

CrossMark
click for updatesCite this: *J. Mater. Chem. A*, 2016, 4, 10409Received 25th May 2016
Accepted 8th June 2016

DOI: 10.1039/c6ta04358e

www.rsc.org/MaterialsA

A simple small molecule as an acceptor for fullerene-free organic solar cells with efficiency near 8%[†]

Miaomiao Li,^{‡,ab} Yongtao Liu,^{‡,ab} Wang Ni,^b Feng Liu,^c Huanran Feng,^{ab} Yamin Zhang,^{ab} Tingting Liu,^a Hongtao Zhang,^{*ab} Xiangjian Wan,^{ab} Bin Kan,^a Qian Zhang,^b Thomas P. Russell^{cd} and Yongsheng Chen^{*ab}

A simple small molecule acceptor named DICTF, with fluorene as the central block and 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)propanedinitrile as the end-capping groups, has been designed for fullerene-free organic solar cells. The new molecule was synthesized from widely available and inexpensive commercial materials in only three steps with a high overall yield of ~60%. Fullerene-free organic solar cells with DICTF as the acceptor material provide a high PCE of 7.93%.

Solution-processed organic solar cells are promising for future renewable energy conversion due to their advantages such as low cost, light weight and flexibility.^{1,2} Owing to the continuous donor material evolution and device optimization,^{3–11} power conversion efficiencies (PCEs) over 10% have been achieved for single junction organic solar cells with a bulk heterojunction (BHJ) architecture using fullerene derivatives as the acceptor.^{12–17} Several fundamental properties make fullerene derivatives excellent acceptor materials for BHJ solar cells, including the low lying lowest unoccupied molecular orbital (LUMO) and thus high electron affinity and high electron mobility.^{18,19} However, these fullerene derivatives have some limitations such as high cost synthesis and purification processes, weak absorption in the visible region, and difficulty in tuning energy levels. In view of these factors, more and more attention has been focused on non-fullerene small molecule

acceptor materials in the past several years,^{20–24} and PCEs over 7% have been achieved.^{25–29} For the design of non-fullerene acceptor materials, several important parameters need to be simultaneously considered such as suitable energy levels, good electron transport properties, strong and broad absorption spectra, and proper miscibility when being blended with donor materials. Besides, in terms of achieving commercialization of organic solar cells, easy accessibility and purification of the active materials are as important as the efficiency of the organic photovoltaic (OPV) devices. Thus, it is highly desirable to develop high-performance non-fullerene acceptor materials with an easy synthesis procedure and low cost.

As a widely used raw material for organic synthesis, fluorene with weak electron-donating ability has been introduced in acceptor materials to obtain a deep-lying highest occupied molecular orbital (HOMO) energy level, and PCEs of 2–4% have been achieved.^{30–34} These fluorene based small molecules showed a wide bandgap with values of ~2.10 eV and relatively narrow absorption. It is worth mentioning that the absorption of acceptor molecules also plays an important role in contributing to the overall device photocurrent. In several previous reports, 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)propanedinitrile has been demonstrated to be a strong electron-withdrawing unit, which could lower the LUMO energy level and thus the band gap of the molecules.^{35–37}

Bearing these in mind, we designed and synthesized a simple small molecule acceptor, named DICTF (Fig. 1a), comprising 9,9-dioctylfluorene as the central building block and 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene)propanedinitrile as the terminal acceptor groups. The new molecule was synthesized from widely available and inexpensive commercial materials in only three steps with a high overall yield of ~60%, indicating great potential for the large-scale production of this new acceptor material. A polymer poly[(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*])dithiophene-2,6-diyl]-*alt*-(2-ethylhexyl-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate-4,6-diyl)], commonly known as PTB7-Th (shown in Fig. 1a) was used as the donor material. The organic solar cell based on PTB7-Th:DICTF exhibits a high PCE of

^aState Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Materials Science and Engineering, Nankai University, Tianjin 300071, China. E-mail: htzhang@nankai.edu.cn; yschen99@nankai.edu.cn

^bKey Laboratory of Functional Polymer Materials and the Centre of Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China

^cMaterials Science Divisions, Lawrence Berkeley National Lab, Berkeley 94720, USA

^dDepartment of Polymer Science and Engineering, University of Massachusetts, Amherst 01003, USA

[†] Electronic supplementary information (ESI) available: Details of the synthesis and characterization of DICTF, TGA, SCLC. See DOI: 10.1039/c6ta04358e

[‡] M. M. Li and Y. T. Liu contributed equally to this work.

