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Wide bandgap copolymers with vertical benzodithiophene dicarboxylate for high-performance polymer solar cells with efficiency

up to 7.49%

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Abstract: In aiming to build novel wide band-gap high-performance photovoltaic donor materials, a vertical benzo[1,2-b:4,5-b]dithiophene-2,6-dicarboxylate (V-BDTC) with weak electron-withdrawing character was primarily developed. And its wide band-gap (WBG) copolymers of PV-BDTC1 and PV-BDTC2 were designed and synthesized, which contain a traditional electron-donating unit of 4,8-disubstituted benzo [1,2-b:4,5-b]dithiophene (BDT) derivative with diethylhexyloxy for the former and diethylhexylthiophenyl for the latter. It is found that the weak electron-withdrawing V-BDTC unit endows its copolymers with a WBG up to 2.09 eV and a deep HOMO energy level of ~5.67 eV. Furthermore, PV-BDTC2 exhibits much better photovoltaic properties than PV-BDTC1 in the solution-processing polymer solar cells (PSCs) with a higher opencircuit voltage (V_{oc}) of 1.03 V and a rising power conversion efficiency (PCE) of 7.49%. To the best of our knowledge, this PCE value here is the highest level recorded for copolymers with a WBG over 2.0 eV in the PSCs to date, along with a remarkable $V_{\rm oc}$ over 1.0 V. This work provides a feasible strategy to develop a novel promising electronwithdrawing building block and its high-performance WBG copolymers based on BDT unit.

Keywords: Vertical benzodithiophene carboxylate, Benzodithiophene, Copolymer, Organic solar cells.

Introduction

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Benzo [1,2-b:4,5-b'] dithiophene (BDT) has emerged as an effective building block for constructing organic photovoltaic materials since the first report in organic solar cells (OSCs).¹ As its inherent structural symmetry and rigid fused aromatic system are available to enhance electron delocalization and improve charge mobility,² numbers of efficient photovoltaic copolymers³⁻⁷ and small molecules (SMs)⁸⁻¹¹ have been developed by incorporating the electron-rich BDT units with other electron-deficient building blocks. High-efficiency photovoltaic materials have been obtained by design the BDT derivatives used as electron-donating building blocks in OSCs.¹²⁻¹⁵ For instance, 5-alkylthiophene-2-yl-substituted benzo[1,2-b:4,5-b] dithiophene (BDTT) moiety has been used extensively to construct two-dimensional (2D)-conjugated polymers in recent years. ^{12,16,17} In general, the derived BDT moieties are mostly modified with alkyl,^{18,19} alkoxy⁴, ²⁰ or aryl groups^{12, 13} at its 4, 8-positions, and incorporated into molecular backbone from its 2, 6-positions, which can be defined as paralleled BDT (P-BDT) unit as shown in Fig. 1. There are also a few reports by Yang et al. on photovoltaic materials based on the vertical BDT (V-BDT) moieties modified with electron-rich units from 2,6-positions. It further provided another potential way to construct the D-A alternating copolymers via incorporation from 4,8-positions of V-BDT.^{21, 22} The typical V-BDT based polymers displayed relatively low HOMO energy level (lower than -5.2 eV) and gave a promising power conversion efficiency (PCE) of 7.1% reported by Nallan et al., in which the PCE value is compared well with that of the reported P-BDT-directed copolymers.²³ While most of effort has been devoted to develop donor units, it is incredible that there is only

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one record that the BDT unit was modified as an electron-accepting building block to

construct conjugated polymers, in which two carboxylate groups were attached into 4, 8-positions of the BDT unit to form a paralleled BDT dicarboxylate (BDTC).²⁴ However, this BDTC-based polymers suffered from an increasing HOMO levels over – 4.8 eV and exhibited a limited PCEs with a lower V_{oc} value (~ 0.5 V) in their solar cells. Therefore, further effort is needed to modify the BDT unit to become electron-withdrawing unit and further obtain its copolymers with lower HOMO energy level. Inspired by the case of the vertical BDT as donor unit, which has made its polymers exhibit a sufficiently decreasing HOMO, in this work, we are full of interest to investigate whether the novel vertical BDTC unit is suitable to use as electron-withdrawing unit and construct its high-performance copolymers in PSCs.



Fig.1 Structural modifications of the BDT unit.

Towards this end, a novel accepter unit of vertical BDTC (V-BDTC) was developed by appending dicarboxylate onto 2, 6-positions of the BDT unit. By copolymerization path-

way of 4, 8-positions of the V-BDTC unit and diethylhexyloxy (or diethylhexylthiophenyl)-substituted BDT unit, two donor-acceptor alternating copolymers, PV-BDT-C1 and PV-BDTC2, have been designed and synthesized. As expected, both V-BDTCbased copolymers display extremely deep HOMO energy level of $-5.56 \sim -5.67$ eV and a very wide optical band gap of $2.07 \sim 2.09$ eV owing to the weak electron-withdrawing property of V-BDTC unit and relatively twisty polymer main chains. However, PV-BDTC2 exhibits more improving photovoltaic properties than PV-BDTC1 in the solution-processing polymer solar cells (PSCs) with a higher open-circuit voltage (V_{oc}) of 1.03 V and an increasing PCE of 7.49%. In principle, an efficient wide band-gap (WBG) polymer ($E_g \ge 1.9 \text{ eV}$) is essential for tandem solar cells to convert high-energy photons and provide high PCE in subcells.²⁵⁻²⁷ As WBG materials often suffer from an inherent defect of a narrow absorption, only a few of them have achieved high PCE over 7%,²⁸⁻³⁰ in particular when the band-gap exceeds 2.0 eV. We believe this WBG copolymer of PV-BDTC2 with high PCE of 7.49% has great potential to be used for tandem cell applications.

