Effects of Vertical Molecular Stratifications and Microstructures on the Properties of Fullerene-Free Organic Solar Cells

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1. Introduction

Organic solar cells (OSCs) are constantly receiving great research attention given their suitability for solution-based fabrication methods, low-cost precursor materials, and thus have high commercialization potential. From the past years, research studies in OSCs have been more concentrated in fullerene-free acceptors (e.g., Y6 and IT-4Cl) blended with polymer donors such as PM6 (also known as PBDB-T-2F) in bulk heterojunctions. Also, several recent reports achieving high power conversion efficiencies (PCEs) of up to over 18% and even enhanced device stability have been possible through complex active layers such as ternary/quaternary blends and upon the incorporation of dopants. Although there is continuous progress improving the performance of OSCs, it can also be observed that there are a number of opposing propositions from different reports in the past few years, which involve (but are not limited to) energy losses and molecular energy offsets. This is
problematic as it will prolong the development of strategies to further advance OSC technology.

Considering that most state-of-the-art OSCs reported recently were from the blends of polymer donors and fullerene-free acceptors, which are generally composed of similar molecular fragments, the effects of vertical phase segregations and film’s microscopic features are then typically disregarded or not given sufficient considerations among former studies.\(^3\) In addition, there are limited experimental methods that can be suitably applied to soft, vulnerable, and disordered organic materials, which leads to inadequacy in understanding the spatial molecular distribution within OSC’s active layers.\(^4\) Xu et al. have reported a lift-off process through a solvent, wherein vertical phase inhomogeneity in poly(3-hexythiophene):fullerene blends has been identified and was attributed to the difference in donor–acceptor surface energies.\(^5\) However, the said lift-off approach will not provide a full view of the active layers as only the buried layer in contact with the substrate can be characterized. A number of similar works concerning phase segregations are also done by Kim et al. for polymer:fullerene blends with additive-assisted separations.\(^6\) Other methods such as x-ray and neutron scattering have also been demonstrated to study the molecular stacking and crystallites within films\(^7\); however, these cannot provide direct identification of donor and acceptor molecules spatial distribution. Further, organic materials can have poor contrast for x-ray scattering, while the limited neutron flux for neutron scattering will also lead to poor resolution.\(^8\) Fortunately, time-of-flight secondary ion mass spectrometry (ToF-SIMS), in combination with argon cluster ion beam as the sputtering source, has been demonstrated to effectively provide the vertical molecular distribution of some polymer:fullerene blends.\(^9\) In general, a primary ion source will impinge the sample surface, which then ejects secondary ions from the fragments of molecules constituting the sample. These secondary ions can be characterized by their mass-to-charge ratio (m/z). Measurements from this method are relatively easier to reproduce in other research laboratories, making it versatile. A more comprehensive discussion about ToF-SIMS is available in our former work.\(^10\)

As previously mentioned, polymer donors and fullerene-free acceptors typically exhibit similar molecular structures, hence acceptors typically exhibit similar molecular structures, hence acceptor surface energies.\(^1\) However, the said lift-off approach has been demonstrated to study the molecular stacking and crystallites within films;\(^2\) however, these cannot provide direct identification of donor and acceptor molecules spatial distribution. Further, organic materials can have poor contrast for x-ray scattering, while the limited neutron flux for neutron scattering will also lead to poor resolution.\(^3\) Fortunately, time-of-flight secondary ion mass spectrometry (ToF-SIMS), in combination with argon cluster ion beam as the sputtering source, has been demonstrated to effectively provide the vertical molecular distribution of some polymer:fullerene blends.\(^4\) In general, a primary ion source will impinge the sample surface, which then ejects secondary ions from the fragments of molecules constituting the sample. These secondary ions can be characterized by their mass-to-charge ratio (m/z). Measurements from this method are relatively easier to reproduce in other research laboratories, making it versatile. A more comprehensive discussion about ToF-SIMS is available in our former work.\(^5\)

