Supporting Information

An 11-nm Molecular Wire that Switches Electrochemically Between an Insulating and a Fully Conjugated State

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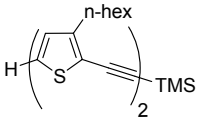
Synthesis

General:

HPLC grade solvents were further purified by passing through an activated alumina column to render them anhydrous and were delivered from a Schlenk manifold. Anhydrous diisopropylamine (DIEA) and THF used in Sonogashira couplings were degassed with argon for 20 min before use. All commercially available materials were obtained from Aldrich used without further purification. Flash column chromatography was performed using Silicycle Ultra Pure Silica Gel Silia-P (60 Å, 40-63μm). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300nb and DPX 300wb spectrometer. Chemical shifts for the proton spectra are reported in ppm (δ) relative to chloroform (δ 7.25). ^{1}H NMR of formamide intermediates **5a-d, 6a-e** and **8-11** revealed complex splitting and multiplets in the aromatic range due to the formation of rotamers. A JEOL HX110 spectrometer was used to obtain mass spectra via fast atomic bombardment (FAB^+). An AB Biosystem Voyager-DE spectrometer was used to obtain mass spectra via MALDI-time of flight (MALDI).

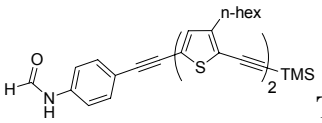
3-*n*-Hexyl-2-iodothiophene,[1] 3-*n*-hexyl-2-[(trimethylsilyl)ethynl]thiophene,[1] 3-*n*-hexyl-2-ethynylthiophene,[1] 3-*n*-hexyl-5-iodo-2-[(trimethylsilyl)ethynl]thiophene,[1] *N*-(4-trimethylsilylethynyl-phenyl)-formamide,[1] *N*-(4-ethynyl-phenyl)-formamide (**4**),[1] *N*-(4-iodo-phenyl)-formamide[2] and 2,5-diiodo-3-*n*-hexylthiophene[3] were prepared following the reported procedures.



[4-*n*-Hexyl-5-(4-*n*-hexyl-thiophen-2-ylethynyl)-thiophen-2-ylethynyl]-trimethylsilane 7. To a solution of 3-*n*-hexyl-2-ethynylthiophene (17.2 g, 89.6 mmol) in THF (100 ml) were added DIEA (19 ml, 0.135 mol), 3-*n*-hexyl-5-iodo-2-[(trimethylsilyl)ethynl]-thiophene (36 g, 92.3 mmol), $Pd(PPh_3)_2Cl_2$ (3.15 g, 4.5 mmol) and CuI (0.45 g, 2.36 mmol). The mixture was stirred and maintained at room temperature in a water bath overnight. After filtration of the solids, the filtrate was concentrated to dryness. Column chromatography (SiO_2, hexanes) provided pure 40 g of **7** (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (1H, d, J = 5.14 Hz), 6.98 (1H, s), 6.89 (1H, d, J = 5.16 Hz), 2.70 (2H, t, J = 7.60 Hz), 2.60 (2H, t, J = 7.60Hz), 1.60 (4H, m), 1.30 (12H, m), 0.86 (6H, m), 0.24 (9H, s). LRMS (FAB^+): 455.6 $[M+H]^+$.

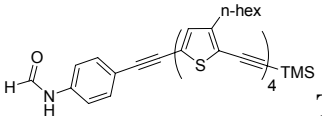
Iodinated bithiophenyl-ethynylene dimer 2. To a solution of DIEA (7.45 ml, 53 mmol) in anhydrous Et_2O (50 ml) at -78°C was added *n*-BuLi (31.3 ml, 1.6 M, 50.2 mmol). The solution was warmed to 0°C for 10 min and recooled to -78°C. Dimer **7** in ether (20 ml) was added dropwise and the solution was stirred at this temperature for 30

minutes. Iodine (13.4 g, 53 mmol) in Et_2O (200 ml) was added and the mixture was stirred at -78°C for 2 h. The temperature was raised to room temperature and stirred overnight. Water (2 ml) was added to quench the reaction. After filtration to remove the solids, the filtrate was washed with aqueous $Na_2S_2O_3$. The organic layer was dried over Na_2SO_4. Column chromatography (SiO_2, hexanes) yielded iodide **2** (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (1H, s), 6.98 (1H, s), 2.70 (4H, m), 1.60 (4H, m), 1.30 (12H, m), 0.89 (6H, m), 0.24 (9H, s). LRMS (FAB^+): 581.9 $[M+H]^+$.