Experimental section

2.1 Measurements.

¹H NMR and ¹³C NMR spectra were collected on a Bruker DPX 400 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS) as internal standard at a resonance frequency of 400 MHz for ¹H and 100 MHz for ¹³C at room temperature. The molecular weight and polydispersity index (PDI) of polymers were determined by Waters 1515 gel permeation chromatography (GPC) using polystyrene as a standard and chloro-

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form (CHCl₃) as the eluent at room temperature and 1,2,4-trichlorobenzene as the eluent errorsset at 160 °C. Thermogravimetric analysis (TGA) was carried out using a Netzsch TG 209 analyzer at a heating rate of 10 °C min⁻¹ up to 600 °C. The differential scanning calorimetry (DSC) was measured on a TA DSCQ-10 instrument at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer. Cyclic voltammograms (CV) were recorded on a CHI 660 electrochemical workstation with a three-electrode setup contain -ing a working electrode of platinum rod, a counter electrode of platinum wire and a reference electrode of Ag/AgCl at scanning rate of 100 mV s⁻¹. The CV measurements were carried out in an anhydrous acetonitrile solution of 0.1 M nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) calibrated with a ferrocene/ferrocenyl couple (Fc/Fc⁺) at room temperature. The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO}) were calculated by the following equations:

$$E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.80) \quad (1)$$
$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\sigma}^{\text{opt}} \quad (2)$$

The theoretical study was performed on the 6-31G^{**} basis set in Gaussian 09 using the density functional theory (DFT), as approximated by the B3LYP. Surface morphologies were recorded by transmission electron microscopy (TEM), which was carried out on a FEI Tecnai T20 with LaB₆ operated at 200 kV. The polymer/PC₇₁BM blend films used as TEM measurement were placed onto a copper grid. Atomic force microscopy (AFM) images were obtained by using a NanoMan VS microscope in tapping-mode. The hole/electron mobilities were measured by using space-charge-limited current (SCLC)

6

method and determined by fitting the dark current to the model of a single carrier SCLC

using the Mott-Gurney equation.



Scheme 1 Synthetic routs of copolymers PV-BDTC1 and PV-BDTC2.

2.2 Materials.

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, TCI) and used without further purification unless stated otherwise. Toluene and tetra-

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hydrofuran (THF) were distilled according to common methods. Column chromategraphy was carried out with Merck silica gel (200-300 mesh). The vertical BDTC derivative of M1 used as one of two monomers was synthesized via four steps according to the literature methods: (1) Oxidization of Compound 1 by chromium trioxide in the presence of acetic anhydrideto give compound $2^{31}_{2}(2)$ Condensation of compound 2 with ethyl 2-mercaptoacetate to afford compound 3^{32} (3) Interesterification of compound 3with 2-butyloctanol to provide compound 4 in 74% yield; (4) Bromination of compound 4 with Br_2 in the presence of FeCl₃ to give the compound 5. Finally, the monomer M1 was obtained by the well-known Stille coupling reaction and then bromination by NBS according to the procedures reported previously.³³

2,5-Dibromobenzene-1,4-dicarbaldehyde (2)

To a suspension of compound 1 (3.9 g, 15mmol), acetic acid (20 mL) and acetic anhydride (40 mL) was added dropwise sulfuric acid (14 mL) at 0 °C under stirring. Then CrO_3 (6.0 g) was added in it in portions. The resulting mixture was stirred vigorously at this temperature for a further 3 h. The formed greenish slurry was poured into ice-water and filtered. The collected white solid was washed with water and cold methanol. The diacetate was then hydrolyzed by refluxing with a mixture of water (20 mL), ethanol (20 mL) and sulfuric acid (2 mL) overnight. After the mixture was cooled, the pale yellow solid was separated by filtration. It was purified by recrystallization from chloroform to afford compound 2 as a light yellow solid (2.0 g, yield 48.0%).¹H NMR (400 MHz, CDCl₃) δ 10.39 (s, 2H), 8.20 (s, 2H).¹³C NMR (100 MHz, CDCl₃) δ 10.39, 8.20, 7.31, 1.66, 0.04.

