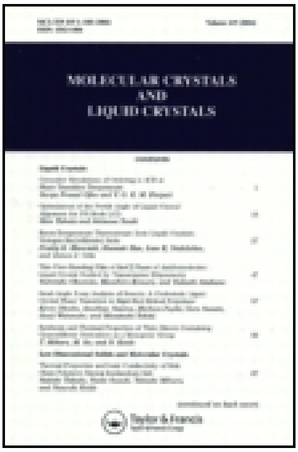

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Small-Molecule Vinazene Acceptors for Bulk Heterojunction Organic Photovoltaics

Eunhee Lim [a] [b] , Sungkoo Lee [b] & Kyeong K. Lee [b]
[a] Department of Chemistry, Kyonggi University, San 94-6, Iui-dong, Yeongtong-gu, Suwon-si, Gyeonggi, 443-760, Republic of Korea
[b] Korea Institute of Industrial Technology (KITECH), Cheonan-si, Chungnam, 331-825, Republic of Korea

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Small-Molecule Vinazene Acceptors for Bulk Heterojunction Organic Photovoltaics

EUNHEE LIM,[1,2,*] SUNGKOO LEE,[2] AND KYEONG K. LEE[2]

[1]Department of Chemistry, Kyonggi University, San 94-6, Iui-dong,
Yeongtong-gu, Suwon-si, Gyeonggi 443-760, Republic of Korea
[2]Korea Institute of Industrial Technology (KITECH), Cheonan-si, Chungnam
331-825, Republic of Korea

*This paper reports the synthesis and characterization of a new vinazene-based small molecule, 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl) vinyl)diketopyrrolopyrrole (**EV-DPP**). The known vinazene-based small molecule, 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c][1,2,5]thiadizole (**EV-BT**), was also prepared for comparison. The benzothiadiazole unit in **EV-BT** was replaced with a DPP unit in **EV-DPP** because DPP units are strong absorbing chromospheres. The UV absorption maxima of **EV-DPP** film (λ_{max} = 386, 573 nm) were greatly red shifted compared to the maxima of **EV-BT** film (λ_{max} = 337, 444 nm). Our preliminary device work showed the possibility of the use of **EV-DPP** as an electron acceptor in OPVs. The P3HT: **EV-DPP** film showed a better power conversion efficiency of 0.02% compared to P3HT: **EV-BT** due to the preferable UV absorption characteristics of **EV-DPP**.*

Keywords organic photovoltaic cells; solar cells; vinazene; Heck coupling; OPV; DPP

Introduction

Organic photovoltaics (OPVs) are a potential candidate for the clean and inexpensive power generation on account of their light weight, flexibility and low cost production [1–3]. Bulk heterojunction solar cells (BHJ) based on interpenetrating networks of electron-donating polymers and electron-accepting derivatives are capable of high efficiency in OPVs. Many groups have shown the fact that OPV devices fabricated with a poly(3-hexylthiophene) (P3HT) donor and a [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) acceptor can achieve a power conversion efficiency (PCE) of nearly 5% [4].

The fullerene core of PCBM readily accepts electrons from a wide range of organic donor materials and exhibits high electron mobility, even in a composite form. Nonetheless, the weak absorption in the visible spectrum and the excessively deep-lying LUMO level of PCBM induce energy loss during the electron transfer process and thereby limit the efficiency of devices, particularly the open circuit voltage (V_{OC}) of the devices [5]. There is a

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[*] Address correspondence to Prof. Eunhee Lim, Department of Chemistry, Kyonggi University, Suwon-si, Gyeonggi 443-760, Republic of Korea (ROK). Tel.: (+82)31-249-9663. E-mail: ehlim@kyonggi.ac.kr

clear need for alternative acceptor materials that exhibit favorable electron-transporting and processing properties, as in the case of PCBM, but that also demonstrate strong absorbance in the solar spectrum.

