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Novel Wide Band Gap Polymers Based on Dithienobenzoxadiazole for Polymer Solar Cells with High Open Circuit Voltages over 1 V[†]

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A new monomer dithieno-[3',2':3,4;2",3":5,6]benzo[1,2-c]xadiazole (fDTBO) is first used as the electron-deficient acceptor to build D-A copolymers in photovoltaic field. Two polymers PBDTT-fDTBO and PBDTO-fDTBO are consisted of fDTBO with thienyl-substituted-benzodithiophene (BDTT) or alkoxy-substituted benzodithiophene (BDTO). Both polymers show deep HOMO around -5.5eV with wide band gap of over 1.9 eV. The polymer solar cells (PSCs) based on two polymers both show over 1V high open circuit voltage (V_{oc}) independent on polymer/PCBM ratios and solvent additives content in PSCs active layer. The power conversion efficiency (PCE) based on PBDTT-fDTBO devices is 4.5% for single junction PSCs, and these polymer can be applied in tandem PSCs due to its wide band gap (up to 1.99 eV). This work demonstrates that fDTBO unit is a promising building block to design high V_{oc} wide band gap photovoltaic polymer.

1 Introduction

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The bulk heterojunction polymer solar cells based on blending of polymer and PCBM have exhibited high PCE of over 10% for single polymer solar cells (PSCs) in recent years¹⁻⁴. In order to achieve higher PCE, the tandem solar cells based on wide band gap (WBG) polymers were needed ⁵⁶⁷ and it may be the most promising route to reach PCE up to 15%.^{8,9} Thus, More and more WBG polymers were synthesized ¹⁰⁻¹³. Generally, the PSCs based on WBG polymers cannot provide very high power conversion efficiency due to the limited light absorption ¹⁴⁻¹⁸. The PCE of PSCs is determined by short-circuit current density (J_{sc}), fill factor (*FF*) and V_{oc}^{19-21} .

Increasing V_{oc} of PSCs is usually as a simple and feasible method to increase the PCE. The V_{oc} is proportional to energy difference between the lowest unoccupied molecular orbital (LUMO) of the fullerene derivatives and the highest occupied molecular orbital (HOMO) of polymers.⁹ Higher V_{oc} may be achieved by deeper HOMO of polymer as the fullerene derivatives remains the same ²². Deep HOMO of polymer also may improve the oxidative stability and decrease energy loss of PSCs devices ^{23, 24}. Typically, there are two molecular structure design strategies to obtain deep HOMO polymer. One is introducing the electron-withdrawing atom (fluorine, sulfur or oxygen) to the conjugated polymer backbone^{25 26}. The other is decreasing the effective conjugate degree by incorporating large side groups or increasing the sinuosity of conjugated backbone ^{27, 28}. Dithienyl-2,1,3-benzothiadiazole (DTBT) is a well-known electron-withdrawing acceptor, and it was first used for D-A copolymer by Andersson et al. in 2003²⁹. As shown in Chart 1, Wei You et al. synthesized a new monomer 4,7-bis (5-bromothiophen-2-yl)-5,6-diuorobenzo-[c][1,2,5]thiadiazole (DTffBT) by introducing F to DTBT for D-A co-polymer with a deeper HOMO.¹³ Li et al. used fusion strategy to synthesis a new monomer dithieno-[3',2':3,4; 2", 3":5,6]benzo[1,2-c] [1,2,5] thiadiazole (fDTBT) by fusing two thienyl units on the benzothiadiazole (BT), and they got a high $V_{\rm oc}$ of 0.84 based on polymer with fDTBT and benzodith iophene (BDT) derivative ³⁰.

