

View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Wen, W. Chen, M. Fan, L. Duan, M. Qiu, M. Sun, L. Han and R. Yang, *J. Mater. Chem. A*, 2016, DOI: 10.1039/C6TA08130D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Shuguang Wen,^a Weichao Chen,^a Meijie Fan,^{a,b} Linrui Duan,^a Meng Qiu,^a Mingliang Sun,^b Liangliang Han,^a* Renqiang Yang^a*

Diketopyrrolopyrrole (DPP)-based π -conjugated polymer is a very promising low band gap electron donor material for polymer solar cell. We have incorporated alkyl groups to the 4-position of the thiophene rings connected to the DPP fragment, which is proven to be beneficial for improving the open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}). Two DPP-based polymers are synthesized with benzo[1,2-b:4,5-b']dithiophene (BDT) as electron-donating segment. The both polymers show good solubility, slightly wide optical band gaps and deep HOMO energy levelswhen incorporating the alkyl groups. Heterojunction solar cells are fabricated with polymer:PC₇₁BM as active layer. V_{oc} and J_{sc} are simultaneously enhanced compared to the device performance of traditional DPP-BDT alternating polymers. Power conversion efficiency (PCE) of 8.11% was obtained, which indicates that rational utilization of backbone torsion is a promising strategy to improve the photovoltaic performance.

Introduction

Published on 27 October 2016. Downloaded by Cornell University Library on 27/10/2016 15:02:19.

In the past decades, polymer solar cells (PSCs) have attracted considerable attention as an approach to direct utilization of sun light due to their advantages such as mechanical flexibility, light weight, low cost and solution processable for large area device fabrication.¹⁻³ Novel materials⁴ and device fabrication methods⁵ have emerged rapidly for improving the photovoltaic performance through optimization of energy level, film morphology, charge carrier mobility and so on. Encouraging power conversion efficiencies (PCEs) of over 10% have been achieved in laboratory for single-junction bulk-heterojunction (BHJ) PSCs.⁶⁻¹¹

Low band gap (LBG) conjugated polymers exhibit bright prospect on photovoltaic application for its wide optical absorption and great potential for tandem solar cell. Diketopyrrolopyrrole (DPP)-based polymers are intensively investigated as representative LBG materials for single and double junction solar cells.¹² These materials show wide absorption range and good coplanar structure, which would be in favor of light harvest and high carrier mobility.¹³ In general, DPP-based polymers are incorporated with long side chains on N-atoms to warrant the solution processability. And the adjacent thiophene is not substituted at 3- and 4- positions in order to keep the planar structure. Yang's group has previously reported that the incorporation of large alkyl group could induce the reduction of PCE



CHEMISTRY Article Online

DOI

^{a.} CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. *Email: hanll@qibebt.ac.cn; yangrq@qibebt.ac.cn

^{b.} Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China

Electronic Supplementary Information (ESI) available: [details of polymer synthesis, hole mobility and device performance]. See DOI: 10.1039/x0xx00000x

distortion of backbone.18

Published on 27 October 2016. Downloaded by Cornell University Library on 27/10/2016 15:02:19.

Scheme 1 Synthetic route and molecular structures of DPPbased copolymers.

Results and discussion

Synthesis and characterization

In order to investigate the effect of backbone twist on the photovoltaic performance, 2-ethylhexyl and cyclohexyl groups are introduced to the 4-position of thiophene group of DPP-monomer with 2-ethylhexyl and 2-butyloctyl side chains on the nitrogen atom, respectively (Scheme 1). The detailed synthetic procedures of DPPbased monomers and copolymers are described in Supporting Information.¹⁷ Two polymers of PDPP-EH and PDPP-CH were prepared by Stille coupling reaction between DPP and BDT monomers. These polymers can be readily soluble in common organic solvents, such as chloroform (CF), tetrahydrofuran (THF), chlorobenzene (CB), and 1, 2-dichlorobenzene (DCB). The numberaverage molecular weights (Mn) of PDPP-EH and PDPP-CH are 158.7 and 148.2 KDa, with polydispersity indexes (PDIs) of 3.25 and 2.62, respectively, as determined by gel permeation chromatography (GPC) with THF as an eluent calibrated with polystyrene standard.

Thermal stabilities of polymers were investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere, as shown in Fig. S1. The decomposition temperatures of PDPP-EH and PDPP-CH at 5% weight loss are 423 and 403 °C, indicating high thermal stability of the polymers for application in optoelectronic devices.

