Self-Assembly and Conductivity of Hydrogen Bonded Oligothiophene Nanofiber Networks

By David A. Stone[1†], Alok S. Tayi[2†], Josh E. Goldberger[1], Liam C. Palmer[1]andSamuel I. Stupp[1,2,3,4]*

[1]Department of Chemistry, Northwestern University, Evanston, IL 60208

[2]Department of Materials Science & Engineering, Northwestern University, Evanston, IL 60208

[3]Fienberg School of Medicine, Northwestern University, Evanston, IL 60208

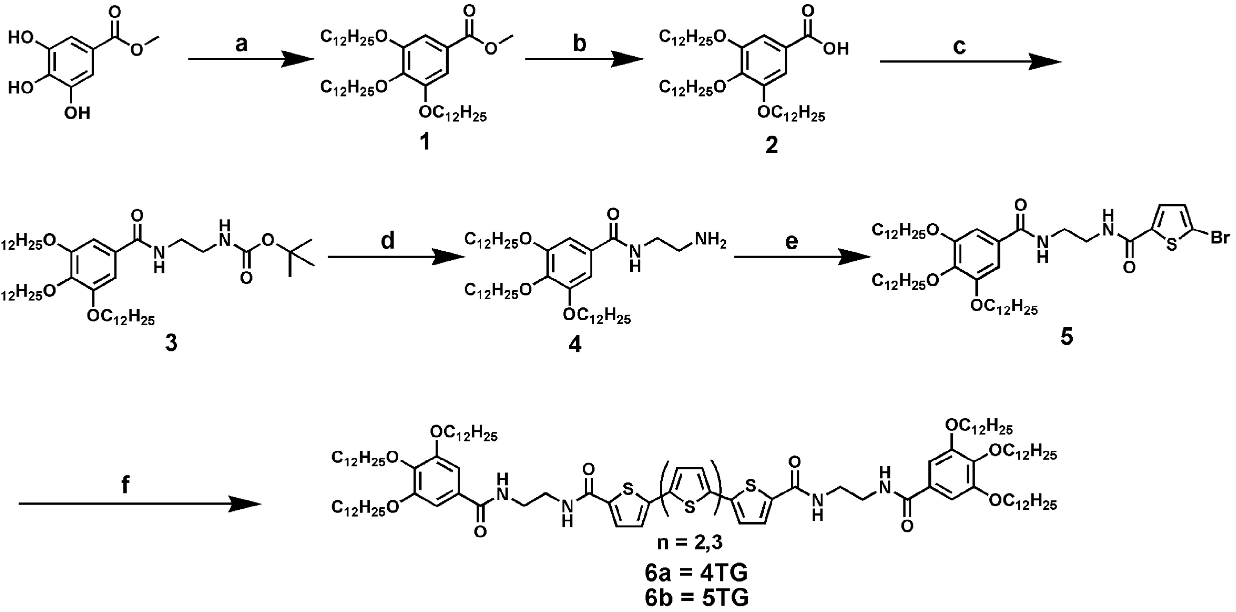
[4]Institute forBioNanotechnology in Medicine, Northwestern University, Evanston, IL 60208

† These authors contributed equally to this work

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. DPTS[12], mono-Boc-protected ethylenediamine[40] and the distannylthiophene derivatives[11] were synthesized according to published procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Varian Inova 500 (500 MHz for ^{1}H and 120 MHz for ^{13}C NMR) spectrometer using the residual solvent proton signal as standard. UV-Vis absorption spectra were collected on a Cary 500 spectrometer and fluorescence was measured on an ISS PC1 spectrofluorometer. Emission spectra were observed by exciting 10 nm higher than the observed absorbance maximum. All optical spectroscopy was collected at 3.0×10^{-6} M.

Transmission Electron Microscopy (TEM) was performed on a JEOL 1230 microscope. Films were prepared by drop casting dilute solutions onto copper grids. All samples werestained with uranyl acetate for 3 min. AFM measurements were taken on a Nanoscope Multimode ScanningProbe Microscope. Films were castonto a freshly cleaned and polished silicon wafer from a solution of 0.1 wt %gel that had been further diluted about 10 times. The silicon wafers were cleaned by soaking in a piranha bath followed by a water bath and then finally in an isopropanol bath for 15 min each.Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis was performed on a Hitachi S4800 microscope.