The band gap is an important parameter for PSCs and it is tuned by electron-rich donor and electron-deficient acceptor unit ³¹. BDT is a good donor unit for high photovoltaic performance, and some WBG polymers based on BDT unit were synthesized and showed high PCEs ³²⁻³⁴. N-alkylthieno [3,4-c]pyrrole-4,6-dione(TPD)^{33, 35-37} derivatives, 2-alkyl-benzo[d] [1,2,3]triazole(TAZ)³⁸ derivatives, thiazolo[5,4d]thiazole(TTz) ^{39, ⁴⁰ derivatives and 1,3-bis (thiophen-2-yl)-5,7-bis(2-ethyl-hexyl) benzo-[1,2-c:4,5-c]dithiophene-4,8-dione (BDD) ⁴¹ et al were main acceptor donors for BDT-based WBG polymers. To the best of our knowledge, the PSCs of wide band gap polymers based on BDT unit rarely show the *V_{oc}* over 1V with high PCE.}

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Hou and coworkers synthesized a new polymer with BDT-F and BDD, and the $V_{\rm oc}$ based on the new polymer was 1.02 V which was reduced to 0.96 V after adding the solvent additives.

The fDTBT was a new promising electron-accepting moiety with good π -electron delocalization and planarity, and we can further get dithieno-[3',2':3,4; 2",3":5,6]benzo[1,2c]zoxadiaz ole (fDTBO) with stronger intermolecular interactions and electron-withdrawing ability by replacing sulfur with oxygen (Chart 1) .The fDTBO unit is first used in photovoltaic field in this work. Compared with sulfur atom, the oxygen had higher electronegativity and electron withdrawing ability, so higher $V_{\rm oc}$ exceeding 1 V can be achieved. In this work, we use fDTBO to build two D-A copolymers: PBDTT-fDTBO and PBDTO-fDTBO. As shown in Scheme 1, two polymers were synthesized by stille coupling with fDTBO and BDTT or BDTO. As a result, PBDTT-fDTBO and PBDTO-fDTBO show high $V_{\rm oc}$ with 1.04V and 1.02V, with wide band gap of 1.99 eV and 1.91 eV, respectively. What's more, the $V_{\rm oc}$ of PSCs devices can maintain above 1V during different polymers/PCBM ratios and solvent additives contents optimization. BHJ PSCs based on PBDTT-fDTBO obtained V_{oc} of 1.04V with decent PCE around 4.52%. We believe the fDTBO unit will be a promising building block to achieve high photovoltaic performances due to its good planarity and strong electron withdrawing.









2 Results and discussion

2.1 Synthesis and Characterization

The synthetic routes of fDTBO, PBDTT-fDTBO and PBDTOfDTBO are shown in Scheme 1. The detailed synthetic routes were described in experimental section and the monomer fDTBO was synthesized according to reported method ⁴². Polymer PBDTT-fDTBO and PBDTO-fDTBO were synthesized by Stille coupling reaction using $Pd_2(dba)_3/P(o-tol)_3$ as catalysts and 5 ml toluene as the solvent. The color of two polymers was both deep red. Both of polymers could only be slowly dissolved in DCB at 90 °C because of their poor solubility. The number-average molecular weights of PBDTT-fDTBO and PBDTO-fDTBO were 88.4kDa and 89.3kDa, with a polydispersity index of 1.40 and 1.93, respectively.

2.2 Thermal analysis

The thermal properties of PBDTT-fDTBO and PBDTO-fDTBO were analyzed by thermogravimetric analysis (TGA). As is shown in Fig. 1, the decomposition temperatures (5% weight loss) of PBDTT-fDTBO and PBDTO-fDTBO are 394 $^{\circ}$ C and 310 $^{\circ}$ C, respectively. This result indicts that both polymers show high thermal stability for PSCs applications.

2.3 Optical properties

The ultraviolet-visible absorption spectra (UV-vis) of these two polymers in thin films and dilute DCB solution is shown in Fig.2. The corresponding optical data is listed in Table 1. In DCB solution, the absorption peak wavelength of PBDTT-fDTBO and PBDTO-fDTBO is at 536 and 530 nm, respectively, which is attributed to intramolecular charge transfer (ICT)⁴³ between BDT unit and fDTBO unit. The sharp shoulder peak of PBDTT-fDTBO and PBDTO-fDTBO at 580 nm and 568 nm is due to the aggregations of the polymer chains. Compared with the absorption spetra in DCB solution, two polymers in thin film

