

Supporting Information

**Overcoming the energy loss in asymmetrical non-fullerene acceptor-based  
polymer solar cells by halogenation of polymer donors**

Qunping Fan,<sup>‡a</sup> Tao Liu,<sup>‡\*b</sup> Wei Gao,<sup>c</sup> Yiqun Xiao,<sup>d</sup> Jiannan Wu,<sup>a</sup> Wenyan Su,<sup>a</sup> Xia  
Guo,<sup>a</sup> Xinhui Lu,<sup>\*d</sup> Chuluo Yang,<sup>c</sup> He Yan,<sup>\*b</sup> Maojie Zhang<sup>\*a</sup> and Yongfang Li,<sup>ae</sup>

<sup>a</sup>Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical  
Engineering and Materials Science, Soochow University, Suzhou 215123, China

\*E-mail addresses: [mjzhang@suda.edu.cn](mailto:mjzhang@suda.edu.cn) (M. Zhang)

<sup>b</sup>Department of Chemistry and Hong Kong Branch of Chinese National Engineering  
Research Center for Tissue Restoration & Reconstruction, Hong Kong University of  
Science and Technology, Clear Water Bay, Kowloon, Hong Kong

\*E-mail addresses: [liutaozhx@ust.hk](mailto:liutaozhx@ust.hk) (T. Liu), [hyan@ust.hk](mailto:hyan@ust.hk) (H. Yan)

<sup>c</sup> Department of Chemistry and Hubei Key Lab on Organic and Polymeric  
Optoelectronic Materials, Wuhan University, Wuhan, 430072, China

<sup>d</sup> Department of Physics, The Chinese University of Hong Kong, New Territories  
999077, Hong Kong

\*E-mail addresses: [xhlu@phy.cuhk.edu.hk](mailto:xhlu@phy.cuhk.edu.hk) (X. Lu)

<sup>e</sup> CAS Research/Education Center for Excellence in Molecular Sciences, CAS Key  
Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences,  
Beijing 100190, China

<sup>‡</sup> These authors contributed equally to this work.

## Materials

All chemicals and solvents were reagent grades and purchased from Alfa Aesar and TCI. PBDB-T ( $M_n=30.9$  kDa, PDI=2.36),<sup>1</sup> PM6 ( $M_n=40.8$  kDa, PDI=2.04),<sup>2</sup> PM7 ( $M_n=31.7$  kDa, PDI=2.21),<sup>3</sup> and IDT6CN-M<sup>4</sup> were synthesized according to the procedure reported in the literatures.

## Experimental Section

*Measurements:* The molecular weights of polymers were measured by high temperature gel permeation chromatography (GPC) using monodispersed polystyrene as the standard and 1,2,4-trichlorobenzene as the eluent at 160 °C. UV-vis absorption spectra were taken on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. A set of samples were analysed on the Thermo Scientific ESCALab 250Xi using UPS. The gas discharge lamp was used for UPS, with helium gas admitted and the HeI (21.22 eV) emission line employed. The helium pressure in the analysis chamber during analysis was about  $2 \times 10^{-8}$  mbar. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. The GIWAXS measurement were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°.<sup>5</sup> The samples for GIWAXS measurements are fabricated on silicon substrates using the same recipe for the devices. The silicon substrates were cleaned stepwise with DI water, acetone, and isopropanol in ultrasonic cleaner for 20 min and then

treated with oxygen plasma before use. The crystal coherence length (CCL) was defined as  $CCL = 0.9 \times (2\pi/\text{FWHM})$  (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak.