2. Results and Discussion

To start with, binary blends of PM6 (a fluorinated polymer donor molecule) and IT-4Cl (a chlorinated fullerene-free acceptor), with their molecular structures shown in Figure 1a, dissolved in o-xylene (a non-halogenated solvent) with 1,8-diodooctane (DIO) additive were chosen. The advantage of this selection is to enable the identification and profiling of PM6 and IT-4Cl molecules (through ToF-SIMS) based on the atomic distribution of F\(^-\) and Cl\(^-\) ions. SIMS is in essence not quantitative without standards (i.e., the intensity of a particular ion fragment is not directly comparable between different samples with different matrix or internal environment), but the relative changes of ion intensities with sputtering time (which is a function of film thickness) describe the vertical uniformity of molecules’ distribution and display any potential segregation that may exist across the layer thickness. Here, different PM6:IT-4Cl blend active layer fabrications have been done: 1) without DIO and with no thermal annealing, xDIO(xTA); 2) with DIO and thermally annealed, DIO(TA); and 3) with DIO and without thermal annealing, DIO(xTA).

The corresponding current density–voltage (J–V) curves of devices based on conventional structure (i.e., Glass/ITO/PEDOT:PSS/Active Layer/PFN-Br/Al) are shown in Figure 1b, and the summary of their photovoltaic performance is in Table S1, Supporting Information. DIO(TA) displays the highest short-circuit current density (J\(_{SC}\)) (17.84 mA cm\(^{-2}\)), but with the lowest open-circuit voltage (V\(_{OC}\)) (0.79 V). In contrast, xDIO(xTA) displays the lowest J\(_{SC}\) (16.78 mA cm\(^{-2}\)) and the highest V\(_{OC}\) (0.87 V). The relative values for J\(_{SC}\) are consistent with the results obtained from the integrated EQE (Table S1, Supporting Information). It is clear that the typically observed trade-off between J\(_{SC}\) and V\(_{OC}\) exists in these samples. From the EQE spectra (Figure 1c), DIO(TA) shows the largest shift toward higher wavelengths (redshift) and also displays a slight improvement in the donor-dominated absorption regime. Overall, from the average of about 20 independent cells, the PCE is highest for DIO(TA) (10.76%), followed by DIO(xTA) (10.31%), and lowest for xDIO(xTA) (9.99%). Inverted structure (i.e., Glass/ITO/ZnO/Active Layer/MoO\(_3\)/Ag) device performances are also measured (Figure S2, Supporting Information) and summarized in Table S1, Supporting Information. Although there is only marginal improvement in PCE for the blends with DIO, their J\(_{SC}\) varied significantly compared with the conventional devices. Specifically, their J\(_{SC}\) increases, which is largest for DIO(TA), followed by DIO(xTA), and smallest for xDIO(xTA). The experimental foundations to demonstrate and understand how the device structure influences J\(_{SC}\) are lacking, especially for fullerene-free systems. In practice, both conventional and inverted structures are being utilized during device fabrication optimization, wherein the configuration with the best PCE will be used for subsequent analysis. However, will the inhomogeneity of donor and acceptor molecules’ vertical distribution significantly influence the device performance? If so, analyses without careful considerations on molecules’ spatial arrangements could be potentially overlooked.

The mass-to-charge ratios (m/z) for F\(^-\) and Cl\(^-\) atomic ions have been identified from the negative SIMS spectra (Figure S1, Supporting Information) and vertical molecular
profiling has been performed in samples adopting the actual conventional device structure (Figure S3, Supporting Information). The cross section of each sample is then illustrated in Figure 2a. From intensity against sputtering time plot (Figure 2b), it can be seen that $F^{-}/C_0$ and $Cl^{-}/C_0$ intensities are considerably uniform from the surface toward the bulk of the active layer. However, there is a significant increase in $Cl^{-}/C_0$ intensity (implying IT-4Cl enrichment) at the interface with the hole transport layer (HTL), which is PEDOT:PSS (i.e., free of F and Cl functionalities). For more meaningful results, the percentage increase of $Cl^{-}/C_0/F^{-}/C_0$ ratio from the bulk to the IT-4Cl enriched layer has been quantified (Table S2, Supporting Information). The increase is more substantial in blends with DIO, i.e., 81% for DIO(xTA), followed by 77% for DIO(TA), compared to 27% for xDIO(xTA). Suggestively, the retained solvent (when no thermal annealing is performed) and DIO provide “pathways” that enhance IT-4Cl diffusion, which is believed to be driven by the difference in PM6 (38.12 mJ m$^{-2}$)$^{[11]}$ and IT-4Cl (42.40 mJ m$^{-2}$)$^{[12]}$ surface energies to adopt the most stable molecular arrangement.

