

ARTICLE

Ultrafast Electron Transfer in All-Small-Molecule Photovoltaic Blends Promoted by Intermolecular Interactions in Cyanided Donors[†]

Guo-dong Wang^a, Zhi-xing Liu^a, Bei-bei Qiu^b, Zhi-guo Zhang^{b,c}, Rui Wang^a, Xiao-yong Wang^a, Jing Ma^d, Yong-fang Li^b, Min Xiao^{a,e}, Chun-feng Zhang^{a*}

a. National Laboratory of Solid State Microstructures, School of Physics, and Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing 210093, China

b. Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

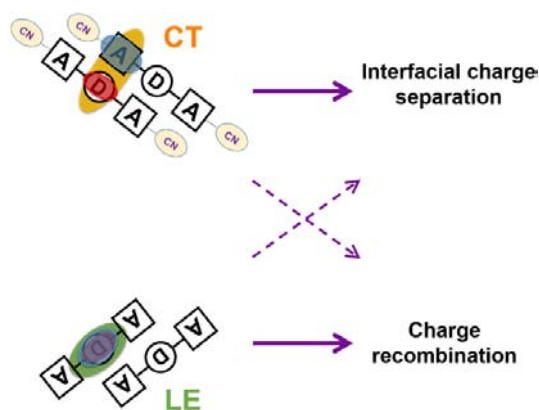
c. State key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

d. Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

e. Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Dated: Received on September 30, 2021; Accepted on October 12, 2021)

Cyano substitution has been established as a viable approach to optimize the performance of all-small-molecule organic solar cells. However, the effect of cyano substitution on the dynamics of photo-charge generation remains largely unexplored. Here, we report an ultrafast spectroscopic study showing that electron transfer is markedly promoted by enhanced intermolecular charge-transfer interaction in all-small-molecule blends with cyanided donors. The delocalized excitations, arising from intermolecular interaction in the moiety of cyano-substituted donor, undergo ultrafast electron transfer with a lifetime of ~ 3 ps in the blend. In contrast, some locally excited states, surviving in the film of donor without cyano substitution, are not actively involved in the charge separation. These findings well explain the performance improvement of devices with cyanided donors, suggesting that manipulating intermolecular interaction is an efficient strategy for device optimization.



Key words: Electron transfer, Organic solar cells, Charge-transfer interaction

I. INTRODUCTION

Organic solar cells (OSCs) have been regarded as cost-effective renewable power suppliers for next-generation flexible electronic devices [1–10]. With

well-defined molecular structures, OSCs using small molecules as both electron donors and acceptors have shown excellent batch-to-batch reproducibility for device performance [11–17], which is essential for practical applications. In the last few years, remarkable processes have been achieved for these all-small-molecule (ASM) OSCs with power-conversion efficiencies (PCEs) raising to $\sim 15\%$ benefiting from the rapid deployment of non-fullerene acceptors (NFAs) [18–21]. Nevertheless, the performance of ASM devices still lags behind the

[†]Part of Special Issue “John Z.H. Zhang Festschrift for celebrating his 60th birthday”.

*Author to whom correspondence should be addressed. E-mail: cfzhang@nju.edu.cn

devices using polymer donors and NFAs (with PCEs >18%) [22, 23]. For device optimization, it is critical to study the charge generation mechanism and elucidate the performance-limited process in ASM blends.

In principle, charge separation of photoexcited excitons primarily sets the upper efficiency limit of an OSC [24–33]. In a polymer/NFA blend, the widely-accepted model describes that a photoexcited exciton diffuses to the donor-acceptor (D-A) interface, forming an interfacial charge-transfer (xCT) state which further dissociates into a charge-separated (CS) state of free charges. For the polymer donors, most of them are co-polymers bearing alternating electron donating and accepting units. The charge-transfer interaction as well as the dipole-dipole interaction results in forming excited states with different degrees of CT character and wavefunction delocalization. Together with the Frenkel excitons (*i.e.*, the linear combinations of electronic excitations of each chromophore in the aggregates), some delocalized states are also excitable with spatially-separated electrons and holes, quoted as the excimer [34, 35], pseudo CT [36] or polaron pairs states [37–41] in previous studies. These weakly bound states with smaller binding energies may act as precursors for efficient charge separation. In the film of NFA, the intermolecular interaction in the acceptor moiety plays a similar role to that in the intermediate for charge separation [42–44]. Similar to NFAs, most high-performance small-molecule donors adopted in the ASM OSCs exhibit acceptor-donor-acceptor (A-D-A) structured architectures [45–48], where strongly electron-withdrawing end groups are attached to electron rich fused ring D unit. It remains elusive whether the intermolecular interaction in the intra-moiety domains affects charge generation in the ASM OSCs.

II. EXPERIMENTS

In this work, we study the charge generation dynamics in the blend films of ASM OSCs using ultrafast transient absorption (TA) spectroscopy. To highlight the effect of intermolecular interaction, we compare two blends consisting of the same acceptor (IDIC: 2,2'-((2Z,2'Z)-((4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile) but two different small-molecule donors with and without cyano substituent on the ester groups (namely, SM and CN-SM

(FIG. 1). With additional electron-withdrawing character induced by the cyano group, intermolecular charge-transfer interaction is enhanced in the donor moiety of CN-SM. In the blend with CN-SM, efficient ultrafast electron transfer from delocalized excited states is characterized with a lifetime of ~ 3 ps. On the contrary, we observe a loss channel of recombination from locally excited (LE) states on a similar time scale without involving in the charge separation process in the blend with SM. These results indicate that the excitation delocalization caused by the intermolecular interaction in the moiety of cyanided donor significantly promotes the efficiency of charge separation, which is confirmed by quantum chemical computation. These findings highlight the significance of intermolecular interaction for optimizing the performance of ASM OSCs which is valuable for future material synthesis and device design.