**Fabrication and characterization of polymer solar cells.** Polymer solar cells with a device structure of ITO/PEDOT:PSS/polymer:IDT6CN-M/PNDIT-F3N-Br/Al were fabricated under conditions as follows: the patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 20 min to improve its work function and clearance. A thin PEDOT:PSS (Heraeus Clevis P VP A 4083) layer (40 nm) was spin-coated onto the ITO substrates and then dried at 150 °C for 15 min in air. The PEDOT:PSS coated ITO substrates were fast transferred to a N<sub>2</sub> filled glove-box for further processing. The polymer:IDT6CN-M (weight ratio of 1:1) were dissolved in chloroform with 0.25% DIO addition, then the mixture was stirred overnight to obtain a blend solution with a total concentration of ~16 mg/mL. The blend solution was spin-cast on the top of PEDOT:PSS layer at 4000 rpm for 40 s. Then it was annealed at 100 °C for 5 min. Subsequently, the active layer coated substrates were quickly transferred to a glove-box integrated thermal evaporator for electrode deposition. A thin PNDIT-F3N-Br layer and Al layer (100 nm) were sequentially evaporated under vacuum of  $5 \times 10^{-5}$  Pa through a shadow mask. The active area of each device was 5.90 mm<sup>2</sup> controlled by a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was ~110 nm.

The current-voltage ( $J$ - $V$ ) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300 W lamp source. To study the charge generation and dissociation processes of the polymer:IDT6CN-M-based PSCs, plots of the photocurrent ( $J_{\text{ph}}$ ) *versus* effective voltage ( $V_{\text{eff}}$ ) of the PSCs were measured. Here,  $J_{\text{ph}}$  and  $V_{\text{eff}}$  are defined as  $J_{\text{ph}} = J_{\text{L}} - J_{\text{D}}$  and  $V_{\text{eff}} = V_0 - V_{\text{appl}}$ , respectively, where  $J_{\text{D}}$  and  $J_{\text{L}}$  are the photocurrent densities in the dark and under the illumination, and  $V_{\text{appl}}$  is the applied bias voltage and  $V_0$  is the voltage at which  $J_{\text{ph}} = 0$ , respectively.<sup>6</sup> Usually,  $V_{\text{eff}}$  determines the electric field in the bulk region and thereby determines the carrier transport and the photocurrent extraction. At high  $V_{\text{eff}}$  values, charge carriers rapidly move toward the related electrodes with minimal recombination. The  $J_{\text{ph}}$  reaches the saturation current density ( $J_{\text{sat}}$ ) at high  $V_{\text{eff}}$  ( $\geq 2 \text{ V}$  in this case). Under the maximum power output conditions, recombination will be strongly competing with the carrier extraction as carriers slow down due to the reduced electric field.

