Journal of Materials Chemistry C



View Article Online

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Cite this: J. Mater. Chem. C, 2019, 7, 15344

Oxygen heterocycle-fused indacenodithiophenebithiophene enables an efficient non-fullerene molecular acceptor†

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To improve the power conversion efficiency (PCE) of solar cells based on non-fullerene acceptors (NFAs), designing low bandgap NFAs of enhanced light-harvesting capability is desirable. Herein, a new set of NFAs based on an oxygen heterocycle-fused indacenodithiophenebithiophene core, were designed and synthesized, all of which achieved low bandgaps around 1.3 eV. An optimal power conversion efficiency of $\sim 8.4\%$ was realized by systematic sidechain engineering. Detailed comparison based on the designed NFAs clarifies that the optimal molecule, **IDTODT-3**, contributes to a moderate phase separation with balanced charge transport and reduced recombination in the blend, and thus performs best. This work verifies the effectiveness of oxygen heterocycle-fusion on realizing LBG, which provides guidelines for designing efficient NFAs via molecule-engineering.

Received 12th September 2019, Accepted 7th November 2019

DOI: 10.1039/c9tc05041h

rsc.li/materials-c

Introduction

Organic solar cells (OSCs) show great potential for photoelectric conversion due to the advantages of low-cost, large-area and flexible device fabrication.¹⁻³ Non-fullerene acceptors (NFAs) are very promising alternatives due to their strong absorption in the visible region, adjustable energy levels and crystallization/ aggregation properties compared with fullerene acceptors.^{4–10} In recent years, considerable efforts have been dedicated to research on acceptor-donor-acceptor (A-D-A) type NFAs since the initial report of 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']*s*-indaceno[1,2-*b*:5,6-*b*']-dithiophene, ITIC.^{11–17} The photovoltaic performance of non-fullerene acceptors was gradually improved by molecular engineering through two main strategies: (a) mainchain engineering,¹⁸ which aims to extend the π -conjugation, enhance the absorption, adjust the energy levels and tune the mobility; and (b) side-chain engineering, which aims to

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9tc05041h

improve the solubility, tune the aggregation and optimize the morphology.^{19,20} Due to such efforts, OSCs based on NFAs have achieved impressive power conversion efficiencies (PCEs) above 15%.²¹

A key parameter limiting the power conversion efficiency (PCE) of OSCs is the short circuit current (J_{sc}) , which is mainly limited by the light absorption of photoactive materials.²² In current well-developed NFA-based solar systems, expanding the spectral coverage of the NFAs has been proved to be efficient and straightforward in enhancing photon-harvesting and increasing the J_{sc} .²³ However, narrowing the optical bandgap (E_g^{opt}) of NFAs too much often brings significant energy loss ($E_{\rm loss}$), as $E_{\rm loss} = E_{\rm g}^{\rm opt} - eV_{\rm oc}$ defines.²⁴ Therefore, most OSCs incorporating low bandgap (LBG) NFAs show promising J_{sc} yet very low open circuit voltage (V_{oc}). Despite a few reports displaying promising PCEs above 10% by using LBG NFAs of less than 1.4 eV E_g^{opt} , most efficient LBG NFAs show band gaps around 1.5–1.7 eV due to better balanced $J_{\rm sc}$ and $V_{\rm oc}$.^{25,26} Therefore, it is urgent to develop new narrow bandgap $(E_{\rm g} < 1.4 \text{ eV})$ NFAs to match with the wide-bandgap polymer donors to further improve the device performance and deeply understand the design strategy of photovoltaic materials, which is also challenging.