III. RESULTS AND DISCUSSION

In ASM OSCs, the active layers are aggregates of A-D-A molecules. Owing to the dipole-dipole and intermolecular charge-transfer interactions, photo excitations create excited states with different degrees of delocalization which may play different roles in charge generation and recombination (FIG. 1(a)) [44, 49–51]. The structures of molecules studied in this work are shown in FIG. 1(b). The molecules are selected as model systems for the complementary absorption spectral coverage of donors and acceptor (FIG. 1(c)), which allows to disentangle the process of electron and hole transfer by selective excitations. With pump at 470 nm or 710 nm, the donor and acceptor are primarily excited to trigger the channels of electron and hole transfer for charge separation. For TA spectroscopic measurements, the pump fluence is $\sim 3 \mu\text{J}/\text{cm}^2$ to minimize the effect of exciton-exciton annihilation as confirmed by fluence-dependent measurements (FIG. S1 in Supplementary materials). The effect of cyano substituent of the donor molecules on the device performance is significant. Using the same acceptor IDIC, the PCE doubles from $\sim 5\%$ to over 10% when the small-molecule donor SM is replaced by CN-SM in ASM OSCs [52].

The electron-withdrawing ability of the cyano substituent is manifested with a markedly enhanced solvent polarity effect of photoluminescence (PL) emission (FIG. 1 (d) and (e)). With increasing the solvent polarity, PL spectra show spectral redshifts while absorption

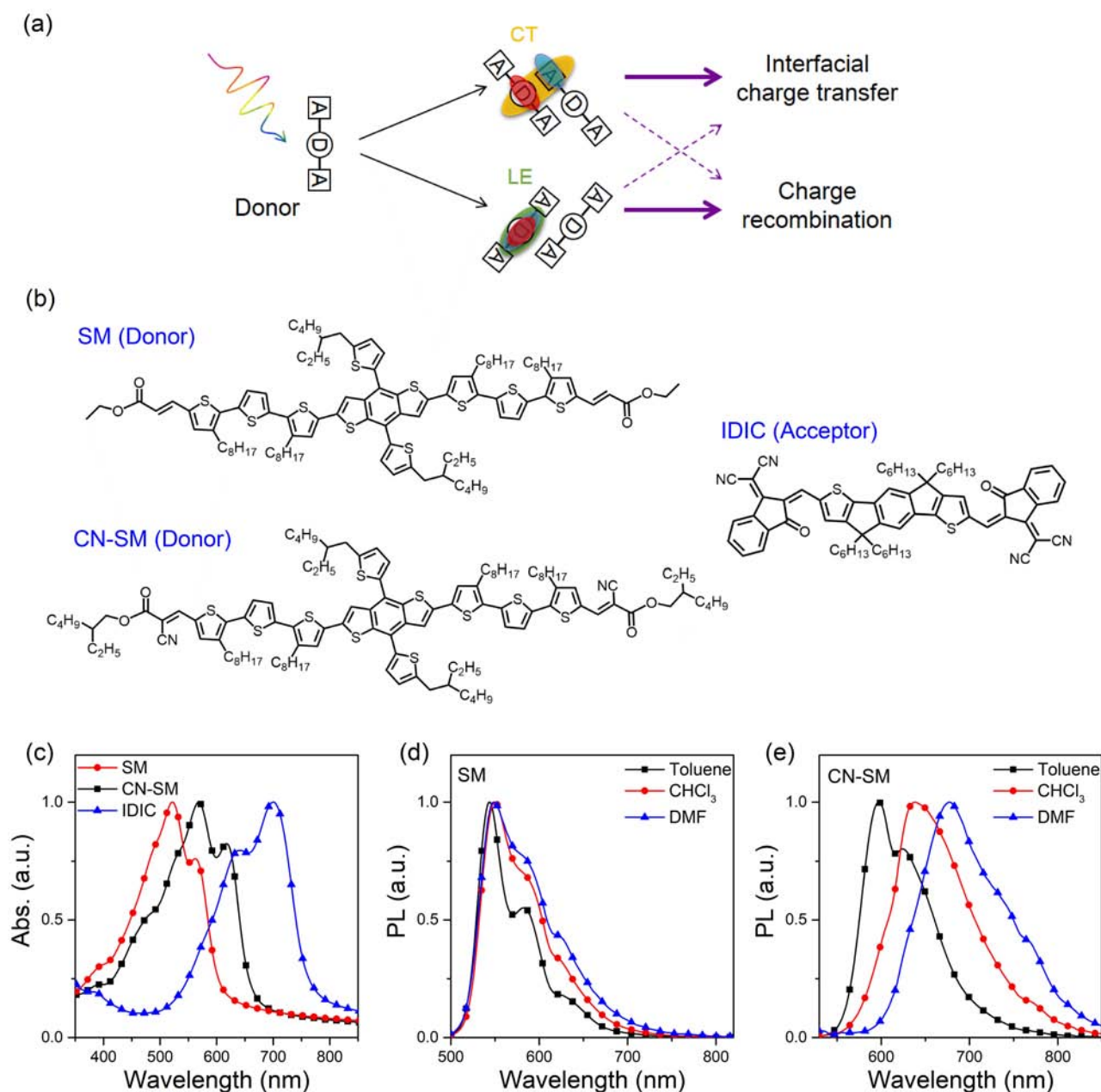


FIG. 1 (a) Schematic representation of the two channels involved in excitations with different degrees of delocalization in A-D-A small molecular donors. (b) Molecular structures of the two donors (SM and CN-SM) and the acceptor (IDIC) studied in this work. (c) The absorption spectra of the films of three samples. PL spectra of (d) SM and (e) CN-SM dissolved in different solvents.

spectra of the acceptors are nearly unchanged (FIG. S2 in Supplementary materials). Redshift of PL emission from CN-SM is more significant than that from SM, which is a clear evidence of a higher degree of charge-transfer character for primary excitations in CN-SM induced by cyano substituent [53–56]. The enhanced electron-withdrawing character may promote the intermolecular charge-transfer integral in the donor moiety,

resulting in delocalization of excited states [57, 58].