Optical and electrochemical properties

The UV-vis absorption spectra of two polymers in chloroform solutions and as thin films are shown in Fig. 1(a) and the data are summarized in Table 1. Two polymers exhibit very similar absorption profiles due to the identical conjugated backbone. The optical band gaps of PDPP-EH (1.53 eV) and PDPP-CH (1.50 eV) are comparatively larger than that of reported DPP-BDT alternating



polymer PBDTT-DPP (1.44 eV),¹⁴ which may be caused by the

Electrochemical cyclic voltammetry (CV) measurements were carried out to determine the HOMO and LUMO levels of conjugated polymers.¹⁹ As shown in Fig. 1(b), the onsets of oxidation potentials of PDPP-EH and PDPP-CH were 0.95 and 0.98 V, respectively, with the corresponding calculated HOMO levels of -5.36 and -5.39 eV,

which are lower than that of PBDTT-DPP. The LUMO levels were

calculated from the equation: $E_{LUMO} = E_{HOMO} + E_g^{opt}$ and the

corresponding LUMO levels of -3.83 and -3.89 eV were obtained,

Fig. 1 (a) UV–vis absorption spectra of PDPP-EH and PDPP-CH in chloroform solutions and as thin films. (b) Cyclic voltammograms of the polymer films measured in Bu_4NPF_6 solution (0.1 M in acetonitrile) at a scan rate of 50 mV s⁻¹.

Table 1	Summary	of o	ptical	and energy	gy levels	s of polymers.

polymers	$\lambda_{sol} (nm)^a$	$\lambda_{\text{film}} (\text{nm})^a$	$\lambda_{\text{onset}} (\text{nm})^b$	$E_g^{opt}(eV)^c$	HOMO $(eV)^d$	LUMO (eV) ^e
PDPP-EH	691, 762	700, 771	810	1.53	-5.36	-3.83
PDPP-CH	683, 763	698, 770	827	1.50	-5.39	-3.89
^a the absorption pea	aks in chloroform s	olution and as thin	films, respectively.	^b the onset absorpti	on of polymer as thin film	n. ^c Calculated from

 $1240/\lambda_{\text{onset}}$. ^{*d*} Determined from the onset of oxidation wave. ^{*e*} Calculated by the equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}^{\text{opt}}$ (eV).

Journal Name

DOI: 10.1039/C6TA08130D

 Table 2 Dihedral angles (deg) along the conjugated backbone for the optimized molecular geometries obtained by DFT evaluated at the B3LYP/6-31G(d) Level



polymer	R	θ_1 (deg)	θ_2 (deg)
PDPP-EH	ethylhexyl	13.30	-39.86
PDPP-CH	cyclohexyl	13.69	-42.17
PBDTT-DPP	Н	9.48	-9.90

Theoretical studies

In order to further investigate the effect of sterically hindered alkyl group on the polymer structure, density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level in Gaussian 09 program.²¹ For computational simplification, the alkyl side chains on the BDT and DPP units were replaced with methyl group and the backbone was simplified to one repeating unit (n = 1). The structures with group of ethylhexyl, cyclohexyl and H on the thiophene unit stand for PDPP-EH, PDPP-CH and PBDTT-DPP, respectively.

The optimized molecular geometries of the models are shown in Fig. S2 and dihedral angels are given in Table 2. The torsion angles of θ_1 are varied from 9.48° to 13.69°, indicating that thiophene and DPP have good coplanar conformation for all three polymers. Comparatively, torsion angle θ_2 shows large difference ranging from -9.9° for PBDTT-DPP to -42.17° for PDPP-CH with the incorporation of alkyl group. PBDTT-DPP shows small torsion angle with a nearly coplanar backbone structure. PDPP-EH and PDPP-CH exhibit large torsion angle on backbone and PDPP-CH with cyclohexyl group is the most twisted. Although the coplanar structure is in favor of stacking effect and charge mobility, it would also induce strong self-aggregation of polymer. Incorporation of long side chain could improve the solubility, while this approach would increase insulating content from the side chain and decrease the crystallinity.22 Interestingly, the appropriate distortion in backbone as the designed polymers would improve the solution processibility and might increase photovoltaic performance.

