

Supporting Information

N-Type Conjugated Materials based on 2-Vinyl-4,5-Dicyanoimidazoles and Their Use in Solar Cells

Richard Yee Cheong Shin¹, Thomas Kietzke¹, Sundarraj Sudhakar¹, Ananth Dodabalapur^{1,2}, Zhi-Kuan Chen¹, and Alan Sellinger^{1*}

1. *Institute of Materials Research & Engineering, 3 Research Link, Singapore 117602, Republic of Singapore*
2. *Microelectronics Research Center, the University of Texas at Austin, Austin, TX, 78758, USA*

*alan-sellinger@imre.a-star.edu.sg

Experimental Section

General Description. All commercially available materials were used as received unless noted otherwise. Cy₂NMe was distilled prior to use. 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole¹ were prepared according to literature procedures. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents.

Instruments

¹H, and ¹³C NMR data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to CDCl₃ or C₄D₈O. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix and silver trifluoroacetate as an ionizing salt when necessary. Differential scanning calorimetry (DSC) was carried out under nitrogen on a DSC Q100 instrument (scanning rate of 10°C.min⁻¹). Thermal gravimetric analysis (TGA) was carried out using TGA Q500 instrument (heating rate of 10°C.min⁻¹). Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. All CV measurements were recorded in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV.s⁻¹). The experiments were performed at

room temperature with a conventional three electrode configuration consisting of a platinum wire working electrode, a gold counter electrode, and a Ag/AgCl in 3 M KCl reference electrode. The measured potentials were converted to SCE (saturated calomel electrode) and the corresponding electron affinity (EA) values, to estimate the LUMO, were derived from the onset potential, based on -4.4 eV as the SCE energy level relative to vacuum ($EA = E_{\text{onset}}^r + 4.4 \text{ eV}$).² UV-Vis spectra were recorded on a Shimadzu model 2501-PC UV-VIS spectrometer and the UV-vis absorption spectroscopic onset was used to calculate the bandgap. Photoluminescence (PL) spectra were measured on a Perkin-Elmer (LS50B) spectrofluorimeter.

Alkyl vinazene. To a solution of vinazene (1.00 g, 6.9 mmol) in 15 mL acetone was added anhydrous K_2CO_3 (1.40 g, 10.1 mmol) and 1-iodohexane (1.40 mL, 9.5 mmol). The solution was refluxed for 24 h, filtered and solvent removed under vacuum. Water (30 mL) was then added to the oily residue and the aqueous layer was extracted three times with 50 mL aliquots of ethyl acetate. The organic layer was dried over magnesium sulfate and the solvent removed under vacuum. The oily residue was recrystallised in EtOH to give pale yellow crystalline solids (1.42 g, 90% yield) after 24 h at 4°C. 1H NMR ($CDCl_3$): δ 0.90 (t, 3 H, $J = 6.8$ Hz), 1.33 (unresolved m, 6 H), 1.80 (q, 2 H, $J = 6.8$ Hz), 4.11 (t, 2 H, $J = 7.2$ Hz), 5.82 (t, 1 H, $J = 6.4$ Hz), 6.52 (d, 2 H, $J = 6.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.4, 26.1, 30.7, 31.1, 46.7, 108.5, 111.9, 112.3, 120.2, 122.5, 126.6, 149.4. The analogue 1-(2-ethylhexyl)vinazene was synthesized using DMF as solvent. After stirring for 24 h at 80°C, the solution was filtered and DMF removed under vacuum. The oily residue was purified by column chromatography (silica gel, 25% ethyl acetate in hexane as eluent). A pale yellow oil was obtained after solvent removal. The oil solidified upon cooling at 4°C for 24 h to give the product as a cream colored solid (34% yield). 1H NMR ($CDCl_3$): 0.89 (t, 3 H, $J = 6.4$ Hz), 0.92 (t, 3 H, $J = 7.6$ Hz), 1.20-1.42 (m, 8 H), 1.80 (septet, 1 H, $J = 6.4$ Hz), 3.98 (d, 2 H, $J = 7.6$ Hz), 5.81 (dd, 1 H, $J = 8.4, 3.6$ Hz), 6.45-6.55 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 10.6, 13.9, 22.9, 23.8, 28.4, 30.4, 41.0, 50.7, 108.7, 111.9, 112.9, 120.5, 122.6, 126.5, 149.8.