Several groups have recently reported high-performance acceptor materials based on vinazene, quinone, and functionalized pentacene, carbazoles, oligothiophene, and bifluorenylidene [2]. Small molecules based on diketopyrrolopyrrole (DPP) derivatives are known to be strongly absorbing donors for OPVs. DPP derivatives are easily synthesized and yield PCEs of more than 4% when blended with PCBM acceptors [2]. A few DPP derivatives have been explored for their use as acceptors in OPVs. The use of inductively electron-withdrawing groups, such as fluoro or fluoroalkyl groups, on the DPP periphery enable the LUMO energy in OPVs to be tuned to yield reasonable V_{OC} values. The best performance was found with a simple trifluoromethylphenyl derivative, which yielded a PCE of 1%. On the other hand, vinazene (4,5-dicyanoc-2-vinylimdazole) derivatives have also been used as acceptor materials in OPVs [6,7]. Various combinations of central cores with the vinazene group offer a unique and versatile means of preparing materials with tunable bandgaps for application in OPVs [4,8,9]. These materials are stable, strongly absorbing chromophores; they can be easily prepared as symmetrical systems with two dicyanoimidazole units flanking an aromatic core [4]. The best performance for a device made of **EV-BT** was a reasonable PCE of 0.75% at a blending ratio of 30:30 (PCz:**EV-BT**) [5].

In this work, we synthesized a new vinazene-based oligomer (**EV-DPP**) using a Heck coupling reaction and fabricated OPV devices using **EV-DPP** as an acceptor material. **EV-DPP** was designed to have a strong electron-accepting unit of DPP, which was an alternative to the benzothiadiazole used in **EV-BT**. The optical properties and photovoltaic characteristics of the oligomer are systematically investigated to establish the relationship between the molecular structure and OPV device performance.

Experimental

Materials

4,7-Dibromobenzo[c][1,2,5]thiadiazole, 3-bromothiophene, bis(tri-tertbutylphosphine) palladium(0) ($Pd[P\text{-}(t\text{-}Bu)_3]_2$), dicyclohexylmethylamine (Cy_2NMe) were purchased from Aldrich. All reagents purchased commercially were used without further purification. 1-(2-Ethylhexyl)vinazene (**4**) and 3,6-bis(5-bromothiophene-2-yl)-2,5-bis(2-ethylhexyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**5**) were prepared according to a literature procedure [10].

Measurements

NMR spectra were recorded on a JNM-ECP 400 MHz (Jeol). UV-vis spectra were obtained using a Shimadzu UV/vis. The oligomer films used in the UV-vis measurements were prepared by spin-coating of oligomer solution in toluene in the same way as the OPV fabrication.

Synthesis

Synthesis of (1Z)-1-amino-1,2-dicyano-3-aza-1,3,5-hexatriene (**Acrodamn**, **2**): Diaminomaleonitrile (5.00 g, 46.2 mmol) (DAMN) and ether (62.5 ml) were added to a 250 ml round-bottom flask. The reaction mixture was stirred in an ice water cooling bath for

15 min. Acrolein (2.85 g, 50.8 mmol) was added to the flask, and the mixture was stirred for 15 min. Several drops of TFA were then added to the mixture. The reaction mixture was poured into pre-cooled hexane. After stirred for 30 min, the reaction mixture was poured ∼ into 375 ml of pre-cooled hexane with rapid stirring. It was then filtered and dried under a vacuum. Acrodamn (**2**, 6.62 g, 98%) was obtained as a beige solid and was used without further purification.

Synthesis of 4,5-dicyano-2-vinylimdazole (**vinazene**, **3**): Lead tetraacetate (21.00 g, 47.6 mmol) and acetonitrile (100 ml) were added to a 250 ml three-neck round-bottom flask and the flask was placed in an ice water cooling bath in an N_2 atmosphere. Crude acrodamn (**2**, 6.62 g, 45.3 mmol) was dissolved in acetonitrile (150 ml) and the mixture was poured into the lead tetraacetate solution over a period of approximately 1 min. The mixture was stirred for 50 min and then filtered. The residual precipitate was washed with ethyl acetate until color was no longer evident in the extract. The organic phase was washed with ether and water and then dried over anhydrous magnesium sulphate. The ether was removed by evaporation under reduced pressure, yielding vinazene (**3**, 6 g, 92%) in the form of an orange clumpy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.62 (dd, 1H), 6.20 (d, 1H), 5.74 (d, 1H).

