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Introduction

Bulk heterojunction organic solar cells (OSCs) are believed to be a promising choice for next generation green energy platforms to address the energy crisis and environmental pollution, due to their attractive features such as low cost, flexibility and large area printing production.^{1–10} The OSC active layer typically consists of

Non-fullerene acceptor engineering with threedimensional thiophene/selenophene-annulated perylene diimides for high performance polymer solar cells[†]

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We report two new propeller-shaped perylene diimide (**PDI**) acceptors based on tetraphenylethylene (**TPE**) as the core and flanked with S/Se-fused **PDIs**, named as **TPE-PDI₄-S** and **TPE-PDI₄-Se**. Compared to the sulfur-annulated counterpart, **TPE-PDI₄-Se** exhibits a blue-shifted absorption spectrum, stronger absorption in the region of 400–600 nm, higher LUMO energy level and twisted molecular geometry. The **TPE-PDI₄-Se** based device with **PBDB-T1** as the donor achieved a power conversion efficiency (PCE) of 7.63% along with a high V_{OC} of 1.08 V, a J_{SC} of 10.28 mA cm⁻² and a high fill factor of 68.8%, a 11.4% boost in PCE with respect to the **TPE-PDI₄-Se** based control device (6.85%). The high photovoltaic performance of the **TPE-PDI₄-Se** based device can be attributed to its relatively high-lying LUMO level, complementary absorption spectra with the donor material, relatively favorable morphology and balanced carrier transport. To the best of our knowledge, a PCE of 7.63% is among the highest values for **TPE** core-based non-fullerene organic solar cells. Overall, our work provides a simple and effective molecule-designing method to promote the PCE of non-fullerene OSCs.

a polymer donor and an acceptor.^{11–17} Fullerene derivatives have been the most investigated acceptors in the past few years and the state-of-the-art single-junction devices based on fullerene derivatives have been reported to reach over 11% power conversion efficiencies (PCEs).¹⁸⁻²⁰ Although fullerenes derivatives have made great contributions to the development of OSCs,^{21,22} they are not the ideal candidates for practical applications because the production of fullerenes is very expensive and the chemical modification of fullerenes remains challenging. Therefore, nonfullerene acceptors (NFAs) composed of large conjugate structures with electron-deficient building blocks to ensure facile charge delocalization and good charge transport have recently emerged as a hot topic in the field of OSCs. They demonstrate lots of advantages, such as structural versatility, adjustable absorption, easy tunability of the energy levels, excellent morphological stability and self-assembly characteristics.3,23-28 In conjunction with device engineering and morphology optimization, these new materials have been intensively studied, for derivatives, 20,33-36 example, ITIC rhodanines,37-39 diketopyrrolopyrroles,40 naphthalimides41,42 and perylene diimides (PDIs).^{28,43} Some NFA based OSCs have achieved over 13% PCE in recent years.²⁹⁻³² Of the myriad of materials explored, those based upon the PDI molecules have been intensely studied in the past few years and the PCEs based on PDI

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acceptors have exceeded 10%.⁴³ **PDIs** demonstrate several excellent properties, such as easy functionalization, strong electron-acceptor character, finely tunable solubility, intense light absorption capability, energy level tunability, and self-assembling properties.^{24–26,28,44–51} Despite these favorable advantages, the strong tendency for π - π stacking between **PDI** molecules leads to the formation of excessively large crystalline domains, which may result in large phase separation in the active layers, thereby limiting the OSC performance.^{52–59}

Many strategies have been adopted to suppress the aggregation tendency including substitution at the imide position, bay position, or non-bay position of the **PDI** units with different functional groups to construct twisted **PDI** dimers and three-dimensional (**3D**)-structure oligomers, for example, triphenylamine,⁵⁵ spirobifluorene,⁶⁰ benzodithiophene,⁶¹ tetraphenylethylene (**TPE**)⁴⁵ and porphyrin.⁴⁶ Furthermore, S,^{50,62,63} Se^{25,48,64} and N⁵³ heteroatoms had been incorporated at the bay positions of **PDI** units to obtain more twisted structures and higher lowest unoccupied molecular orbital (LUMO) levels. Despite the great progress in conjugated multidimensional **PDIs**, the development of high-performance OSC acceptors based on **PDI** dyes and a deep understanding of their optoelectronic properties and structure–property relationships remain the key issues that the chemistry and materials science communities face.

