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

Richard Yee Cheong Shin,[†] Thomas Kietzke,[†]
Sundarraj Sudhakar,[†] Ananth Dodabalapur,[†,‡]
Zhi-Kuan Chen,[†] and Alan Sellinger*,[†]

Institute of Materials Research & Engineering,
3 Research Link, Singapore 117602, Republic of Singapore,
and Microelectronics Research Center, the University of
Texas at Austin, Austin, Texas 78758

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Organic light-emitting diodes (OLEDs), field-effect transistors (FETs), and solar cells based on π-conjugated materials have been extensively studied in the past decade because of their low-cost processing, simple packaging, and compatibility with flexible substrates.[1−3]

To date, the most widely investigated organic semiconductors are p-type (hole transporting) materials based on aromatic amines and thiophene materials.[2,4,5] To further advance the area of high-performance organic electronic devices, we need organic n-type semiconductors with high electron mobilities and controllable HOMO and LUMO energy levels.[6−8] For example, organic solar cells incorporating heterojunctions of p- and n-type conjugated materials show much better performance than devices based on only one specific material. In this case, the heterojunction helps photogenerated excitons dissociate into free charge carriers.[3,9−11]

In this communication, we report the synthesis, characterization, and preliminary organic solar-cell device results of solution processable n-type conjugated materials based on 2-vinyl-4,5-dicyanoimidazoles, marketed as Vinazene.[12] Previously, Vinazene has been used as a monomer or comonomer in the preparation of imidazole containing polymers and as high-nitrogen-containing heterocyclic molecules.[13,14] To the best of our knowledge, the Heck chemistry of vinazenes or their use in organic electronic applications has not been reported thus far. The vinazene materials can be easily prepared in high yields through one step Heck coupling reactions with dibromoaromatics, as shown in Scheme 1.[15] Solubility can be controlled by alkylation of the 1 position with haloalkyl groups of varying lengths. Both the HOMO and LUMO energy levels of the materials can be easily tuned over a wide range by simply changing the central aromatic segments. The widely tunable energy levels and bandgaps make these materials attractive for potential application as emissive and/or electron-transporting materials for OLEDs and organic solar cells.

Vinazene derivatives **V−DP**, **V−F**, **V−BT**, and **V−TBT** from Scheme 1 were synthesized from the Heck coupling of 1-alkyl-2-vinyl-4,5-dicyanoimidazole (1-alkylvinazenes) with various dibromoaromatics in DMF using bis(tri-t-butylphosphine)-palladium(0) [Pd[P(t-Bu)$_3$]$_2$] as catalyst, and dicyclohexylmethylamine (Cy$_2$NMe) as base/HBr scavenger.[16] Initial products were synthesized using a butyl group in the 1 position, but the resultant solubility was low. Subsequently, hexyl and 2-ethylhexyl groups provided materials with enhanced solubility. The products were isolated in moderate to high yields by precipitation in ethanol followed by recrystallization.

The thermal properties of the materials have been analyzed by DSC and TGA and the results are presented in Table 1. All the materials melt above 205 °C and have relatively high thermal stability (>380 °C) under N$_2$.

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* Corresponding author. E-mail: alan-sellinger@imre.a-star.edu.sg.
[†] Institute of Materials Research & Engineering.
[‡] University of Texas at Austin.

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(15) General procedure for the preparation of the vinazene derivatives. **Alkyl Vinazene.** To a solution of vinazene (1.00 g, 6.9 mmol) in 15 mL of acetone was added anhydrous K$_2$CO$_3$ (1.40 g, 10.1 mmol) and 1-iodohexane (1.40 mL, 9.5 mmol). The solution was refluxed for 24 h and filtered and the was solvent removed under a 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 was removed under a vacuum. The oily residue was recrystallized in EtOH to give pale yellow crystalline solids (1.42 g, 90% yield) after 24 h at 4 °C. ^{1}H 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. **Heck Reactions.** In a glovebox, the aryl halide, Cy$_2$NMe, Pd[P(t-Bu)$_3$]$_2$, DMF, and alkyl vinazene were added to an oven-dried Schlenk flask equipped with a stir bar. The flask was taken out of the glove box and connected to a Schlenk line; the reaction mixture was then stirred at 80 °C for 20 h. Upon reaction completion, the mixture was cooled to room temperature and filtered. Ethanol was added to the filtrate while stirring to precipitate out the product, which was washed with EtOH followed by hexane. The product obtained was recrystallized from DMF/EtOH or THF/EtOH. Reaction conditions for the synthesis of **V-BT**: 4,7-dibromo-2,1,3-benzothiadiazole (88 mg, 0.30 mmol), 1-hexylvinazene (171 mg, 0.75 mmol), Cy$_2$NMe (0.161 mL, 0.75 mmol), Pd[P(t-Bu)$_3$]$_2$ (3.1 mg, 0.006 mmol, 1 mol %), and DMF (2 mL). After workup, the product was obtained as an orange solid (155 mg, 88% yield). ^{1}H NMR (CDCl$_3$): 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). ^{13}C NMR (CDCl$_3$): 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 C$_{32}$H$_{32}$N$_{10}$S: 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. MS (MALDI-TOF): m/z 589 (M + H); calcd. for C$_{32}$H$_{32}$N$_{10}$S, 588.

