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• ARTICLES •

A new oligobenzodithiophene end-capped with 3-ethyl-rhodanine groups for organic solar cells with high open-circuit voltage

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A new solution-processable small-molecule donor material, named DRBDT₃, cor gobenzo[1,2-b:4,5-b'] dithiophene as the backbone and 3-ethyl-rhodanine as the end-capped group has been do ynthesized for application in d and organic photovoltaic cells. The oligobenzodithiophene derivative exhibits osorption m 300 to 640 nm. The film of $\times 10^{-4} \text{ cm}^2$ ∇^{-1} s⁻¹. The new molecule shows a DRBDT₃ shows highly long-range ordering assembly and high mobility of deep highest-occupied molecular orbital energy level. The device based on DRB the donor and PC71BM as the acceptor oltage exhibits a power conversion efficiency of 4.09% with a high ope 9 V under AM.1.5G illumination (100 $mWcm^{-2}$).

Keywords: small molecule, organic solar cell, oligober

1 Introduction

Organic photovoltaic cells (OPVs) ive attracted an induring th creasing amount of attention past ded de, due to their advantages of solution abili veight, low cost, and potential in the f flexible devices rica [1-9]. Many efforts have been de to improve the power conversion efficiency (PCE) polymer-based OPVs (P-OPVs) [10-15] PCEs over 🐝 have been achieved [16-21] in the past few years. Compared to polymer materials, small molecules exhibit competitive advantages such as well-defined structure and therefore less batch-to-batch variation, easier band structure control, etc. [22-31]. To date, solution-processed small-molecule-based OPVs (SM-OPVs) have achieved PCEs higher than 8% [32-35] through design and synthesis of new small- molecule materials and optimization of device fabrication [36-41].

Benzo[1,2-b:4,5-b'] dithiophene (BDT) as an electron-donating unit has been widely used in P-OPVs h open-circuit voltage

[3,42-45]. The symmetric and plain conjugated structure could facilitate the formation of π - π stacking. Devices based on BDT-based polymer are able to afford high PCEs of more than 9% [16, 17]. A series of BDT-based polymers including homopolymers and copolymers has been reported by Yang's group [40]. Among these BDT-based polymers, BDT-based homopolymer shows the deepest highest-occupied molecular orbital (HOMO) energy level, which could lead to a high Voc in OPV devices because open circuit voltage (V_{oc}) mainly depends on the difference between the HOMO energy level of the donor material and the lowest unoccupied molecular orbital (LUMO) energy level of the acceptor material [5, 46]. John P. Ferraris et al. reported a BDT-based homopolymer, named O-PBDT, which exhibits a PCE of 1.56% with a high V_{oc} of 0.83 V and a relatively low short-circuit current density (J_{sc}) of 4.18 mA cm⁻² [47]. The relatively low J_{sc} of O-PBDT is believed to be due to the narrow absorption band with absorption onset at 560 nm. To enhance the J_{sc} , it is essential to reduce the band gap, which is decided by the difference between the HOMO energy level and the LUMO energy level of the donor material. Decreasing the LUMO energy level of the donor molecule while retaining the deep HOMO energy level could be an efficient way to obtain high V_{oc} and J_{sc} , and thus high PCEs. Another homopolymer, poly(3-hexylthiophene) (P3HT) which has been widely investigated in P-OPV, also shows a large band gap. By reducing the number of conjugated units of P3HT and introducing electron-accepting end-groups, a series of high- photovoltaic-performance oligothiophene derivatives have been designed and synthesized [48]. Importantly, these oligothiophene derivatives show low band gaps, a result that could be attributed to the introduction of electron-accepting end groups. Inspired by the achievement of low-band-gap oligothiophene-derivative SM-OPVs, we think that introducing electro-accepting terminal units to oligobenzo[1,2-b:4,5-b'] dithiophene could be an efficient way to extend the absorption band of BDT-based donor material, retain the deep HOMO energy level, and thereby achieve a high PCE.