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Table 1.Optical absorption properties and molecular levels of two polymers

polymers	λ _{max} film (nm)	λ _{max} solution (nm)	λ _{onset} film (eV)	Eg ^{opt} (eV)	E _{ox} (V)	HOMO ^{cv} (eV)	LUMO ^{cv} (eV)	E _g DFT (eV)	HOMO ^{DFT} (eV)	LUMO ^{DFT} (eV)
PBDTT-fDTBO	369, 546 ,596	361, 534, 580	648	1.91	1.23	-5.64	-3.73	2.63	-5.48	-2.85
PBDTO-fDTBO	392, 532, 571	403, 530, 564	623	1.99	1.15	-5.56	-3.57	2.74	-5.39	-2.65



Fig.2 UV-vis absorption spectra of PBDTT-fDTBO and PBDTO-fDTBO in dilute DCB solution and in thin films

have stronger intermolecular force, and show about 13 nm red-shifted. In addition, the localized π - π * transitions can bring about absorption peak in short-wavelength area. The absorption spectra of PBDTT-fDTBO showed red-shifted compared with the spectra of PBDTO-fDTBO which may be ascribed to the 2D conjugated structures of the polymer PBDTT-fDTBO. The optical band gap (E_g^{opt}) of PBDTT-fDTBO and PBDTO-fDTBO are 1.91 eV and 1.99 eV respectively, which were calculated from their absorption onset of thin film.

2.4 Electrochemical properties

The electrochemical properties of two polymers were measured by cyclic voltammetry (CV) .The CV curves are shown in Fig.3 and detailed onset oxidation potentials (E_{ox}) and HOMO , LUMO energy levels are shown in Table 1. The E_{ox} of PBDTT-fDTBO and PBDTO-fDTBO were 1.23V and 1.15V vs saturated calomel electrode (SCE), respectively. Half-wave potential of theferrocene/ferrocenium (Fc/Fc⁺) redox couple was as the internal standard, and the potential ($E_{1/2}^{(Fc/Fc^+)}$) vs SCE was measured to be 0.39 V. The HOMO of PBDTT-fDTBO





and PBDTO-fDTBO were calculated by $E_{HOMO} = -e(E_{ox}+4.8-E_{1/2}^{(Fc/Fc^+)})$ and the corresponding LUMO were calculated by HOMO and $E_g^{opt 44}$. These two polymers both had deep HOMO energy levels regardless of the donor unit, which were mainly attributed to the strong electron-withdrawing group fDTBO unit. Thus high V_{oc} of PSCs could be expected when polymers based on fDTBO unit blended with PCBM.

2.5 Theoretical Calculations

In order to understand the optoelectronic properties of two polymers, density functional theory (DFT) calculations were carried out using Gaussian 09 program. The optimized molecular geometries were recognized as the minimum energy conformations when calculating vibrational frequencies at the same level. Some methods were implemented to simplify the calculations, such as choosing one repeating unit and replacing alky side chains by methyl groups. The optimized molecular geometry and frontier molecular orbitals are shown in Fig. 4 and detailed energy levels are depicted in Table 1. The simulated data from the DFT calculations coincided well with

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experimental results estimated from the cyclic voltammograms. Two polymers showed similar distributions of electron density .The LUMO was mainly delocalized in the fDTBO unit, while the HOMO was located both in donor unit and acceptor unit.

2.6 Hole mobility

Hole mobility is an another import parameter influencing the PSCs performances. It was measured by space-charge-limitedcurrent (SCLC) with polymer and $PC_{71}BM$ blend film. As shown in Fig. 5, the hole mobility of PBDTT-fDTBO and PBDTO-fDTBO is 3.11×10^{-4} and $2.90 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The polymer PBDTT-fDTBO has higher hole mobility than PBDTO-fDTBO, which may induce the PSCs device based on PBDTT-fDTBO showing higher performances. The hole mobilities values of two polymers make a great difference, which should be partly attributed to the difference of their structures. Previous reports have revealed that 2D-structure can enhance the hole mobility effectively ^{48,49}. The polymer PBDTT-fDTBO is based on alkylthienyl-substituted BDT (2D structure) and PBDTOfDTBO is based on alkoxyl-substituted BDT, thus PBDTT-fDTBO exhibits higher hole mobility.



