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基于小分子NDT高效异质结的超快动力学研究 (特激)

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摘 要:利用飞秒瞬态吸收光谱对三个经不同处理且光电性能有明显差异的 NDT 基异质结薄膜(无已 基取代混合膜,已基取代混合膜以及已基取代并做溶剂退火处理的混合膜)进行了研究。结果显示这 三个异质结薄膜,其电荷分离态大部分都是由激子态直接演化来的,并没有经过电荷转移态。在这三 个混合膜中,已基取代并做溶剂退火处理的混合膜表现出最大电荷分离产率,已基取代但不经过溶剂 退火处理的混合膜拥有最长的电荷分离态寿命。结合它们的电子-空穴迁移率,从动力学的角度给出 了已基取代及溶剂退火处理增强光电转换效率的原因在于提高了电荷分离态寿命、增强了电荷分离产 率以及平衡了电子-空穴迁移率。此研究可为将来优化光电转换效率提供参考。 关键词:超快动力学;有机光伏材料;瞬态吸收光谱;小分子;化学修饰;溶剂退火

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Ultrafast Dynamics Investigation on Efficient NDT-based Small Molecule Heterojunctions (Invited)

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Abstract: Three heterojunction blend films composed of NDT-based small molecule with different treatment and performance (null substituents, hexyl-substituents, hexyl-substituents with solvent vapor annealing treatment) were investigated by femtosecond transient absorption spectroscopy. The transient absorption results show that the charge separation state is mainly evolved from exciton state directly for all

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the three heterojunctions. The largest charge separation yield is found in the hexyl-substituents blend film with solvent vapor annealing treatment and the longest charge separation state lifetime is found in the hexyl-substituents blend film without solvent vapor treatment. In combination with the electron-hole mobility results, a dynamics viewpoint of the increased charge separation state lifetime, the enhanced charge separation yield and the more balanced electron-hole mobility were provided for the explanation of the enhanced power conversion efficiency after hexyl-substituents and solvent vapor annealing treatment. This work also offers a guideline for performance optimization in the future.

Key words: Ultrafast dynamics; Organic photovoltaic materials; Transient absorption spectroscopy; Small molecules; Chemical modification; Solvent vapour annealing

OCIS Codes: 320.7150; 300.6530; 160.4890; 320.7163

0 Introduction

As a new generation of photovoltaic technology, organic solar cells have attracted extensive attention in recent years due to their advantages of low cost, light weight and solution processing^[1-6]. The latest research results showed that the Power Conversion Efficiency (PCE) of polymer–based Organic Solar Cells (OSCs) has exceeded 18%^[6-9]. Compared with polymer–based OSCs, All–Small–Molecule Organic Solar Cells (ASM–OSCs) are considered to have greater commercialization prospects due to their definite structure, easy synthesis of materials and small batch to batch differences^[10]. With the enormous devote of researchers, thousands of small molecular organic solar cell materials have been designed. The diversity of small molecule material and steady increase in PCE values bring a bright future for ASM–OSCs, which have stimulated great interest as an emerging alternative to the polymer counterparts^[11-17].

In the field of material engineering, many methods were employed to improve the device performance, such as rational design for both donor and acceptor materials and the good matching between them^[12, 18], chemical modification on the potential materials^[19-22] and thermal annealing or solvent vapor annealing treatment^[23-26] for crystallinity and morphology modulation. Currently, the power conversion efficiency of ASM–OSCs has reached 15.39%^[27], but it is still lower than that of polymer–based OSCs. For further development of ASM–OSCs, in–depth and comprehensive investigation is necessary.