In this study, we report two new propeller-shaped smallmolecule acceptors, named **TPE-PDI₄-S** and **TPE-PDI₄-Se** based on tetraphenylethylene (**TPE**) as the core and flanked with S/Se-fused **PDIs**. The introduction of S and Se atoms to the **PDIs** results in the obviously increased lowest unoccupied molecular orbital (LUMO) level of -3.81 eV and -3.77 eV, respectively. By incorporating the as-synthesized crystallographic polymer donor, **PBDB-T1** (Fig. S4, ESI†), organic solar cells based on **TPE-PDI₄-Se** show a PCE of 7.63%, much higher than those of **TPE-PDI₄-S** (6.85%) and **TPE-PDI₄** (5.53%),⁴⁵ with an open-circuit voltage (V_{OC}) of 1.078 V, a J_{SC} of 10.287 mA cm⁻² and a high FF of 68.8%. To the best of our knowledge, the resulting PCE of 7.63% is among the highest values of **TPE** as core based non-fullerene organic solar cells so far.

Results and discussion

Synthesis and characterization

The synthesis of **TPE-PDI₄-S** and **TPE-PDI₄-Se** is illustrated in Schemes 1 and 2. The precursor **PDI-S-Br** was synthesized starting from a previously reported method.⁶² Compound **PDI-NO₂** reacted with S in NMP solvent to give compound **PDI-S**, which was then treated with liquid Br₂ at room temperature to produce monomer **PDI-S-Br** (Scheme 1). Afterwards, compound **PDI-S-Br** was reacted with **TPE-PDI₄** (Scheme 2) *via* a Suzuki coupling reaction to yield target compound **TPE-PDI₄-S**. The synthetic route of **TPE-PDI₄-Se** was similar to **TPE-PDI₄-S** (Scheme 2). The as-synthesized materials were fully characterized by ¹H and ¹³C NMR, matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS), and the original data are provided in the ESI.[†] Both acceptors exhibited





Scheme 1 Synthetic routes of TPE-Pin₄, PDI-S-Br and PDI-Se-Br.



Scheme 2 Synthetic routes of the two acceptors.

excellent solubility in common organic solvents, such as chloroform, toluene and *o*-dichlorobenzene (*O*-DCB) at room temperature. These conjugated molecules also exhibit excellent thermal stability with a decomposition temperature ($T_{\rm d}$, 5% weight loss) of >400 °C for both acceptors in a nitrogen atmosphere, while heating the solids in air at 200 °C for two hours did not lead to a detectable change in the ¹H NMR spectra.

Optical and electrochemical properties

The optical absorption spectra of **TPE-PDI₄-S** and **TPE-PDI₄-S** in solution and thin-films were obtained (Fig. 1) and the corresponding data are summarized in Table 1. In CH₂Cl₂ solution, both acceptors exhibited similar absorption profiles and showed very high absorption in the range of 400–600 nm, which is characteristic of **PDI** chromophores. **TPE-PDI₄-S**



Fig. 1 (a) The normalized absorption spectra of $TPE-PDI_4-S$ and $TPE-PDI_4-Se$ in 10 μ M dichloromethane solutions. (b) The normalized absorption spectra of $TPE-PDI_4-S$ and $TPE-PDI_4-Se$ blend films.

