Macromolecular Research Article

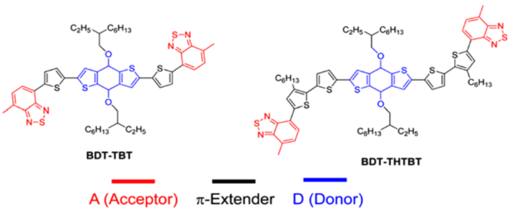
DOI 10.1007/s13233-018-6066-4 www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

Synthesis of Conjugated Materials Based on Benzodithiophene - Benzothiadazole and Their Application of Organic Solar Cells

Nadhila Sylvianti[†,1]
Youn Hwan Kim[†,1]
Dong Geun Kim[1]
Ratna Dewi Maduwu[1]
Ho Cheol Jin[1]
Doo Kyung Moon[2]
Joo Hyun Kim[*,1]

[1] Department of Polymer Engineering, Pukyong National University, Busan 48547, Korea
[2] Department of Materials Chemistry and Engineering, Konkuk Univerisity, Seoul 05029, Korea

Received November 6, 2017 / Revised November 28, 2017 / Accepted December 28, 2017



Abstract: Electron acceptor-donor-acceptor type oligomers based on benzothiadiazole (BT) unit and a (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (BDT) unit have been designed and prepared as electron-donating materials, which are 2,6-[5-(7-methyl-benzo[1,2,5]thiadiazol-4-yl)-thiophen-2-yl]-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene) (**BDT-TBT**) and 2,6-[5'-(3'-hexyl-[2,2']bithiophenyl-5-yl)-7-methyl-benzo[1,2,5]thiadiazole]-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene) (**BDT-THTBT**), for Organic Solar Cells (OSCs) with PC$_{71}$BM as electron-accepting materials. The HOMO energy level is elevated by the number of thiophene ring as a p-bridge, which lowers the band gap. Inverted-type organic solar cells (OSCs) with a configuration of ITO/ZnO/**BDT-TBT** (or **BDT-THTBT**):PC$_{71}$BM/MoO$_3$/Al are fabricated. OSC based on **BDT-THTBT** exhibits the highest power conversion efficiency (PCE) of 1.04% with the best J_{sc} of 4.20 mA/cm^2.

Keywords: conjugated oligomer, benzodithiophene, benzothiadiazole, thiophene, organic solar cell.

1. Introduction

Bulk-heterojunctions (BHJ) organic solar cells (OSCs), which blending electron donor-acceptor materials in a common solution, have been attracted in both research field and industry due to their great promise for the low-cost production, mechanical flexibility and high-performance renewable energy source.[1,2] Several attempts to increase the efficiencies have been attempted, such as developing new molecular structures with low band-gap and engineering new device architectures.[3-5] As a results, OSCs with a power conversion efficiency (PCE) up to 11% have been achieved.[6,7] In contrast with polymer solar cells, small molecule donor materials occupy specific advantages such as uniform molecular weight distribution, highly pure materials due to easy to purify, and possess the higher capability to self-assemble into ordered domain.[8-11] The compelling breakthrough has been made for small molecules organic solar cells with high PCEs over 10%.[12,13] Evolving new molecular structure with low band-gap is one of the promising ways to get high PCEs. Blending electron-donor unit with highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels and electron withdrawing units with low HOMO/LUMO levels is necessary to reduce the band gap.[14] Having advantages such as a large planar conjugated structure and the competence to efficiently form cofacial p-p stacking, benzodithiophene (BDT) is well-known electron rich molecules that achieve high PCEs OSCs.[15-18] As a proper electron withdrawing moiety, 2,1,3-benzothiadiazole (BT) derivatives are frequently used because of their high ability to lower the band gap with electron donating moiety in the BHJ type OSCs with high PCEs reported.[19-21] Increasing the conjugation length of the small molecules is crucial to decrease the band gap. Besides elevating the HOMO energy levels, introducing thiophene unit into the oligomer will shrink the band gap.[22,23] Alkyl chains were additionally applied in the thiophene unit to increase the required solubility of the compounds, which can improve the performances of the OSCs.[24] Using the stille-coupling reaction, we synthesized acceptor (A)-donor (D)-acceptor (A) type oligomer consist of a central BDT unit as the electron donor and BT as the electron acceptor for application as donor materials in OSCs, which are 2,6-[5-(7-methyl-benzo[1,2,5]thiadiazol-4-yl)-thiophen-2-yl]-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene) (**BDT-TBT**) and 2,6-[5'-(3'-hexyl-[2,2']bithiophenyl-5-yl)-7-methyl-benzo[1,2,5]thiadiazole]-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene) (**BDT-THTBT**) (Shown in Scheme 1). Utilizing those oligomers with [6,6]-phenylC$_{71}$-butyric acid methyl ester (PC$_{71}$BM) as the active layer, we fabricated inverted OSCs to observe the effect of the combination between electron donor (BDT) and electron acceptor (BT) in addition to increased number of thiophene rings with additional alkyl chain. In view of this, we report the syn-