To verify that the observed IT-4Cl enriched layer is not just instrumental effects concerning the interface with HTL, vertical profiling of PM6:IT-4Cl blends from precursor solutions with a low concentration of either PM6 or IT-4Cl was also performed (Figure S4, Supporting Information). As expected, for low PM6 concentration, no enrichment can be realized as the active layer is mainly dominated by the acceptor. Similarly, for low IT-4Cl concentration, there is also no enrichment, which can be ascribed to the enhanced intermolecular attraction with the donor molecules. Thus, the observed IT-4Cl enriched layer is confirmed not to be instrumental nor interfacial effects. For inverted devices with structure Glass/ITO/ZnO/Active Layer, a similar trend for IT-4Cl enrichment was deduced (Figure S5, Supporting Information).

The observed $J_{SC}$ enhancement for inverted devices can then be understood as an improvement in the overall charge collection as the acceptor enrichment at the bottom of active layers can facilitate electron transport from the active layer to the electron transport layer (ETL). This is in contrast to the conventional structured devices, where the acceptor enrichment is closer to the underlying HTL providing insufficient routes (i.e., donor domains) for hole extraction, and thus increasing the probability of electron–hole encounter for recombination. These are well supported by the relative changes in $J_{SC}$ such that the improvement by adopting an inverted device structure is more sizeable in blends with more pronounced IT-4Cl enrichment. Consequently, without knowing the spatial molecular distribution within active layers, it will be very challenging to precisely understand and attribute the enhanced device performance of a particular donor:acceptor heterojunction compared to other systems.

Energy loss is another metric commonly used to assess the performance of OSCs. The energy loss can be estimated from the difference between the optical band gap ($E_g$) and $V_{OC}$. Generally, for systems with low bandgap fullerene-free acceptors, $E_g$ is estimated on the basis of neat acceptor thin film absorption.

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**Figure 1.** Precursor molecules and device performance: chemical structure of PM6 and IT-4Cl (a), current density–voltage curves (b), and EQE (c) for conventional structure-based devices (i.e., Glass/ITO/PEDOT:PSS/Active Layer/PFN-Br/Al).
and photoluminescence (PL) intersection (neat acceptor films means without blending with donor molecules). Remember that the molecular arrangement in actual device active layers (i.e., a blend for donors and acceptors) can be different from such simplified neat thin films. Yet, the potential influence of microscopic features on optoelectronic properties is typically not given enough attention. Consequently, this study further investigates the effects of microscopic differences between thin films of neat donor/acceptor and their corresponding blends adopting different fabrications (i.e., xDIO(xTA), DIO(TA), and DIO(xTA)). For the blended thin films, microscopic differences associated with domain aggregations have been confirmed from the larger dimensions of surface domains/hills for DIO(TA), followed by DIO(xTA), compared to xDIO(xTA) (Figure 2c) as obtained through atomic force microscope (AFM) characterizations. Further, the most aggregated sample displays less uniform size distribution of surface hills, which are also supported by the AFM surface roughness (Figure 2d), such that DIO(TA) demonstrates the highest roughness (2.75 nm) compared to xDIO(xTA) (1.54 nm) and DIO(xTA) (2.06 nm).