In 2011, naphthalenedithiophene-based donor material was firstly introduced in the application of the photovoltaic device by Marks group^[28]. As an important part of the enedithiophene family, naphthalenedithiophene (NDT)-based molecules have been widely used as polymer donors, small molecule donors, and even non-fullerene molecular acceptors^[12, 29-31]. Currently, the best performance obtained on NDT-based ASM-OSCs is around 10% by WEI Zhixiang's group^[32]. NDT has a more extended π -conjugated system and a larger planar heteroarene structure, which leads to enhanced π -orbital overlapping, strong intermolecular interaction, and efficient charge transport, however, for ASM-OSCs based on NDT donors, encouraging PCEs are rarely reported. Recently, ZHU Xiaozhang's group synthesized NDT-based molecule with hexyl substituents at β position of thiophene, named as NDT-Hex, and obtained a higher PCE than that of null substituents. Moreover, the PCE is further increased after Solvent Vapor Annealing (SVA) treatment^[33]. Although the positive effect of the side chain modification and SVA treatment on PCE is explained in the aspect of morphology, the investigation from the viewpoint of photo-generated carrier dynamics is lacking.

In organic solar cells, photophysical processes leading to photocurrent generation are usually described as: 1) the active layer materials of organic solar cells absorb sunlight photons and consequently generate electronhole (E-H) pairs (exciton); 2) the exciton diffuses toward the donor-acceptor (D-A) interface, where an intermediate Charge Transfer (CT) state is formed after an ultrafast CT reaction; 3) the CT state then further splits into free charges (Charged Separation, CS) by breaking the E-H pair binding energy under the driving force offered by the energy difference of the interface; 4) the free charges drift-diffuse in the bulk materials and are eventually collected by the cathode and anode electrodes. Each step is accompanied by loss processes, for example, incomplete photon absorption, exciton recombination, geminate recombination, bimolecular recombination and so on. As PCE is a measure of the ability to convert solar energy to electric energy through all the above photophysical processes, any factors that can influence the above photophysical processes could affect the final PCE. It is generally believed that the higher charge separation yield, the more conducive to the generation of free charges, a more balanced carrier mobility and a longer lifetime of CS state are facilitated to the charge transport and collection, which positively contribute to the overall PCE. In short, PCE is a comprehensive measurement index, before further investigation on the photo-generated carrier dynamics, one cannot conclude an improved PCE is benefited from which photophysical processes. To study the effect of the side chain modification and SVA treatment on PCE of NDT-based ASM-OSCs from the aspect of dynamic, we applied femtosecond Transient Absorption (fs-TA) measurement on heterojunctions composed of NDT (NDT-Hex) as donors and PC₇₁BM as acceptors. We extracted the lifetime of CS state and the CS yield through Global Analysis (GA) of TA spectra and discussed their contribution to the PCE upon side chain modification and SVA treatment.

1 Materials and methods

1.1 Sample preparation

The synthetic details and the spectroscopic characterization of materials used here have been reported elsewhere^[33]. Starting materials were obtained from Adamas, Aldrich or J&K, and used as received. All blends were spun from chloroform with 10 mg mL⁻¹ for 1: 0.8 blends (D: A mass ratio) in an argon-protected glovebox. All heterojunction films were prepared on thin glass substrates, which were cleaned by detergent, deionized water, acetone and isopropanol and then exposed to ultraviolet-ozone chamber for 20 min. The substrates were subsequently placed in an argon-filled glovebox and spun at 1 500 r/min for 60 s.

1.2 UV-Vis absorption spectra measurements

All steady-state spectra of samples were measured using Agilent Technologies Cary 60 UV-Vis spectrophotometer. The spectral range of the source is $200 \sim 1\ 100\ nm$.

1.3 Femtosecond pump-probe absorption spectroscopy

Fs-TA spectra were acquired on a home-build TA system. The output of a Ti: Saphire laser system (Astrella, Coherent company, The United States) was split to generate pump and probe beams. About 0.6 W of 800 nm laser pulse was introduced to a noncollinear optical parametric amplifier (Topas White, Light Conversion, Lithuania) to generate visible pump beam. About 3 mW of 800 nm laser pulse was focused onto a sapphire crystal to generate a supercontinuum and used as a probe beam. To eliminate polarization selection effects, the angle between the polarizations of pump and probe beams was set to the magic angle (54.7°). The transmitted probe beam through the sample was sent to a spectrometer and collected by a CCD. The delay time between pump and probe is controlled by a high-resolution delay stage. No significant sample degradation was observed throughout the TA experiments. Repeat measurements were done on several different spots for each sample to ensure the reliable results. Global analysis of the dispersion-corrected data was done using CarpetView software package.