---

Acknowledgments: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20174010201460) and was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2015015683).

***Corresponding Author:** Joo Hyun Kim (jkim@pknu.ac.kr)

[†] N. Sylvianti and Y. H. Kim equally contributed to this research.

thesis, characterization, optical and electrochemical properties also the photovoltaic performances of the devices based on those materials.

2. Results and discussion

2.1. Synthesis of BDT-TBT and BDT-THTBT

Scheme 1 shows the synthetic route of **BDT-TBT** and **BDT-THTBT**, which were synthesized by the Stille coupling reaction between 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (**6**) and compound **3** or compound **5.** 3-Hexylthiophene ring was incorporated into the conjugated backbone to investigate the effect of conjugated spacer in conjugated structure. BT and BDT are introduced as D and A to lower the band gap of material. The chemical structures of synthesized compounds in this research were confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analysis (EA). **BDT-TBT** and **BDT-THTBT** exhibit good solubility in organic solvents such as chloroform, chlorobenzene and toluene. As shown in Figure 1, **BDT-TBT** and **BDT-THTBT** exhibited no thermal transitions such as glass transition and melting behavior up to 200 °C.

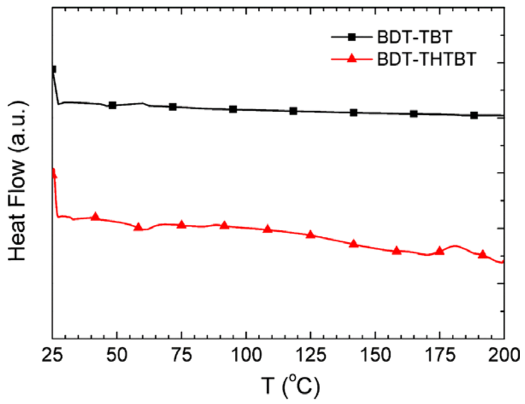
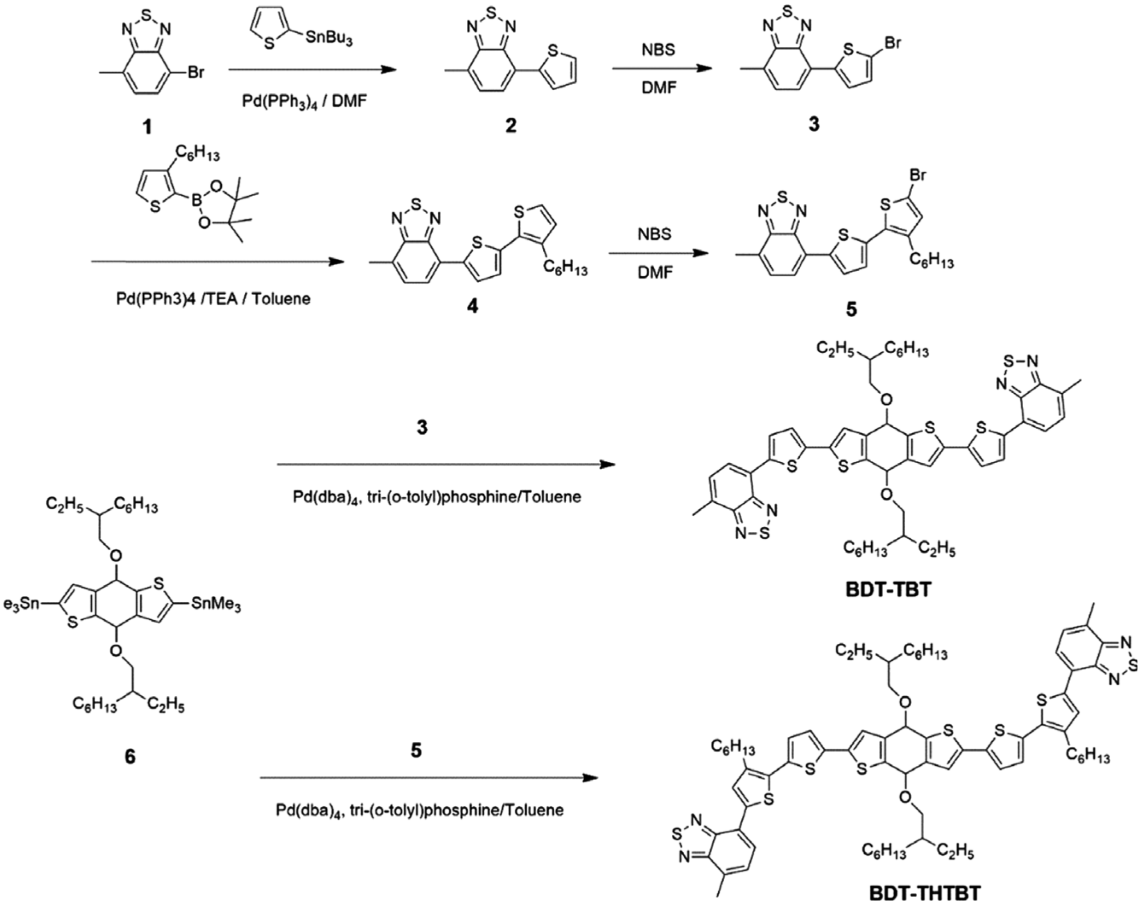


Figure 1. DSC thermograms of **BDT-TBT** and **BDT-THTBT**.

2.2. Optical and electrochemical properties

As shown in Figure 2(a), the UV-Visible spectra of **BDT-TBT** and **BDT-THTBT** in chloroform solution exhibit two broad absorption bands at 350 - 410 and 420 - 550 nm, respectively. The π-π^* transition of conjugated backbone are appeared at 350-410 nm region. Another broad absorption band at 420-550 nm region associated to the typical intramolecular charge transfer (ICT). The maximum absorption of the **BDT-TBT** and **BDT-THTBT** film were red-shifted compared to those of solution due to intermolecular interaction. This phenomena propose that the film displays more intimate intermolecular contacts relative to the solution. As shown in Figure 2(b), the absorption wavelength and the band gap of **BDT-THTBT** film showed at 546 nm and 2.04 eV, respectively, which are 23 nm and 0.12 eV red-shifted compared to that of **BDT-TBT** film because of extended



Scheme 1. Synthesis of **BDT-TBT** and **BDT-THTBT** and their chemical structure.

