

A New Nonfullerene Electron Acceptor with a Ladder Type Backbone for High-Performance Organic Solar Cells

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Organic solar cells (OSC) are one of the promising green energy alternatives for future renewable energy conversion, due to advantages such as low cost, low weight, and flexibility.^[1–5] The past decade has witnessed dramatic progress in this area, and power conversion efficiency (PCE) over 10% has been achieved for single junction organic solar cells with bulk-heterojunction architecture using fullerene derivatives as the acceptor, mainly due to the development of novel donor materials and device optimization.^[6–11] The great success of the fullerene derivative acceptors in OSCs is attributed to several fundamental properties including high electron affinity and electron mobility, isotropic charge transport, as well as formation of appropriate phase separation.^[12,13] However, the fullerene derivatives have some intrinsic drawbacks, such as weak absorption in the visible region, high cost in the synthesis and purification processes, etc. To address these issues, nonfullerene electron acceptor materials with good light absorption, facile synthesis, fine-tuned energy levels, and low cost, have developed rapidly in recent years.^[14,15] Currently, many nonfullerene acceptors including the newly emerged and excellent 3,9-bis(2methylene-(3(1,1dicyanomethylene)indanone))-5,5,11,11-tetrakis(4hexylphenyl)-dithieno[2,3d:2',3'd']sindaceno[1,2b:5,6b']dithiophene (ITIC) (as shown in Figure 1a), etc. have been designed and excellent performance has been achieved for the devices based on these materials.^[16–18]

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For the nonfullerene molecules design, many strategies such as the incorporation of n-type molecules/blocks, i.e., perylene diimide and naphthalene derivatives, and the use of electron withdrawing units as the end units have been explored.^[19–32] Among them, small molecules with acceptor–donor–acceptor (A–D–A) backbone structures seem to be the most successful ones. This echoes the success of using small molecules with A–D–A structures as the donor materials for the widely studied [6,6]-phenyl-C61/C71-butyricacidmethylester (PCBM) based systems. In the last few years, we have reported a series of small molecules with mainly thiophene-based A–D–A structures as the donors with fullerene derivatives as the acceptors and PCEs over 10% have been achieved.^[11,33–35] It has been found that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of those molecules are mainly determined by their electron donor core units and electron withdrawing terminal units, respectively. Furthermore, their absorptions, mobilities, and molecule packing modes at solid states could also be tuned through delicate molecule design. Based on these results and the recent development of in nonfullerene acceptors, it is intrinsic to design new acceptors with the much successful A–D–A backbone systems. Very recently, we have reported a rather a simple acceptor molecule named 2,2'-(((9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (DICTF), which has a A–D–A structure and fluorene as the central block and 2-(2,3-dihydro-3-oxo-1H-inden-1-ylidene)propanedinitrile (INCN) as the end group.^[23] DICTF in thin films showed good absorption in the range of 400–700 nm and gave a decent PCE of 7.93% when combining with the polymer poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th) as the donor material. It has been well-known that for many organic optoelectronic materials, the introduction of a ladder type backbone with fused rings is an effective strategy to both tune the rigidity of the molecular geometries and adjust the optoelectronic properties such as absorption, energy levels, etc.^[36–39] With these in mind, herein, we designed a new acceptor following the above strategy by fusing the fluorene core in DICTF with the adjacent thiophene units to obtain the ladder type molecule 2,9-bis(2methylene(3(1,1dicyanomethylene)indanone))7,12-dihydro-4,4,7,7,12,12-hexaoctyl-4H-cyclopenta[2'',1'':5,6;3'',4'':5',6']diindeno[1,2-b:1',2'-b']dithiophene (FDICTF) (Figure 1a). With this small change, the absorption and band structure are tuned as expected. The impact of such a small change in molecular structure on the optical, electrochemical properties,