Fig.4 Optimized molecular geometries and frontier molecular orbitals from DFT calculations on PBDTT-fDTBO and PBDTO-fDTBO



Fig.5 Current density (J)-voltage (V) curves for PBDTT-fDTBO and PBDTO-fDTBO based devices.

Table	2	Photovoltaic	properties	of	two	polymers	with differe	nt
polyme	er/P	C ₇₁ BM ratios w	ithout Chloro	onap	hthale	ene (GN) 0.10)39/C6RA0795	1B

polymer	D/A	$V_{\rm oc}(V)$	J _{sc} (mA/cm ²)	FF(%)	PCE _{max} /PCE _{ave} (%)
PBDTT-fDTBO	1:1	1.07	2.72	40.13	1.16/1.10
PBDTT-fDTBO	1:2	1.05	5.53	49.57	2.88/2.75
PBDTT-fDTBO	1:3	1.06	3.56	53.59	2.02/1.87
PBDTO-fDTBO	1:1	1.03	3.78	43.66	1.69/1.55
PBDTO-fDTBO	1:2	1.02	5.41	50.67	2.80/2.75
PBDTO-fDTBO	1:3	1.00	3.30	41.38	1.36/1.25

Table 3 Photovoltaic properties of two polymers/ $PC_{71}BM$ (1:2) with different CN amounts

polymer	CN	V _{oc} (V)	J _{sc} (mA/cm ²)	FF(%)	PCE _{max} /PCE _{ave} (%)
PBDTT-fDTBO	0	1.05	5.53	49.57	2.88/2.75
PBDTT-fDTBO	1	1.02	5.32	40.12	2.18/2.13
PBDTT-fDTBO	2	1.03	5.33	48.38	2.66/2.51
PBDTT-fDTBO	3	1.04	7.95	54.59	4.52/4.36
PBDTT-fDTBO	4	1.04	7.57	55.02	4.33/4.23
PBDTO-fDTBO	0	1.02	5.41	50.67	2.80/2.75
PBDTO-fDTBO	1	1.01	3.33	45.15	1.52/1.48
PBDTO-fDTBO	2	1.00	3.30	44.26	1.46/1.40
PBDTO-fDTBO	3	1.01	3.31	46.65	1.48/1.39

2.7 Photovoltaic properties

The bulk heterojunction(BHJ) polymer solar cells were fabricated with the traditional structure of ITO/PEDOT (poly (3,4-ethylenedioxythiophene)):PSS(poly(styrenesulfonate))/

PBDTT-fDTBO(PBDTO-fDTBO):PC₇₁BM/Ca/Al to investigate the photovoltaic properties of two polymers. These polymers blended with PC₇₁BM were heated to 80 °C for 1 hour before spin-coated as the active layer due to their poor solubility. As shown in Table 2, 3 and Fig.6, different ratios of polymer/PC₇₁BM and different proportions of solvent additives (CN) ⁴⁵ had obvious influences on the photovoltaic properties of PSCs devices. With different D/A ratios and the proportion of CN devices performances were tested, and the optimal D/A ratios of two polymers were both probed to be 1:2 and the optimal proportion of CN of PBDTT-fDTBO and PBDTO-fDTBO was 3% and 0% , respectively. In addition, the V_{oc} of PSCs based on two polymers both showed over 1V with different polymer /PC₇₁BM ratios and CN proportions .

