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High efficiencies of 7.58% is obtained in non-fullerene OSCs using **PM-PDI**₃ as the acceptors and **PDBT-T1** as the donor.

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Methane-Perylene Diimides-Based Small Molecule Acceptors for **High Efficiency Non-Fullerene Organic Solar Cells**

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We reported perylene diimide (PDI) small molecules based on diphenylmethane, triphenylmethane, and tetraphenylmethane cores, named as PM-PDI2, PM-PDI3 and PM-PDI4, respectively. The OSCs performances of PM-PDI3 and PM-PDI₄ are comparable. The PM-PDI₃ based device with PDBT-T1 as the donor achieved a highest power conversion efficiency (PCE) of 7.58% along with a high open-circuit voltage (V_{oc}) of 0.98 V, a short-circuit current density (J_{sc}) of 11.02 mA cm⁻² and a high fill factor (FF) of 69.9%, a 1.32 times boost in PCE with respect to the PM-PDI₂ based control device (3.26%). The high photovoltaic performance of the PM-PDI₃ based device can be attributed to its relatively high-lying LUMO level, complementary absorption spectra with the polymer donor material PDBT-T1, relatively favorable morphology and improved exciton dissociation and charge collection efficiency. A PCE of 7.58% is among the highest efficiency of phenyl-methane as core based non-fullerene organic solar cells. Overall, this work provides a new approach to enhance the performance of non-fullerene acceptors.

Introduction

In the past decade, organic solar cells (OSCs) consisting of donors and acceptors as active layers, have attracted increasing attention owing to their advantages of light weight, low cost, solution-processing ability and their potential application in flexible devices.¹⁻¹¹ Fullerene derivatives, have been dominant electron acceptors in OSCs for the past few decades, and their success is attributed to their outstanding electron- withdrawing ability and charge transport $properties.^{12\mathchar`-14}$ However, they suffer from some intrinsic drawbacks, such as poor spectral absorption, limited tunablity of chemical structures and energy level, high-cost purification morphological instability, hindering the further and commercialization of fullerene OSCs.15 Therefore, research on non-fullerene acceptors (NFA) is of significance.

NFA materials, possessing the favorable electron-accepting and transporting properties, are believed to excel fullerene and have undergone rapid development. A variety of high performance fullerene-free acceptors have been invented,16-19 especially for the systems of ITIC ^{18, 20-30} and perylene diimides (PDIs).^{31, 32} Recently, Zou group reported single-junction OSCs devices based on Y6 exceeded a power conversion efficiency (PCE) of 16%;³³ Chen group reported the highest PCE of 17.3% in tandem devices based on PBDB-T:F-M and PTB7-Th:O6T-4F:PC71BM, ³⁴ demonstrating the great potential of nonfullerene acceptors for future commercialization.

Perylene diimide (PDI) small molecule is competitive among the various non-fullerene acceptors. They have several advantages: (1) easy to large-scale preparation and purification;³⁵ (2) adjustability of molecular structure, energy levels, and absorption range (PDI moiety provide several substitution sites, including the bay position,^{36, 37} the non-bay position ³⁸and the nitrogen atoms.);³⁹ (3) high electron mobilities in the order of 101-10-3 cm² V-1s-1.40

PDIs tend to form large aggregates domains due to their large and planar structures, which may aggravate geminate recombination and deteriorate device performance. Accordingly, we need to make efforts to suppress the formation of 1D π stacking while trying to retain sufficient intermolecular LUMO-LUMO overlap for adequate electron transport. This can be achieved by constraining two or more PDIs to be non-planar and/or with the introduction of a conjugated bridge.^{41, 42} Previously, Yan group reported that a PDI dimer featuring spirobifluorene linker, named as SF-PDI₂. which achieved an impressive PCE of 9.50% with a high Voc of 1.11 V with the low bandgap polymer P3TEA. ³¹ Our group developed a star-shaped PDI trimer TPA-PDI₃ with a triphenylamine (TPA) core, which displayed weak molecular aggregation, strong absorption as well as energy levels matched with the donor of PBDB-T, OSCs based on PBDB-T: TPA-PDI₃ gave a PCE of 5.84 %.^{36b} Yan group used the ringfusion strategy to obtain a novel PDI tetramer named FTTB-PDI4, and achieved a PCE of 10.58% by matching FTTB-PDI4 with the polymeric donor P3TEA, which is the highest value for PDI small molecule-based OSCs.32

Despite the above-mentioned advantages of PDIs derivatives,

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Scheme 1. The synthesis routes of PM-PDI₂, PM-PDI₃ and PM-PDI₄.