To a dry one-neck 250 mL flask filled with 100 mL DMF were added compound **2** (2.7g, 9.3 mmol), ethyl 2-mercaptoacetate (3.0 g, 28 mmol), K₂CO₃ (4.1 g, 30 mmol) and CuO nanopowder (180 mg, 0.3 mmol). Protected by N₂ flow, the reaction mixture was heated to 80 °C and stirred overnight. After cooled to room temperature, the mixture was poured into water. The aqueous phase was extracted with chloroform (3 × 25 mL). The organic layer was combined and dried over Na₂SO₄. The solvent was removed off under vacuum and the residue was purified by column chromatgraphy to provide compound **3** as a light yellow solid (1.2 g, yield 38.7%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 2H), 8.10 (s, 2H), 4.43 (d, *J* = 6.7 Hz, 4H), 1.69 – 1.31 (m, 6H).¹³C NMR (100 MHz, CDCl₃) δ 162.55, 139.23, 138.32, 135.87, 129.42, 119.34, 110.02, 61.88, 14.35.

Benzo[1,2-b:4,5-b']dithiophene-2,6-bis(2'-butyloctyl) dicarboxylate (4)

Titanium (IV) oxide bis(2,4-pentaedionate)(20mg,0.08 mmol) was added to a suspension of compound **3** (1.0 g, 3 mmol) and 2-butyloctanol(2.0 g, 11 mmol) in anhydrous toluene (40 mL). The mixture was heated to reflux for 10 h under Dean-Stark conditions. Then 5mL water was added to the Dean-Stark trap to help removal of the generated ethanol. Further titanium (IV) oxide bis(2,4-pentaedionate) (50 mg) and 2-butyloctanol (1.0 g) were added and the mixture was heated to reflux for further 10 h. After cooled to room temperature, the mixture was poured into water. The aqueous phase was extracted with dichloromethane (CH₂Cl₂, 3×25 mL) and the combined organic layer was dried over Na₂SO₄. The solvent was removed off under vacuum and residue was purified by column chromatography to afford compound **4** as a light yellow solid (1.36 g, yield

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74.1%). ¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 2H), 8.09 (s, 2H), 4.28 (d, J = 5.6 Hz, 2H), 1.47 – 1.12 (m, 32H), 0.89 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 162.64, 141.35, 139.27, 138.34, 136.72, 135.95, 129.89, 129.30, 122.31, 119.32, 69.88, 68.62, 66.72, 37.45, 34.15, 31.82, 31.44, 31.11, 29.63, 29.00, 27.78, 26.76, 23.74, 23.00, 22.66, 15.21, 14.10, 14.05. Elementary analysis calcd for C₃₆H₅₄O₄S₂: C
70.31, H 8.85, S 10.43. Found: C 71.74, H 8.83, S 10.17.

4,8-Dibromobenzo[1,2-b:4,5-b']dithiophene-2,6-bis(2'-butyloctyl)dicarboxylate (5)

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To a mixture of compound **4** (1.36 g, 2.2 mmol) and anhydrous FeCl₃ (150 mg) in chloroform (80mL), bromine (0.24 mL, 4.6 mmol) was added dropwise at room temperature protected from light. The mixture was refluxed overnight. Monitored by TLC, bromine was further added if it was necessary. The mixture was cooled down to room temperature and poured into aqueous of NaHSO₃ (100 mL). The aqueous solution was extracted with CH₂Cl₂ and the organic layer was collected. The solvent was removed off under vacuum and residue was purified by column chromatography using a mixture solvent of hexane and CH₂Cl₂ (4:1, *v*:*v*) as eluent to give **5** as a light yellow powder (1.35g, yield 80%). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 2H), 4.30 (d, *J* = 5.6 Hz, 4H), 1.82 (d, *J* = 5.6 Hz, 2H), 1.48 – 1.16 (m, 32H), 0.91 (dt, *J* = 15.6, 6.4 Hz, 12H).¹³C NMR (100 MHz, CDCl₃) δ 161.99, 141.20, 137.68, 136.93, 129.74, 111.46, 69.08, 37.39, 31.84, 31.42, 31.09, 29.62, 29.01, 26.76, 23.00, 22.68, 14.14, 14.09. Elementary analysis calcd for C₃₆H₅₂Br₂O₄S₂: C 55.96, H 6.68, S 8.30. Found: C 56.20, H 5.59, S 8.61.

4,8-Di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-bis(2'-butyloctyl)dicarbo -xylate (6)

/iew Article Online A solution of compound **5** (0.77 g, 1.0 mmol), tributyl(thiophen-2-yl)stannane^{O(101039/C6TA07364F} 3.0 mmol) and Pd(PPh₃)₄ (60 mg) in 60 mL toluene was degassed with nitrogen and heated to reflux for overnight. Cooled down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH₂Cl₂ (50 mL×3). The organic layer was washed with brine, dried over anhydrous MgSO4, then distillated to remove off the solvent. The residue was purified by column chromategraphy using a mixture solvent of hexane and CH_2Cl_2 (2:1, v:v) as eluent to give compound **6** as a yellow solid (0.72 g, yield 92.5%). ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 2H), 7.59 (d, J = 4.9 Hz, 2H), 7.51 (d, J = 3.0 Hz, 2H), 7.34 - 7.27 (m, 2H), 4.23 (d, J = 5.8 Hz, 4H), 1.77 (d, J = 4.9 Hz,2H), 1.63 (dd, J = 15.6, 8.2 Hz, 2H), 1.47 – 1.09 (m, 32H), 0.90 (dt, J = 15.2, 7.0 Hz, 12H).¹³C NMR (100 MHz, CDCl₃) δ 162.58, 141.27, 137.95, 137.51, 136.07, 129.72, 128.70, 127.77, 127.29, 126.23, 68.82, 37.37, 31.77, 31.45, 31.10, 29.59, 28.96, 28.29, 26.77, 26.72, 22.96, 22.64, 17.31, 14.09, 14.03, 13.58. MALDI-TOF MS m/z: calcd for C44H58 O4S4, 778.32; found, 778.25. Elementary analysis calcd for C44H58O4S4: C 67.82, H 7.50, S 16.46. Found: C 69.25, H 7.54, S 16.26.