The best photovoltaic performance of PSCs device based on polymer PBDTT-fDTBO was 4.52% with a V_{oc} of 1.04 V, a J_{sc} of 7.95 mA/cm² and *FF* of 54.59%, while the PCE of PBDTO-fDTBO based PSCs device reached maximum value of 2.88%, with a V_{oc} of 1.05V, J_{sc} of 5.53mA/cm² and *FF* of 49.57%. Wei-Shi Li ³⁰ group synthesized several polymers based on BDT and DTBT (fDTBT) and the polymer PBDT₁₆-fDTBT achieved the best photovoltaic performance. The PSCs based on PBDT₂₀-DTBT showed maximum PCE of 3.98% with V_{oc} of 0.76V, and the PSCs based on PBDT₁₆-fDTBT showed maximum PCE of 4.50% with V_{oc} of 0.85V. Thus, the V_{oc} of our polymer PBDTT-fDTBO





Fig.6 J-V curves of PSCs based on PBDTT-fDTBO and PBDTO-fDTBO with different CN amounts.

or PBDTO-fDTBO based device was nearly 0.2 V higher than $V_{\rm oc}$ of PBDT₁₆-fDTBT, which agreed well with our expectation. Furthermore, the higher $V_{\rm oc}$ of PBDTT-fDTBO based PSCs agreed well with CV curves.

The external quantum efficiency (EQE) spectra of the optimized polymer solar cells based on PBDTT-fDTBO and PBDTO-fDTBO are shown in Fig.7. The EQE curves exhibited absorption region from 300 to 640 nm. The maximum EQE of PBDTT-fDTBO based PSCs devices was 58.63% at 480nm, while the maximum EQE of PBDTO-fDTBO based PSCs devices was 43.76% at 530 nm. The calculated current densities from the EQE curves were 8.02 and 5.40 mA/cm² of PBDTT-fDTBO and PBDTO-fDTBO respectively, which were consistent with the J_{sc} obtained by J-V curves.

2.8 Morphology Characterization

The influences of CN on the morphology characterizations of the blended films were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM).



Fig.7 EQE curves of the PSCs based on PBDTT-fDTBO:PC₇₁BM (1:2) and PBDTO-fDTBO:PC₇₁BM (1:2).

As shown in Fig.8 (a, b, e, f), the surface of PBDTT-fDTBO /PC₇₁BM blended film without CN was smooth with the rootmean-square (RMS) roughness value of 0.7 nm. While 3% CN was added, the RMS value of the blended film was 1.35 nm due to larger domains. Meanwhile, the surface of PBDTO-fDTBO/PC71BM blended film without CN and with 3% CN showed similar RMS value of 0.91 nm and 0.89 nm, respectively. As shown in Fig.8 (c, d, g, h), the aggregations of PC₇₁BM and PBDTO-fDTBO without CN was more evident than those with CN, while the aggregations of polymer PBDTT-fDTBO and PC₇₁BM became evident after adding 3% CN. (Fig.8 (a, b, e, f)). What's more, the better surface morphology and phase separation of PBDTT-fDTBO was another reason for its higher hole mobility.

3 Conclusion

In summary, new monomer fDTBO is first used as acceptor to build D-A copolymers in photovoltaic polymer field. The PSCs based on two polymers both showed high V_{oc} of above 1 V, and the PSCs devices can remained 1 V high V_{oc} during polymer/PCBM ratios and solvent additives content optimization. Compared with the polymer PBDT16-fDTBT, the V_{oc} of our polymer increased nearly 0.2 V. Therefore, this may provide us a new strategy by replacing the sulfur atom with oxygen for achieving stable higher V_{oc} photovoltaic devices.

4 Experimental section

4.1 Materials

All solvents and chemicals were purchased by reagent companies, and all of the solvents except toluene and tetrahy drofuran (THF) were used directly. Toluene and THF were used

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Fig.8 AFM (a, b) topography and TEM (c, d) images of the PBDTT-fDTBO:PC₇₁BM (1:2) without and with 3% CN AFM (e, f) topography and TEM (g, h) images of the PBDTO-fDTBO:PC₇₁BM (1:2) without and with 3% CN

for water sensitive reactions after dried by sodium under argon atmosphere. Compound BDTT, BDTO, fDTBO were synthesized according to reported methods. $^{\rm 42,\,46,\,47}$