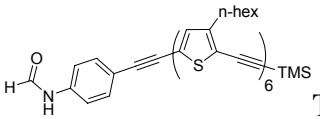
TMS-protected alkyne monoformamide dimer 8. Iodide **2** (10.0 g, 17.2 mmol) was coupled to alkyne **4** (2.65 g, 18.3 mmol) as described for **7** using DIEA (4.96 ml, 34.6 mmol), $Pd(PPh_3)_2Cl_2$ (121 mg, 0.172 mmol) and CuI (65 mg, 0.345 mmol) to give **8** as a pure solid (84%) after purification via column chromatography (SiO_2, 10:1 v/v $CHCl_3$/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.32 H, d, J = 11.2 Hz), 8.38 (0.54 H, s), 7.50 (4H, m), 7.17 (0.7 H, s), 7.04 (0.46 H, s), 7.02 (1H, s), 6.98 (1H, s), 2.66 (4H, m), 1.60 (4H, m), 1.30 (12H, m), 0.89 (6H, m), 0.25 (9H, s). LRMS (FAB^+) 599.2 $[M+H]^+$.

Alkyne dimer 5a. To a solution of dimer **8** (10 g, 16.7 mmol) in 1:1 CH_2Cl_2/CH_3OH (40 ml) was added K_2CO_3 (6.9 g, 50 mmol). The mixture was stirred at room temperature overnight under argon. After pouring into water (200 ml), the aqueous layer was extracted with CH_2Cl_2. The combined organic extract was washed with brine solution and dried over Na_2SO_4. Pure alkyne **5a** was obtained after purification via column chromatography (SiO_2, 10:1 v/v $CHCl_3$/EtOAc) in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.36H, d, J = 11.4 Hz), 8.38 (0.57 H, s), 7.50 (4H, m), 7.17 (0.71H, s), 7.04 (0.46 H, s), 7.02 (1H, s), 6.98 (1H, s), 3.48 (1H, s), 2.66 (4H, m), 1.60 (4H, m), 1.30 (12H, m), 0.89 (6H, m). LRMS (FAB^+): 526.9 $[M+H]^+$.



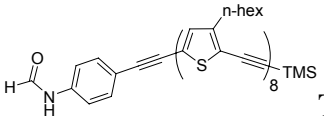
TMS-protected alkyne monoformamide tetramer 9. Alkyne dimer **5a** (5.60 g, 10.9 mmol) was coupled to iodide **2** (7.0 g, 12.1 mmol), worked up and purified as described for **8** to give pure tetramer **9** in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.29 H, d, J = 11.2 Hz), 8.38 (0.48H, s), 7.50 (4H, m), 7.22 (overlapped with solvent peak), 7.04 (0.56 H, s), 7.05 (4H, m), 2.66 (8H,m), 1.60 (8H, m), 1.30 (24H, m), 0.89 (12H, m), 0.26 (9H, s). LRMS (FAB^+): 978.4 $[M+H]^+$.

Alkyne tetramer 5b. Tetramer **9** (6.2 g, 6.39 mmol) was deprotected as described for **5a** to give pure alkyne **5b** in 94% yield after purification via column chromatography (SiO_2, 4:1 v/v $CHCl_3$/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.32H, d, J = 11.4 Hz), 8.38 (0.52H, s), 7.71 (0.38H, d, J = 11.3 Hz), 7.50 (4H, m), 7.22 (overlapped with solvent peak), 7.04 (0.66 H, s), 7.05 (4H, m), 2.66 (8H, m), 1.62 (8H, m), 1.34 (24H, m), 0.92 (12H, m). LRMS (FAB^+): 906.6 $[M+H]^+$.



TMS-protected alkyne monoformamide hexamer 10. Alkyne tetramer **5b** (4.20 g, 4.3 mmol) was coupled to iodide **2** (4.0 g, 6.9 mmol) as described for **8** to give pure hexamer **10** in 64% yield after purification via column chromatography on silica gel (SiO_2, 20:1 v/v $CHCl_3$/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.25 H, d, *J* = 11.2Hz), 8.38 (0.49H, s), 7.50 (4H, m), 7.15 (0.65H, s), 7.04 (0.66H, s), 7.05 (6H, m), 2.66 (12H, m), 1.60 (12H, m), 1.34 (36H, m), 0.92 (18H, m), 0.26 (9H, s). LRMS (FAB^+): 1358.5 $[M+H]^+$.

Alkyne hexamer 5c. Hexamer **10** (3.8 g, 2.8 mmol) was deprotected, worked up and purified as described for **5a** to give alkyne **5c** in 75% yield. ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.73 (0.32H, d, *J* = 11.4 Hz), 8.38 (0.52H, s), 7.71 (0.28H, d, *J* = 11.3Hz), 7.50 (4H, m), 7.18 (0.67H, s), 7.05 (6.6H, m), 3.48 (1H, s), 2.66 (12H, m), 1.62 (12H, m), 1.33 (24H, m), 0.89 (18H, m). LRMS (FAB^+): 1286.4 $[M+H]^+$.



TMS-Protected alkyne monoformamide octamer 11. Alkyne hexamer **5c** (1.7 g, 1.3 mmol) was coupled iodide **2** (2.0 g, 3.4 mmol), worked up and purified as described for **8** to give pure octamer **11** in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.32 H, d, *J* = 11.2Hz), 8.38 (0.52H, s), 7.50 (4H, m), 7.15 (0.72H, s), 7.05 (8.66H, m), 2.66 (16H, m), 1.60 (16H, m), 1.34 (48H, m), 0.92 (24H, m), 0.26 (9H, s). LRMS (FAB^+): 1739.3 $[M+H]^+$.

