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Boosting Photovoltaic Thermal Stability of Fullerene Bulk Heterojunction Solar Cells through Charge Transfer Interactions

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Fullerene-based bulk heterojunction organic solar cells (BHJ-OSCs) represent one of the current state-of-the-art organic solar cells. Nonetheless, most of these devices still suffer from adverse performance degradation due to thermally induced morphology changes of active layers. We herein demonstrate that the photovoltaic performance stability of BHJ-OSCs can be profoundly enhanced with an appositely functionalized 9-fluorenylidene malononitrile. The latter, through charge transfer (CT) interactions with the donor polymer, enabling formation of a "frozen" 3-dimensional mesh-like donor polymer matrix, which effectively restrains free movement of embedded fullerene molecules and suppresses their otherwise uncontrolled aggregation. 9-Fluorenylidene malononitrile derivatives with multiple CT interaction sites are particularly effective as preservation of power conversion efficiency of over 90% under severe thermal stress has been accomplished. The generality of this novel strategy has been affirmed with several common donor polymers, manifestingthis to be hitherto the most efficient approach to stabilized fullerene-based BHJ-OSCs.

1. Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) with active layers comprising a polymer electron donor and a fullerene electron acceptor have been a prevalent topic of intense research.¹⁻² One of the primary driving forces stems from their perceived facile solution processability, which would enable high-throughput roll-to-roll fabrication leading to lowcost manufacturing.³⁻⁴ Other potential attributes relate to their lightweight and structural flexibility characteristics which may be useful for portable devices and other niche applications.⁵⁻⁷ Fullerene acceptors have been widely studied in bulk heterojunction organic solar cells (BHJ-OSCs) owing to their reasonably high electron mobility, solution processability and compatibility with many donor polymer materials.⁸⁻¹⁰ They have also provided excellent photovoltaic properties with stateof-the-art donor polymers. However, most of the fullerene based BHJ-OSCs suffer from rapid performance degradation over time, particularly upon exposure to elevated temperatures.11-14 This is largely due to the propensity of

fullerene acceptors to aggregate into undesirably large and discontinuous domains in the active layer.¹²⁻¹³ Such polymer donor/fullerene acceptor phase segregation not only leads to reduced donor-acceptor (D-A) interfaces with detrimental effects to exciton separation and diffusion, but also disruption of charge conduction pathways. Accordingly, the morphology of active layers plays a decisive role in impacting the photovoltaic performance of BHJ-OSCs.14-21 While many strategies including solvent annealing, incorporation of ternary components, cross-linkable fullerene derivatives, etc. have been engaged to optimize and stabilize active layer morphology with varying degrees of success, it remains extremely challenging to sustain thermal stability without sacrificing the photovoltaic performance.²²⁻²⁵ A favorable active layer morphology, besides being compositionally graded in vertical direction for charge collection and having favorable molecular orientation for charge transport, should possess a continuous network of nanodomains of semiconducting materials for efficient exciton dissociation and charge transport.26-30

We herein report our structural engineering strategy to enhance the thermal stability of active layer morphology, thereby helping preserve and sustain photovoltaic performance of fullerene-based BHJ-OSCs under greatly exaggerated thermal exposure. Our strategy involves "freezing" of donor polymer matrix through charge transfer (CT) interactions with an appropriate electron-deficient compound such as 9fluorenylidene malononitrile derivative, leading to formation of a presumably three-dimensional (3D) "mesh-like" donor polymer matrix network in the active layer. When uniformly dispersed in this mesh-like polymer network structure, fullerene

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PCFM (I)

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acceptor molecules can be visualized as being captured within the network "cavities", capable of forming nanodomains but are substantially restrained in movement from aggregating to undesirably large domains even under prolonged thermal exposure. This would enable stable and continuous fullerene nanodomain structures for efficient exciton dissociation and transport, thus sustained photovoltaic performance over prolonged thermal exposure. The beneficial effects of such a 3D mesh-like polymer matrix in sustaining thermal photovoltaic performance stability have been unequivovally supported by the experimental results of charge transport, trap density, and morphological studies of active layer in the presence of an appropriate 9-fluorenylidene malononitrile derivative.

