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Simultaneously Achieved High Open-Circuit Voltage and Efficient Charge Generation by Fine-tuning Charge-Transfer Driving Force in Non-fullerene Polymer Solar Cells

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Keywords: benzotriazole; voltage loss; charge generation; driving force; non-fullerene acceptor

Abstract

To maximize the short-circuit current density (J_{SC}) and the open circuit voltage (V_{OC}) simultaneously is a highly important but challenging issue in organic solar cells (OSCs). In this study, a benzotriazole-based p-type polymer (J61) and three benzotriazole-based non-fullerene small molecule acceptors (BTA1-3) were chosen to investigate the energetic driving force for the efficient charge transfer. The lowest unoccupied molecular orbital (LUMO) energy levels of small molecule acceptors could be fine-tuned by modifying the end-capping units, leading to high V_{OC} (1.15-1.30 V) of OSCs. Particularly, the LUMO energy level of BTA3 satisfies the criteria for efficient charge generation, which results in a high V_{OC} of 1.15 V, nearly 65% external quantum efficiency, and a high power conversion efficiency (PCE) of 8.25%. This is one of the highest V_{OC} in the high-performance OSCs reported to date. Our results imply that it is promising to achieve both high J_{SC} and V_{OC} to realize high PCE with the carefully designed non-fullerene acceptors.

Introduction

Recently, the power conversion efficiencies (PCEs) of single-junction organic solar cells (OSCs) have reached ~13% with systematic material design and device optimization.^[1] Though these efficiency values are promising, they still lag behind the Si or perovskite solar cells and are not commercially competitive yet. One of the most important factors that limit the PCE of OSCs is the relatively modest open-circuit voltage (V_{OC}) due to their large energy loss (E_{loss}) from the optical band gap.^[2] The E_{loss} can be expressed by the equation: $E_{loss} = E_{opt, min} - qV_{OC}$, where $E_{opt, min}$ is the lower excited singlet state of the blend film in OSCs and e is the elementary charge. In the Si or perovskite solar cells, E_{loss} are around 0.30-0.55 eV,^[2-3] while E_{loss} in OSCs are typically in the range of 0.7-1.0 eV.^[4] **Figure 1** summarizes the relationship between $E_{opt, min}$ and V_{OC} in promising OSCs reported to date. Because of the large E_{loss} , V_{OC} of the devices with $E_{opt, min}$ between 1.5 and 2.1 eV can seldom exceed 1.0 V. Thus, a key challenge facing the field of OSCs is to decrease E_{loss} and increase V_{OC} . V_{OC} has been proved to be correlated to the energy levels of frontier orbitals for the donor and acceptor materials in OSCs. Two feasible methods to improve V_{OC} have been proposed: one is to lower the highest occupied molecular orbital (HOMO) energies of the electron donors and the other is to uplift the lowest unoccupied molecular orbital (LUMO) level of the electron acceptors.^[5] In fact, these efforts have been devoted to increase V_{OC} , but only a handful molecules with $V_{OC} > 1.1$ V can achieve moderate PCEs (> 4%) (as shown in **Figure 1**). It is well-known that the increase of V_{OC} usually accompanies with the decrease of the quantum efficiency for the charge generation. To overcome this trade-off is one of the most pressing issues in OSCs.

Figure 1. Plot of V_{OC} against $E_{opt,min}$ in organic solar cells with high PCE reported to date. The list of the data is available in Supporting Information.

An intuitive way to quantify E_{loss} between $E_{opt,min}$ and qV_{OC} is to divide the loss into two parts: the loss in the formation of charge transfer (CT) states and the loss in the charges or CT states recombination.^[6] The former comes from the energy offset (ΔG_{CS}^{eff}) of exciton dissociation ($\Delta G_{CS}^{eff} = E_{opt,min} - E_{CT}$), which is corresponding to the driving force for the charge separation.^[7] The latter is a loss linked to the geminate and non-geminate recombination during the process of CT states generation, split and charge transport.^[8] Hence, decreasing the energy loss by the raising the energy of the CT state (E_{CT}) while still keeping the efficient charge separation could be an effective way to break the troublesome trade-off. The pertinent question is how much of the minimal driving force is required for the efficient charge separation. However, in this regard, synthetic chemists face a formidable challenge: it is still unclear that how the molecular structural factors contribute to the low E_{loss} and to attain high V_{OC} and quantum efficiency simultaneously.

Herein, we design and synthesize three molecular electron acceptors by changing the substituent in the end-capping units to systematically fine-tune the molecular orbitals energies. The acceptors have similar π -conjugated backbones comprising of indacenodithiophene (IDT), benzotriazole (BTA) and end-capped units. As shown in **Figure 2**, BTA1 contains two

rhodanine units as the end-capped groups, while replacing a sulfur atom in rhodanine with an oxygen atom generates compound BTA2, and introducing a dicyanomethylene group in rhodanine produces BTA3. Considering that the LUMO energy level mainly depends on the electron withdrawing segment in the Donor-Acceptor (D-A)-type copolymer, it is supposed that the same electron-withdrawing building units (BTA) in both the donor and acceptor may contribute to realize the close LUMO levels.^[9] Thus, in this study, a 2D-conjugated donor-acceptor copolymer (J61) containing fluorine substituted benzotriazole was chosen as the electron donor. Based on this similarity in the electron accepting units, we can study the effect of the small LUMO-LUMO offsets on the charge generation. In addition, we have shown that OSCs with BTA1 and BTA2 in the combination with poly(3-hexylthiophene) (P3HT), exhibited higher V_{OC} (1.0 and 1.2 V)^[10] than that of P3HT:PC₆₁BM (phenyl-C₆₁-butyric acid methyl ester) based OSCs (~0.6 V).^[11] Based on the above analysis, these systems in this report are expected to achieve high V_{OC} .^[1c, 12]

Figure 2. Chemical structures of the J61 and the acceptors BTA_x ($x=1-3$) with different end-capped groups.

Results and Discussion

BTA_x were synthesized by a simple two-step reactions (**Scheme S1**); Stille-coupling reaction to generate dialdehyde intermediate, followed by a Knoevenagel condensation with

three different end-capping units to afford BTA x ($x=1-3$) with a yield of 70-80%. As can be seen from thermogravimetric analysis (TGA) (**Figure S1**), the temperature with the 5% weight loss (T_d) of BTA1-3 are as high as 386, 405 and 396 °C, respectively, which indicates that all of them are thermally stable enough for the application in OSCs.

Figure 3. a) The normalized UV-vis absorption spectra of pure J61 and BTA x ($x = 1-3$) in films. b) Energy diagram of the frontier molecular orbitals based on the cyclic voltammetry (CV) experiments and density functional theory (DFT).

The ultraviolet-visible (UV-vis) absorption spectra are displayed in **Figure 3a** and **Figure S2** and the data are summarized in **Table S1**. Film of BTA1 shows the absorption onset at around 663 nm. The introduction of O atom instead of S atom in BTA2 leads to the blue-shifted absorption with the onset at 620 nm compared with BTA1. When the strong electron-withdrawing dicyanomethylene group employed for BTA3, red-shifted absorption and extended absorption edge up to around 704 nm are observed. Accordingly, the optical bandgaps of BTA x ($x = 1, 2, 3$) films are estimated as 1.87, 2.00, and 1.76 eV, respectively. Accompanied with the increase of the electron deficiency at the end-capping units, the absorption spectra are becoming more complementary with that of J61 in the order of BTA2, BTA1, and BTA3. Thus, blend film of J61:BTA3 shows the broadest absorptions spanning the wavelength range from around 300 to 700 nm (**Figure S2b**), which is beneficial in enhancing light harvesting accompanied with an increasing J_{SC} .^[13]

Based on the cyclic voltammetry (CV) measurements in **Figure S3**, the HOMO levels of BTA x ($x=1, 2, 3$) were estimated to be -5.46 eV, -5.43 eV, and -5.49 eV, respectively. HOMO level of J61 is taken from the literature.^[12] LUMO levels of J61 and BTA x ($x=1, 2, 3$) are estimated to be -3.38 eV, -3.59 eV, -3.43 eV and -3.73 eV, respectively, by adding the optical bandgap to their HOMO levels. The decrease of the LUMO levels from BTA2, via BTA1 to BTA3 is observed as the increase of the electron deficiency in the acceptor units. The highest LUMO levels of BTA2 implies possibly largest V_{OC} .^[7d, 14] The LUMO–LUMO energy offsets between the donor and the acceptors (BTA2, 1, 3) are respectively 0.05, 0.21, 0.35 eV and the HOMO–HOMO energy offsets are respectively 0.11, 0.14, 0.17 eV. This gradual change of energy offsets will offer an excellent parameter for the study on the charge generation process.^[15]

The energy levels are also calculated using density functional theory (DFT) at B3LYP/6-31G(d) level. The results are listed in **Figure 3b** and the orbital electron distributions of their HOMO/LUMO levels are shown in **Figure S4**. For all the three molecules, the HOMO level is primarily delocalized from the IDT-based central donor unit to some part of the acceptor unit, whereas the LUMO level is delocalized on the entire π -conjugated main chain. DFT calculations predict the LUMO/HOMO levels of J61 and BTA x ($x=1, 2, 3$) to be $-2.69/-4.82$, $-2.93/-5.06$, $-2.74/-4.99$, and $-3.15/-5.26$ eV, respectively. The LUMO offsets between J61 and three acceptors (BTA2, BTA1 and BTA3) are calculated to be 0.05, 0.24 and 0.46 eV, respectively, while the HOMO offsets are calculated to be 0.17, 0.24, 0.44 eV, respectively. The theoretical calculation data match well with the experimental results. Underestimation of HOMO and LUMO energy levels in DFT calculations could primarily come from the effects of the polarization energy in the thin films^[16].