Alkyne octamer 5d. Octamer **11** (1.5 g, 0.86 mmol) was deprotected, worked up and purified as described for **5a** to give pure alkyne **5d** in 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (0.29H, d, *J* = 11.4Hz), 8.38 (0.49H, s), 7.50 (4H, m), 7.18 (0.61H, s), 7.05 (8.6H, m), 3.48 (1H, s), 2.66 (16H, m), 1.62 (16H, m), 1.33 (48H, m), 0.89 (24H, m). LRMS (FAB^+): 1667.9 $[M+H]^+$.

General Sonogashira coupling procedure for the synthesis of diformamides 6a-e. A solution of 2,5-diiodo-3-*n*-hexylthiophene (0.5 mmol), alkyne (1.5 mmol), DIEA (0.40 ml, 3.0 mmol) in THF (5 ml) was stirred at room temperature for 0.5 h under argon. Then $Pd(PPh_3)_2Cl_2$ (9.0 mg, 0.025 mmol) and CuI (9.5 mg, 0.05 mmol) was added to this solution. The resulting mixture was allowed to stir overnight at room temperature. After removal of the solids via filtration, the filtrate was concentrated to dryness. Column chromatography (SiO_2, 0-2:1 v/v CH_2Cl_2/EtOAc) provided pure diformamides **6a-e** in 80-92% yield as a yellow to dark-red solid.

Diformamide 6a. Yield: 80%. Chromatography condition: EtOAc as eluent. ^{1}H NMR (300 MHz, $CDCl_3$/CD_3CN): δ 8.67 (0.54H, d, *J* = 11.4Hz), 8.28 (1.45H, s), 8.00 (2H, br, s), 7.57-7.40 (7.2H, m), 7.05 (2H, m), 2.65 (2H, t, *J* = 7.4Hz), 1.62 (2H, m), 1.33 (6H, m), 0.89 (3H, t, J=7.40Hz). LRMS (FAB^+): 455.3 $[M+H]^+$.

Diformamide 6b. Yield: 95%. Chromatography condition: 1:1 v/v CH_2Cl_2/EtOAc as eluent. ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.71 (0.79H, d, *J* = 11.4Hz), 8.37 (1.18H, s), 7.57-7.40 (8.9H, m), 7.05 (6.59H, m), 2.65 (10H,m), 1.62 (10H, m, br), 1.33 (30H, m), 0.88 (15H, br). LRMS (FAB^+): 1215.9 $[M+H]^+$.

Diformamide 6c. Yield: 82%. Chromatography condition: 2:1 v/v CH_2Cl_2/EtOAc as eluent. ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.71 (0.61H, d, *J* = 11.4Hz), 8.37 (1.0H, s), 7.57-7.40 (8.0H, m), 7.05 (11.7 H, m), 2.65 (18H, m, br), 1.62 (18H, m, br), 1.33 (54H, m), 0.90 (27H, br). LRMS (MALDI): 1977.5 $[M+H]^+$.

Diformamide 6d. Yield: 84%. Chromatography condition: 2:1 v/v CH_2Cl_2/EtOAc as eluent. ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.71 (0.59H, d, *J* = 11.4Hz), 8.37 (1.1H, s), 7.57-7.40 (7.24H, m), 7.05 (15.7H, m), 2.65 (26H, m, br), 1.62 (26H, m, br), 1.33 (78H, m), 0.90 (39H, br). LRMS (MALDI): 2739.2 $[M+H]^+$.

Diformamide 6e. Yield: 92%. Chromatography condition: 2:1 v/v CH_2Cl_2/EtOAc as eluent. ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.71 (0.62H, d, *J* = 11.4Hz), 8.37 (1.1H, s), 7.57-7.40 (7.38H, m), 7.05 (19.7H, m), 2.65 (34H, m, br), 1.62 (34H, m, br), 1.33 (102H, m), 0.90 (51H, br). LRMS (MALDI): 3501.5 $[M+H]^+$.

General dehydration procedure for the synthesis of diisocyanides 3a-e. To a solution of diformamide **6a-e** (0.2 mmol) in 1:3 Et_3N/CH_2Cl_2 (40 ml) under argon at 0^{o}C was added triphosgene (0.44 mmol). After stirring at 0^{o}C for 4 h, the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and loaded onto silica gel. The column was flashed with CH_2Cl_2 to give pure diisocyanides **3a-e** in 77-91% yield as a yellow to dark-red solid.

Diisocyanide 3a. Yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (4H, d, *J* = 8.6 Hz), 7.34 (4H, d, *J* = 8.6Hz), 7.07 (1H, s), 2.71 (2H, t, *J* = 7.3 Hz), 1.64 (2H, m), 1.33 (6H, br), 0.88 (3H, t, *J* = 7.2Hz). LRMS (FAB^+): 419.4 $[M+H]^+$.