Now that microscopic variations between each sample have already been established, the absorption and PL spectra were obtained to describe their optoelectronic properties. The addition of DIO demonstrates bathochromic shifts with significant enhancement of the acceptor absorption (Figure 3a), supporting the enhanced $J_{SC}$ for DIO(TA) devices (Figure 1b and Figure S2, Supporting Information). This is also an indication of better molecular ordering, aggregation, and enhanced chromophore for IT-4Cl.[13] Consequently, the EQE of DIO(TA) (Figure 1c) is the most redshifted. Molecular ordering can arise from the aggregations of conjugated molecules, which improves the backbone planarization and has been experimentally demonstrated to cause absorption shifts toward higher wavelengths.[14] Even though xDIO(xTA) displays the least IT-4Cl enrichment, which has been discussed to be the preferred case for hole extraction in conventional devices (when considering the vertical morphology).
as compared to DIO(TA) and DIO(xTA), it still exhibits the lowest J_{SC} (Figure 1b) due to poor domain aggregations which concern the lateral morphology. In contrast, thermal annealing slightly reduces the donor absorption in DIO(TA), suggesting retarded PM6 self-aggregation.[15] Interestingly, DIO(TA) still manages to exhibit slightly better EQE at the donor-dominated absorption regime (Figure 1c), implying enhanced charge transport property, which is expected as a consequence of more continuous percolation pathways enabled by aggregations.[16] These are in agreement with PL quenching (referenced to neat IT-4Cl) (Figure 3b), which is largest (or most efficient) for the least aggregated xDIO(xTA), followed by DIO(xTA), and least for the most aggregated DIO(TA). This confirms that more efficient PL quenching is indicative of highly intermixed blend constituents (smaller domains), which increases the donor–acceptor interfacial area for charge transfer.[11] However, the too-large donor–acceptor interfacial area will also stimulate the recombination of free charges,[17] as reflected from the lower J_{SC} for xDIO(xTA)-based device. Further, the mentioned aggregations can also be inferred from the normalized PL spectra (Figure 3c), wherein hypsochromic shift and broadened PL for xDIO(xTA) film, compared to DIO(TA) and DIO(xTA), have been obtained, which are known to be consequences of smaller domain sizes.[18]

This work then illustrates that absorption and emission features of the same donor:acceptor blends may significantly change relative to the microstructures of fabricated thin films. As mentioned earlier, E_g based on neat acceptor thin films is widely used as the reference for energy loss calculations in most OSC studies. Some of which leads to captivating claims of overcoming (by tens of meV lower) the empirically observed minimum energy loss (i.e., 0.60 eV)[19] to achieve high device quantum efficiency. To shed light, Figure 3d shows the estimated E_g from the corresponding absorption and PL spectra intersections (Figure S7, Supporting Information) of neat IT-4Cl and the blends. Variations of up to around 60 meV can be observed. DIO(TA) (1.55 eV) displays the smallest E_g, while it is highest for xDIO(xTA) (1.61 eV). These are consistent with the observations from other systems, such as PM6:BTP-4Cl, as reported recently.[20] Intuitively, such discrepancies can generally be expected in this class of materials, and energy losses from former reports could potentially be over/underestimated.

Time-resolved PL (TRPL) was also performed to describe the corresponding dynamics of excited states, more precisely for hole transfer, as IT-4Cl has a much lower E_g than PM6. The exponential fittings and summary of obtained lifetimes are provided in Figure 4a–c (Figure S8, Supporting Information, for neat IT-4Cl) and summarized in Table S3, Supporting Information. As expected, upon exciting the acceptor, the neat IT-4Cl has a

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Figure 3. Absorption and emission spectra: normalized absorption relative to the maximum for PM6 and IT-4Cl, while relative to DIO(TA) maximum for the blends (a), normalized to IT-4Cl PL (b), normalized to individual maximum PL (c), and illustration of the estimated E_g values (d).
much longer excited state weighted average lifetime ($\tau_{\text{ave}}$) (148 ps) compared to blends which are known to be a consequence of charge transfer.\cite{21} A single exponential function is able to fit the lifetime of xDIO(xTA), which implies a common recombination center, while a biexponential function is needed for blends with DIO. The shift from single to biexponential fittings demonstrates the existence of recombination centers with both fast ($\tau_A$) and slow ($\tau_B$) components. This associates well with