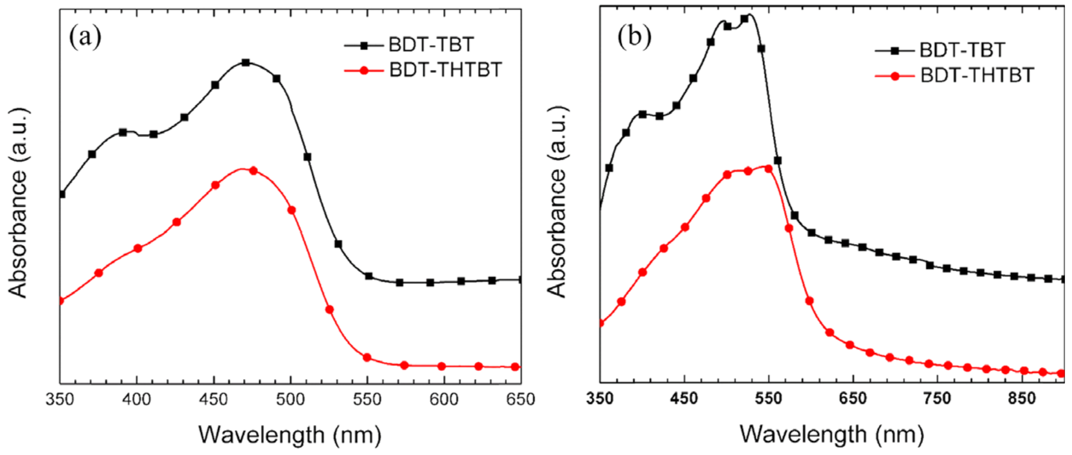


Figure 2. UV-Visible spectrum of **BDT-TBT** and **BDT-THTBT** (a) in chloroform solution and (b) film.

π-conjugation length by insertion of HT unit in the backbone. In addition, the molar extinction coefficients (ε) of **BDT-TBT** and **BDT-THTBT** are 5.67×10^4 and 7.33×10^4 M^{-1} cm^{-1}, respectively, indicating stronger ICT in **BDT-THTBT** than that of **BDT-TBT**.

The HOMO energy level of **BDT-TBT** and **BDT-THTBT** was determined by cyclic voltammetry (CV) measurements. As shown in Figure 3(a), one can easily notice that **BDT-TBT** and **BDT-THTBT** have quasi-reversible oxidation behavior. The HOMO level of **BDT-TBT** and **BDT-THTBT** were -5.43 eV and -5.33 eV, respectively, which are estimated from the onset potential of oxidation corresponding CV. The LUMO energy levels of **BDT-TBT** and **BDT-THTBT** were -3.29 and -3.31 eV, respectively. These are calculated based on the HOMO energy level and the optical band gap. The HOMO energy levels of **BDT-THTBT** was increased by 0.1 eV. This is consistent with increasing the number of thiophene ring in molecule. Introducing thiophene ring as a π-extender leads to an elevation of the HOMO energy level and decreasing the band gap. The LUMO energy levels of **BDT-TBT** and **BDT-THTBT** were higher than that of $PC_{71}BM$ (-3.96 eV). Compared with **BDT-TBT** which contain same conjugation backbone (BDT), introducing hexylthiophene unit effectively decrease the band gap and elevates HOMO energy level. As illustrated in Figure 3(b), dissociation of excitons and charge transporting process are energetically favorable.

2.3. Photovoltaic properties

By applying **BDT-TBT** and **BDT-THTBT** as donor materials and $PC_{71}BM$ as acceptor materials, the devices were fabricated with an inverted type structure, of ITO/ZnO (15 nm)/donor: $PC_{71}BM$/MoO_3 (20 nm)/Ag (100 nm). The photovoltaic parameters were tested with different blend ratios of donor and $PC_{71}BM$, and the optimum blend ratio was 1:1 (w/w) for both **BDT-TBTT** and **BDT-THTBT**. In addition, the effect of 1,8-diiodooctane (DIO, 0.5 vol.%) as processing additive on the photovoltaic performances were tested. DIO shows negative effect on the photovoltaic parameters. The current density (J) – voltage (V) curves of OSCs under AM 1.5G simulated illumination and the dark condition are shown in Figure 4 and the corresponding short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) of the devices are summarized in Table 1. For **BDT-TBT**, the highest PCE was 0.69% at the 3:3 blend ratio of **BDT-TBT** and $PC_{71}BM$. The V_{oc}, J_{sc}, and FF of the devices based **BDT-TBT** were 0.84 V, 2.56 mA/cm^2, and 31.9%. **BDT-THTBT** achieved higher PCE than that of **BDT-TBT**, which was 1.04%. The V_{oc}, J_{sc}, and FF of the devices based on **BDT-THTBT** were 0.82 V, 4.20 mA/cm^2, and 30.1%, respectively. As shown in Table 1, the J_{sc} devices based on **BDT-THTBT**:$PC_{71}BM$ (1:1) is 1.64 mA/cm^2 higher than that of the