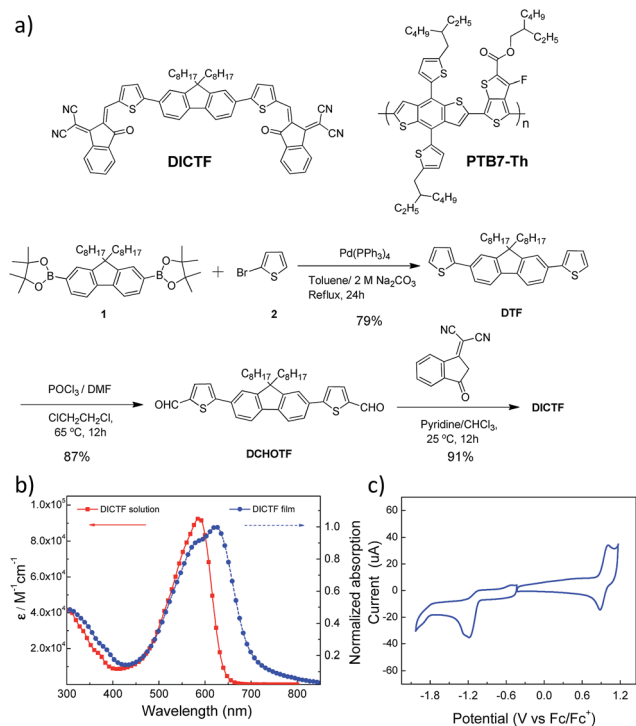


Fig. 1 (a) Chemical structures of DICTF and PTB7-Th, and the synthetic route of DICTF. (b) Absorption spectra of DICTF in chloroform solution and the as-cast film. (c) Cyclic voltammogram of DICTF in a dichloromethane solution of 0.1 mol L⁻¹ Bu₄NPF₆ with a scan rate of 100 mV s⁻¹.

7.93%, which is comparable to that of the control device based on PTB7-Th:PC₇₁BM. The results demonstrate that DICTF is a very promising alternative to fullerene derivatives for organic solar cells.

The synthetic route of DICTF is shown in Fig. 1a. All the starting materials were purchased from commercial suppliers and used without further purification. DTF was synthesized using the Suzuki coupling reaction. The intermediate of dialdehyde DCHOTF was obtained by the Vilsmeier–Haack reaction. The target molecule (DICTF) was then prepared by the Knoevenagel condensation of DCHOTF with 2-(2,3-dihydro-3-oxo-1H-inden-1-ylidene)propanedinitrile. The details are provided in the ESI.† Thermogravimetric analysis (TGA) indicates that DICTF exhibits excellent thermal stability up to 320 °C under a N₂ atmosphere (Fig. S2†).

The UV-Vis absorption spectra of DICTF in chloroform solution and in thin film are shown in Fig. 1b. DICTF in chloroform (10⁻⁶ M) shows an absorption peak at 587 nm with a maximum absorption coefficient of 9.3 × 10⁴ M⁻¹ cm⁻¹. In the solid state, the DICTF film shows a red-shifted maximum absorption peak at 624 nm and a broad absorption band in the visible light region. The relatively broad absorption of DICTF could contribute to the total absorption of the active layer. The optical bandgap of DICTF is 1.82 eV, estimated from the onset of the film absorption spectrum. The electrochemical properties of DICTF were investigated by cyclic voltammetry with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the

vacuum level) as the internal calibration. The HOMO and LUMO energy levels of DICTF, which are -5.67 and -3.79 eV, respectively, are estimated based on the onset oxidation potential and the onset reduction potential of the redox curve as shown in Fig. 1c. The deep HOMO energy level of DICTF is much lower than those of typical high efficiency donor materials (-5.0 to -5.3 eV).^{5,7} In addition, the relatively high-lying LUMO energy level of DICTF compared to that of PCBM (~-3.90 eV) indicates that an increased V_{oc} could be expected by using DICTF as an electron acceptor material in OPV devices.