Along with rapid progress on NFAs, interesting LBG NFA cases reporting encouraging PCEs shed new light on designing such type of materials. As is well-known, realizing LBG of acceptors relies mainly on energy level tuning, which can be achieved either by enhancing the electron-donating ability of the central core to elevate the highest occupied molecular

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orbital (HOMO) energy level, or by strengthening the accepting ability of the terminal unit to decrease the lowest unoccupied molecular orbital (LUMO) energy level. Both applications would result in an improved ICT and reduced bandgap. Recently, Hou et al. reported a new LBG NFA, IEICO-4F, which shows an ultra-narrow band gap of 1.24 eV and records an impressive $J_{\rm sc}$ of 25.3 mA cm⁻². The key of this design is the realization of an enhanced intramolecular charge transfer (ICT) effect by the apt introduction of alkoxy groups and fluorine atoms onto the central D and terminal A moieties.²⁴ Extending the length of the conjugate plane is also an effective way to raise the HOMO level and narrow the E_g^{opt} . Cheng et al. found an obvious E_{g}^{opt} decrease by comparing a fused NFA DTFT9-FIC (E_{g}^{opt} : 1.48 eV) with a non-fused DTFT5-FIC (E_{g}^{opt} : 1.65 eV), which was attributed to the extension of the conjugated π plane.³¹ Introducing a carbon-oxygen (C-O) bridge into the A-D-A molecules has been viewed to be an alternative way to realize enhanced ICT. By introducing an O-atom into the IDT core, we obtained NDBTP and NBDTP-F, both demonstrating that the incorporation of an oxygen heterocycle efficiently narrows the E_{g}^{opt} while has least influence on the LUMO of NFAs.^{27,28} Ding et al. reported COi8DFIC with an E_{g}^{opt} of 1.26 eV and a PCE above 12%, which also witnesses the effectiveness of enhanced ICT.¹⁹ By a comparative study on a series of NFAs having the same terminal electron-accepting groups, but different C-O bridged electrondonating cores, they suggested that the device performance highly relates to the electron-donating core of the constructed NFAs.

Inspired by the above progress on LBG NFAs achieved by oxygen heterocycle-incorporation, we were motivated to develop new LBG NFAs through further optimizing the fused central cores. By incorporating oxygen heterocycles into the indacenodithiophenebithiophene (IDTDT) core (Fig. 1), we constructed three new NFAs with E_g^{opt} all below 1.4 eV. As indicated by a Gaussian theoretical calculation at the B3LYP/6-31G* level (Fig. S1, ESI†), the introduction of fused oxygen heterocycles contributes to a more deep-loading LUMO than the HOMO, which benefits a narrowed bandgap. Systematic side chain engineering^{29–33} was conducted with an optimized molecule and photovoltaic performance achieved. Among all three LBG NFAs of different alkyl chain substituents, the **IDTODT-3** molecule

Fig. 1 Chemical structure of IDTODTs with varied alkyl chain substituents.

achieves a PCE of 8.34%, which shows favourable molecular packing and blending morphology. The molecule displays good potential for tandem solar cell applications.³⁴

Results and discussion

Material synthesis and characterization

The synthetic routes of IDTODT-1, IDTODT-2 and IDTODT-3 are shown in Scheme 1. Precursors 1-11 were prepared according to the published procedures with synthetic and characteristic details (¹H NMR, ¹³C NMR and mass spectra) provided in the ESI.[†] Compounds 12 and 15 were synthesized through Stille- and Negishi-coupling reactions, respectively while compounds 13 and 16 were synthesized through a sequence of diaddition and acid-facilitated intramolecular cyclization. All the final products were achieved through a Knoevenagel condensation reaction. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability. As shown in Fig. S2 (ESI⁺), all the materials show good thermal stability with decomposition temperatures (T_d) at 312.4 °C, 260.8 °C and 300.0 °C for **IDTODT-1**, **IDTODT-2** and IDTODT-3, respectively, T_d defined by 5% weight loss. The normalized ultraviolet-visible (UV-vis) optical absorption spectra of the three materials in chloroform and in film states are shown in Fig. S3 (ESI[†]) and Fig. 2. The three IDTODTs exhibit similar absorption in the solution state with maximal absorption peaks all appearing at 788 nm, yet show different maximal absorption coefficiencies (ε). Comparably, **IDTODT-3** show a larger ε (4.27 \times 10^5 m^{-1}) than the other two molecules ($3.33 \times 10^5 \text{ m}^{-1} \text{ cm}^{-1}$ for **IDTODT-1** and $2.74 \times 10^5 \text{ m}^{-1} \text{ cm}^{-1}$ for **IDTODT-2**, respectively). The three molecular acceptors show similar bathochromic shifts of 32 nm (IDTODT-1), 33 nm (IDTODT-2) and 30 nm (IDTODT-3), which suggests similar molecule packing mode in their respective pristine films. The optical bandgaps are estimated to be 1.32 eV, 1.35 eV and 1.34 eV for IDTODT-1, IDTODT-2 and IDTODT-3 respectively, calculation based on the onsets of film absorption. The molecules are all optically complementary with the PBDB-T polymer donor.