4,8-Bis(5-bromothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-bis(2'-butyloctyl) dicarboxylate (M1)

To a solution of compound **6** (0.72 g, 0.93 mmol) dissolved in 30 mL THF was added *N*-bromosuccinimide (0.344 g, 1.95 mmol) in portions over a course of 30 min protected from light and stirred for another 24 h at room temperature. Then 100 mL water was added to quench the reaction. The mixture was extracted with CH_2Cl_2 . The resulting organic phase was washed with brine and dried over anhydrous MgSO₄. The solvent was

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removed off under reduced pressure and the residue was purified by column chromate – graphy on silica gel using a mixture solvent of hexane and CH₂Cl₂ (2:1, *v:v*) as eluent to give **M1** as an orange solid (0.70 g, yield 82.0%).¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 0.8 Hz, 2H), 7.29 (m, 4H), 4.27 (d, J = 5.8 Hz, 4H), 1.82 (s, 2H), 1.51 – 1.18 (m, 32H), 0.91 (dd, J = 12.3, 6.7 Hz, 12H).¹³C NMR (100 MHz, CDCl₃) δ 162.36, 141.13, 139.25, 137.37, 136.42, 130.68, 129.25, 129.17, 125.46, 114.53, 68.99, 37.31, 31.80, 31.41, 31.08, 29.61, 28.96, 26.72, 23.00, 22.68, 14.15, 14.10. Elementary analysis calcd for C₄₄H₅₆Br₂O₄S₄: C 56.40, H 6.02, S 13.69. Found: C 58.97, H 5.94, S 15.07.

Synthesis of PV-BDTC1

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In a dry 25 mL flask, monomer **M1** (187 mg, 0.2 mmol), BDT(154 mg, 0.2 mmol), Pd₂(dba)₃ (3.2 mg) and P(*o*-Tol)₃ (6.1 mg) were dissolved in a degassed toluene (6 mL). The mixture was stirred and heated for 24 h at 100 °C. Cooled down to room temperature, it was dropped into acetone to form polymer precipitation. The resulting polymer was collected by filtration through 0.45 μ m Teflon filter and was resolved in toluene, then quickly passed through a short column. Its further purification was carried out by Soxhlet-extraction with methanol, diethyl ether, and then chloroform. The collected chloroform fraction was concentrated to a small volume and precipitated by adding dropwise this solution into acetone. Finally, the polymer was collected by filtration using a 0.45 μ m Teflon filter and dried under vacuum at 40 °C overnight (200 mg, yield 90%). Molecular weight: $M_n = 31.7$ kDa; $M_w/M_n = 2.9$.

Synthesis of PV-BDTC2

Using a similar polymerization procedure of PV-BDTC1 described above to prepare

PV-BDTC2. A mixture of **M1** (140 mg, 0.15 mmol) and **BDTT** (136 mg, 0.15 mmol) D^{1100}_{1000} (130 mg) was polymerized for 24 h to give **PV-BDTC2** (150 mg, yield 73%). Molecular weight: $M_{\rm n} = 35.2 \text{ kDa}; M_{\rm w}/M_{\rm n} = 1.7.$

2.3 Solar Cells Fabrication and Characterization

A traditional bulk heterojunction sandwich structure was used in the solar cell fabrication. The ITO/glass substrates were ultrasonic-cleaned by detergent, deionizer water, acetone and isopropanol for 15 min each in sequence. The resulting substrates were dried under a stream of nitrogen and subjected to the treatment of Ar/O_2 plasma for 5 min. A layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) film (40 nm) was spin-coated on ITO and baked at 150 °C for 10 min in a glove box. A blend solution of polymeric donor materials (PV-BDTC1 or PV-BDTC2) and [6,6]-phenyl-C-71-butyric acid methyl ester (PC₇₁BM) in o-dichlorobenzene (DCB) was then spun cast onto the PEDOT:PSS layer. A mixing concentration of PV-BDTC1 or PV-BDTC2 is 10 mg mL⁻¹ in DCB. The photoactive layer with an optimal thickness of 90 nm was prepared with different polymers/PC₇₁BM weight ratios and DIO concentrations at 1800 rpm for 40 s. Finally, 20 nm calcium and 100 nm aluminum films were successively deposited on the active layer through a shadow mask at a vacuum pressure of~ 5×10^{-5} Pa to form the top electrode. The active area was 0.04 cm² for each cell. EQE spectra were performed in a QEX10 solar cell measurement system. The hole mobilities of PV-BDTC2 in both pure and blend films were investigated by employing the hole-only devices with a structure of $ITO/MoO_3/polymer$ (or polymer/ $PC_{71}BM$ blend)/ MoO₃/Al. The electron mobilities of blend films were performed in the electron-only

devices with a structure of ITO/Al/polymer/PC71BM blend/Al.