Photovoltaic properties

The photovoltaic properties of polymers PDPP-EH and PDPP-CH were investigated by fabricating the BHJ solar cells with the conventional structure of ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al. The active layers were spin-coated from DCB solution and 1, 8-diiodooctane (DIO) was added to optimize the blend film morphology. All devices were characterized under a solar simulator AM 1.5G at 100 mW/cm². The details of the device fabrication and characterization are given in the supporting information. The *J-V* curves are shown in Fig. 2a and the photovoltaic parameters are summarized in Table 3. The reported polymer PBDTT-DPP with

identical backbone to PDPP-EH/CH is used as the reference and the photovoltaic properties are cited directly from the angle 6TA08130D

Firstly, polymer/PC71BM blend ratios (w/w) of 1:1, 1:2 and 1:3 were evaluated (Table S1) and it was found that the ratio of 1:2 (w/w) showed the best performance for both polymers. PDPP-EH and PDPP-CH exhibited good PCEs of 7.25% and 6.66%, respectively. As DIO was added, the efficiency of PDPP-EH was reduced to 6.24%. Interestingly, the efficiency of PDPP-CH was increased to 8.11%, mainly due to the increase of J_{SC} from 14.6 to 17.5 mA/cm². Compared to the reported polymer PBDTT-DPP, PDPP-EH and PDPP-CH exhibit higher V_{OC} , J_{SC} and PCEs. The V_{OC} is increased as predicted, which is in accordance with their HOMO levels.23 Meanwhile, the J_{SC} is also increased, which indicates that an improved molecular packing and film morphology are formed upon the introduction of steric hindered alkyl groups. However, PDPP-CH shows a slightly lower FF compared to PDPP-EH, which indicates more intrinsic charge traps are formed in the blend film. Structure disorder could induce the formation of charge traps and recombination.²⁴ PDPP-CH is more twisted and the crystallization is weaker than PDPP-EH, which can be concluded from XRD pattern. Therefore, PDPP-CH exhibits a slightly lower FF value.

The external quantum efficiency (EQE) curves for the best devices of PDPP-EH and PDPP-CH are shown in Fig. 2b. Both polymers exhibit broad photo-response from 400 to 800 nm. The J_{SC} values integrated from the EQE spectra are 14.6 and 16.9 mA/cm², respectively, which are consistent well with J_{SC} obtained from the J-V measurements.



Fig. 2 (a) *J-V* curves of polymer solar cells based on PDPP-EH and PDPP-CH under illumination of AM 1.5G, 100 mW cm⁻². (b) EQE

Published on 27 October 2016. Downloaded by Cornell University Library on 27/10/2016 15:02:19.

curves of the best PSCs based on the two polymers PDPP-EH and PDPP-CH.

Table 3 The photovoltaic parameters of the devices based on the two polymers under illumination of AM 1.5G, 100 mW cm⁻²

$V_{OC}(V)$	$J_{\rm SC}~({\rm mA/cm^2})$	FF	PCE $(\%)^d$
0.75	15.1	0.64	7.25 (7.09)
0.74	13.4	0.63	6.24 (6.13)
0.76	14.6	0.60	6.66 (6.48)
0.76	17.5	0.61	8.11 (8.01)
0.73	14.0	0.65	6.6
	Voc (V) 0.75 0.74 0.76 0.76 0.73	V_{OC} (V) J_{SC} (mA/cm2)0.7515.10.7413.40.7614.60.7617.50.7314.0	$\begin{array}{c cccc} V_{OC}\left(V\right) & J_{SC}\left(mA/cm^2\right) & FF \\ \hline 0.75 & 15.1 & 0.64 \\ 0.74 & 13.4 & 0.63 \\ 0.76 & 14.6 & 0.60 \\ 0.76 & 17.5 & 0.61 \\ 0.73 & 14.0 & 0.65 \\ \end{array}$

^a The	polyn	ner/P	C71BI	M blen	ding	ratio	: 1/2	(w/	w),	solvent:	D	CB.
^b DIO	(1%,	v/v)	was	added.	^c Ref	14.	^d Va	lues	in	parenthes	es	are
average data from over 10 devices.												