Despite the progress mentioned above, more efforts should be made to improve photovoltaic performances towards commercialization. Therefore, it is of importance to design and synthesize new acceptor materials, and investigate the relationship between molecular structure and OSCs performance.⁴³

Bearing these considerations in mind, we designed and synthesized phenyl-methane based PDI dimer, PDI trimer and tetramers, named PM-PDI₂, PM-PDI₃ and PM-PDI₄, respectively. Their structures are shown in Scheme 1. Their photophysicial and electrochemical properties, molecular simulations, charge transport and photovoltaic properties were investigated in detail. All these acceptor molecules have a central phenyl-substituted methane core and the peripheral PDI units are directly linked to the benzene. $PM-PDI_2$ is a Vtype molecule, which contains two flanked PDI units; PM-PDI₃ is a star-shape C3-symmetrical molecule with three peripheral PDI units; and **PM-PDI₄** is a C4-symmetrical molecule with four PDI units linked to the central benzene. The influences of the varied molecular geometries on the photophysical properties, the active layers morphologies and the photovoltaic performances are studied in detail.

Results and discussion

Material synthesis and characterization

The synthesis routes to all three compounds are shown in Scheme 1. The precursor of borate ester (1-3) was synthesized according to boylation coupling reaction of corresponding bromide with bis(pinacolato)diboron catalyzed with Pd(dppf)Cl₂. Another precursor of monobromo-PDI (4) was obtained via bromination of PDIs according to the known procedures.⁴⁴ Then the final products of **PM-PDI₂**, **PM-PDI₃**



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Fig. 1 Absorption spectra of PBDB-T1, PM-PDI₂, PM-PDI₃ and PM-PDI₄ films.

and PM-PDI₄ were obtained by reacting the borate ester and monobromo-PDI through Suzuki coupling reaction in the presence of $Pd(PPh_3)_4$. The purification of **PM-PDI₂** was easy due to relatively less by-products, but the purification of PM-PDI₃ and PM-PDI₄ were very different due to multiple reaction sites, and we purified them by repeated column chromatograph. All of the new compounds have been fully characterized by ¹H NMR, ¹³C NMR and FT-IR. Although the satisfactory mass spectra of PM-PDI₂ and PM-PDI₄ were not available owing to the influence of matrix, ion detection mode and concentration of samples, the molecular ion peaks (MALDI-TOF-MS) of these three compounds have been successfully acquired (Fig. S15-S17). All of the new compounds have been fully characterized by ¹H NMR, ¹³C NMR, FT-IR and high-resolution mass spectra (HRMS). The three target products are highly soluble in general organic solvents, such as dichloromethane, tetrahedronfunan (THF), orthodichlorobenzene (o-DCB), and chloroform room at temperature. Such good solubility is mainly ascribed to the tridimensional molecular scaffold. The thermal properties were evaluated by thermal gravimetric analysis (TGA) performed under nitrogen atmosphere. The three target products have the decomposition temperature (5% weight loss) of above 300 °C (Fig. S18).

Optical and electrochemical properties



Fig. 2 CV curves of PM-PDI₂, PM-PDI₃, PM-PDI₄ and mono PDI (shown in Fig. S1).