Diisocyanide 3b. Yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (4H, d, *J* = 8.6 Hz), 7.34 (4H, d, *J* = 8.6Hz), 7.07 (5H, m), 2.69 (10H, m), 1.64 (10H, m), 1.33 (30H, br), 0.88 (15H, m). LRMS (V): 1179.5 $[M+H]^+$.

Diisocyanide 3c. Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (4H, d, *J* = 8.6 Hz), 7.34 (4H, d, *J* = 8.6Hz), 7.07 (9H, m), 2.69 (18H, m), 1.64 (18H, m), 1.33 (54H, br), 0.88 (27H, m). LRMS (MALDI): 1941.8 $[M+H]^+$.

Diisocyanide 3d. Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (4H, d, *J* = 8.6Hz), 7.34 (4H, d, *J* = 8.6Hz), 7.07 (13H, m), 2.69 (26H, m), 1.64 (26H, m), 1.33 (78H, br), 0.88 (39H, m). LRMS (MALDI): 2701.2 $[M+H]^+$.

Diisocyanide 3e. Yield: 87%. ^{1}HNMR (300 MHz, $CDCl_3$): δ 7.50 (4H, d, *J* = 8.6Hz), 7.34 (4H, d, *J* = 8.6 Hz), 7.07 (17H, m), 2.66 (34H, m), 1.64 (34H, m), 1.33 (102H, br), 0.88 (51H, m). LRMS (MALDI): 3463.7 $[M+H]^+$.

Experimental

Infra-red spectroscopy of Platinum Nanoparticle Coupled to Isocyanides 3a-e:

Platinum nanoparticles were prepared according to literature procedures[4] to yield a 9 mM platinum solution in toluene in which the nanoparticles were stabilized by the weakly coordinating tetraoctylammonium bromide. Solutions of isocyanides in CH_2Cl_2 were prepared and mixed with the nanoparticle solutions to reach an approximate 1:1 ratio of isocyanide to platinum. After 1 hour, mixtures were dried on CaF_2 plates, vacuum-dried and analyzed by transmission IR. Isocyanides **3a-e** were also analyzed by IR without Pt treatment.

Surface Preparation for Ellipsometry:

Silicon wafers (prime grade) were purchased from Silicon Sense. Platinum and titanium were purchased from Aldrich. A 10 nm layer of titanium was evaporated on the silicon substrate followed by 35 nm of platinum, using a Semicore SC20002T electron beam evaporator. Deposition rate varied from 0.1 nm/min for the titanium layer and the first 7 nm of the platinum to 0.5 nm/min for the final 15 nm.

Self-Assembled Monolayer Formation for Ellipsometry:

Freshly evaporated Pt substrates were immersed in solutions of diisocyanides (10^{-5}-10^{-6} M in CH_2Cl_2) for at least 36 h. The substrates were then thoroughly rinsed with CH_2Cl_2, sonicated for ~1 min in CH_2Cl_2, rinsed with CH_2Cl_2 and ethanol, dried, and measured immediately.

Ellipsometry:

Film thickness was measured on a Rudolph Research/Auto EL Ellipsometer equipped with a He-Ne laser (λ = 632.8 nm) at an incidence angle of 70° with respect to the surface normal. Optical constants (n_s and k_s) of the Pt substrates were measured prior to the SAM measurements. The refractive index of the conjugated SAM was assumed to be 1.55.[5] Each film thickness was averaged over at least 5 measurements.

Calculation of Tilt Angle by Ellipsometry:

Molecular modeling to obtain theoretical end-to-end lengths of diisocyanides **3a-e** was performed using Chem 3D Pro's MM2 Force Fields, optimized to the minimum RMS gradient of 0.100. Experimental thicknesses for **3a-e** of 1.70±0.12, 3.95±0.17, 5.38±0.78, 6.98±0.41, 7.28±0.20 nm were plotted against the thicknesses calculated by molecular modeling of 2.1, 4.4, 6.6, 8.8 and 11.0 nm respectively (Figure S1). The resulting linear curve fit gave a slope value of 0.64. Assuming a constant tilt angle from the surface normal for **3a-e**, $\sin^{-1}(0.64) \approx 40°$.

Cyclic Voltammetry:

Electrochemistry was performed on a BAS CV-50W voltammetric analyzer with a three-electrode cell in a CH_2Cl_2 solution (0.1 M Bu_4NPF_6 or 0.1M $Bu_4[B(C_6F_5)_4]$ as an electrolyte) at different scan rates (100-5000 mV/s). Solvent was dried and deoxygenated before use. The working electrode was a platinum disk electrode (BAS, d = 1.6 mm), the

counter electrode was a platinum wire, and a Ag/AgCl (3 M NaCl) electrode were used as the reference electrode, calibrated against the oxidation of ferrrocene (0.47 V vs Ag/AgCl). All oxidation potential values are reported against this Fc/Fc+ oxidation couple.