The frontier orbital energy levels of the three NFAs were determined by electrochemical cyclic voltammetry (CV) measurement. The highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels for **IDTODT-1**, **IDTODT-2** and **IDTODT-3** were -5.35/-3.90, -5.38/-3.95 and -5.39/-3.96 eV respectively, measured using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard (see Table 1 and Fig. S3, ESI⁺).

Photovoltaic performance

Bulk-heterojunction solar cells of conventional device structure (ITO/PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrenesulfonate)/active layer(**IDTODT-1**, **IDTODT-2** or **IDTODT-3**: PBDB-T)/PDINO³⁵/Al) were fabricated to investigate the photovoltaic performance of the three NFAs. Detailed optimization of the device performance was performed by adjusting the annealing temperature, film thickness, *etc.* (see Tables S1–S6, ESI†). Fig. 3a shows the typical current density–voltage (*J–V*) curves and external









Fig. 2 (a) Normalized UV-vis absorption of IDTODT-1, IDTODT-2 and IDTODT-3 films. (b) Energy level diagrams of IDTODT-1, IDTODT-2 and IDTODT-3.

Table 1 Optical and electrochemical data of IDTODT-1, IDTODT-2 and IDTODT-3

Molecule	$\lambda_{\max}^{\mathrm{sol}}\left(nm\right)$	$\lambda_{\max}^{\operatorname{film}}\left(nm\right)$	$E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$	HOMO (eV)	LUMO (eV)
IDTODT-1 IDTODT-2 IDTODT-3	814 788 788	846 821 818	1.32 1.34 1.34	-5.35 -5.38 -5.39	$-3.90 \\ -3.95 \\ -3.96$

quantum efficiency (EQE) for the optimal PBDB-T:NFAS PSCs with detailed photovoltaic parameters summarized in Table 2. The PBDB-T:**IDTODT-3** device obtains a PCE of 8.34% with an open-circuit voltage ($V_{\rm oc}$) of 0.794 V, a short-circuit current ($J_{\rm sc}$) of 17.32 mA cm⁻², and a fill factor (FF) of 60.63%, which surpasses the PCEs of the other two devices. Comparatively, the PBDB-T: **IDTODT-3** device demonstrates a stronger photo response with EQEs all exceeding 50% in the wavelength range from 500 nm to 840 nm, whose maximum value reaches 58.89% at 580 nm. The calculated $J_{\rm sc}$ values by EQE integration are 14.35, 15.24 and 17.29 mA cm⁻² for **IDTODT-1**, **IDTODT-2** and **IDTODT-3** devices, respectively, all agreeing well with those by direct J-V measurement (errors less than 1%).

Fig. 3c and d shows the dependence of $J_{\rm sc}$ on the light intensity ($P_{\rm light}$) and that of photocurrent density ($J_{\rm ph}$) to the effective voltage ($V_{\rm eff}$), which were plotted to investigate the charge generation, extraction and recombination conditions. The $J_{\rm sc}$ - $P_{\rm light}$ correlation can be expressed by $J_{\rm sc} \propto P_{\rm light}^{\alpha}$, where α reflects the degree of carrier recombination. An α closer to 1 suggests less bimolecular recombination. As shown, the α value of the **IDTODT-3** device is 0.958, larger than those of **IDTODT-1**



Fig. 3 (a) J-V, (b) EQE, (c) $J_{sc}-P_{light}$ and (d) $J_{ph}-V_{eff}$ curves of the optimized devices based on **IDTODT-1**, **IDTODT-2** and **IDTODT-3**.