The photoluminescence (PL) spectra of the pure PTB7-Th film and the PTB7-Th:DICTF blend films were measured and the results are shown in Fig. S3.† The pure PTB7-Th film exhibited a PL emission band in the range of 670–850 with a peak at 750 nm. Compared with the pure PTB7-Th film, the PTB7-Th:DICTF blend film exhibited a significantly decreased PL emission, indicating good molecule miscibility and efficient charge transfer between PTB7-Th and DICTF. The results demonstrate that DICTF could be an efficient electron acceptor material.

BHJ organic solar cells were fabricated using PTB7-Th as the electron donor material and DICTF as the electron acceptor material with a device structure of glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulphonate) (PEDOT:PSS)/PTB7-Th:DICTF/*N,N'*-bis(propylene-dimethylamine)-3,4:9,10-perylene diimide (PDIN)/Al, using a solution process. PDIN is a perylene diimide derivative, developed as a cathode interlayer by Li *et al.*,³⁸ and its structure is shown in Fig. S4.† The optimization process of the device performance can be found in Table S1–S3.† The optimized D/A weight ratio of PTB7-Th:DICTF is 1 : 1.4. The current density–voltage (*J*–*V*) curves of the devices (with D/A weight ratio of 1 : 1.4) without and with a thermal annealing (TA) treatment measured under 100 mW cm⁻² simulated sunlight illumination are shown in Fig. 2a, and the device parameters of V_{oc}, J_{sc}, FF and PCE are summarized in Table 1. The device based on the PTB7-Th:DICTF blend film without post-treatment showed a PCE of 6.82% with a V_{oc} of 0.87 V, a J_{sc} of 15.55 mA cm⁻² and an FF of 0.51. For the blend film after 100 °C thermal annealing for 10 min, the PCE increased to 7.93%. The control device based on PTB7-Th:PC₇₁BM with PDIN as the interface layer exhibited a V_{oc} of 0.79 V, a J_{sc} of 16.91 mA cm⁻² and an FF

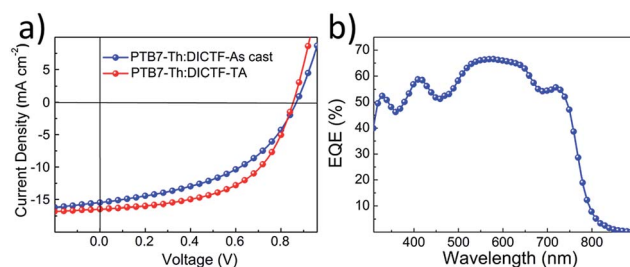


Fig. 2 (a) Characteristic current density versus voltage (*J*–*V*) curves of PTB7-Th:DICTF based devices without and with thermal annealing and (b) the external quantum efficiency (EQE) curves of the optimized PTB7-Th:DICTF based devices.

Table 1 Device performance parameters of the BHJ solar cells based on the PTB7-Th:DICTF (1 : 1.4, w/w) blend films

Treatment	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE ^{a,b} [%]
None	0.86 ± 0.01	15.23 ± 0.32	0.50 ± 0.01	6.54 ± 0.28 (6.82)
TA	0.85 ± 0.01	16.33 ± 0.28	0.55 ± 0.01	7.63 ± 0.30 (7.93)

^a Average values of 30 devices. ^b The best PCEs are provided in parentheses.

of 0.62 and a slightly higher PCE of 8.28%. Compared with the devices based on the PTB7-Th:PC₇₁BM blend, the device based on the PTB7-Th:DICTF blend exhibited a higher V_{oc} , which was correlated with the high lying HOMO energy level of DICTF. The external quantum efficiency (EQE) spectrum of the optimized OPV device with the PTB7-Th:DICTF blend is shown in Fig. 2b. The optimized device showed a broad photo-to-current response from 300 to 850 nm with a maximum value of 67% and over 60% across the range of 500–660 nm, indicating an efficient photoelectron conversion process.

The bulk charge mobility properties of the PTB7-Th:DICTF blend films were measured by the space-charge limited current (SCLC) method. The hole and electron mobilities were measured with device structures of ITO/PEDOT:PSS/PTB7-Th:DICTF/Au and Al/PTB7-Th:DICTF/Al, respectively (Fig. S5[†]). The blend films without annealing showed a hole mobility of $2.28 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $5.85 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. After thermal annealing, the hole and electron mobilities increased to 3.82×10^{-4} and $1.93 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Importantly, the blend film with thermal annealing exhibited higher and more balanced hole and electron mobility, which was consistent with the higher FF.