To further investigate the relationship between molecular structure and photovoltaic properties, hole mobility was measured via the space-charge-limited current (SCLC) method with a hole-only device configuration of ITO/PEDPOT:PSS/polymer:PC₇₁BM /Au.²⁵ *J-V* curves are shown in Fig. S3. The hole mobilities (μ_{hole}) of the optimized polymer:PC₇₁BM blend for PDPP-EH and PDPP-CH were determined to be 4.1×10^{-4} cm² V⁻¹ s⁻¹ and 2.2×10^{-4} cm² V⁻¹ s⁻¹, respectively, which are similar to that of PBDTT-DPP (2.9×10^{-4} cm² V⁻¹ s⁻¹).¹⁴ As is well known, backbone distortion could break out the coplanarity of the polymer and the mobility would thus be decreased. Interestingly, PDPP-EH and PDPP-CH still exhibit even higher hole mobilities, which would probably result from the wellformed bicontinuous interpenetrating network and/or molecular packing in the blend films.²⁶ Furthermore, high μ_{hole} is also beneficial to obtain high *J*sc and FF values.²⁷



Fig. 3 TEM images of polymer/PC₇₁BM blends (1:2 weight ratio cast from *o*-dichlorobenzene) for PDPP-EH (a, b) and PDPP-CH (c, d) without (a, c) and with 1% DIO (b, d).

To understand the influence of side chain on the photovoltaic performance, the morphology of blend film was examined by

tapping-mode atomic force microscopy (AFM) and transmission electron microscopy (TEM). In AFM images (Fig. 1849), (the soft face of PDPP-EH blend film obtained without DIO shows evenly distributed small grains. As DIO added, the surface becomes much coarser and the root-mean-square (rms) roughness increases from 1.66 to 12.2 nm, which is probably caused by the aggregation of polymer and PC71BM in the active layer.²⁸ As for the blend film of PDPP-CH, the surface morphology showed mild evolution and the rms roughness increased slightly from 1.71 nm to 3.35 nm upon the addition of DIO. The increase of roughness may result from the stronger crystallization and phase separation of blend film, which would lead to a more efficient charge dissociation and transport. Meanwhile, TEM was used to explore the bulk morphology of blend film (Fig. 3). In TEM images, the bright regions are polymers-rich domains and the dark regions are PCBM-rich domains. A bicontinuous network is formed for PDPP-EH blend film without DIO, however, the network is disturbed and a severe aggregation is observed as the addition of DIO. As a result, the PCE is dropped from 7.25% to 6.24%. Compared to PDPP-EH, blend film PDPP-CH exhibits a quite homogeneous phase separation without DIO. More clearly interpenetrating network is observed with the addition of DIO, which could facilitate exciton dissociation and charge transport.²⁹ The morphology results are fairly well consistent with the photovoltaic performance of the two polymers.

The microstructures of the blending films were further characterized by X-ray diffraction (XRD) of polymer:PC71BM films processed with or without DIO, as shown in Fig. 4. The blend films only show a wide (100) lamellar diffraction peak in the out-of-plane direction, indicating the edge-on orientations are formed in both blend films. The two polymers exhibit small lamellar distance of 14.7 and 15.0 Å for PDPP-EH and PDPP-CH, respectively. As DIO is added, the lamellar distance are slightly increased to 14.8 and 15.2 Å, respectively, which indicates longer packing distance between side chains of neighboring polymer backbones induced by addition of DIO.26 Furthermore, the lamellar stacking exhibits quite small distance compared to the widely reported conjugated polymers, such as P3HT (~17 Å)³⁰ and PTB7 (~18 Å)³¹, especially much smaller than thiophene-flanked DPP-based polymers (~20 Å).^{12a} This compact packing is probably caused by the twisted backbone, which has been reported to decrease the lamellar spacing.³² The coherence length ζ of the polymer gives information about the lattice disorder, which was calculated by Scherrer equation.33 Compared to PDPP-EH, PDPP-CH/DIO exhibits a smaller coherence length (7.8 nm vs 10.8 nm) with a low intensity, which indicates a weaker crystallization formed in the blend film. The lower crystallization induced by the disruption of molecular packing would be one reason for lower FF value of PDPP-CH. Furthermore, the π -stacking diffraction is not observed in the films, which is probably ascribed to the backbone distortion of the polymers.



Fig. 4 X-ray diffraction patterns of polymer:PC71BM blend films.