The effect of cyano substituent on the primary excitations in the donor films is characterized by TA spectroscopy. In FIG. 2, we compare the TA data recorded from the neat films of SM and CN-SM. The TA spectra for both samples exhibit similar spectral profiles for primary excitation, including the bleach in the visible absorption band and excited-state absorption (ESA) in

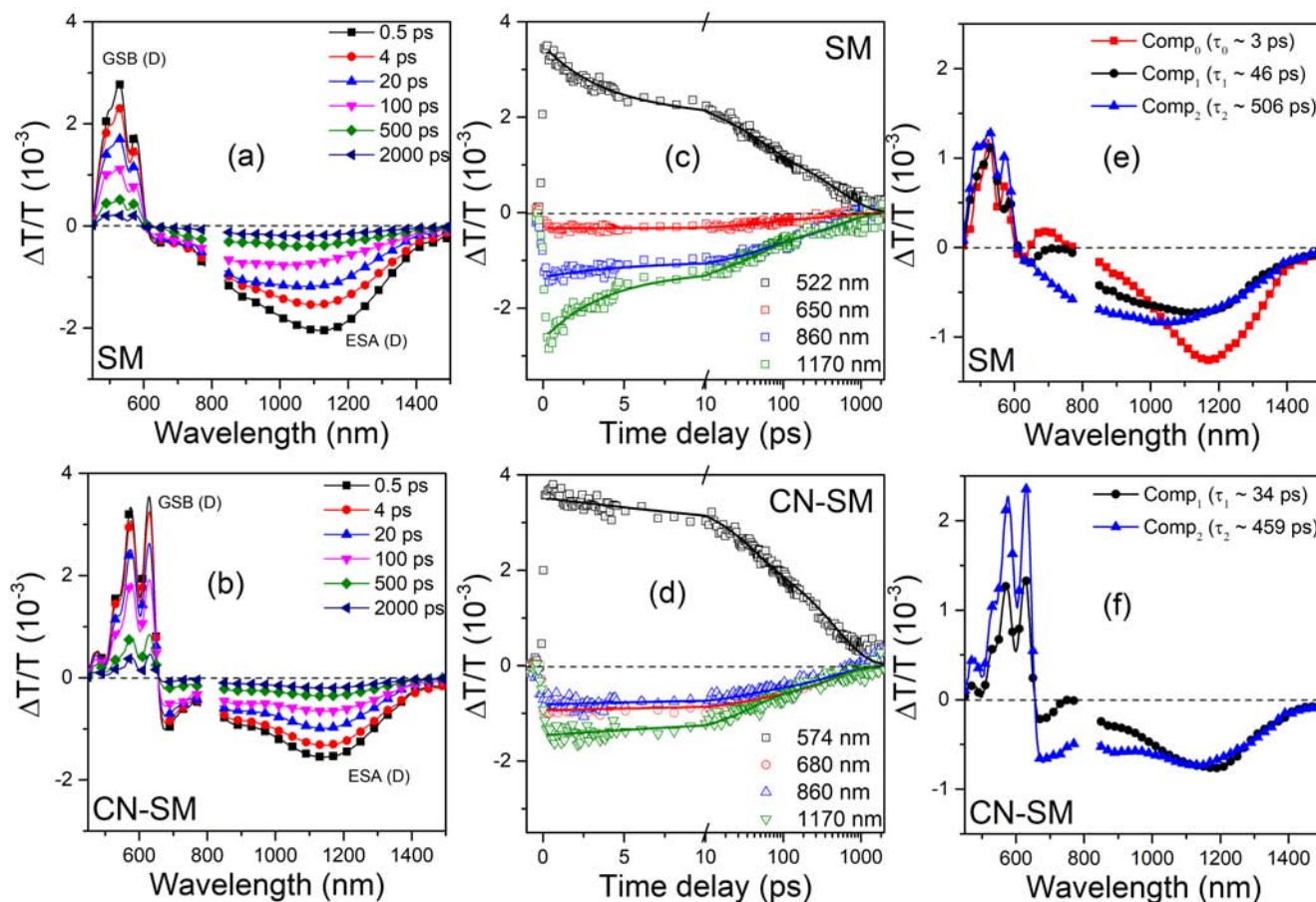


FIG. 2 TA spectra recorded at different time delays in the neat films of (a) SM and (b) CN-SM with pump at 470 nm, respectively. Time-resolved kinetic curves at different probe wavelength of (c) SM and (d) CN-SM, the additional fast decay shown in SM kinetic curves. The spectral features from global fitting of (e) SM and (f) CN-SM.

the near-infrared band (FIG. 2 (a, b)). Nevertheless, the dynamics shows markedly difference in the two samples especially for the signals at the early stages. The ESA feature recorded from the SM film shows a slight blue shift with a fast decay component with lifetime of ~ 3 ps in the range of 900–1300 nm (FIG. 2 (a, c)). Such a spectral transfer component is not observed in the ESA signal of CN-SM (FIG. 2 (b, d)). To elucidate the dynamics difference between the two samples, global fitting has been performed to extract different decay components (FIG. 2 (e, f), FIG. S3 in Supplementary materials). The dynamics of excited states in the SM film can be fitted with three exponential decay components with lifetime parameters of ~ 3 ps, ~ 46 ps, and ~ 506 ps, respectively. Only two components with lifetime parameters of ~ 34 ps and ~ 459 ps, similar to the two slower components in the SM sample, are required to reproduce the dynamics in the CN-SM film (FIG. 2(e)–(f)). The slowest components in both samples, also observable in the solution samples, are proba-

bly related to the intersystem crossing as supported by the triplet sensitization measurements (FIGS. S4–S6 in Supplementary materials). The different aspects for the two relatively fast components can be explained by considering the effect of excitation delocalization. The components with lifetimes on the 10 s of ps are related to the recombination of delocalized excitations in the film samples. The fastest component with the lifetime of ~ 3 ps, only present in the film of SM, can be ascribed to the short-lived localized excitations. In the CN-SM sample, the delocalized excitation dominates with enhanced intermolecular charge-transfer interaction induced by the cyano substituent while local excitations still contribute significantly in the SM sample.

To verify the above assignments, we survey the intermolecular charge-transfer interaction in these films by quantum chemistry computation. Initially, the molecular packings in the CN-SM films are characterized by grazing-incidence wide-angle X-ray scattering (GIWAXS) method [59] (FIG. 3 (a) and (b)). In the in-