Synthesis of 4,5-Dicyano-2-ethylhexyl-2-vinylimidazole (1-(2-ethylhexyl)vinazene, **4**): K_2CO_3 (8.17 g, 59.0 mmol) and 1-bromo-2-ethylhexane (8.03 g, 41.6 mmol) were added to a solution of vinazene (**3**) in DMF (90 ml). The solution was stirred at 80°C for 24 h and then quenched with water (30 ml). The aqueous layer was extracted three times with diethyl ether. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The yellow liquid residue was purified by a silica-gel column chromatograph (ethyl acetate:hexane = 1:3) to yield a clear light-yellow liquid product (**4**, 1.46 g, 13.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.62 (dd, 1H), 6.20 (d, 1H), 5.74 (d, 1H), 4.3 (dd, 1H), 1.72 (m, 1H), 1.27 (m, 4H), 0.85 (m, 2H).

Syntheses of the oligomers (**EV-DPP** and **EV-BT**): 4,7-Bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2yl)vinyl)diketopyrrolopyrrole (**EV-DPP**) and 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyaniomidazol-2-yl)vinyl)benzo[c][1,2,5]thiadiazole]-2,7-diyl (**EV-BT**) were synthesized using the Heck coupling reaction of 1-(2-ethylhexyl)vinazene and the corresponding dibromoaryl compounds, 3,6-bis(5-bromothiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**4**) and 4,7-dibromobenzo [c][1,2,5]thiadiazole, respectively.

Synthesis of **EV-DPP**: 1-(2-ethylhexyl)vinazene (188 mg, 0.73 mmol), **4** (200 mg, 0.29 mmol), Cy_2NMe (143 mg, 0.73 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (0.003 mg, 0.006 mmol), and DMF (1.29 ml) were added to an oven-dried flask in a glove box. The flask was taken out of the glove box and the reaction mixture was stirred at 85°C overnight. At the end of the reaction, the mixture was cooled to room temperature and filtered through a glass sinter. Ethanol was added to the filtrate while stirring to precipitate the product, which was collected and washed with ethanol and hexane. The product was obtained as a dark violet solid after recrystallization from THF/ethanol (0.05 g, 21.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.8 (d, 2H), 8.7 (d, 2H), 6.52 (d, 4H), 5.8 (d, 4H), 4.0 (m, 22H), 1.65 (m, 16H), 1.27 (m, 24H), 0.89 (m, 34H).