2. Results and discussion

Through systematic studies on the electronic interactions of electron-deficient compounds with electron donor polymers, we observed that certain 9-fluorenylidene malononitrile derivatives (Figure 1) were capable of interacting with donor polymers through CT interactions. Strong CT interactions of this nature may be expected to lead to physical "crosslinking" of donor polymer, thus a suitably functionalized 9-fluorenylidene malononitrile derivative with a low-lying lowest unoccupied molecular orbital (LUMO) or high electron affinity may satisfy as a suitable CT crosslinking or polymer matrix freezing agent. From this perspective, a dimeric or trimeric acceptor containing 9-fluorenylidene malononitrile moieties would be particularly efficient. These materials, which carry multiple active sites for CT interactions within a single molecule, would enable formation of a 3D mesh-like polymer network structure. This "cavities" containing network would impede the movements of embedded fullerene molecules, suppressing their diffusion and otherwise uncontrolled aggregation into relatively large domains. Our results showed that incorporation of a minute quantity of an appropriate 9-fluorenylidene malononitrilie derivative in the active layers of fullerene-based BHJ-OSCs effectively hampered fullerene aggregation, resulting in sustained photovoltaic performance characteristics. Preservation of photovoltaic performance of over 90% of PCEs after extended thermal exposure at high temperatures (~ 100 °C for over 20 hours) had been experimentally accomplished. To the best of our knowledge, this represents hitherto best approach to enhancing the thermal stability of fullerene-based BHJ-OSCs.

2.1 Molecular Design of 9-Fluorenylidene Malononitrile Additives

As CT interaction involves electron transfer from the highest occupied molecular orbital (HOMO) of an electron donor to the LUMO of an electron acceptor, a higher HOMO level and a lower LUMO level would generally favor CT interactions. The electron affinity of an electron acceptor, which measures its capacity to accept an electron, correlates directly with its LUMO level. The LUMO level of a fluorenylidene malononitrile acceptor can be readily



Figure 1 Chemical structures of 9-fluorenylidene malononitrile derivatives.

1-NPCFM (II)

manipulated through substitution on the fluorenylidene malononitrile nucleus with electron withdrawing functionalities such as carbonyl, carboxylic, nitro groups, etc. to achieve the desirable electron affinity. Its physical properties such as polymer compatibility and solubility characteristics to facilitate solution processing can also be modulated with appropriate alkyl or carboxylic ester substitution. Accordingly, 9fluorenylidene malononitrile derivatives are attractive electronic agents which can be employed to interact with the electron donor-acceptor (D-A) polymers commonly utilized as donor polymers in BHJ-OSCs. Specifically, with a reasonably low lying LUMO, a 9-fluorenylidene malononitrile can effectively form CT bonding with the donor moieties of a D-A polymer, leading to a physically crosslinked donor polymer network. Depending on the mode and efficacy of CT interactions, the crosslinked donor polymer matrix with varying degrees of crosslink density can exert modulating effects on the movements of fullerene molecules. This will have decisive consequences on the distribution and stability of fullerene acceptor dispersions, thus the micro- and nanostructural morphology of active layer.

The fluorenylidene malononitrile derivatives that were utilized in our studies as electronic agents or additives are depicted in Scheme S1. Details of their synthesis and characterizations are described in the experimental section. We selected carboxylic ester and nitro substitutions to modulate the solubility and LUMO of 9-fluorenylidebne malononitrile chromophore as these offered ease of synthesis and attainment of desirable LUMOs. Three small molecular 9-fluorenvlidene malononitrile derivatives, PCFM (I), 1-NPCFM (II), and 2-NPCFM (III), differing structurally in the number of nitro substitutions, and thus their LUMO levels in the descending order of -3.87 eV, -4.13 eV, and -4.32 eV, respectively from vacuum were investigated. Since crosslinking of a polymer would be far more effective with a divalent or polyvalent agent, we therefore also designed appropriate fluorenylidene malononitrile dimer and trimer for our studies.

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2-NPCFM (III)

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Figure 2 Photovoltaic thermal stability of PTB7:PC71BM BHJ-OSCs with different 9-fluorenylidene malononitrile derivatives. (a-d) J-V characteristics, (e) summary plots of photovoltaic characteristics.