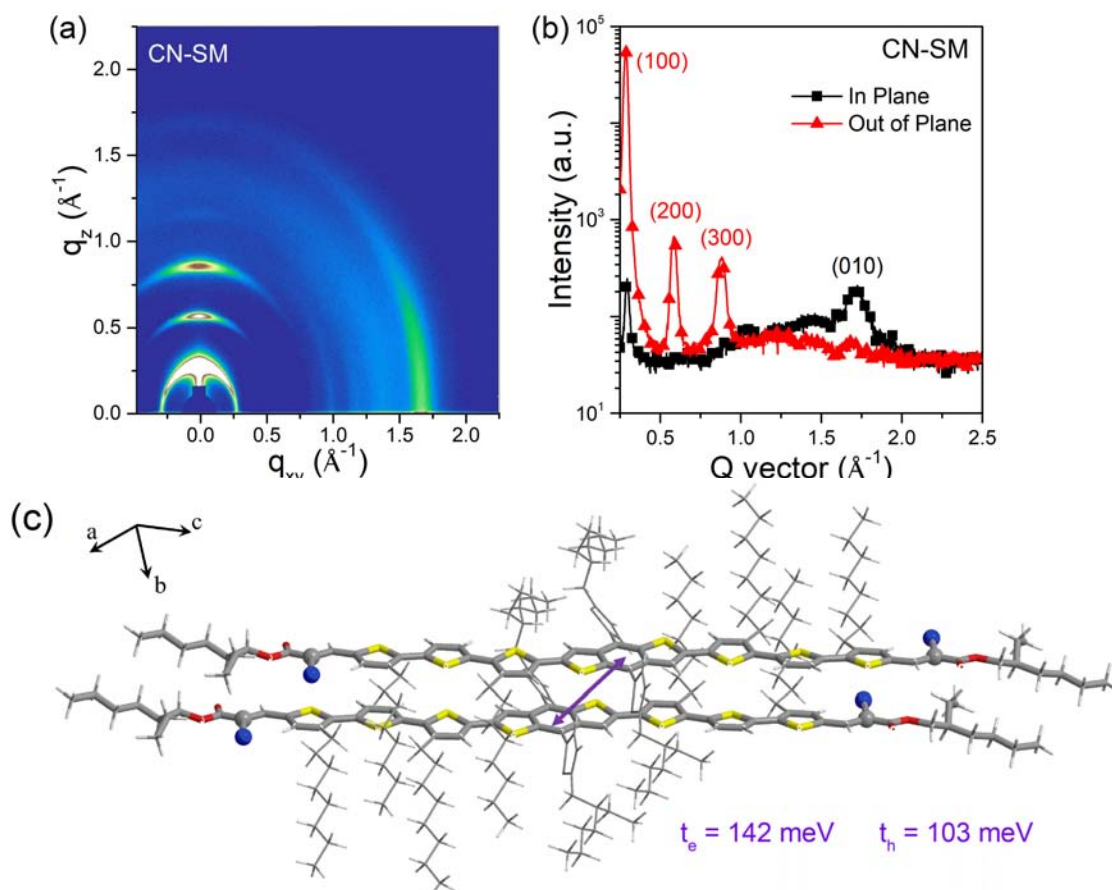


FIG. 3 (a) Grazing-incidence wide-angle X-ray scattering image of CN-SM. (b) Line cuts of the GIWAXS images of the neat film of CN-SM. (c) Calculated charge transfer integrals of the closest molecule in the film of CN-SM.

plane direction, the signal recorded from the CN-SM film shows a pronounced peak (010) at 1.71 \AA^{-1} , corresponding to a π - π stacking distance of 3.68 \AA . The short intermolecular separation facilitates significant spatial overlap between the highest occupied and the lowest unoccupied molecular orbitals (HOMOs and LUMOs, respectively) on neighboring molecules [60, 61]. To quantify the intermolecular interaction, we calculate the charge-transfer integral for the nearest molecules in the films with optimized structures (FIGS. S7, S8 and Table S1 in Supplementary materials). In the CN-SM films, the values for electron transfer integral (t_e) and hole transfer integral (t_h) are calculated to be $\sim 142 \text{ meV}$ and $\sim 103 \text{ meV}$, respectively. In the SM film, the molecule separation distance is similar to that of CN-SM (see FIG. S9, Table S2 and S3 in Supplementary materials). Nevertheless, the calculated values of charge-transfer integrals (t_e of $\sim 49 \text{ meV}$ and t_h of $\sim 72 \text{ meV}$) are much smaller. The computation results support that the electron withdrawing ability of the cyano substituent promotes the intermolecular charge-

transfer interaction, which can explain the differences for the primary excitations for SM and CN-SM considering certain structure diversity in the film samples. The large intermolecular interaction results in the primary channel of charge-transfer excitations in the CN-SM films while some local excitations survive in the SM films with relatively weak intermolecular interaction.

Next, we study the impact of the delocalized excitation on the interfacial charge separation process in the blends of active layers. In the ASM devices with NFAs, both channels of electron transfer and hole transfer contribute substantially to the charge generation. The dynamics of hole transfer in the two blend films with SM or CN-SM is shown in FIG. 4 by selectively pumping the acceptor IDIC at 710 nm. The hole transfer process is manifested with a speedup in the decay of the excited dynamics of primary excitations in the acceptor together with a rise of the signal of the excited states in the donor. The TA spectra after hole transfer show spectral features similar to that at the CS state as characterized by the photo-induced absorption (PIA)

