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# Vinazene end-capped acceptor-donor-acceptor type small molecule for solution-processed organic solar cells

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ABSTRACT

An acceptor-donor-acceptor (A-D-A) type molecule based on dioctyltertthiophene-benzo[1,2-*b*:4,5-*b*′]dithiophene-dioctyltertthiophene central donor and vinazene terminal acceptor was designed and synthesized for solution-processed small molecule bulk-heterojunction (BHJ) solar cells. The thermal and optochemical properties, BHJ morphology and solar cell performance were investigated. The BHJ morphology was systematically optimized by thermal annealing, solvent vapor annealing, and the use of solvent additives. Processed by a combination of thermal annealing and solvent vapor annealing treatments, **V-BDT**:$PC_{71}BM$ device showed an optimized PCE of 3.73% with a $V_{OC}$ of 0.89 V, an $J_{SC}$ of 6.88 mA $cm^{-2}$ and a FF of 0.61.

## 1. Introduction

Solution-processed small-molecule organic solar cells (SMOSCs) have been studied intensively due to their intrinsic advantages of definite molecule structure, high purity, good batch-to-batch reproducibility, and ease of functionalization compared to their polymeric counterparts [1–4]. In recent years, numerous efforts have been devoted to suitable molecular design and device optimization, and impressive power conversion efficiencies (PCEs) of about 10% have been achieved for a single-junction solar cell, which is comparable with the polymer materials [5–9]. Bazan, Heeger and co-workers reported highly efficient $D^1$-A-$D^2$-A-$D^1$-type oligomers containing a dithieno[3,2-*b*:2′,3′-*d*]silole central unit flanked by two asymmetric electron deficient heterocycle moieties such as [1,2,5] thiadiazolo[3,4-*c*]pyridine, fluorinated benzothiadiazole [10–15]. By systematic optimization of the acceptor blocks in a series of donor molecules, PCEs up to 9% have been achieved [6,10]. We synthesized and investigated an $A^1$-D-$A^2$-D-$A^1$-type small molecule CNDPP consisting of a DPP central unit flanked by two dioctylterthiophene donor units, and found that solvent additive had a profound effect in the BHJ morphology, achieving a PCE of 5% [16]. Chen et al. developed a series of soluble oligothiophene-based A-D-A-type small molecular materials end-capping with various terminal units such as alkyl cyanoacetate, 3-ethylrhodanine, etc., reaching an excellent PCE of 10% [8,17–19]. Their design strategy could efficiently solve the poor film quality problem for general small molecules, and exhibits high carrier mobilities and wide absorptions with high coefficients. The replacement of the central thiophene with a benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT), forming a donor architecture of dioctyltertthiophene-BDT-dioctyltertthiophene (3T-BDT-3T), could enhance the coplanarity of the A-D-A structure as well as the electron density at the D unit [7,20–23]. They demonstrated that 3T-BDT-3T-based SMs have emerged as one of the most efficient and successful families of SM donor materials, exhibiting a PCE range of 8%–9% [22,23]. In addition, the terminal A units have strong influence on optoelectronic properties and the BHJ morphology and consequently on the photovoltaic performance [17,24]. For example,

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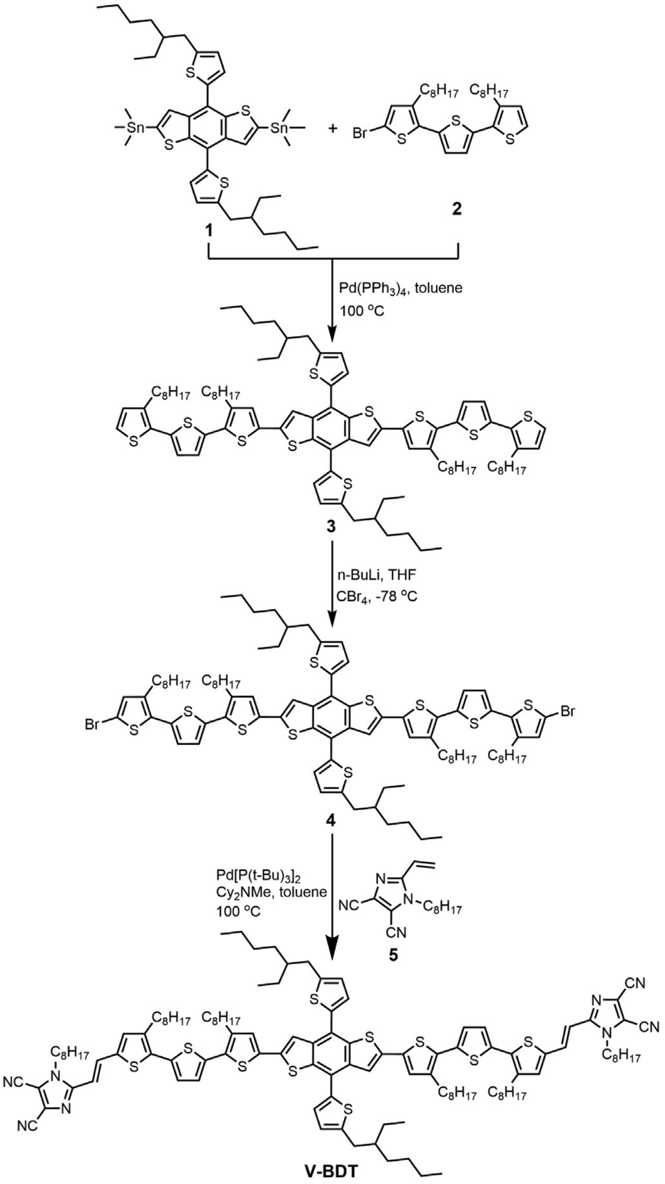
rhodanine-terminated oligomers showed a much improved short circuit current density ($J_{SC}$) than that of alkyl cyanoacetate-terminated compounds, and thus showing a significantly higher PCE [21].

