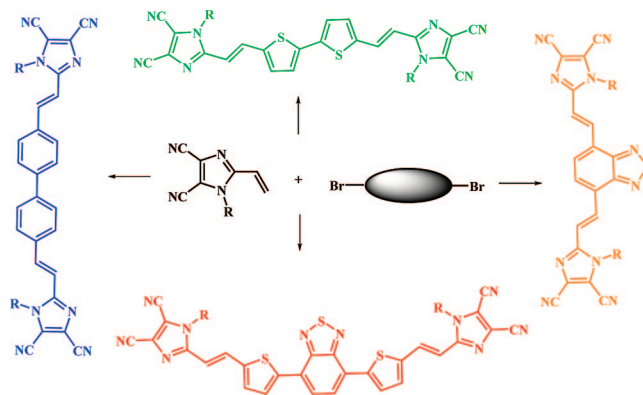# Electron-Accepting Conjugated Materials Based on 2-Vinyl-4,5-dicyanoimidazoles for Application in Organic Electronics

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We report the Heck coupling of 2-vinyl-4,5-dicyanoimidazole (vinazene) with selected di- and trihalo aromatics in an effort to prepare linear and branched electron-accepting conjugated materials for application in organic electronics. By selecting the suitable halo-aromatic moiety, it is possible to tune the HOMO−LUMO energy levels, absorption, and emission properties for a specific application. In this regard, materials with strong photoluminescence from blue → green → red are reported that may have potential application in organic light-emitting diodes (OLEDs). Furthermore, derivatives with strong absorption in the visible spectrum, coupled with favorable HOMO−LUMO levels, have been used to prepare promising organic photovoltaic devices (OPVs) when combined with commercially available semiconducting donor polymers.

Introduction

Over the past two decades there have been extensive efforts to develop organic semiconductors due to their potential for application in organic light-emitting diodes (OLEDs),[1−7] field effect transistors (OFETs),[8−17] and photovoltaic cells (OPVs).[18−27] Both electron-donor (hole-transporting) and electron-acceptor (electron-transporting) materials with thermal/chemical stability, solution processability, charge carrier mobility, and controllable HOMO−LUMO energy levels are essential for these applications. With regard to new materials development, to date most studies have focused on *donor* semiconductors based on aromatic amines and thiophenes, with significantly less work being reported on new *acceptor* materials.[28−35] For example,

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cyano phenylvinylene polymers (CN-PPVs), perylene dianhydrides and diimides, and fullerenes are the most widely studied acceptor materials in the areas of OPVs and OFETs. Since the mid-1990s, fullerene compounds have been the most utilized acceptor materials for use in solution processable OPVs providing power conversion efficiencies (PCE) in the range of $2-5\%$ when combined with selected donor materials.[26,36−38] Despite their success, fullerenes tend to have low absorption coefficients in the visible range, are difficult to synthesize and purify, are very expensive, and lead to devices with relatively low open circuit voltages (Voc).

Recently, several groups have reported high-performance accepting materials by introducing cyano or fluoro electron-withdrawing substituents into π-conjugated systems mostly for application in OFETs[39−45] with very few new acceptors being reported for application in OPVs. Along these lines, our group has previously reported on novel solution processable accepting materials based on 2-vinyl-4,5-dicyanoimidazoles (vinazene).[46,47] As an extension of this work, we herein report a more complete synthesis and characterization study of this family of n-type conjugated materials based on vinazene where by simply changing the central aromatic segments we could easily tune the optical properties and HOMO−LUMO energy levels of the resultant products. Previously, vinazene has been used as a monomer and/or comonomer in the preparation of dicyanoimidazole-containing polymers with high nitrogen content.[48−50] To the best of our knowledge, we have been the first to synthesize 4,5-dicyanoimidazole-based derivatives for use in organic electronic applications.

Results and Discussion

Synthesis. The vinazene-based n-type materials were synthesized through the Heck coupling reaction between 1-alkyl-2-vinyl-4,5-dicyanoimidazole (1-alkylvinazenes) with selected di- and tribromoaromatics. The synthetic procedure is shown in Scheme 1a−1b.