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RESULTS AND DISCUSSION

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3.1 Synthesis and Thermal properties

The synthetic route of both V-BDTC based copolymers of PV-BDTC1 and PV-BDTC2 is summarized in Scheme 1. They were obtained in good yields over 70% by Stille coupling reaction of trimethylstannyl-substituted benzo[1,2-b:4,5-b']dithiophene derivatives of BDTSnMe₃ or BDTTSnMe₃ with monomer M1. Both polymers are soluble in common organic solvents such as chloroform, toluene and DCB at room temperature. Number-average molecular weight (M_n) and polydispersity (PDI= M_w/M_n) of PV-BDTC1 and PV-BDTC2 are 31.7 kDa (2.93) and 35.2 kDa (1.70) at room temperature, respective -ly. However, the resulting M_n values are decreased to 25.0 kDa for PV-BDTC1 with a PDI value of 1.96 and 32.0 kDa for PV-BDTC2 with a PDI value of 2.04 at 160 °C due to the different molecular aggregation effect. The larger M_n (PDI) difference value between room temperature and 160 °C is exhibited for PV-BDTC1. It implies that PV-BDTC1 has stronger molecular aggregation than PV-BDTC2 in room temperature.

Polymers	Solution		Film			<i>E</i>	<i>E</i>	T.
	λ _{abs} (nm)	ε_{\max}^{a} (Lg ⁻¹ cm ⁻¹)	λ _{abs} (nm)	fwhm (nm) ^b	E_{g}^{opt} (eV) ^c	(eV)	$(eV)^{d}$	^{I}d (°C)
PV-BDTC1	483	35	520	186	2.07	-5.56	-3.49	326
PV-BDTC2	479	34	514	177	2.09	-5.67	-3.58	357

Table 1 Optical, electrochemical and thermal properties of PV-BDTC1 and PV-BDTC2.

^{*a*}Absorption coefficient from the peak at long wavelength. ^{*b*}Full width at half-maximum. ^{*c*} Band gap estimated from optical absorption band edge of the film. ^{*d*} E_{LUMO} (eV) = $E_{HOMO} + E_g^{opt}$.

The thermal properties of PV-BDTC1 and PV-BDTC2 are evaluated with TGA and

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DSC. The recorded TGA and DSC curves are shown in Fig. 2a and Fig. 2b, respectively. The corresponding data are summarized in Table 1. High decomposition temperatures (T_d) of 326 °C for PV-BDTC1 and 357 °C for PV-BDTC2 are observed during the heating process at a 5% weight loss, respectively. It indicates that PV-BDTC2 exhibits higher thermal stability than PV-BDTC1, that because alkoxy groups are eliminated earlier than aryl groups from their parent BDT unit, which is consistent with the observations for other similar systems.^{34,35} On the other hand, no distinct endothermic and exothermic peaks are exhibited for both polymers during the heating and cooling processes between 50 and 300 °C, as shown in Fig. 2b. It implies that both PV-BDTC1 and PV-BDTC2 tend to present an amorphous state.



Fig. 2 TGA (a) and DSC (b) curves of PV-BDTC1 and PV-BDTC2.

3.2 Optical Properties

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Fig.3 displays the UV–vis absorption spectra of PV-BDTC1 and PV-BDTC2 in dilute solutions and in their thin films. The absorption maximums are listed in Table 1. Similar absorption spectra are observed for both polymers. Furthermore, these absorption profiles exhibit a red-shifted peak in low-lying energy region by about 35 nm from in solution to in solid state. In solutions, PV-BDTC1 and PV-BDTC2 display an absorption peak at 483 nm with a molar extinction coefficient (ε_{max}) of 35 Lg⁻¹ cm⁻¹ and 479 nm with a ε_{max} value

of 34 Lg⁻¹ cm⁻¹, respectively. Obviously, PV-BDTC2 shows a slightly blue-shifted absorption profile compared to PV-BDTC1 in this solution state. It implies that PV-BDTC1 with alkoxyl side chain adopts a slightly more coplanar orientation than PV-BDTC2 with aryl side chain on the BDT unit, which is further supported by theoretical calculation in Table S1 (see electron supporting information, ESI).



Fig. 3 UV-vis spectra of PV-BDTC1 and PV-BDTC2 in CHCl₃ solutions and thin films.