To investigate the photovoltaic properties of the three acceptors, photovoltaic devices are fabricated with a conventional device structure of indium tin oxide (ITO)/

poly(3,4ethylenedioxythiophene):poly(styrene sulfonate)(PEDOT:PSS)/ J61:BTAx ($x=1-3$) /Ca/Al. The detail optimization conditions are shown in **Table S2-4**. **Figure 4** shows the current density–voltage (J – V) curves, and the corresponding external quantum efficiency (EQE) spectra of the optimized devices. The photovoltaic performance data are listed in **Table 1** for comparison.

Figure 4. a) J - V curves under the illumination of AM1.5G, 100 mW/cm^2 and b) EQE spectra for the optimized OSCs based on J61:BTAx (1:1, w/w).

Table 1. Photovoltaic performance parameters of the optimized OSCs based on J61:BTAx (1:1, w/w)

Devices	V_{OC} (V) ^{a)}	J_{SC} (mA cm^{-2}) ^{a), b)}	Fill Factor (FF) (%) ^{a)}	PCE (%) ^{a)}	μ_h ^{c)} $\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	μ_e ^{c)} $\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
J61:BTAA2	1.29	0.84 (0.82)	23.88	0.26	0.98	0.24
	1.29 $\pm$ 0.02	0.83 $\pm$ 0.06	24.31 $\pm$ 0.72	0.26 $\pm$ 0.003		
J61:BTAA1	1.24	5.21 (5.09)	46.71	3.02	1.91	0.54
	1.26 $\pm$ 0.20	5.09 $\pm$ 0.11	46.51 $\pm$ 0.50	2.98 $\pm$ 0.04		
J61:BTAA3	1.15	10.84 (10.53)	66.17	8.25	3.26	2.17
	1.15 $\pm$ 0.01	10.43 $\pm$ 0.38	67.14 $\pm$ 1.20	8.03 $\pm$ 0.14		

^{a)} The average PCE value was calculated from ten devices for each condition. The numbers in the upper rows are the best values. ^{b)} The numbers in parentheses are calculated from EQE spectra. ^{c)} Calculated from the space charge-limited current (SCLC) method.

As expected from the energy levels, J61:BTAA2 based device exhibits the highest V_{OC} of 1.29 V and J61:BTAA1 based device is not far behind with a value of 1.24 V. With the deepest

LUMO level of acceptor, V_{OC} of J61:BTA3 based device drops down to 1.15 V. In contrast, the J_{SC} increases as the LUMO levels become deeper. J61:BTA2 shows the smallest J_{SC} of 0.84 mA cm⁻², followed by J61:BTA1 with a modest J_{SC} of 5.21 mA cm⁻². J61:BTA3 exhibits the largest J_{SC} of 10.84 mA cm⁻² among these three combinations. The calculated J_{SC} values from the EQE curves (**Figure 4b**) agree well with the J_{SC} values obtained from the J - V curves within a 5% mismatch (**Table 1**). As a consequence, the PCE values of the best devices based on BTA2, BTA1, and BTA3 increased from 0.26% to 3.02% and 8.25%, respectively. To the best of our knowledge, the V_{OC} of 1.15 V together with a PCE of 8.25% observed for J61:BTA3 OSC is one of the highest V_{OC} in the high performance non-fullerene OSCs reported to date (**Figure 1**).^[17] Here, the high V_{OC} (1.15 V) and efficient charge generation observed in J61:BTA3 will offer opportunities to simultaneously realize a high V_{OC} and high J_{SC} for tandem devices.

To determine the cause of the very high V_{OC} in the three devices, we have analyzed the energy loss in detail. The detailed balance theory has been used to quantify the energy losses. The energy losses contains the radiative recombination loss ($E_{opt,min} - qV_{OC}^{SQ}$ and $qV_{OC}^{SQ} - qV_{OC}^{rad}$) and the non-radiative recombination loss ($q\Delta V_{OC}^{non-rad} = -kT\ln(EQE_{EL})$). Note that V_{OC}^{SQ} is the theoretical maximum voltage by the Shockley-Queisser limit, where the EQE is assumed to be step-wise function of the energy of absorbed photon. V_{OC}^{rad} is the open-circuit voltage when there is only radiative recombination. k is the Boltzmann constant, T is temperature and EQE_{EL} is radiative quantum efficiency of the solar cell when charge carriers are injected into the device in the dark (**Figure S5**).^[2, 8, 17a] The calculation results of all kinds of energy losses have been listed in **Table 2**. The details of the derivation process are in Supporting Information. The first loss of ($E_{opt,min} - qV_{OC}^{SQ}$) is unavoidable, which is correlated to the E_g and the spectrum^[2, 18] and this value in our systems equals roughly 0.22-0.3 eV. The second loss of ($qV_{OC}^{SQ} - qV_{OC}^{rad}$) is caused by the fact that the EQE of a practical Photovoltaic

device cannot be step-wise function and it is mainly from the sub-bandgap absorption. This kind of loss in OSCs is relatively larger when compared to inorganic solar cells, because the existence of the charge transfer state which lies far below the onset of strong absorption and energy disorders in organic semiconductors.^[2] In our cases, this loss is estimated to be 0.082 eV for BTA2 and 0.037 eV for BTA1, and only 0.022 eV for BTA3, which is much smaller than those for the previously reported OSCs (0.67 eV for P3HT:PC₆₁BM and 0.20 eV for PTB7:PC₇₁BM).^[2] The non-radiative recombination loss in the OSCs based on J61:BTAx ($x=1, 2, 3$) is 0.285 eV, 0.257 eV and 0.309 eV, respectively, estimated from the relatively high EQE_{EL} value of 4.5×10^{-5} , 1.5×10^{-5} and 6×10^{-6} , which is smaller than those for the previously reported OSCs (typically > 0.35 eV)^[2, 8] and close to those for the inorganic solar cells (~ 0.25 eV).^[18] Hence, these small voltage losses give rise to the ultra-high voltage, and the calculated values of V_{OC} based on these above analysis are 1.30 eV for BTA2, 1.26 eV for BTA1 and 1.14 eV for BTA3, which is consistent with that obtained in our experiments.

Table 2. The energy of the $E_{opt,min}$, V_{OC} , V_{OC}^{SQ} , V_{OC}^{rad} , $\Delta V_{OC}^{non-rad}$, E_{CT} , and ΔG_{CS}^{eff} of the optimized solar cells.

Materials	$E_{opt,min}$ (eV)	qV_{OC} (eV)	qV_{OC}^{SQ} (eV)	$E_{opt,min} - qV_{OC}^{SQ}$ (eV)	qV_{OC}^{rad} (eV)	$qV_{OC}^{SQ} - qV_{OC}^{rad}$ (eV)	$q\Delta V_{OC}^{non-rad}$ (eV)	E_{CT} (eV)	ΔG_{CS}^{eff} (eV)
J61:BTA2	1.94	1.30	1.640	0.300	1.558	0.082	0.257	1.91	0.03
J61:BTA1	1.87	1.26	1.579	0.221	1.542	0.037	0.285	1.80	0.07
J61:BTA3	1.76	1.14	1.474	0.286	1.452	0.022	0.309	1.65	0.11

The similar chemical structures and the optical properties of the three devices give rise to dramatic difference in J_{SC} and FF. In order to investigate the origin of this difference in J_{SC} , firstly, EQE spectra are measured to evaluate the spectral response of the devices. The three kinds of devices show the similar EQE curves in **Figure 4b** but the maximum values of EQE are remarkably increased from 6% in J61:BTA1 to 34% in J61:BTA1 and further to 62% in J61:BTA3, respectively, indicating that the difference in J_{SC} is a result of different electrical or excitonic processes in the devices. Then, the charge-transport properties of the three devices

are also measured. The plots of the current density vs. voltage are shown in **Figure S6** and the data are summarized in **Table 1**. Among the three systems, J61:BTA3 blend film gives the highest hole mobility(μ_h) and electron mobility (μ_e) values (3.26×10^{-4} and 2.17×10^{-4} cm² V⁻¹ s⁻¹, respectively) and a small μ_h/μ_e ratio of 1.5, which are partly responsible for the highest J_{SC} and FF.^[19]

Figure 5. (a) 2D GIWAXS patterns of the optimized blend films. (b) Line profiles of the scattering images in the out-of-plane (q_z) and the in-plane (q_{xy}) directions.

Figure 6. a), b) and c) the height images for the J61:BTA2, J61:BTA1, and J61:BTA3 blend film, respectively; d), e), and f) the phase images for the J61:BTA2, J61:BTA1, and J61:BTA3 blend film, respectively.