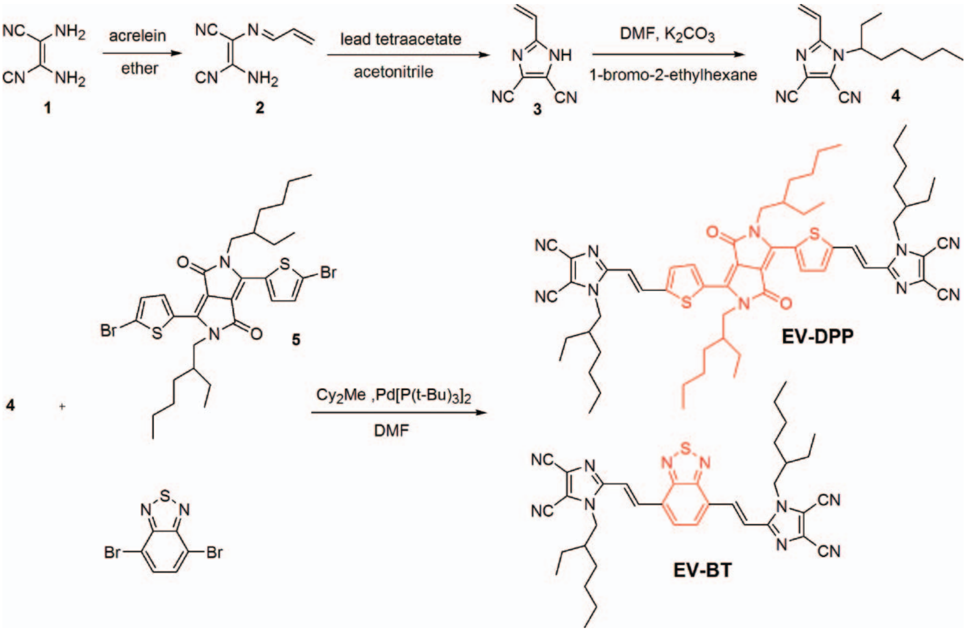
Synthesis of **EV-BT**: **EV-BT** was prepared as for **EV-DPP** using 4,7-dibromo-2,1,3-benzothiadiazole (160 mg, 0.5 mmol), resulting in a yellow solid [4]. (0.02 g, 3.17 mmol) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33(d, 2H), 8.06 (d, 1H), 7.74 (s, 2H), 4.30 (t, 4H), 1.95 (g, 4H), 1.37 (m, 12H), 0.90 (t, 6H).

Fabrication of OPV device

OPV devices were fabricated with the configuration ITO/PEDOT:PSS/P3HT:oligomer/LiF/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, isopropyl alcohol, and methanol. The poly(ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) was spin-coated on the substrate (3500 rpm, 40 nm) and annealed at 120°C for 30 min. The active layer consisting of P3HT and oligomer was spin-coated from a toluene solution. Prior to use, a toluene solution of P3HT and oligomer with the total concentration of 36 mg/ml was stirred at 60°C overnight to ensure complete dissolution. The solution was filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane syringe before applied dropwise onto the substrates. Next, the LiF (1 nm) and Al metal layer (100 nm) was deposited as the cathode electrode. The area of the device was 4 mm^2. The current-voltage (J-V) characteristics of the P3HT:oligomer films were measured with a Keithley 2400 source-measure unit in air under white light illumination of AM 1.5 (100 mW/cm^2).

Results and Discussion

We used the Heck coupling reaction to synthesize two vinazene-based small molecules, namely **EV-BT** and **EV-DPP**. The syntheses of **EV-BT** and **EV-DPP** are shown in **Scheme 1**. 1-(2-Ehylhexyl)vinazene (**4**) can be easily prepared in high yields from a three-step reaction. The benzothiadiazole unit in **EV-BT** was replaced with a DPP unit in **EV-DPP** because DPP units are strong absorbing chromospheres.



Scheme 1. Synthetic route via Heck coupling to the 1-(2-ehylhexyl)vinazene (**4**) and vinazene-based oligomers (**EV-BT** and **EV-DPP**).

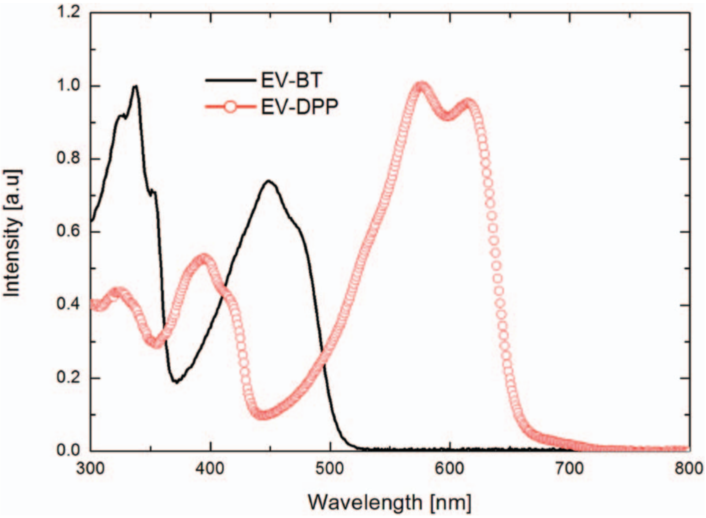


Figure 1. UV-vis absorption spectra of **EV-BT** and **EV-DPP** in toluene.

