

Full Experimental Section

Materials. Starting reagents were purchased from Aldrich and used without purification, except where noted. Lead(II) thiocyanate was dried in a vacuum desiccator containing phosphorus(V) oxide. N-bromosuccinimide (NBS) was recrystallized from water. Butyllithium was a 1.6 M hexanes solution. Solvents were purchased from Anachemia or Caledon and purified prior to use: dichloromethane, diethyl ether, and tetrahydrofuran (THF) by passage through an alumina column under N₂; alcohols by distillation from magnesium under N₂. Oligothiophenes 2,2'-bithiophene (T₂) and 2,2':5',2''-terthiophene (T₃) were synthesized by Grignard couplings of thienylmagnesium bromide (TMgBr) to 2-bromothiophene (BrT) and 2,5-dibromothiophene (Br₂T) respectively, using the Kumada catalyst [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl₂).¹ Monobromination to create 5-bromo-2,2'-bithiophene (BrT₂) and 5-bromo-2,2':5',2''-terthiophene (BrT₃) was accomplished by the method of Bäuerle.² 5,5'-Dicyano-2,2'-bithiophene (T₂CN₂)³ and -2,2':5',2''-terthiophene (T₃CN₂)⁴ were synthesized by the literature methods. All thiocyanation reactions were performed in a darkroom under an atmosphere of N₂.

Instruments. FT-IR spectra were recorded as nujol mulls on a Nicolet 380 FT-IR spectrometer; vibrational frequencies are reported as wavenumbers (cm⁻¹), with an experimental resolution of 4 cm⁻¹. NMR spectra were recorded on a Varian Unity Inova 500 at room temperature in CDCl₃ or DMSO-*d*₆ solutions, referenced to TMS added to the sample or to the residual protonated solvent peak. Fluorescence measurements were taken on a Perkin Elmer LS50B luminescence spectrometer, while UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 11 UV/vis spectrometer; both were recorded as dichloromethane solutions. Combustion analyses were performed on a CEC (SCP) 240-XA Analyzer. Gradient vacuum sublimations and crystal growth for X-ray crystallography were performed on an Applied Test Systems model 3210 split tube furnace attached to a series 2404 3-zone temperature control system. Melting points were recorded on an Electrothermal 9100 apparatus and are uncorrected. Atomic force microscopic images were taken using a PicoSPM (Agilent Technologies).

Electrochemical capacitance measurements were performed in a three-electrode system using a VoltaLab 40 potentiostat PGZ301. Electrochemical software VoltaMaster 4 (Version 5.1) was used for data acquisition. The amplitude of the modulation potential and the frequency were 10 mV

and 25 Hz, respectively. A platinum coil was used as the counter electrode, and was flame annealed before the measurements. A saturated calomel electrode (SCE) was used as the reference, and was connected to the investigated electrolyte through a salt bridge. The electrolyte was 0.05 M KClO₄ made with pure water (18.2 MΩ·cm). The electrolyte was deaerated with ultra-pure argon (99.999%) before the measurements, and argon was passed over the top of the solution during the experiment. Measurements were conducted at room temperature (20 ± 2°C).

2-Ethylthiophene (TEt). Thiophene (T, 15.0 g, 0.18 mol) was dissolved in 120 mL of THF. An equimolar amount of *n*-butyllithium was added dropwise at -78°C, which was allowed to stir until the temperature warmed to -25°C. The solution was recooled to -78°C whereupon bromoethane (19.4 g, 0.18 mol) was added. The solution was warmed to room temperature and stirred 12 h. The solution was poured into an equal volume of water, extracted into 2 x 100 mL of diethyl ether, and dried with MgSO₄. The solvent was rotary evaporated and the resultant oil fractionally vacuum distilled to give 12.1 g (0.11 mol, 61%) of pure TEt. ¹H NMR: δ 7.10 (d, *J*_{AB} 5.0 Hz, 1 H), 6.91 (dd, *J*_{AB} 3.5 Hz, *J*_{AC} 5.0 Hz, 1 H), 6.79 (d, *J*_{AB} 3.5 Hz, 1 H), 2.86 (q, *J*_{AB} 7.5 Hz, 2 H), 1.31 (t, *J*_{AB} 7.5 Hz, 3H) ppm. This material was used without further characterization.