In 2007, Sellinger et al. firstly introduced electron-withdrawing 2-vinyl-4,5-dicyanoimidazole (vinazene) unit to end-cap with fluorene, benzothiadiazole, etc., as the nonfullerene acceptor for solar cell applications, and VE-BT exhibited a PCE of 1.4% using poly[3-(4-*n*-octyl)-phenylthiophene] (POPT) as the donor [25–28]. Vinazene derivatives can be easily synthesized in high yields through one-step Heck coupling reactions with dibromoaromatics, and exhibit good solubility and film-forming properties by varying the alkyl chain of the *N*-position of imidazole. Those results reveal the great potential of this new class of end-capping acceptor moiety. Herein, we designed and synthesized a small molecule named **V-BDT** based on the 3T-BDT-3T architecture end-capped with vinazene units (Scheme 1). The thermal properties, optical and electrochemical properties were investigated. Bulk-heterojunction (BHJ) devices were fabricated using **V-BDT** as the donor and PCBM as the acceptor. And the devices were systematically optimized by thermal annealing (TA), solvent vapor annealing (SVA), as well as the use of solvent additives. Optimized PCE of 3.73% was achieved with an open circuit voltage ($V_{OC}$) of 0.89 V, a $J_{SC}$ of 6.88 mA cm$^{-2}$ and a fill factor (FF) of 0.61 after dual TA and SVA treatments.



**Scheme 1.** Synthetic route of **V-BDT**.

## 2. Experimental section

### 2.1. Materials

Tetrahydrofuran (THF) and toluene were dried over sodium and distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Commercial grade reagents were used without further purification unless otherwise stated. Compound **1** was purchased from SunaTech Inc. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS Heraeus Clevios PVP AI 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG. $PC_{61}BM$ was purchased from Solarmer Energy, Inc. $PC_{71}BM$ was purchased from Sigma-Aldrich Co. LLC. The monomer **2** and vinazene were synthesized according to the literatures [28,29].

### 2.2. General measurement and characterization

The $^{1}H$ NMR and $^{13}C$ NMR spectra of the synthesized chemicals were recorded on a Brucker Avance III 500 MHz NMR spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Brucker Autoflex Speed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 4000 instrument at a heating rate of 10 °C min$^{-1}$ under $N_2$ atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC 7 instrument with approximately 5 mg samples at a heating rate of 10 °C min$^{-1}$ under $N_2$. UV–vis spectra in chloroform solution and thin films were recorded on a Perkin Elmer Lambda 750 UV–vis spectrophotometer. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Time-resolved emission studies were performed with an Edinburgh FL 920 photon counting system with a hydrogen-filled lamp as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function, using a software package provided by Edinburgh Instruments. Cyclic voltammetry (CV) was performed at a scanning rate of 50 mV s $^{-1}$ on an AUTOLAB PGSTAT30 potentiostat/galvanostat system (Ecochemie, Netherlands), which was equipped with a three-electrode cell. The material was cast onto a glass carbon disk as a working electrode, and Pt wire was used as the counter electrode. Ag/Ag$^{+}$ was used as the reference electrode. Tetrabutylammonium hexafluorophosphate (n-$Bu_4NPF_6$, 0.1 mol L$^{-1}$) was used as the supporting electrolyte. The X-ray diffraction (XRD) spectrum was recorded by a D8 Advance XRD instrument operated with Cu K$\alpha$ radiation. Thin solid films for the XRD experiments were deposited on quartz glass substrates following the same procedures (conditions) as used for OPV devices fabrication. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. Thin film samples for AFM measurement were deposited on ITO/ZnO substrates following the same procedures as used for OPV devices fabrication. Transmission electron microscopy (TEM) tests were performed on a Tecnai G2 F20 S-Twin 200 kV field-emission electron microscope (FEI). Specimens for the TEM experiments were obtained by transferring the floated blend films from the water onto the 200 mesh copper grid.