showed a maximum molar extinction coefficient of 9.08×10^4 M^{-1} cm⁻¹ at 553 nm, which is higher than that of **TPE-PDI₄-Se** $(6.21 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \text{ at } 557 \text{ nm})$ most likely due to the synergistic effect of π - π interactions and multiple heteroatomheteroatom interactions.⁶¹ The absorption spectra of the two acceptors in films were similar to those in solution, which manifests weak intermolecular aggregations in the solid state. Compounds TPE-PDI4-S and TPE-PDI4-Se exhibit optical absorption onsets of 585 and 596 nm, respectively. This redshift can be attributed to a less twisted conjugated structure afforded by four **TPE-Se** subunits. The optical bandgaps (E_{α}^{opt}) of TPE-PDI₄-S and TPE-PDI₄-Se were estimated to be 1.69 and 1.77 eV, respectively, from the empirical formula: $E_{g}^{\text{opt}} = 1240/$ λ_{onset} . In addition, the absorption spectra of TPE-PDI₄-S and TPE-PDI₄-Se with PBDB-T1 are well complemented to ensure full harvesting of light in the visible spectrum (Fig. 1b and Fig. S1, ESI[†]).

Redox properties were determined by cyclic voltammetry (CV) in dry dichloromethane with TBAPF₆ (tetrabutylammonium hexa-fluorophosphate) as a supporting electrolyte (0.1 M) and Ag/Ag⁺ as a reference and Fc/Fc⁺ (0.259 V) as a standard (Fig. S2 (ESI⁺) and

Table 1). No significant change in the redox properties of the two acceptors was observed. Both acceptors showed no obvious oxidation waves within the measurement range. In the negative potential region, an irreversible reduction wave of -0.51 V and -0.55 V was observed, which is assigned to the reduction of the PDI groups. The LUMO energy levels were calculated according to the equation $E_{\text{LUMO}} = -[q(E_{\text{red}} - E_{\text{Fc/Fc+}}) + 4.8] \text{ eV.}^{43}$ Since S and Se annulated polycyclic aromatics increase the electron-donating ability and electron density, TPE-PDI4-S and TPE-PDI4-Se exhibited higher LUMO levels and larger bandgaps than TPE-PDI4. The highest occupied molecular orbital (HOMO) energy levels for TPE-PDI₄-S and TPE-PDI₄-Se were calculated to be -5.97 and -5.94 eV, respectively, according to the equation E_{HOMO} = $-(E_{LUMO} + E_{g}^{opt})$ eV.⁴³ As shown in Fig. 2b, the larger energy offset of 1.63 eV (LUMO-LUMO) for TPE-PDI₄-Se and PBDB-T1 than those of TPE-PDI₄-S and PBDB-T1 (1.59 eV) can produce a higher V_{OC} for **TPE-PDI₄-Se** based PSCs.

Theoretical analysis

To gain deep insights into the properties of TPE-PDI₄-S and TPE-PDI₄-Se at the molecular level, density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level,⁶⁵ where the long alkyl chain was simplified to isopropyl groups. The LUMO energy levels of TPE-PDI₄-S and TPE-PDI₄-Se are mainly located on the PDI units. However, the HOMO energy levels of both acceptors are mainly distributed on the tetraphenylethene core along with the PDI unit (Fig. 3). This may hint that photoinduced charge transfer occurred from the TPE core to the PDI units. Moreover, the dihedral angles between PDIs with linked benzene for TPE-PDI₄-S are 72.1° and 81.9°, 85.1° and 76.5° respectively (Fig. S3, ESI†). The dihedral angles between PDIs with linked benzene for TPE-PDI₄-Se are 86.1°, 80.1°, 79.6° and 69.4°, respectively (Fig. S3, ESI[†]). This indicates that the introduction of S/Se-fused PDIs in the TPE core reduced the obvious intramolecular twisting between the PDIs, which may influence the π - π stacking and lead to different aggregation behaviors. The LUMO/HOMO energy levels of TPE-PDI₄-S and TPE-PDI₄-Se are -3.79/-5.91 eV and -3.81/ -5.89 eV through DFT calculations (Table S1, ESI⁺), respectively. The calculated values are consistent with the values by CV measurements.