Conclusions

Published on 27 October 2016. Downloaded by Cornell University Library on 27/10/2016 15:02:19

In summary, two DPP-BDT alternating conjugated copolymers PDPP-EH and PDPP-CH were designed and synthesized with alkyl groups of 2-ethylhexyl and cyclohexyl incorporated to the 4-position of thiophene unit, respectively. The influence of sterically hindered groups on the structural, optical, electrochemical and photovoltaic properties of the two polymers were fully investigated and compared to the reported PBDTT-DPP without side chains on the thiophene unit. Polymers PDPP-EH and PDPP-CH show slightly wider band gaps and lower HOMO levels. Theoretical calculations reveal that two polymers show more twisted backbone than PBDTT-DPP and hence the coplanar structure is broken. Both polymers exhibit higher PCEs (7.25% for PDPP-EH and 8.11% for PDPP-CH) than PBDTT-DPP (6.6%). TEM image indicates that a bicontinuous fibril network is obviously formed in PDPP-CH:PC71BM blend as addition of DIO, which is beneficial for obtaining high J_{SC} value. Our work demonstrates that the appropriate twisted backbone is an effective strategy to improve PSC performance.

Experimental section

Materials and reagents

All reactions and manipulations were carried out under Ar with the use of standard inert atmosphere. Common solvents were dried by standard procedures. Deuterated chloroform, 1, 8-diiodooctane and *o*-dichlorobenzene were purchased from Sigma-Aldrich. All column chromatography was performed with the use of silica gel 200-300 mesh. 2,6-Bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-b:4,5-b']dithiophene, monomers and polymers were synthesized according to the literature methods.¹⁷ Unless stated otherwise, other reagents were purchased from commercial sources, and used without further purification.

Instruments

¹H NMR and ¹³C NMR spectra were performed in a Bruker AVANCE-III 600 MHz spectrometer using solutions in CDCl₃ and chemical shifts were recorded in ppm units with TMS as the internal standard. UV-vis spectra were recorded on a Lambda25 spectrophotometer. The electrochemical measurements were carried

ARTICLE

out under nitrogen on a deoxygenated solution of tetra-nbutylammonium hexafluorophosphate (0.1 MD/ml@ceron/iteile0with a computer-controlled CHI660C electrochemical workstation, a Pt working electrode, a platinum-wire auxiliary electrode, and an SCE as the reference electrode. Potentials were referenced to the ferrocenium/ferrocene(Fc/Fc⁺) couple by using ferrocene as a standard. The HOMO levels of the polymers were determined using the oxidation onset value. TGA measurements were performed on STA-409at a heating rate of 10 °C/min under N2 atmosphere. All GPC analyses were made using THF as eluant and polystyrene standard as reference. Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using an Agilent 5400 instrument. Bright field transmission electron microscopy (TEM) data were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. The structure of the films was analyzed using X-ray diffraction (Bruker D8 ADVANCE). The ground-state geometries of BDT-DTBT molecules were fully optimized with DFT method under B3LYP/6-31G(d,p) level.

Photovoltaic Device Fabrication and Characterization

The PSCs were fabricated with a configuration of ITO/PEDOT:PSS/ polymers:PC71BM/Ca/Al. A thin layer of PEDOT:PSS (30 nm, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was spincast on pre-cleaned ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150 °C for 30 min in air, then the device was transferred into glovebox, where the active layer (100 nm) of the blend of the polymer and PC71BM was spin coated on the PEDOT:PSS layer. Finally, a Ca (10 nm)/Al (100 nm) metal top electrode was thermal evaporated onto the active layer under about 2 \times 10⁻⁴ Pa. The active area of the device was 0.1 cm² defined by shadow mask. The current density-voltage (J-V) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW/cm² (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Space charge limited current measurements

Hole mobility was measured using the space charge limited current (SCLC) model, using a device configuration of ITO/PEDOT:PSS/polymer/Au by taking current-voltage in the range of 0-5 V and fitting the results to a space charge limited current for hole-only device. In the presence of carrier traps in the active layer, a trap-filled-limit (TFL) region exists between the ohmic and trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized by using the Mott-Gurney square law,

$$J = \frac{9\varepsilon\mu V^2}{8L^3}$$

where ε is the static dielectric constant of the medium and μ is the carrier mobility, *V* is the voltage drop across the device, and *L* is the polymer thickness.

ARTICLE

General procedure for the synthesis of polymers

Monomer 1 (0.2 mmol), monomer 2 (0.2 mmol), Pd₂(dba)₃ (1.8 mg, 0.002 mmol) and P(*o*-tol)₃ (3.6 mg, 0.012 mmol) were dissolved into 6 mL toluene in a 25 mL round bottom flask protected by argon. The flask was purged three times with successive vacuum and argon filling cycles. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 18 h at 110 °C under argon atmosphere. After cooling, the mixture was cooled to room temperature and precipitated in 200 mL methanol. The precipitate was filtered and washed with methanol and hexane successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight.