1.4 Dynamics model and global analysis

The fs-TA data are analyzed globally using a target model based on the method discussed in detail in previous articles^[34-35]. The data of pure donor films was fitted to obtain the recombination rate of Exciton (EX) and the formation and recombination rates of Intramolecular Charge Transfer (ICT). For blends, a new CS state is introduced into the whole target model due to efficient exciton separation. In this model, the formation of CS is simply separated to two main routes^[36]. One comes from the initial exciton considering the partial populations at the interfaces (fast delocalization due to strong vibronic coupling), and the other origins from the further splitting of CT during the charge diffusion.

2 Experimental results and discussion

The chemical structures of NDT and NDT-Hex are shown in Fig. 1. Both molecules are comprised of an electron-rich NDT core and two electron-deficient units. The mainly structure difference of them is the hexyl group is introduced at β -position on the side chain of NDT-Hex molecules. Fig. 2 shows the normalized UV-Vis absorption spectra of neat films and blend films. As shown in Fig. 2(a), NDT and NDT-Hex solid films share very similar absorption profiles, both the neat films exhibit "two-peaks" feature above the absorption

onset. It is also noted that the relative strengths of the two peaks are different, which suggests different packing states. As explained in previous study^[33], the introduction of hexyl group on the side chain enlarges the steric hindrance and affect the π -planarity, which is not conducive to the close packing of NDT-Hex molecules during the film formation process. The absorption spectra of blend films were also given for comparison, which shows that the addition of acceptors of PC₇₁BM mainly contributes to the absorption in the short wavelength region.



Fig. 1 Chemical structure of NDT and NDT-Hex small molecule donors



Fig. 2 Normalized UV-Vis absorption spectra

To unravel the effect of side chain modification and SVA treatment on the photoelectric processes in the heterojunction film, fs-TA spectroscopy was conducted on neat films and blend films. A low pump fluence was implemented to eliminate the effects of multiphoton absorption and annihilation processes between excitons and/ or charges. All samples were measured under the same condition.

Figs. 3(a) and (d) show the TA carpet of neat films upon excitation with 610 nm optical pump. The pump here only excites the donor material, which is also confirmed by zero TA signal when the sample is replaced by neat PC₇₁BM film. NDT and NDT-Hex shows similar TA response. Both of them are composed of one negative band and a part of positive band in the probe spectral region. The shape of negative band resembles the shape of the ground-state absorption, and thus this band is assigned to the Ground-State Bleaching (GSB) of donor material^[37-38]. The TA signal decays over ~100 ps but does not fall to zero. The positive band around 720 nm is attributed to the Excited State Absorption (ESA). Figs.3(c) and (f) present the normalized typical TA traces at 640 nm (GSB) and 720 nm (ESA). Interestingly, the dynamics behaviors of the two neat films are almost the same, which means although the hexyl group affect the molecules packing state or film morphology, the relaxation of the excited states for neat films, like charge transfer, charge recombination etc. occurred within molecules and thus are not sensitive to the packing state or film quality.

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Fig. 3 TA measurement results of neat films

Fig.4 shows the TA results of three heterojunction films (NDT:PC₇₁BM, NDT-Hex:PC₇₁BM and NDT-Hex:PC₇₁BM-SVA). The spectral features of blend films are almost identical to those of neat films with one GSB band and part of ESA band. Fig. 4(g) and (h) presents the normalized TA traces of the three blend films at the probe wavelength of 640 nm and 720 nm. The TA signals of the blend film persist to the time scale longer than that in neat film, suggesting other competing processes, such as intermolecular charge transfer and charge separation in blend films. The TA traces in blend films shows that the decay of 640 nm is slowest for NDT-Hex: PC₇₁BM film while the other two films show similar fast decay. In contrast, in the TA trace of 720 nm (ESA), NDT: PC₇₁BM exhibits fastest dynamics decay and NDT-Hex: PC₇₁BM and NDT-Hex: PC₇₁BM exhibits fastest dynamics decay and NDT-Hex: PC₇₁BM and NDT-Hex: PC₇₁BM film while the other, the initial EX state and the followed CT and CS states are severely overlapped in spectra, obviously, it's difficult to conclude interconversion dynamics only from the overall TA traces.