Alkylation of vinazene with various alkyl bromides and iodides (butyl and hexyl) in DMF or acetone using K_2CO_3 as base gave the desired products in good yield after recrystallization in ethanol. Vinazene with a branched alkyl group at the 1-position (ethylhexyl) was also synthesized to further enhance the solubility of the final n-type products. Ethylhexyl vinazene was obtained as an oil after purification by column chromatography, which solidified on cooling. This material was found to be unstable if stored at room temperature for a few days, readily converting into a brown insoluble product due to photoinitiated polymerization of the active vinyl group on vinazene.[49]

The Heck coupling reaction between 1-alkylvinazene and aromatic bromides was carried out in anhydrous DMF using bis(tri-*tert*-butylphosphine)palladium(0) [Pd[P(tBu)$_3$]$_2$] as catalyst and dicyclohexylmethylamine (NCy$_2$Me) as base/HBr scavenger (Scheme 1b).[51] The final products were obtained by precipitation of the reaction mixture into ethanol followed by recrystallization of the crude product in DMF/ethanol or THF/ethanol. The yields range from 75 to 88%, except for compounds **2**, **7**, **9**, **12**, **13**, and **14**. The lower yields (41% to 55%) for these compounds are mainly due to the relatively poor solubility. In selected cases, we used ethylhexylvinazene to increase the product solubility as compared to their hexylvinazene analogues. Trivinazene substituted products **15** and **16** have also been synthesized using similar reaction conditions with 1,3,5-tribromobenzene and 1,3,5-tris(4-bromophenyl)benzene as the core moiety in yields of 58% and 87%, respectively, as shown in Scheme 2.

The structure and purity of all the final products have been characterized and confirmed by ^{1}H NMR, ^{13}C NMR, elemental analysis, and MALDI-TOF mass spectra measurements.