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The absorption spectra of PM-PDI₂, PM-PDI₃ and PM-PDI₄ are shown in Fig. 1 and Figs S2-3 and corresponding data are provided in Table 1. The three PDI acceptors demonstrated similar absorption spectra in solution. PM-PDI₂ in dichloromethane solution showed a broad absorption in the range of 450-600 nm with a maximum at 534 nm. PM-PDI₃ and PM-PDI₄ demonstrated almost same absorption spectra with $PM-PDI_2$, but the molar extinction coefficient ϵ values of PM- $\textbf{PDI}_{2},~\textbf{PM-PDI}_{3}$ and $\textbf{PM-PDI}_{4}$ solutions ascend from 1.44 \times 10^{5} to 1.90×10^5 to 2.09×10^5 M⁻¹ cm⁻¹ with increasing number of PDI units. From the solution to the film, the absorption edges red-shift by ca. 50 nm, suggesting the intermolecular $\pi - \pi$ stacking of these acceptors in the solid state. PM-PDI2, PM-PDI₃ and PM-PDI₄ pure films exhibit optical absorption onsets of 598 nm, 596 nm and 596 nm, respectively. As illustrated in Fig. 1, the main absorption of PDBT-T1 is in the range from 400 to 700 nm, which complements the absorption spectrum of PM-PDI₂, PM-PDI₃ and PM-PDI₄. The optimal band gaps (Eg^{opt})



Fig. 3 Molecular energy level diagrams of electron donors and acceptors. (LUMO levels were calculated from the HOMO levels and optical bandgap.)

of three PDIs derivatives estimated from the film absorption edges are 2.07, 2.08 and 2.08 eV, respectively.

The electrochemical properties of **PM-PDI₂**, **PM-PDI₃** and **PM-PDI₄** in dichloromethane solutions were investigated by cyclic voltammetry (CV) as shown in Fig. 2. The LUMO energy levels of these molecules were calculated from the onset reduction potentials according to the equation of $E_{LUMO} = -e (E_{red} + 4.80)$ (eV), assuming the Fc/Fc⁺ to be -4.8 eV.^{32} The HOMO energy levels were estimated from the equation $E_{HOMO} = E_{LUMO} - E_g^{opt}$ (eV). The corresponding energy levels data were summarized in Table 1. The LUMO levels up-shift from -3.90 to -3.86 eV, with the increased number of PDI units. The high-lying LUMO of **PM-PDI₄** potentially contributes to the high open-circuit voltage. It is worth noting that **PM-PDI₂** exhibits lower LUMO energy levels than **PM-PDI₃** and **PM-PDI₄**, which should be attributed to the relatively lower dipole moment of symmetric structure.

Theoretical analysis

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To gain deep insight into the structural and electronic properties of **PM-PDI₂**, **PM-PDI₃** and **PM-PDI₄**, density function theory (DFT) calculation⁴⁵⁴⁵ (B3LYP/6-31G*)⁴⁵ was performed on the three molecules. The optimized configurations and orbital distributions of HOMO and LUMO energy levels are illuminated in Fig. S6. The electron clouds of HOMO energy levels were delocalized throughout the PDI core, while the LUMO energy levels are dominated by perylene diimides core.

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Moreover, the distinct dihedral angles (Fig.S6), between adjacent PDIs indicate that the flanking 1PDIS⁹/iPTPhenyA methane core form the large steric repulsion, especially for **PM-PDI**₃ and **PM-PDI**₄, suggesting that the more introduction of PDIs units, results in a more twisted molecular configuration. Furthermore, the theoretically predicted HOMO and LUMO energy levels and bandgap of three compounds fit quite well with the values obtained by CV experiment (Table 2 and S1).

Photovoltaic Properties

We used polymeric donor (PDBT-T1) and PDI acceptors (PM-PDI₂, PM-PDI₃ and PM-PDI₄) to construct OSCs with a conventional device configuration: ITO glass/ PEDOT:PSS / active layers / Zracac /Al. Where ITO is indium tin oxide, PEDOT is poly(3,4-ethylenedioxythiophene) and PSS is poly(styrenesulfonate). The p-type polymer PDBT-T1 was selected as the donor material because of complementary absorption and the matched energy levels with these three



Fig. 4 (a) J - V curves of PDBT-T1:PM-PDI₂, PDBT-T1:PM-PDI₃ and PDBT-T1:PM-PDI₄-based devices. (b) IPCE curves of the devices.