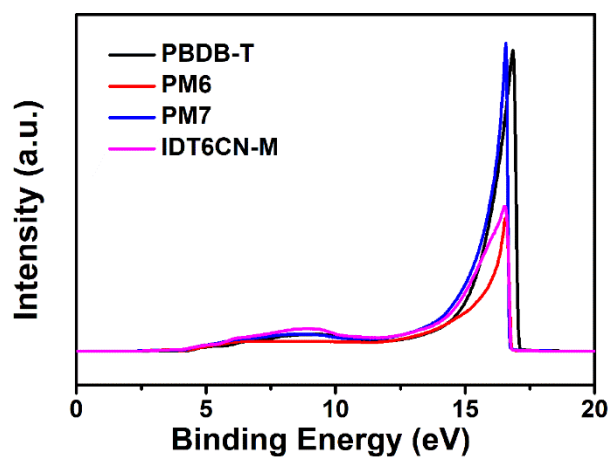
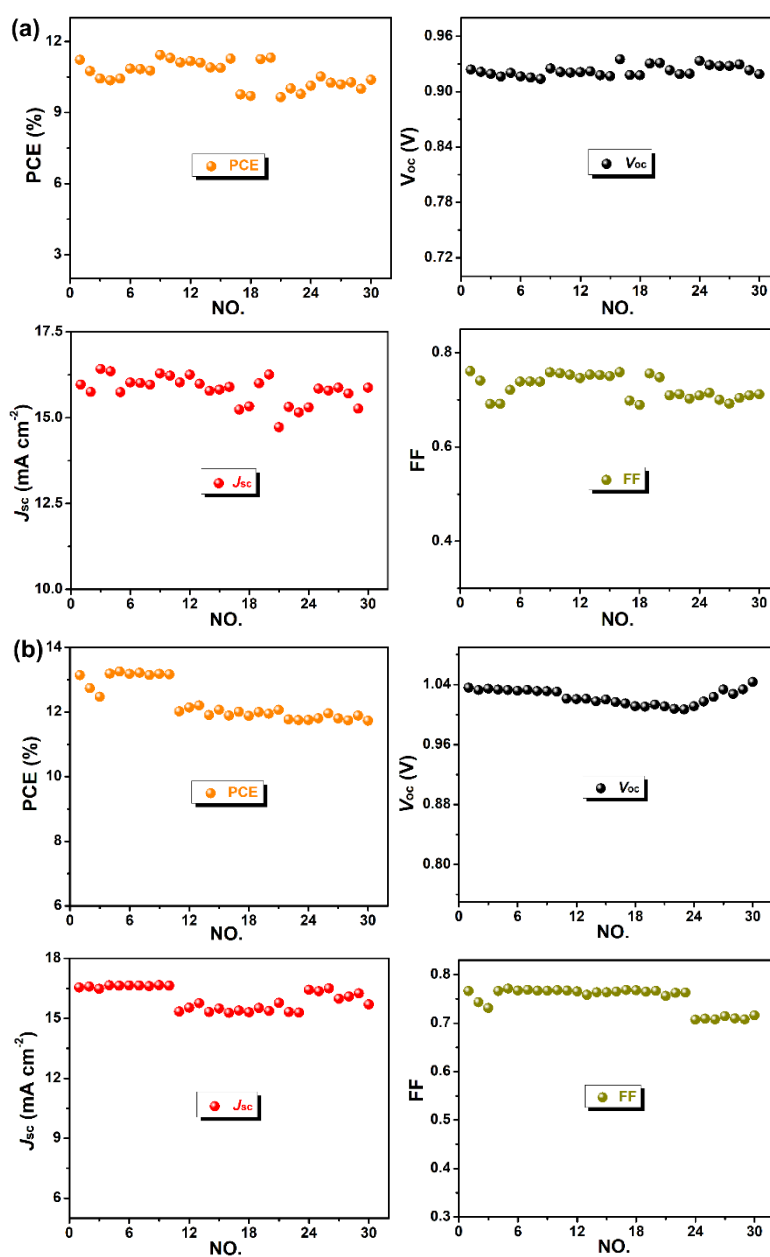
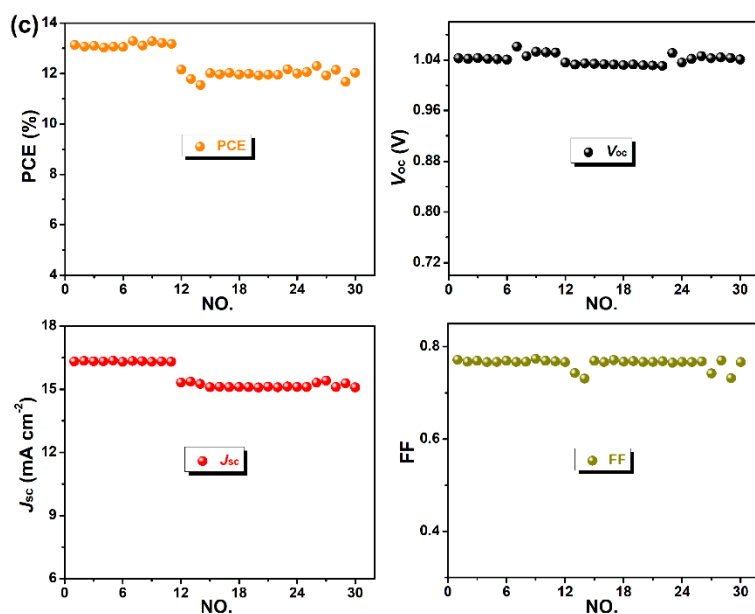


Fig. S1 UPS spectra of the active layer materials in films.