 Table 2
 Photovoltaic parameters for the optimal PBDB-T:IDTODT-1,

 PBDB-T:IDTODT-2 and PBDB-T:IDTODT-3 devices

Acceptor	$V_{\rm oc}$ (V)	$J_{ m sc} \ (m mA\ cm^{-2})$	$J_{ m sc}^{ m int}$ (mA cm ⁻²)	FF	PCE (%)
IDTODT-1	0.802	14.49	14.35	59.10	$\begin{array}{c} 6.87[6.77\pm0.09]\\ 6.99[6.90\pm0.10]\\ 8.34[8.27\pm0.06]\end{array}$
IDTODT-2	0.770	15.28	15.24	59.25	
IDTODT-3	0.794	17.32	17.29	60.63	

All average values with standard deviations were calculated from over 10 devices.

and **IDTODT-2** devices, which may partially explain its relatively high J_{sc} . As shown in Fig. 3d, when the V_{eff} exceeds 2.0 V, the J_{ph} of the three devices gradually saturates, where all photogenerated excitons dissociate and were efficiently collected. For devices based on **IDTODT-1**, **IDTODT-2** and **IDTODT-3**, the J_{sat} values were 16.06, 16.03 and 18.00 mA cm⁻², respectively. We calculated the probability of charge dissociation and collection P(E,T) by $P(E,T) = J_{ph}/J_{sat}$. The P(E,T)s under short-circuit and maximum power output condition in the **IDTODT-3**-based device are 96.2% and 77.8%, respectively, both higher than those of the other two devices (**IDTODT-2**, 95.3% and 75.1%; **IDTODT-1**, 90.2% and 73.7%). Comparatively, the **IDTODT-3**based device shows more efficient exciton dissociation and collection than the others, which is consistent with the EQE results.

The charge transporting behavior within all three devices was examined by measuring the hole mobility (μ_h) and electron mobility (μ_e) *via* a space-charge-limited-current (SCLC) method. The hole-only device of ITO/PEDOT:PSS/active layer/MoO₃/Ag structure and electron-only device of ITO/ZnO/active layer/ PFN/Al structure are constructed, respectively. The mobility data are summarized in Table 3 with the corresponding *J*-*V* curves shown in Fig. S4 (ESI†). We find that in the PBDB-T: **IDTODT-3** device, a more balanced μ_h/μ_e ratio was achieved. Since a more balanced charge transport benefits the decrease of recombination, we attribute this to be a reason for its relatively high J_{sc} and better device performance.

The morphological differences between all three blends were characterized by transmission electron microscopy (TEM) and atomic force spectroscopy (AFM). As shown in Fig. 4a, the PBDB-T:**IDTODT-3** blend shows better interpenetrating networks compared to the other blends. From their AFM images (Fig. 4d–f), we observed obvious root-mean-square (RMS) differences, which are 1.63 nm, 0.87 nm and 1.26 nm, respectively. The moderate RMS of the PBDB-T:**IDTODT-3** blend suggests good balance between the miscibility and crystallization demands, which therefore contributes to a better performance compared to the others. Comparatively, the PBDB-T:**IDTODT-1** blend exhibits better miscibility yet insufficient phase separation while the **IDTODT-2** blend shows a too large phase separation due to worse miscibility, both of which disfavor achieving a high device performance.

Grazing incidence X-ray diffraction (GIXD) was further conducted to investigate the microstructures of the neat and blend thin films to better understand the performance variation of IDTODTs. The two-dimensional (2D) GIXD patterns and the corresponding line-cuts of neat PBDB-T, neat IDTODTs, and their blends at optimal conditions are shown in Fig. S5 (ESI†) and Fig. 5. PBDB-T showed a (100) diffraction peak in the in-plane (IP) direction at 0.29 Å⁻¹ and a (010) diffraction peak in the out-of-plane (OOP) direction at 1.65 Å⁻¹. The corresponding inter-lamellae spacings are 21.5 and 3.80 Å. As enhanced π - π stacking diffraction in the OOP direction indicates, the polymer crystalline regime takes preferential face-on orientation. The neat films of **IDTODT-1** and **IDTODT-2** show similar packing structure exhibiting alkyl-stacking peaks at 0.27 and 0.29 Å, which