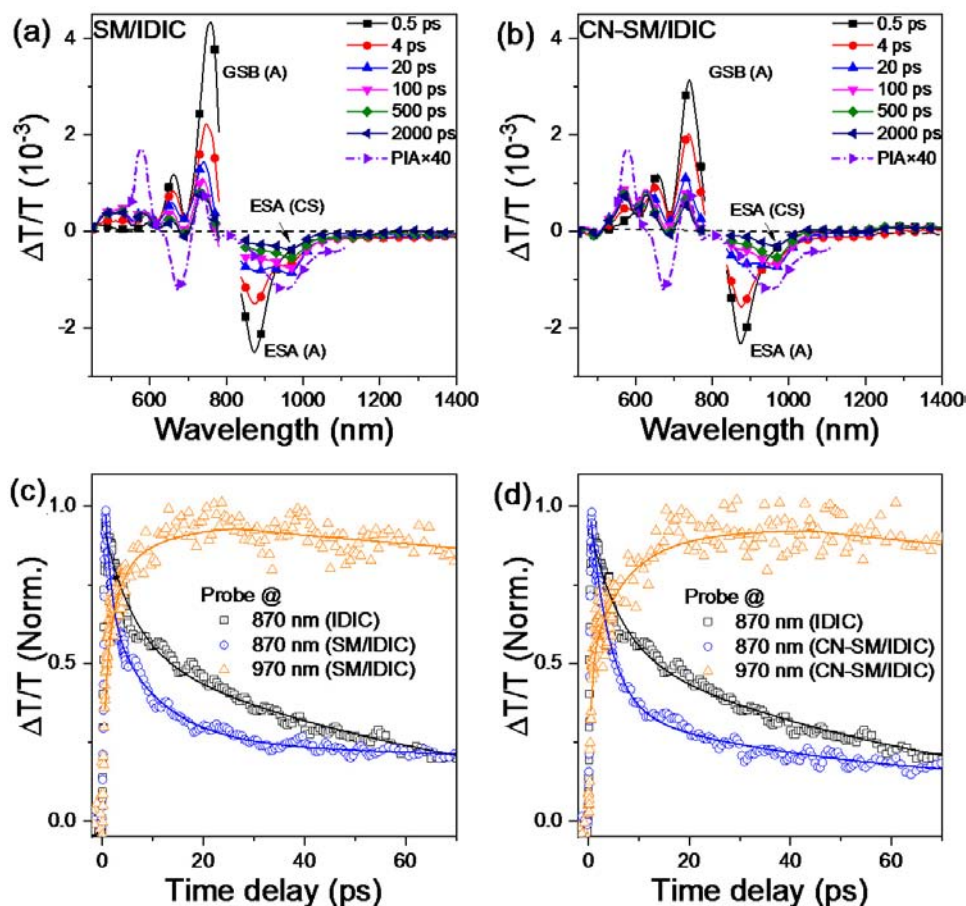


FIG. 4 Hole transfer dynamics in the blend films. TA spectra recorded at different time delays in the blend films of (a) SM/IDIC and (b) CN-SM/IDIC with optical pump at 710 nm compared with the PIA spectra at CS states upon weak excitation, respectively. Time-resolved kinetic curves probed at 870 nm and 970 nm in the blend films of (c) SM/IDIC and (d) CN-SM/IDIC compared with the kinetic curve probed at 870 nm in the neat film of IDIC.

spectra upon weak continuous-wave excitation [62–64]. The hole transfer processes in the blend films with SM and CN-SM show similar dynamic behaviors with the fast decay component probed at 870 nm being shortened from ~ 18 ps in neat IDIC film to ~ 3 ps in both blend films (FIG. 4(c, d) and FIG. S10 in Supplementary materials). On a same time scale, the ESA signals at 970 nm in both blends show rising behaviors as charge separation from the channel of hole transfer. The similar dynamics of hole transfer in the two blends suggests that the donor/acceptor interfacial interactions are similar in the blends with two different donors [31]. The similar hole transfer dynamics implies that nanoscale morphologies and molecular stacking features at the donor/acceptor interfaces are similar for interfacial charge dynamics in both samples [65–67], which is consistent with the results by GIWAXS measurements (FIG. S11 in Supplementary materials).

Strikingly, electron transfer shows markedly differ-

ence in the two blends with SM and CN-SM. FIG. 5 (a) and (b) show the TA data recorded from the two blend films with optical pump at 470 nm which is selected to avoid the major band of acceptor absorption. Nevertheless, some direct optical excitation of the acceptor is also presented. As a result, the TA data are entangled with signals from electron and hole transfer processes. Fortunately, the signal in the spectral range >1100 nm is not observed in either the signal of photo-excitation in the neat IDIC film (FIG. S12 in Supplementary materials) or the hole transfer process from acceptor to donor (FIG. 4), which is solely contributed by the excited states in the donors. The signals in this wavelength range allow us to extract the dynamics of interfacial electron transfer process triggered by the excitations in the two donors. We compare the kinetics probed at the major ESA features at 1170 nm in the neat donor films and the blend films with SM (FIG. 5(c)) and CN-SM (FIG. 5(d)), respectively. In

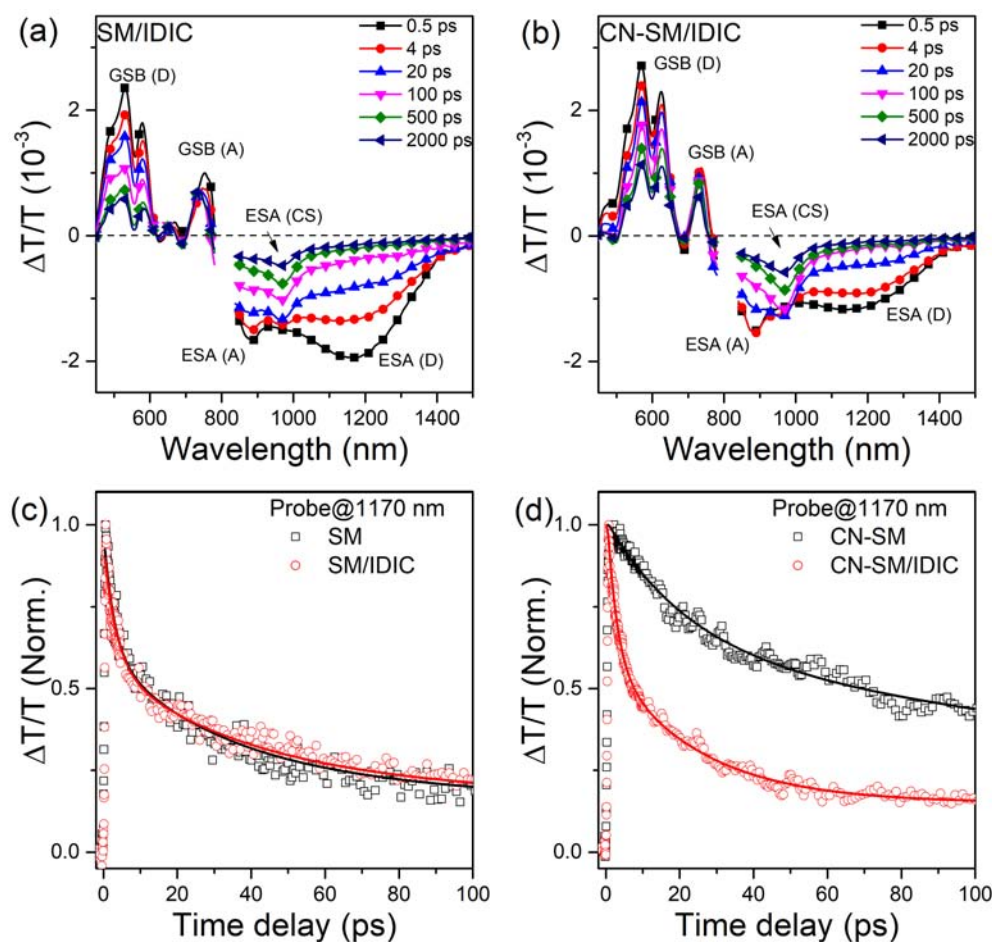


FIG. 5 Electron transfer dynamics in the blend films. TA spectra recorded at different time delays in the blend films of (a) SM/IDIC and (b) CN-SM/IDIC with optical pump at 470 nm, respectively. Time-resolved kinetic curves probed at 1170 nm in the blend films of (c) SM/IDIC and (d) CN-SM/IDIC compared with the kinetics in the neat donor samples.