**Figure 4.** Excited states dynamics and molecular energy levels: xDIO(xTA) monoexponential TRPL fitting with the instrument response frequency (a), biexponential TRPL fittings for DIO(TA) (b), DIO(xTA) (c), UPS spectral onset of films fabricated through o-xylene solvent with Gaussian fits and the estimated onset energies (relative to vacuum) as inset (d), and UPS onset of neat IT-4Cl films fabricated from different solvents (e). For TRPL, 780 nm laser was used for excitation, while the summation of emissions from 820 to 900 nm was used for detection. As a note, no deconvolution was performed in the blend UPS spectra. Thus, the onset energies provided are not intended to coherently describe IEs, but rather only to give quantitative estimates on how IEs can be affected.
the discussed aggregations. The fast component can be assigned to those excited states generated near the donor–acceptor interfaces; correspondingly, slow dynamics can be expected for those excited states generated inside large domains owing to charge diffusion reaching the interface before charge transfer, which leads to longer emission lifetimes. Overall, the obtained $\tau_{\text{ave}}$ (about 20 ps) for the samples considered are within comparable limits. Thus, for a more comprehensive view of exciton dynamics, both the fast and the slow decay times can be considered, reflecting the microscopic property of the samples.

Ultimately, arguments about the significance of donor:acceptor ionization energy (IE) offset exist in a number of recent reports\textsuperscript{[22]} such that some systems with offset lower than 500 meV (by tens to hundreds of meV) are found to exhibit drastically lower quantum efficiencies, while reports for other systems do not display similar behavior. IEs obtained from ultraviolet photoelectron spectroscopy (UPS) onset energies relative to vacuum are typically regarded as better representative energetics in devices\textsuperscript{[23]} thus this method has increasingly been used for more conservative studies. Similar to other methods, measurements based on neat thin films are commonly regarded to quantitatively describe the energy level alignments of donor and acceptor molecules constituting the device active layer. However, it is often neglected that when energetically dissimilar materials (electron donors and acceptors) are mixed to fabricate solid thin films/devices, the resultant multiphase system is likely to have energetics different from that of the neat constituents owing to factors such as intermolecular attractions. To address this, blended thin films fabricated with varying precursor solution donor-to-acceptor ratios (1:4 and 4:1) were studied in addition to neat thin films. This also sought to illustrate how the identified vertical stratification across the active layer thickness (i.e., having nonidentical donor-to-acceptor ratios caused by the previously discussed vertical phase segregations) can influence the IEs. As a note, samples are thermally annealed to enhance the film conductivity for enhanced spectral resolution.

As an initial basis, gas-phase IEs of single molecules from time-dependent density functional theory (TD-DFT) calculations were also reported (Figure S9, Supporting Information). Looking at the UPS onset region (Figure 4d), the IEs for both neat IT-4Cl ($\sim 5.15$ eV) and PM6 ($\sim 4.96$ eV) films using o-xylene solvent were identified. Also, the blend with 1:4 ratio displays only marginal spectral difference compared to neat IT-4Cl, which suggests that the influence of PM6 is minimal (onset and cutoff regions are in Figure S10, Supporting Information). However, based on the Gaussian fits, the blend with 4:1 ratio displays a distinct spectral feature compared to both the neat films. This spectrum may correspond mainly to PM6, IT-4Cl, or their spectral convolution. Although upon considering the cutoff regions (shown in Figure S10, Supporting Information), it can apparently be attributed principally to IT-4Cl. In any case, this demonstrates an evolution of donor and/or acceptor UPS spectra upon variation in the donor-to-acceptor ratio, such that onset energies vary up to about 100 meV herein (inset of Figure 4d). In practice, the actual blend components ratio (or the resulting nanomorphology) in device active layers was not meant to be diligently replicated upon fabrication of simplified thin films. Also, there are donor–acceptor interfacial effects that have been introduced recently, such as band bending\textsuperscript{[24]} which can also contribute to these observed spectral changes. To better exemplify the effects concerning nanomorphology, onset energies of neat IT-4Cl thin films were fabricated using the same precursor composition as with the o-xylene-based solution, but from chloroform ($\sim 4.63$ eV) and chlorobenzene ($\sim 4.72$ eV) solvents were also determined (Figure 4e). As demonstrated from previous studies\textsuperscript{[23]} these solvents have different film-forming properties as compared to o-xylene. Also, IT-4Cl possesses polar ends, making chloroform and chlorobenzene (i.e., polar solvents) more widely used among former reports. Accordingly, the onset energies obtained using the mentioned halogenated solvents have significantly varied relative to when o-xylene is used, but closer to DFT estimations. As with the $E_g$ such differences could be more notable on other systems. It is then suggestive that distinguishable IEs can be expected from a set of samples with the same composition, but having different microstructures depending on film fabrication and the intrinsic properties of precursor materials. On top of the estimated onset energy variations, it is more important to highlight the illustrated spectral transformations, which must be recognized among future related studies for a more precise interpretation of results.