Preparation for Solution CV:
Substrate concentrations were 0.08 to 1.0 mM, depending on the substrate solubility in CH_2Cl_2. The reported E_{pa} values correspond to quasi-reversible oxidations ($\Delta E>60mV$, $i_{pa}/i_{pc}\approx1$, $i \propto \upsilon^{1/2}$). The different spectra obtained from using Bu_4NPF_6 vs. $Bu_4[B(C_6F_5)_4]$ as the electrolyte is shown in Figure S2.

Surface Preparation for SAM CV:
Prior to submersion into the isocyanide-containing CH_2Cl_2 solution, the platinum disk electrodes were polished sequentially with aqueous slurries of 1.0-, 0.3- and 0.05-μm alumina. The electrodes were immersed in the solution for at least 12 hours to form the monolayer. After immersion, the electrodes were rinsed thoroughly and sonicated in CH_2Cl_2 for ~1 minute to remove any physisorbed compounds. Surface coverage of the SAM was determined first by measuring the decrease in the oxidation of 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl/H_2O due to the passivation effects of the SAM (Figure S3). The E_{pa} values correspond to oxidations that follow adsorbed monolayer characteristics ($\Delta E<60mV$, $i_{pa}/i_{pc}\approx1$, $i \propto \upsilon$).

UV/Vis and Fluorescence Spectroscopy
Absorbance spectra were obtained using a Perkin Elmer Lambda 19 UV/Vis/NIR Spectrometer. Emission spectra were obtained using a Perkin Elmer LS50B Luminescence Spectrometer. Sample solutions were in the 10μM range in CH_2Cl_2 (Figure S4).

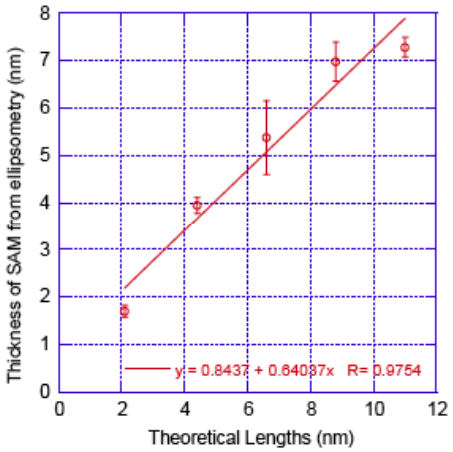


Figure S1: Plot of theoretical lengths vs SAM thickness obtained via ellipsometry.

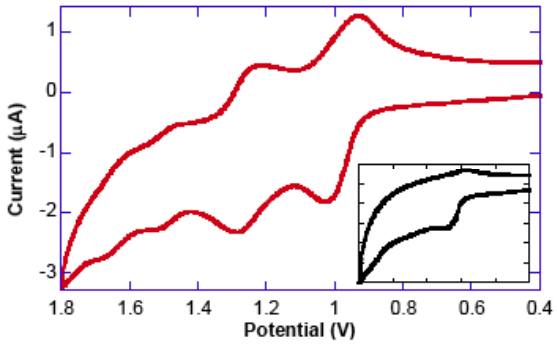


Figure S2: CV voltammograms of OTE **4b** using $Bu_4[B(C_6F_5)_4]$ (red) as electrolyte versus Bu_4PF_6 (inset, black).

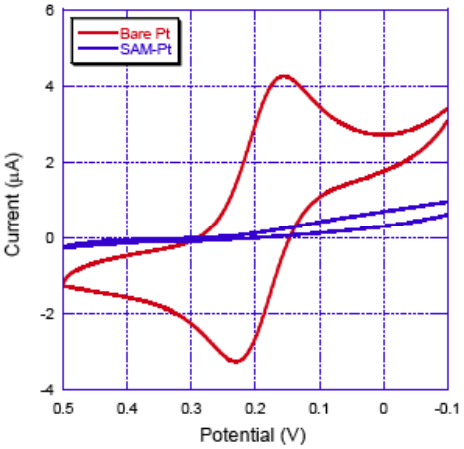


Figure S3: Cylic volammograms in a solution of $K_3[Fe(CN)_6]$/KCl (1 mM/0.1 M in H_2O) on Pt electrodes before (red) and after (blue) immersion in a CH_2Cl_2 solution of **3b** for 12 h.