Procedure for Heck reactions. In a glovebox, the aryl halide, Cy₂NMe, Pd[P(*t*-Bu)₃]₂, DMF, and the olefin (alkyl vinazene) were added to an oven-dried Schlenk flask equipped with a stir bar. The Schlenk flask was taken out of the glove box, connected to the nitrogen line, and the reaction mixture was stirred at 80 °C for 20 h. At the end of the reaction, the reaction mixture was cooled to room temperature and filtered over a glass sinter (Por. 4). Ethanol was added to the filtrate while stirring to precipitate out the product which was collected and washed with EtOH and then hexane. The product obtained was then recrystallized from DMF/EtOH or THF/EtOH at 4°C.

V-DP. Using 4,4'-dibromobiphenyl (125 mg, 0.40 mmol), 1-ethylhexylvinazene (256 mg, 1.0 mmol), Cy₂NMe (0.214 mL, 1.0 mmol), Pd[P(*t*-Bu)₃]₂ (4.1 mg, 0.008 mmol), and DMF (2 mL). After workup, the product was obtained as yellow solids (108 mg, 41% yield). ¹H NMR (CDCl₃): δ 0.91 (t, 6 H, *J* = 6.0 Hz), 0.98 (t, 6 H, *J* = 7.2 Hz), 1.32-1.46 (m, 16 H), 1.86 (unresolved m, 2 H), 4.07 (d, 4 H, *J* = 7.2 Hz), 6.81 (d, 2 H, *J* = 15.6 Hz), 7.63 (d, 4 H, *J* = 8.0 Hz), 7.69 (d, 4 H, *J* = 8.0 Hz), 7.90 (d, 2 H, *J* = 15.6 Hz). ¹³C NMR (CDCl₃): δ 10.8, 14.1, 23.0, 23.9, 28.6, 30.4, 41.2, 50.5, 108.8, 110.5, 112.0, 112.8, 122.8, 127.7, 128.3, 134.5, 139.7, 141.7, 150.3. Anal. Calcd for C₄₂H₄₆N₈: C, 76.10; H, 6.99; N, 16.90. Found: C, 76.04; H, 6.82; N, 16.99. **MALDI-TOF-MS (dithranol) *m/z*: 663 (M + H); calcd. for C₄₂H₄₆N₈ = 662.**

V-BT. Using 4,7-dibromo-2,1,3-benzothiadiazole (88 mg, 0.30 mmol), 1-hexylvinazene (171 mg, 0.75 mmol), Cy₂NMe (0.161 mL, 0.75 mmol), Pd[P(*t*-Bu)₃]₂ (3.1 mg, 0.006 mmol), and DMF (2 mL). After workup, the product was obtained as orange solids (155 mg, 88% yield). ¹H NMR (CDCl₃): δ 0.90 (t, 6 H, *J* = 7.2 Hz), 1.37 (unresolved m, 12 H), 1.95 (q, 4 H, *J* = 7.2 Hz), 4.30 (t, 4 H, *J* = 7.2 Hz), 7.74 (s, 2 H), 8.06 (d, 2 H, *J* = 15.6 Hz), 8.33 (d, 2 H, *J* = 15.6 Hz). ¹³C NMR (CDCl₃): δ 14.0, 22.5, 26.2, 30.8, 31.2, 46.9, 108.6, 111.9, 112.7, 117.4, 123.2, 129.4, 132.5, 135.5, 150.2, 153.8. Anal. Calcd for C₃₂H₃₂N₁₀S: C, 65.28; H, 5.48; N, 23.79; S, 5.45. Found: C, 64.75; H, 5.37; N, 24.06; S, 5.19. **MALDI-TOF-MS (dithranol) *m/z*: 589 (M + H); calcd. for C₃₂H₃₂N₁₀S = 588.**

V-TBT. Using 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (137 mg, 0.30 mmol), 1-hexylvinazene (171 mg, 0.75 mmol), Cy₂NMe (0.161 mL, 0.75 mmol), Pd[P(*t*-Bu)₃]₂ (3.1 mg, 0.006 mmol), and DMF (2 mL). After workup, the product was obtained as dark red solids (179 mg, 79% yield). ¹H NMR (CDCl₃): δ 0.93 (t, 6 H, *J* = 6.8 Hz), 1.39 (unresolved m, 12 H), 1.88 (q, 4 H, *J* = 6.8 Hz), 4.19 (t, 4 H, *J* = 7.2 Hz), 6.64 (d, 2 H, *J* = 15.6 Hz), 7.37 (d, 2 H, *J* = 4.0 Hz), 7.96 (s, 2 H), 8.01 (d, 2 H, *J* = 15.2 Hz), 8.09 (d, 2 H, *J* = 4.0 Hz). ¹³C NMR (C₄D₈O): δ 14.4, 23.5, 27.1, 31.6, 32.3, 47.2, 109.7, 111.5, 112.9, 113.5, 123.5, 126.9, 129.7, 132.3, 132.9, 142.2, 143.4, 151.0, 153.6. Anal. Calcd for C₄₀H₃₆N₁₀S₃: C, 63.80; H, 4.82; N, 18.60; S, 12.78. Found: C, 63.58; H, 4.61; N, 18.57; S, 12.72. **MALDI-TOF-MS (dithranol) *m/z*: 752 (M); calcd. for C₄₀H₃₆N₁₀S₃ = 752.**