Table 3 The α value, *P*(*E*, *T*), and SCLC mobilities of PBDB-T:**IDTODT-1**, PBDB-T:**IDTODT-2** and PBDB-T:**IDTODT-3** devices

Acceptor	$P(E,T)_{J_{\rm sc}}$	$P(E,T)_{\rm MP}$	$\mu_{\rm h}~(\rm cm^2~V~s^{-1})$	$\mu_{\rm e} \left({\rm cm}^2 ~{\rm V}~{\rm s}^{-1} \right)$	$\mu_{\rm h}/\mu_{\rm e}$
IDTODT-1 IDTODT-2 IDTODT-3	90.2 95.3 96.2	73.7 75.1 77.8	$egin{array}{llllllllllllllllllllllllllllllllllll$	$egin{array}{llllllllllllllllllllllllllllllllllll$	8.41 2.39 2.28

 $P(E,T)_{\rm MP}$ is the charge dissociation probability at maximum power output.



Fig. 4 TEM (a-c) and AFM (d-f) images of PBDB-T:IDTODT-1, PBDB-T: IDTODT-2 and PBDB-T:IDTODT-3 blend films.

corresponds to the inter-lamellae spacing of 22.6 and 21.5 Å, respectively. The crystalline regime of these two molecules also takes preferential face-on orientation in their neat films while exhibiting a broad π - π stacking peak centered at 1.74 and 1.77 Å⁻¹ in the OOP direction, respectively. The neat IDTODT-3 shows a slightly broad (100) alkyl-stacking peak at 0.313 Å with a smaller inter-lamellae spacing of 20.1 Å in the IP direction. It also shows a π - π stacking peak centered at 1.71 Å with a smaller inter-lamellae spacing of 3.67 Å. This indicates the closer packing of IDTODT-3 crystallites than the others. We further probed the packing states for all three blend films by analyzing (010) π - π stacking peaks in the OOP direction. Comparatively, the IDTODT-3 blend shows a (010) peak centered around 1.67 Å with a d-spacing of 3.76 Å, while those of IDTODT-1 and IDTODT-2 blends are 3.82 Å and 3.72 Å, respectively. After blending with PBDT-T, the π - π stacking within IDTODT-1 crystallites increases, which suggests the possible formation of large IDTODT-1 domains. This accounts for a large RMS of the **IDTODT-1** blend film with a small μ_e . The **IDTODT-2** crystallites show a decreased π - π stacking, which results in a favorable blending morphology of a small RMS. Therefore, both high $\mu_{\rm h}$ and $\mu_{\rm e}$ were observed. However, due to a relatively low absorption coefficient, the light-capturing ability of

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Fig. 5 2D GIXS images and corresponding line-cuts of (a) **IDTODT-1**, (b) **IDTODT-2** and (c) **IDTODT-3** pristine films and (d) PBDB-T:**IDTODT-1**, (e) PBDB-T:**IDTODT-2** and (f) PBDB-T:**IDTODT-3** blend films.

the **IDTODT-2** blend film is limited, which produces low J_{sc} and enlarged energy loss. Thus it only shows a PCE comparable to **IDTODT-1**'s. Comparably, the **IDTODT-3** blend demonstrates a moderate crystal coherence length of 17.4 Å compared to the **IDTODT-1** blend (17.1 Å) and **IDTODT-2** blend (18.8 Å), suggesting a moderate crystallization in its blends, which is consistent with the morphological observation and mobility measurement results.

To well define the phase separation condition within the three devices, we preformed photoinduced force microscopy (PiFM) measurement. Fig. S6 (ESI⁺) shows the PiFM images of three PBDB-T:IDTODT blends. PBDB-T:IDTODT-1 shows a pronounced coarse fiber network with a typical fiber length and diameter around 100 nm and 25 nm, respectively. However, the dominant component within these phases can hardly be determined as a distinctive PBDD-T-rich area and IDTODT-1-rich area are both absent (the red area in the upper half cannot be attributed to be the PBDB-T-rich phases, which were probably caused by the heat-induced drifting as they were not observed at the bottom half). The PBDB-T:IDTODT-1 film features a typical well-miscible blending morphology with insufficient phase separation. In contrast, more obvious phase separation in both PBDB-T:IDTODT-2 and PBDB-T:IDTODT-3 blends was observed. As shown, the red and green areas in both Pifm images are well distinguishable. In detail, the PBDB-T:IDTODT-2 blend shows more large acceptor-rich domains (marked in green)