Grazing incidence wide-angle X-ray scattering (GIWAXS, **Figure 5** and **Figure S7**) and atom force microscope (AFM) studies are performed to confirm if the morphology differences can explain the observed results as described above. As shown in **Figure 5**, all of the blends

exhibit an obvious (010) diffraction peak in the out-of-plane direction at $q_z = 1.75 \text{ \AA}^{-1}$, which suggests that J61 adopt the face-on orientation in all of the blend films. Differently, both the J61:BTA2 and J61:BTA1 films appear to have dual texture: the (100) diffraction peaks show both out-of-plane and in-plane orientations.^[20] While the J61:BTA3 film displays homogeneous lamellar texture judged by the presence of (100) peaks from J61 and BTA3 in the in-plane direction at $q_{xy} = 0.25$ and $0.33 \text{ \AA}^{-1}$, respectively. The higher crystalline behavior and the face-on orientation in J61:BTA3 film can be correlated with the higher carries mobilities observed.^[21] **Figure 6** indicates that J61:BTA1 film shows the highest root-mean-square (RMS) roughness value of 4.12 nm and the presence of large domains, on the order of hundreds of nanometers in diameter. Unfortunately, J61:BTA1 films can not exhibit fine film morphology even if solvent additives are applied in these blends (**Figure S8**). While both the J61:BTA2 and J61:BTA3 blends present fine microstructures with the lower roughness of 0.54 nm and 0.82 nm, respectively. The similar phase-segregated morphologies with a size of 20-30 nm and 30-40 nm, respectively, can also be observed in their phase images. There are minor morphological differences between the J61:BTA2 and J61:BTA3 blends, but the latter gives much higher J_{SC} than the former. J61:BTA2 based active layer could be regarded as more homogenous than the J61:BTA1 based active layer, while the J_{SC} of the latter device is much larger. Based on our results on the blended and the pristine materials as described above, we conclude that differences in morphology can not rationalize the differences in J_{SC} , which is unlikely the main cause.

Figure 7. The PL spectra obtained from: a) from the neat J61, BTA2 (excited at $\lambda = 532$ nm) and their blend film; b) from the neat J61, BTA1 (excited at $\lambda = 562$ nm) and their blend film; c) from the neat J61, BTA3 (excited at $\lambda = 597$ nm) and their blend film. The neat J61 and blend films are excited at $\lambda = 550$ nm.

Another possible reason for the changes of the photocurrent is the exciton generation and separation under illumination. Steady-state photoluminescence (PL) quenching studies are performed on the J61:BTA1-3 blends and shown in **Figure 7**. At the excitation wavelength of 550 nm, the J61 is responsible for 54% of the J61:BTA1 device absorption, 58% for J61:BTA2, 64% for J61:BTA3. Emission from the blend with BTA2 is close to the emission of the pristine J61 film and the PL quantum efficiency is about 66.3% as strong as from pure J61 (**Figure 7a**). The inefficient quenching of polymer excitons are usually attributed to two reasons: the excitons may be formed in large domains and recombine before they reach the heterojunction, or they may reach the heterojunction but can not undergo electron transfer before recombining. Due to the homogeneous morphology of the J61:BTA2 film (as shown in **Figure 6a**), the low PL quenching efficiency (33.2%) should be mainly attributed to the inefficient electron transfer. In addition, considering that about 46% of excitons start on the BTA2, the very low PL quantum efficiency of BTA2 in J61:BTA2 blend indicates that excitons initially generated on the BTA2 could undergo efficient hole transfer to the polymer. For blends of J61 with BTA1, PL spectra with a band shape very similar to pure BTA1 are obtained. This implies that excitons initially

generated on the J61 can transfer to the BTA1, and then decay from BTA1 singlet state. The emission of BTA1 may originate from hundreds nanometer-sized domains observed in phase images (**Figure 6b**).^[22] In the blend of J61 with BTA3, the emission from J61 is strongly quenched (99.7%) compared to its pristine film, which indicates near unity quantitative charge separation upon J61 and BTA3 excitation, and thus partially explains its greatly increased photocurrent.

Table 3. The calculated quenching efficiency in PL and fitting parameters of PL decay dynamics of the various films.

Film	$\Delta\text{PL}_0^{\text{a)}$	τ_1 (ps)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_{avg} (ps)
J61	-	223	67.30	1.05	32.70	493
BTA2	-	201	91.15	1.82	8.85	344
BTA1	-	165	93.82	1.74	6.18	262
BTA3	-	710	96.17	3.47	3.83	816
J61:BTA2	33.2%	211	68.23	1.39	31.77	586
J61:BTA1	48.2%	81.4	91.22	2.93	8.78	332
J61:BTA3	99.7%	49.8	97.15	2.80	2.85	128

a) ΔPL was estimated by the PL intensity of the blend film relative to that of the neat polymers.

Time resolved PL (TRPL) measurements are also applied to estimate the charge transfer efficiency. The normalized TRPL spectra and their fitted curves with bi-exponential decay model are displayed in **Figure S9** and the TRPL lifetime data are summarized in **Table 3**. The PL lifetime τ_1 of the J61:BTA2 blends is 211 ps, which is close to that of the neat J61 film (223 ps) and the fast decay fraction f_1 is 68.23% whereas the slow decay fraction f_2 is 31.77%, which implies the absence of efficient photoinduced electron transfer from the donor J61 to the acceptor BTA2, and more excitons undergo radiative recombination instead of generating electron transfer.^[23] The values of τ_1 obtained in both J61:BTA1 and J61:BTA3 are obviously decreased down to 81.4 and 49.8 ps, which proves that the presence of charge transfer at the donor/acceptor (D/A) interfaces. The fast decay fraction f_1 in J61:BTA1 film is a little lower than that of J61:BTA3 film (91.22% vs. 97.15%), whereas the slow decay fraction f_2 is higher

(8.78% vs. 2.85%). It can be inferred that the exciton generated in the donor J61 can more quickly separate at the D/A interface in the J61:BTA3 film.^[24]

Figure 8. EL spectra of the pure films and the blend films at different applied voltage: a) J61:BTA2; b) J61:BTA1; c) J61:BTA3.

The above phenomena suggest that with the increase of the LUMO level of the acceptor, the CT state energy increases and gradually approaches the single-state (S_1) energy, resulting in the exciton separation efficiency decreases.^[6c] Hence, we further explored the driving force required for the efficient charge transfer and photocurrent generation by measuring electroluminescence (EL) spectra. Fourier-transform photocurrent spectroscopy external quantum efficiency (FTPS-EQE) measurements are performed to quantify the energy of the CT state. As shown in **Figure 8**, the EL spectra of pure films and J61:BTAx ($x=1-3$) based blend films at different applied voltage are compared. Only at low applied voltage, a weak CT peak at low energy can be observed, and as the increase of the applied voltage, the CT peak gradually blue-shifts and disappears. At low applied voltages, the injected carriers tend to populate the low energy states and recombine accompanied with emitting photons with low energy. As the applied voltage increases, the higher energy states are gradually populated accompanied with a blue-shift emission. The LUMO-LUMO offset (~ 0.05 eV) between J61 and BTA2 and the HOMO-HOMO offsets (~ 0.14 eV, ~ 0.17 eV) between J61 and BTA1, 3 are very small. So the injected carriers have a probability recombination in the pristine materials, forming singlet state

excitons and emitting. This can explain the EL spectrum of the neat and blend films in **Figure 8** overlap to a large extent. The emission of singlet states usually have relatively high EQE_{EL} than that of CT states. This can explain why the non-radiative recombination energy loss (0.285 eV-0.309 eV) in our systems is smaller compared with normal OPVs. For all these three devices, the shape of EL spectrum demonstrates weak dependence on applied voltage. This indicates a small disorder in all three blends, matching well with a sharp cutoff absorption tail in EQE-FTPS spectrum of these three devices (**Figure S7**).^[25] This can explain why the loss of $(V_{OC}^{SQ} - V_{OC}^{Rad})$ is very small in our devices.

Marcus formula are used to estimate the energy of CT states by fitting the low-energy shoulder of the EL spectra and FTPS-EQE spectra (**Figure S5**).^[6c, 26]

$$EL_{PV}(E) = \frac{f}{E\sqrt{4\pi\lambda\kappa T}} \exp\left(\frac{-(E_{CT}-\lambda-E)^2}{4\lambda\kappa T}\right) \quad (1)$$

$$EQE_{PV}(E) = \frac{f}{E\sqrt{4\pi\lambda\kappa T}} \exp\left(\frac{-(E_{CT}+\lambda-E)^2}{4\lambda\kappa T}\right) \quad (2)$$

In Equations (1) and (2), E is the photon energy, k is the Boltzmann constant, and T is the temperature. The fit parameters are E_{CT} , the reorganization energy, λ , and a factor proportional to the number of states, f . The CT energy in J61:BTAX($x=1, 2, 3$) is estimated to be 1.80, 1.91 and 1.65 eV, respectively. The decreased CT energy from BTA2, via BTA1, to BTA3 is a consequence of the decreased LUMO energy. $E_{opt,min}$ in J61:BTA2 film equals the singlet state energy of J61, while in J61:BTA1 and J61:BTA3 film, $E_{opt,min}$ equals the singlet state energy of the acceptor. Thus, the according ΔG_{CS}^{eff} increases from 0.03 eV for J61:BTA2, via 0.07 eV for the J61:BTA1, to 0.11 eV for J61:BTA3. It is obvious that the trend in ΔG_{CS}^{eff} follows the trend in J_{SC} . For J61:BTA2 system, E_{CT} is so close to the energy of singlet excited state that the population of the CT state becomes energetically less favorable and back electron transfer from the CT state to the singlet excited state might occur. The back electron transfer can be in direct competition with CT state dissociation into free charge carriers, giving a very small

photocurrent below 1 mA cm^{-2} .^[6c, 27] The gradually increased ΔG_{CS}^{eff} could inhibit the back electron transfer and promote the CT state dissociation into free charge carriers. In the J61:BTA1 system, with an increased ΔG_{CS}^{eff} of 0.07 eV, they exhibit an enhanced photocurrent above 5.21 mA cm^{-2} . When ΔG_{CS}^{eff} further increased up to 0.11 eV in J61:BTA3 based device, an obviously enhancement of photocurrent occurs, which suggests that a driving force of 0.11 eV for charge transfer is enough to sufficiently inhibit repopulation of the singlet excited state and for efficient charge generation.