2-Bromo-5-ethylthiophene (BrTEt). The above TEt (12.1 g, 0.11 mol) was dissolved in 200 mL THF. In the dark, NBS was added portionwise over the course of three hours and the solution stirred a further 12 hours. The solution was poured into an equal volume of water, extracted into 2 x 100 mL of diethyl ether, and dried with Na₂SO₄. The solvent was rotary evaporated and the resultant oil fractionally vacuum distilled to give 7.2 g (38 mmol, 35%) of pure BrTEt. ¹H NMR: δ 6.84 (d, *J*_{AB} 3.5 Hz, 1 H), 6.54 (d, *J*_{AB} 3.5 Hz, 1 H), 2.77 (q, *J*_{AB} 7.5 Hz, 2 H), 1.27 (t, *J*_{AB} 7.5 Hz, 3H) ppm. This material was used without further characterization.

5-Ethyl-2,2'-bithiophene (EtT₂). The Grignard reagent TMgBr was generated from BrT (5.2 g, 32 mmol) and magnesium (0.78 g, 32 mmol) in 40 mL of ether. This was added via cannula (at 0°C) to a solution of BrTEt (5.6 g, 29 mmol) and Ni(dppp)Cl₂ (0.3 g, 0.6 mmol) in 25 mL of ether. The solution was allowed to stir at room temperature for 16 h. The solution was poured into an equal volume of saturated aqueous NH₄Cl solution, extracted into 3 x 100 mL ether, and dried over MgSO₄. Following rotary evaporation of the solvent and fractional vacuum distillation of the

resultant oil, 4.1 g (21 mmol, 72%) of pure T₂Et was isolated. ¹H NMR: δ 7.14 (d, J_{AB} 5 Hz, 1 H), 7.08 (d, J_{AB} 3.5 Hz, 1 H), 6.98-6.96 (m, two overlapping signals, 2H), 6.67 (d, J_{AB} 3.5 Hz, 1 H), 2.81 (q, J_{AB} 7.5 Hz, 2 H), 1.29 (t, J_{AB} 7.5 Hz, 3H) ppm. This material was used without further characterization.

2,2'-Bithiophene-5-thiocarbonitrile (T₂SCN). To a solution of bithiophene (T₂, 5.0 g, 30 mmol) and potassium thiocyanate (27 g, 0.24 mol) in 300 mL of methanol at 0°C was added dropwise a solution of bromine (9.6 g, 60 mmol) in 100 mL of methanol. The mixture was stirred for 1.5 h, during which time a white precipitate formed. The mixture was poured onto ice and filtered to give impure (contained T₂SCN₂) T₂SCN. Recrystallization from hexane yielded 2.25 g (33%) of pure material. Mp: 56-57°C. ¹H NMR: δ 7.34 (d, J_{AB} 3.5 Hz, 1 H), 7.32 (d, J_{AB} 5 Hz, 1 H), 7.23 (d, J_{AB} 3.5 Hz, 1 H), 7.12 (d, J_{AB} 4 Hz, 1 H), 7.06 (dd, J_{AB} 5 Hz, J_{AC} 3.5 Hz, 1H) ppm. IR: 2155 (s), 1200 (m), 1077 (w), 1047 (w), 987 (m), 887 (w), 799 (s), 710 (s), 665 (m) cm⁻¹. UV-vis: λ_{max} = 322 nm, ε_{max} = 1.40 × 10⁴ L·mol⁻¹·cm⁻¹. Anal Calcd for C₉H₅NS₃: C, 48.4; H, 2.3; N, 6.3%. Found: C, 48.5; H, 2.4; N, 6.3%.