Synthesis



Synthesis of oligiothiophene gelator. (a) $C_{12}H_{25}Br$, K_2CO_3, acetone, 18-crown-6, reflux; (b) NaOH, water/THF/MeOH; (c) *N*-Boc-ethylenediamine, EDC, DCM; (d) 4M HCl/dioxane; (e) 5-bromo-2-thiophene-carboxylic acid, EDC, DPTS, DCM; (f) 2,2'- di(tributylstannyl)bithiophene, $Pd(PPh_3)_4$, DMF, 100°C for **6a**, 2,2'- di(tributylstannyl)terthiophene, $Pd(PPh_3)_4$, DMF, 100°C for **6b**.

Methyl 3,4,5-tris(dodecyloxy)benzoate(**1**): In a 500 mL round bottom flask, **1** (3.00 g, 16.3 mmol), K_2CO_3 (13.51 g, 99.7 mmol), 18-crown-6 (1.29 g, 4. 88 mmol), and 1-bromododecane (16.25 g, 65.2 mmol) were added to 250 mL of acetone. The reaction mixture was refluxed overnight and cooled to room temperature. The solution was filtered and the acetone was evaporated. The resulting residue was dissolved in ether and extracted three times with sat. $NaCO_3$ (aq). The organic layer was then dried with Na_2SO_4 and concentrated. The crude product was purified by column chromatography (silica gel; dichloromethane/hexanes, 30:70) to yield 10.87 g (96%) of the compound as a waxy while solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.27 (s, 2H, Ar H), 4.04-4.01 (m, 6H, OCH_2), 3.90 (s, 3H, $COOCH_3$), 1.84-1.73 (m, 6H, CH_2), 1.48 (qn, J = 8 Hz, 6H; CH_2), 1.38-1.27 (m, 48H, CH_2), 0.89 (t, J = 7.5 Hz, 9H; CH_3); ^{13}C NMR (120 MHz, $CDCl_3$, δ): 167.1, 153.0, 142.5, 124.8, 108.1, 73.7, 69.3, 52.3, 32.1, 30.5, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 26.2, 22.9, 14.3.

3,4,5-tris(dodecyloxy)benzoic acid (2): In a 250 mL round bottom flask, **1** (5.00g, 7.30 mmol) was dissolved in 100 mL of THF. NaOH (3.00 g, 73.0 mmol) dissolved in 100 mL of water was then added to the solution along with a few drops of methanol. The reaction mixture was refluxed for 16 hours, allowed to cool to room temperature and then acidified with 2 M HCl. The organic layer was then evaporated leaving a white precipitate in the aqueous layer. The precipitate was dissolved with dichloromethane and separated from the aqueous layer. The aqueous layer was extracted three times with dichloromethane. The combined organic layer was then extracted three times with 2 M HCl (aq). The organic layer was then dried with Na_2SO_4 and concentrated. The desired product was afforded after purification by column chromatography (silica gel; ethyl acetate/hexanes, 40:60) as 4.88 g (99%) of a waxy white solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.31 (br s, 1H, COOH), 7.27 (s, 2H, Ar H), 4.04-4.01 (m, 6H, OCH_2), 1.84-1.73 (m, 6H, CH_2), 1.48-1.46 (m, 6H; CH_2), 1.38-1.27 (m, 48H, CH_2), 0.89 (t, J = 7.5 Hz, 9H; CH_3); ^{13}C NMR (120 MHz, $CDCl_3$, δ):153.0, 143.3, 123.8, 108.7, 73.7, 69.3, 32.1, 30.5, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5,29.4, 26.3, 26.2, 22.9, 14.3.