We note that ΔG_{CS}^{eff} follows the same trend as the charge transfer efficiency and J_{SC} observed in the devices. The estimated driving force also explains the observations made in PL and EL. These correlations indicate the driving force plays an important role in the generation of the free charges in these blends. The present results indicate that a driving free energy of $\sim 0.11 \text{ eV}$ is required for efficient charge generation.

Conclusions

In this report, three non-fullerene acceptor materials with gradually varied band levels have been carefully engineered by modifying end-capping units to investigate the effect of the driving force on the V_{OC} and J_{SC} generation. The high LUMO levels and low energy loss around 0.6 eV endow these three materials ultrahigh V_{OC} ($>1.15\text{V}$). With the increase of the V_{OC} , the corresponding J_{SC} and PCE of them decrease obviously. There is a threshold value of ΔG_{CS}^{eff} to ensure the efficient charge generation. Only when the driving force for charge transfer is preserved to be enough, a higher power conversion efficiency could be achieved. In this system, only the J61:BTA3 devices simultaneously achieved a high V_{OC} of 1.15 V and efficient charge generation, yielding excellent performance of 8.25%. At the same time, we also notice that in some other systems, the combinations where the E_{CT} approaches the energy of singlet excitons can work efficiently.^[17a] This means that the amount of driving force needed for efficient charge separation may significantly depend on the donor and acceptor materials. Further detailed

investigations are currently ongoing. In any case, consistent with previous reports, our results further indicate that previously empirical notification of 0.3 eV driving force is not necessary.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Acknowledgements

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References

- [1] a) S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, *Adv. Mater.* **2016**, 28, 9423; b) F. Zhao, S. Dai, Y. Wu, Q. Zhang, J. Wang, L. Jiang, Q. Ling, Z. Wei, W. Ma, W. You, C. Wang, X. Zhan, *Adv. Mater.* **2017**, 29, 1700144; c) Y. Yang, Z. G. Zhang, H. Bin, S. Chen, L. Gao, L. Xue, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2016**, 138, 15011; d) H. Bin, L. Gao, Z. G. Zhang, Y. Yang, Y. Zhang, C. Zhang, S. Chen, L. Xue, C. Yang, M. Xiao, Y. Li, *Nat. Commun.* **2016**, 7, 13651; e) D. Deng, Y. Zhang, J. Zhang, Z. Wang, L. Zhu, J. Fang, B. Xia, Z. Wang, K. Lu, W. Ma, Z. Wei, *Nat. Commun.* **2016**, 7, 13740; f) W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, 139, 7148.

- [2] J. Yao, T. Kirchartz, M. S. Vezie, M. A. Faist, W. Gong, Z. He, H. Wu, J. Troughton, T. Watson, D. Bryant, J. Nelson, *Phys. Rev. Appl.* **2015**, *4*, 014020.
- [3] a) R. R. King, D. Bhusari, A. Boca, D. Larrabee, X. Q. Liu, W. Hong, C. M. Fetzer, D. C. Law, N. H. Karam, *Prog. Photovolt: Res. Appl.* **2011**, *19*, 797; b) A. H.-B. Martin A. Green, Henry J. Snaith, *Nat. Photon.* **2014**, *8*, 506.
- [4] M. Wang, H. Wang, T. Yokoyama, X. Liu, Y. Huang, Y. Zhang, T. Q. Nguyen, S. Aramaki, G. C. Bazan, *J. Am. Chem. Soc.* **2014**, *136*, 12576.
- [5] a) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, *Adv. Mater.* **2006**, *18*, 789; b) X. Gong, M. Tong, F. G. Brunetti, J. Seo, Y. Sun, D. Moses, F. Wudl, A. J. Heeger, *Adv. Mater.* **2011**, *23*, 2272.
- [6] a) T. Markvart, *Appl. Phys. Lett.* **2007**, *91*, 064102; b) A. Maurano, R. Hamilton, C. G. Shuttle, A. M. Ballantyne, J. Nelson, B. O'regan, W. Zhang, I. McCulloch, H. Azimi, M. Morana, *Adv. Mater.* **2010**, *22*, 4987; c) M. A. Faist, T. Kirchartz, W. Gong, R. S. Ashraf, I. McCulloch, J. C. de Mello, N. J. Ekins-Daukes, D. D. Bradley, J. Nelson, *J. Am. Chem. Soc.* **2012**, *134*, 685.
- [7] a) K. Vandewal, S. Albrecht, E. T. Hoke, K. R. Graham, J. Widmer, J. D. Douglas, M. Schubert, W. R. Mateker, J. T. Bloking, G. F. Burkhard, A. Sellinger, J. M. Frechet, A. Amassian, M. K. Riede, M. D. McGehee, D. Neher, A. Salleo, *Nat Mater* **2014**, *13*, 63; b) K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganas, J. V. Manca, *Nat Mater* **2009**, *8*, 904; c) T. M. Burke, S. Sweetnam, K. Vandewal, M. D. McGehee, *Adv. Energy Mater.* **2015**, *5*, 1500123; d) S. D. Dimitrov, J. R. Durrant, *Chem. Mater.* **2014**, *26*, 616.
- [8] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, J. V. Manca, *Phys. Rev. B* **2010**, *81*, 125204.
- [9] Y. Li, *Acc. Chem. Res.* **2012**, *45*, 723.
- [10] a) B. Xiao, A. Tang, J. Zhang, A. Mahmood, Z. Wei, E. Zhou, *Adv. Energy Mater.* **2016**, 1602269; b) B. Xiao, A. Tang, J. Yang, Z. Wei, E. Zhou, *ACS Macro Lett.* **2017**, 410.

- [11] G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, *Adv. Funct. Mater.* **2007**, *17*, 1636.
- [12] H. Bin, Z.-G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2016**, *138*, 4657.
- [13] a) F. Liu, Z. Zhou, C. Zhang, J. Zhang, Q. Hu, T. Vergote, F. Liu, T. P. Russell, X. Zhu, *Adv. Mater.* **2017**, *29*, 1606574; b) A. Tang, L. Li, Z. Lu, J. Huang, H. Jia, C. Zhan, Z. a. Tan, Y. Li, J. Yao, *J. Mater. Chem. A* **2013**, *1*, 5747.
- [14] G. Zhao, Y. He, Y. Li, *Adv. Mater.* **2010**, *22*, 4355.
- [15] a) K. H. Hendriks, A. S. Wijpkema, J. J. van Franeker, M. M. Wienk, R. A. Janssen, *J. Am. Chem. Soc.* **2016**, *138*, 10026; b) S. Shoaee, T. M. Clarke, C. Huang, S. Barlow, S. R. Marder, M. Heeney, I. McCulloch, J. R. Durrant, *J. Am. Chem. Soc.* **2010**, *132*, 12919; c) S. D. Dimitrov, A. A. Bakulin, C. B. Nielsen, B. C. Schroeder, J. Du, H. Bronstein, I. McCulloch, R. H. Friend, J. R. Durrant, *J. Am. Chem. Soc.* **2012**, *134*, 18189; d) H. Ohkita, S. Cook, Y. Astuti, W. Duffy, S. Tierney, W. Zhang, M. Heeney, I. McCulloch, J. Nelson, D. D. C. Bradley, J. R. Durrant, *J. Am. Chem. Soc.* **2008**, *130*, 3030.
- [16] H. Yoshida, K. Yamada, J. y. Tsutsumi, N. Sato, *Phys. Rev. B* **2015**, *92*.
- [17] a) 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, H. Yan, *Nat. Energy* **2016**, *1*, 16089; b) Y. Zhang, X. Guo, B. Guo, W. Su, M. Zhang, Y. Li, *Adv. Funct. Mater.* **2017**, 1603892; c) 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. Durrant, I. McCulloch, *Energy Environ. Sci.* **2016**, *9*, 3783.
- [18] a) T. Kirchartz, U. Rau, M. Kurth, J. Mattheis, J. H. Werner, *Thin Solid Films* **2007**, *515*, 6238; b) K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov, H. J. Bolink, *Sci Rep* **2014**, *4*, 6071.
- [19] H. Zhou, Y. Zhang, J. Seifert, S. D. Collins, C. Luo, G. C. Bazan, T.-Q. Nguyen, A. J.

Heeger, *Adv. Mater.* **2013**, 25, 1646.

[20] J. W. Jung, F. Liu, T. P. Russell, W. H. Jo, *Adv. Mater.* **2015**, 27, 7462.

[21] J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. Bao, *J. Am. Chem. Soc.* **2011**, 133, 20130.

[22] Z. Tang, B. Liu, A. Melianas, J. Bergqvist, W. Tress, Q. Bao, D. Qian, O. Inganas, F. Zhang, *Adv. Mater.* **2015**, 27, 1900.

[23] a) N. R. Banerji, S. Cowan, E. Vauthey, A. J. Heeger, *J. Phys. Chem. C* **2011**, 115, 9726;
b) A. A. Y. Guilbert, L. X. Reynolds, A. Bruno, A. MacLachlan, S. P. King, Mark A. Faist, E. Pires, J. E. Macdonald, N. Stingelin, S. A. Haque, J. Nelson, *ACS Nano* **2012**, 6, 3868.

[24] Y. Fu, B. Wang, J. Qu, Y. Wu, W. Ma, Y. Geng, Y. Han, Z. Xie, *Adv. Funct. Mater.* **2016**, 26, 5922.

[25] F. Gao, S. Himmelberger, M. Andersson, D. Hanifi, Y. Xia, S. Zhang, J. Wang, J. Hou, A. Salleo, O. Inganäs, *Adv. Mater.* **2015**, 27, 3868.

[26] N. A. Ran, J. A. Love, C. J. Takacs, A. Sadhanala, J. K. Beavers, S. D. Collins, Y. Huang, M. Wang, R. H. Friend, G. C. Bazan, T. Q. Nguyen, *Adv. Mater.* **2016**, 28, 1482.