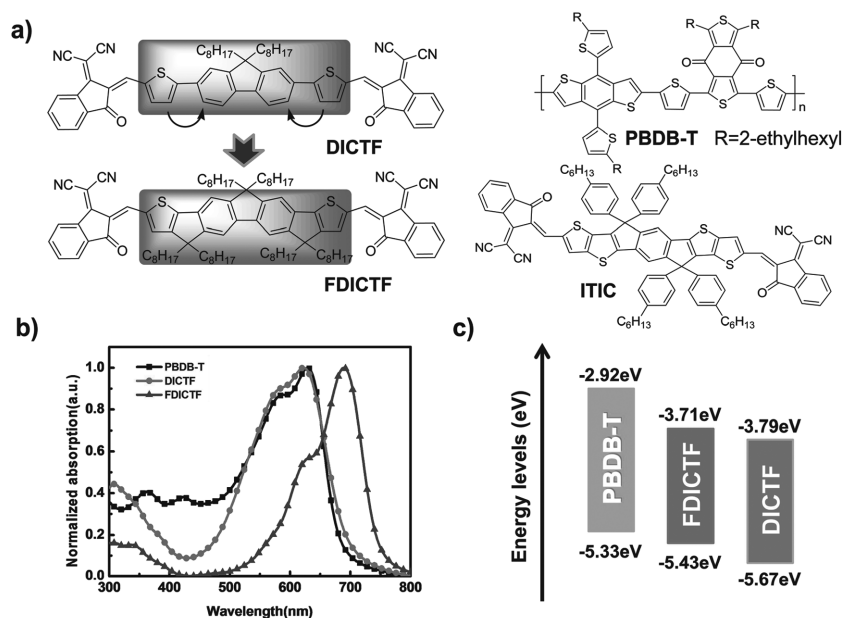
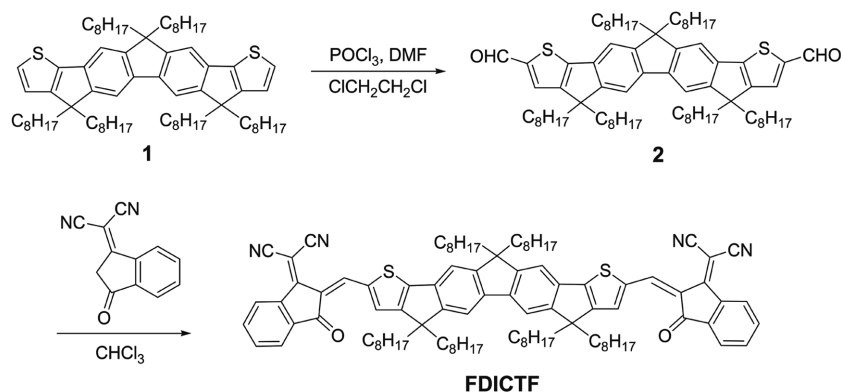


Figure 1. a) Chemical structures of DICTF, FDICTF, ITIC, and PBDB-T. b) Absorption spectra of DICTF, FDICTF, and PBDB-T in thin films. c) Estimated energy levels of DICTF, FDICTF, and PBDB-T from electrochemical cyclic voltammetry.

morphologies, and device performance were systematically investigated. Devices based on PTB7-Th:FDICTF gave a PCE of 7.87%, which is comparable with that of PTB7-Th:DICTF shown in Table S3 in the Supporting Information.^[23] For better complementary absorptions and matched energy levels, a middle gap polymer poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5'-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T) was chosen as the donor to fabricate the devices with FDICTF for further detailed device studies. A high PCE of 10.06% was achieved for the PBDB-T:FDICTF based devices, compared with the relatively moderate PCE (5.93%) of the devices of PBDB-T:DICTF. These results indicate that the utilization of a ladder backbone structure with fused rings as the core units in A–D–A type molecules might be an effective strategy for designing high-performance nonfullerene acceptors.

The synthetic route of FDICTF is shown in Scheme 1. The detailed procedures are provided in the Supporting



Scheme 1. Synthetic route of FDICTF.

Information. The fused core 1 was synthesized according to the literature method.^[40] Intermediate 2 was prepared by Vilsmeier–Haack reaction of 1 using POCl₃ and DMF (N,N-Dimethylformamide). Subsequent Knoevenagel condensation between 2 and INCN afforded the target molecule in high yield. The chemical structure of FDICTF was fully characterized by ¹H and ¹³C NMR and matrix assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). It exhibits good solubility in common organic solvents, such as dichloromethane, chloroform, and *ortho*-dichlorobenzene at room temperature. Thermal characteristics with thermogravimetric analysis (Figure S1, Supporting Information) under nitrogen atmosphere indicates it has good thermal stability with a weight-loss lower than 5% up to 336 °C and meets the requirement of device fabrication.