**Fig. S2** Summary of the photovoltaic parameters from 30 independent PSCs based on (a) PBDB-T:IDT6CN-M, (b) PM6:IDT6CN-M, and (c) PM7:IDT6CN-M.

**Table S1.** GIWAXS test performance parameters of the PBDB-T, PM6, PM7, and IDT6CN-M pure films and the related as-cast or thermal annealed blend films.

	in plane			out of plane		
	location ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	CCL ( $\text{\AA}$ )	location ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	CCL ( $\text{\AA}$ )
PBDB-T	0.29	21.67	58.5	1.69	3.72	20.2
PM6	0.29	21.67	54.4	1.75	3.59	22.4
PM7	0.29	21.67	51.1	1.70	3.70	18.4
IDT6CN-M	0.34	18.48	31.7	1.83	3.43	29.4
PBDB-T:IDT6CN-M	0.30	20.94	90.5	1.79	3.16	26.2
PM6:IDT6CN-M	0.30	20.94	92.6	1.78	3.18	30.2
PM7:IDT6CN-M	0.30	20.94	89.7	1.74	3.25	27.9

**Table S2.** The photovoltaic data of the single-junction PSCs with  $V_{oc}$  over 1.0 V.

D:A	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)	$E_{loss}$ (eV)	Ref.
<b>PM6:IDT6CN-M</b>	<b>1.04</b>	<b>16.6</b>	<b>77.1%</b>	<b>13.3</b>	<b>0.56</b>	<b>This work</b>
<b>PM7:IDT6CN-M</b>	<b>1.05</b>	<b>16.4</b>	<b>77.5%</b>	<b>13.3</b>	<b>0.55</b>	<b>This work</b>
PvBDTTAZ:O-IDTBR	1.08	16.26	63.6%	11.6	0.55	[7]
P3HT:BTA1	1.02	7.34	70%	5.24	0.83	[8]
PB3T:IT-M	1.00	18.9	63%	11.9	0.60	[9]
PBT7-Th:DTNR	1.08	15.72	56%	9.51	0.50	[10]
PCDTBT:P-BNBP-T	1.30	5.41	45.51%	3.20	0.53	[11]
P3TEA:SF-PDI <sub>2</sub>	1.11	13.27	64.3%	9.5	0.61	[12]
DRCNST:TPH	1.04	11.59	51%	6.16	0.56	[13]
PCE10:IDTBR:IDFBR	1.03	17.2	60%	11.0	0.52	[14]
PIDTT-TID:PC <sub>71</sub> BM	1.00	12.6	53%	6.7	0.49	[15]
PffBT4T-2DT:IDTBR	1.07	15.0	62%	9.95	0.51	[16]
P3TEA:FTTB-PDI4	1.13	13.87	65.9%	10.37	0.53	[17]
P3HT:SF(DPPB) <sub>4</sub>	1.14	8.29	55%	5.16	0.63	[18]
PBDB-T:ITCC	1.01	15.9	71%	11.4	0.66	[19]
P3HT:BTA2	1.22	6.15	60%	4.5	0.78	[20]
PffBT4T:EH-IDTBR	1.04	13.6	66.1%	9.4	0.55	[21]
PBDTSF-FBT:ITIC	1.03	17.09	66.3%	11.66	0.68	[22]
PBDT-ODZ:ITIC-Th	1.06	17.10	68.1%	12.34	0.50	[23]