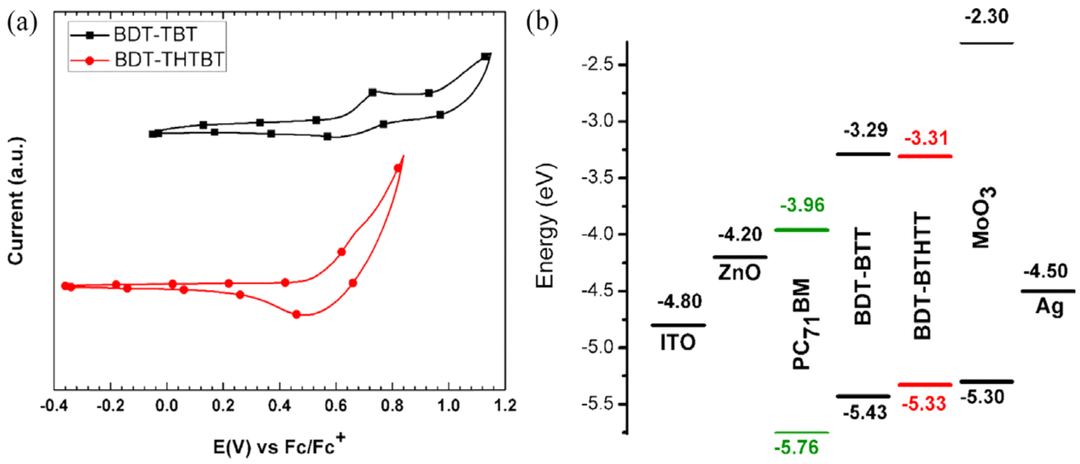


Figure 3. (a) Cyclic voltammograms of **BDT-TBTT** and **BDT-THTBT** and (b) the energy level diagrams of the components in the device.

Table 1. The best photovoltaic parameters of OSCs. The averages for the photovoltaic parameters of each device are given in parentheses

Donor	Blend ratio[a]	DIO (vol%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
BDT-TBT	1:1	0	2.56 (2.58±0.02)	0.84 (0.83±0.01)	31.9 (31.5±0.33)	0.69 (0.67±0.01)
	1:2	0	2.34 (2.32±0.03)	0.84 (0.82±0.01)	33.0 (32.0±0.78)	0.65 (0.61±0.03)
	1:1	0.5	1.91 (1.83±0.08)	0.88 (0.84±0.04)	35.7 (36.0±0.25)	0.60 (0.55±0.05)
	1:2	0.5	1.74 (1.73±0.01)	0.85 (0.83±0.02)	35.7 (34.6±0.78)	0.53 (0.49±0.02)
BDT-THTBT	1:1	0	4.20 (4.15±0.03)	0.82 (0.82±0.00)	30.1 (30.0±0.19)	1.04 (1.02±0.01)
	1:2	0	3.71 (3.73±0.02)	0.80 (0.79±0.01)	32.2 (31.8±0.37)	0.96 (0.93±0.02)
	1:1	0.5	4.06 (3.98±0.09)	0.83 (0.84±0.01)	27.7 (27.5±0.51)	0.93 (0.92±0.01)
	1:2	0.5	3.59 (3.55±0.03)	0.76 (0.76±0.00)	31.7 (31.5±0.20)	0.86 (0.86±0.01)

[a]Mass ratio of donor to $PC_{71}BM$.

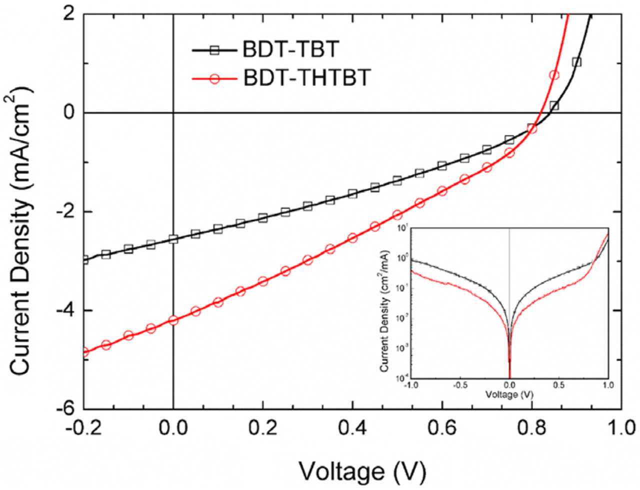


Figure 4. Current density-voltage curves of OSCs based on **BDT-TBT** and **BDT-THTBT** under AM 1.5G simulated illumination with an intensity of 100 mW/cm^2 and the dark condition.