FDICTF in chloroform solution exhibits strong absorption in the 550–720 nm region with a very high maximum extinction coefficient of $2.7 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 665 nm, which is three times of that of DICTF ($9.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 587 nm) (Figure S2, Supporting Information). As shown in Figure 1b, the film of FDICTF shows strong absorption in the wavelength region from 500 to 770 nm, and the absorption onset of 760 nm corresponds to an optical bandgap of 1.63 eV. In contrast, the optical bandgap of DICTF films estimated from the absorption edge (681 nm) is 1.82 eV. In addition, the maximum absorption peak of FDICTF in thin films shows a significant redshift of 65 nm compared with that of DICTF. This is consistent with the fact that, compared with molecule DICTF, FDICTF has an increased effective π -conjugation by bridging the adjacent fluorene with the thiophene units and a better coplanarity would be expected (also see below). The absorption data of DICTF and FDICTF are summarized in Table 1.

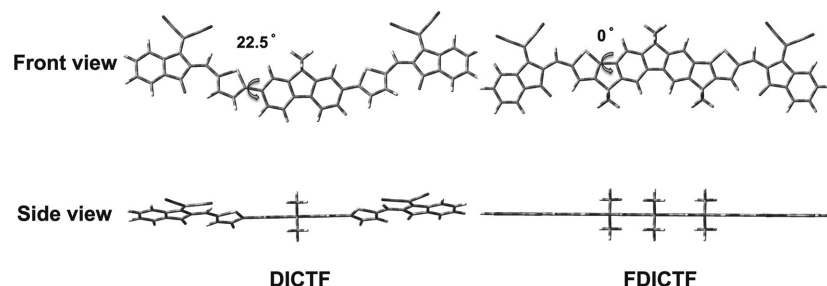
The electrochemical behavior of FDICTF has been investigated by cyclic voltammetry (CV) (Figure S4, Supporting Information). The energy levels were estimated from the oxidation and reduction wave in CV spectra, and the measurement was referenced by the energy level of Fc/Fc⁺ (−4.8 eV below vacuum).^[41] The results are presented in Figure 1c and Table 1. The fused structure in FDICTF facilitates the first oxidation and reduction event, as it occurs at a lower oxidation and reduction potential compared with DICTF, which leads to higher HOMO (−5.43 eV) and LUMO (−3.71 eV) energy levels.^[37] In addition, the LUMO offsets between FDICTF/DICTF and the donor PBDB-T (−2.92 eV) are larger than 0.7 eV, sufficient to provide the driving force for exciton dissociation.^[17]

In order to compare the chemical geometry structure of the two molecules of DICTF and FDICTF, density functional theory at the

Table 1. Optical and electrochemical data of DICTF and FDICTF.

Molecules	UV-vis				CV		
	$\lambda_{\text{max}}^{\text{sol}}$ [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	$\lambda_{\text{max}}^{\text{film}}$ [nm]	$E_{\text{g}}^{\text{opt}}$ [eV] ^{a)}	HOMO [eV]	LUMO [eV]	E_{g}^{cv} [eV]
DICTF	587	9.3×10^4	624	1.82	-5.67	-3.79	1.88
FDICTF	665	2.7×10^5	689	1.63	-5.43	-3.71	1.72

^{a)}Optical bandgap was obtained from the onset wavelength of the film.

**Figure 2.** Optimized molecular geometries of DICTF and FDICTF at B3LYP/6-31G*.

B3LYP/6-31G* level were performed.^[42,43] Frequency analysis was followed to ensure that the optimized geometries were at stable states, and the octyl groups were replaced by methyl ones for simplification. As shown in **Figure 2**, dihedral angles of 22.5° and 0° were obtained between the thiophene and fluorene units in DICTF and FDICTF, respectively. And the different electronic communication in each building block due to the difference of dihedral angles are consistent with the electron cloud distributions at frontier molecular orbitals (Figure S5, Supporting Information). Therefore, the improved planarity and thus better π -electron delocalization of FDICTF is expected to cause its bathochromically shifted absorption.