Therefore, we designed and synthesized a new solutionprocessable small-molecule-donor material, named DRBDT₃, that comprises three benzo[1,2-b:4,5-b'] dithiophene units end-capped with 3-ethyl-rhodanine (Scheme 1). This new oligobenzodithiophene derivative shows a broad absorption, from 300 to 640 nm. Importantly, compared with O-PBDT [47], DRBDT₃ indeed shows a reducing LUMO energy level of -3.40 eV while retaining the deep HOMO energy level of -5.34 eV. The OPV device based on the DRBDT₃:PC₇₁BM-blend film shows a PCE of 4.09% with a high V_{oc} of 0.99V, a J_{sc} of 8.26 mA cm⁻², and factor (FF) of 0.50. Note that the device based on olig zo[1,2-b:4,5-b'] dithiophene shows a higher V_{oc} a BDT-based homopolymer, and thus affords bet photovo taic performance than the BDT-based homop ymer (F of 1.56% [47]). These results demonst ligot zo[1,2-b:4,5-b'] dithiophene derivative could be ing donor materials for SM-OPVs.



2 Experimental

2.1 General experimental

All reactions and manipulations were carried out under argon atmosphere using standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification.

2.2 Synthesis procedures

The synthesis routes of DRBDT₃ are shown in Scheme 2. 2,6-dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene (1) and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyltoxy) benzo[1,2-b:4,5-b'] dithiophene (3) were synthesized according to the literature [42].



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of compound 1 (4.20 g, 6.94 mmol) in anhydrous solutio mL) was degassed twice with argon and cooled to solution of n-BuLi (3.5 mL, 2 M in cyclohexane, 7 s added dropwise to the THF solution and the mol) hixture was stirred at -78°C for 1 h under argon atmosphere. Subsequently, anhydrous DMF (1.0 mL, 13.3 mmol) was added dropwise at -78°C. Then the cooling bath was removed and the mixture was stirred at room temperature overnight. The mixture was then poured into water (200 mL) and extracted with ethyl acetate; next, the combined organic layer was washed with water and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure by a rotating evaporator and the resulting oil was purified by silica gel chromatography (petroleum ether and dichloromethane = 3:1 as eluent) to give a red oil (2.15 g, 3.83 mmol, 56 % yield). ¹H NMR (400 MHz, CDCl₃): δ 10.09 (s, 1H), 8.14 (s, 1H), 7.46 (s, 1H), 4.22 (d, 2H), 4.13 (d, 2H), 1.81 (m, 2H), 1.70-1.45(m, 8H), 1.38(m, 8H), 1.01(t, 6H), 0.94(t, 6H). 13 C NMR(100 MHz, CDCl3): δ 184.43, 146.05, 143.58, 142.70, 134.34, 131.95, 131.44, 130.20, 130.08, 123.29, 117.57, 40.63, 30.35, 29.16, 23.79, 23.09, 14.14, 11.29. MS (MALDI-TOF): calcd for C₂₇H₃₇BrO₃S₂ [M⁺], 552.14; found: 552.08.

Synthesis of DCHOBDT₃

A solution of 2 (1.57 g, 2.84 mmol) and 3 (1 g, 1.29 mmol) in dry toluene (40 mL) was degassed twice with argon,

followed by the addition of Pd(PPh₃)₄ (30 mg, 0.026 mmol). After stirring at 100°C for 24 h under argon, the mixture was poured into water (200mL) and extracted with chloroform. The organic layer was washed with water and then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using a mixture of petroleum and dichloromethane ether (1:2) as eluant to afford compound DCHOBDT₃ (1.22 g, 68%). ¹H NMR (400 MHz, CDCl₃): δ 9.94 (s, 2H), 7.95 (s, 2H), 7.44 (s, 4H), 4.20 (m, 12H), 1.90-1.40 (m, 54H), 1.35-0.90 (m, 36H). ¹³C NMR(100 MHz, CDCl₃): δ 184.24, 146.44, 144.34, 144.25, 142.35, 138.74, 136.25, 135.39, 132.62, 131.77, 131.46, 130.59, 129.41, 128.44, 118.60, 117.59, 40.71, 30.49, 30.45, 30.37, 29.73, 29.32, 29.29, 29.24, 23.89, 23.83, 23.23, 23.18, 14.33, 14.27, 14.24, 11.41, 11.39. MS (MALDI-TOF): calcd for $C_{80}H_{110}O_8S_6$ [M⁺], 1390.65; found: 1390.65.