Fig. 4 TA measurement results of blend films

To address the above issue, Global Analysis (GA) procedure was applied to all the blend films based on the model described in the method part as shown in Fig.5(a) where three states were involved (EX state, CT state, CS state). The CT state refers to the situation in which the hole delocalized on the Highest Occupied Molecular Orbital (HOMO) of a donor molecule and the electron on the Lowest Unoccupied Molecular Orbital (LUMO) of an adjacent acceptor $PC_{71}BM$ molecule, while the electron-hole pairs are still strongly bound by coulomb interactions. After the CT state dissociated, the carriers can undergo several ultrafast hops, allowing them to separate before the CS state thermal relaxation and the carrier entering the normal polaron hopping regime. The formation of CT/CS states is usually fast, as a result, the other longer process (such as traps and triplet states) are not involved in the limited time window. Species-Associated Difference Spectra (SADS) and the kinetics of the corresponded components for NDT: $PC_{71}BM$ film are shown in Figs. 5(b) and (c) as an example. The CT/CS spectral features basically match with EX but with a slight difference at \sim 650 nm. In CT/ CS states, the distance between electrons and holes is already large, which minimize the binding energy of electron-hole pairs and leads to GSB peak red shifts^[39-40]. The concentration over time shows that the EX decay is on a time scale of \sim ps. As shown in Fig.5(c), the population of CT state is one order magnitude smaller than the population of CS state, which means for the blend film, the formation of CS state is mostly from the EX states directly without going through CT state. The SADS and components population dynamics of NDT-Hex: PC₇₁BM and NDT-Hex: PC₇₁BM-SVA films show similar results.

The time constants from the GA fit for all blend samples are listed in Table 1. With these parameters, the CS yield was calculated by the equation of $\eta_{CS} = \frac{k_1}{k_1 + k_2 + k_A} \times \frac{k_3}{k_3 + k_B} + \frac{k_2}{k_1 + k_2 + k_A}$ for the three blend films. The CS yield of the three blend films are also listed in Table 1. Apparently, the CS yield is largest for NDT-Hex: PC₇₁BM-SVA film as the process from EX state to CS state (~0.4 ps) is much faster than other

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Fig. 5 The results of the global analysis based on the dynamics model for NDT : $PC_{71}BM$ blend film

relaxation processes, which indicates that most excitons generated by photon absorption can become separated charges, conducive to PCE improvement. This is consistent with the fact that the best device performance was obtained on the solar cells with NDT-Hex: PC₇₁BM-SVA as active layer. SVA treatment can modulate the morphology of films, and the appropriate phase separation and surface roughness are conducive to charge separation^[41-43]. Moreover, the previous charge transporting study by Space Charge-Limited Current (SCLC) method showed the electron and hole mobility ratio is 12.03, 1.88 and 1.32 for NDT: PC₁₁BM, NDT-Hex: PC₇₁BM and NDT-Hex: PC₇₁BM-SVA, respectively^[33]. The more balanced charge transport is another reason for the highest PCE of NDT-Hex: PC71BM-SVA heterojunction. However, for NDT-Hex blend film, the CS yield is smaller than that of NDT blend film, which seems to be contradicted with the PCE measurement results that the PCE of NDT-Hex blend film is slightly higher than that of NDT blend film. In fact, CS yield is just one of many factors that can affect the PCE. The following photophysical processes after charge separation also matter. We noticed that the lifetime of CS state is longer for NDT-Hex blend film from GA fit (The large uncertainty of CS state lifetime is caused by the limited time window. Even that, the longer CS state lifetime for NDT-Hex: $PC_{71}BM$ is still valid as shown in Figs.4(g) and (h), NDT-Hex: $PC_{71}BM$ shows slower decay in TA traces). The longer lifetime of CS states indicates that the bimolecular recombination rate is reduced and the carriers have more chance to be collected by electrodes^[44]. Comparing with NDT blend film, although the CS yield of NDT-Hex blend film is slightly smaller, its longer CS lifetime and more balanced mobility could give rise to the higher PCE than that of NDT blend film.