2.2 Photovoltaic Performance

For our photovoltaic evaluation, we utilized a device structure of ITO/PEDOT:PSS/active layer/LiF/Al. The active layer of control device was composed of donor polymer, poly{4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-divl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4b]thio phene-4,6-divl} or PTB7 and fullerene acceptor, [6,6]-phenyl-C₇₁-butyric acid methyl ester or PC₇₁BM, while for those of experimental devices under investigation, less than 1 weight percent (wt%) of 9-fluorenylidene malononitrile derivative was incorporated. The devices were thermally annealed at different temperatures for 20 hours each before electrical characterization was carried out using AM 1.5G illumination with a 100 mW/cm^2 solar simulator. Figure 2 shows the current-voltage (J-V) characteristics of control device and 9fluorenyildene malononitrile-incorporated devices at different annealing temperatures. The device parameters and detailed photovoltaic performance [short circuit current density (J_{sc}), open circuit voltage (Voc), fill factor (FF) and power conversion efficiency (PCE)] are summarized in Table S1. When added in minor quantity (<1 wt%) into the active layer, PCFM (I) was found to be beneficial in preserving the thermal stability of photovoltaic performance of fullerene BHJ-OSC devices, and the optimum quantity was found to be about 0.8% by weight. Specifically, both the as-prepared control and PCFMincorporated devices without thermal annealing exhibited essentially similar photovoltaic performance characteristics. Upon thermal treatment at 100 °C for 20 hours, the PCFMincorporated device showed preservation of over 85% of its original PCE while the control device exhibited severe performance deterioration with over 30% drop in PCE (from

7.7% to 5.3%). The latter was due largely to degradation in FF (from 62% to 47%) and concomitant decrease in J_{sc} (by 2 mA/cm²). These experimental observations were in agreement with our hypothesis that the CT interaction of PCFM with donor polymer, PTB7, led to donor polymer crosslinking. The crosslinked donor polymer matrix effectively suppressed thermally induced migration and ensuing aggregation of fullerene molecules into undesirably large domains, thus effectively preventing disruption in exciton dissociation and charge transport. On the other hand, utilization of stronger electron acceptors such as 1-NPCFM (II) or 2-NPCFM (III) as active layer additives invoked over 20% drop in PCE even without thermal treatment (Figure S1 and Table S1). The negative effects of 1-NPCFM and 2-NPCFM could be attributed to their much higher electron affinities (or significantly lower LUMOs), which rendered them excellent electron traps, adversely interfering in charge transport as well as mitigating their CT interactions with donor polymer in crosslinking upon electron acceptance.

The dimeric and trimeric 9-fluorenylidene malononitrile derivatives, **BDFB (IV)** and **TDFA (V) (Table 1)**, which would greatly enhance CT interactions with donor polymers, were also synthesized for investigation. These materials, which carried similar 9-fluorenylidene malononitrile moieties within their molecules, possessed approximately the same LUMO levels as that of PCFM (ca. -3.9 to -3.8 eV), and were not expected to negatively interfere in charge transport in the active layer. As prepared without thermal annealing, both the devices with BDFB and TDFA additives exhibited similar performance characteristics as the control device (Jsc \approx 16 mA/cm², V_{oc} \approx 0.76 V, FF \approx 64%, PCE \approx 7.8%). Upon heating at 100 °C for 20

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Table 1

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Figure 3 Plots of current-density versus electric field at room temperature of (a) hole-only and (b) electron-only devices with and without BDFB additive.

Annealing Temperature	Hole μ_0 (cm ² V ⁻¹ s ⁻¹)		Electron μ_0 (cm ² V ⁻¹ s ⁻¹)	
	Without BDFB	With BDFB	Without BDFB	With BDFB
Room temperature	1.2×10^{-4}	1.2×10^{-4}	1.4×10^{-4}	1.1×10^{-4}
100 °C	$9.9 imes 10^{-6}$	$7.9 imes10^{-5}$	2.4×10^{-6}	$6.4 imes 10^{-5}$

hours, both BDFB and TDFA-incorporated devices were observed to perform admirably well, preserving over 90% of their original PCEs. The dimeric fluorenylidene malononitrile additive, BDFB, was particularly effective as essentially no change in J_{sc} was noted with its overall PCE degraded only about 7% from its original value. It should be noted that all J_{sc} 's were in agreement with their external quantum efficiency (EQE) measurements (Figure S2).

Hole and electron mobility as measured at room temperature.