***tert*-Butyl 2-(3,4,5-tris(dodecyloxy)benzamido)ethylcarbamate (3)**: To a solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (1.06 g, 5.55 mmol), 4-dimethylaminopyridine/*p*-toluenesulfonic acid (DPTS) (1.50, 4.81 mmol), and **2** (2.50 g, 3.70 mmol) in 300 mL of dichloromethane was added *N*-Boc-ethylenediamine (0.77 g, 4.81 mmol). The reaction was stirred at RT overnight. The reaction mixture was extracted three times with 2M HCl (aq) and the organic layer was dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 95:5) to yield 2.90 g (96%) of the compound as a waxy while solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.37 (br s, 1H, NH), 7.07 (s, 2H, Ar H), 5.09 (br s, 1H, NH), 4.02 (t, J = 6 Hz, 4H; OCH_2), 3.99 (t, J = 6 Hz, 2H; OCH_2), 3.53 (app q, J = 5 Hz, 2H; CH_2), 3.39 (app q, J = 5 Hz, 2H; CH_2), 1.80 (qn, J = 7.5 Hz, 4H; CH_2), 1.74 (qn, J = 8 Hz, 2H; CH_2), 1.49-1.44 (m, 6, CH_2), 1.43 (s, 9H, CH_3), 1.39-1.23 (m, 48H, CH_2), 0.89 (t, J = 7.5 Hz, 9H; CH_3); ^{13}C NMR (120 MHz, $CDCl_3$, δ): 167.7, 157.9, 153.2, 141.1, 129.1, 105.7, 80.1, 73.6, 69.4, 42.6, 40.4, 32.2, 32.1, 32.1, 30.5, 30.0, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.6, 28.5, 26.3, 22.9, 14.3.

***N*-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide** (**4**): In a 100 mL round bottom flask, compound **3** (1.50, 1.80 mmol) was dissolved in 3 M HCl in ethyl acetate. The reaction was monitored by TLC. When the reaction had completed, typically 2 h, the reaction was evaporated *in vacuo* to remove the solvent and acid. The product was dried under high vacuum and used without further purification.

***N*-(2-(3,4,5-tris(dodecyloxy)benzamido)ethyl)-5-bromothiophene-2-carboxamide** (**5**): To a solution of 5-bromothiophene-2-carboxylic acid (0.19 g, 0.96 mmol), DPTS (0.32 g, 1.04 mmol), and EDC (0.23 g, 1.20 mmol) in dichloromethane (100 mL) was added **5** (0.61 g, 0.80 mmol). The reaction mixture was stirred overnight at RT. The reaction is then extracted 3 times with sat. $NaHCO_3$ (aq), then the organic layer is dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 95:5) to yield 0.63 g (86%) of the compound as a waxy while solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.73 (br s, 1H, NH), 7.50 (br s, 1H, NH), 7.37 (d, J = 4 Hz, 1H; Ar H), 7.03 (s, 2H, Ar H), 6.99 (d, J = 4 Hz, 2H; Ar H), 4.06-3.97 (m, 6H, OCH_2), 3.60 (app s, 4H, CH_2), 1.80 (qn, J = 8 Hz, 4H; CH_2), 1.74 (qn, J = 8 Hz, 2H; CH_2), 1.49-1.43 (m, 6H, CH_2), 1.39-1.24 (m, 48H, CH_2), 0.89 (t, J = 7 Hz, 9H; CH_3); ^{13}C NMR (120 MHz, $CDCl_3$, δ): 169.2, 162.7, 153.3, 141.3, 140.5, 131.0, 128.8, 128.7, 118.6, 105.7, 73.8, 69.4, 41.3, 40.8, 32.2, 30.6, 29.9, 29.6, 26.4, 22.9, 14.2.

4TG (**6a**): A 100 mL flask was flame dried and cooled under nitrogen. In 50 mL of DMF, 2-(tributylstannyl)-5-(5-(tributylstannyl)bithiophene (0.15g 0.21 mmol) and **5** (0.41g, 0.46 mmol) were dissolved. The solution was then degassed by the freeze-pump-thaw method three times. Tetrakistriphenylphosphinepalladium(0) (0.012 g, 5% cat loading) was added to the solution and allowed to react overnight at 100 °C. The reaction was allowed to cool to room temperature and then filtered through a silica plug. The collected solution was evaporated to yield a yellow solid.

The crude solid was recrystallized three times with chloroform/methanol to give 0.25g of the desired product as a yellow solid (30.6% yield). ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (9:1), δ): 7.45 (d, J = 4 Hz, 2H; Ar H), 7.11 (d, J = 4 Hz, 2H; Ar H), 7.07 (d, J = 4.5 Hz, 2H; Ar H), 7.06 (d, J = 3.5 Hz, 2H; Ar H), 6.99 (s, 4H, Ar H), 3.97 (t, J = 6 Hz, 8H; OCH_2), 3.93 (t, J = 6.5 Hz, 4H; OCH_2), 3.54 (br s, 8H, CH_2), 1.76 (qn, J = 7.5 Hz, 8H; CH_2), 1.68 (qn, J = 7.5, 4H; CH_2), 1.44-1.38 (m, 12H, CH_2), 1.32-1.16 (m, 96H, CH_2), 0.83-0.80 (m, 18H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.2, 163.6, 153.1, 141.9, 140.9, 137.1, 137.0, 135.7, 129.3, 128.8, 125.8, 124.9, 124.1, 105.7, 73.7, 69.2, 40.6, 39.9, 32.0, 30.4, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.8, 14.2.