The optical band gaps are estimated to be 2.07 eV for PV-BDTC1 and 2.09 eV for PV-BDTC2 from their absorption band edges (E_g^{opt}) in thin films. Moreover, a very broad absorption window in a range of 300-600 nm with a full width at half-maximum (fwhm) of 186 nm for PV-BDTC1 and 177 nm for PV-BDTC2 is observed at the same time. Some investigations have shown that wide band-gap (WBG) and low band-gap (LBG) polymers can be simultaneously used in polymer tandem solar cells to obtain high performance solar cells, in which the high-energy and the low-energy photons are efficiently absorbed by WBG and LBG polymers, respectively.^{26,36,37} In this work, such high E_{g}^{opt} over 2.0 eV and absorption feature should endow their great potential to be used as novel WBG materials.

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In order to explore the influence of the acceptor of $PC_{71}BM$ on the absorption of them polymeric blend films, the absorption spectra of the polymer/PC71BM blend films were measured and shown in Fig. S1 (see ESI). In comparison with absorption spectra of the pure films and the blend films in Figure 3 and Figure S1, it is found that the acceptor of PC71BM plays an important role in tuning photo-response region from 600 nm to 700 nm for the blend films, which should result in extension of EQE response. The similar phenomenon was observed in other reported blend films. The large extension of photo response here should be related to the polymer structure and the D-A interaction between the polymer and PC₇₁BM.³⁸

3.3 Electrochemical Properties

Fig. 4 depicts the oxidative curves of PV-BDTC1 and PV-BDTC2 measured by the CV method. A reversible oxidative behavior is observed with an onset of oxidation potential at 0.76 V for PV-BDTC1 and 0.87 V for PV-BDTC2 vs Fc/Fc⁺, respectively. According to these onsets of oxidation and the energy level of ferrocene (4.8 eV below vacuum level),³⁹ the HOMO energy level is estimated at -5.56 eV for PV-BDTC1 and -5.67 eV for PV-BDTC2.

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Fig. 4 The oxidation curves of PV-BDTC1 and PV-BDTC2.

The electrochemical results reveal that attaching two carboxylate substitutions on the BDT unit has made their polymers exhibit lower HOMO energy levels around – 5.6 eV, which is available to increase open-circuit voltages (V_{oc}) for their photovoltaic devices. Similar phenomena were also recorded in the literatures.^{40,41} On the other hand, the LUMO energy levels were calculated to be –3.49 and –3.58 eV for PV-BDTC1 and PV-BDTC2, respectively, based on the equation $E_{LUMO} = E_{HOMO} + E_g^{opt}$. The offset of LUMO energy level between one of polymers and PC₇₁BM is ~0.4 eV, which should be able to provide sufficient driving force for exciton dissociation.⁴²

3.4 Theoretical Calculations

To further understand the relationship among structures and energy levels of polymers, we performed theoretical simulations for their molecular geometries and frontier orbitals with the hybrid density functional theory (DFT) at the B3LYP/6-31G(d) level using Gaussian 09W. It is suggested this method would over delocalize the wave-functions in conjugated systems and favor more planar structures, but the calculated results are still

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comparable to some extent as both polymers share the same molecular backbone.^{DOI:49.1679/C6TA07364F} optimal geometries and wave functions (HOMO and LUMO) of PV-BDTC1 and PV-BDTC2 are shown in Fig. 5. And dihedral angles of the optimal geometries of PV-BDTC1 and PV-BDTC2 are summarized in Table S1 (see ESI). It shows that the electron densities of LUMO and HOMO are most localized on electron- deficient V-BDTC unit and electron-rich BDT moiety, respectively. In comparison with the LUMO and LUMO +1 orbitals of both polymers, there is little change in the electron density distribution, which reveals the electron-accepting feature of V-BDTC moiety resulting from the substitution of dicarboxylate functional group on vertical BDT unit. A similar phenomenon is also found from HOMO to HOMO-1 owing to the electron-rich property of BDT unit. Compared to their optimal geometries and dihedral angles of two polymers, it is further found that the dihedral angles between donor BDT and thiophene space is 20.39° in PV-BDTC1, and 27.36° in PV-BDTC2. It further confirms that PV-BDTC2 has a slightly twisty polymeric main chain, which is consistent with those results obtained from UVvis spectra and CV properties.

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PV-BDTC1	PV-BDTC2
Side view	Side view
47.98° 02 24.13° 04 04 04 20.39° 41.30° Top view	47.99° 02 03 04 27.36° 25.76° Top view



Fig. 5 Optimized molecular geometries, molecular frontier orbitals of LUMO+1, LUMO, HOMO, and HOMO-1 for PV-BDTC1 and PV-BDTC2.

3.5 Photovoltaic Properties

The processing conditions of the bulk-heterojunction polymer solar cells based on polymers of PV-BDTC1 and PV-BDTC2 were preliminarily optimized by varying polymer/PC₇₁BM weight ratios from 1:1 to 1:2.5 and 1,8-diiodoctane (DIO) additive con