Synthesis of DRBDT₃

To a CHCl3 (60 mL, anhydrous) solution of DCHOBDT₃ (0.30 g, 0.215 mmol), 3-ethyl-rhodanine (0.50 g, 3.10 mmol) and three drops of piperidine were added. The resulting solution was refluxed at 70°C for 12 h under argon. Then the mixture was poured into water (200mL) and extracted with chloroform. The organic layer was washed with water and then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using a mixture of petroleun and dichloromethane ether (1:1) as eluant; next, the q solid was recrystallized using hexane and chlorofor afford DRBDT₃ (0.23 g, 64%). ¹H NMR (400 MJ δ 7.71 (s, 2H), 7.49 (s, 2H), 7.29 (s, 2H), 23 (s, 2H) 4.25-4.05 (m, 16H), 1.90-1.40 (m, 54H), 26 (t, 6 1.20-1.10 (m, 18H), 1.10-1.00 (m, 18 MHz, CDCl₃): 192.01, 166.98, 145 1, 143.96 138.19, 136.68, 136.15, 134.01, 13 8, 131. 131.14, 129.20, 128.90, 128.17, 123. 117.31. 29.38, 40.72, 39.86, 30.51, 30.47 30.4 29.34, 29.31, 23.87, 23.30, 23.22, 14.41, 14 2.29, 11.43. MS $_{0}N_{2}O_{8}S_{10}$ [M⁺], 1676.72; (MALDI-TOF): calcd for C_{90} found: 1676.68.

2.4 Measurements and instruments

The H¹ and C¹³ nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Autoflex III instrument. The transmission-electron microscope (TEM) investigation was performed on a Philips Technical G2 F20 at 200 kV. The thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 10°C min⁻¹ heating rate. UV–vis spectra were obtained with

a JASCO V-570 spectrophotometer. X-ray diffraction (XRD) experiments were performed on a Bruker D8 FOCUS X-ray

diffractometer with Cu–K α radiation ($\lambda = 1.5406$ Å) at a generator voltage of 40 kV and a current of 40 mA. Atomic-force microscope (AFM) investigation was performed using Bruker MultiMode 8 in tapping mode. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium pherophorus hexafluoride (Bu₄NPF₆, 0.1 M) in dichloromethan was used as the supporting electrolyte; the scan rate mV s⁻¹. Hole mobility was measured by a space-cha ge-limite current (SCLC) method using a diode ration **W**f ITO/PEDOT:PSS/ conf donor:PC71BM/4 ark current density in the range of 0fitting the results to а harge-lim spaceform where SCLC is described by:

$$\frac{e_r \mu_0 V^2}{8L^3} \exp(0.89\beta \sqrt{\frac{V}{L}})$$

If the provided the second density; *L* is the film thickness of the active Leer; μ_0 is the hole mobility; ε_r is the relative lielectric constant of the transport medium; ε_0 is the provided the provided of the space (8.85×10^{-12} F m⁻¹); $V (= V_{appl} - V_{bi})$ is the internal voltage of the device; V_{appl} is the applied ltage of the device; and V_{bi} is the built-in voltage due to a relative work-function difference of the two electrodes.

The current density-voltage (*J-V*) characteristics of th ephotovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination-simulated 100 mW cm⁻² AM1.5G irradiation using a xenon-lamp-based solar simulator (Oriel 96000, AM1.5G) in an argon-filled glove box. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode. The external quantum efficiency (EQE) value of the encapsulated device was obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air. Photon flux was determined by a calibrated silicon photodiode.

2.5 Fabrication of organic solar cells

The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/donor:acceptor/ZnO/Al. The ITOcoated glass substrates were cleaned by ultrasonic treatment in detergent followed by deionized water, acetone, and isopropyl alcohol, under ultrasonication for 15 min each, and then dried by a nitrogen flow. A thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 µm) was spin-coated (3000 rpm, ca. 40 nm thick) onto the ITO surface. After being baked at 150°C for 20 min, the substrates were transferred into an argon-filled glove box. Then the active layer was spin-coated from different ratios of donor (8 mg/mL):PC₇₁BM-blend chloroform solution at 1700 rpm for 20 s each. Next, ZnO particle suspension [49] was used to spin-coat the ZnO layer on top of the active layers. Thermal annealing was carried out on a digitally controlled hot plate at various temperatures after ZnO spin-coating in an argon-filled glove box. Finally, a 50 nm Al layer was deposited onto the ZnO film under high vacuum (< 2×10^{-4} Pa). The thickness of the ZnO and the active layer were measured using a Dektak 150 profilometer. The effective area of each cell was 4 mm², defined by masks for the solar-cell devices discussed in this work.