5TG (**6b**): Prepared and purified following a similar procedure as **6a**, but using (tributylstannyl)-5-(5-(tributylstannyl)terthiophene. Product collected as an orange solid in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (9:1), δ): 7.90 (br s, 2H, NH), 7.78 (br s, 2H, NH), 7.40 (d, J = 4 Hz, 2H; Ar H), 7.07 (d, J = 4 Hz, 2H; Ar H), 7.03-7.00 (m, 10H, Ar H), 3.98 (t, J = 6.5 Hz, 8H; OCH_2), 3.95 (t, J = 6.5 Hz, 4H; OCH_2), 1.78 (qn, J = 8 Hz, 8H; CH_2), 1.70 (qn, J = 8 Hz, 4H; CH_2), 1.47-1.40 (m, 12H, CH_2), 1.38-1.19 (m, 96H, CH_2), 0.86-0.83 (m, 18H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.1, 163.4, 153.2, 141.9, 141.4, 137.3, 137.0, 136.2, 135.5, 129.3, 128.9, 125.7, 124.9, 124.7, 124.0, 106.1, 73.7, 69.5, 40.6, 40.1, 32.0, 20.4, 28.8, 29.7, 29.6, 20.5, 29.4, 26.2, 26.1, 22.7, 14.0.

Device Fabrication and Measurement:

All top-contact conductivity devices, using 4TG, 5TG, and P3HT materials, were fabricated in the same manner. First, a 0.1wt% solution in chlorobenzene was prepared for each conductive molecule. Thin film depositions were performed on cleaned glass substrates. Onto glass, 4 μL of the solution was deposited in 1 μL increments. After each deposition, the film was allowed to air dry and then placed under vacuum for approximately 15 minutes. This forced remnant solvent out of the thin film.

When sufficiently dry, a copper evaporation mask was adhered to the polymer film. We employed copper transmission electron microscopy grids (SPI Quad) as the shadow mask. Using this mask, 200 nm gold was evaporated on the surface of the nanofiber film. Though most groups employ bottom contact geometry, the alkylated exterior may hinder charge injection. Thus, top-contact geometry provided pervasive electronic contact to much of the nanofiber thin-film.

Four-probe conductivity measurements were performed using a Keithley 2400 SMU. Based on the resistance, thickness, and device length and width, a conductivity value was calculated for each measurement. To ensure that conduction was due to the nanofibers, not metal, we performed numerous photoconductivity experiments to verify. Furthermore, scanning electron microscopy and energy dispersive X-ray spectroscopy proved that little metal existed in the semiconducting channel.

Field Effect Mobility Measurements

FET devices were fabricated by spincoating 5TG thin films onto a degenerately doped Si wafer with 300nm of SiO_2. **5TG** was solubilized in a mixture of 90:10 (by volume) dichlorobenzene and methanol to limit aggregation while drying. This procedure resulted in ~ 60 nm thick **5TG** films. AFM showed that this process still produced 1D supramolecular nanostructures. FET curves from these devices are shown in **Figure S8**. Mobilities were very low, likely due to the short persistence length of the dichlorobenzene/methanol cast fibers. The mobility of 5TG devices was found to be 2.34×10^{-7} cm^2/Vs.