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-centrations from 1 wt% to 4 wt% under an illumination of AM1.5G simulated solar light at 100 mW/cm². The recorded photovolatic parameters of these solar cells are summarized in Table S1 and S2 (see ESI). It is shown that an optimized PV-BDTC1/ PC₇₁BM (or PV-BDTC2/PC₇₁BM) weight ratio was 1:2. However, the DIO additive made different influnce on photovoltaic performance in the PV-BDTC1 and PV-BDTC2 based cells. An optimized DIO concentration of 3 wt% was obtained in the PV-BDTC2based cells only. In contrast, adding DIO made the PV-BDTC1-based cells exhibit lower photovoltaic properties. Fig. 6 depicts the typical current density-voltage (J-V) characteristics of two polymers in these devices at optimized processing conditions and the resulting device parameters are summarized in Table 2. A PCE of 3.25% with a $V_{\rm oc}$ of 0.93 V in the PV-BDTC1-based cells and an increasing PCE of 5.62% with a V_{oc} of 1.04 V in the PV-BDTC2-based cells are observed at an optimized polymer/PC71BM weight ratio of 1:2 without any post treatment. When 3% DIO additive is added, a sufficiently enhanced PCE of 7.49% with greater J_{sc} of 10.37 mA cm⁻² and fill factor (FF) of 70.0% is achieved for the PV-BDTC2-based devices except for a slightly decreased V_{oc} of 1.03 V. However, this V_{oc} value over 1.0 V in the PV-BDTC2-based devices is still higher among the reported PSCs, which would be ascribed to its deeper HOMO energy levels of -5.67 eV. To the best of our knowledge, this PCE value in the PV-BDTC2- based devices represents the highest value so far for PSCs based on polymers with bandgaps over 2.0 eV.

Table 2. Photovoltaic parameters of the optimized polymer/PCBM-based solar cells based on PV-BDTC1 and PV-BDTC2.

22

Polymer/accepter	D/A ratio	V _{oc} (V)	$\frac{J_{\rm sc}^a}{(\rm mAcm^{-2})}$	FF (%)	PCE (%)	$J_{\rm sc}^{b}$ DOI: 10.1 (mA cm ⁻²)	View Article Online PCE(TAVE) ^{64F} (%)
PV-BDTC1/PC71BM	1:2	0.93	5.90	59.39	3.25	5.75	3.15
PV-BDTC1/PC61BM	1:2	0.91	5.99	39.5	2.25	5.88	2.13
PV-BDTC2/PC71BM	1:2	1.04	8.93	60.8	5.61	8.82	5.53
PV-BDTC2/PC71BM ^d	1:2	1.03	10.37	70.0	7.49	10.10	7.33
PV-BDTC2/PC ₆₁ BM ^d	1:2	1.02	9.87	61.2	6.32	9.55	6.18
${}^{a}J_{sc}$ measured from solar additive.	cells. ^b J	sc estimate	d from EQE	spectra. '	² Obtained	from 20 devices	<i>^d</i> 3%DIO

Additionally, an average PCE of 7.33% was further obtained in twenty PV-BDTC2 based devices, indicating this class of devices has good reproducibility. In order to explore the influence of PCBM acceptor, the photovoltaic properties of the polymer/ PC₆₁BM devices were also examined, and depicted in Table 2 and Figure S2 (see ESI). A lower PCE value was observed in both polymer/ $PC_{61}BM$ devices owing to its weaker absorption in visible region compared to the polymer/PC₇₁BM devices. In comparison with all these devices, the PV-BDTC2/PC71BM device exhibited the best photovoltaic properties whether the acceptor material is $PC_{71}BM$ or $PC_{61}BM$. The recorded EQE curves of the optimized polymer/PC71BM and polymer/PC61BM blend films under illumination of monochromatic light, as respectively shown in Fig. 6b and Fig. S2, further support why PV-BDTC2 exhibit better photovoltaic performance than PV-BDTC1 in the devices. The photo-response wave-length ranges of the EQE curves were well-consistent with the UV-vis absorption ranges for the polymer/ $PC_{71}BM$ blend films (see Fig. S1). The maximum EQE values of 78% and 50% are respectively observed for the PV-BDTC2/PC71BM and PV-BDTC1/PC71BM blend films, which is higher than those corres

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-ponding values for the PV-BDTC2/PC₆₁BM and PV-BDTC1/PC₆₁BM blend films. The measured J_{sc} values of 10.10 and 5.75 mA/cm² respectively in the PV-BDTC2 and PV-BDTC1 based devices here are agreed well with the J_{sc} values estimated from the EQE charcteristics. Therefore, the higher photo response efficiency for the PV-BDTC2/ PC₇₁BM blend film can promote its solar cells exhibit higher J_{sc} values, then better photovoltaic performance.



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Fig. 6 (a) J - V curves of the optimized polymer/PC₇₁BM-based solar cells under a

view Article Online view Article Online Simulated AM 1.5 G irradiation (100 mW cm⁻²); (b) *EQE* curves of the optimized

polymer/PC₇₁BM-based solar cells under illumination of monochromatic light.

3.6 Film Morphology and Charge mobility

To analyze the origin of photovoltaic performance differences between the PV -BDTC1- and PV-BDTC2-based solar cells, we carried out the investigation on their mor -phologies of the polymer/PC₇₁BM blend films by TEM. Fig. 7 shows the TEM images of these polymer/PC₇₁BM blend films with/without 3 wt% DIO solvent additive at a polymer/PC₇₁BM weight ratio of 1:2. It is seen that nanoscale phase separation of polymer and PC₇₁BM is observed in both polymer/PC₇₁BM blend films without DIO additive. The fibrillar-like light regions are attributed to the polymer aggregation.⁴⁴



Fig. 7 TEM images of the polymers/PC₇₁BM blend films at a D/A weight ratio of $1:2^{.1039/C6TA07364F}$ with or without DIO additive.