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SCHEME 1.   (a) Alkylation of Vinazene and (b) Heck Couplings of Aryl Dibromides with Alkylvinazene
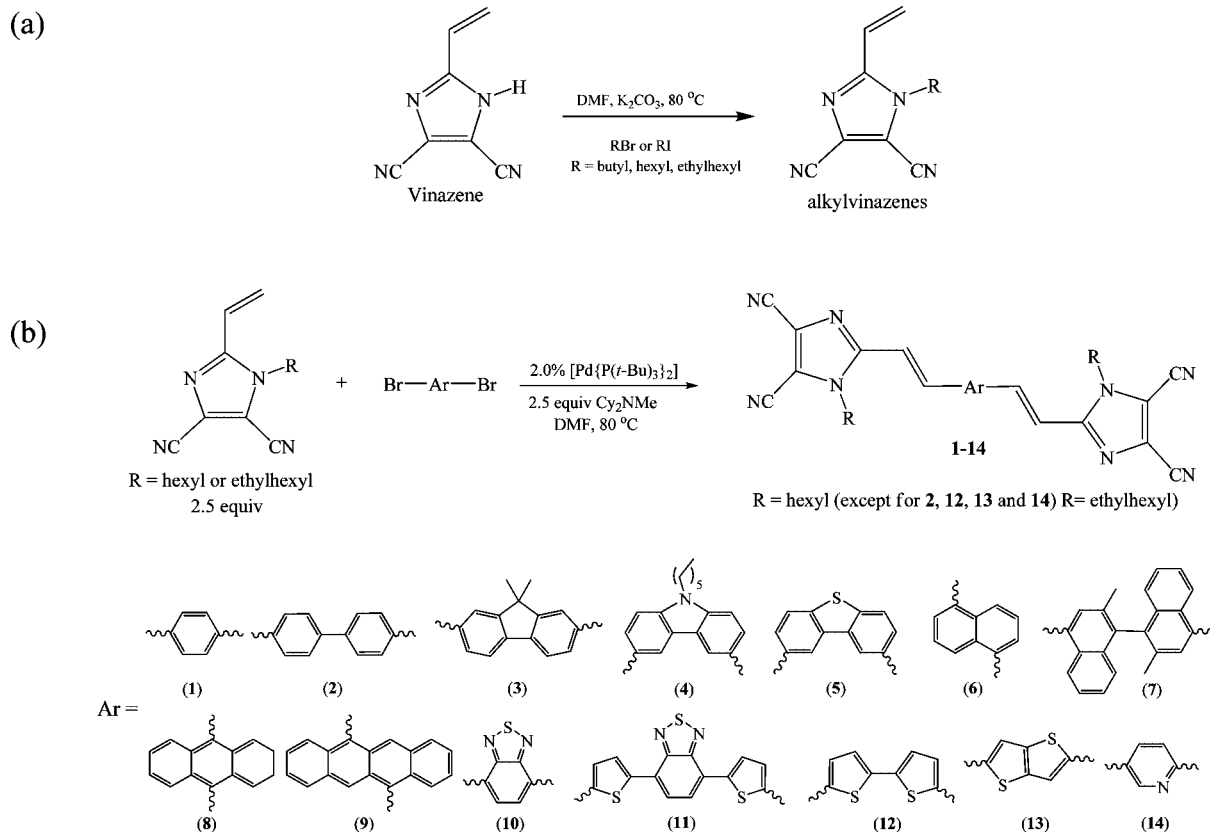
SCHEME 2.   Heck Couplings of Aryl Tribromides with Alkylvinazene
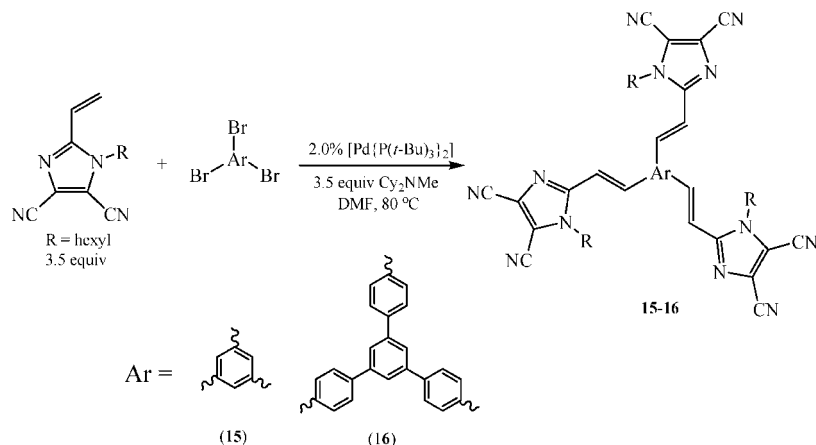
Optical Properties. The optical properties of all the compounds were measured by UV−vis and fluorescence spectroscopy in toluene and are shown in Table 1. The absorption spectra of the compounds provide information on the extent of π-conjugation between the central aromatic segment and the linked alkylvinazenes. The representative absorption and emission spectra for compounds **6**, **11**, **12**, and **15** are shown in Figure 1.

The π−π* transition bands of these compounds are located in the 300−600 nm range with the remaining absorption peaks located in 331−520 nm region. These values are strongly dependent on the nature of the central aromatic ring. For example, compound **1** with a phenylene bridge showed a maximum absorption peak at 376 nm. When the phenylene group is replaced with biphenylene (compound **2**) or binaph-

thalene (compound **7**), the absorption peaks are blue-shifted to 369 and 362 nm, respectively, due to the twisted conformation between the two phenyl/naphthyl rings resulting in disruption of conjugation. However, when the biphenyl rings are fixed in a more planar configuration, such as **3** (fluorene), the overall conjugation length is increased thereby causing a red shift of λ_{max} by 21 nm (λ_{max}: 390 nm) compared to compound **2**. When the linkage of the central group is shifted from the para to the meta position (compounds **4** and **5**), the absorption bands are also significantly blue-shifted.

In addition to planarity, the electron-donating nature of the central aromatic group also plays a crucial role in the optical properties. For example, when the bithienylene or thienothiophene groups are used as building blocks (compound **12** and **13**), red shifts of 40−60 nm are observed compared to compound **3**.