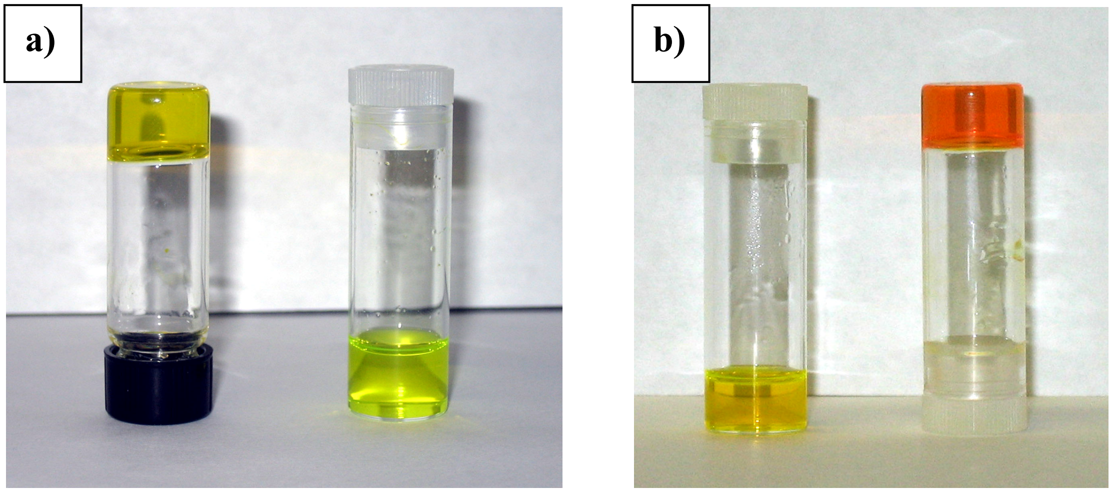


Figure S1. Photographs of 1 wt % samplesa) **4TG** and b) **5TG** in toluene (gel) and THF (solution). Inverted vials show formation of a self-supporting gel.Red-shifting of the absorbance is visible by eye with both materials.

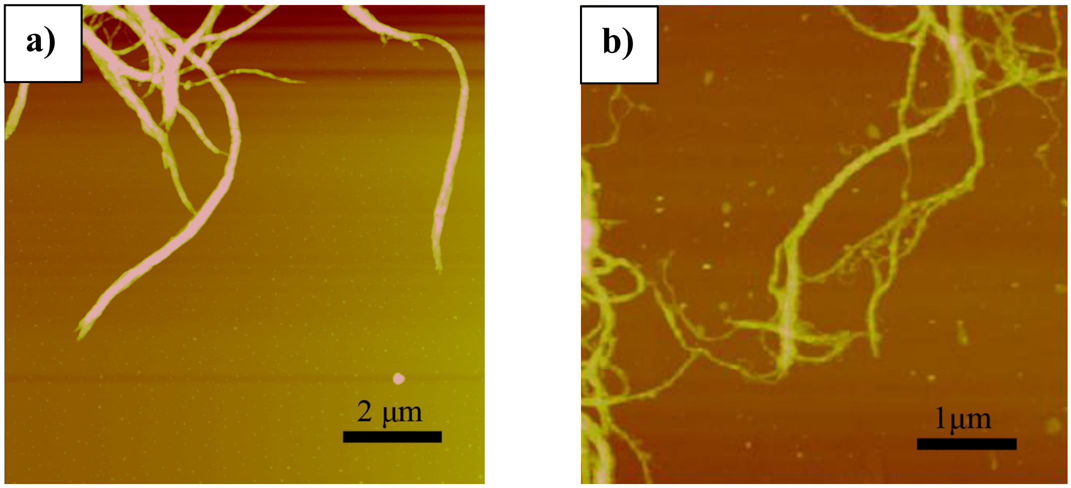


Figure S2. AFM micrographs: thin film from chlorocyclohexane of a) **4TG** and b) **5TG**.Films were prepared by dropcasting approximately 1µL of a 0.01 wt% gel on silicon. After dropcasting, the substrate was left in air at ambient conditions until all the solvent was thoroughly evaporated. This process took approximately 15 minutes for the dropcast solvent to fully evaporate.