Photovoltaic properties

Photovoltaic properties of **TPE-PDI₄-S** and **TPE-PDI₄-Se** as acceptors were investigated in OSC devices with a structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS)/PBDB-T1:acceptor/zirconium

Table 1 Basic properties of TPE-PDI ₄ -S and TPE-PDI ₄ -Se													
Acceptors	λ_{\max}^{a} (nm)	$\varepsilon_{\max}^{a} \left(M^{-1} \ cm^{-1} \right)$	$\lambda_{\text{onset}}^{a}$ (nm)	$\lambda_{\max}^{b}(nm)$	$\lambda_{\text{onset}}^{b}$ (nm)	$E_{g}^{\text{opt }c}\left(\mathrm{eV} ight)$	HOMO (eV)	$LUMO^{d}$ (eV)	$\mu_{\rm e}^{\ e} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$				
TPE-PDI ₄ -S TPE-PDI ₄ -Se	502 510	$\begin{array}{c} 1.73 \times 10^5 \\ 1.85 \times 10^5 \end{array}$	540 553	508 517	585 596	2.12 2.08	$-5.91 \\ -5.89$	-3.79 -3.81	$\begin{array}{c} 4.53 \times 10^{-4} \\ 4.82 \times 10^{-4} \end{array}$				

^{*a*} In a dichloromethane solution. ^{*b*} In a neat film. ^{*c*} Calculated from the empirical 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.



Fig. 2 (a) Device configuration of the studied OSCs. (b) Estimated energy levels of PBDB-T1, TPE-PDI₄-S and TPE-PDI₄-Se from electrochemical CV.



acetylacetonate (ZrAcAc)/Al. The wide-bandgap polymer of PBDB-T1 (Fig. S4, ESI[†]) was used as the donor due to its complementary absorption and compatible energy levels with TPE-PDI₄-S and TPE-PDI₄-Se. Dichlorobenzene was employed as the processing solvent and the total concentration of donor and acceptor was 20 mg ml⁻¹ with a donor: acceptor weight ratio of 1:1. The optimal annealed temperature was 100 °C. The current density-voltage (J-V) curves of the TPE-PDI₄-S and TPE-PDI₄-Se based PSCs are shown in Fig. 4a and the cell parameters are summarized in Table 2. The PBDB-T1:TPE-PDI4-Se based devices achieved a high PCE of 7.63% along with a $V_{\rm OC}$ of 1.078V, a J_{SC} of 10.287 mA cm⁻² and a FF of 68.8%, which surpass those of PBDB-T1:TPE-PDI4-S based PSCs (PCE = 6.85%, $V_{\rm OC}$ = 1.051 V, $J_{\rm SC}$ = 9.839 mA cm⁻², FF = 66.3%). The enhancements of FF and J_{SC} for TPE-PDI₄-Se compared with TPE-PDI₄-S, illustrated lower loss of FF and J_{SC} with selenization. This indicated that selenophene-fused PDIs perform better than the thiophene-fused PDIs.

The external quantum efficiency (EQE) spectra of both acceptor based optimized OSCs are shown in Fig. 4b. The J_{SC} values obtained by integrating the EQE curves with an AM1.5 G reference spectrum are in accordance with those obtained from J-V measurements (within 5% mismatch). The optimized TPE-PDI₄-Se based device showed a broad photo-to-current





Fig. 4 (a) J-V curves and (b) EQE spectra

response from 300 to 700 nm with a maximum value of 63%, indicating a relatively efficient photoelectron conversion process.