Table 1	Target fitting parameters and the corresponding CS efficiency obtained from the broadband transient absorption				
data of NDT-based blend films					

	NDT:PC ₇₁ BM	NDT-Hex:PC ₇₁ BM	NDT-Hex:PC ₇₁ BM-SVA
$ au_{ m A}/ m ps$	1.9 ± 0.4	1.7 ± 0.3	1.7 ± 0.3
$ au_1/\mathrm{ps}$	22 ± 7	20 ± 6	20 ± 6
$ au_{ m \scriptscriptstyle B}/ m ps$	68 ± 33	70 ± 37	70 ± 37
$ au_2/\mathrm{ps}$	1.4 ± 0.2	2 ± 0.5	0.40 ± 0.03
$ au_{ m _3}/ m ps$	5.9 ± 1.0	5.8 ± 2.0	3.5 ± 0.6
$ au_{ m c}/{ m ps}$	157 ± 60	280 ± 180	134 ± 48
CS yield	0.59 ± 0.06	0.49 ± 0.07	0.81 ± 0.03

3 Conclusion

Three heterojunction films (NDT: $PC_{71}BM$, NDT-Hex: $PC_{71}BM$ and NDT-Hex: PC71BM-SVA) were investigated by TA spectroscopy. The dynamics results showed that the chemical modification and SVA treatment can alter several photophysical processes in the blend films. Solely focusing on one process cannot well explain the overall PCE. The highest CS yield and best balanced electron-hole mobility of NDT-Hex: $PC_{71}BM$ -SVA give

rise to the largest PCE among the three blend films. The longer CS lifetime and better balanced electron-hole mobility of NDT-Hex: $PC_{71}BM$ leads to a higher PCE than that of NDT: $PC_{71}BM$. This work shows that the CS yield, CS lifetime and electron-hole mobility are all important factor for PCE improvement, thus for the device optimization, these three factors should all be considered to ensure the PCE is improved essentially.