acceptors (See Fig. 3 and Fig. S1). The processing solvent for the active layer is chlorobenzene (DCB) with a total concentration of 20 mg/mL. The detailed device fabrications and measurements are demonstrated in Supporting Information. The optimal conditions for preparing the devices were obtained by changing film thickness, annealing

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temperatures and additives carefully. The optimized weight ratio of D / A was 1:1 and the optimized film thickness is ca. 95 nm. The optimized ratio of 1,8-Diiodooctane (DIO) was 0.25%. Figure 4a illustrates the current density-voltage (J-V) curves of OSCs based on PDBT-T1:PM-PDI2, PDBT-T1:PM-PDI3, and PDBT-T1:PM-PDI₄, and the detailed photovoltaic parameters are shown in Table 2. The PDBT-T1:PM-PDI₄-based device yields a PCE of 7.52%, with an open-circuit voltage (V_{0c}) of 1.01 V, a J_{SC} of 11.20 mA cm⁻² and a fill factor (FF) of 0.67. In contrast, the PDBT-T1:PM-PDI2-based device exhibits a low PCE of 3.26%, with an enhanced V_{OC} (0.98 V) but reduced J_{SC} (8.49 mA cm⁻²) and FF (39.3%). PDBT-T1:PM-PDI₃ showed an impressive PCE as high as 7.58%, with a V_{OC} of 0.98 V, a J_{SC} of 11.02 mA cm⁻² and a FF of 69.9% under the illumination of AM 1.5G, 100 mW cm⁻². Benefiting from the increased J_{sc} and FF in PDBT-T1:PM-PDI3 and PDBT-T1:PM-PDI4-based OSCs, both devices exhibit higher PCEs than the PDBT-T1:PM-PDI2 counterpart.

The incident photon-to-current conversion efficiency (IPCE) spectra of the optimal devices based on **PM-PDI₂**, **PM-PDI₃** and **PM-PDI₄** are displayed in Fig. 4b. J_{SC} s integrated from IPCE



Fig. 5 Dark current density-voltage characteristics for a) hole-only and b) electron-only devices with optimized PDBT-T1: PM-PDI₂, PDBT-T1: PM-PDI₃ and PDBT-T1: PM-PDI₄ BHJ films.

match well with the values from the J-V curves within 4% error (Table 2). We can see that the IPCE curves for all the three types of devices cover a broad and strong photoresponse range from 300 to 700 nm. The IPCE values of **PM-PDI**₃ and **PM-PDI**₄-based solar cells are distinctly higher than the counterpart of **PM-PDI**₂.

Active Layer Charge Transport

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To clarify the charge mobilities in the OSOs1deVices?We have measured electron and hole mobilities in the blend films by the space charge limited current (SCLC) method. Hole-only diodes with the structure of ITO/MoO_x/active layers/MoO_x/Al and electron-only diodes with the structure of ITO/ZnO/active layer/Zracac/Al were fabricated and measured to extract the hole (μ_h) and electron (μ_e) mobilities of **PM-PDI**_x pure films, and PDBT-T1:PM-PDI_x blend films (Fig. 5, S4 and Table S2.) The $\mu_e s$ values of $\text{PM-PDI}_2,~\text{PM-PDI}_3$ and PM-PDI_4 pristine films changed from 5.78 \times 10⁻⁴ to 7.08 \times 10⁻⁴ to 7.39 \times 10⁻⁴ cm²V⁻¹s⁻¹ with increasing number of PDI units. **PM-PDI**_x pure films, and PDBT-T1:PM-PDI, blend films have µs in the same magnitude, which implied that efficient electron-transport pathways are unaffected to a great extent by the presence of the donor polymer. The μ_h / μ_e of three blend films were 2.19, 1.70 and 1.75, respectively. PM-PDI₃ and PM-PDI₄ -based blend films showed increased hole and electron mobility and more balanced μ_h and μ_e , which benefits to the charge transport and corresponds with high fill factor.46