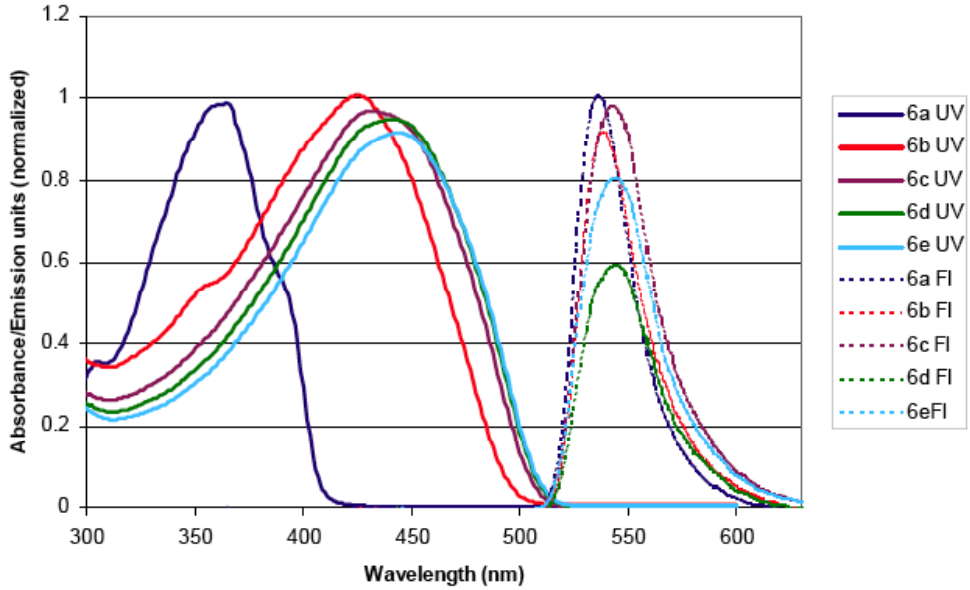


Figure S4: Overlay of normalized absorbance (solid) and emission (dotted) spectra of OTE **6a-e**.

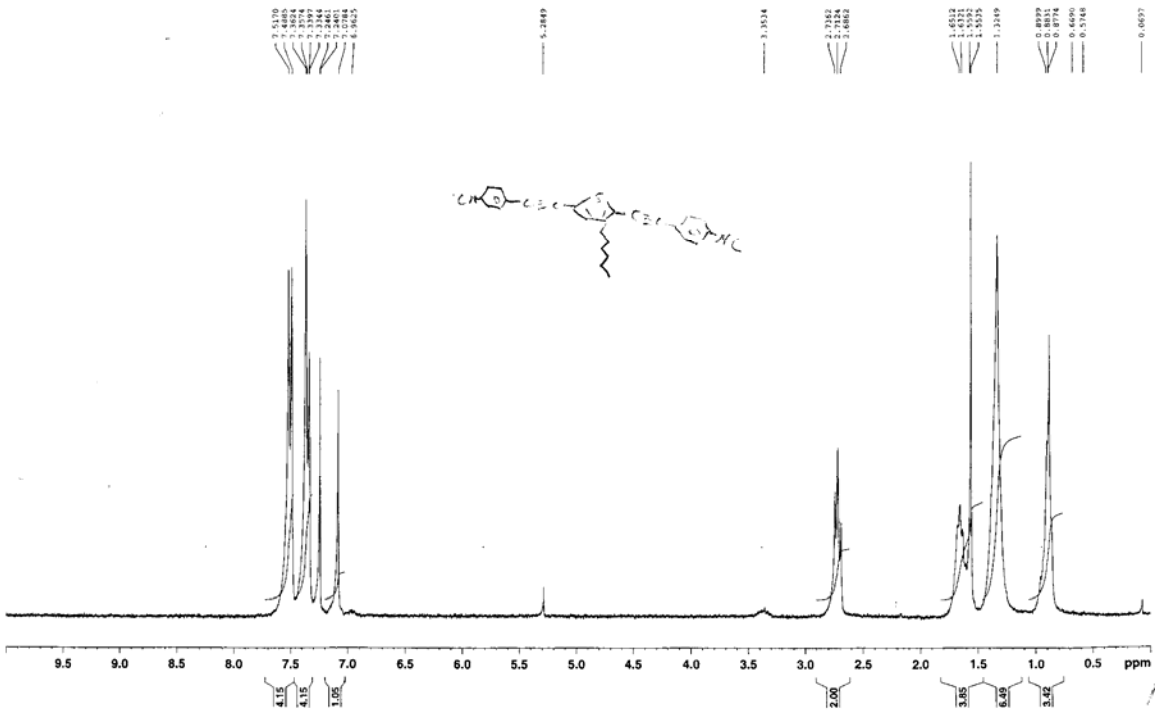


Figure S5: ^{1}HNMR of Diisocyanide 3a.