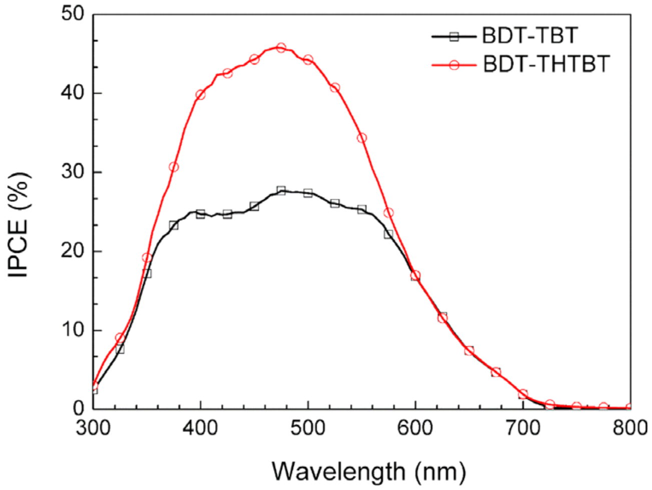


Figure 5. IPCE spectra of OPVs based on **BDT-TBT**:$PC_{71}BM$ (3:3) (square) and **BDT-THTBT**:$PC_{71}BM$ (3:3) (circle).

devices based on **BDT-TBT**:$PC_{71}BM$ (1:1). This is due to the extended conjugation length by insertion of HT unit.[25] However, the V_{oc} devices based on **BDT-THTBT**:$PC_{71}BM$ (1:1) is slightly decrease than that of the devices based on BDT-TBT:$PC_{71}BM$ (1:1) due to the elevation of HOMO energy levels. Broadly, lower HOMO energy level is affirmative for the improvement of the V_{oc}.[26] Therefore, the lower V_{oc} can be associated with the loss in charge carriers at the electrodes. Consistent with the value of V_{oc}, the FF devices based on **BDT-THTBT** is marginally lower than that of the devices based on **BDT-TBT**. The incident photon conversion efficiency (IPCE) spectra of the **BDT-TBT**:$PC_{71}BM$ and **BDT-THTBT**:$PC_{71}BM$ based on OSCs are showed in Figure 5 to verify the accuracy of measurements. The IPCE spectra are well correlated with the J_{sc} values of the devices.

3. Conclusions

A-D-A structured oligomers based on BDT as a D and BT as an A involving different alkyl chain in thiophene as p-conjugated bridge have been synthesized by the Stille coupling reaction. Thiophene rings as a p-extender lead to an elevation of the HOMO energy level as well as decreasing of the band gap. As a results, the **BDT-THTBT** based OSCs exhibit the best PCE of 1.04%. These results signify that increasing the number of thiophene with additional alkyl chain would enhance the performances of OSCs.

Supporting information: Information is available regarding the experimental procedure for the preparation of BDT-TBT and BDT-THTBT, fabrication and analysis of organic solar cells. The materials are available *via* the Internet at http://www.springer.com/13233.