[27] E. T. Hoke, K. Vandewal, J. A. Bartelt, W. R. Mateker, J. D. Douglas, R. Noriega, K. R. Graham, J. M. J. Fréchet, A. Salleo, M. D. McGehee, *Adv. Energy Mater.* **2013**, 3, 220.

Table of contents entry

The existence of the driving force in organic solar cells (OSCs) often creates a problematic trade-off between the open-circuit voltage and short-circuit current. Here, fine-tuning driving force by gradually decreasing the acceptor energy level has afforded high open-circuit voltage (>1.15 V) and efficient charge generation ($>60\%$) at the same time, which is instructive to the development of more efficient OSCs.

Keyword

benzotriazole, voltage loss, charge generation, driving force, non-fullerene acceptor

Authors

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Title

Simultaneously Achieved High Open-Circuit Voltage and Efficient Charge Generation by Fine-tuning Charge-Transfer Driving Force in Non-fullerene Polymer Solar Cells

ToC figure

Supporting Information

Simultaneously Achieved High Open-Circuit Voltage and Efficient Charge Generation by Fine-tuning Charge-Transfer Driving Force in Non-fullerene Polymer Solar Cells

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Experiment Section

Instrumentation

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained using a Bruker AVANCE III HD 400 with tetramethylsilane as an internal standard. Mass spectra (MALDI-TOF) were carried on a Micromass GCT-MS spectrometer. UV-vis spectra were identified with a Lambda 950 spectrophotometer. Electrochemical CV was conducted on an electrochemical workstation (VMP3 Biologic, France) with a Pt disk coated with a molecular film, a Pt plate, and an Ag/AgCl electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol L⁻¹ tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆) acetonitrile solution. The *J*-*V* curves were obtained in air with a Keithley 2420 source measure unit. The photocurrent was measured under illumination using an Oriel Newport 150W solar simulator (AM 1.5G), and the light intensity was calibrated with a Newport reference detector (Oriel PN

91150 V). The EQE measurements of the devices were performed in air with an Oriel Newport system (Model 66902). The thickness of the active layer was measured on a Kla-TencorAlpha-StepD-120 Stylus Profiler. AFM images were obtained on a Multimode Digital Instrument in tapping mode. The samples were prepared with the optimized device fabrication conditions. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were measured at the SPring-8 on beamline BL46XU. The sample was irradiated at a fixed angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.39 keV ($\lambda = 1 \text{ \AA}$), and diffracted X-rays were captured at an exposure time of 1 s by a two-dimensional detector (PILATUS 300K) located at a distance of $L=174 \text{ mm}$ from the sample. The samples were spin-coated onto the PEDOT:PSS/Si substrate. PL and TRPL spectra were measured with Nanolog FL3-iHR320. EL spectra were detected using a light guide positioned close to the sample. The bias was applied on the devices using a Keithley 2400 Source Meter. The detector was a Newton EM-CCD Si array detector at -60°C with a Shamrock SR-303i spectrograph from Andor Tech. EQE_{EL} values were obtained from an in-house-built system comprising a Hamamatsu silicon photodiode 1010B, a Keithley 2400 Source Meter for supplying voltages and recording injected current, and a Keithley 485 picoammeter for measuring the emitted light intensity. FTPS-EQE was measured using a Vertex 70 from Bruker Optics, equipped with a quartz tungsten halogen lamp, quartz beam splitter and external detector option. A low-noise current amplifier (SR570) was used to amplify the photocurrent produced on illumination of the photovoltaic devices with light modulated by the Fourier transform infrared spectroscope (FTIR). The output voltage of the current amplifier was fed back into the external detector port of the FTIR, to be able to use the FTIR's software to collect the photocurrent spectrum. The thickness of the active layer was measured on a Kla-TencorAlpha-StepD-120 Stylus Profiler.

Photovoltaic device fabrication

The OSCs devices were fabricated with a configuration of ITO/PEDOT:PSS/J61:BTAx/Ca/Al. A thin layer of PEDOT:PSS (30 nm, Baytron PH1000) was spin-cast on pre-cleaned ITO-coated

glass at 3000 rpm. After baking at 150 °C for 20 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The Donor: Acceptor (D:A) ratio of 1:1 (w/w) was dissolved chloroform (CF) with a total concentration of 10 mg/mL for 1 hour at 60 °C and then the active layers was spin-coated from the above solution with a speed of 1200 rpm. The thickness of the photoactive layer is in the range of 90–100 nm. The effects of solvents, additive concentrations, thermal annealing temperature, and blend ratios on device performance were also examined. Finally, a Ca (20 nm)/Al (80nm) metal top electrode was thermal evaporated onto the active layer under about 2×10^{-6} Pa. The active area of the device was 0.04 cm² defined by shadow mask.

Carrier Mobilities.

Hole mobility: The hole mobility of the polymer was investigated by the space charge limited current (SCLC) method. The hole only mobility of the blend films was measured with the device structure of ITO/PEDOT:PSS/active layer (~100 nm)/Au (80 nm) while the electron only mobility of the blends was measured with the device structure of ITO/TiO_x/active layer(~100 nm)/Al (80 nm).

The SCLC model is described by modified Mott-Gurney law:

$$J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)\exp[0.89\beta(V/L)^{0.5}]$$

where J stands for current density, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{CV}^{-1} \text{m}^{-1}$), ϵ_r is the relative dielectric constant of the transport medium (assuming that 3.0), μ is the carrier mobility, V is the internal potential in the device and L is the thickness of the active layer, β is the field activation factor.

The Energy Loss

According to Shockley's theory, the junction current density of the diode is expressed as:

$$J_d = J_0[\exp(qV/kT) - 1] \quad (1)$$

where k is the Boltzmann constant, T is the temperature and J_0 is the reverse saturation current density and V is the output voltage.^[1]

However, in fact, the current density J in the solar cells is closely linked to series resistance R_s and shunt resistance R_{sh} , so the expression can be written as:

$$J = \frac{R_{sh}}{R_{sh} + R_s} \left\{ J_0 \left[\exp \left(\frac{q(V - JR_s)}{nkT} \right) - 1 \right] + \frac{V}{R_{sh}} \right\} - J_{ph} \quad (2)$$

The open-circuit voltage is the voltage where recombination current and photocurrent J_{ph} are equal, where $V = V_{OC}$, $J = 0$, and with the assumption that $R_{sh} \gg R_s$, V_{OC} can be expressed as''

$$V_{OC} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) \quad (3)$$

n is the ideality factor of the diode.

This definition is general for any recombination mechanism. Considering radiative recombination only, $J_0 = J_{0,rad}$ and $n=1$ in formula (3), we can obtain V_{OC}^{rad} as follows:

$$V_{OC}^{rad} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0^{rad}} + 1 \right) \quad (4)$$

The expression for J_{ph} and J_0^{rad} are given by:

$$J_{SC} = q \int_0^\infty EQE_{PV}(E) \varphi_{AM1.5}(E) dE \quad (5)$$

$$J_0^{rad} = q \int_0^\infty EQE_{PV}(E) \varphi_{BB}(E) dE \quad (6)$$

Hereby is q the elementary charge, $\varphi_{AM1.5}(E)$ is the standard AM1.5 solar illumination spectrum and $\varphi_{BB}(E)$ the black body spectrum of the solar cell.^[2]

Based on the Shockley-Queisser theory,^[1b] the general quantum efficiency $EQE_{PV}^{SQ}(E)$ is defined as:

$$EQE_{PV}^{SQ}(E) = 1, E \geq E_{gap}; \quad EQE_{PV}^{SQ}(E) = 0, E < E_{gap}; \quad (7)$$

So, the saturation current in the SQ limit, J_0^{SQ} , can also obtained:

$$J_0^{SQ} = q \int_{E_{gap}}^\infty EQE_{PV}^{SQ}(E) \varphi_{BB}(E) dE = q \int_{E_{gap}}^\infty \varphi_{BB}(E) dE \quad (8)$$

Now, we can calculate the value of the V_{OC}^{SQ} and V_{OC}^{rad} from the FTPS-EQE.

Materials and Synthesis.

All the reagents were purchased from Alfa, Aldrich, TCI or Wako and used without further purification. Solvents were bought from the Beijing Chemical Plant. The precursor 1 was bought from the reagent plant and the precursor 2, 3 and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile were synthesized according to the reported procedure. BTA1 and BTA 2 were synthesized according the routes that we have previously reported.^[3]

Scheme S1. The synthetic route of the compound of 3 and 4.

The synthesis of BTA3.

Compound 3 (719 mg, 0.50 mmol), 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (724 mg, 3.75 mmol), chloroform (100 mL) and pyridine (2 mL) were added to a two-necked round-bottom flask. The mixture was purged with nitrogen for 10 min and then refluxed for 48 hours. After cooling to room temperature, the mixture was poured into methanol (300 mL) and stirred for 10 minutes, then filtered. The residue was purified by column chromatography on silica gel with CHCl_3 as an eluent yielding a black solid (708 mg, 80%). ^1H NMR (400 M, CDCl_3): δ (ppm) 8.33 (s, 2H), 8.11 (s, 2H), 7.71-7.69 (d, $J = 8$ Hz, 2H), 7.55 (s, 2H), 7.55-7.53 (d, $J = 8$ Hz, 2H), 7.25-7.27 (d, $J = 8$ Hz, 8H), 7.12-7.10 (d, $J = 8$ Hz, 8H), 4.80-4.84 (t, 4H), 4.32-4.37 (q, 4H), 2.56-2.60 (t, 8H), 2.21-2.24 (m, 4H), 1.56-1.63 (m, 8H), 1.26-1.44 (m, 50H), 0.84-0.88 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 166.82, 166.69, 157.54, 154.18, 144.90, 142.92, 141.82, 141.50, 141.20, 135.67, 132.32, 131.45, 129.63, 128.50, 127.97, 124.96, 121.41, 120.95, 118.10, 117.35, 113.30, 112.55, 63.19, 57.28, 55.10, 40.50, 35.62, 31.74, 31.39, 29.82, 29.20, 29.10, 28.94, 26.57, 22.63, 22.62, 14.20, 14.11. MS(MALDI-TOF): m/z : calcd. for $\text{C}_{110}\text{H}_{122}\text{N}_{12}\text{O}_2\text{S}_4$, 1771.87; Found: 1771.9 ;

Thermal properties

Figure S1. TGA curves of BTA0-2 with a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an atmosphere of N_2 .