References

- [1] LIG, ZHUR, YANG Y. Polymer solar cells[J]. Nature Photonics, 2012, 6 (3): 153-161.
- [2] SUN Y, WELCH G C, LEONG W L, et al. Solution-processed small-molecule solar cells with 6.7% efficiency [J]. Nature Materials, 2012, 11 (1): 44-48.
- [3] ZHAO J, LI Y, YANG G, et al. Efficient organic solar cells processed from hydrocarbon solvents [J]. Nature Energy, 2016, 1: 15027.
- [4] YAN C, BARLOW S, WANG Z, et al. Non-fullerene acceptors for organic solar cells[J]. Nature Reviews Materials, 2018, 3(3): 18003.
- [5] CUI Y, YAO H, ZHANG J, et al. Single-junction organic photovoltaic cells with approaching 18% efficiency [J]. Advanced Materials, 2020, 32 (19): 1908205.
- [6] LIU Q, JIANG Y, JIN K, et al. 18% Efficiency organic solar cells[J]. Science Bulletin, 2020, 65 (4): 272-275.
- [7] QIN J, ZHANG L, ZUO C, et al. A chlorinated copolymer donor demonstrates a 18.13% power conversion efficiency[J]. Journal of Semiconductors, 2021, 42 (1): 010501.
- [8] JIN K, XIAO Z, DING L. 18.69% PCE from organic solar cells[J]. Journal of Semiconductors, 2021,42(6): 060502.
- [9] SALIM M B, NEKOVEI R, JEYAKUMAR R. Organic tandem solar cells with 18.6% efficiency [J]. Solar Energy, 2020, 198: 160-166.
- [10] MISHRA A, BAEUERLE P. Small molecule organic semiconductors on the move: promises for future solar energy technology[J]. Angewandte Chemie-International Edition, 2012, 51 (9): 2020-2067.
- [11] DUTTA P, YANG W, EOM S H, et al. Development of naphtho [1, 2-b: 5, 6-b'] dithiophene based novel small molecules for efficient bulk-heterojunction organic solar cells[J]. Chemical Communications, 2012, 48 (4): 573-575.
- [12] DUAN Y A, GENG Y, LI H B, et al. Theoretical characterization and design of small molecule donor material containing naphthodithiophene central unit for efficient organic solar cells[J]. Journal of Computational Chemistry, 2013, 34 (19): 1611–1619.
- [13] FERNANDEZ D, VITERISI A, CHALLURI V, et al. Understanding the limiting factors of solvent-annealed smallmolecule bulk-heterojunction organic solar cells from a chemical perspective[J]. ChemSusChem, 2017, 10 (15): 3118-3134.
- [14] LI H, ZHAO Y, FANG J, et al. Improve the performance of the all-small-molecule nonfullerene organic solar cells through enhancing the crystallinity of acceptors[J]. Advanced Energy Materials, 2018, 8 (11): 1702377.
- [15] SHI Y, YANG C, LI H, et al. A-π-D-π-A small-molecule donors with different end alkyl chains obtain different morphologies in organic solar cells[J]. Chinese Chemical Letters, 2019, 30 (4): 906-910.
- [16] LOU S J, LOSER S, LUCK K A, et al. Charge generation mechanism tuned via film morphology in small molecule bulkheterojunction photovoltaic materials[J]. Journal of Materials Chemistry C, 2020, 8 (43): 15234–15252.
- [17] WEI Z, LU K, ZHOU R, et al. Research progress of small molecule donors with high crystallinity in all small molecule organic solar cells[J]. Acta Chimica Sinica, 2021, 79 (3): 284–302.
- [18] CUI Y, YAO H, HONG L, et al. Achieving over 15% efficiency in organic photovoltaic cells via copolymer design[J]. Advanced Materials, 2019, 31 (14): 1808356
- [19] ZHANG S Q, QIN Y P, ZHU J, et al. Over 14% efficiency in polymer solar cells enabled by a chlorinated polymer donor[J]. Advanced Materials, 2018, 30 (20): 1800868.
- [20] CUI Y, YAO H, ZHANG J, et al. Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages[J]. Nature Communications, 2019, 10: 2515.
- [21] JIANG H X, LI X M, WANG H, et al. Appropriate molecular interaction enabling perfect balance between induced crystallinity and phase separation for efficient photovoltaic blends [J]. ACS Applied Materials & Interfaces, 2020, 12 (23): 26286-26292.
- [22] LI H, WU Q, ZHOU R, et al. Liquid-crystalline small molecules for nonfullerene solar cells with high fill factors and power conversion efficiencies[J]. Advanced Energy Materials, 2019, 9 (6): 1803175.
- [23] NI W, LI M M, KAN B, et al. Fullerene-free small molecule organic solar cells with a high open circuit voltage of 1.15 V[J]. Chemical Communications, 2016, 52 (3): 465-468.
- [24] WANG W, CHEN B, JIAO X, et al. A new small molecule donor for efficient and stable all small molecule organic solar cells[J]. Organic Electronics, 2019, 70: 78-85.
- [25] ZHANG H, WANG C, LI X, et al. The effect of processing conditions on performance of small-molecule organic solar

cells[J]. Solar Energy, 2017, 157: 71-80.