TABLE 1. Physical Properties of Vinazene Derivatives

compd	$T_g{}^a$ (°C)	$T_m{}^a$ (°C)	$T_d{}^b$ (°C)	UV−vis$\lambda_{max}{}^c$ (nm)	UV−vis onset (nm)	PL $\lambda_{max}{}^c$ (nm)	Φ^d	HOMO/LUMO^f (eV)	bandgap (eV) (from CV)^f	bandgap (eV) (from UV$_{onset}$)^g
1	59	250	382	376	421	(413) 437	0.56	−6.00/−2.98	3.02	2.95
2	na	208	402	369	419	(417) 442	0.76	−5.95/−2.85	3.10	2.96
3	na	238	387	390 (409)	435	427, 453	0.74	−5.82/−2.85	2.97	2.85
4	na	226	410	321, 386	431	426 (455)	0.05	−5.47/−		2.88
5	na	257	414	331	400	397, 411	0.02	−5.83/−2.76	3.07	3.10
6	na	215	396	392	468	467, 496	0.57	−5.83/−−3.10	2.73	2.65
7	89	na	393	362	418	445	0.09	−5.85/−2.78	3.07	2.97
8	53	279	376	422	508	592	0.29	−5.61/−3.26	2.35	2.44
9	86	na	343	516	596	638	0.07^e	−5.34/−3.41	1.93	2.08
10	na	205	381	337, 448	517	516	0.48	−6.02/−3.50	2.52	2.40
11	na	266	400	390, 520	628	606	0.13^e	−5.52/−3.45	2.07	1.97
12	na	244	382	450	519	506, 541	0.19	−5.57/−3.09	2.48	2.39
13	na	264	400	430, 448	482	476, 507	0.09	−5.70/−3.10	2.60	2.58
14	45	na	300	379	430	443	0.69	−5.60/−2.90	2.70	2.91
15	na	247	405	331	380	399 (425)	0.36	−/−2.93		3.26
16	115	na	400	351	396	(408) 436	0.12	−5.99/−2.79	3.20	3.13

^{a} Obtained from DSC measurements. ^{b} Obtained from TGA measurements (temperature at 5% weight loss). ^{c} Measured in a toluene solution. ^{d} Using quinine sulfate as standard. ^{e} Using rhodamine 6G as standard. ^{f} Calculated from CV data. ^{g} Calculated from UV−vis absorption spectral band edge. na = not detected. Data in parentheses are shoulders in UV and PL spectra.
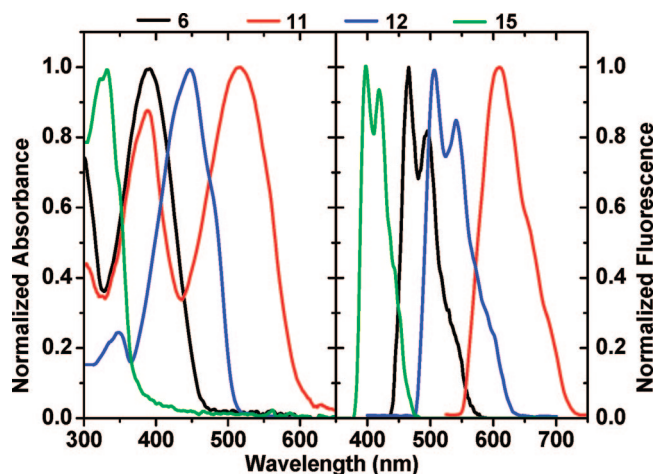

FIGURE 1. UV−vis and PL spectra of selected compounds in toluene.

This large red shift is ascribed to the electron-donating effect of the sulfur atom and the more coplanar configuration of the bithienyl/thienothiophene rings. The effective conjugation length can be also controlled by using fused aromatic groups such as naphthalene, anthracene, and tetracene. For example, when 1,4-naphthalene (compound **6**), 9,10-anthracene (compound **8**), or 5,11-tetracene (compound **9**) is used as the central groups, the absorption peaks are red-shifted by 16, 46, and 140 nm, respectively, in comparison with compound **1**.