Optoelectrical properties

Figure S2. a) The UV-vis absorption spectra of BTA1-3 in chloroform solution. b) the UV-vis absorption spectra of J61:BTA1-3 based blend films with D/A = 1:1.

Figure S3. Cyclic voltammograms of the BTA1-3 on the Pt electrode measured with 0.1m Bu_4NPF_6 in CF solution with Ag/AgCl as the reference electrode.

Figure S4. The simulated molecular geometries and frontier molecular orbitals obtained by DFT calculation at B3LYP/6-31G(d) level.

Figure S5. a) The EL spectra of all the three devices on a log-lin scale. The dashed lines are simultaneous fits using Equations (1), fit to the low-energy peak of the EL. b) Semilogarithmic plots of the EQE as measured by Fourier-transform photocurrent spectroscopy (FTPS) of their corresponding OPV devices. The dashed lines are simultaneous fits using Equations (2).

Figure S6. (a) Hole and (b) electron mobility plots from SCLC methods. Note: the red rhombus represents BTA0; the black del operator represents BTA1; the blue sphere is the BTA2.

Figure S7. (a) 2D GIWAXS patterns of the neat films. (b) The out of plane linecuts (q_z) and in-plane linecuts (q_{xy}) of the neat films.

The neat J61 showed a (100) diffraction peak in the in-plane direction at $0.25 \text{ \AA}^{-1}$ and an obvious (010) diffraction peak in the out-of-plane direction at $1.75 \text{ \AA}^{-1}$, revealing the semicrystalline structure and strong preference for face-on orientation in the pristine film. The

neat films of BTA2 and BTA1 show a broad alkyl-stacking peak at $0.34 \text{ \AA}^{-1}$ with no azimuthal dependence and a diffusive diffraction arc around $1.35 \text{ \AA}^{-1}$, which indicating both the BTA2 and BTA1 are amorphous in their pure films. While for BTA3 film, an obvious (100) reflection at $0.33 \text{ \AA}^{-1}$ in the in plane direction and a strong (010) reflection at $1.73 \text{ \AA}^{-1}$ in the out of plane direction can be found, exhibiting a prominent face-on orientation. Thus, the introduction of dicyanomethylene as the electron-withdrawing unit increased its self-organization behavior and crystallinity.

Figure S8. The height images (a-d) and phase images (e-h) for the J61:BTA1 with 0.8% CN and 0.8% DPE as solvent additive, ODCB as solvent and ODCB as solvent with annealing, respectively.

Figure S9. The normalized TRPL spectra excited at 590 nm a) for all the blend films; and b) J61:BTA2, c) J61:BTA1 and d) J61:BTA1 blend films. For comparison, kinetics of the neat films of J61, BTA2, BTA1 and BTA3 are also measured under the same condition. Solid lines are the fitting curves based on bi-exponential model functions.

Table S1. The optoelectrical properties of the small molecules.

Compounds	the solutions			blend films			E_{red}^a (V)	E_{ox}^a (V)	E_{HOM}^a (eV)	E_{LUMO}^a (eV)
	ϵ_{max} (L/mol/cm)	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_{g} (eV)				
BTA2	1.10×10^5	557	603	561	620	2.00	-0.87	1.13	-5.43	-3.48
BTA1	1.13×10^5	592	651	562	663	1.87	-0.77	1.08	-5.46	-3.55
BTA3	1.14×10^5	613	676	593	704	1.76	-0.78	1.14	-5.49	-3.57

^a copulated from the CV measurements.

Photovoltaic performance

Table S2. The photovoltaic performance of J61:BTA_x ($x=0-2$) under different D/A ratios after thermal annealing at 100 °C, 10 min.

devices	D/A	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
J61 ⁽¹⁾ : BTA2	1:1	1.38±0.005	0.39±0	26.27±0.78	0.14±0.005
J61 ⁽²⁾ :BTA2	1.5:1	1.25±0.02	0.72±0	24.33±0.68	0.22±0.01
	1:1	1.28±0.01	0.71±0.1	24.56±1.40	0.24±0.002
	1:1.5	1.28±0.01	0.72±0.06	23.93±0.62	0.24±0.01

J61 ⁽¹⁾ :BTA1	1.5:1	1.33±0.007	4.14±0.16	45.19±1.39	2.49±0.007
	1:1	1.34±0.007	4.28±0.20	45.33±0.39	2.60±0.09
	1:1.5	1.33±0	4.08±0.13	46.28±0.74	2.51±0.13
J61 ⁽²⁾ : BTA1	1:1	1.26±0.20	5.09±0.11	46.51±0.50	2.98±0.04
J61 ⁽¹⁾ :BTA3	1.5:1	1.18±0	9.38±0.03	58.36±1.01	6.46±0.06
	1:1	1.18±0.006	9.48±0.20	59.98±0.35	6.71±0.16
	1:1.5	1.18±0	6.73±0.18	54.25±0.06	4.31±0.11
J61 ⁽²⁾ : BTA3	1:1	1.16±0.005	10.61±0.04	59.86±1.68	7.37±0.21

The average PCE value was calculated from ten devices for each condition. J61⁽¹⁾ and J61⁽²⁾ represent the different batches of J61.

Table S3. The photovoltaic performance of J61:BTA_x(x=0-2) under different solvent with 1:1 (D:A) after thermal annealing at 100 °C, 10 min.

devices	solvent	V _{OC} (V) ^a	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
J61 ⁽¹⁾ :BTA1	CF	1.33±0.009	4.02±0.22	46.61±0.42	2.49±0.11
	CB	1.34±0.005	3.79±0.02	44.14±0.42	2.24±0.02
	<i>o</i> -DCB	1.29±0.03	3.40±0.16	41.76±0.72	1.83±0.15
J61 ⁽¹⁾ :BTA3	CF	1.16±0.006	9.48±0.20	59.98±0.35	6.71±0.16
	CB	1.20±0.005	4.56±0.24	65.91±0.18	3.60±0.007
	<i>o</i> -DCB	1.19±0.007	4.63±0.04	61.68±0.01	3.39±0.007

The average PCE value was calculated from ten devices for each condition.

Table S4. The photovoltaic performance of J61:BTA_x(x=0-2) under different thermal annealing temperature.

devices	annealing temperature (°C)	V _{OC} (V) ^a	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
J61 ⁽²⁾ :BTA2	r.t.	1.11	0.58	20.14	0.13
	90	1.16±0.02	0.89±0.007	23.24±0.83	0.24±0.007
	100	1.29±0.02	0.83±0.06	24.31±0.72	0.26±0.003
	130	1.10±0.01	0.86±0.007	25.46±0.62	0.24±0
	150	1.22±0.11	0.79±0.007	27.0±2.81	0.26±0
J61 ⁽¹⁾ :BTA1	r.t.	1.34±0.04	3.41±0.11	33.48±0.07	1.53±0.05
	90	1.33±0.005	3.93±0.099	40.75±0.74	2.13±0.007
	100	1.33±0.009	4.02±0.22	46.61±0.42	2.49±0.11
	110	1.33±0.005	3.60±0.23	48.23±0.04	2.31±0.16
	130	1.33±0.006	3.14±0.007	53.80±0.54	2.25±0.02
	150	1.32±0	2.75±0.09	52.67±2.30	1.91±0.02
J61 ⁽²⁾ :BTA1	100	1.26±0.20	5.09±0.11	46.51±0.50	2.98±0.04
J61 ⁽¹⁾ :BTA3	100	1.18±0.006	9.48±0.20	59.98±0.35	6.71±0.16
	130	1.15±0.008	10.27±0.75	59.91±0.69	7.09±0.69
	150	1.11±0.005	8.44±0.08	60.50±0.68	5.65±0.02
J61 ⁽²⁾ :BTA3	130	1.16±0.01	10.43±0.38	67.14±1.20	8.03±0.14

The average PCE value was calculated from ten devices for each condition. J61⁽¹⁾ and J61⁽²⁾ represent the different batches J61.