2.3 Charge Carrier Transport and Subgap Absorption Properties

To understand the role and mechanism of 9-fluorenylidene malononitrile in thermal stabilization of photovoltaic performance of fullerene-based BHJ-OSCs, we accordingly conducted more detailed characterization studies on the devices with the most efficient dimeric additive, BDFB. The charge transport properties of active layers under thermally annealed conditions were investigated using space-charge-limited-current (SCLC) model to measure the current density-voltage (J-V) characteristic, and extract zero-field hole and electron mobility. Corresponding single-carrier diodes were employed for measurements. Electric-field dependent current of the samples was measured and carrier mobility was extracted using following equation:

$$J_{SCL} d = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 exp(0.89\beta\sqrt{F}) F^2$$

where J_{SCL} is the space-charged-limited current density, *d* is the thickness of tested layer, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the polymer, μ_0 is the zero-field mobility, β is the field-dependent coefficient, and *F* is the average electrical field applied on the sample.³¹⁻³²

At room temperature, both the control and BDFBincorporated active layer (BHJ) films displayed approximately similar hole and electron mobility. ($\sim 1 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). Upon thermal annealing at 100 °C for 20 hours, the control BHJ film showed one order of magnitude drop in hole mobility (10^{-4} to 10^{-5} cm²V⁻¹s⁻¹) and nearly two orders of magnitude decrease in electron mobility (10^{-4} to 10^{-6} cm²V⁻¹s⁻¹). This imbalance of electron and hole mobility would account for the observed lower FF of the control device.³³ On the other hand, the BDFB-incorporated BHJ film suffered comparatively smaller degradations in both hole (1.2×10^{-4} to 7.9×10^{-5} cm²V⁻¹s⁻¹) and electron mobility (1.1×10^{-4} to 6.4×10^{-5} cm²V⁻¹s⁻¹) (**Figure 3** and Table S1), thus manifesting the stabilization effect of BDFB additive on the BHJ film morphology.

The defect and trap densities of thermally annealed BHJ films were analyzed by photothermal deflection spectroscopy (PDS) to probe the subgap absorptions.³⁴⁻³⁷ For simplicity and clarity, we showed only the PDS spectra of each film before and after annealing at 100 °C for 20 hours (**Figure 4**; see Figure S3 for detailed spectral properties). For the control films, we observed a noticeable increase in the subgap absorption after thermal annealing as compared to BDFB-incorporated films. The subgap absorption was quantified by estimating the nominal trap state density (*N*) of the films using optical sum rule:³⁸

$$N = \frac{cnm}{2\pi^2 \hbar e^2} \int \alpha_{sub}(E) \, dE$$

E is the photon energy, *c* is the speed of light, *n* is the refractive index, *m* is the effective mass of electron, *e* is the elementary charge, \hbar is the Planck constant. α_{sub} represents the subtracted subgap absorption by Urbach absorption. $[\alpha_{sub}(E) = \alpha(E) - \alpha_u(E)$, where $\alpha_u = \alpha_0 \exp(hv - E_g/E_u)$ for $E < E_g$, and E_u is the Urbach energy.³⁹] The increased trap densities after thermal stress are presented in Table S3. As can be noted, the BDFB-incorporated film exhibited one order lower in trap density increment as compared to control film. These results suggest that the additive BDFB impeded trap generation during thermal

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Figure 4 Photothermal deflection spectra of control and BDFB-incorporated BHJ films. The region shaded in light blue indicates the raise in subgap trap states upon thermal stress.

stress, and the traps were likely due to unfavorable morphology changes. These observations were also in agreement with the observed stable FF of BDFB-incorporated BHJ-OSC devices as similar relationship between FF and trap density had earlier been reported.^{37,40-41}