The various combinations of central cores with the vinazene acceptor offer a unique and versatile method to prepare materials with tunable band gaps for application in organic photovoltaics. For example, lower band gap materials have a higher potential to harvest photons from sunlight.[52,53] For the materials synthesized here, band gaps are tuned from 2.95 eV (wide band gap material) to 2.08 eV (low band gap material) by selecting the appropriate central aromatic moiety. It is well known that the band gaps of conjugated molecules can be lowered by mixing different electron-donating and electron-withdrawing blocks in the conjugated backbone to form an alternating donor and acceptor structure. The lower band gap of such an alternating structure is attributed to the increase of quinoidal character of the ground state in the molecule.[54−56] Following this strategy, a central segment of 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole was incorporated to form a donor−acceptor (D−A−D) structure (compound **11**), which showed a maximum absorption of 520 nm. The band gap calculated from the absorption onset of this compound (**11**) is 1.97 eV (which is the lowest band gap among all materials in this study). From the above discussion, it is clear that by changing the central moiety one can effectively tune the band gap of materials using structure−property relationships. The range of absorption bands as well as energy levels (from wide band gap to low band gap materials) of all these new n-type materials (acceptor) provide more opportunities to match p-type materials (donor) for OPV applications, as will be demonstrated later in this manuscript.

The fluorescence spectra of selected materials are shown in Figure 1. Compounds **9** and **11** exhibit strong red photoluminescence (PL) emission at 638 and 606 nm, respectively. This is attributed to the interaction of the HOMO and LUMO of the donor and acceptor segments respectively within the molecule. The PL quantum efficiency also depends strongly on the central aromatic group (see values in Table 1). For example, high PL efficiencies were obtained with the central aromatic groups such as 2,5-pyridyl, biphenyl, and fluorene (69−76%), moderate efficiencies with phenylene, benzothiadiazole, and naphthalene (48−57%), and low efficiencies with 3,6-carbazole, 3,6-dibenzothiophene, 2,2′-dimethylbinaphthyl, and tetracene (2−9%).

Electrochemical Properties. Cyclic voltammetry (CV) was used to determine the electrochemical properties of the materials. All CV measurements were recorded (Figures S1−S16 Supporting Information) 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

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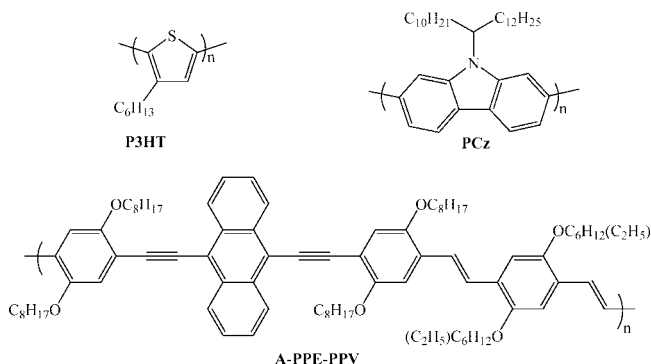
FIGURE 2. Selected donor polymers used with compound **10** for preparing organic solar cell devices.

TABLE 2. Organic Solar Cell Device Data Using Compound 10 with Selected Donor Polymers

	P3HT:**10** (hexyl)	A-PPE-PPV:**10** (hexyl)	PCz:**10** (ethylhexyl)
anneal temp (°C)	140	80	80
Voc[a] (V)	0.67	0.98	1.36
Isc[a] (mA/cm²)	1.79	1.20	1.14
fill factor (%)	37.3	35.0	49.0
IPCE[a] max (%)	14.0	12.2	18.5
PCE[a] (%)	0.45	0.42	0.75

[a] Voc is open circuit voltage; Isc is short-circuit current density; IPCE is incident photon to conversion efficiency; PCE is power conversion efficiency.

electrode), and the corresponding ionization potential (IP) and electron affinity (EA) values were derived from the onset redox potentials, based on -4.4 eV as the SCE energy level relative to vacuum (EA $= E_{\text{red-onset}} + 4.4$ eV, IP $= E_{\text{ox-onset}} + 4.4$ eV).