featuring a rough diameter around 100 nm while in the PBDB-T: **IDTODT-3** blend, they are more slim and scattered, which features a rough value around 50 nm. Comparatively, the PBDB-T:**IDTODT-3** blend shows a moderate phase separation, though the scale is still large compared to other high PCE systems. We attribute this to be a reason for the relatively inferior performance of IDTODTs.

Conclusions

In summary, three oxygen heterocycle-fused NFAs were designed and synthesized. By systematic side-chain engineering, an efficient NFA based on an indacenodithiophenebithiophene core with an optimal power conversion efficiency of $\sim 8.4\%$ was achieved. A detailed comparative study clarifies that the optimal molecule, **IDTODT-3**, shows a moderate phase separation with balanced charge transport and reduced recombination, and thus performs best. This work demonstrates the effectiveness of oxygen heterocycle-incorporation in realizing LBG and provides strategic guidelines towards designing efficient NFAs *via* molecule-engineering.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Basic Research Program of China (973 Program) (No. 2014CB643502), the National Key R&D Program of China (2017YFA0204700), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12010200), and the National Natural Science Foundation of China (21572234, 21661132006 and 61505225) for their financial support.

References

- 1 C. Brabec, U. Scherf and V. Dyakonov, *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies,* Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany, 2014.
- 2 J. B. Zhao, Y. K. Li, G. F. Yang, K. Jiang, H. R. Lin, H. Ade, W. Ma and H. Yan, *Nat. Energy*, 2016, 1, 15027.
- 3 C. B. Nielsen, S. Holliday, H. Y. Chen, S. J. Cryer and I. McCulloch, *Acc. Chem. Res.*, 2015, **48**, 2803.
- 4 Y. Z. Lin and X. W. Zhan, Acc. Chem. Res., 2016, 49, 175.
- 5 Z. Yao, X. Liao, K. Gao, F. Lin, X. Xu, X. Shi, L. Zuo, F. Liu, Y. Chen and A. K. Jen, *J. Am. Chem. Soc.*, 2018, **140**, 2054.
- 6 S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade and J. Hou, *Adv. Mater.*, 2016, **28**, 9423.
- 7 S. X. Li, W. Q. Liu, M. M. Shi, J. Q. Mai, T. K. Lau, J. H. Wan,
 X. H. Lu, C. Z. Li and H. Z. Chen, *Energy Environ. Sci.*, 2016,
 9, 604.
- 8 Y. Li, N. Zheng, L. Yu, S. Wen, C. Gao, M. Sun and R. Yang, *Adv. Mater.*, 2019, **31**, e1807832.
- 9 Y. Cui, H. Yao, L. Hong, T. Zhang, Y. Xu, K. Xian, B. Gao, J. Qin, J. Zhang, Z. Wei and J. Hou, *Adv. Mater.*, 2019, 31, e1808356.
- 10 W. Xu and F. Gao, Mater. Horiz., 2018, 5, 206.
- 11 Y. Lin, J. Wang, Z. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
- 12 W. Liu, J. Zhang, Z. Zhou, D. Zhang, Y. Zhang, S. Xu and X. Zhu, *Adv. Mater.*, 2018, **30**, 1800403.
- 13 S. Li, L. Zhan, C. Sun, H. Zhu, G. Zhou, W. Yang, M. Shi, C. Z. Li, J. Hou, Y. Li and H. Chen, *J. Am. Chem. Soc.*, 2019, 141, 3073.
- 14 T. Li, S. Dai, Z. Ke, L. Yang, J. Wang, C. Yan, W. Ma and X. Zhan, Adv. Mater., 2018, 30, 1705969.
- 15 H. Feng, Y. Q. Q. Yi, X. Ke, J. Yan, Y. Zhang, X. Wan, C. Li, N. Zheng, Z. Xie and Y. Chen, *Adv. Energy Mater.*, 2019, 9, 1803541.