Table S5. Eg, Voc, and PCE for various polymer solar cells.

polymer/Fullerence	Eg (eV)	Voc (V)	PCE (%)	References
PM6:PC71BM	1.8	0.98	9.2	[4]
PDTBT-TT:PC71BM	1.59	0.78	9.18	[5]
PTB7-Th:PC71BM	1.63	0.8	9.35	[6]
TBTIT-h:PC71BM	1.6	0.72	9.1	[7]
PBDF-T1:PC71BM	1.83	0.92	9.43	[8]
PPDTBT:PC71BM	1.72	0.81	5.08	[9]
PPDT2FBT:PC71BM	1.76	0.86	7.26	
PBDT-T8-TPD:PC61BM	1.85	1	6.17	[10]
PBDTT:PC71BM	2.13	0.93	6.12	[11]
PBDFTPD(2EH/C8):PC71BM	1.85	0.97	7.4	[12]
PBDTTPD(2EH/C8):PC71BM	1.97	0.94	7.1	
PDCBT:PC71BM	1.9	0.91	7.20	[13]
PBDTT-LTPD:PC71BM	1.88	1.02	7.27	[14]
P2:PC71BM	1.84	0.94	5.77	[15]
PzNDTTPD:PC71BM	2.04	0.95	4.40	[16]
PBDTT-tTPD:PC71BM	1.86	0.84	6.81	[17]
PzNDTT-TPD1:PC71BM	1.94	0.86	7.50	[18]
PzNDTT-TPD2:PC71BM	1.98	0.88	3.68	
PBT1:PC71BM	1.77	0.83	6.88	[19]
PffBX4T-2DT:PC71BM	1.65	0.875	9.10	[20]
PITFBT:PC71BM	1.82	0.9	9.14	[21]
PffBT-T4-2O:PC71BM	1.63	0.82	10.5	[22]
P1:PC71BM	1.72	0.85	1.42	[23]
P2:PC71BM	1.77	0.87	9.26	
PT-tTPD:PC71BM	1.75	0.86	9.21	[24]
PThBDTP:PC71BM	1.86	0.96	9.13	[25]
PBDTDPP:PC71BM	1.31	0.82	5.2	[26]
PDPP2T-BT-co-DTP:PC71BM	1.19	0.52	3.7	[27]
BBTI-1:PC71BM	1.44	0.64	8.3	[28]
P(BTI-F):PC71BM	1.86	1.11	1.6	[29]
P3FTBT1F:PC71BM	2.00	1.08	4.6	[30]
P3HT:PC61BM	1.9	0.61	4.4	[31]
P3HT: Indene - C60	1.9	0.84	6.5	[32]
PNTz4T:PC71BM	1.56	0.71	10.1	[33]
PNOz4T:PC71BM	1.52	0.96	8.9	[34]
PIDTT-TID:PC71BM	1.49	1.0	6.7	[35]
PIPCP:PC71BM	1.47	0.86	6.15	[36]
PDPP2TzDTP:PC71BM	1.47	0.92	5.1	[37]
PBDTTPD(2EH/C7):PC71BM	1.73	0.97	8.5	[38]
PNNT-12HD:PC71BM	1.68	0.82	8.2	[39]
PffBT4T-2OD:PC71BM	1.65	0.77	10.5	[40]

polymer/Non-Fullerence	Eg (eV)	Voc (V)	PCE (%)	References
PBDTTT-C-T:Bis-PDI-T-EG	1.58	0.85	4.03	[41]
PBDTTT-C-T:S(TPA-PDI)	1.58	0.87	3.22	[42]
P3HT:SF-DPPEH	1.79	1.10	3.63	[43]
PTB7-Th:TP-PDI	1.58	0.87	4.1	[44]
PTB7:DTDfBT(TDPP)2	1.55	0.81	5.0	[45]

PDBT-T1:SdiPBI-S	1.77	0.90	7.16	[46]
PTB7-Th:hPDI4	1.68	0.80	8.30	[47]
PTB7-Th:TPB	1.68	0.79	8.47	[48]
PCDTBT-C12:SM1	1.97	1.04	2.78	[49]
PCDTBT-C12:SM2	1.97	1.11	0.74	
PCDTBT-C12:SM3	1.97	1.09	0.56	
PCDTBT-C12:SM4	1.97	1.24	0.13	
PDCBT:ITIC	1.59	0.94	10.16	[50]
PBDB-T: ITIC	1.59	0.90	11.22	[51]
PBDB-T: IT-M	1.60	0.94	12.05	
PBDB-T: IT-DM	1.63	0.97	11.29	
PTB7-Th: IC-2IDT-IC	1.57	0.93	4.38	[52]
PDBT-T1: IC-1IDT-IC	1.77	0.92	7.39	
P3HT:O-IDTBR	1.63	0.72	6.3	[53]
P3HT:4D	1.72	1.18	3.86	[54]
J61:ITIC	1.59	0.89	9.53	[55]
PDBT-T1:ITIC-Th	1.60	0.88	9.6	[56]
PSEHTT:DBFI-EDOT	1.77	0.93	8.1	[57]
PBDTT-FTTE:DBFI-EDOT	1.57	0.95	6.7	
J51:N2200	1.48	0.83	8.27	[58]
PTB7-Th:PDI-V	1.58	0.74	7.57	[59]
PTB7-Th:PNDI-T10	1.55	0.83	7.6	[60]
PTB7-Th:P-BNBP-Se	1.58	1.03	4.26	[61]
PTB7-Th:P-BNBP-T	1.58	1.12	2.27	
PBDTT-FTTE:PNDIS-HD	1.59	0.81	7.73	[62]
P3TEA:SF-PDI2	1.72	1.11	9.5	[63]
P3HT:F4TBT4	1.90	1.26	4.12	[64]
P3HT:PFTBT	1.90	1.19	1.86	
PffBT4T-2DT:FBR	1.61	1.12	7.8	[65]
PffBT4T-2DT:IDTBR	1.61	1.07	9.95	
PffBT4T-2OD:BAF-4CN	1.60	0.77	8.4	[66]
PTB7-Th:ATT-1	1.58	0.87	10.07	[67]
PTZ1:PMI-F-PMI	1.97	1.30	6.0	[68]
PBDB-T:IDT-BOC6	1.63	1.01	9.6	[69]
PBDB-T:ITCC	1.67	1.01	11.4	[70]
PBDB-T:NFBTD	1.56	0.87	10.42	[71]
PDBT-T1/SdiPBI-BT	1.80	0.95	6.61	[72]
PDBT-T1/diPBI-BT	1.80	0.99	5.73	
PTzBI:ITIC	1.57	0.87	10.24	[73]
PBDB-T:PBIPor	1.48	0.73	7.4	[74]

Figure S11. ^1H NMR curve of BTA3.

Figure S10. ^{13}C NMR curve of BTA3.

Reference

- [1] a) N. K. Elumalai, A. Uddin, *Energy Environ. Sci.* **2016**, 9, 391; b) W. Shockley, H. J. Queisser, *J. Appl. Phys.* **1961**, 32, 510.
- [2] G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, 21, 1323.
- [3] a) B. Xiao, A. Tang, J. Yang, Z. Wei, E. Zhou, *ACS Macro Lett.* **2017**, 410; b) B. Xiao,

- A. Tang, J. Zhang, A. Mahmood, Z. Wei, E. Zhou, *Adv. Energy Mater.* **2016**, 1602269.
- [4] M. Zhang, X. Guo, W. Ma, H. Ade, J. Hou, *Adv. Mater.* **2015**, 27, 4655.
- [5] S. Zhang, B. Yang, D. Liu, H. Zhang, W. Zhao, Q. Wang, C. He, J. Hou, *Macromolecules* **2016**, 49, 120.
- [6] S. H. Liao, H. J. Jhuo, Y. S. Cheng, S. A. Chen, *Adv. Mater.* **2013**, 25, 4766.
- [7] W. Yue, R. S. Ashraf, C. B. Nielsen, E. Collado-Fregoso, M. R. Niazi, S. A. Yousaf, M. Kirkus, H.-Y. Chen, A. Amassian, J. R. Durrant, I. McCulloch, *Adv. Mater.* **2015**, 27, 4702.
- [8] L. Huo, T. Liu, B. Fan, Z. Zhao, X. Sun, D. Wei, M. Yu, Y. Liu, Y. Sun, *Adv. Mater.* **2015**, 27, 6969.
- [9] T. L. Nguyen, H. Choi, S. J. Ko, M. A. Uddin, B. Walker, S. Yum, J. E. Jeong, M. H. Yun, T. J. Shin, S. Hwang, J. Y. Kim, H. Y. Woo, *Energy Environ. Sci.* **2014**, 7, 3040.
- [10] J. Yuan, Z. Zhai, H. Dong, J. Li, Z. Jiang, Y. Li, W. Ma, *Adv. Funct. Mater.* **2013**, 23, 885.
- [11] T. K. Tae Eui Kang, Cheng Wang, Seunghyup Yoo, Bumjoon J. Kim, *Chem. Mater.* **2015**, 27, 2653.
- [12] C. C. Julien Warnan , Abdulrahman El Labban , Michael Ryan Hansen ,, M. F. T. Christopher Tassone , Pierre M. Beaujuge, *Adv. Mater.* **2014**, 26, 4357.
- [13] X. G. Maojie Zhang , Wei Ma , Harald Ade , Jianhui Hou, *Adv. Mater.* **2014**, 26, 5880.
- [14] B. Xia, K. Lu, Y. Zhao, J. Zhang, L. Yuan, L. Zhu, Y. Yi, Z. Wei, *Adv. Sci.* **2015**, 2, 1500021.
- [15] J. Jo, A. Pron, P. Berrouard, W. L. Leong, J. D. Yuen, J. S. Moon, M. Leclerc, A. J. Heeger, *Adv. Energy Mater.* **2012**, 2, 1397.
- [16] S. Shi, P. Jiang, S. Yu, L. Wang, X. Wang, M. Wang, H. Wang, Y. Li, X. Li, *J. Mater. Chem. A* **2013**, 1, 1540.
- [17] J.-H. Kim, J. B. Park, F. Xu, D. Kim, J. Kwak, A. C. Grimsdale, D.-H. Hwang, *Energy Environ. Sci.* **2014**, 7, 4118.
- [18] X. Zhu, J. Fang, K. Lu, J. Zhang, L. Zhu, Y. Zhao, Z. Shuai, Z. Wei, *Chem. Mater.* **2014**, 26, 6947.
- [19] D. Qian, W. Ma, Z. Li, X. Guo, S. Zhang, L. Ye, H. Ade, Z. a. Tan, J. Hou, *J. Am. Chem. Soc.* **2013**, 135, 8464.
- [20] J. Zhao, Y. Li, A. Hunt, J. Zhang, H. Yao, Z. Li, J. Zhang, F. Huang, H. Ade, H. Yan, *Adv. Mater.* **2016**, 28, 1868.
- [21] D. C. Meng Wang, Zhigang Yin, Shan-Ci Chen, Cheng-Feng Du, Qingdong Zheng, *Adv. Mater.* **2016**, 28, 3359.
- [22] H. Hu, K. Jiang, G. Yang, J. Liu, Z. Li, H. Lin, Y. Liu, J. Zhao, J. Zhang, F. Huang, Y. Qu, W. Ma, H. Yan, *J. Am. Chem. Soc.* **2015**, 137, 14149.
- [23] Y. Liu, W. Zhao, Y. Wu, J. Zhang, G. Li, W. Li, W. Ma, J. Hou, Z. Bo, *J. Mater. Chem. A* **2016**, 4, 8097.
- [24] J.-H. Kim, J. B. Park, I. H. Jung, A. C. Grimsdale, S. C. Yoon, H. Yang, D.-H. Hwang, *Energy Environ. Sci.* **2015**, 8, 2352.
- [25] J. Cao, L. Qian, F. Lu, J. Zhang, Y. Feng, X. Qiu, H. L. Yip, L. Ding, *Chem. Commun. (Camb)* **2015**, 51, 11830.
- [26] J. Woong Jung, J. Woong Jo, F. Liu, T. P. Russell, W. Ho Jo, *Chem. Commun.* **2012**, 48, 6933.
- [27] W. Li, K. H. Hendriks, A. Furlan, A. Zhang, M. M. Wienk, R. A. J. Janssen, *Chem. Commun.* **2015**, 51, 4290.
- [28] C. B. Nielsen, R. S. Ashraf, N. D. Treat, B. C. Schroeder, J. E. Donaghey, A. J. White, N. Stingelin, I. McCulloch, *Adv. Mater.* **2015**, 27, 948.
- [29] H. Li, S. Sun, S. Mhaisalkar, M. T. Zin, Y. M. Lam, A. C. Grimsdale, *J. Mater. Chem. A* **2014**, 2, 17925.
- [30] M. Wang, H. Qin, L. Wang, J. Wei, D. Cai, Z. Yin, Y. Ma, S.-C. Chen, C. Tang, Q. Zheng,