3 Results and discussion

3.1 Synthesis and thermal property



Figure 1 TGA curves of DRBDT₃ with a heating rate of $^{\circ}C/min$ un N_2 atmosphere.

As shown in Scheme 1, the intermed as DCHO synthesized by a Stille coupling read p 2 and 3 on betw under argon atmosphere in presend f Pd(P $n_3)_4$ as the catalyst for 24 h. The targe sule D was then m prepared by the Knoevenagel n of DCHOBDT₃ on with 3-ethyl-rhodanine under at on atmosphere in the presence of piperidine as the catalyst or 12 h. DRBDT₃ shows good solubility in common solvents. The thermal property of DRBDT₃ was investigated by TGA. As shown in Figure 1, compound DRBDT₃ exhibited good thermal stability with 5% weight-loss temperature at 337°C under N_2 atmosphere.

Table 1 Optical and electrochemical data of DRBDT₃.

3.2 Optical properties and electrochemical properties



right 2 a) Absolution spectra of B-CO 1₃ in chlorolorm solution and in as-cast film; b) Cyce ; yes annuar am of DRBDT₃ in a dichloromethane solution of $0.1 \text{ mol } L^{-1}$ where a scan rate of 100 mV s⁻¹.

ption spectra of DRBDT₃ in diluted chloroform UV olid state are shown in Figure 2a. DRBDT₃ in solution and plution shows a maximum absorption peak at 536 nm paximal coefficient of 1.20×10^5 M⁻¹cm⁻¹. The vith a RBDT film cast from CHCl₃ shows a red-shifted maxiorption peak at 572 nm with a broader absorption m 300 to 640 nm. The optical band gap of DRBDT₃ nđ estimated from the onset of the absorption spectra. A cyclic voltammogram was used to investigate the electrochemical properties of DRBDT₃. Ferrocene/ferrocenium of the (Fc/Fc^{+}) redox couple (4.8 eV below the vacuum level) was used as the internal calibration. The HOMO and LUMO energy levels of DRBDT₃ were estimated based on the onset oxidation potential and the onset reduction potential of the redox curve as shown in Figure 2b; they are -5.34 and -3.40 eV, respectively. Note that, compared with O-PBDT, the new oligobenzodithiphene derivative end-capped with 3-ethyl-rhodanine indeed shows a decreasing LUMO energy level, which also demonstrates that the LUMO energy level of the A-D-A-structure small molecule mainly depends on the acceptor moiety. The electrochemical band gap of DRBDT₃ is 1.94 eV, which is consistent with the value of the optical band gap. The data for the optical and electrochemical properties are summarized in Table 1.

Compound	λ_{max} solution/nm	€ solution/M ⁻¹ cm ⁻¹	λ _{max} film/nm	ε film∕cm⁻¹	E_{g}^{opt} film/eV	$E_g^{\ CV}/eV$	HOMO/eV	LUMO/eV
DRBDT ₃	536	1.20×10 ⁵	572	6.8×10 ⁴	1.97	1.94	-5.34	-3.40



Figure 3 a) XRD pattern of pristine DRBI film spin om CHCl3 onto the glass substrate. b) J-V character only device tics of a h PC₇₁BM/Au with the configuration ITO/PED)/DR BD PSS (30 (30 nm). c) J-V characteristics of the configu--only ration ITO/Al (30 nm)/DRBDT3:P 30 nn e solid line represents the fit using a model of single with field-independent mobility. The $J_{\rm D}$ -V characteristics are cted for the built-in voltage $V_{\rm bi}$ that arises from the work-function different between the contacts.