the blend film with CN-SM, the lifetime of early-stage decay probed at 1170 nm is shortened from ~ 31 ps in the neat donor film to about ~ 3 ps in the blend film, indicating that over 90% of photo-excited excitons undergo the ultrafast electron transfer channels of charge separation. In contrast, the early-stage dynamics in the blend with SM remains nearly unchanged from that in the neat SM film, implying the electron transfer process is much less efficient. As noted above, the differences between the interfacial morphologies are not significant in the blends with SM and CN-SM. The difference in the electron transfer behavior is probably related to the different forms of the excited states in the two blends. Since the early-stage dynamics is primarily governed by the local excitations in the film of SM, the absence of ultrafast electron transfer in the SM/IDIC blend suggests that the local excitation states are not actively involved in the interfacial charge separation of the ASM OSC blends. These results suggest that the intermolecular

charge-transfer interaction in the CN-SM films plays an essential role for efficient charge separation.

The above results suggest that the delocalization of the primary excited states in ASM OSCs is essential for photocharge generation as that in the polymer/NFA OSCs. In polymers, the delocalized excited states inherently arise from the intrachain and interchain interaction between the conjugated units and the interplay between electronic and vibration degrees of freedom [34, 39–41, 68]. For small molecules, photo excitations are generally localized at individual molecules. Fortunately, the degree of excitation delocalization in a film of small molecules may be significantly enhanced by the intermolecular interaction in the molecular aggregates. Engineering the ending groups is an effective approach to manipulate the charge-transfer interaction between small molecules [69, 70], which is valuable for future device optimization.

IV. CONCLUSION

We have used TA spectroscopy complemented by quantum chemical computations to study the dynamics of photo-charge generation in the ASM blends with the donors of SM and CN-SM. The electron withdrawing ability of the cyano substituent promotes the intermolecular charge-transfer interaction which significantly suppresses the formation of localized excitations in the donor aggregates. The delocalized excitations in the blends with CN-SM donor and IDIC acceptor undergo highly electron transfer process with lifetime of ~ 3 ps, which can well explain the improvement of device performance in comparison with the system without cyano substituent. The experimental data suggest a scenario similar to that in polymer solar cells where the delocalized states act as precursors for interfacial charge separation in the ASM devices. The finding in this work suggests a strategy to optimize the device by manipulating intermolecular interaction through molecule engineering.

Supplementary materials: Experimental methods, supporting spectral results and computation details are available. Fluence-dependent measurements (FIG. S1), absorption spectra of solution samples (FIG. S2), global fitting data (FIG. S3), triplet sensitization measurements (FIGs. S4–6), calculation structures (FIGs. S7–S8), GIWAXS data of SM (FIG. S9), hole transfer dynamics (FIG. S10), GIWAXS data of blends (FIG. S11), TA spectra of IDIC (FIG. S12), calculated crystal lattice parameters (Table S1), predicted structures of SM and CN-SM (Tables S2–3), as well as calculated charge transfer integrals (Table S4) are given.

V. ACKNOWLEDGMENTS

This work is supported by the National Key R&D Program of China (No.2018YFA0209100 and No.2017YFA0303703), the National Natural Science Foundation of China (No.21922302, No.21873047, No.91850105, and No.91833305), and the Fundamental Research Funds for the Central Universities (No.0204-14380126). Chun-feng Zhang acknowledges financial support from the Tang Scholar Program. The authors acknowledge Dr. Xue-wei Wu at Nanjing University for the technical assistance.

- [1] G. Li, R. Zhu, and Y. Yang, *Polymer Solar Cells Nat. Photon.* **6**, 153 (2012).
- [2] Y. Huang, E. J. Kramer, A. J. Heeger, Bazan, and G. C. Bulk, *Chem. Rev.* **114**, 7006 (2014).
- [3] L. Y. Lu, T. Y. Zheng, Q. H. Wu, A. M. Schneider, D. L. Zhao, and L. P. Yu, *Chem. Rev.* **115**, 12666 (2015).
- [4] P. Cheng, G. Li, X. W. Zhan, and Y. Yang, *Nat. Photon.* **12**, 131 (2018).
- [5] G. J. Hedley, A. Ruseckas, and I. D. W. Samuel, *Chem. Rev.* **117**, 796 (2017).
- [6] O. Inganaes, *Adv. Mater.* **30**, 1800388 (2018).
- [7] C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, and X. Zhan, *Nat. Rev. Mater.* **3**, 18003 (2018).
- [8] A. Karki, A. J. Gillett, R. H. Friend, and T. Q. Nguyen, *Adv. Energy Mater.* **11**, 2003441 (2021).
- [9] J. Hou, O. Inganas, R. H. Friend, and F. Gao, *Nat. Mater.* **17**, 119 (2018).
- [10] G. Zhang, J. Zhao, P. C. Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang, and H. Yan, *Chem. Rev.* **118**, 3447 (2018).
- [11] Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan, and A. Heeger, *Nat. Mater.* **11**, 44 (2012).
- [12] A. Mishra and P. Baeuerle, *Angew. Chem. Int. Ed.* **51**, 2020 (2012).
- [13] Q. Zhang, B. Kan, F. Liu, G. Long, X. Wan, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T. P. Russell, and Y. Chen, *Nat. Photon.* **9**, 35 (2015).
- [14] L. Yang, S. Zhang, C. He, J. Zhang, H. Yao, Y. Yang, Y. Zhang, W. Zhao, and J. Hou, *J. Am. Chem. Soc.* **139**, 1958 (2017).
- [15] Y. Huo, X. T. Gong, T. K. Lau, T. Xiao, C. Yan, X. Lu, G. Lu, X. Zhan, and H. L. Zhang, *Chem. Mater.* **30**, 8661 (2018).
- [16] R. Zhou, Z. Jiang, C. Yang, J. Yu, J. Feng, M. A. Adil, D. Deng, W. Zou, J. Zhang, K. Lu, W. Ma, F. Gao, and Z. Wei, *Nat. Commun.* **10**, 5393 (2019).
- [17] K. Gao, S. B. Jo, X. Shi, L. Nian, M. Zhang, Y. Kan, F. Lin, B. Kan, B. Xu, Q. Rong, L. Shui, F. Liu, X. Peng, G. Zhou, Y. Cao, and A. K. Y. Jen, *Adv. Mater.* **31**, 1807842 (2019).
- [18] J. Gao, J. Ge, R. Peng, C. Liu, L. Cao, D. Zhang, B. Fanady, L. Hong, E. Zhou, and Z. Ge, *J. Mater. Chem. A* **8**, 7405 (2020).
- [19] D. Hu, Q. Yang, H. Chen, F. Wobben, V. M. Le Corre, R. Singh, T. Liu, R. Ma, H. Tang, L. J. A. Koster, T. Duan, H. Yan, Z. Kan, Z. Xiao, and S. Lu, *Energy Environ. Sci.* **13**, 2134 (2020).
- [20] J. Qin, C. An, J. Zhang, K. Ma, Y. Yang, T. Zhang, S. Li, K. Xian, Y. Cui, Y. Tang, W. Ma, H. Yao, S. Zhang,