Synthesis of PBDTT-fDTBO and PBDTO-fDTBO The 4.1.1mixture of compound fDTBO (78.01mg,0.2mmol), BDTT (242.63mg,0.2mmol) or BDTO (221.79,0.2mmol), Pd2dba3 (2.67 mg), P(o-tol)₃ (5.34 mg) and toluene (5ml) were added into 25ml flask, and then it was cooled to -78 $^\circ$ C to remove the oxygen dissolved in toluene. The reaction was stirred at 110 $^\circ\mathrm{C}$ for 24 or 15 hours and then was dropped into methanol after cooling to the room temperature. The raw solid after filtration was further conducted by Soxhlet extraction in turn using acetone, hexane, dichloromethane and chloroform. Finally, the dark red solid (158mg, 69% yield; or 142mg , 57% yield) was got. These two polymers could not be recorded by nuclear magnetic resonance due to their poor solubility. Elemental analysis was conducted, and the results were as follows. PBDTT-fDTBO, elemental analysis calcd (%) for C₆₈H₉₂N₂OS₆: C 71.28%, H 8.09%, found: C 71.12%, H 8.27%. PBDTO-fDTBO, elemental analysis calcd (%) for $C_{60}H_{88}N_2O_3S_4$: C 71.10%, H 8.75%, found: C 70.86%, H 9.02%.

4.2 Measures

¹H NMR (nuclear magnetic resonance) and ¹³C NMR spectra were tested by the Bruker DRX with 600MHZ spectrometer with tetramethylsilane (TMS) as zero for a standard. Elemental analysis data was recorded on a Vario El Cube elementar analyzer. Under a nitrogen atmosphere, TGA curves were recorded by a SDT Q600 with a heating rate of 10°C min⁻¹. The molecular weights (M_n) of two polymers were performed by GPC with polystyrene as the standard and THF as the solvent at 35 °C. UV-vis absorption spectra were got with solvents and thin films using the Hitachi U-4100 spectrophotometer. CV curves were recorded by a CHI 660D electrochemical workstation using the standard three-electrode system with solution electrochemical cell а Tetrabutylammonium phosphorus hexafluoride (0.1 M) in acetonitrile (under an argon atmosphere) at a scan rate of 100 mV/s. In the three-electrode system, Pt electrode with the polymer film was as the working electrode, SCE was as the reference electrode and Pt wire was as the auxiliary electrode at the ambient temperature. The DFT calculations were measured by Gaussian 09 program at the B3LYP/6-31G(d,p)

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4.3 Fabrication and characterization of PSCs

Conventional polymer solar cells devices were fabricated with of ITO/PEDOT:PSS/PBDTT-fDTBO(PBDTOstructure the fDTBO):PC71BM/Ca/AI . The ITO-coated glasses were cleaned in the ultrasonic bath with water, and washed with acetone, toluene, methanol and isopropyl alcohol subsequently. After about 20 min oxygen plasma treatment, the layer of PEDOT:PSS (30 nm) was spin-coated onto the ITO glasses and then dried at 120 °C under argon atmosphere for 20 min. The polymer blended with PC71BM (1:1, 1:2 and 1:3) were dissolved in CN/DCB (0%, 1%, 2% or 3%) solution. The solution was maintained at 90 °C for 1 hour before being spin-coated as the active layer (90 nm) onto the ITO/PEDOT:PSS substrate. At last Ca (10 nm) and Al (100 nm) layers were in sequence thermal evaporated onto the active layer with a pressure of $3*10^{-4}$ Pa. The active area of the PSCs device in this work was about 0.1 cm². The current density-voltage characteristics were measured by a Keithley 2420 source measurement under illumination (AM 1.5 G, 100 mW/cm²) from a Newport solar simulator. A standard silicon solar cell was used to calibrate the light intensity. The external quantum efficiency (EQE) of the PSCs were recorded by a certified Newport incident photon conversion efficiency (IPCE) measurement system.