- 16 H. Yao, Y. Chen, Y. Qin, R. Yu, Y. Cui, B. Yang, S. Li,
 K. Zhang and J. Hou, *Adv. Mater.*, 2016, 28, 8283.
- 17 J. Hou, O. Inganas, R. H. Friend and F. Gao, *Nat. Mater.*, 2018, **17**, 119.
- 18 D. He, F. Zhao, L. Jiang and C. Wang, *J. Mater. Chem. A*, 2018, **6**, 8839.
- 19 Z. Xiao, S. Yang, Z. Yang, J. Yang, H. L. Yip, F. Zhang, F. He, T. Wang, J. Wang, Y. Yuan, H. Yang, M. Wang and L. Ding, *Adv. Mater.*, 2018, **30**, e1804790.
- 20 F. Zhao, C. Wang and X. Zhan, Adv. Energy Mater., 2018, 8, 1703147.
- 21 G. Liu, J. Jia, K. Zhang, X. E. Jia, Q. Yin, W. Zhong, L. Li, F. Huang and Y. Cao, *Adv. Energy Mater.*, 2019, 9, 1803657.
- M. M. Li, W. Ni, H. R. Feng, B. Kan, X. J. Wan, Y. M. Zhang,
 X. Yang and Y. S. Chen, *Chin. J. Chem.*, 2015, 33, 852.
- 23 X. Liao, X. Shi, M. Zhang, K. Gao, L. Zuo, F. Liu, Y. Chen and A. K. Jen, *Chem. Commun.*, 2019, 55, 8258.
- 24 H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang and J. Hou, Angew. Chem., Int. Ed., 2017, 56, 3045.
- 25 J.-L. Wang, K.-K. Liu, L. Hong, G.-Y. Ge, C. Zhang and J. Hou, ACS Energy Lett., 2018, 3, 2967.
- 26 D. He, F. Zhao, J. Xin, J. J. Rech, Z. Wei, W. Ma, W. You, B. Li, L. Jiang, Y. Li and C. Wang, *Adv. Energy Mater.*, 2018, 8, 1802050.
- H. Wu, H. Fan, S. Xu, C. Zhang, S. Chen, C. Yang, D. Chen,
 F. Liu and X. Zhu, *Sol. RRL*, 2017, 1, 1700165.
- 28 H. Wu, H. Fan, S. Xu, L. Ye, Y. Guo, Y. Yi, H. Ade and X. Zhu, Small, 2019, 15, e1804271.
- 29 Z. Luo, H. Bin, T. Liu, Z.-G. Zhang, Y. Yang, C. Zhong, B. Qiu, G. Li, W. Gao, D. Xie, K. Wu, Y. Sun, F. Liu, Y. Li and C. Yang, *Adv. Mater.*, 2018, **30**, 1706124.
- 30 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 and X. Zhan, *J. Am. Chem. Soc.*, 2016, **138**, 4955.
- 31 F. Zhao, S. Dai, Y. Wu, Q. Zhang, J. Wang, L. Jiang, Q. Ling, Z. Wei, W. Ma, W. You, C. Wang and X. Zhan, *Adv. Mater.*, 2017, 1700144.
- 32 Y. Yang, Z.-G. Zhang, H. Bin, S. Chen, L. Gao, L. Xue,
 C. Yang and Y. Li, *J. Am. Chem. Soc.*, 2016, 138, 15011.
- 33 T. Liu, W. Gao, Y. Wang, T. Yang, R. Ma, G. Zhang, C. Zhong, W. Ma, H. Yan and C. Yang, *Adv. Funct. Mater.*, 2019, 29, 1902155.
- 34 Z. Zheng, S. Q. Zhang, M. J. Zhang, K. Zhao, L. Ye, Y. Chen,
 B. Yang and J. H. Hou, *Adv. Mater.*, 2015, 27, 1189.
- 35 Z. G. Zhang, B. Y. Qi, Z. W. Jin, D. Chi, Z. Qi, Y. F. Li and J. Z. Wang, *Energy Environ. Sci.*, 2014, 7, 1966.