The structural order of the pristine DRBDT₃ film spin-coated from CHCl₃ solution was investigated by XRD analysis. As shown in Figure 3a, we observed a strong diffraction peak at 2θ =5.49°, corresponding to a d₁₀₀-spacing value of 16.09 Å for first order. The d₁₀₀-spacing value is the distance between the planes of the main conjugation chains of DRBDT₃, which are separated by alkyloxy side-chains. The second- and third-order diffraction peaks, at 2θ =11.05° and 16.65°, are also clearly evident. The results of XRD show that DRBDT₃ has some long-range ordering at the solid state. The hole mobility of DRBDT₃/PC₇₁BM (w/w, 1:0.8) blend film was measured by SCLC method. As plotted in Figures 3b and 3c, the calculated hole mobility and electron mobility of the blend films were $1.21 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ and $1.43 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$, respectively. The blend films showed balanced hole and electron transport which could be beneficial for charge collection. The high hole mobility of DRBDT₃ was ascribed to the strong and ordered packing of DRBDT₃, as demonstrated by the XRD results above.

3.4 Photovoltaic properties



a) J-V curve of optimized device based on DRBDT₃:PC₇₁BM (.8, w): b) EQE of devices based on DRBDT₃:PC₇₁BM (1:0.8, w/w) or without thermal annealing.

Table 2 Device-performance parameters of the BHJ solar cells based on DRBDT₃:PC₇₁BM-blend films with different donor:acceptor blend ratios.

Blend ratio	V_{oc}/V	$J_{sc}/mA \text{ cm}^{-2}$	FF	PCE (%)
1:0.5	0.98	7.90	0.48	3.72
1:0.8	0.99	8.26	0.50	4.09
1:1	0.99	7.96	0.49	3.86

SM-OPV devices were fabricated using DRBDT₃ as the electron donor material and PC₇₁BM as the electron acceptor material with а conventional device structure of glass/ITO/PEDOT:PSS/DRBDT₃:PC₇₁BM/ZnO/Al, using the solution spin-coating process. The typical J-V curve of the test results is displayed in Figure 4a and the results are summarized in Table 2. The optimized device based on DRBDT₃:PC₇₁BM-blend film shows a PCE of 4.09% with a high $V_{\rm oc}$ of 0.99 V, a J_{sc} of 8.26 mA cm⁻² and FF of 0.50. The high V_{oc} of the device based on DRBDT₃ is consistent with its deep HOMO energy level. The external quantum efficiency (EQE) spectrum of the optimized device is shown in Figure 4b. From the EQE curve, we can see that the DRBDT₃-based device exhibits a moderate response, from 330 nm to 640 nm, with the maximum EQE value of 58% at 420 nm.

3.5 Morphology of the DRBDT₃:PC₇₁BM-blend film



Figure 5 AFM (a) and TEM (b) images of DRBDT₃:PC₇₁BM-blend film.

The morphology of DRBDT₃:PC₇₁BM blend film was investigated by atomic-force microscopy (AFM) and transmission-electron microscopy (TEM). As shown in Figure 5a, root mean square (*rms*) roughness of DRBDT₃:PC₇₁BM blend film was 1.72 nm. The surface of the blend film was uniform and smooth, indicating the good film quality of the DRBDT₃:PC₇₁BM-blend film. From Figure 5b, we can see that the DRBDT₃:PC₇₁BM fil exhibited an interpenetrating network with the widt of 50~60 nm. The domain size is much larger than the exi charge diffusion length (10~20 nm), [50] lengths to a relatively low photocurrent, which is consistent with the result of EQE.

4 Conclusions

In conclusion, we designed and nthes a new oligobenzo[1,2-b:4,5-b'] dithiophe e comprising of three benzo[1,2-b:4,5-b'] dithic nene units as the central building block and 3-ethyl-rhodat pe as terminal units. The new molecule shows a broad absorption, from 300 to 640 nm, and a deep HOMO energy level of -5.34 eV. The optimal device based on DRBDT₃/PC₇₁BM-blend film shows a PCE of 4.09% with a high V_{oc} of 0.99V, a short-circuit current of 8.26 mA cm⁻², and a fill factor of 0.50. Furthermore, this new oligobenzo[1,2-b:4,5-b'] dithiophene derivative exhibits a much better photovoltaic performance than BDTbased homopolymer. These results demonstrate that oligobenzodithiophene derivatives would be potential smallmolecule donor materials for OPVs.

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