Morphology characterization

The surface morphology measurements of BHJ active layer were performed using atomic force microscopy (AFM). As can be seen from AFM height images (Fig. 6), **PDBT-T1:PM-PDI**₂ blend film displayed a smooth and uniform morphologies with slightly larger root mean square (RMS) surface roughness of 1.81 nm than **PDBT-T1:PM-PDI**₃ and **PDBT-T1:PM-PDI**₄, which could be attributed to the stronger PDI aggregation therein. In contrast, **PDBT-T1:PM-PDI**₃ and **PDBT-T1:PM-PDI**₄ demonstrated relatively clear and delicate nanofibrillar structures; and no strong molecule aggregation between **PDBT-T1** and the two acceptors occurred, which are beneficial for charge transport and extraction.

Exciton dissociation and charge extraction

Charge collection and exciton dissociation in active layers were also investigated and the corresponding curves of photocurrent density versus effective voltage of the optimal OSCs are shown in Fig. 7a. The saturation photocurrent density (J_{sat}), exciton dissociation efficiency (η_{diss}) and charge collection efficiency (η_{coll}) can be estimated from the curves of J_{ph} and V_{eff} . The exciton dissociation efficiency ($\eta_{diss} = J_{SC}/J_{sat}$) and charge collection efficiency ($\eta_{coll} = J_{max}/J_{sat}$) were calculated under the short circuit and maximum power output conditions, are 74.6%, 92.8% and 90.8%, respectively, and corresponding η_{coll} are 39.4%, 77.6% and 74.2%. The much higher η_{diss} and η_{coll} values of **PM-PDI₃** and **PM-PDI₄**-based device demonstrates its higher exciton dissociation and charge collection efficiency, corresponding with their higher J_{Sc} and FF.⁴⁷

Charge-recombination

We investigated charge recombination by measuring J_{sc} at different light intensities (*P*), as shown in Fig. 7b, and the corresponding data were summarized in Table S3. The relationship between J_{sc} and *P* can be describe using $J_{sc} \propto P^{s}$, when S = 1 indicates that all the free carriers are collected and swept out before recombination, when S < 1, indicates a

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certain degree of bimolecular recombination.⁴⁸ The recombination parameters *S* are 0.872, 0.971 and 0.940 for the devices with **PDBT-T1:PM-PDI₂**, **PDBT-T1:PM-PDI₃** and **PDBT-T1:PM-PDI₄** BHJ films, respectively, suggesting weak

bimolecular recombination⁴⁹ of **PDBT-T1:PM-PDI**_{3 e} and **PDBT-T1:PM-PDI**₄ -based devices, which are consistent/witho their higher J_{SC} and FF.



Fig. 6 Film morphology images, AFM height (A-C) and phase (D-F) images of blend films. A, D) PDBT-T1: PM-PDI₂, RMS = 1.81 nm; B, E) PDBT-T1: PM-PDI₃, RMS = 1.23 nm; C, F) PDBT-T1: PM-PDI₄, RMS = 1.17 nm.

Table 1. Basic Properties of PDBT-T1: PM-PDI ₂ , PDBT-T1: PM-PDI ₃ and PDBT-T1: PM-PDI ₄ .												
Acceptors	λ _{max} ^{a)} (nm)	ε _{max} ^{a)} (M ⁻¹ cm ⁻¹)	λ _{onset} ^{a)} (nm)	λ _{max} ^{ь)} (nm)	λ _{onset} ^{b)} (nm)	Eg ^{opt c)} (eV)	HOMO (eV)	LUMO ^{d)} (eV)	μ _e ^{e)} (cm² V ⁻¹ s ⁻¹)			
PM-PDI₂	533	1.44×10^{5}	576	540	598	2.07	-5.97	-3.90	5.78 × 10 ⁻⁴			
PM-PDI ₃	534	1.90 × 10 ⁵	576	510	596	2.08	-5.97	-3.89	7.08 × 10 ⁻⁴			
PM-PDI ₄	535	2.09 × 10 ⁵	576	541	596	2.08	-5.94	-3.86	7.39 × 10 ⁻⁴			

^{a)} In a dichloromethane solution. ^{b)} In a neat film. ^{c)} Calculated from empirical the formula: $E_g^{opt} = 1240/\lambda_{onset}$. ^{d)} Cyclic voltammetry (CV) method by measuring in dichloromethane. ^{e)} Measured by the space charge limited current (SCLC) method.