J. Mater. Chem. A **2015**, 3, 21672.

- [31] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, 4, 864.
- [32] G. Zhao, Y. He, Y. Li, *Adv. Mater.* **2010**, 22, 4355.
- [33] V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nat. Photon.* **2015**, 9, 403.
- [34] K. Kawashima, Y. Tamai, H. Ohkita, I. Osaka, K. Takimiya, *Nat. Commun.* **2015**, 6, 10085.
- [35] 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, E. Wang, *Adv. Energy Mater.* **2016**, 6, 1600148.
- [36] M. Wang, H. Wang, T. Yokoyama, X. Liu, Y. Huang, Y. Zhang, T. Q. Nguyen, S. Aramaki, G. C. Bazan, *J. Am. Chem. Soc.* **2014**, 136, 12576.
- [37] W. Li, K. H. Hendriks, A. Furlan, M. M. Wienk, R. A. Janssen, *J. Am. Chem. Soc.* **2015**, 137, 2231.
- [38] C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. Frechet, M. D. McGehee, P. M. Beaujuge, *J. Am. Chem. Soc.* **2013**, 135, 4656.
- [39] I. Osaka, T. Kakara, N. Takemura, T. Koganezawa, K. Takimiya, *J. Am. Chem. Soc.* **2013**, 135, 8834.
- [40] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, 5, 5293.
- [41] 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, J. Yao, *Adv. Mater.* **2013**, 25, 5791.
- [42] Y. Lin, Y. Wang, J. Wang, J. Hou, Y. Li, D. Zhu, X. Zhan, *Adv. Mater.* **2014**, 26, 5137.
- [43] X.-F. Wu, W.-F. Fu, Z. Xu, M. Shi, F. Liu, H.-Z. Chen, J.-H. Wan, T. P. Russell, *Adv. Funct. Mater.* **2015**, 25, 5954.
- [44] Y. Cai, L. Huo, X. Sun, D. Wei, M. Tang, Y. Sun, *Adv. Energy Mater.* **2015**, 5, 1500032.
- [45] J. W. Jung, W. H. Jo, *Chem. Mater.* **2015**, 27, 6038.
- [46] D. Sun, D. Meng, Y. Cai, B. Fan, Y. Li, W. Jiang, L. Huo, Y. Sun, Z. Wang, *J. Am. Chem. Soc.* **2015**, 137, 11156.
- [47] 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, C. Nuckolls, *Nat. Commun.* **2015**, 6, 8242.
- [48] Q. Wu, D. Zhao, A. M. Schneider, W. Chen, L. Yu, *J. Am. Chem. Soc.* **2016**, 138, 7248.
- [49] J. Zhang, X. Zhang, H. Xiao, G. Li, Y. Liu, C. Li, H. Huang, X. Chen, Z. Bo, *ACS Appl. Mater. Interfaces* **2016**, 8, 5475.
- [50] Y. Qin, M. A. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T. J. Shin, H. Y. Woo, J. Hou, *Adv. Mater.* **2016**, 28, 9416.
- [51] S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, *Adv. Mater.* **2016**, 28, 9423.
- [52] Y. Lin, T. Li, F. Zhao, L. Han, Z. Wang, Y. Wu, Q. He, J. Wang, L. Huo, Y. Sun, C. Wang, W. Ma, X. Zhan, *Adv. Energy Mater.* **2016**, 6, 1600854.
- [53] 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, I. McCulloch, *Nat. Commun.* **2016**, 7, 11585.
- [54] A. G. Anushri Rananaware, JingLiang Li, Ante Bilic, Lathe Jones, Suresh Bhargava, Sheshanath V. Bhosale, *Chem. Commun.* **2016**, 52, 8522.
- [55] H. Bin, Z.-G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2016**, 138, 4657.
- [56] Y. Lin, F. Zhao, Q. He, L. Huo, Y. Wu, T. C. Parker, W. Ma, Y. Sun, C. Wang, D. Zhu, A. J. Heeger, S. R. Marder, X. Zhan, *J. Am. Chem. Soc.* **2016**, 138, 4955.

- [57] Y. J. Hwang, H. Li, B. A. Courtright, S. Subramaniyan, S. A. Jenekhe, *Adv. Mater.* **2016**, 28, 124.
- [58] L. Gao, Z. G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei, Y. Li, *Adv. Mater.* **2016**, 28, 1884.
- [59] Y. Guo, Y. Li, O. Awartani, J. Zhao, H. Han, H. Ade, D. Zhao, H. Yan, *Adv. Mater.* **2016**, 28, 8483.
- [60] Z. Li, X. Xu, W. Zhang, X. Meng, W. Ma, A. Yartsev, O. Inganäs, M. R. Andersson, R. A. Janssen, E. Wang, *J. Am. Chem. Soc.* **2016**, 138, 10935.
- [61] Z. Ding, X. Long, C. Dou, J. Liu, L. Wang, *Chem. Sci.* **2016**, 7, 6197.
- [62] Y.-J. Hwang, B. A. E. Courtright, A. S. Ferreira, S. H. Tolbert, S. A. Jenekhe, *Adv. Mater.* **2015**, 27, 4578.
- [63] 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, H. Yan, *Nat. Energy* **2016**, 1, 16089.
- [64] Y. Fu, B. Wang, J. Qu, Y. Wu, W. Ma, Y. Geng, Y. Han, Z. Xie, *Adv. Funct. Mater.* **2016**, 26, 5922.
- [65] 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. Durrant, I. McCulloch, *Energy Environ. Sci.* **2016**, 9, 3783.
- [66] V. G. Suman, Anirban Bagui, Surya Prakash Singh, *Adv. Funct. Mater.* **2016**, 27, 1603820.
- [67] F. Liu, Z. Zhou, C. Zhang, T. Vergote, H. Fan, F. Liu, X. Zhu, *J. Am. Chem. Soc.* **2016**, 138, 15523.
- [68] Y. Zhang, X. Guo, B. Guo, W. Su, M. Zhang, Y. Li, *Adv. Funct. Mater.* **2017**, 1603892.
- [69] Y. Liu, Z. Zhang, S. Feng, M. Li, L. Wu, R. Hou, X. Xu, X. Chen, Z. Bo, *J. Am. Chem. Soc.* **2017**, 139, 3356.
- [70] 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, J. Hou, *Adv. Mater.* **2017**, 1700254.
- [71] B. Kan, H. Feng, X. Wan, F. Liu, X. Ke, Y. Wang, Y. Wang, H. Zhang, C. Li, J. Hou, Y. Chen, *J. Am. Chem. Soc.* **2017**, 139, 4929.
- [72] C. Zhang, T. Liu, W. Zeng, D. Xie, Z. Luo, Y. Sun, C. Yang, *Mater. Chem. Front.* **2017**, 1, 749.
- [73] B. Fan, K. Zhang, X. F. Jiang, L. Ying, F. Huang, Y. Cao, *Adv. Mater.* **2017**, 1606396.
- [74] A. Zhang, C. Li, F. Yang, J. Zhang, Z. Wang, Z. Wei, W. Li, *Angew. Chem. Int. Ed. Engl.* **2017**, 56, 2694.