Cyclic voltammograms of vinazene compounds **1**−**16** were used to estimate the LUMO (electron affinity) and HOMO (ionization potential) values which are shown in Table 1. Compounds **1**, **2**, **10**, and **16** showed the lowest HOMO values (furthest from vacuum) compared to the other derivatives of the series. The lower HOMO values indicate the higher oxidative stability of the materials, which is a key requirement for organic electronics. The LUMO values vary from -2.76 to -3.50 eV and again demonstrate the wide range of materials for band gap engineering obtained using this strategy. The optical band gaps calculated from the UV−vis absorption onset,[5,57] and the electrochemical band gaps obtained from cyclic voltammetry, are found to be in good agreement as shown in Table 1. The lowest band gap calculated for the compound **9** and **11** are around 2.0 eV due to higher conjugation length of blocks used as a central moiety.

Thermal Properties. The thermal behavior of all the materials was determined by a repeating heating−cooling cycle using differential scanning calorimetry (DSC) (see Table 1). Compounds **1**, **7**−**9**, **14**, and **16** showed glass transition temperatures varying from 45 to 115 °C. The highest T_g was reported for compound **16** due to the two phenyl rings that enhance the rigid nature of the branched material. All compounds showed melting peaks except **7**, **9**, **14**, and **16** despite heating to 300 °C. This observation also indicates the stiff nature of the material due to the fused aromatic structure of the central moiety. Thermal decomposition (T_d) analysis of all the materials was carried out using thermogravimetric analysis (TGA). T_d, 5 wt % loss, for all compounds were observed in the 300−414 °C range. These values clearly indicate the high thermal stability of the materials, which is a prerequisite for eventual device lifetime and various processing conditions of organic devices.

Photovoltaic Properties. After careful screening of all the materials prepared in this study, the hexyl and ethylhexyl versions of compound **10** were found to be the most promising for application in OPV devices when combined with the selected donor polymers shown in Figure 2.[46,47,58,59]

The first-order screening process involved selecting materials with suitable HOMO and LUMO levels to match with commercially available donor polymers such as regioregular poly(3-hexylthiophene) (P3HT), which has reported HOMO−LUMO levels of -5.2 and -3.3 eV, respectively. Based on this criterion, suitable vinazene-based compounds included compounds **8**−**13**, which were all tested in OPV devices with P3HT. Of these six materials, compound **10** showed the best performance and was selected for further optimization. For the convenience of the reader, we have compiled published OPV device data based on compound **10** in Table 2. Details of the device preparation and testing can be found in the provided references. Although the initial PCEs reported here are roughly $5\times$ lower than those achieved by C_{60}-based fullerene-based acceptors (PCBM) combined with donor polymers such as regioregular poly(3-hexylthiophene) P3HT, our materials show some very promising properties. For example, a majority of the white light illumination (solar simulator, AM 1.5 and 100mW/cm²) is absorbed by compound **10** and not the donor polymer. This is in contrast to the traditional P3HT:PCBM system where P3HT absorbs most of the light. Furthermore, the LUMO level of compound **10** (-3.50 eV) is 0.5 eV lower than that of PCBM (-4.00 eV) resulting in higher Voc values for OPV devices. This can be seen in Table 2 where the Voc values are tuned from $0.67-1.36$ V depending on the donor polymer. For the compound **10**:PCz system where 1.36 V is achieved, almost all the visible light is absorbed by compound **10** as PCz is a high band gap polymer and absorbs primarily in the UV region. In this case, derivatives such as PCBM could not be efficiently utilized with PCz as both materials primarily absorb in the UV region. As a result, compound **10** is a very versatile acceptor material that can be used with many donor systems. Further optimization of processing conditions, active layer morphology, donor polymer, and materials design will likely lead to improving the ultimate PCEs. In fact, improved device efficiencies of 1.1% have recently been prepared using compound **10** with other donor polymers and the results will be reported shortly. Finally, we are currently building a solar cell lifetime setup to compare devices prepared with these new acceptors with the more traditional fullerene based materials.