References

(1) S. Oh, S. Badgujar, D. H. Kim, W. E. Lee, N. Khan, M. Jahandar, S. Rasool, C. E. Song, H. K. Lee, W. S. Shin, J. C. Lee, S. J. Moon, and S. K. Lee, *J. Mater. Chem. A*, **5**, 15923 (2017).
(2) Y. Q. Yi, H. Feng, M. Chang, H. Zhang, X. Wan, C. Li, and Y. Chen, *J. Mater. Chem. A*, **5**, 17204 (2017).
(3) S. Somasundaram, S. Jeon, and S. Park, *Macromol. Res.*, **24**, 226 (2016).
(4) Y.-H. Ha, J. E. Lee, M.-C. Hwang, Y. J. Kim, J.-H. Lee, C. E. Park, and Y.-H. Kim, *Macromol. Res.*, **24**, 457 (2016).
(5) H. Y. Kim, M. H. Choi, Y. W. Han, D. K. Moon, and J. R. Haw, *J. Ind. Eng. Chem.*, **33**, 209 (2016).
(6) N. Gasparini, L. Lucera, M. Salvador, M. Prosa, G. D. Spyropoulus, P. Kubis, H. J. Egeelhaf, C. J. Brabec, and T. Ameri, *Energy Environ. Sci.*, **10**, 885 (2017).
(7) D. Deng, Y. Zhang, J. Zhang, Z. Wang, L. Zhu, J. Fang, B. Xia, Z. Wang, K. Lu, W. Ma, and Z. Wei, *Nat. Commun.*, **7**, 13740 (2016).
(8) Y. Liu, C. C. Chen, Z. Hong, J. Gao, Y. Yang, H. Zhou, L. Dou, G. Li, and Y. Yang, *Sci. Rep.*, **3**, 3356 (2013).
(9) R. Xin, J. Feng, C. Zeng, W. Jiang, L. Zhang, D. Meng, Z. Ren, Z. Wang,

and S. Yan, *ACS Appl. Mater. Interfaces*, **9**, 2739 (2017).

(10) R. Dominguez, N. F. Montcada, P. Cruz, E. Palomares, and F. Langa, *Phys. Chem. Chem. Phys.*, **19**, 3640 (2017).

(11) Q. Zhang, B. Kan, F. Liu, G. Long, X. Wang, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T. P. Russell, and Y. Chen, *Nat. Photonics*, **9**, 35 (2015).

(12) W. Chen and Q. Zhang, *J. Mater. Chem. C*, **5**, 1275 (2017).

(13) N. Liang, W. Jiang, J. Hou, and Z. Wang, *Mater. Chem. Front.*, **1**, 1291 (2017).

(14) J. Ku, Y. Lansac, Y. H. and J. Jang, *Phys. Chem. C*, **115**, 21508 (2011).

(15) Y. Eom, C. E. Song, W. S. Shin, S. K. Lee, and E. Lim, *J. Ind. Eng. Chem.*, **45**, 338 (2017).

(16) L. Ye, X. Jiao, H. Zhang, S. Li, H. Yao, H. Ade, and J. Hou, *Macromolecules*, **48**, 7156 (2015).

(17) H. Yao, L. Ya, H. Zhang, S. Li, S. Zhang, and J. Hou, *Chem. Rev.*, **116**, 7397 (2016).

(18) R. K. Pai, T. N. Ahipa, and B. Hemavathi, *RSC Adv.*, **6**, 23760 (2016).

(19) Y. Jeon, T. M. Kim, J. J. Kim, and J. I. Hong, *New J. Chem.*, **39**, 9591 (2015).

(20) M. Karakus, D. H. Apaydin, D. E. Yildiz, L. Toppare, and A. Cirpan, *Polymer*, **53**, 1198 (2012).

(21) N. Sylvianti, Y. W. Kim, M. A. Marsya, D. K. Moon, and J. H. Kim, *Synth. Met.*, **221**, 127 (2016).

(22) P. Chen, K. Nakano, K. Suzuki, K. Hashimoto, T. Kikitsu, D. Hashizume, T. Koganezawa, and K. Tajima, *ACS Appl. Mater. Interfaces*, **9**, 4758 (2017).

(23) E. Bundgaard and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, **91**, 954 (2007).

(24) F. Zhang, D. Wu, Y. Xu, and X. Feng, *J. Mater. Chem.*, **21**, 17590 (2011).

(25) N. V. Elumalai and A. Uddin, *Energy Environ. Sci.*, **9**, 391 (2016).

(26) X. Jiang, Y. Yang, J. Zhu, T. K. Lau, P. Cheng, X. Lu, X. Zhan, and X. Chen, *J. Mater. Chem. C*, **5**, 8179 (2017).