PDPP-EH, GPC: Mn= 158.7 kg mol⁻¹, PDI = 3.25, Td = 423 °C.¹H NMR (600 MHz, CDCl₃) δ (ppm): 9.11-8.80 (br, 2H), 7.80-6.92 (br, 6H), 4.03 (br, 4H), 2.87 (br, 8H), 1.80-0.79 (br, 90H).

PDPP-CH, GPC: Mn= 148.2 kg mol⁻¹, PDI = 2.62, Td = 403 °C.¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.94 (br, 2H), 7.80-6.93 (br, 6H), 4.04 (br, 4H), 3.13 (br, 4H), 2.88 (br, 4H), 1.88-0.71 (br, 94H).

Acknowledgements

This work was supported by National Natural Science Foundation of China (21202181, 51503219, 51573205, 61405209), Department of Science and Technology of Shandong Province (ZR2015EQ002, 2015GGX104007), and the Qingdao Institute of Bioenergy and Bioprocess Technology Director Innovation Foundation for Young Scientists (QIBEBT-DIFYS-201507).

Notes and References

- (a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, Science, 1995, 270, 1789. (b) J. W. Chen and Y. Cao, Acc. Chem. Res., 2009, 42, 1709.
- 2 R. F. Service, Science, 2011, 332, 293.
- 3 B. C. Thompson and J. M. J. Frechet, Angew. Chem. Int. Ed., 2008, 47, 58.
- 4 (a) Y. J. Cheng, S. H. Yang and C. S. Hsu, *Chem. Rev.*, 2009, 109, 5868. (b) Y. F. Li, *Acc. Chem. Res.*, 2012, 45, 723. (c) P.-L. T. Boudreault, A. Najari and M. Leclerc, *Chem. Mater.*, 2010, 23, 456.(d) X. Wang, Q. Su, Y. Li, C. Cheng, Y. Xia, L. He, H. Li, G. Shu, and F. Wang, *Synth. Met.*, 2016, 220, 433.
- 5 (a) G. Li, C. W. Chu, V. Shrotriya, J. Huang and Y. Yang, *Appl. Phys. Lett.*, 2006, 88, 253503. (b) J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, 317, 222. (c) Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.*, 2011, 23, 4636.
- 6 Y. H. Liu, J. B. Zhao, Z. K. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. R. Lin, H. Ade and H. Yan, *Nat. Commun.*, 2014, 5, 5293.
- 7 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.

- 8 J. D. Chen, C. H. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. F. Li and J. X. Tang, Adv. Mater., 2015, 27 pt0350.1039/C6TA08130D
- 9 J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, *Nat. Energy*, 2016, 1, 15027.
- 10 V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya and H. Murata, *Nat. Photonics*, 2015, 9, 403.
- 11 S. Zhang, L. Ye and J. Hou, *Adv. Energy Mater.*, DOI: 10.1002/aenm.201502529.
- 12 (a) L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, 6, 180. (b) W. Li, K. H. Hendriks, A. Furlan, W. S. C. Roelofs, S. C. J. Meskers, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2014, 26, 1565. (c) K. H. Hendriks, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk and R. A. J. Janssen, *Angew. Chem. Int. Ed.*, 2013, 52, 8341.
- 13 (a) X. Guo, A. Facchetti and T. J. Marks, *Chem. Rev.*, 2014, 114, 8943. (b) C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, 2013, 25, 1859. (c) Y. Li, P. Sonar, L. Murphy and W. Hong, *Energy Environ. Sci.*, 2013, 6, 1684.
- 14 L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li and Y. Yang, J. Am. Chem. Soc., 2012, 134, 10071.
- 15 (a) S. Ko, E. Verploegen, S. Hong, R. Mondal, E. T. Hoke, M. F. Toney, M. D. McGehee and Z. Bao, J. Am. Chem. Soc., 2011, 133, 16722. (b) S. Ko, E. T. Hoke, L. Pandey, S. Hong, R. Mondal, C. Risko, Y. Yi, R. Noriega, M. D. McGehee, J.-L. Brédas, A. Salleo and Z. Bao, J. Am. Chem. Soc., 2012, 134, 5222.
- 16 L. Han, W. Chen, T. Hu, J. Ren, M. Qiu, Y. Zhou, D. Zhu, N. Wang, M. Sun and R. Yang, ACS Macro Lett., 2015, 4, 361.
- 17 W. Li, A. Furlan, K. H. Hendriks, M. M. Wienk and R. A. J. Janssen, J. Am. Chem. Soc., 2013, 135, 5529.
- (a) M. R. Andersson, M. Berggren, O. Inganäs, G. Gustafsson, J. C. Gustafsson-Carlberg, D. Selse, T. Hjertberg and O. Wennerström, *Macromolecules*, 1995, **28**, 7525. (b) B. Themans, W. R. Salaneck and J. L. Brédas, *Synth. Met.*, 1989, **28**, 359.
- 19 Y. F. Li, Y. Cao, J. Gao, D. L. Wang, G. Yu and A. J. Heeger, Synth. Met., 1999, 99, 243.
- 20 (a) H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, 3, 649. (b) L. J. A. Koster, V. D. Mihailetchi and P. W. M. Blom, *Appl. Phys. Lett.*, 2006, 88, 093511.
- 21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J.