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Scheme 1. Heck Couplings of Aryl Dibromides and 1-Alkylvinazene

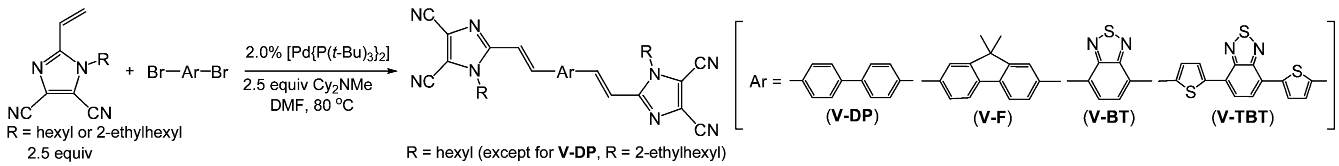

Table 1. Physical Properties of Vinazene Oligomers

compd	T_m (°C)[a]	T_d (°C)[b]	UV−vis $\lambda_{\max}$ (nm)[c]	PL $\lambda_{\max}$ (nm)[c]	Φ[d]	HOMO/LUMO (band gap) (eV)[f]
V−DP	208	402	369	417 (sh), 442	0.76	−5.74/−2.84 (2.90)
V−F	238	387	390, 409 (sh)	427, 453	0.74	−5.57/−2.84 (2.73)
V−BT	205	381	337, 448	516	0.48	−5.87/−3.49 (2.38)
V−TBT	266	400	390, 520	606	0.13[e]	−5.24/−3.44 (1.80)

[a] Obtained from DSC measurement. [b] Obtained from TGA measurement (temperature at 5% weight loss under N_2). [c] Measured in a toluene solution. [d] Using quinine sulfate as standard. [e] Using rhodamine 6G as standard. [f] Calculated from CV data and UV−vis absorption spectra band edge.

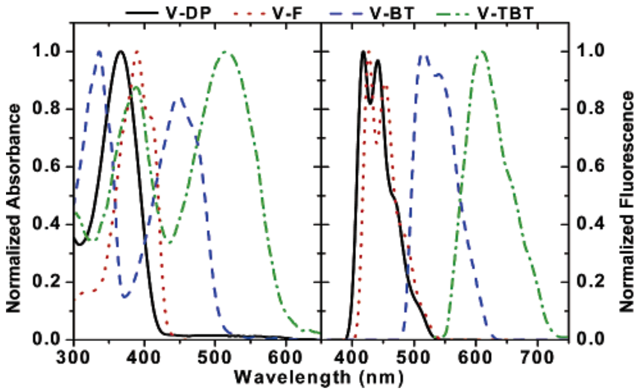

Figure 1. UV−vis and fluorescence spectra of the vinazene derivatives

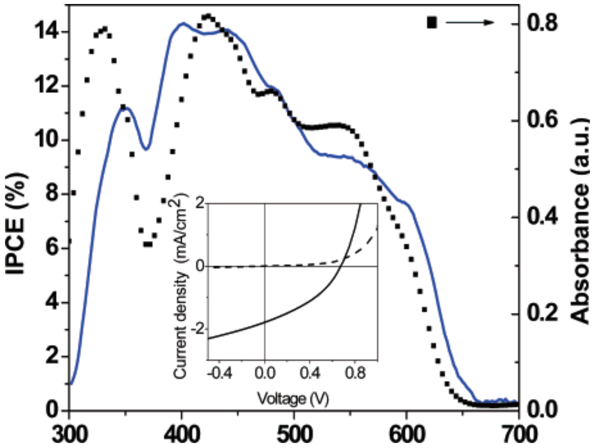

Figure 2. IPCE spectra for **V−BT:P3HT** (1:1) devices annealed at 140 °C for 10 min prior the cathode evaporation. For comparison, the absorbance spectrum of a 1:1 blend is shown. The inset shows the I(V) characteristics under illumination with AM 1.5 irradiation (1000 W/m^2, solid line) and under dark conditions (dashed line).

The photophysical properties of the compounds were measured by UV−vis and fluorescence spectroscopy in toluene. The compounds show strong absorption and emission in the 330−520 and 410−610 nm (Figure 1) ranges, respectively. Furthermore, the molecules exhibit high photoluminescence (PL) quantum efficiencies and emission from blue to red, as shown in Table 1 and Figure 1.

Cyclic voltammetry (CV) and the UV−vis absorption band edge were used to estimate the ionization potential (HOMO), electron affinity (LUMO), and band gap of the vinazene materials[7,17] (see the Supporting Information, Figures S1−S4). From these results, we observed that the HOMO−LUMO and band gap values could be systematically tuned by changing the central aromatic group as shown in Table 1. For example, values ranging from −5.24 to −5.87 eV (HOMO) and −2.84 to −3.49 eV (LUMO) could be obtained using this strategy.