The photoluminescence (PL) spectra of the pure donor/acceptor films and the blend films were measured and the results were shown in Figures S6 and S7 in the Supporting Information. The pure PBDB-T film exhibits a PL emission band in the range of 650–850 nm. DICTF and FDICTF show similar PL emission in the region of 700–820 nm. Compared with the pure films, the blend films exhibit a significant PL quenching, indicating that efficient photoinduced charge transfer occurs in the films between the donor and acceptor molecules, which is a prerequisite for achieving high photovoltaic performance.^[44]

For better complementary absorptions and matched energy levels, polymer PBDB-T was chosen as the donor material to blend with FDICTF for detailed device studies using a conventional device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)/active

layer/*N,N'*-bis(propylenedimethylamine)-3,4,9,10-perylene diimide (PDIN) /Al. PDIN is a perylene diimide derivative (as shown in **Figure 3b**), developed as cathode interlayer by Li and co-workers, which can modify the work function of the electrode and be beneficial to charge extraction efficiency and reduce recombination losses.^[45] Similar devices using the newly emerged nonfullerene acceptor DICTF were also fabricated and optimized for comparison. The optimized device performance data were summarized in **Table 2**, and the corresponding *J*-*V* characteristics were shown in **Figure 3c**. More detailed device parameters were provided in the Supporting Information (Tables S1 and S2). Benefitting from their high-lying LUMO energy levels, devices based on DICTF and FDICTF as acceptors blending with PBDB-T as donors all gave a high open-circuit voltage (V_{oc}) of over 0.90 V. However, compared with PBDB-T:DICTF system, PBDB-T:FDICTF based devices showed much higher short-circuit current density (J_{sc}), due to their much better complementary absorption and stronger absorption coefficient as shown in **Figure S3** in the Supporting Information, which is consistent with external quantum efficiency (EQE) studies (**Figure 3d**). The

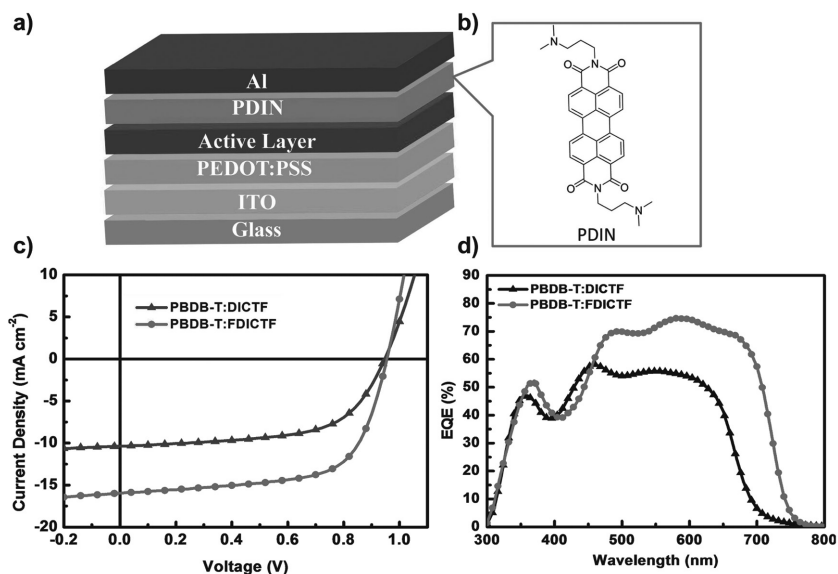
**Figure 3.** a) Device structure of the OSCs. b) The chemical structure of PDIN. c) Current density-voltage (*J*-*V*) characteristics and d) EQE spectra of OSCs based on FDICTF and DICTF at optimized conditions.

Table 2. Device performance parameters of OSCs based on PBDB-T measured at simulated 100 mW cm⁻² AM 1.5G illumination.

Acceptor	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%] ^{a,b)}
DICTF	0.93 ± 0.01	10.30 ± 0.20	0.59 ± 0.01	5.65 ± 0.28 (5.93)
FDICTF	0.94 ± 0.01	15.81 ± 0.28	0.66 ± 0.01	9.81 ± 0.25 (10.06)
PC ₇₁ BM	0.86 ± 0.01	12.16 ± 0.23	0.68 ± 0.01	7.11 ± 0.22 (7.33)

^{a)}Average values from 20 devices; ^{b)}The best PCEs are provided in parentheses.

optimized device of FDICTF shows high and broad photo-to-current response from 300 to 770 nm with a maximum value of 75% and over 70% across the range of 500–700 nm, indicating an efficient photoelectron conversion process. While the EQE of PBDB-T:DICTF devices gave rather low values. Based on these results, the maximum PCEs for the two acceptors reached 10.06% and 5.93%, respectively, at optimized conditions. The PCE value of FDICTF-based devices was higher than that of the control device based on PBDB-T:PC₇₁BM ([6,6]-phenyl-C71-butyric acid methyl ester) (7.33%, as shown in Table 2), and was among the highest values reported for nonfullerene acceptor solar cells.^[16–18]