- B. Xu, C. He, and J. Hou, *Sci. China Mater.* **63**, 1142 (2020).
- [21] Y. Huo, H. L. Zhang, and X. Zhan, *ACS Energy Lett.* **4**, 1241 (2019).
- [22] Y. Cui, H. Yao, J. Zhang, K. Xian, T. Zhang, L. Hong, Y. Wang, Y. Xu, K. Ma, C. An, C. He, Z. Wei, F. Gao, and J. Hou, *Adv. Mater.* **32**, 1908205 (2020).
- [23] Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang, and L. Ding, *Sci. Bull.* **65**, 272 (2020).
- [24] T. M. Clarke and J. R. Durrant, *Chem. Rev.* **110**, 6736 (2010).
- [25] A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne, and R. H. Friend, *Science* **335**, 1340 (2012).
- [26] S. M. Falke, C. A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A. De Sio, A. Rubio, G. Cerullo, E. Molinari, and C. Lienau, *Science* **344**, 1001 (2014).
- [27] S. Gelinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan, and R. H. Friend, *Science* **343**, 512 (2014).
- [28] A. C. Jakowetz, M. L. Bohm, J. Zhang, A. Sadhanala, S. Huettner, A. A. Bakulin, A. Rao, and R. H. Friend, *J. Am. Chem. Soc.* **138**, 11672 (2016).
- [29] D. M. Stoltzfus, J. E. Donaghey, A. Armin, P. E. Shaw, P. L. Burn, and P. Meredith, *Chem. Rev.* **116**, 12920 (2016).
- [30] T. F. Hinrichsen, C. C. S. Chan, C. Ma, D. Palecek, A. Gillett, S. Chen, X. Zou, G. Zhang, H. L. Yip, K. S. Wong, R. H. Friend, H. Yan, A. Rao, and P. C. Y. Chow, *Nat. Commun.* **11**, 5617 (2020).
- [31] A. Karki, J. Vollbrecht, A. J. Gillett, S. S. Xiao, Y. Yang, Z. Peng, N. Schopp, A. L. Dixon, S. Yoon, M. Schrock, H. Ade, G. N. M. Reddy, R. H. Friend, and T. Q. Nguyen, *Energy Environ. Sci.* **13**, 3679 (2020).
- [32] A. Karki, J. Vollbrecht, A. J. Gillett, P. Selter, J. Lee, Z. Peng, N. Schopp, A. L. Dixon, M. Schrock, V. Nadazydy, F. Schauer, H. Ade, B. F. Chmelka, G. C. Bazan, R. H. Friend, and T. Q. Nguyen, *Adv. Energy Mater.* **10**, 2001203 (2020).
- [33] M. Saladina, P. S. Marques, A. Markina, S. Karuthedath, C. Wopke, C. Gohler, Y. Chen, M. Allain, P. Blanchard, C. Cabanetos, D. Andrienko, F. Laquai, J. Gorenflot, and C. Deibel, *Adv. Funct. Mater.* **31**, 2007479 (2021).
- [34] O. G. Reid, R. D. Pensack, Y. Song, G. D. Scholes, and G. Rumbles, *Chem. Mater.* **26**, 561 (2014).
- [35] S. A. Jenekhe and J. A. Osaheni, *Science* **265**, 765 (1994).
- [36] B. S. Rolczynski, J. M. Szarko, H. J. Son, Y. Liang, L. Yu, and L. X. Chen, *J. Am. Chem. Soc.* **134**, 4142 (2012).
- [37] D. Di Nuzzo, D. Viola, F. S. U. Fischer, G. Cerullo, S. Ludwigs, and E. Da Como, *J. Phys. Chem. Lett.* **6**, 1196 (2015).
- [38] R. Wang, Y. Yao, C. Zhang, Y. Zhang, H. Bin, L. Xue, Z. G. Zhang, X. Xie, H. Ma, X. Wang, Y. Li, and M. Xiao, *Nat. Commun.* **10**, 398 (2019).
- [39] A. De Sio, F. Troiani, M. Maiuri, J. Rehault, E. Sommer, J. Lim, S. F. Huelga, M. B. Plenio, C. A. Rozzi, G. Cerullo, E. Molinari, and C. Lienau, *Nat. Commun.* **7**, 13742 (2016).
- [40] R. Tautz, E. Da Como, C. Wiebeler, G. Soavi, I. Dumsch, N. Froehlich, G. Grancini, S. Allard, U. Scherf, G. Cerullo, S. Schumacher, and J. Feldmann, *J. Am. Chem. Soc.* **135**, 4282 (2013).
- [41] R. Tautz, E. Da Como, T. Limmer, J. Feldmann, H. J. Egelhaaf, E. von Hauff, V. Lemaure, D. Beljonne, S. Yilmaz, I. Dumsch, S. Allard, and U. Scherf, *Nat. Commun.* **3**, 970 (2012).
- [42] R. Wang, C. Zhang, Q. Li, Z. Zhang, X. Wang, and M. Xiao, *J. Am. Chem. Soc.* **142**, 12751 (2020).
- [43] Q. Guo, Q. Guo, Y. Geng, A. Tang, M. Zhang, M. Du, X. Sun, and E. Zhou, *Mater. Chem. Front.* **5**, 3257 (2021).
- [44] G. Zhang, X. K. Chen, J. Xiao, P. C. Y. Chow, M. Ren, G. Kupgan, X. Jiao, C. C. S. Chan, X. Du, R. Xia, Z. Chen, J. Yuan, Y. Zhang, S. Zhang, Y. Liu, Y. Zou, H. Yan, K. S. Wong, V. Coropceanu, N. Li, C. J. Brabec, J. L. Bredas, H. L. Yip, and Y. Cao, *Nat. Commun.* **11**, 3943 (2020).
- [45] H. Bin, Y. Yang, Z. G. Zhang, L. Ye, M. Ghasem, S. Chen, Y. Zhang, C. Zhang, C. Sun, L. Xue, C. Yang, H. Ade, and Y. Li, *J. Am. Chem. Soc.* **139**, 5085 (2017).
- [46] Z. Zhou, S. Xu, J. Song, Y. Jin, Q. Yue, Y. Qian, F. Liu, F. Zhang, and X. Zhu, *Nat. Energy* **3**, 952 (2018).
- [47] B. Qiu, Z. Chen, S. Qin, J. Yao, W. Huang, L. Meng, H. Zhu, Y. Yang, Z. G. Zhang, and Y. Li, *Adv. Mater.* **32**, 1908373 (2020).
- [48] Y. Wang, Y. Wang, B. Kan, X. Ke, X. Wan, C. Li, and Y. Chen, *Adv. Energy Mater.* **8**, 1802021 (2018).
- [49] S. Athanasopoulos, H. Baessler, and A. Koehler, *J. Phys. Chem. Lett.* **10**, 7107 (2019).
- [50] K. H. Park, W. Kim, J. Yang, and D. Kim, *Chem. Soc. Rev.* **47**, 4279 (2018).
- [51] J. Shi, A. Isakova, A. Abudulimu, M. van den Berg, O. K. Kwon, A. J. Meixner, S. Y. Park, D. Zhang, J. Gierschner, and L. Luer, *Energy Environ. Sci.* **11**, 211 (2018).
- [52] B. Qiu, L. Xue, Y. Yang, H. Bin, Y. Zhang, C. Zhang, M. Xiao, K. Park, W. Morrison, Z. G. Zhang, and Y. Li, *Chem. Mater.* **29**, 7543 (2017).
- [53] S. Ellinger, K. R. Graham, P. Shi, R. T. Farley, T. T. Steckler, R. N. Brookins, P. Taraneekar, J. Mei, L. A. Padilha, T. R. Ensley, H. Hu, S. Webster, D. J. Hagan,