2.4 Active Layer Morphology Analysis

To shed light on the effect of 9-fluorenylidene malononitrile additive on molecular ordering and nanoscale phase separation of PC71BM in the BHJ film, grazing incidence wide-angle and small-angle X-ray scattering (GIWAXS and GISAXS) measurements were conducted.42-44 Two-dimensional (2D) GIWAXS patterns of BHJ films, with and without BDFB additive, thermally annealed at different temperatures are presented in Figure S4. For all these films, ring-like lamellar and p-p stacking peaks were observed at approximately the same position ($q \approx 0.34$ Å⁻¹ and 1.75 Å⁻¹), indicating that addition of BDFB did not exert any observable effects on the molecular packing in the BHJ films. In sharp contrast, the influence of BDFB on nanoscale phase separation was distinctly noted in GISAXS measurements. Figure 5(a) shows the 2D GISAXS patterns with the corresponding intensity integrals along qr direction. The intensity integral [Figure 5(b)] of the control film (without BDFB) shifted to lower q in the medium q region (~ 0.01–0.05 Å⁻¹) and turned up in the low q region (< 0.006 Å⁻¹) after thermal annealing (100 °C for 20 hr), demonstrating severe morphology instability of the control film. For the film with BDFB, the intensity integral displayed significantly less changes under similar conditions, reflecting the efficacy of BDFB in freezing the film morphology. The estimated domain sizes of aggregated PC71BM clusters (Rg_PC71BM) from the fitting results, and the amorphous intermixing phase are summarized in Table S2. The percentage changes in domain size were presented in Figure 5(c). As can be noted, the domain size of control film was more than double for both phases at annealing temperature of 100 °C, while for the BDFB-incorporated film, the domain size increments were less than about 40% at the same annealing temperature.

Transmission electron microscopy (TEM) was also performed to visualize the effects of BDFB incorporation in the BHJ film. The TEM images for the BHJ films with and without BDFB incorporation are shown in Figure 6. The TEMs of both BHJ films with and without BDFB additive show relatively uniform morphology before heating. After thermal annealing, substantial fullerene and donor polymer aggregations were visibly noted in the film without BDFB (bright and dark spots/regions), while the film with BDFB additive retained its relatively uniform morphology even after thermal annealing. In addition, a continuous mesh-like network structure of donor polymer matrix was visually evident in the BHJ film with BDFB additive, which was significantly more pronounced after heating. These observations correlated well with the X-ray scattering results, and provided unequivocal affirmation on the formation of "frozen" 3D mesh-like network structure of donor polymer matrix in the BDFB-incorporated BHJ films.

2.5 Charge Transfer Interactions

The combined results of charge transport studies and structural morphology analysis of active layer compositions with and without 9-fluorenylidene malononitrile additive such as BDFM unequivocally point to the role of 9-fluorenylidene malononitrile additive as a capable CT crosslinking agent for donor polymer such as PTB7 through CT interactions. The resulted crosslinked donor polymer matrix effectively restrained thermally-induced fullerene migration and impeded its microscale aggregation, leading to enhanced stability of BHJ nanophase morphology in the active layer. To substantiate the existence of CT interaction between BDFM and PTB7, we conducted spectroscopic and steady-state photoluminescence studies of PTB7 films with and without BDFM. Figure 7(a) shows the UV-vis absorption spectra of the PTB7 films with and without 0.8 wt% of BDFM. In the presence of BDFM additive, slight redshifts of vibrational absorption peaks at 608 nm (0-1) and 660 nm (0-0) to 625 nm and 675 nm respectively, together with a concomitant increase in (0-0) vibrational peak intensity at the expense of (0-1) peak were observed. These ARTICLE

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Figure 5 (a) 2D GISAXS patterns of PTB7:PC₇₁BM BHJ films with and without BDFB additive before and after heating at 100 °C for ~20 hours; (b) corresponding in-plane linecut and best fittings; and (c) percentage changes in domain size as estimated from GISAXS.

results clearly manifested higher degrees of molecular ordering in the BDFM-incorporated film.⁴⁵⁻⁴⁶ Moreover, steady-state photoluminescence (PL) studies showed that BDFM effectively quenched the photoluminescence of PTB7 [**Figure 7(b**)]. Specifically, incorporation of 0.8% by weight of BDFM into the PTB7 film led to a two-third decrease in its photoluminescence intensity. It was thus reasonable to assume that the free movement of fullerene was restricted by the resulting 3D mesh-like donor polymer matrix structure formed from the CT interactions of BDFB and the donor polymer upon BDFB addition. Other weak intermolecular interactions such as



Figure 6 TEM images of control and BDFB-incorporated BHJ films before and after heating at 100°C for ~20 hours.

van der Waals force are too weak to pull together or physically crosslink the donor polymers. The CT interactions are much stronger, much like the hydrogen bonding which has been shown to crosslink fluorine-containing donor polymers.²⁵

A schematic diagram portraying CT interactions leading to a crosslinked donor matrix is depicted in **Figure 8**. Such a 3D mesh-like donor polymer matrix would effectively impede free movements of fullerene molecules, preventing them from forming undesirably large domains even subjected to external thermal stimulus. This would result in a more stable charge transport environment with reduced trap density, and better photovoltaic performance.