The microstructural features of the pure DICTF films, the pure PTB7-Th films and their blend films with different treatments were investigated by two dimensional grazing-incidence wide-angle X-ray scattering (GIWAXS) (Fig. 3a). The line-cut profiles in the out-of-plane (OOP) direction and the in-plane (IP) direction are summarized in Fig. 3b and c, respectively. As shown in Fig. 3a, the as-cast pure DICTF film showed a weak (100) diffraction peak along the in-plane (IP) direction, and a relatively strong (010) diffraction peak along the OOP direction, indicating a greater preference for a face-on molecular orientation. The (100) and (010) peaks are located at 0.40 and 1.80 \AA^{-1} , corresponding to an interchain distance of 15.7 \AA and a π - π stacking distance of 3.49 \AA , respectively. From the GIWAXS pattern of the pure PTB7-Th film, it can be seen that the PTB7-Th polymer crystallites also took a face-on orientation with (100) diffraction in the IP direction and (010) diffraction in the OOP direction. The (100) peak in the pure film is located at 0.27 \AA^{-1} , giving an alkyl-to-alkyl spacing of 23.3 \AA . The (010) peak is located at 1.60 \AA^{-1} , giving a π - π stacking distance of 3.93 \AA . In the PTB7-Th:DICTF blend films, DICTF and PTB7-Th still adopted a face-on orientation, which is favorable for effective charge transport in the photovoltaic devices. In addition, the blend film with thermal annealing showed stronger diffraction peaks, indicating improved molecule packing which facilitated exciton diffusion and charge transport.

The morphology of the PTB7-Th:DICTF blend films was investigated by atomic force microscopy (AFM) and

transmission electron microscopy (TEM). As shown in Fig. 4, the blend films without and with thermal annealing are smooth and uniform with a low root-mean-square (rms) surface roughness of 0.96 and 1.01 nm, respectively. Both of the PTB7-Th:DICTF blend films without and with thermal annealing are uniform and there is no large phase separation, indicating good miscibility between PTB7-Th and DICTF. Compared to the as-cast film, the film with thermal annealing exhibited slightly increased interpenetrating networks of donor and acceptor phases. The excellent morphology of the PTB7-Th:DICTF blend films benefits exciton dissociation and charge transport, thus leading to high J_{sc} .

In order to investigate the morphological stability of the PTB7-Th:DICTF blend films, the blend films were heated at $100 \text{ }^\circ\text{C}$ for several hours. As shown in Fig. S6,[†] after annealing for 480 min, the PTB7-Th:DICTF blend films still showed a similar morphology compared to those with only annealing for 10 min. The devices based on the blend films with thermal annealing for different times were also fabricated. The corresponding OPV device performances are shown in Table S4.[†] It can be seen that thermal annealing for 480 min has little impact on the

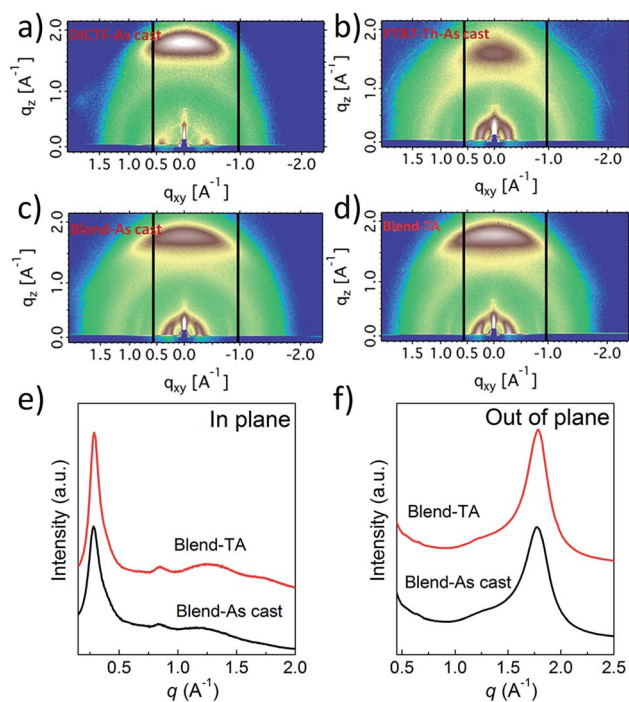


Fig. 3 (a) GIWAXS images of DICTF (a), and PTB7-Th (b) pure films and PTB7-Th:DICTF (c and d) blend films. (e) In-plane line-cuts of GIWAXS patterns of the PTB7-Th:DICTF blend films. (f) Out-of-plane line-cuts of GIWAXS patterns of the PTB7-Th:DICTF blend films.