- E. W. Van Stryland, K. S. Schanze, and J. R. Reynolds, *Chem. Mater.* **23**, 3805 (2011).
- [54] G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma, and Z. Y. Wang, *Chem. Mater.* **20**, 6208 (2008).
- [55] S. Wang, X. Yan, Z. Cheng, H. Zhang, Y. Liu, and Y. Wang, *Angew. Chem. Int. Ed.* **127**, 13260 (2015).
- [56] L. Yao, S. Zhang, R. Wang, W. Li, F. Shen, B. Yang, and Y. Ma, *Angew. Chem. Int. Ed.* **53**, 2119 (2014).
- [57] H. Tamura and I. Burghardt, *J. Am. Chem. Soc.* **135**, 16364 (2013).
- [58] N. J. Hestand and F. C. Spano, *Chem. Rev.* **118**, 7069 (2018).
- [59] J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Salleo, and M. F. Toney, *Chem. Rev.* **112**, 5488 (2012).
- [60] G. A. DiLabio and E. R. Johnson, *J. Am. Chem. Soc.* **129**, 6199 (2007).
- [61] S. Grimme, *Angew. Chem. Int. Ed.* **47**, 3430 (2008).
- [62] A. Distler, P. Kutka, T. Sauermann, H. J. Egelhaaf, D. M. Guldi, D. Di Nuzzo, S. C. J. Meskers, and R. A. J. Janssen, *Chem. Mater.* **24**, 4397 (2012).
- [63] C. W. Schlenker, K. S. Chen, H. L. Yip, C. Z. Li, L. R. Bradshaw, S. T. Ochsenbein, F. Z. Ding, X. S. S. Li, D. R. Gamelin, A. K. Y. Jen, and D. S. Ginger, *J. Am. Chem. Soc.* **134**, 19661 (2012).
- [64] D. Baran, N. Gasparini, A. Wadsworth, C. H. Tan, N. Wehbe, X. Song, Z. Hamid, W. Zhang, M. Neophytou, T. Kirchartz, C. J. Brabec, J. R. Durrant, and I. McCulloch, *Nat. Commun.* **9**, 2059 (2018).
- [65] A. K. K. Kyaw, D. H. Wang, C. Luo, Y. Cao, T. Q. Nguyen, G. C. Bazan, and A. J. Heeger, *Adv. Energy Mater.* **4**, 1301469 (2014).
- [66] M. Morana, H. Azimi, G. Dennler, H. J. Egelhaaf, M. Scharber, K. Forberich, J. Hauch, R. Gaudiana, D. Waller, Z. H. Zhu, K. Hingerl, S. S. van Bavel, J. Loos, and C. J. Brabec, *Adv. Funct. Mater.* **20**, 1180 (2010).
- [67] F. Etzold, I. A. Howard, N. Forler, D. M. Cho, M. Meister, H. Mangold, J. Shu, M. R. Hansen, K. Muellen, and F. Laquai, *J. Am. Chem. Soc.* **134**, 10569 (2012).
- [68] Z. Guo, D. Lee, R. D. Schaller, X. Zuo, B. Lee, T. Luo, H. Gao, and L. Huang, *J. Am. Chem. Soc.* **136**, 10024 (2014).
- [69] G. Li, X. Zhang, L. O. Jones, J. M. Alzola, S. Mukherjee, L. W. Feng, W. Zhu, C. L. Stern, W. Huang, J. Yu, V. K. Sangwan, D. M. DeLongchamp, K. L. Kohlstedt, M. R. Wasielewski, M. C. Hersam, G. C. Schatz, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **143**, 6123 (2021).
- [70] G. Jia, S. Zhang, L. Yang, C. He, H. Fan, and J. Hou, *Acta Phys. Chim. Sin.* **35**, 76 (2019).