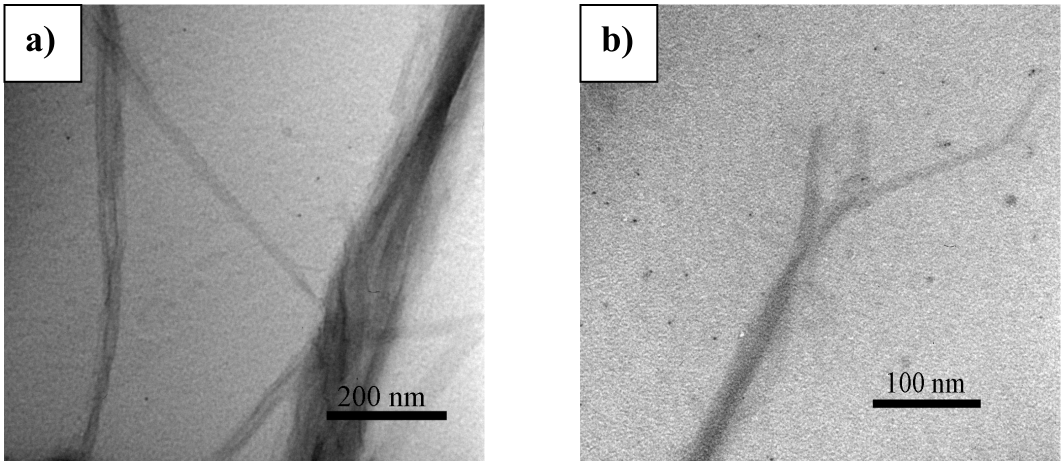


Figure S3. TEM micrographs: film cast from chlorocyclohexane of a) **4TG** and b) **5TG**. Close up imaging shows the large bundles are comprised of smaller nanofibers. Films were prepared by dispersing approximately 1μL of a 0.1 wt% gel onto a copper TEM grid. The substrate was then left in air at ambient conditions until all the solvent was thoroughly evaporated. This process took approximately 15 minutes for the dropcast solvent to fully evaporate.

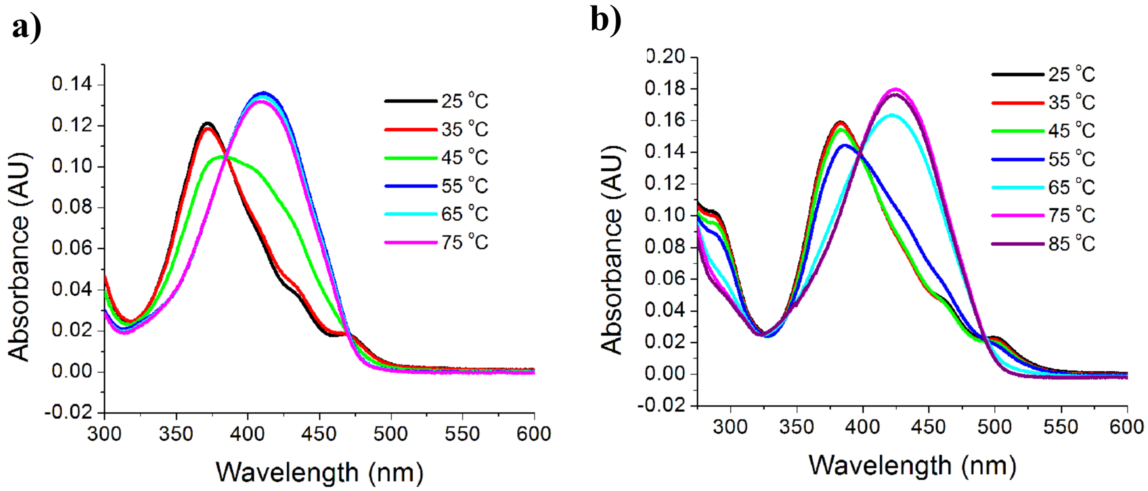


Figure S4. Variable temperature absorbance spectra for a) **4TG** and b) **5TG**. All spectra are collected at equal concentrations (3×10^{-6} M) and equilibrated for 10 min at each temperature before data collection.

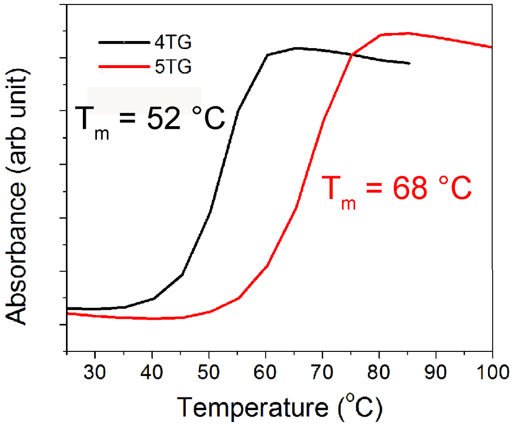


Figure S5. Absorption measured at the maximum of the unassembled state for **4TG** (416 nm) and **5TG** (432 nm) as a function of temperature. Melting point is taken as inflection point of the curve. All spectra are collected at equal concentrations (3 × 10^{-6} M) and equilibrated for 10 min at each temperature before data collection.