PTZ1:PMI-F-PMI	1.30	7.0	63.5%	6.0	0.61	[24]
J61:BTAA3	1.15	10.84	66.17%	8.25	0.60	[25]
DBT-T1:6a	1.001	12.53	71.7%	9.28	0.77	[26]
PBCIT:ITIC	1.01	13.95	60.05%	8.46	0.63	[27]
DR3TSBDT:DTBTF	1.15	7.42	45%	3.64	0.59	[28]
P3HT:F4TBT4	1.26	5.83	56.1%	4.12	0.65	[29]
PBDTS-TDZ:ITIC	1.10	17.78	65.4%	12.80	0.48	[30]
PTB7-Th:IDTT-T	1.015	15.7	57%	9.1	0.57	[31]
PBPD-Th:ITIC	1.01	18.1	59%	10.8	0.54	[32]
PTZ6:ITIC	1.01	14.1	72.3%	10.3	0.58	[33]
P4TIN:PC <sub>61</sub> BM	1.06	15.17	52%	8.36	0.61	[34]
PBDB-T:IDT-BOC6	1.01	17.52	54%	9.60	0.62	[35]
PBTA-PSF:ITIC	1.01	18.51	74.4%	13.91	0.67	[36]

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## References

1. D. Qian, L. Ye, M. Zhang, Y. Liang, L. Li, Y. Huang, X. Guo, S. Zhang, Z. Tan and J. Hou, *Macromolecules*, 2012, **45**, 9611.
2. M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 4655.
3. Q. Fan, Q. Zhu, Z. Xu, W. Su, J. Chen, J. Wu, X. Guo, W. Ma, M. Zhang and Y. Li, *Nano Energy*, 2018, **48**, 413.
4. W. Gao, M. Zhang, T. Liu, R. Ming, Q. An, K. Wu, D. Xie, Z. Luo, C. Zhong, F. Liu, F. Zhang, H. Yan and C. Yang, *Adv. Mater.*, 2018, **30**, 1800052.



5. T. Yang, W. Wen, G. Yin, X. Li, M. Gao, Y. Gu, L. Li, Y. Liu, H. Lin, X. Zhang, B. Zhao, T. Liu, Y. Yang, Z. Li, X. Zhou and X. Gao, *Nucl. Sci. Tech.*, 2015, **26**, 020101.
6. P. W. M. Blom, V. D. Mihailetschi, L. J. A. Koster and D. E. Markov, *Adv. Mater.*, 2007, **19**, 1551.
7. S. Chen, Y. Liu, L. Zhang, P. C. Y. Chow, Z. Wang, G. Zhang, W. Ma and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 6298.
8. B. Xiao, A. Tang, J. Zhang, A. Mahmood, Z. Wei and E. Zhou, *Adv. Energy Mater.*, 2017, **7**, 1602269.
9. D. Liu, B. Yang, B. Jang, B. Xu, S. Zhang, C. He, H. Y. Woo and J. Hou, *Energy Environ. Sci.*, 2017, **10**, 546.
10. Y. Ma, M. Zhang, Y. Tang, W. Ma and Q. Zheng, *Chem. Mater.*, 2017, **29**, 9775.
11. Z. Ding, X. Long, B. Meng, C. Dou, J. Liu and L. Wang, *Nano Energy*, 2017, **32**, 216.
12. J. Liu, S. Chen, D. Qian, B. Gautam, G. Yang, J. Zhao, J. Bergqvist, F. Zhang, W. Ma, H. Ade, O. Inganäs, K. Gundogdu, F. Gao and H. Yan, *Nat. Energy*, 2016, **1**, 16089.
13. N. Liang, D. Meng, Z. Ma, B. Kan, X. Meng, Z. Zheng, W. Jiang, Y. Li, X. Wan, J. Hou, W. Ma, Y. Chen and Z. Wang, *Adv. Energy Mater.*, 2017, **7**, 1601664.
14. D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, M. Neophytou, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant and I. McCulloch, *Nat. Mater.*, 2017, **16**, 363.