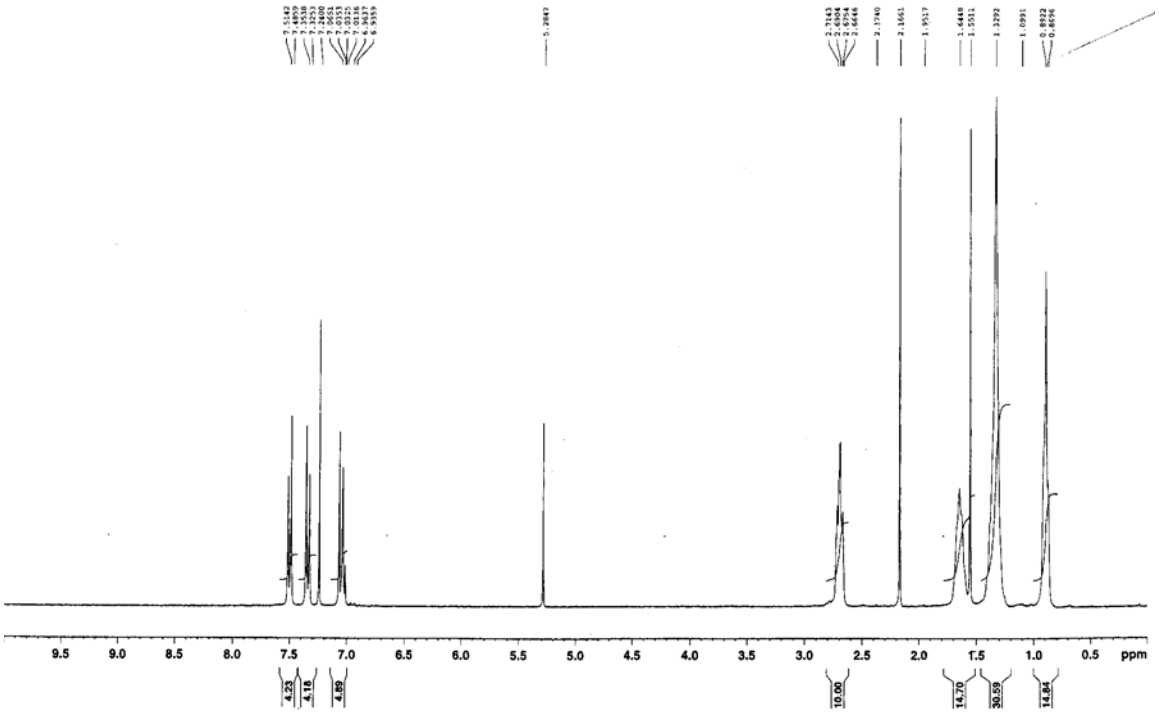


Figure S6: ^{1}HNMR of Diisocyanide 3b.

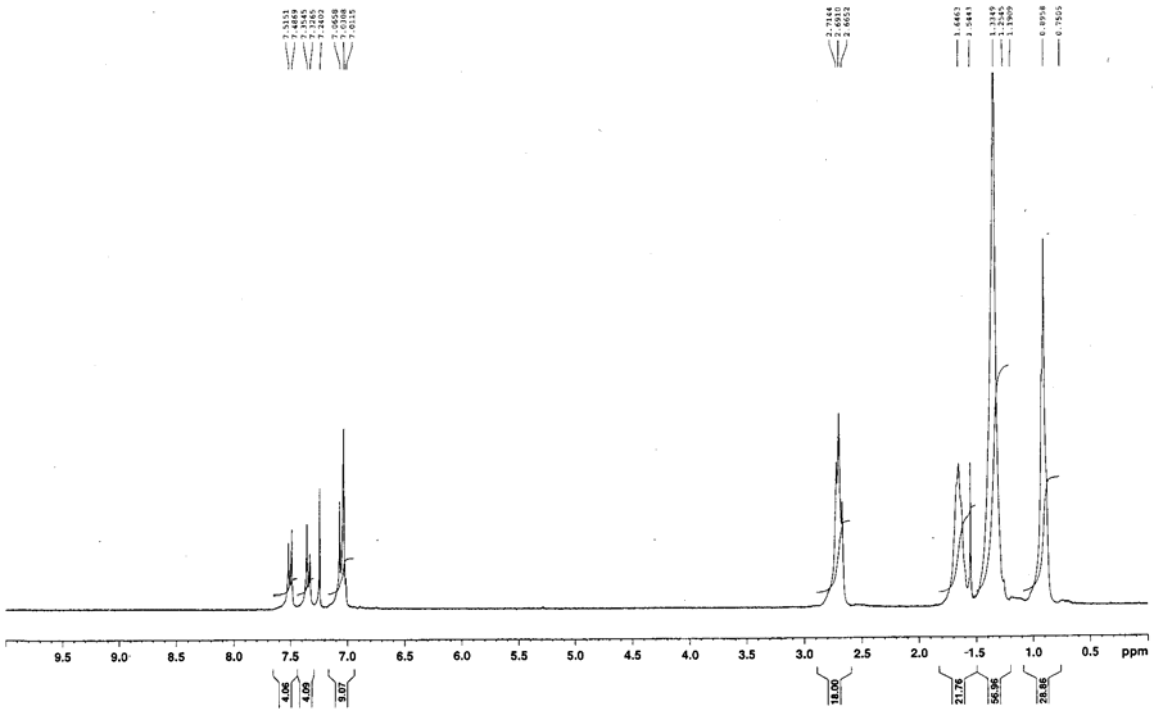


Figure S7: ^{1}H NMR of Diisocyanide 3c.