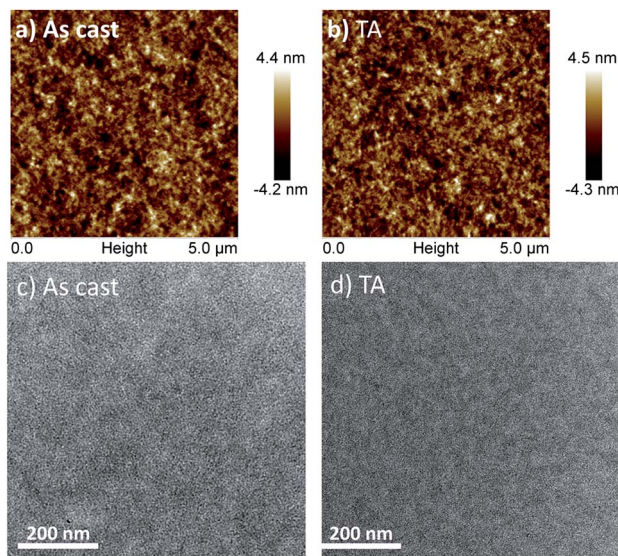


Fig. 4 Tapping-mode AFM height images of the active layers of the PTB7-Th:DICTF blend films, (a) without annealing and (b) with thermal annealing. TEM images of the PTB7-Th:DICTF blend films from CHCl_3 , (c) without annealing and (d) with thermal annealing.

photovoltaic performance. The results demonstrate that the PTB7-Th:DICTF blend films show good morphological stability.

In summary, a new small molecule DICTF was designed and synthesized through a simple synthetic route with high yield. The new molecule exhibited suitable energy levels and strong absorption in the visible light region. The device based on PTB7-Th as the donor material and DICTF as the acceptor material exhibited a high PCE of 7.93%, which is comparable to that of the device based on PTB7-Th:PC₇₁BM. The rather simple acceptor molecule DICTF provides a good example of a successful trade-off between conversion efficiency, and cost and scalability in terms of possible large-scale production. The results demonstrate that DICTF is a very promising acceptor material for organic solar cells.

Acknowledgements

The authors gratefully acknowledge the financial support from MoST (2014CB643502), NSFC (51373078, 51422304 and 91433101), PCSIRT (IRT1257) and Tianjin city (13RCGFGX01121). TPR and FL were supported by Polymer-Based Materials for Harvesting Solar Energy (PhaSE), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under award number DE-SC0001087.