2,2'-Bithiophene-5,5'-dithiocarbonitrile (T₂SCN₂). To a 0°C solution of bithiophene (T₂, 5.0 g, 30 mmol) and ammonium thiocyanate (18.3 g, 0.24 mol) in 400 mL of methanol was added dropwise a solution of bromine (19.2 g, 0.12 mol) in 100 mL of methanol. Solution was stirred for 2 h at room temperature then poured onto ice to yield a white precipitate, which was isolated by suction filtration. After recrystallization in acetonitrile and vacuum sublimation (temperature gradient 90-60°C), 1.80 g (21.4%) of yellow blocks were isolated. Mp: 154-159°C. ¹H NMR: δ 7.38 (d, J_{AB} 4 Hz, 1 H), 7.17 (d, J_{AB} 4 Hz, 1 H) ppm. IR: 2152 (s), 1209 (m), 995 (m), 873 (m), 804 (s) cm⁻¹. UV-vis: λ_{max} = 327 nm, ε_{max} = 2.82 × 10⁴ L·mol⁻¹·cm⁻¹. Anal Calcd for C₁₀H₄N₂S₄: C, 42.8; H, 1.7; N, 10.3%. Found: C, 42.8; H, 1.4; N, 10.0%.

5-Ethyl-2,2'-bithiophene-5'-thiocarbonitrile (EtT₂SCN). To a solution of ethyl bithiophene (EtT₂, 4.0 g, 21 mmol) and ammonium thiocyanate (12.8 g, 0.17 mol) in 300 mL of methanol at 0°C was added dropwise a solution of bromine (13.4 g, 84 mmol) in 50 mL of methanol. The solution was stirred at room temperature for 2 hours, during which time a fine white precipitate formed. The

solution was then poured into water and the white solid collected by suction filtration. Crude yield was 4.5 g (85%). The material was recrystallized from ethanol to give analytically pure material. Mp: 69-70°C. ¹H NMR: δ 7.30 (d, J_{AB} 4 Hz, 1 H), 7.04 (d, J_{AB} 3.5 Hz, 1 H), 7.02 (d, J_{AB} 4 Hz, 1 H), 6.73 (d, J_{AB} 3.5 Hz, 1 H), 2.84 (q, J_{AB} 7.5 Hz, 2 H), 1.32 (t, J_{AB} 7.5 Hz, 3 H) ppm. UV-vis: λ_{\max} = 333 nm, ϵ_{\max} = 2.52×10^4 L·mol⁻¹·cm⁻¹. IR: 2155 (m), 1511 (m), 1198 (m), 985 (w), 872 (m), 792 (s) cm⁻¹. Anal Calcd for C₁₁H₉NS₃: C, 52.6; H, 3.6; N, 5.6. Found: C, 52.1; H, 3.6; N, 5.6.

5-Bromo-2,2'-bithiophene-5'-thiocarbonitrile (BrT₂SCN). A solution of BrT₂ (7.4 g, 30 mmol) and ammonium thiocyanate (9.2 g, 0.12 mol) was slurried in 400 mL of methanol at 0°C. A solution of bromine (9.62 g, 60 mmol) in 100 mL of methanol was added dropwise, with stirring, to the thiophene solution. The resultant mixture was stirred for 1 h at 0°C then warmed to room temperature and stirred a further 2 h. The mixture was added to 1 L of ice water and the resultant solid isolated by suction filtration. Recrystallization in acetonitrile afforded 5.8 g (19.2 mmol, 64%) of pure BrT₂SCN. Single crystals for X-ray crystallography were grown by vacuum sublimation over a temperature gradient of 70-50°C. Mp: 102-103°C. ¹H NMR: δ 7.33 (d, J_{AB} 4 Hz, 1 H), 7.05 (d, J_{AB} 4 Hz, 1 H), 7.02 (d, J_{AB} 4 Hz, 1 H), 6.97 (d, J_{AB} 4 Hz, 1 H) ppm. IR: 2154 (m), 1545 (w), 1197 (m), 970 (w), 867 (m), 799 (s), 787 (s) cm⁻¹. UV-vis: λ_{\max} = 328 nm, ϵ_{\max} = 2.49×10^4 L·mol⁻¹·cm⁻¹. Anal Calcd for C₉H₄BrNS₃: C, 35.8; H, 1.3; N, 4.6%. Found: C, 35.6; H, 1.5; N, 4.5%.