Morphology characterization

The surface morphology of the OSC active layer was investigated using atomic force microscopy (AFM). The as-cast blend films of **PBDB-T1:TPE-PDI₄-S** and **PBDB-T1:TPE-PDI₄-Se** displayed smooth and uniform morphologies with root mean square (RMS) surface roughness of 0.95 and 0.93 nm (Fig. 5b and d), respectively. No strong molecule aggregation between **PBDB-T1** and the two acceptors occurred. Moreover, both blend films exhibited clear nanofibrillar structures, which is beneficial for the charge transport.

Active layer charge transport

Space charge limited current (SCLC) measurements were performed to determine the hole and electron mobilities of TPE-PDI₄-S and TPE-PDI₄-Se neat and blend films (Fig. 6). The electron mobilities of both acceptor neat films were found to be 4.53 × 10⁻⁴ and 4.82 × 10⁻⁴ cm² V⁻¹ s⁻¹, respectively (Table 1). After annealing at 100 °C, the hole/electron mobility of PBDB-T1:TPE-PDI₄-S and PBDB-T1:TPE-PDI₄-Se blend films were 3.01 × 10⁻⁴ cm² V⁻¹ s⁻¹/1.15 × 10⁻⁴ cm² V⁻¹ s⁻¹ and 3.21 × 10⁻⁴ cm² V⁻¹ s⁻¹/1.37 × 10⁻⁴ cm² V⁻¹ s⁻¹ with $\mu_{\rm h}/\mu_{\rm e}$ of 2.61 and 2.34, respectively (Table S2, ESI†). Thermal annealing increases hole and electron mobility and reduces the ratio of $\mu_{\rm h}/\mu_{\rm e}$ for the TPE-PDI₄-S and TPE-PDI₄-Se based blend films.

Exciton dissociation and charge extraction

The exciton dissociation and charge extraction of PBDB-T1: TPE-PDI₄-S and PBDB-T1:TPE-PDI₄-Se based OSCs were

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Table 2 Performance of the optimized OSC devices based on PBDB-T1: acceptor (1:1, w/w)

Active layer	Annealing (°C)	$V_{\rm OC}$ (V)	$J_{ m SC}~({ m mA~cm^{-2}})$	FF (%)	PCE_{max} (%)	PCE (%)
PBDB-T1 : TPE-PDI4-S PBDB-T1 : TPE-PDI4-Se	100 100	$\begin{array}{c} 1.051 \; (1.052 \pm 0.007) \\ 1.078 \; (1.070 \pm 0.006) \end{array}$	$\begin{array}{l} 9.839 \ (9.632 \pm 0.161) \\ 10.287 \ (10.011 \pm 0.201) \end{array}$	$\begin{array}{c} 0.663 \; (0.660 \pm 0.004) \\ 0.688 \; (0.682 \pm 0.007) \end{array}$	6.85 7.63	$\begin{array}{c} 6.688 \pm 0.192 \\ 7.305 \pm 0.214 \end{array}$



Fig. 5 The AFM height images for: (a) a **TPE-PDI₄-S** neat film; (b) a **PBDB-T1:TPE-PDI₄-S** blend film; (c) a **TPE-PDI₄-Se** neat film; (d) a **PBDB-T1: TPE-PDI₄-Se** blend film.



Fig. 6 Dark current density-voltage characteristics for (a) hole-only and (b) electron-only devices with optimized **PBDB-T1:TPE-PDI4-S** and **PBDB-T1:TPE-PDI4-Se** OSC films.

investigated by performing the photocurrent density *versus* effective voltage. Where $J_{\rm ph} = J_{\rm L} - J_{\rm D}$ ($J_{\rm L}$ and $J_{\rm D}$ are the current density under illumination and dark, respectively)



Fig. 7 (a) $J_{\rm ph}$ versus $V_{\rm eff}$ curves. (b) Light intensity dependence of $J_{\rm SC}$.