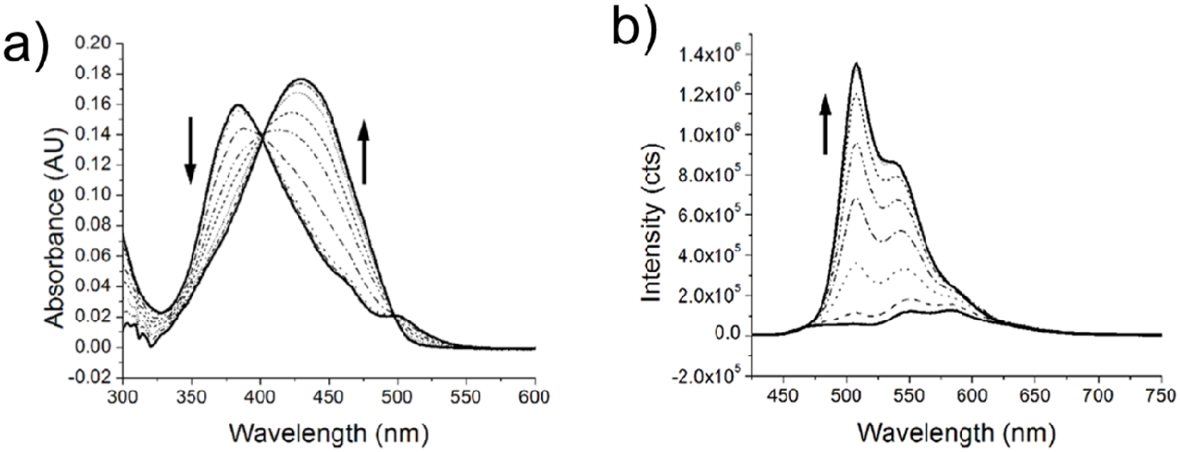


Figure S6. Absorbance (a) and fluorescence (b) spectra of **5TG** in CCH from 0 to 10 vol % CH_3OH indicating nanofibers disassembly. All spectra were obtained at 3.0 × 10^{-6}M.

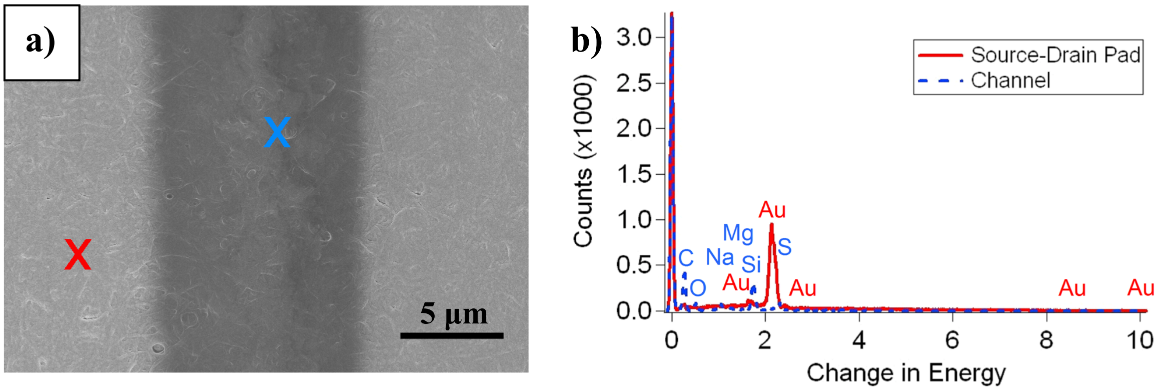


Figure S7. a) SEM image showing a **5TG** device. b) Energy Dispersive X-Ray SEM (EDX) showing elemental composition on a gold pad and with in an organic channel. In the organic channel there is no gold signal present.