It is clear that the PV-BDTC2/PC₇₁BM blend film exhibits smaller domain size than the PV-BDTC1/PC₇₁BM blend film, which can provide larger interface area for efficient exciton diffusion and charge separation. This can be explained why the PV-BDTC2based devices show higher J_{sc} and FF than the PV-BDTC1-based devices without the DIO additive. When DIO is employed, for the case of PV-BDTC1, the size of polymer/ PC₇₁BM domains instead increases, which should limit the donor/acceptor interface and result in a decreased performance.^{45,46} In contrast, for the case of PV-BDTC2, a more uniform image with better bicontinuous morphology is observed under the presence of 3 wt% DIO, this is also confirmed by the atomic force microscopy (AFM) images featured with interpenetrating network (see ESI figure S2), thus giving rise to a remarkably increased *FF* and PCE values.

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To further understand the device performance differences of the PV-BDTC2-based solar cells with/without DIO additive, charge transport behavior for hole and electron mobilities were deduced from the space-charge-limited current (SCLC) measurements.⁴⁷ Fig. 8 shows the current–voltage (*J–V*) characteristics and SCLC fittings of these holeand electron-only devices. The corresponding hole and electron mobilities are summarized in Table 3. A hole mobility (μ_h) of $8.2 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and an electron mobility (μ_e) of $2.28 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, as well as a μ_e/μ_h value of 2.77 are observed in the PV-BDTC2/ PC₇₁BM based hole- and electron-only devices, respectively. While 3 wt% DIO was added, the μ_h and μ_e values are increased to 9.7 ×10⁻⁴ and 2.32 × 10⁻³ cm² \text{V}^{-1} \text{s}^{-1} with a

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 $J_{\rm sc}$ and overall performance.^{48,49}



Fig. 8 *J*–*V* curve of the hole/electron-only PV-BDTC2/PC₇₁BM-based devices: (a) hole-only characteristics of pure films and blend films (with or without 3% DIO). (b) electron-only characteristics of the blend films (with or without 3% DIO).

Table 3 Hole and electron mobilities of PV-BDTC2/PC71BM in the hole- and

Samples	Hole mobility $\mu_h/cm^2V^{-1}S^{-1}$	Electron mobility $\mu_e/cm^2V^{-1}S^{-1}$	μ_{e}/μ_{h}
PV-BDTC2	2.26×10^{-3}		
PV-BDTC2:PC71BM	8.22×10^{-4}	2.28×10^{-3}	2.77
PV-BDTC2:PC71BM (3% DIO)	9.72×10^{-4}	2.32×10^{-3}	2.38

Conclusion

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In summary, a novel vertical dicarboxylate substituted benzodithiophene of V-BDTC was primarily used as an electron-withdrawing building block to construct D-A copolymers. Its copolymers of PV-BDTC1 and PV-BDTC2 with alkoxy- and thiophenylsubstituted benzodithiophene (BDT) units have been obtained, respectively. Wide band gaps of 2.07~2.09 eV with remarkable deep HOMO levels of -5.56 to -5.67 eV were observed in both copolymers. However, the better photovoltaic properties were exhibited in the PV-BDTC2-based solar cells with an impressive PCE up to 7.49% and high $V_{\rm oc}$ of 1.03 V at a PV-BDTC2/PC₇₁BM weight ratio of 1:2 and a DIO concentration of 3 wt%. Its relatively wide optical band gap over 2.0 eV with high absorption coefficient, high hole mobility, much balanced hole/electron mobility, and excellent film morphology of the PV-BDTC2/PC71BM blend film are responsible for the remarkably improved photovoltaic performance of the PV-BDTC2-based solar cells. The PCE maximum with a high $V_{\rm oc}$ over 1.0 V obtained in this work is the highest level recorded for the conventional BHJ PSCs based on WBG (>2.0 eV) polymers. The work provides a feasible strategy to develop a novel family of the BDT-based D-A copolymers. It further indicates that

V-BDTC is a potential electron-deficient building block in D-A-type copolymers and ^{View Article Online} PV-BDTC2 is a promising WBG donor material for high-performance PSCs. Interestingly, there remains considerable scope to fully explore the potential of the V-BDTC-based

copolymers in photovoltaic applications, such as choosing more suitable donor units to construct novel copolymers, optimization of the device processing technique and use in tandem solar cells.

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Wide bandgap copolymers with vertical benzodithiophene dicarboxylate for high-performance polymer solar cells with efficiency up to 7.49%

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A novel vertical carboxylate functionalized benzodithiophene V-BDTC unit was designed as an election-accepting block to build D-A type copolymers. Two wide band gap polymers of PV-BDTC1and PV-BDTC2 were prepared with V-BDTC unit. A high V_{oc} of 1.03 V and a significant PCE of 7.49% were achieved based on this kind of polymers.