Of the vinazene-based materials synthesized to date, **V−BT** has the most promising properties for solar-cell applications. Its LUMO level is sufficiently low to provide an efficient charge transfer of the photogenerated electron from the donor polymer, such as polyphenylenevinylene (**PPV**) derivatives or thiophene polymers, to **V−BT**.

For the solar-cell devices, the following structures were fabricated: glass/ITO/PEDOT:PSS (40 nm)/active layer (70 nm)/Ca (30 nm)/Ag (100 nm), where PEDOT:PSS is 2.5% poly(ethylenedioxythiophene)-polystyrene sulfonic acid in water, and the active layer is 5.0 mg/mL **V−BT** and 5.0 mg/mL regioregular poly(3-hexylthiophene-2,5-diyl) (**P3HT**) in chloroform. The PEDOT:PSS and active layer were spin-coated under a nitrogen atmosphere, whereas the Ca and Ag were thermally sublimed (preparation and characterization details can be found in the Supporting Information). We found that annealing the active layer at 140 °C for 10 min prior to cathode deposition provided the optimum device efficiencies.

The solar-cell devices demonstrated very good photoresponses in the range from 300 to 650 nm, as shown in Figure 2, reaching external quantum efficiencies exceeding 14% for 1:1 ratios of **V−BT:P3HT**. Other ratio variations provided lower efficiencies. The photoresponse resembles the absorbance of the active layer, demonstrating that both materials contribute equally to the photocurrent.

Under white light illumination with a solar simulator (AM 1.5, 1000 W/m^2), an open circuit voltage of $V_\mathrm{oc} = 0.67$ V was achieved with a corresponding fill factor and power conversion efficiency of 37% and $\eta = 0.45\%$, respectively. To the best of our knowledge, this is the highest power conversion efficiency reported for organic solar cells comprising a blend of **P3HT** as donor and a non-fullerene based acceptor.[18,19] As fullerene derivatives are expensive and

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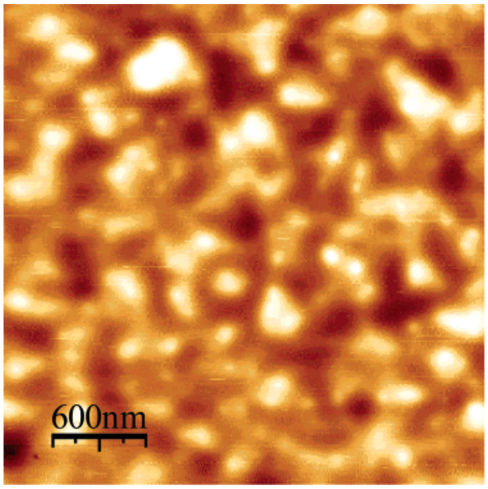

Figure 3. Atomic force microscopy (AFM) image of the **V−BT:P3HT** (1:1) blend layer annealed at 100 °C obtained in tapping mode.

involve much more complicated syntheses, vinazene derivatives are quite an attractive alternative for low-cost electron acceptors. Furthermore, vinazene derivatives are much easier to prepare than cyano-PPV derivatives that are also used as acceptors in organic solar cells.[20] In combination with donor polymers having a lower HOMO level, such as **PPV** derivatives, open circuit voltages exceeding 1.2 V could be reached using **V−BT** as an acceptor. Further studies on this system are under way and will be presented in a forthcoming paper.

Images from atomic force microscopy (AFM) reveal the active layers having a phase-separated morphology with feature sizes around 100 nm in diameter (Figure 3), even after annealing at temperatures well below the glass transition of P3HT ($T_{g,P3HT} = 120$ °C). Annealing at temperatures higher than 120 °C initially showed an optimum device power efficiency at 140 °C ($\eta = 0.45\%$). However, further annealing at 160 °C led to a power efficiency decrease with an associated increase in phase-separated feature sizes (∼1 μm). Because the exciton diffusion length in polymers is estimated to be only about 5−10 nm, most likely not all photogenerated excitons reach the heterointerface and hence limit the device efficiency. Further work is under way to modify the **V−BT** with 2-ethylhexyl solubilizing groups so that a finer phase separation may occur to possibly provide higher solar-cell device efficiencies.

In conclusion, we have reported the synthesis and characterization of a new family of n-type conjugated materials based on the Heck reaction of 2-vinyl-4,5-dicyanonimidazole with selected dibromoaromatics. The materials are easily prepared in high yields from one-step reactions using commercially available materials. The materials optoelectronic properties, such as Abs, PL, HOMO−LUMO are easily tuned by selecting the proper aromatic central segment. Initial organic solar cells using **P3HT** as donor and **V−BT** as electron acceptor show high external quantum efficiencies exceeding 14%, making this novel class of materials a promising candidate for future highly efficient and low-cost organic solar cells.

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Supporting Information Available: Experimental procedures and cyclic voltammograms. This material is available free of charge via Internet at http://pubs.acs.org.

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