V-F. Using 2,7-dibromo-9,9'-dimethylfluorene (106 mg, 0.30 mmol), 1-hexylvinazene (171 mg, 0.75 mmol), Cy₂NMe (0.161 mL, 0.75 mmol), Pd[P(*t*-Bu)₃]₂ (3.1 mg, 0.006 mmol), and DMF (2 mL). After workup, the product was obtained as yellow solids (148 mg, 76% yield). ¹H NMR (CDCl₃): δ 0.91 (t, 6 H, *J* = 6.8 Hz), 1.38 (unresolved m, 12 H), 1.57 (s, 6 H), 1.89 (q, 4 H, *J* = 6.8 Hz), 4.21 (t, 4 H, *J* = 7.2 Hz), 6.80 (d, 2 H, *J* = 15.6 Hz), 7.59 (d, 2 H, *J* = 8.4 Hz), 7.59 (overlapping s, 2 H), 7.78 (d, 2 H, *J* = 7.6 Hz), 7.95 (d, 2 H, *J* = 15.6 Hz). ¹³C NMR (CDCl₃): δ 14.0, 22.5, 26.2, 27.2, 30.8, 31.2, 46.7, 47.2, 108.7, 109.8, 112.0, 112.3, 121.2, 122.2, 123.0, 127.2, 134.9, 140.7, 140.9, 150.2, 155.2. Anal. Calcd for C₄₁H₄₂N₈: C, 76.13; H, 6.54; N, 17.32. Found: C, 76.01; H, 6.90; N, 17.57. **MALDI-TOF-MS (dithranol) *m/z*: 647 (M + H); calcd. for C₄₁H₄₂N₈ = 646.**

References.

1. Hou, Q.; Xu, Y.; Yang, W.; Yuan, M.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2002**, *10*, 2887.
2. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