Notes and references

- 1 A. J. Heeger, *Chem. Soc. Rev.*, 2010, **39**, 2354.
- 2 F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 394.
- 3 J. E. Coughlin, Z. B. Henson, G. C. Welch and G. C. Bazan, *Acc. Chem. Res.*, 2013, **47**, 257.
- 4 Y. Li, *Acc. Chem. Res.*, 2012, **45**, 723.
- 5 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao and L. Yu, *Chem. Rev.*, 2015, **115**, 12666.
- 6 A. Mishra and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2012, **51**, 2020.
- 7 J. Roncali, P. Leriche and P. Blanchard, *Adv. Mater.*, 2014, **26**, 3821.
- 8 L.-M. Chen, Z. Hong, G. Li and Y. Yang, *Adv. Mater.*, 2009, **21**, 1434.
- 9 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323.
- 10 H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, **45**, 607.
- 11 C. Duan, A. Furlan, J. J. van Franeker, R. E. M. Willems, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2015, **27**, 4461.
- 12 J.-D. Chen, C. Cui, Y.-Q. Li, L. Zhou, Q.-D. Ou, C. Li, Y. Li and J.-X. Tang, *Adv. Mater.*, 2015, **27**, 1035.
- 13 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photonics*, 2015, **9**, 174.
- 14 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 and Y. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 3886.
- 15 S. Zhang, L. Ye, W. Zhao, B. Yang, Q. Wang and J. Hou, *Sci. China: Chem.*, 2015, **58**, 248.
- 16 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Commun.*, 2014, **5**, 5293.
- 17 C. Liu, C. Yi, K. Wang, Y. Yang, R. S. Bhatta, M. Tsige, S. Xiao and X. Gong, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4928.
- 18 Y. He and Y. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1970.
- 19 D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martin, *Chem. Soc. Rev.*, 2009, **38**, 1587.
- 20 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
- 21 A. a. F. Eftaiha, J.-P. Sun, I. G. Hill and G. C. Welch, *J. Mater. Chem. A*, 2014, **2**, 1201.
- 22 Y. Lin and X. Zhan, *Mater. Horiz.*, 2014, **1**, 470.
- 23 A. Sharenko, C. M. Proctor, T. S. van der Poll, Z. B. Henson, T.-Q. Nguyen and G. C. Bazan, *Adv. Mater.*, 2013, **25**, 4403.
- 24 C. B. Nielsen, S. Holliday, H.-Y. Chen, S. J. Cryer and I. McCulloch, *Acc. Chem. Res.*, 2015, **48**, 2803.
- 25 H. Li, Y.-J. Hwang, B. A. E. Courtright, F. N. Eberle, S. Subramanian and S. A. Jenekhe, *Adv. Mater.*, 2015, **27**, 3266.
- 26 D. Sun, D. Meng, Y. Cai, B. Fan, Y. Li, W. Jiang, L. Huo, Y. Sun and Z. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 11156.
- 27 D. Meng, D. Sun, C. Zhong, T. Liu, B. Fan, L. Huo, Y. Li, W. Jiang, H. Choi, T. Kim, J. Y. Kim, Y. Sun, Z. Wang and A. J. Heeger, *J. Am. Chem. Soc.*, 2016, **138**, 375.
- 28 Y. Zhong, M. T. Trinh, R. Chen, G. E. Purdum, P. P. Khlyabich, M. Sezen, S. Oh, H. Zhu, B. Fowler, B. Zhang, W. Wang, C.-Y. Nam, M. Y. Sfeir, C. T. Black, M. L. Steigerwald, Y.-L. Loo, F. Ng, X. Y. Zhu and C. Nuckolls, *Nat. Commun.*, 2015, **6**, 8242.
- 29 S. Li, W. Liu, M. Shi, J. Mai, T.-K. Lau, J. Wan, X. Lu, C.-Z. Li and H. Chen, *Energy Environ. Sci.*, 2016, **9**, 604.
- 30 S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson and I. McCulloch, *J. Am. Chem. Soc.*, 2015, **137**, 898.

- 31 Y. Kim, C. E. Song, S.-J. Moon and E. Lim, *Chem. Commun.*, 2014, **50**, 8235.
- 32 K. N. Winzenberg, P. Kemppinen, F. H. Scholes, G. E. Collis, Y. Shu, T. Birendra Singh, A. Bilic, C. M. Forsyth and S. E. Watkins, *Chem. Commun.*, 2013, **49**, 6307.
- 33 W. Ni, M. Li, B. Kan, F. Liu, X. Wan, Q. Zhang, H. Zhang, T. P. Russell and Y. Chen, *Chem. Commun.*, 2016, **52**, 465.
- 34 S. Li, J. Yan, C.-Z. Li, F. Liu, M. Shi, H. Chen and T. P. Russell, *J. Mater. Chem. A*, 2016, **4**, 3777.
- 35 G. He, Z. Li, X. Wan, J. Zhou, G. Long, S. Zhang, M. Zhang and Y. Chen, *J. Mater. Chem. A*, 2013, **1**, 1801.
- 36 Y. Lin, Z.-G. Zhang, H. Bai, J. Wang, Y. Yao, Y. Li, D. Zhu and X. Zhan, *Energy Environ. Sci.*, 2015, **8**, 610.
- 37 H. Bai, Y. Wang, P. Cheng, J. Wang, Y. Wu, J. Hou and X. Zhan, *J. Mater. Chem. A*, 2015, **3**, 1910.
- 38 Z.-G. Zhang, B. Qi, Z. Jin, D. Chi, Z. Qi, Y. Li and J. Wang, *Energy Environ. Sci.*, 2014, **7**, 1966.