and $V_{\rm eff} = V_0 - V_{\rm a}$, (V_0 is the voltage at $J_{\rm ph} = 0$ and $V_{\rm a}$ is the measured voltage under different current densities).²⁰ As shown in Fig. 7a and Table S3 (ESI[†]), the $J_{\rm ph}$ s of two OSCs reached saturation at voltages approaching 3 V, and the $J_{\rm sat}$ values after annealing were 10.508 mA cm⁻² and 10.981 mA cm⁻² for **PBDB-T1:TPE-PDI₄-S** and **PBDB-T1:TPE-PDI₄-Se** based OSCs, respectively. After annealing treatment, the probabilities of exciton dissociation calculated from $J_{\rm ph}/J_{\rm sat}$ under short circuit conditions and probabilities of charge collection calculated from $J_{\rm ph}/J_{\rm sat}$ at the maximal power output condition were 93.6% and 72.5% for **PBDB-T1:TPE-PDI₄-Se**, respectively. Obviously, the **PBDB-T1:TPE-PDI₄-Se** based OSCs showed higher exciton dissociation and charge collection efficiencies than those of **PBDB-T1:TPE-PDI₄-S**, which contributed to a large $J_{\rm SC}$ and FF.

Charge recombination reduces the amount of photogenerated electrons and leads to low PCEs. In order to understand charge recombination probabilities in PSCs, the current densities under different light intensities were measured on their optimized devices. The linear relationship between J_{SC} and the light intensity in logarithmic coordinates $(\ln(J_{SC}) \propto \ln(P)^S)$ is depicted in Fig. 7b, where *S* is the recombination constant reflecting the bimolecular recombination degree. It is generally believed that if more free charges can be effectively collected at the electrodes prior to recombination, the slope of *S* is closer to 1.⁶⁶ As shown in

Fig. 7b, the *S* values for **PBDB-T1:TPE-PDI₄-Se** were calculated to be 0.91, which is larger than that of **PBDB-T1:TPE-PDI₄-S** (0.90). The higher *S* value indicates that the **PBDB-T1:TPE-PDI₄-Se** based device has less bimolecular recombination and enhances the utilization rate of excitons and improves the transport properties of carriers, facilitating the enhancement of J_{SC} and FF.