The morphology of the blend films was investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in the AFM images (Figure 4a,b), the root-mean-square roughness of the optimized films of PBDB-T:FDICTF and PBDB-T:DICTF gave values of 3.4 and 3.2 nm, respectively. The TEM images of two optimized films are shown in Figure 4c,d. There are clear fiber structures and

phase separation in the PBDB-T:FDICTF blending film with interpenetrating structures. From the chemical structures, such morphology difference could be due to FDICTF having a more planar backbone and larger steric effect than DICTF, leading to relatively inferior miscibility with the polymer PBDB-T in contrast to DICTF. In contrast, no clear phase separation was observed in the PBDB-T:DICTF film. These differences should contribute to the improvement of the exciton dissociation efficiency and carrier mobility in the OSC devices of PBDB-T:FDICTF. These results are also consistent with the higher J_{sc} and fill factor (FF) of PBDB-T:FDICTF devices compared with that of PBDB-T:DICTF devices.

The molecular stacking of a pure FDICTF film was investigated by X-ray diffraction (XRD) analysis (Figure S8, Supporting Information). There is no clear peak in the XRD pattern of FDICTF, indicating its amorphous nature, which is probably attributed to the steric effect of the out-of-plane side-chains. This steric molecular geometry owing to the octyl groups at the sp³-hybridized bridging carbon atoms might prevent excessive π - π stacking and suppress strong intermolecular aggregation effectively in the acceptor phases.

The bulk charge mobility properties of the optimized PBDB-T:DICTF and PBDB-T:FDICTF blend films were measured by the space-charge limited current method. The hole and electron mobilities were measured with device structures of ITO/PEDOT:PSS/active layer/Au and Al/active layer/Al, respectively. As shown in Figure S9 (Supporting Information), the PBDB-T:DICTF blend films show hole mobility of 1.56×10^{-5} cm² V⁻¹ s⁻¹ and electron mobility of 1.49×10^{-5} cm² V⁻¹ s⁻¹. For PBDB-T:FDICTF, the hole and electron mobilities increased to 3.37×10^{-5} and 2.40×10^{-5} cm² V⁻¹ s⁻¹, respectively. Both the improved and balanced electron and hole mobilities should have contribution to the observed higher values of J_{sc} and FF for FDICTF-based devices.

In summary, we have designed and synthesized an A–D–A type nonfullerene acceptor with a ladder fused structure. A simple change by fusing the thiophene unit in the previous simple molecule DICTF has led to a stronger and better complementary absorption and tunable molecular energy levels. For the morphology control in the active layer, the out-of-plane chains on the fused core of FDICTF can effectively prevent overaggregation in the acceptor phases, contributing to the formation of a favorable interpenetrating donor/acceptor network with a suitable degree of phase separation in the active layers. Devices with the polymer donor PBDB-T gave a high PCE of 10.06%, which is much higher than that of the control devices with fullerene counterparts. The results demonstrate that using a ladder A–D–A structure as the backbone in acceptor molecules is an effective strategy to design new and high-performance nonfullerene acceptors. Considering the wide structure