Conclusions

We have reported the synthesis and characterization of a new family of n-type conjugated materials based on the Heck reaction of 1-alkylvinazenes with selected bromoaromatics. The materials are easily prepared in high yields from minimal step reactions while the optoelectronic properties, such as UV−vis, PL, HOMO−LUMO are easily tuned by selecting the proper central aromatic segment. The materials may be tuned for solution

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processability and high thermal stability which are key parameters for processing and device lifetime. We are currently investigating their applications as emissive and/or electron transporting materials for OLEDs as well as continued studies on related materials for use in organic photovoltaic cells.

Experimental Section

Materials. Commercially available materials were used as received unless noted otherwise. Dicyclohexylmethylamine (Cy$_2$NMe) was distilled prior to use. *N*-Hexyl-3,6-dibromocarbazole, 5,11-dibromotetracene,[60] 4,4′-dibromo-2,2′-dimethyl-1,1′-binaphthyl,[61] and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole[62] were prepared according to literature procedures. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents.

Synthesis. The synthetic routes for the alkylation of vinazene and Heck couplings are shown in Schemes 1 and 2, and their synthetic procedures are provided as follows:

Synthesis of 1-Alkylvinazenes. To a solution of vinazene (2.00 g, 0.014 mol) in 30 mL of DMF was added 2.80 g (0.020 mol) of anhydrous K$_2$CO$_3$ and 1-iodohexane (2.80 mL, 0.019 mmol). The solution was stirred at 80 °C for 24 h and then quenched with 30 mL of water. The aqueous layer was extracted three times with 50 mL of diethyl ether. The organic layer was dried over magnesium sulfate, and the solvent was removed under vacuum. The oily residue was recrystallized in EtOH to give pale yellow crystalline solids (2.22 g, 70% 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.

The analogue 1-(2-ethylhexyl)vinazene was synthesized from 1-bromo-2-ethylhexane using similar conditions. After being stirred for 24 h, 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 removal of solvent. The oil solidified upon cooling 4 °C for 24 h to give the product as a cream-colored solid (34% yield). ^{1}H 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.

General Procedure for Heck reactions. In a glovebox, the aryl halide, Cy$_2$NMe, 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 glovebox and connected to the nitrogen line, and the reaction mixture was stirred at 85 °C for 20 h. At the end of the reaction, the mixture was cooled to room temperature and filtered through 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 followed by hexane. In cases where the product could not be precipitated out, EtOH was added and the solution kept at 4 °C until precipitation occurred. The product obtained was then recrystallized from DMF/EtOH or THF/EtOH followed by cooling.

Compound 1. Reaction system: 1,4-dibromobenzene (71 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), and DMF (2 mL). After workup, the product was obtained as yellow solids (120 mg, 75% yield). ^{1}H NMR (CDCl$_3$): δ 0.90 (t, 6 H, *J* = 7.2 Hz), 1.36 (unresolved m, 12 H), 1.86 (q, 4 H, *J* = 6.8 Hz), 4.19 (t, 4 H, *J* = 7.6 Hz), 6.80 (d, 2 H, *J* = 16.0 Hz), 7.60 (s, 4 H), 7.87 (d, 2 H, *J* = 15.6 Hz). ^{13}C NMR (CDCl$_3$): δ 14.0, 22.5, 26.2, 30.8, 31.2, 46.7, 108.6, 111.2, 111.8, 112.5, 123.0, 128.4, 136.6, 139.5, 149.7. Anal. Calcd for C$_{32}$H$_{34}$N$_8$: C, 72.43; H, 6.46; N, 21.12. Found: C, 72.27; H, 6.79; N, 21.29. MS (MALDI-TOF): *m/z* 531.37 (M + 1), calcd for C$_{32}$H$_{34}$N$_8$ 530.29.

Supporting Information Available: Detailed experimental procedures and compound characterization data for all products, NMR spectra (^{1}H), and cyclic voltammogram traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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