Table 2. Performance of the optimized OSCs devices based on PDBT-T1: PM-PDI₂, PDBT-T1: PM-PDI₃ and PDBT-T1: PM-PDI₄ (1:1, w/w).

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		V _{oc} ^{a)}	J _{SC} ^{a)}	J _{SC} ^{b)}	FF ^{a)}	PCE ^{a)}				
Active layer	Additive	(V)	(mA cm ⁻²)	(mA cm ⁻²)	(%)	(%)				
		0.978	8.490		0.393	3.26				
PDBT-T1:PM-PDI ₂	0.25% DIO	(0.972±0.010)	(8.218±0.221)	8.211	(0.392±0.006)	(3.131±0.192)				
		0.984	11.022		0.699	7.58				
PDBT-T1:PM-PDI ₃	0.25% DIO	(0.987±0.009)	(10.765±0.241)	10.668	(0.690±0.011)	(7.331±0.205)				
		1.007	11.203		0.667	7.52				
PDB1-11:PM-PDI ₄	0.25% DIO	(0.993±0.011)	(10.875±0.238)	10.946	(0.661±0.005)	(7.137±0.212)				
^{a)} Values are for the highest-PCE device, with average values obtained from 20 devices listed in parentheses. ^{b)} J _{sc} value from the integration										
of the EQE spectra are within 4% error of those from J-V curves.										

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Fig. 7 (a) Light intensity dependence of J_{SC} of the devices. (b) J_{ph} versus V_{eff} of the optimized devices

In addition to the OSCs performance, the acceptor's cost still deserves the attention of materials scientists. Facile synthesis and the high yields for such PDI-based acceptors enable ready materials access at greatly reduced cost. Taking **PM-PDI**₃ for example, the synthetic cost of PDI material was estimated to be 620 RMB /g (\approx 90 \$/g) based on the price of solvents and chemicals supplied in China (Table S4), which is far less than the price of fused-ring electron acceptors represented by ITIC. Furthermore, if large-scale preparation is performed, the cost is expected to further reduced, showing the distinctive advantage of PDIs materials for industrial applications.

Conclusions

In conclusion, we designed and synthesized three methaneperylene diimides-based small molecular acceptors, **PM-PDI₂**, **PM-PDI₃** and **PM-PDI₄**, and investigated the effects of PDIs' number on photophysical, electronic, charge-transport, photovoltaic, and morphological properties. **PM-PDI₃** and **PM-PDI₄** exhibit relatively stronger absorption profile, upshifted LUMO energy level and a higher electron mobility than **PM-PDI₂**, which endow **PM-PDI₃** and **PM-PDI₄** with better prospects for OSC applications. Furthermore, **PDBT-T1:PM-PDI₃** and **PDBT-T1:PM-PDI₄** active layers delivered a high PCE of 7.58% and 7.52%, outcompeting **PDBT-T1:PM-PDI₂**. Notably, compared with **PM-PDI₄**, the slightly enhanced PCE of **PM-PDI₃** mainly attributed to improved FF of 69.9%, which is one of the highest FF for the PDI-based OSCs to date. Our results demonstrated that PDIs' number in PDI small molecules had a significant impact on the photovoltaic performance.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 L. Lu, M. A. Kelly, W. You and L. Yu, *Nat. Photon.*, 2015, **9**, 491.
- 2 G. Li, W.-H. Chang and Y. Yang, Nat. Rev. Mater., 2017, 2, 17043.
- 3 A. Polman, M. Knight, E. C. Garnett, B. Ehrler and W. C. Sinke, *Science*, 2016, **352**, 6283.
- 4 R. Ganesamoorthy, G. Sathiyan and P. Sakthivel, Sol. Energ. Mat. Sol. C., 2017, 161, 102.
- 5 P. Cheng, G. Li, X. Zhan and Y. Yang, *Nat. Photon.*, 2018, **12**, 131.
- 6 Y. Lin and X. Zhan, Acc. Chem. Res., 2016, 49, 175.
- 7 J. Hou, O. Inganäs, R. H. Friend and F. Gao, *Nat. Mater.*, 2018, **17**, 119.
- 8 C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder and X. Zhan, *Nat. Rev. Mater.*, 2018, **3**, 18003.
- 9 G. Zhang, J. Zhao, P. C. Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang and H. Yan, *Chem. Rev.*, 2018, **118**, 3447.
- 10 F. Shen, J. Xu, X. Li and C. Zhan, J. Mater. Chem. A., 2018, 6, 15433.
- 11 C. Li, H. Fu, T. Xia and Y. Sun, *Adv. Energy. Mater.*, 2019, 1900999. doi: 10.1002/aenm.201900999.
- M. Li, K. Gao, X. Wan, Q. Zhang, B. Kan, R. Xia, F. Liu, X. Yang, H. Feng, W. Ni, Y. Wang, J. Peng, H. Zhang, Z. Liang, H.-L. Yip, X. Peng, Y. Cao and Y. Chen, *Nat. Photon.*, 2016, **11**, 85.
- 13 J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, Nat. Energy., 2016, 1, 15027.
- 14 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.*, 2016, 7, 13740.