Figure 1 shows the absorption spectra of **EV-DPP** and **EV-BT** in toluene. The absorption spectra of the oligomers have two absorption bands, which can be assigned to the π-π^* transition of the conjugated backbone in shorter wavelengths and the intramolecular charge transfer (ICT) interactions between the thiophene donor and the benzothiadiazole acceptor units in longer wavelengths [11]. The absorption peaks of **EV-BT** appear at 337 nm and 444 nm, which is a good match with the previously reported result [5]. Importantly, the UV absorption spectrum of **EV-DPP** with two absorption maxima at 386 nm and 573 nm was greatly red shifted compared to those of **EV-BT**. The optical properties of conjugated materials strongly depend on the nature of the central aromatic ring [10]. The red-shifted broad UV-visible absorption of **EV-DPP** is preferable for good OPV performance because materials with a lower bandgap are more capable of harvesting photons from sunlight. **Figure 2** shows the UV-vis absorption spectrum of **EV-DPP** film together with the spectrum of PCBM. PCBM is a well-known acceptor material for OPV application and PCBM film has absorption maximum at 333 nm. The **EV-DPP** film has UV-vis absorption maxima at 397 nm and 590 nm, which are much more red-shifted than the absorption maximum of PCBM. This clearly red-shifted UV-vis absorption of **EV-DPP** is indicative of good film aggregation. Although PCBM is widely used as an electron acceptor with a wide range of organic donor materials, it is known to be a non-ideal material for photovoltaic applications on account of its weak absorption in the visible spectrum [5]. From this point of view, DPP-containing materials such as **EV-DPP**, which have strong absorption in the low energy region, can be a good replacement for the PCBM acceptor in OPVs [12,13].

OPV cells were fabricated using the vinazene derivatives (**EV-DPP** and **EV-BT**) as electron acceptors. The device configuration was ITO/PEDOT:PSS/P3HT:oligomer/LiF/Al. **Figure 3** shows the current density versus voltage (J-V) curves for the P3HT:**EV-DPP** devices. In this work, the blending ratio of P3HT and **EV-DPP** was adjusted to 1:2. Our preliminary device achieved a power conversion efficiency of 0.02% with P3HT:**EV-DPP** blended film, while the device with P3HT:**EV-BT** did not perform in the device. The superior performance of **EV-DPP** over that of **EV-BT** can be explained by the preferable optical

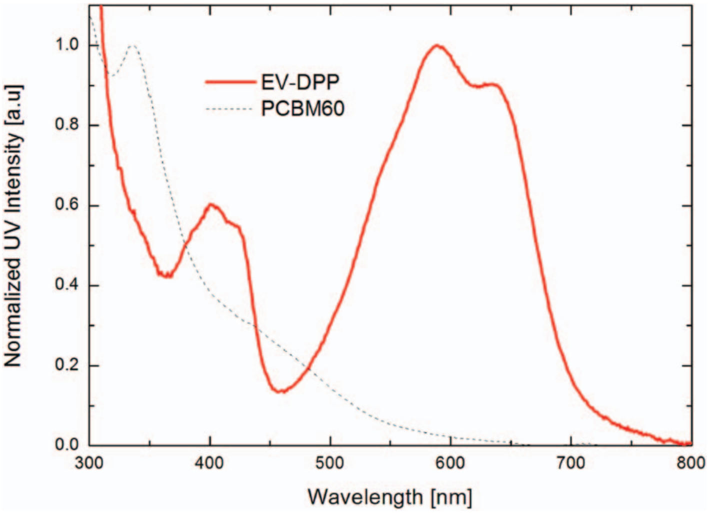


Figure 2. Normalized absorption spectra of the **EV-DPP** and PCBM films.

properties of **EV-DPP**, as shown in the UV-absorption spectra. Atomic force microscopy (AFM) image of the active layer (P3HT:**EV-DPP**) showed a phase-separated morphology (**Figure 4**). Because the **EV-BT** device from the literature had a power conversion efficiency of 0.75% (PCz:**EV-BT** = 30: 30) [5], our future work will be focused on the optimization of the device fabrication conditions and the use of different donor materials, such as polycarbazole.