3. Conclusion

In conclusion, this work experimentally illustrated the existence of vertical molecular stratification on a polymer:fullerene-free system and demonstrates how such stratification governs the photovoltaic device performance. The enrichment of acceptor domains near the HTL (for conventional devices) hinders hole transport, while its enrichment near ETL (for inverted devices) favors the electron transport, as suggested from the correspondingly obtained $J_{SC}$ values. Owing to the different nature of molecular stratifications, the $J_{SC}$ and EQE were identified to be highly dependent on device structures. In essence, without spatial molecular characterization, it will be very challenging to precisely identify the sources of device improvements when comparing different blends of donor and acceptor molecules. Further, the thin-film microstructure was also found to influence its optoelectronic properties. Specifically, $E_g$ and UPS onset energies of neat and set of blended thin films display differences upon variation on the sample fabrication, blend constituents’ ratio, and the choice of precursor solvent. As the actual device active layer can have vertical molecular stratification and its nanomorphology/composition could be different relative to simplified thin films, the energy loss quantifications and energy offset analyses could then be greatly affected. All these will result in less precise understanding of OSCs’ photovoltaic and optoelectronic properties, as well reflected from a number of opposing propositions from different reports lately. This study then highlights the importance of spatial molecular characterization. Also, as thin films are the most versatile way to describe active layers, it could then be worthy to also understand how significant a particular optoelectronic property will depend on thin-film microstructure, leading to more accurate correlations relative to device metrics. These are sought to introduce more precise data interpretations in future studies and accelerate the advancements in OSCs.
4. Experimental Section

Experimental details are available in the Supporting Information.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contribution

T.A.D.P.: experiments, conceptualization, methodology, and writing; R.M.: thin film fabrication; A.S.: device fabrication; Z.X. and Z.J.: TRPL setup and measurements; J.W., D.B., and H.Y.: equipment; L.W.: TOF-SIMS; and K.S.W.: supervisory, funding, and writing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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[1] a) K. Weng, L. Ye, L. Zhu, J. Xu, J. Zhou, X. Feng, G. Lu, S. Tan, F. Liu, Y. Sun, Nat. Commun. 2020, 11, 1; b) Y. Zhou, M. Li, H. Lu, H. Jin, X. Wang, Y. Zhang, S. Shen, Z. Ma, J. Song, Z. Bo, Adv. Funct. Mater. 2021, 31, 2101742; c) H. Huang, X. Li, C. Sun, I. Angunawela, B. Qiu, J. Du, S. Qin, L. Meng, Z. Zhang, H. Ade, J. Mater. Chem. C 2020, 8, 7718.

[2] a) Y. Lin, Y. Firdaus, M. I. Nugraha, F. Liu, S. Karuthedath, A. H. Emwas, W. Zhang, A. Seithkan, M. Neophytou, H. Faber, Adv. Sci. 2020, b) J. Song, C. Li, L. Zhu, J. Guo, J. Xu, X. Zhang, K. Weng, K. Zhang, J. Min, X. Hao, Adv. Mater. 2019, 31, 1905645; c) G. Chai, Y. Chang, J. Zhang, X. Xu, L. Yu, X. Zou, X. Li, Y. Chen, S. Luo, B. Liu, F. Bai, Z. Luo, H. Yu, J. Liang, T. Liu, K. S. Wong, H. Zhou, Q. Peng, H. Yan, Energy Environ. Sci. 2021, 14, 3469; d) L. Arunagiri, Z. Peng, X. Zou, H. Yu, G. Zhang, Z. Wang, J. Y. L. Lai, J. Zhang, Y. Zheng, C. Cui, F. Huang, Z. Yau, K. S. Wong, P. C. Y. Chow, H. Ade, H. Yan, Joule 2020, 4, 1790; e) T. Liu, T. Yang, R. Ma, L. Zhan, Z. Luo, G. Zhang, Y. Li, K. Gao, Y. Xiao, J. Yu, X. Zou, H. Sun, M. Zhang, T. A. Dela Peha, Z. Xing, H. Liu, X. Li, G. Li, J. Huang, C. Duan, K. S. Wong, X. Lu, X. Guo, F. Gao, H. Chen, F. Huang, Y. Li, Y. Li, Y. Cao, B. Tang, H. Yan, Joule 2021, 5, 914; f) R. Ma, Y. Tao, Y. Chen, T. Liu, Z. Luo, Y. Guo, Y. Xiao, J. Fang, G. Zhang, X. Li, X. Guo, Y. Yi, M. Zhang, X. Lu, Y. Li, H. Yan, Sci. China Chem. 2021, 64, 581; g) Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang, L. Ding, Sci. Bull. 2020, 65, 272.