- 15 B. Kan, H. Feng, X. Wan, F. Liu, X. Ke, Y. Wang, Y. Wang, H. Zhang, C. Li, J. Hou and Y. Chen, J. Am. Chem. Soc., 2017, 139, 4929.
- 16 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.
- 17 Q. An, W. Gao, F. Zhang, J. Wang, M. Zhang, K. Wu, X. Ma, Z. Hu, C. Jiao and C. Yang, *J. Mater. Chem. A*, 2018, **6**, 2468.
- 18 W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang and J. Hou, J. Am. Chem. Soc., 2017, 139, 7148.
- 19 T. J. Aldrich, M. Matta, W. Zhu, S. M. Swick, C. L. Stern, G. C. Schatz, A. Facchetti, F. S. Melkonyan and T. J. Marks, J. Am. Chem. Soc., 2019, 141, 3274.
- 20 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
- 21 Q. An, X. Ma, J. Gao, F. Zhang, Sci. Bull. 2019, 64, 504.
- 22 H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang and J. Hou, Angew. Chem. Int. Ed., 2017, 56, 3045.
- 23 N. D. Eastham, J. L. Logsdon, E. F. Manley, T. J. Aldrich, M. J. Leonardi, G. Wang, N. E. Powers-Riggs, R. M. Young, L. X. Chen, M. R. Wasielewski, F. S. Melkonyan, R. P. H. Chang and T. J. Marks, *Adv. Mater.*, 2018, **30**, 1704263.
- 24 X. Yi, B. Gautam, I. Constantinou, Y. Cheng, Z. Peng, E. Klump, X. Ba, C. H. Y. Ho, C. Dong, S. R. Marder, J. R. Reynolds, S.-W. Tsang, H. Ade and F. So, *Adv. Func. Mater.*, 2018, **28**, 1802702.
- 25 Z. Fei, F. D. Eisner, X. Jiao, M. Azzouzi, J. A. Röhr, Y. Han, M. Shahid, A. S. R. Chesman, C. D. Easton, C. R. McNeill, T. D. Anthopoulos, J. Nelson and M. Heeney, *Adv. Mater.*, 2018, **30**, 1705209.
- 26 Z. Yao, X. Liao, K. Gao, F. Lin, X. Xu, X. Shi, L. Zuo, F. Liu, Y. Chen and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2018, **140**, 2054.
- Z. Zheng, Q. Hu, S. Zhang, D. Zhang, J. Wang, S. Xie, R. Wang, Y. Qin, W. Li, L. Hong, N. Liang, F. Liu, Y. Zhang, Z. Wei, Z. Tang, T. P. Russell, J. Hou and H. Zhou, *Adv. Mater.*, 2018, **30**, 1801801.