2,2':5',2''-Terthiophene-5,5''-dithiocarbonitrile (T₃SCN₂). At 0°C in the dark, thiocyanogen was generated by adding a solution of bromine (10.7 g, 67 mmol) in 60 mL of dichloromethane dropwise to a solution of lead(II) thiocyanate (27 g, 84 mmol) in 60 mL of dichloromethane. The mixture was allowed to come to room temperature with stirring over the next 3 h, after which it was added via cannula to a solution of T₃ (4.2 g, 17 mmol) in 60 mL of dichloromethane at 0°C. This solution was left stirring in the dark for one hour during which time the temperature raised to 25°C. Workup was accomplished by pouring into an equal volume of saturated aqueous sodium thiosulfate solution, extraction into 3 x 100 mL of dichloromethane, and drying with magnesium sulfate. Rotary evaporation gave 5.0 g (14 mmol, 82%) of crude T₃SCN₂. Column chromatography (silica gel, 10% dichloromethane/90% hexanes) gave analytically pure material. Mp: 147-149°C. ¹H NMR: δ 7.36 (d, J_{AB} 3.5 Hz, 2 H), 7.16 (s, 2 H), 7.14 (d, J_{AB} 4 Hz, 1 H) ppm. IR: 2158 (s), 777 (s) cm⁻¹. UV-vis:

$\lambda_{\max} = 369 \text{ nm}$, $\epsilon_{\max} = 2.81 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Anal Calcd for $\text{C}_{14}\text{H}_6\text{N}_2\text{S}_5$: C, 46.4; H, 1.7; N, 7.7%. Found: C, 46.3; H, 2.1; N, 7.6%.

5-Bromo-2,2':5',2''-terthiophene-5''-dithiocarbonitrile (BrT₃SCN). At 0°C in the dark, thiocyanogen was generated by adding a solution of bromine (1.74 g, 11 mmol) in 25 mL of dichloromethane dropwise to a solution of lead(II) thiocyanate (4.1 g, 13 mmol) in 25 mL of dichloromethane. The mixture was allowed to come to room temperature with stirring over the next 3 hours, after which it was added via cannula to a solution of T₃Br (2.8 g, 8.6 mmol) in 150 mL of THF at 0°C. This solution was left stirring at room temperature for 16 h. Workup was accomplished by pouring into an equal volume of saturated aqueous sodium thiosulfate solution, extraction into 3 x 100 mL of dichloromethane, and drying with magnesium sulfate. Rotary evaporation gave 1.9 g (5 mmol, 58%) of crude BrT₃SCN. Analytically pure material was isolated after purification via silica column (100% hexanes removed unreacted T₃Br, followed by 25% dichloromethane to isolate the desired product). Mp: 91-94°C. ¹H NMR: δ 7.34 (d, J_{AB} 4 Hz, 1 H), 7.12 (d, J_{AB} 3.5 Hz, 1 H), 7.10 (d, J_{AB} 4 Hz, 1 H), 7.04 (d, J_{AB} 4 Hz, 1 H), 7.00 (d, J_{AB} 4 Hz, 1 H), 6.94 (d, J_{AB} 4 Hz, 1 H). IR: 2156 (m), 852 (m), 789 (s) cm^{-1} . UV-vis: $\lambda_{\max} = 370 \text{ nm}$, $\epsilon_{\max} = 1.53 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Anal Calcd for $\text{C}_{13}\text{H}_6\text{BrNS}_4$: C, 40.6; H, 1.6; N, 3.6%. Found: C, 41.0; H, 2.0; N, 3.4%.