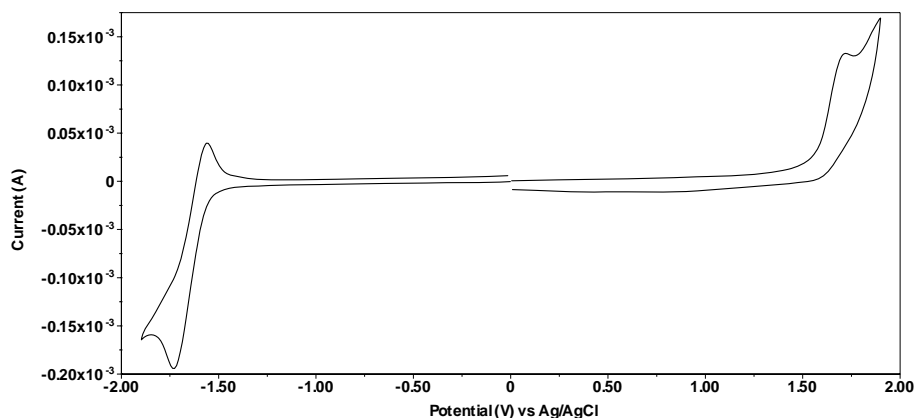


Figure S1. Cyclic voltammogram of V-DP

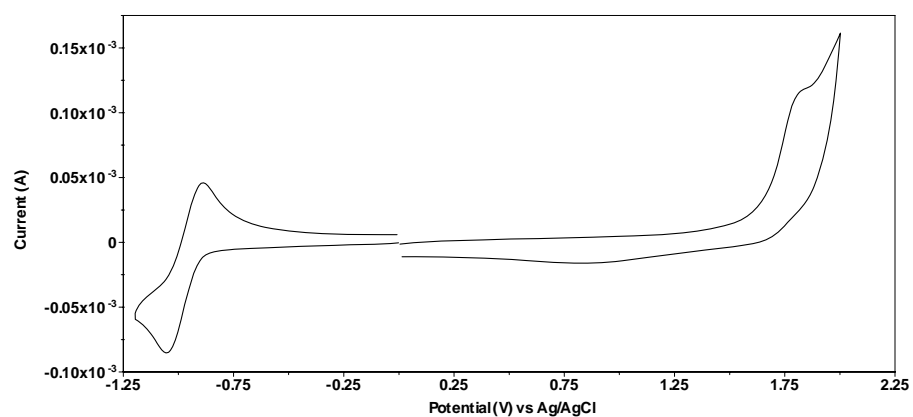


Figure S2. Cyclic voltammogram of V-BT

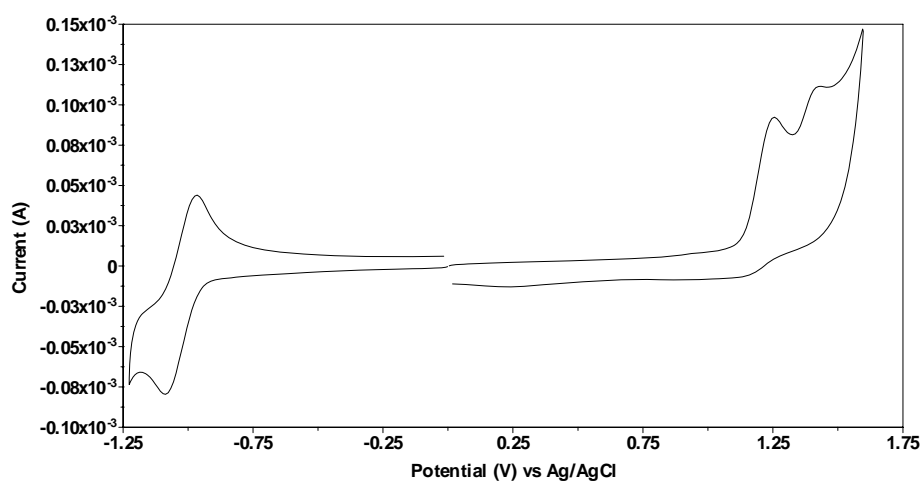


Figure S3. Cyclic voltammogram of V-TBT

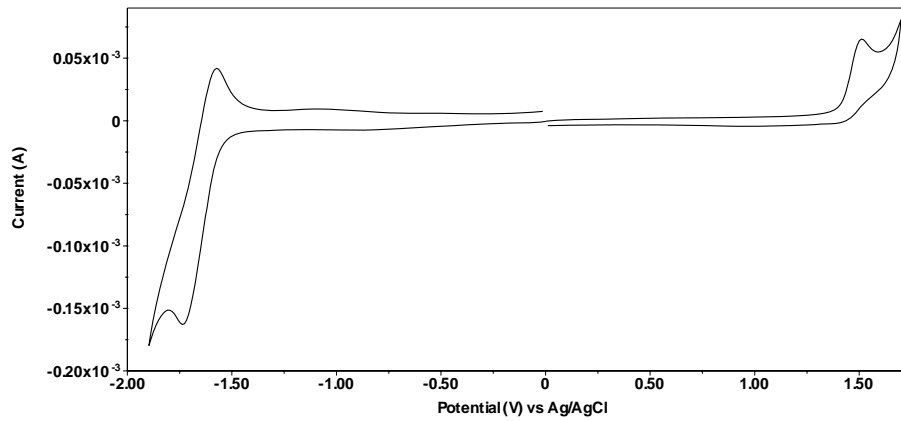


Figure S4. Cyclic voltammogram of V-F

Device preparation and characterization:

For device fabrication, an approximately 40 nm thick layer of poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) was spin-coated onto commercial glass substrates covered with indium-tin-oxide (140 nm). The PEDOT:PSS films were dried on a hot plate under a nitrogen atmosphere for 30 min at 120°C. Next, the active layer of the presented device was spin coated from a 1:1 by weight solution at 2000 RPM and annealed at 140°C for 10 min. The devices were completed by evaporating a 30 nm Ca layer protected by 100 nm of Ag at a base pressure of 2×10^{-6} mbar. The effective solar cell area as defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 0.14 cm². All device preparation and characterization were performed under nitrogen atmosphere.

To characterize the solar cells the incident-photon-to-current-efficiency (IPCE) was measured. The IPCE is a measure of the external quantum efficiency and is defined as:

$$\text{IPCE} = \frac{\text{no. of electrons}}{\text{no. of photons}} = \frac{hcI_{\text{SC}}}{e\lambda P_{\text{light}}}$$

where λ is the incident wavelength, I_{SC} the short-circuit current, e the elementary charge, h the Planck constant, c the speed of light, and P_{light} the incident light power.

The IPCE as a function of wavelength was measured with a home built setup consisting of an Oriel 300 Watt Xe-lamp in combination with an Oriel Cornerstone 130 monochromator and a SRS 830 Lock In amplifier. The number of photons incident on the

device was calculated for each wavelength by using a calibrated Si-diode as reference. The white light measurements were performed using a Steuernagel 535 solar cell simulator (1000W/m^2) and a Keithley 2400 Source/Measure unit.