- 28 W. Li, L. Ye, S. Li, H. Yao, H. Ade and J. Hou, Adv. Mater., 2018, **30**, 1707170.
- 29 R. Yu, H. Yao, L. Hong, Y. Qin, J. Zhu, Y. Cui, S. Li and J. Hou, *Nat. Commun.*, 2018, 9, 4645.
- 30 B. Fan, X. Du, F. Liu, W. Zhong, L. Ying, R. Xie, X. Tang, K. An, J. Xin, N. Li, W. Ma, C. J. Brabec, F. Huang and Y. Cao, *Nat. Energy.*, 2018, **3**, 1051.
- 31 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.
- 32 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.
- J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu,
 C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski,
 Y. Li and Y. Zou, *Joule*, 2019, **3**, 1140.
- 34 L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao and Y. Chen, *Science*, 2018, **361**, 1094.
- 35 A. Nowak-Król, K. Shoyama, M. Stolte and F. Würthner, Chem. Comm., 2018, 54, 13763.
- 36 (a) G. Li, S. Wang, T. Liu, P. Hao, Z. Liu, F. Li, L.-M. Yang, Y. Zhang, D. Li, S. Yang, J. Zhao, J. Li, H. Yan and B. Tang, *J. Mater. Chem. C.*, 2018, 6, 12601; (b) G. Li, Y. Zhang, T. Liu, S. Wang, D. Li, J. Li, F. Li, L.-M. Yang, Z. Luo, C. Yang, H. Yan, P. Hao, Q. Shang and B. Tang, *J. Mater. Chem. C.*, 2018, 6, 11111.
- 37 (a) J. Yi, Y. Wang, Q. Luo, Y. Lin, H. Tan, H. Wang and C.-Q. Ma, *Chem. Comm.*, 2016, **52**, 1649; (b) L. Yang, Y. Chen, S. Chen, T. Dong, W. Deng, L. Lv, S. Yang, H. Yan and H. Huang, *J. Power Sources.*, 2016, **324**, 538.

- 38 H. Wang, L. Chen and Y. Xiao, J. Mater. Chem_{View Article} 2019, 835.
 DOI: 10.1039/C9TC03457A
- 39 H. Fu, D. Meng, X. Meng, X. Sun, L. Huo, Y. Fan, Y. Li, W. Ma, Y. Sun and Z. Wang, J. Mater. Chem. A., 2017, 5, 3475.
- 40 X. Zhang, Z. Lu, L. Ye, C. Zhan, J. Hou, S. Zhang, B. Jiang, Y. Zhao, J. Huang, S. Zhang, Y. Liu, Q. Shi, Y. Liu and J. Yao, *Adv. Mater.*, 2013, **25**, 5791.
- 41 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.
- 42 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.
- 43 A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini,
 C. J. Brabec, D. Baran and I. McCulloch, *Chem. Soc. Rev.*,
 2019, 48, 1596.
- 44 Q. Yan and D. Zhao, Org. Lett., 2009, 11, 3426.
- 45 R. D. F. Gaussian 09, M. J. et al. Gaussian, Inc., Wallingford, CT, 2009, see supporting information for full citation.
- 46 Q. An, J. Wang, F. Zhang, Nano Energy, 2019, 60, 768.
- 47 X. Ma, M. Luo, W. Gao, J. Yuan, Q. An, M. Zhang, Z. Hu, J. Gao, J. Wang, Y. Zou, C. Yang and F. Zhang, *J. Mater. Chem.* A, 2019, **7**, 7843.
- 48 T. Liu, L. Huo, S. Chandrabose, K. Chen, G. Han, F. Qi, X. Meng, D. Xie, W. Ma, Y. Yi, J. M. Hodgkiss, F. Liu, J. Wang, C. Yang and Y. Sun, *Adv. Mater.*, 2018, **30**, 1707353.
- 49 Z. Hu, F. Zhang, Q. An, M. Zhang, X. Ma, J. Wang, J. Zhang, J. Wang, ACS Energy Lett., 2018, 3, 555.