Conclusions

In summary, two new non-fullerence acceptors of TPE-PDI₄-S and TPE-PDI₄-Se, were designed and synthesized by employing tetraphenylethene as the central core unit and PDI-S and PDI-Se as the end-groups. TPE-PDI₄-S and TPE-PDI₄-Se show wide optical bandgaps of 2.12 eV and 2.08 eV, respectively, with relatively high-lying LUMO levels. The TPE-PDI₄-Se based OSCs with PBDB-T1 as the donor achieved high PCEs of 7.63%, with a $V_{\rm OC}$ of 1.078 V, a $J_{\rm SC}$ of 10.287 mA cm⁻² and a FF of 68.8%, a 11.4% boost in PCE with respect to the TPE-PDI₄-S based device. Our results demonstrate that using suitable 3D core and Se-annulated PDI end groups to construct SMAs is a simple and efficient approach to achieve high performance OSCs. Taking these excellent advantages into consideration, we expect that the combination of the Se-annulated PDI ending group with other 3D conformation cores will create more promising and practical acceptors.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 G. Li, W.-H. Chang and Y. Yang, *Nat. Rev. Mater.*, 2017, 2, 17043.
- 2 L. Lu, M. A. Kelly, W. You and L. Yu, *Nat. Photonics*, 2015, 9, 491.
- 3 Y. Lin and X. Zhan, Acc. Chem. Res., 2016, 49, 175.
- 4 A. Polman, M. Knight, E. C. Garnett, B. Ehrler and W. C. Sinke, *Science*, 2016, **352**, 6283.
- 5 R. Ganesamoorthy, G. Sathiyan and P. Sakthivel, Sol. Energy Mater. Sol. Cells, 2017, 161, 102.
- 6 P. Cheng, G. Li, X. Zhan and Y. Yang, *Nat. Photonics*, 2018, 12, 131.
- 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 C. B. Nielsen, S. Holliday, H.-Y. Chen, S. J. Cryer and I. McCulloch, *Chem. Res.*, 2015, **48**, 2803.
- M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, 18, 789.
- 12 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.
- 13 Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li and L. Yu, J. Am. Chem. Soc., 2009, 131, 56.
- 14 C.-Z. Li, H.-L. Yip and A. K. Y. Jen, *J. Mater. Chem.*, 2012, 22, 4161.
- 15 S. Xiao, Q. Zhang and W. You, Adv. Mater., 2017, 29, 1601391.
- 16 R. Stalder, J. Mei, K. R. Graham, L. A. Estrada and J. R. Reynolds, *Chem. Mater.*, 2014, 26, 664.
- 17 N. M. Randell, C. L. Radford, J. Yang, J. Quinn, D. Hou, Y. Li and T. L. Kelly, *Chem. Mater.*, 2018, **30**, 4864.
- 18 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. Photonics*, 2016, **11**, 85.
- 19 J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, *Nat. Energy*, 2016, 1, 15027.
- 20 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.
- 21 B. M. Savoie, A. Rao, A. A. Bakulin, S. Gelinas, B. Movaghar, R. H. Friend, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 2014, **136**, 2876.
- 22 A. Weu, T. R. Hopper, V. Lami, J. A. Kreß, A. A. Bakulin and Y. Vaynzof, *Chem. Mater.*, 2018, **30**, 2660.
- 23 X. Zhan, Z. a. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow,
 Y. Li, D. Zhu, B. Kippelen and S. R. Marder, *J. Am. Chem. Soc.*, 2007, **129**, 7246.
- 24 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.
- 25 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.
- 26 Q. Wu, D. Zhao, A. M. Schneider, W. Chen and L. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7248.
- 27 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.
- 28 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.
- 29 J.-D. Chen, Y.-Q. Li, J. Zhu, Q. Zhang, R.-P. Xu, C. Li, Y.-X. Zhang, J.-S. Huang, X. Zhan, W. You and J.-X. Tang, *Adv. Mater.*, 2018, **30**, 1706083.

- 30 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.
- 31 X. Xu, T. Yu, Z. Bi, W. Ma, Y. Li and Q. Peng, *Adv. Mater.*, 2018, **30**, 1703973.
- 32 S. Zhang, Y. Qin, J. Zhu and J. Hou, *Adv. Mater.*, 2018, **30**, 1800868.
- 33 T. Liu, Z. Luo, Q. Fan, G. Zhang, L. Zhang, W. Gao, X. Guo,
 W. Ma, M. Zhang, C. Yang, Y. Li and H. Yan, *Energy Environ. Sci.*, 2018, DOI: 10.1039/C8EE01700J.
- 34 H. Bin, L. Gao, Z.-G. Zhang, Y. Yang, Y. Zhang, C. Zhang, S. Chen, L. Xue, C. Yang, M. Xiao and Y. Li, *Nat. Commun.*, 2016, 7, 13651.
- 35 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, 27, 1170.
- 36 J. Wang, J. Zhang, Y. Xiao, T. Xiao, R. Zhu, C. Yan, Y. Fu, G. Lu, X. Lu, S. Marder and X. Zhan, *J. Am. Chem. Soc.*, 2018, 140, 9140.
- 37 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 and I. McCulloch, *Nat. Commun.*, 2016, 7, 11585.
- 38 D. Baran, T. Kirchartz, S. Wheeler, S. Dimitrov, M. Abdelsamie, J. Gorman, R. S. 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.
- 39 Z. Ji, X. Xu, G. Zhang, Y. Li and Q. Peng, *Nano Energy*, 2017, 40, 214.
- 40 A. Tang, C. Zhan, J. Yao and E. Zhou, *Adv. Mater.*, 2017, 29, 1600013.
- 41 Y. Liu, L. Zhang, H. Lee, H.-W. Wang, A. Santala, F. Liu, Y. Diao, A. L. Briseno and T. P. Russell, *Adv. Energy Mater.*, 2015, 5, 1500195.
- 42 J. Choi, K.-H. Kim, H. Yu, C. Lee, H. Kang, I. Song, Y. Kim, J. H. Oh and B. J. Kim, *Chem. Mater.*, 2015, **27**, 5230.
- 43 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.
- 44 H. Wang, L. Chen and Y. Xiao, *J. Mater. Chem. C*, 2017, 5, 12816.
- 45 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 and H. Yan, *Adv. Mater.*, 2015, 27, 1015.