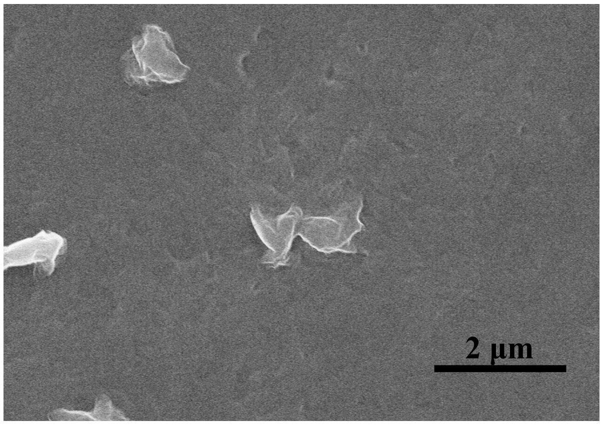


Figure S8. Representative SEM image showing amorphous morphology of a **5TG** film cast from chloroform.

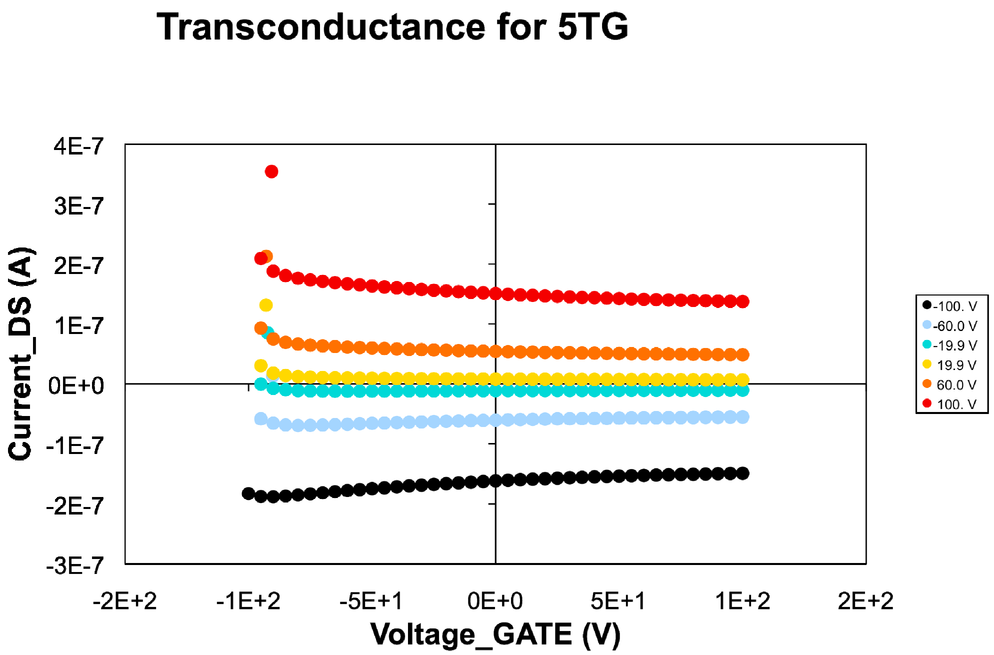


Figure S9. Representative transconductance curves for **5TG** field-effect transistors. Devices were fabricated on Si/SiO_2 substrates by spincoating.

Electrode Metal	**Avg. Cond. (S/cm)**
Titanium	3.5×10^{-8}
Aluminum	1.0×10^{-7}
Silver	4.1×10^{-7}
Gold	8.8×10^{-6}
Nickel	2.6×10^{-5}

Table S1. Table of average conductivities measured with varying metal electrodes.

Solvent	**4TG**[a][b]	**5TG**
Acetonitrile	I	I
Chlorobenzene	G (3 mg/mL)	G (3 mg/mL)
Chlorocyclohexane	G (<1 mg/mL)	G (<1 mg/mL)
Chloroform	S	S
1,2-Dichloroethane	G (2 mg/mL)	G (3 mg/mL)
Dichloromethane	S	S
DMF	P	P
Ethanol	I	I
Hexanes	P	P
Pentane	P	P
Styrene	G (<1 mg/mL)	G (<1 mg/mL)
Tetrahydrofuran	S	G (5 mg/mL)
Thiophene	G (5 mg/mL)	S
Toluene	G (<1 mg/mL)	G (<1 mg/mL)

Table S2. Table of solubilities of **4TG** and **5TG** in organic solvents. [a] **I**is insoluble in solvent; **S** is soluble in solvent; **P** is soluble at high temperatures, but precipitates upon cooling, **G** is gel formation. [b] number in parentheses is minimum concentration need to form a gel.