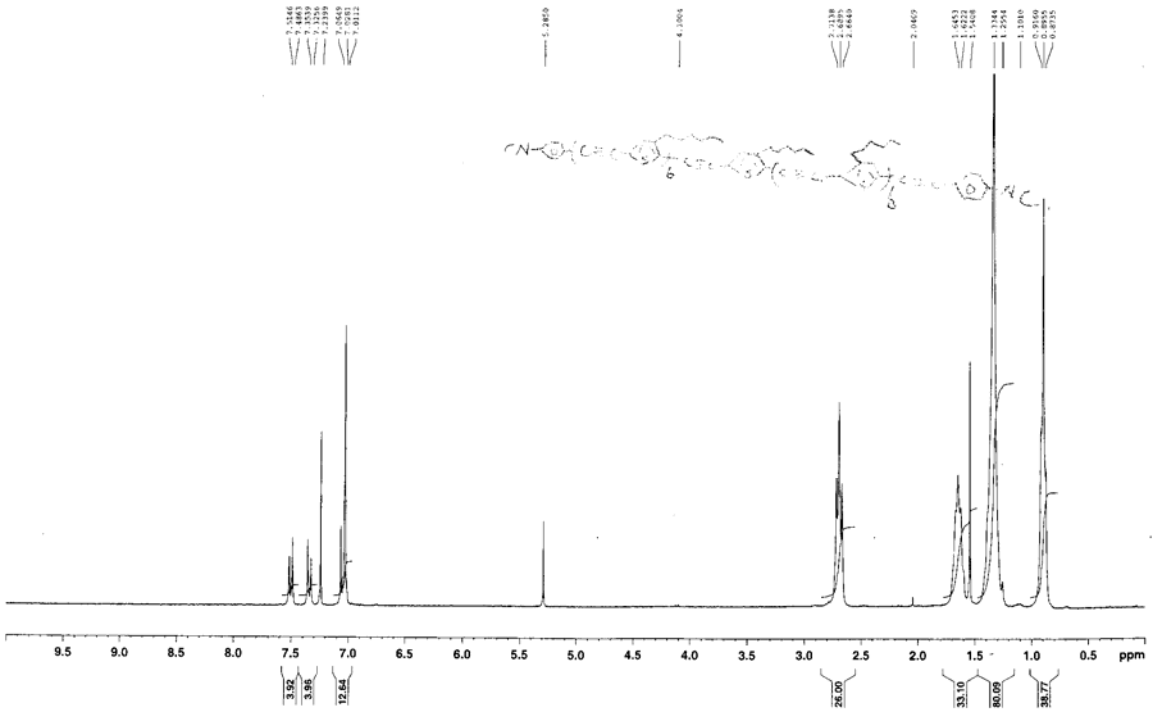


Figure S8: ^{1}H NMR of Diisocyanide 3d.

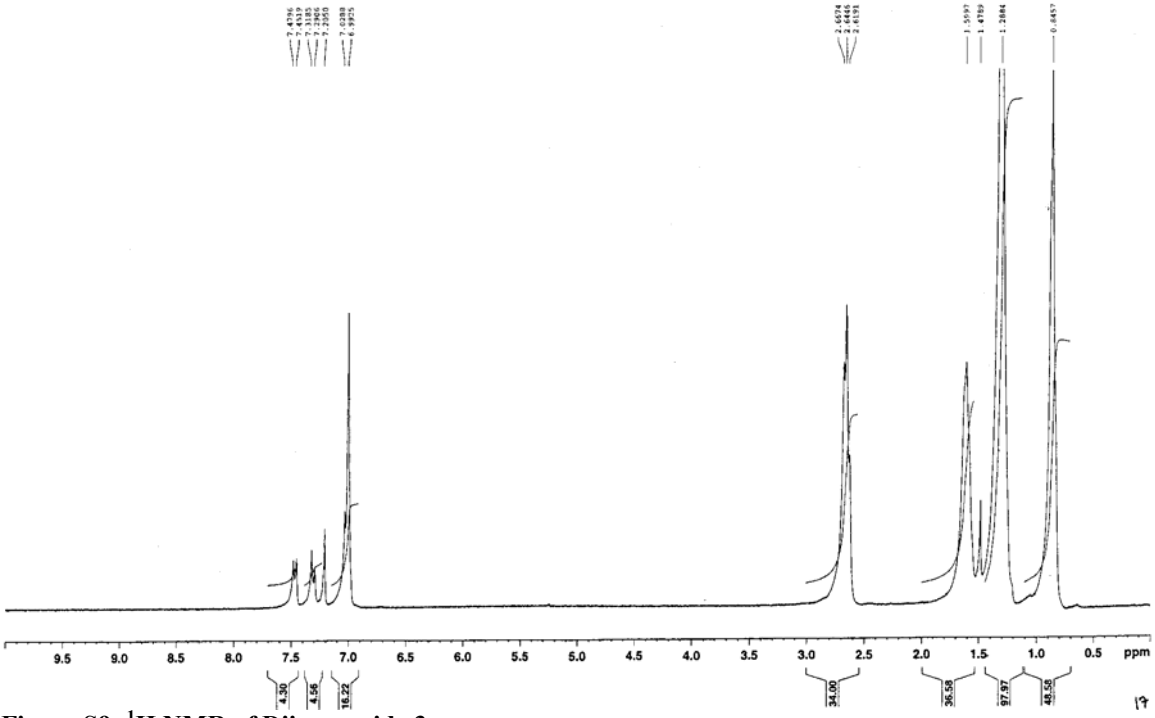


Figure S9: ^{1}H NMR of Diisocyanide 3e.

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