[3] J. Zhang, M. H. Futschers, V. Lami, F. U. Kosasih, C. Cho, Q. Gu, A. Sadhanala, A. J. Pearson, B. Kan, G. Divitini, Adv. Energy Mater. 2019, 9, 1902145.

[4] B.-Y. Yu, W.-C. Lin, W.-B. Wang, S.-i. Iida, S.-Z. Chen, C.-Y. Liu, C.-H. Kuo, S.-H. Lee, W.-L. Kao, G.-J. Yen, Acs Nano 2010, 4, 833.

[5] Z. Xu, L. M. Chen, G. Yang, C. H. Huang, J. Hou, Y. Wu, G. Li, C. S. Hsu, Y. Ang, Adv. Funct. Mater. 2009, 19, 1227.

[6] a) M. Kim, J. Lee, S. B. Jo, D. H. Sin, H. Ko, H. Lee, S. G. Lee, K. Cho, J. Mater. Chem. A 2016, 4, 15522; b) M. Kim, J. H. Kim, H. H. Choi, J. H. Park, S. B. Jo, M. Sim, J. S. Kim, H. Jinnai, Y. D. Park, K. Cho, Adv. Energy Mater. 2014, 4, 1300612.

[7] a) S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, Adv. Mater. 2016, 28, 9423; b) J. T. Rogers, K. Schmidt, M. F. Toney, E. J. Kramer, G. C. Bazan, Adv. Mater. 2011, 23, 2284.

[8] P. Müller-Buschbaum, Polym. J. 2013, 45, 34.

[9] a) V. S. Smentkowski, G. Zorn, A. Misner, G. Parthasarathy, A. Couture, E. Tallarek, B. Hagenhoff, J. Vacuum Sci. Technol. A: Vacuum Surf. Films 2013, 31, 030601; b) J. Y. Baek, C. M. Choi, S. J. Lee, B. K. Min, H. S. Kang, D. C. Choo, J. Y. Sung, S. J. Jin, M. C. Choi, Appl. Surf. Sci. 2020, 507, 144887; c) S. J. Lee, C. M. Choi, B. K. Min, J. Y. Baek, J. Y. Eo, M. C. Choi, Bull. Korean Chem. Soc. 2019, 40, 877.

[10] a) T.-T. Wang, C.-M. Chan, in Wiley Encyclopedia of Composites, Wiley, Hoboken, NJ, p. 1.

[11] a) J. Wu, G. Li, J. Fang, X. Guo, L. Zhu, B. Guo, Y. Wang, G. Zhang, L. Arunagiri, F. Liu, Nat. Commun. 2020, 11, 1.

[12] H. Jiang, G. Qin, L. Zhang, F. Pan, Z. Wu, Q. Wang, G. Wen, W. Zhang, Y. Cao, J. Chen, J. Mater. Chem. C 2021, 9, 249.

[13] C. Labanti, M. J. Sung, J. Luke, S. Kwon, R. Kumar, J. Hong, J. Kim, A. A. Bakulin, S.-K. Kwon, Y.-H. Kim, ACS Nano 2021, 15, 7700.

[14] M. Li, H. Bin, X. Jiao, M. M. Wink, H. Yan, R. A. Janssen, Angew. Chem. Int. Ed. 2020, 132, 856.