- 46 A. Zhang, C. Li, F. Yang, J. Zhang, Z. Wang, Z. Wei and W. Li, Angew. Chem., Int. Ed., 2017, 56, 2694.
- 47 H. Wang, L. Chen and Y. Xiao, J. Mater. Chem. A, 2017, 5, 22288.
- 48 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.
- 49 T. J. Sisto, Y. Zhong, B. Zhang, M. T. Trinh, K. Miyata, X. Zhong, X. Y. Zhu, M. L. Steigerwald, F. Ng and C. Nuckolls, *J. Am. Chem. Soc.*, 2017, **139**, 5648.
- 50 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.
- 51 T. Liu, D. Meng, Y. Cai, X. Sun, Y. Li, L. Huo, F. Liu, Z. Wang, T. P. Russell and Y. Sun, *Adv. Sci.*, 2016, 3, 1600117.
- 52 Y. Cai, L. Huo, X. Sun, D. Wei, M. Tang and Y. Sun, *Adv. Energy Mater.*, 2015, 5, 1500032.
- 53 A. D. Hendsbee, J.-P. Sun, W. K. Law, H. Yan, I. G. Hill, D. M. Spasyuk and G. C. Welch, *Chem. Mater.*, 2016, 28, 7098.
- 54 Y. Lin, J. Wang, S. Dai, Y. Li, D. Zhu and X. Zhan, *Adv. Energy Mater.*, 2014, 4, 1400420.
- 55 Y. Lin, Y. Wang, J. Wang, J. Hou, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2014, 26, 5137.
- 56 S. Rajaram, R. Shivanna, S. K. Kandappa and K. S. Narayan, J. Phys. Chem. Lett., 2012, 3, 2405.
- 57 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.
- 58 R. Singh, E. Aluicio-Sarduy, Z. Kan, T. Ye, R. C. I. MacKenzie and P. E. Keivanidis, J. Mater. Chem. A, 2014, 2, 14348.
- 59 D. Zhao, Q. Wu, Z. Cai, T. Zheng, W. Chen, J. Lu and L. Yu, *Chem. Mater.*, 2016, 28, 1139.
- 60 J. Lee, R. Singh, D. H. Sin, H. G. Kim, K. C. Song and K. Cho, *Adv. Mater.*, 2016, 28, 69.
- 61 Z. Luo, T. Liu, W. Cheng, K. Wu, D. Xie, L. Huo, Y. Sun and C. Yang, *J. Mater. Chem. C*, 2018, **6**, 1136.
- 62 W. Fan, N. Liang, D. Meng, J. Feng, Y. Li, J. Hou and Z. Wang, *Chem. Commun.*, 2016, **52**, 11500.
- 63 C. Zhang, T. Liu, W. Zeng, D. Xie, Z. Luo, Y. Sun and C. Yang, *Mater. Chem. Front.*, 2017, 1, 749.
- 64 Z. Luo, W. Xiong, T. Liu, W. Cheng, K. Wu, Y. Sun and C. Yang, Org. Electron., 2017, 41, 166.
- 65 Gaussian 09, revision A.1, Gaussian, Inc., Wallingford, CT, 2009, see ESI[†].
- 66 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.