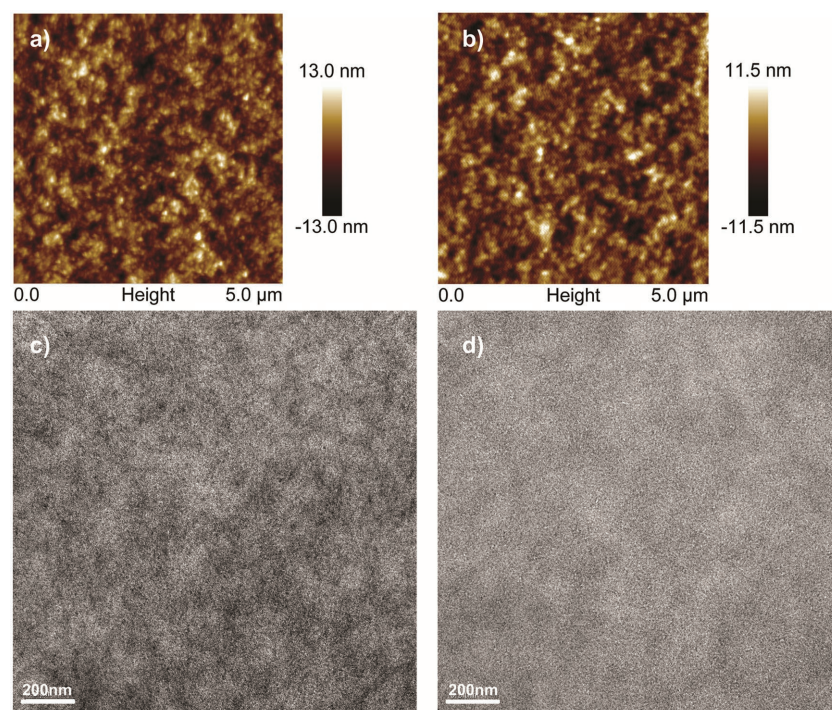


Figure 4. Tapping-mode AFM height images of the active layers of a) PBDB-T:FDICTF blend films and b) PBDB-T:DICTF blend films. TEM images of c) PBDB-T:FDICTF blend films and d) PBDB-T:DICTF blend films.