[15] B. Du, R. Geng, W. Tan, Y. Mao, D. Li, X. Zhang, D. Liu, W. Tang, W. Huang, T. Wang, J. Energy Chem. 2021, 54, 131.

[16] Y. Liu, D. Tang, K. Zhang, P. Huang, Z. Wang, K. Zhu, Z. Li, L. Yuan, J. Fan, Y. Zhou, B. Song, ACS Omega 2017, 2, 2489.

[17] a) V. Wandelov, J. Widmer, T. Heumuller, C. J. Brabec, M. D. McGehee, K. Leo, M. Riede, A. Salles, Adv. Mater. 2014, 26, 3839.

[18] a) J. Jia, P. Zhang, Z. Lin, R. Anthony, U. Kortshagen, S. Huang, B. Putthen-Veettil, G. Conibeer, I. Perez-Wurfl, RSC Adv. 2015, 5, 55119.

[19] W. Li, K. H. Hendriks, A. Furlan, M. M. Wink, R. A. Janssen, J. Am. Chem. Soc. 2015, 137, 2231.

[20] a) T. A. Dela Peha, J. I. Khan, N. Chaturvedi, R. Ma, Z. Xing, J. Gorenfloft, A. Sharma, F. L. Ng, D. Baran, H. Yan, K. S. Wong, ACS Energy Lett. 2021, 6, 3408.

[21] a) M. A. Alamoudi, J. I. Khan, Y. Firdaus, K. Wang, D. Andrienko, P. M. Beaujuge, F. Laquai, ACS Energy Lett. 2018, 3, 802; b) R. Singh, R. Shivanna, A. Iosifidis, H.-J. R. Butt, G. Floudas, K. Narayan, P. E. Keivanidis, ACS Appl. Mater. Interfaces 2015, 7, 24876.
[22] a) S. Karuthedath, J. Gorenflo, Y. Firdaus, N. Chaturvedi, C. S. De Castro, G. T. Harrison, J. I. Khan, A. Markina, A. H. Balawi, T. A. Dela Peña, W. Liu, R.-Z. Liang, A. Sharma, S. H. K. Paleti, W. Zhang, Y. Lin, E. Alarousu, D. H. Anjum, P. M. Beaujuge, S. De Wolf, I. McCulloch, T. D. Anthopoulos, D. Baran, D. Andrienko, F. Laquai, Nature Materials 2021, 20, 378; b) A. Classen, C. L. Chochos, L. Lüer, V. G. Gregoriou, J. Wortmann, A. Osvet, K. Forberich, I. McCulloch, T. Heumüller, C. J. Brabec, Nature Energy 2020, 5, 711; c) T. Kim, J. Heo, J. Y. Lee, Y. J. Yoon, T. H. Lee, Y. S. Shin, I.-S. Kim, H. Kim, M. S. Jeong, I.-W. Hwang, B. Walker, P. S. Jo, B. Lim, J. Y. Kim, ACS Appl. Mater. Interfaces 2019, 11, 7208; d) Y. Xie, W. Wang, W. Huang, F. Lin, T. Li, S. Liu, X. Zhan, Y. Liang, C. Gao, H. Wu, Y. Cao, Energy Environ. Sci. 2019, 12, 3556.

[23] a) J.-L. Bredas, Mater. Horizons 2014, 1, 17; b) J. Sworakowski, Synthet. Met. 2018, 235, 125.

[24] M. Schwarze, K. S. Schellhammer, K. Ortstein, J. Benduhn, C. Gaul, A. Hinderhofer, L. P. Toro, R. Scholz, J. Kublitzki, S. Roland, Nat. Commun. 2019, 10, 1.

[25] a) H. Zhang, H. Yao, J. Hou, J. Zhu, J. Zhang, W. Li, R. Yu, B. Gao, S. Zhang, J. Hou, Adv. Mater. 2018, 30, 1800613; b) C. Sprau, F. Buss, M. Wagner, D. Landerer, M. Koppitz, A. Schulz, D. Bahro, W. Schabel, P. Scharfer, A. Colsmann, Energy Environ. Sci. 2015, 8, 2744.