- [26] WANG Y L, WANG Y, ZHU L, et al. A novel wide-bandgap small molecule donor for high efficiency all-smallmolecule organic solar cells with small non-radiative energy losses[J]. Energy & Environmental Science, 2020, 13 (5): 1309-1317.
- [27] GE J, HONG L, SONG W, et al. Solvent annealing enables 15.39% efficiency all-small-molecule solar cells through improved molecule interconnection and reduced non-radiative loss[J]. Advanced Energy Materials, 2021: 2100800.
- [28] LOSER S, BRUNS C J, MIYAUCHI H, et al. A naphthodithiophene-diketopyrrolopyrrole donor molecule for efficient solution-processed solar cells[J]. Journal of the American Chemical Society, 2011, 133 (21): 8142-8145.
- [29] SHINAMURA S, OSAKA I, MIYAZAKI E, et al. Linear- and angular-shaped naphthodithiophenes: selective synthesis, properties, and application to organic field-effect transistors [J]. Journal of the American Chemical Society, 2011, 133 (13): 5024-5035.
- [30] TAKIMIYA K, OSAKA I. Naphthodithiophenes: emerging building blocks for organic electronics[J]. Chemical Record, 2015, 15 (1): 175-188.
- [31] ZHU X W, LU K, LI H, et al. Naphthodithiophene-based donor materials for solution processed organic solar cells[J]. Chinese Chemical Letters, 2016, 27 (8): 1271-1276.
- [32] CHANG Y, CHANG Y, ZHU X, et al. Constructing high-performance all-small-molecule ternary solar cells with the same third component but different mechanisms for fullerene and non-fullerene systems[J]. Advanced Energy Materials, 2019, 9 (16): 1900190.
- [33] XIA C, WU H, FAN H, et al. Efficient NDT small molecule solar cells with high fill factor using pendant group engineering[J]. Journal of Materials Chemistry C, 2020, 8 (22): 7561-7566.
- [34] STOKKUM I H MVAN, LARSEN D S, GRONDELLE RVAN. Global and target analysis of time-resolved spectra[J]. Biochimica Et Biophysica Acta-Bioenergetics, 2004, 1657 (2-3): 82-104.
- [35] HIPPIUS C, STOKKUM I H MVAN, ZANGRANDO E, et al. Excited state interactions in calix 4 arene-perylene bisimide dye conjugates: Global and target analysis of supramolecular building blocks[J]. Journal of Physical Chemistry C, 2007, 111 (37): 13988-13996.
- [36] WANG X, KAN B, KUANG Z, et al. Unveiling the molecular symmetry dependence of exciton dissociation processes in small-molecular heterojunctions[J]. Journal of Physical Chemistry C, 2018, 122 (47): 26851-26856.
- [37] RUCKEBUSCH C, SLIWA M, PERNOT P, et al. Comprehensive data analysis of femtosecond transient absorption spectra: A review[J]. Journal of Photochemistry and Photobiology C-Photochemistry Reviews, 2012, 13 (1): 1-27.
- [38] BERERA R, GRONDELLE RVAN, KENNIS J T M. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems[J]. Photosynthesis Research, 2009, 101 (2-3): 105-118.
- [39] GELINAS S, RAO A, KUMAR A, et al. Ultrafast long-range charge separation in organic semiconductor photovoltaic diodes[J]. Science, 2014, 343 (6170): 512-516.
- [40] JAKOWETZ A C, BOEHM M L, SADHANALA A, et al. Visualizing excitations at buried heterojunctions in organic semiconductor blends[J]. Nature Materials, 2017, 16 (5): 551–557.
- [41] LI M, LIU F, WAN X, et al. Subtle balance between length scale of phase separation and domain purification in smallmolecule bulk-heterojunction blends under solvent vapor treatment[J]. Advanced Materials, 2015, 27 (40): 6296-6302.
- [42] SUN K, XIAO Z, HANSSEN E, et al. The role of solvent vapor annealing in highly efficient air-processed small molecule solar cells[J]. Journal of Materials Chemistry A, 2014, 2 (24): 9048–9054.
- [43] XIE L, YANG C, ZHOU R, et al. Ternary organic solar cells based on two non-fullerene acceptors with complimentary absorption and balanced crystallinity[J]. Chinese Journal of Chemistry, 2020, 38 (9): 935–940.
- [44] YANG B, YUAN Y, HUANG J. Reduced bimolecular charge recombination loss in thermally annealed bilayer heterojunction photovoltaic devices with large external quantum efficiency and fill Factor[J]. Journal of Physical Chemistry C, 2014, 118 (10): 5196-5202.