varieties, it is believed that great breakthrough in nonfullerene acceptors based OSCs could be realized through delicate molecule design and device optimization in the near future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, 270, 1789.
- [2] L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, *Adv. Mater.* **2013**, 25, 6642.
- [3] A. J. Heeger, *Chem. Soc. Rev.* **2010**, 39, 2354.
- [4] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2009**, 93, 394.
- [5] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, 11, 15.
- [6] J. D. Chen, C. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. Li, J. X. Tang, *Adv. Mater.* **2015**, 27, 1035.
- [7] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, 5, 5293.
- [8] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, *Nat. Photonics* **2015**, 9, 174.
- [9] C. Liu, C. Yi, K. Wang, Y. Yang, R. S. Bhatta, M. Tsige, S. Xiao, X. Gong, *ACS Appl. Mater. Interfaces* **2015**, 7, 4928.
- [10] S. Zhang, L. Ye, W. Zhao, B. Yang, Q. Wang, J. Hou, *Sci. China Chem.* **2015**, 58, 248.
- [11] B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni, G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang, Y. Cao, T. P. Russell, Y. Chen, *J. Am. Chem. Soc.* **2015**, 137, 3886.
- [12] T. Liu, A. Troisi, *Adv. Mater.* **2013**, 25, 1038.
- [13] Y. He, Y. Li, *Phys. Chem. Chem. Phys.* **2011**, 13, 1970.
- [14] Y. Lin, Y. Li, X. Zhan, *Chem. Soc. Rev.* **2012**, 41, 4245.
- [15] J. E. Anthony, *Chem. Mater.* **2011**, 23, 583.
- [16] Y. Lin, F. Zhao, Q. He, L. Huo, Y. Wu, T. C. Parker, W. Ma, Y. Sun, C. Wang, D. Zhu, A. J. Heeger, S. R. Marder, X. Zhan, *J. Am. Chem. Soc.* **2016**, 138, 4955.
- [17] W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, J. Hou, *Adv. Mater.* **2016**, 28, 4734.
- [18] H. Bin, Z. G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2016**, 138, 4657.
- [19] Y. Liu, C. Mu, K. Jiang, J. Zhao, Y. Li, L. Zhang, Z. Li, J. Y. L. Lai, H. Hu, T. Ma, R. Hu, D. Yu, X. Huang, B. Z. Tang, H. Yan, *Adv. Mater.* **2015**, 27, 1015.
- [20] Q. Wu, D. Zhao, A. M. Schneider, W. Chen, L. Yu, *J. Am. Chem. Soc.* **2016**, 138, 7248.
- [21] Y. J. Hwang, B. A. Courtright, A. S. Ferreira, S. H. Tolbert, S. A. Jenekhe, *Adv. Mater.* **2015**, 27, 4578.
- [22] W. Ni, M. Li, B. Kan, F. Liu, X. Wan, Q. Zhang, H. Zhang, T. P. Russell, Y. Chen, *Chem. Commun.* **2016**, 52, 465.
- [23] M. Li, Y. Liu, W. Ni, F. Liu, H. Feng, Y. Zhang, T. Liu, H. Zhang, X. Wan, B. Kan, Q. Zhang, T. P. Russell, Y. Chen, *J. Mater. Chem. A* **2016**, 4, 10409.
- [24] Y. J. Hwang, T. Earmme, B. A. Courtright, F. N. Eberle, S. A. Jenekhe, *J. Am. Chem. Soc.* **2015**, 137, 4424.
- [25] S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C. H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant, I. McCulloch, *Nat. Commun.* **2016**, 7, 11585.
- [26] J. W. Jung, J. W. Jo, C. C. Chueh, F. Liu, W. H. Jo, T. P. Russell, A. K. Jen, *Adv. Mater.* **2015**, 27, 3310.
- [27] S. Li, W. Liu, M. Shi, J. Mai, T.-K. Lau, J. Wan, X. Lu, C.-Z. Li, H. Chen, *Energy Environ. Sci.* **2016**, 9, 604.
- [28] Y. Zhou, T. Kurosawa, W. Ma, Y. Guo, L. Fang, K. Vandewal, Y. Diao, C. Wang, Q. Yan, J. Reinspach, J. Mei, A. L. Appleton, G. I. Koleilat, Y. Gao, S. C. B. Mannsfeld, A. Salleo, H. Ade, D. Zhao, Z. Bao, *Adv. Mater.* **2014**, 26, 3767.
- [29] Y. Zhong, M. T. Trinh, R. Chen, W. Wang, P. P. Khlyabich, B. Kumar, Q. Xu, C.-Y. Nam, M. Y. Sfeir, C. Black, M. L. Steigerwald, Y.-L. Loo, S. Xiao, F. Ng, X. Y. Zhu, C. Nuckolls, *J. Am. Chem. Soc.* **2014**, 136, 15215.
- [30] K. Gao, L. Li, T. Lai, L. Xiao, Y. Huang, F. Huang, J. Peng, Y. Cao, F. Liu, T. P. Russell, R. A. Janssen, X. Peng, *J. Am. Chem. Soc.* **2015**, 137, 7282.
- [31] J.-L. Wang, Z. Wu, J.-S. Miao, K.-K. Liu, Z.-F. Chang, R.-B. Zhang, H.-B. Wu, Y. Cao, *Chem. Mater.* **2015**, 27, 4338.
- [32] P. Josse, C. Dalinot, Y. Jiang, S. Dabos-Seignon, J. Roncali, P. Blanchard, C. Cabanetos, *J. Mater. Chem. A* **2016**, 4, 250.
- [33] B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng, Y. Chen, *J. Am. Chem. Soc.* **2014**, 136, 15529.
- [34] Q. Zhang, B. Kan, F. Liu, G. Long, X. Wan, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T. P. Russell, Y. Chen, *Nat. Photonics* **2014**, 9, 35.
- [35] W. Ni, M. Li, X. Wan, Y. Zuo, B. Kan, H. Feng, Q. Zhang, Y. Chen, *Sci. China Chem.* **2014**, 58, 339.
- [36] R. Chen, Y. Wang, T. Chen, H. Li, C. Zheng, K. Yuan, Z. Wang, Y. Tao, C. Zheng, W. Huang, *J. Phys. Chem. B* **2015**, 119, 583.
- [37] B. Kobin, L. Grubert, S. Blumstengel, F. Henneberger, S. Hecht, *J. Chem. Mater.* **2012**, 22, 4383.
- [38] M. Forster, K. O. Annan, U. Scherf, *Macromolecules* **1999**, 32, 3159.
- [39] J. Roncali, *Chem. Rev.* **1997**, 97, 173.
- [40] C.-Y. Chang, Y.-J. Cheng, S.-H. Hung, J.-S. Wu, W.-S. Kao, C.-H. Lee, C.-S. Hsu, *Adv. Mater.* **2012**, 24, 549.
- [41] J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, 7, 551.
- [42] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [43] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- [44] H. Yao, R. Yu, T. J. Shin, H. Zhang, S. Zhang, B. Jang, M. A. Uddin, H. Y. Woo, J. Hou, *Adv. Energy Mater.* **2016**, 6, 1600742.
- [45] Z.-G. Zhang, B. Qi, Z. Jin, D. Chi, Z. Qi, Y. Li, J. Wang, *Energy Environ. Sci.* **2014**, 7, 1966.