15. C. Wang, X. Xu, W. Zhang, J. Bergqvist, Y. Xia, X. Meng, K. Bini, W. Ma, A. Yartsev, K. Vandewal, M. R. Andersson, O. Inganäs, M. Fahlman and Ergang Wang, *Adv. Energy Mater.*, 2016, **6**, 1600148.
16. D. Baran, T. Kirchartz, S. Wheeler, S. Dimitrov, M. Abdelsamie, J. Gorman, R. Ashraf, S. Holliday, A. Wadsworth, N. Gasparini, P. Kaienburg, H. Yan, A. Amassian, C. J. Brabec, J. R. Durrant and I. McCulloch, *Energy Environ. Sci.*, 2016, **9**, 3783.
17. J. Zhang, Y. Li, J. Huang, H. Hu, G. Zhang, T. Ma, P. C. Y. Chow, H. Ade, D. Pan and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 16092.
18. 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.
19. H. Yao, L. Ye, J. Hou, B. Jang, G. Han, Y. Cui, G. M. Su, C. Wang, B. Gao, R. Yu, H. Zhang, Y. Yi, H. Y. Woo, H. Ade and J. Hou, *Adv. Mater.*, 2017, **29**, 1700254.
20. B. Xiao, A. Tang, J. Yang, Z. Wei and E. Zhou, *ACS Macro Lett.*, 2017, **6**, 410.
21. G. Zhang, R. Xia, Z. Chen, J. Xiao, X. Zhao, S. Liu, H.-L. Yip and Y. Cao, *Adv. Energy Mater.*, 2018, **8**, 1801609.
22. G. Zhang, X. Xu, Z. Bi, W. Ma, D. Tang, Y. Li and Q. Peng, *Adv. Funct. Mater.*, 2018, **28**, 1706404.
23. X. Xu, Z. Li, Z. Bi, T. Yu, W. Ma, K. Feng, Y. Li and Q. Peng, *Adv. Mater.*, 2018, **30**, 1800737.

24. Y. Zhang, X. Guo, B. Guo, W. Su, M. Zhang and Y. Li, *Adv. Funct. Mater.*, 2017, **27**, 1603892.
25. A. Tang, B. Xiao, Y. Wang, F. Gao, K. Tajima, H. Bin, Z.-G. Zhang, Y. Li, Z. Wei and E. Zhou, *Adv. Funct. Mater.*, 2018, **28**, 1704507.
26. D. Meng, H. Fu, C. Xiao, X. Meng, T. Winands, W. Ma, W. Wei, B. Fan, L. Huo, N. L. Doltsinis, Y. Li, Y. Sun and Z. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 10184.
27. P. Chao, Z. Mu, H. Wang, D. Mo, H. Chen, H. Meng, W. Chen and F. He, *ACS Appl. Energy Mater.*, 2018, **1**, 2365.
28. 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.
29. Y. Fu, B. Wang, J. Qu, Y. Wu, W. Ma, Y. Geng, Y. Han and Z. Xie, *Adv. Funct. Mater.*, 2016, **26**, 5922.
30. X. Xu, T. Yu, Z. Bi, W. Ma, Y. Li and Q. Peng, *Adv. Mater.*, 2018, **30**, 1703973.
31. B. He, B. Yang, M. A. Kolaczowski, C. A. Anderson, L. M. Klivansky, T. L. Chen, M. A. Brady and Y. Liu, *ACS Energy Lett.*, 2018, **3**, 1028.
32. Q. Fan, Z. Xu, X. Guo, X. Meng, W. Li, W. Su, X. Ou, W. Ma, M. Zhang and Y. Li, *Nano Energy*, 2017, **40**, 20.
33. B. Guo, W. Li, X. Guo, X. Meng, W. Ma, M. Zhang and Y. Li, *Nano Energy*, 2017, **34**, 556.
34. S.-F. Liao, C.-T. Chen and C.-Y. Chao, *ACS Macro Lett.*, 2017, **6**, 969.
35. Y. Liu, Z. Zhang, S. Feng, M. Li, L. Wu, R. Hou, X. Xu, X. Chen and Z. Bo, *J. Am. Chem. Soc.*, 2017, **139**, 3356.

36. X. Li, G. Huang, N. Zheng, Y. Li, X. Kang, S. Qiao, H. Jiang, W. Chen, R. Yang,  
*Sol. RRL*, 2019, **3**, 1900005.