Journal of Materials Chemistry A Accepted Manuscript

View Article Online DOI: 10.1039/C6TA08130D

Fox, Gaussian 09, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.

- 22 A. T. Yiu, P. M. Beaujuge, O. P. Lee, C. H. Woo, M. F. Toney, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2012, **134**, 2180.
- 23 (a) Y. Zhang, J. Zou, C.-C. Cheuh, H.-L. Yip and A. K. Y. Jen, *Macromolecules*, 2012, **45**, 5427. (b) D. Muhlbacher, M. Scharber, M. Morana, Z. G. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, **18**, 2884.
- 24 (a) N. Gasparini, X. Jiao, T. Heumueller, D. Baran, G. J. Matt1, S. Fladischer1, E. Spiecker, H. Ade, C. J. Brabec and T. Ameri1, *Nat. Energy*, 2016, 1, 16118. (b) Y. Yang, W. Chen, L. Dou, W.-H. Chang, H.-S. Duan, B. Bob, G. Li and Y. Yang, *Nat. Photonics*, 2015, 9, 190.
- 25 (a) Y. Chen, Z. Du, W. Chen, Q. Liu, L. Sun, M. Sun and R. Yang, Org. Electron., 2014, 15, 405. (b) S. C. Price, A. C. Stuart and W. You, *Macromolecules*, 2010, 43, 4609.
- 26 H. Choi, S.-J. Ko, T. Kim, P.-O. Morin, B. Walker, B. H. Lee, M. Leclerc, J. Y. Kim and A. J. Heeger, *Adv. Mater.*, 2015, 27, 3318.
- 27 (a) S. C. Price, A. C. Stuart, L. Q. Yang, H. X. Zhou and W. You, J. Am. Chem. Soc., 2011, 133, 4625. (b) J. Min, Z. G. Zhang, S. Y. Zhang and Y. F. Li, Chem. Mater., 2012, 24, 3247.
- 28 W. Li, Y. Zhou, B. V. Andersson, L. M. Andersson, Y. Thomann, C. Veit, K. Tvingstedt, R. Qin, Z. Bo, O. Inganäs, U. Würfel, F. Zhang, Org. Electron., 2011, 12, 1544.
- 29 (a) Y. Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. P. Yu, *Adv. Mater.*, 2010, **22**, E135. (b) J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497. (c) P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster and D. E. Markov, *Adv. Mater.*, 2007, **19**, 1551.
- 30 Y. C. Huang, C. S. Tsao, C. M. Chuang, C. H. Lee, F. H. Hsu, H. C. Cha, C. Y. Chen, T. H. Lin, C. J. Su, U. S. Jeng and W. F. Su, *J. Phys. Chem. C*, 2012, **116**, 10238.
- 31 B. A. Collins, Z. Li, J. R. Tumbleston, E. Gann, C. R. McNeill and H. Ade, Adv. Energy Mater., 2013, 3, 65.
- 32 C. J. Mueller, E. Gann, C. R. Singh, M. Thelakkat and C. R. Mcneill, *Chem. Mater.*, 2016, **28**, 7088.
- 33 J. Rivnay, R. Noriega, R. J. Kline, A. Salleo, M. F. Toney, *Phys. Rev. B*, 2011, 84, 045203.



Two DPP-BDT alternating conjugated polymers with twisted backbone were synthesized and high efficiency of 8.11% was obtained in photovoltaic device.