To demonstrate the generality of the present approach of utilizing 9-fluorenylidene malononitrile as an effective BHJ morphology stabilizer, two other different donor polymers, namely poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1, 2-b;4,5-b']-dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluoro thieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] or PTB7-Th, and regioregular poly(n-hexythiophene) or P3HT, were utilized. Figure S8 summarizes the thermal stability of photovoltaic properties of BHJ-OSC devices using PTB7-Th:PC71BM and P3HT:PC₆₁BM active layers with and without BDFM additive. The corresponding J-V curves of devices are presented in Figure S9. With PTB7-Th as the donor polymer, the device with BDFM additive maintained very good photovoltaic performance after heating at 100 °C for 20 hours, showing excellent thermal stability as compared to the device without BDFM additive. Likewise, the P3HT device with BDFM additive also demonstrated excellent thermal stability in its photovoltaic performance after annealing at 70°C. The corresponding P3HT device without BDFM additive exhibited a significant drop in PCE under similar thermal annealing conditions, due largely to a significant loss in FF. It should be

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Figure 7 (a) Normalized UV-vis spectra and (b) steady-state photoluminescence spectra of thin films of PTB7 and PTB7 with 0.8 wt% of BDFB additive (excitation wavelength = 470 nm).

mentioned that in the case of P3HT, 70°C was used as the annealing temperature as these devices could not withstand 100°C for 20 hours. These results have once again affirmatively demonstrated the general utility and efficacy of this strategy for the stabilization of photovoltaic performance of fullerene-based BHJ-OSCs.

3. Conclusions

Through molecular design, charge transport, and spectroscopic studies, together with grazing incidence wideangle and small-angle X-ray scattering analysis, we have unequivocally demonstrated that an ultra-low concentration of appositely functionalized 9-fluorenylidene malononitrile derivative is extremely efficient in enhancing the thermal stability of fullerene-based BHJ-OSCs. The stabilization stems from the CT interactions of 9-fluorenylidene malononitrile with the donor polymer in locking up the donor polymer chains, leading to formation of a frozen 3D mesh-like donor polymer matrix in the active layer. This has provided effective



Figure 8 Schematic diagram of PTB7:PC₇₁BM active layer with BDFB additive showing CT-induced crosslinked donor polymer matrix with nanophase PC₇₁BM morphology.

impediment to thermally-induced diffusion and aggregation of embedded fullerene molecules in the crosslinked donor polymer matrix, thus imparting significantly enhanced thermal stability to the BHJ morphology of the active layer. A suitably low LUMO level of close to -4 eV would be required for CT interactions without adversely impacting charge transport properties; much lower LUMO levels leads to electron trapping, lower charge transport rates, and thus lower PCEs. 4-Alkoxycarbonyl-9-fluorenylidene malononitrile derivative, which has a LUMO level of about -3.9 eV, represents an effective agent for the stabilization of fullerene-based BHJ-OSCs with common donor polymers such as PTB7, PTB7-Th or P3HT. The dimeric 9-fluorenvlidene malononitrile derivative, BDFM, which carries two electron-deficient sites for CT interaction within a single molecule, is particularly effective. As much as over 90% of PCE could be preserved even after severe thermal stress of exposure to 100 °C for 20 hours. To the best of our knowledge, this is hitherto most effective strategy to enhance thermal stability of fullerenebased OSCs.

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Author contributions

Device fabrication/characterization, photothermal deflection spectroscopic and charge transport studies were carried out by C. H. Y. Ho, H. Yin, K. L. Chiu, L. K. Ma, S. H. Cheung. Molecular design and synthesis were conducted by H. Cao and

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Y. Lu. T.-K. Lau and X. Lu conducted grazing incidence X-ray scattering experiments and morphology analysis. External quantum efficiency and steady-state photoluminescence studies were conducted by H.-W. Li, Y. Cheng and S.-W. Tsang. B. S. Ong and S. K. So were responsible for the overall project direction. The manuscript was prepared with inputs from all members of the team.