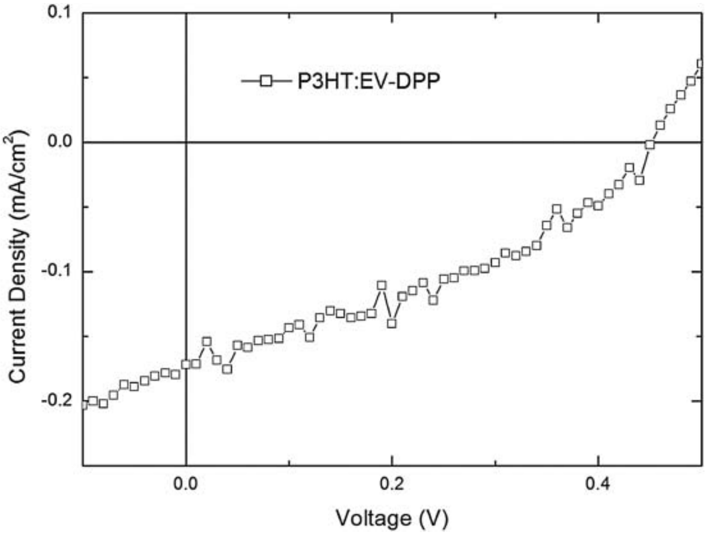


Figure 3. *J*-*V* curves of the P3HT: **EV-DPP** device.

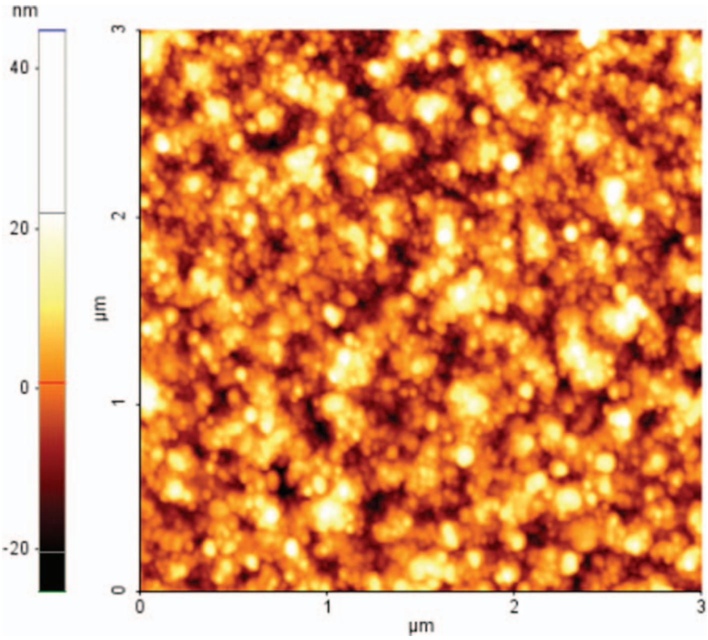


Figure 4. AFM image of the P3HT: **EV-DPP** film.

Conclusion

We synthesized a new vinazene-based small-molecule (**EV-DPP**) containing diketopyrrolopyrrole unit via Heck reaction. Through its optical and photovoltaic properties, we concluded that vinazene derivatives could be a new family of n-type conjugated materials in OPV application. In our preliminary device work, **EV-DPP** showed better performance compared to the reference material **EV-BT** due to the preferable absorption spectra and good phase separation.

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