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References

- 1 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao and L. Yu, Chem Rev, 2015, 115, 12666.
- 2 Z. Wu, C. Sun, S. Dong, X. F. Jiang, S. Wu, H. Wu, H. L. Yip, F. Huang and Y. Cao, J Am Chem Soc, 2016, 138, 2004.
- 3 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, Nat Commun, 2014, 5, 5293.
- 4 S. H. Liao, H. J. Jhuo, P. N. Yeh, Y. S. Cheng, Y. L. Li, Y. H. Lee, S. Sharma and S. A. Chen, Sci Rep, 2014, 4, 6813.
- 5 A. R. b. M. Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. da Silva and J. Jang, Energy Environ. Sci., 2015, 8, 303.
- 6 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao, G. Li and Y. Yang, Nat Commun, 2013, 4, 1446.
- 7 V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya and H. Murata, Nature Photonics, 2015, 9, 403.
- 8 M. Lenes, G.-J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra,
- J. C. Hummelen and P. W. M. Blom, Adv Mater., 2008, 20,2116
- 9 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, Adv Mater, 2006, 18, 789-794.
- 10 Q. Liu, X. Bao, Y. Yan, Z. Du, V. A. L. Roy, D. Zhu, M. Sun, C. S. Lee and R. Yang, J Mater Sci, 2014, 50, 2263.
- 11 V. Tamilavan, J. Lee, R. Agneeswari, D. Y. Lee, S. Cho, Y. Jin, S. H.

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Advances Accepted

Park and M. H. Hyun, Polymer, 2015, 80, 95.

View Article Online 12 W. Li, A. Furlan, W. S. Roelofs, K. H. Hendriks, G. W3yar6Rauissen, M. M. Wienk and R. A. Janssen, Chem. Commun., 2014, 50, 679.

13 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, J Am. Chem. Soc., 2011, 133, 4625.

14 J. Huang, X. Wang, C. Zhan, Y. Zhao, Y. Sun, Q. Pei, Y. Liu and J. Yao, Polym. Chem, 2013, 4, 2174.

15 M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, Angewandte Chemie, 2003, 115, 3493-3497.

16 S. Subramaniyan, H. Xin, F. S. Kim, N. M. Murari, B. A. E. Courtright and S. A. Jenekhe, Macromolecules, 2014, 47, 4199-4209. 17 J. Gilot, M. M. Wienk and R. A. Janssen, Adv Mater, 2010, 22, E67-71.

18 V. Tamilavan, K. H. Roh, R. Agneeswari, D. Y. Lee, S. Cho, Y. Jin, S. H. Park and M. H. Hyun, J POLYM SCI POL CHEM, 2014.

19 L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street and Y. Yang, Adv Mater, 2013, 25, 6642.

20 L. Ye, S. Zhang, L. Huo, M. Zhang and J. Hou, Acc. Chem. Res., 2014. 47. 1595.

21 J. Ren, X. Bao, L. Han, J. Wang, M. Qiu, Q. Zhu, T. Hu, R. Sheng, M. Sun and R. Yang, Polym. Chem., 2015, 6, 4415.

22 J. Wang, M. Xiao, W. Chen, M. Qiu, Z. Du, W. Zhu, S. Wen, N. Wang and R. Yang, Macromolecules, 2014, 47, 7823.

23 D. Veldman, S. C. J. Meskers and R. A. J. Janssen, Adv Funct Mater, 2009, 19, 1939.

24 K. Vandewal, Z. Ma, J. Bergqvist, Z. Tang, E. Wang, P. Henriksson, K. Tvingstedt, M. R. Andersson, F. Zhang and O. Inganäs, Adv Funct Mater, 2012, 22, 3480.

25 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, Nature Photonics, 2009, 3, 649-653.

26 Y. Huang, L. Huo, S. Zhang, X. Guo, C. C. Han, Y. Li and J. Hou, Chem. Commun., 2011, 47, 8904.

27 D. Liu, C. Gu, M. Xiao, M. Qiu, M. Sun and R. Yang, Polym. Chem., 2015. 6. 3398.

28 R. S. Kularatne, F. J. Taenzler, H. D. Magurudeniya, J. Du, J. W. Murphy, E. E. Sheina, B. E. Gnade, M. C. Biewer and M. C. Stefan, J Mater Chem, 2013, 1, 15535.

