cm^{-1}, C-N 1200 cm^{-1}, C-H out of plane vibration of thiophene ring 800 cm^{-1}.

Synthesis of 2,3-Di(5,5”-dihexyl-[2,2’;3’,2’’]terthiophene-5’-yl)thiophene-5-carbo-xylic acid (2-mercapto-ethyl)-amide ($HSC_2$7T6C). A solution of NHS7T6C (210.9 mg, 0.20 mmol), cysteamine (19.5 mg, 0.25 mmol) and 0.5 mL of triethylamine in 10 mL of CH_2Cl_2 was stirred at room temperature overnight. The mixture was concentrated in vacuo and the residue was purified by flash chromatography (25% hexane-$CHCl_3$) affording $HSC_2$7T6C (159 mg, 78%) as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.79 (s, 1H), 7.29 (br, 1H), 7.21 (s, 1H), 7.14 (s, 1H), 6.91 (d, 1H, J= 3.6 Hz), 6.83 (d, 2H, J= 3.3 Hz), 6.76 (d, 1H, J= 3.3 Hz), 6.63 (m, 2H), 6.57 (m, 2H), 3.81 (m, 2H), 3.02 (t, 2H, J= 6.3 Hz), 2.71 (m, 8H), 1.62 (m, 9H), 1.29 (m, 24H), 0.87 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.94, 147.82, 147.46, 146.38, 146.09, 136.44, 136.15, 134.50, 134.10, 133.99, 133.75, 132.14, 131.96, 131.89, 131.83, 131.66, 131.63, 131.47, 130.93, 130.80, 130.61, 129.92, 129.83, 127.70, 127.50, 126.49, 126.19, 124.13, 124.03, 39.52, 37.91, 31.54, 30.10, 28.76, 22.59, 14.15, 14.01. FT-IR (KBr): N-H 3325 cm^{-1}, CH_2 asymmetric stretch 2928 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, amide I 1628 cm^{-1}, amide II 1543 cm^{-1}, C-H out of plane vibration of thiophene ring 799 cm^{-1}.

Synthesis of 2,3-Di(5,5”-dihexyl-[2,2’;3’,2’’]terthiophene-5’-yl)thiophene-5-carbo-xylic acid (11-mercapto-undecyl)-amide (HSC_{11}7T6C). A solution of NHS7T6C (316.5 mg, 0.30 mmol), 11-mercaptoundecylamine (67.5 mg, 0.33 mmol) and 0.5 mL of triethylamine in 10 mL of CH_2Cl_2 was stirred at room temperature overnight. The mixture was concentrated in vacuo and the residue was purified by flash chromatography (25% hexane-$CHCl_3$) affording HSC_{11}7T6C (326 mg, 95%) as a yellow liquid. ^{1}H NMR ($CDCl_3$): 7.52 (s, 1H), 7.24 (s, 1H), 7.16 (s, 1H), 6.93 (m, 2H), 6.86 (m, 2H), 6.64 (m, 4H), 6.26 (br, 1H), 3.43 (q, 2H, J= 6.0 Hz), 2.77 (m, 8H), 2.67 (t, 2H, J= 7.5 Hz), 1.63 (m, 12H), 1.30 (m, 38H), 0.89 (t, 12H, J= 6.5 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.23, 147.83, 147.54, 146.39, 146.16, 137.04, 135.51, 134.48, 134.08, 134.00, 133.69, 132.16, 131.94, 131.89, 131.83, 131.60, 131.19, 130.79, 130.73, 129.90, 129.84, 127.72, 127.68, 127.53, 127.48, 126.47, 126.23, 124.15, 123.97, 40.17, 39.19, 31.52, 30.11, 30.07, 29.63, 29.50, 29.30, 29.15, 28.74, 28.42, 26.95, 22.54, 14.10, 14.04. FT-IR (KBr): N-H 3298 cm^{-1}, CH_2 asymmetric stretch 2924 cm^{-1}, CH_2 symmetric stretch 2855 cm^{-1}, amide I 1624 cm^{-1}, amide II 1558 cm^{-1}, C-H out of plane vibration of thiophene ring 798 cm^{-1}.

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