X-ray crystallography.

Structure of BrT₂SCN. Single crystal data was collected using the Smart Apex CCD (Bruker) equipped with an area detector utilizing graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data collection was performed by scans of 0.3° in θ in three and half groups of 600 frames at 0°, 90°, 180° and 270° with an exposure time of 30 seconds. The data were corrected for Lorentz and polarization effects. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements using the APEX II package. The space group was determined on the basis of the systematic absences using the APEX II package. Structure solution and refinement using the SHELXTL package of APEX II were successful in the *C2/c* space group. The structure solution via direct method led to the identification of the heavy atoms and the refinement on F^2 using the least square method resulted in the reported R value.

Structure of T₂SCN₂. Crystal cell refinement and data reduction were carried out using DENZO reflection data, systematic absences were consistent with the monoclinic space group $P2_1/n$. The SHELXTL-NT V6.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier synthesis allowed the remaining atoms to be located. The hydrogen atoms were calculated geometrically and were included as riding on their respective carbon atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Full details of the structures have also been deposited with the Cambridge Crystallographic Data Center as CCDC 729272 (T₂SCN₂) and 729271 (BrT₂SCN). This information may be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Band Structure Calculations. Calculations were performed using the program CAESAR (version 2.0) on a PC running Windows XP, which uses an Extended Hückel level of theory. This program is published by PrimeColor Software and is available free of charge on the internet (www.primec.com).