29 M. Z. Svensson, F.; Veenstra, S. C.; Verhees, W. J. H.; and J. C. K. Hummelen, J. M.; Inganas, O.; Andersson, M. R, Adv. Mater, 2003, 15.988.

30 C.-Y. Mei, L. Liang, F.-G. Zhao, J.-T. Wang, L.-F. Yu, Y.-X. Li and W.-S. Li, Macromolecules, 2013, 46, 7920.

31 L. Huo and J. Hou, Polym. Chem, 2011, 2, 2453.

32 J. Yuan, Y. Zou, R. Cui, Y.-H. Chao, Z. Wang, M. Ma, Y. He, Y. Li, A. Rindgen, W. Ma, D. Xiao, Z. Bo, X. Xu, L. Li and C.-S. Hsu, Macromolecules, 2015, 48, 4347.

33 J. Yuan, H. Dong, M. Li, X. Huang, J. Zhong, Y. Li and W. Ma, Adv Mater, 2014, 26, 3624.

34 J. Wolf, F. Cruciani, A. El Labban and P. M. Beaujuge, Chem Mater, 2015. 27. 4184.

35 Y. Zhang, S. K. Hau, H.-L. Yip, Y. Sun, O. Acton and A. K. Y. Jen, Chem Mater, 2010, 22, 2696.

36 A. N. Y.Zou, P. Berrouard, and B. B. R. d. A. c. S. Beaupré, Y. Tao , M. Leclerc , J. Am. Chem. Soc. , 2010, 132, 5330.

37 E. T. Hoke, K. Vandewal, J. A. Bartelt, W. R. Mateker, J. D. Douglas, R. Noriega, K. R. Graham, J. M. J. Fréchet, A. Salleo and M. D. McGehee, Adv. Energy Mater., 2013, 3, 220-230.

38 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, J. Am. Chem. Soc. 2011, 133, 8057.

39 L. Huo, X. Guo, S. Zhang, Y. Li and J. Hou, Macromolecules, 2011, 44, 4035.

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- 40 Z. G. Zhang, J. Min, S. Zhang, J. Zhang, M. Zhang and Y. Li, *Chem Commun (Camb)*, 2011, **47**, 9474.
- 41 M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv Mater*, 2015, **27**, 4655.
- 42 C. A. R. Frank A. Arroyave, and John R. Reynolds, *Ogr Lett*, 2012, **14**, 6138.
- 43 Y.-J. Cheng, J.-S. Wu, P.-I. Shih, C.-Y. Chang, P.-C. Jwo, W.-S. Kao and C.-S. Hsu, *Chem Mater*, 2011, **23**, 2361.
- 44 Q. Liu, X. Bao, S. Wen, Z. Du, L. Han, D. Zhu, Y. Chen, M. Sun and R. Yang, *Polym. Chem*, 2014, **5**, 2076.

45 W. Nie, C. M. Macneill, Y. Li, R. E. Noftle, D. L. Carroll and R. C. Coffin, *Macromol Rapid Commun*, 2011, **32**, 1163.

46 M.-H. P. Jianhui Hou, Shaoqing Zhang, Yan Yao, Li-Min Chen, Juo-Hao Li, and and Y. Yang, *Macromolecules*, 2008, **41**, 6012.

- 47. C. Duan, A. Furlan, J. J. van Franeker, R. E. Willems, M. M. Wienk
- and R. A. Janssen, Adv Mater, 2015, 27,4461.
- 48. Y. F. Li, Y. P. Zou, Adv. Mater. 2008, 20, 2952
- 49. L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li, J. H. Hou, Angew. Chem., Int. Ed. 2011, 50, 9697

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Novel Wide Band Gap Polymers Based on Dithienobenzoxadiazole for Polymer Solar Cells with High Open Circuit Voltages over 1V

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Just by replacing sulfur with oxygen atom, the V_{oc} of PBDT-fDTBO based PSCs is 0.2 V higher than PBDT-fDTBT based devices.