Figure S1: Band structure of BrT₂SCN

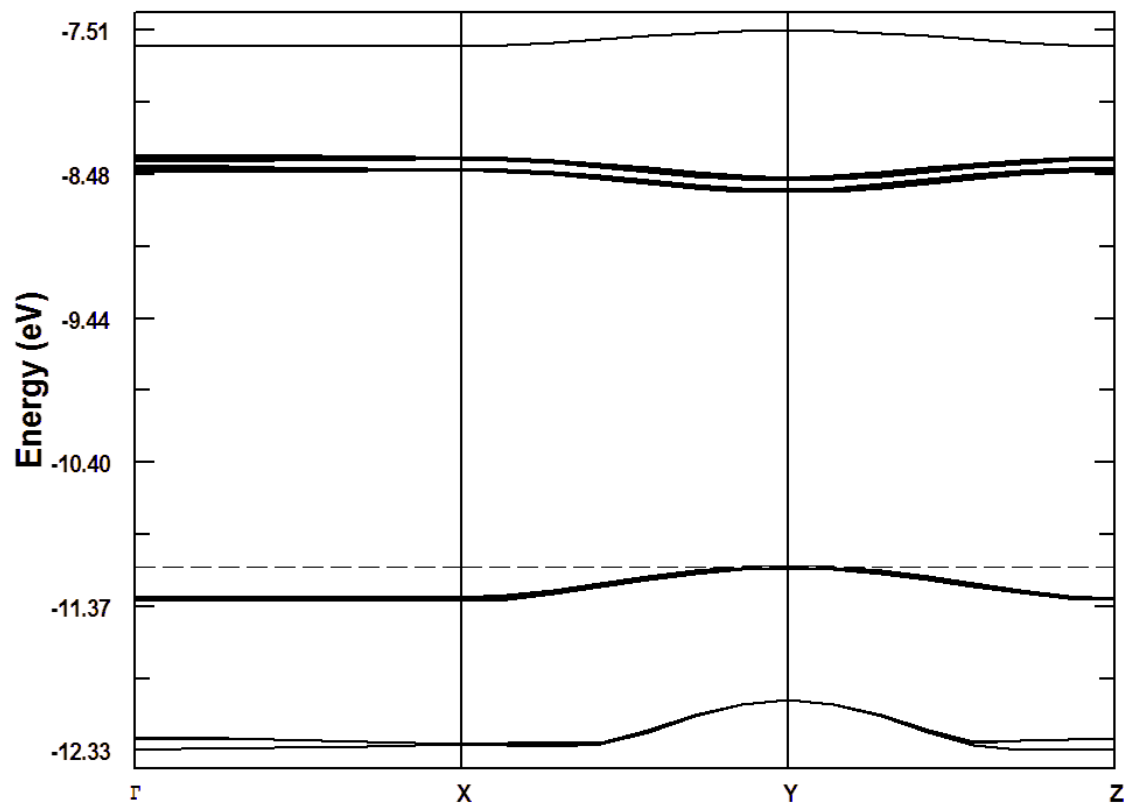
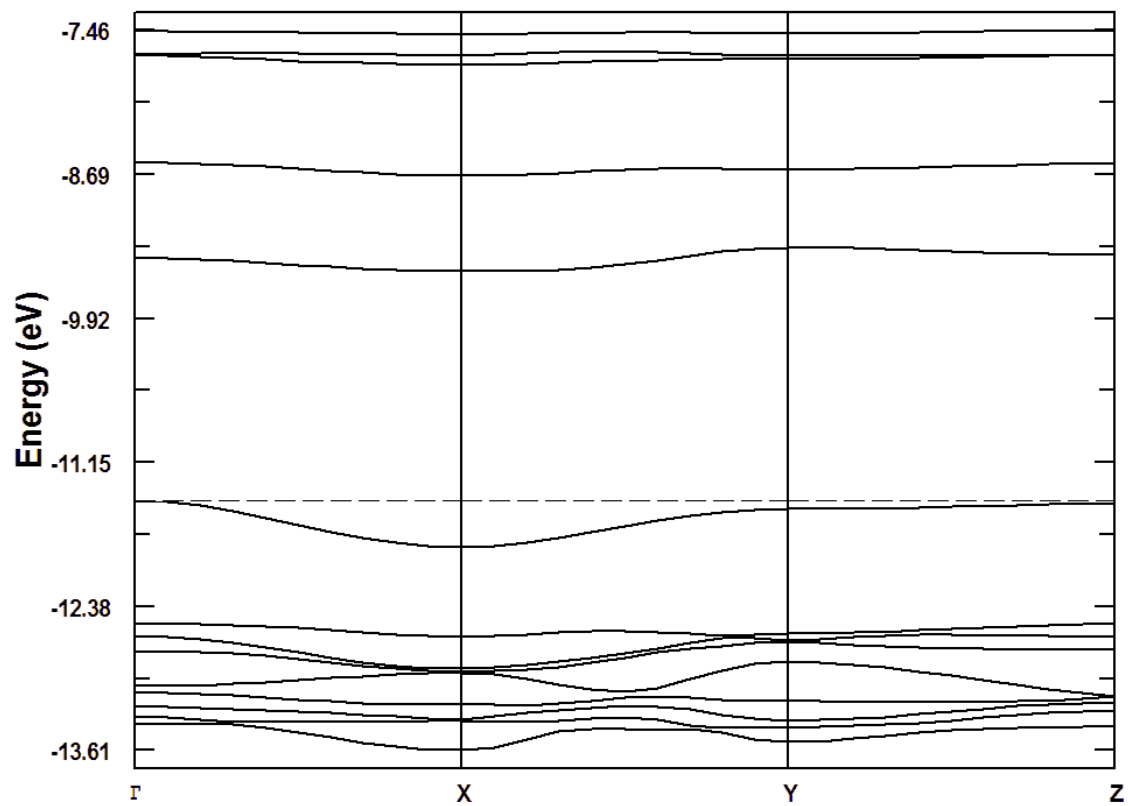


Figure S2: Band structure of T_2CN_2 .



References

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