References

- L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, Adv. Mater., 2013, 25, 6642–6671.
- 2 A. J. Heeger, Adv. Mater., 2014, 26, 10-28.
- 3 F. C. Krebs, S. A. Gevorgyana, J. Alstrupa, J. Mater. Chem., 2009, 19, 5442-5451.
- 4 R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen, F. C. Krebs, *Materials Today, 2012*, **15**, 36-49.
- 5 H. Kang, G. Kim, J. Kim, S. Kwon, H. Kim, K. Lee, *Adv. Mater.*, 2016, **28**, 7821-7861.
- 6 Q. Lin, H. Huang, Y. Jing, H. Fu, P. Chang, D. Li, Y. Yao, Z. Fan, J. Mater. Chem. C, 2014, 2, 1233-1247.
- 7 M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sariciftci, S. Bauer, *Nat. Comm., 2012*, 3, 770-776.
- J. Zhao, A. Swinnen, G. V. Assche, J. Manca, D. Vanderzande, B. V. Mele, J. Phys. Chem. B, 2009, 113, 1587–1591.
- 9 S. Berthoa, I. Haeldermansa, A. Swinnena, W. Moonsa, T. Martensa, L. Lutsenb, D. Vanderzandea, J. Mancaa, A. Senesc, A. Bonfiglioc, *Sol. Energ. Mat. Sol.*, 2007, **91**, 385-389.
- 10 J. U. Lee, J. W. Jung, J. W. Jo, W. H. Jo, *J. Mater. Chem., 2012,* **22**, 24265-24283.
- S. B. Dkhil, M. Pfannmöller, M. I. Saba, M. Gaceur, H. Heidari, C. Videlot-Ackermann, O. Margeat, A. Guerrero, J. Bisquert, G. Garcia-Belmonte, A. Mattoni, S. Bals, J. Ackermann, *Adv. Energy Mater.*, 2017, 4, 1601486.
- 12 L. Derue, O. Dautel, A. Tournebize, M. Drees, H. Pan, S. Berthumeyrie, B. Pavageau, E. Cloutet, S. Chambon, L. Hirsch, A. Rivaton, P. Hudhomme, A. Facchetti, G. Wantz, Adv. Mater., 2014, 26, 5831-5838.
- 13 O. Oklobia, T.S. Shafai, Sol. Energ. Mat. Sol., 2013, 117, 1-8.
- 14 M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. D. C. Bradley, J. Nelson, *Nat. Mater.*, 2008, 7, 158-164.
- 15 J. K. J. van Duren, X. Yang, J. Loos, C. W. T. Bulle-Lieuwma, A. B. Sieval, J. C. Hummelen, R. A. J. Janssen, *Adv. Funct. Mater.*, 2004, **14**, 425-434.
- 16 H. Hoppe, N. S. Sariciftci, J. Mater. Chem., 2006, 16, 45-61.
- 17 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Comm., 2014*, **5**, 5293–5300.
- 18 I. A. Howard, R. Mauer, M. Meister, F. Laquai, J. Am. Chem. Soc., 2010, 132, 14866-14876.
- 19 Z. Xiao, Y. Yuan, B. Yang, J. VanDerslice, J. Chen, O. Dyck, G. Duscher, J. Huang, Adv. Mater., 2014, 26, 3068-3075.
- 20 G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, Adv. Funct. Mater., 2007, 17, 1636-1644.
- 21 J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, A. J. Heeger, *J. Am. Chem. Soc.*, 2008, 130, 3619–3623.
- 22 L. Derue, O. Dautel, A. Tournebize, M. Drees, H. Pan, S. Berthumeyrie, B. Pavageau, E. Cloutet, S. Chambon, L. Hirsch, A. Rivaton, P. Hudhomme, A. Facchetti, G. Wantz, Adv. Mater., 2014, 26, 5831-5838.
- 23 Y.-J. Cheng, C.-H. Hsieh, P.-J. Li, C.-S. Hsu, Adv. Funct. Mater., 2011, 21, 1723-1732.

- 24 B. C. Schroeder, Z. Li, M. A. Brady, G. C. Faria, R. S. Ashraf, C. J. Takacs, J. S. Cowart, D. T. Duong, K. H. Chiu, C.-H. Tan, J. T. Cabral, A. Salleo, M. L. Chabinyc, J. R. Durrant, I. McCulloch, Angew. Chem. Int. Ed., 2014, 53, 12870-12875.
- 25 P. Cheng, C. Yan, T.-K. Lau, J. Mai, X. Lu, X. Zhan, Adv. Mater., 2016, 28, 5822-5829.
- 26 M. Jørgensen, K. Norrman, F. C. Krebs, Sol. Energ. Mat. Sol., 2008, 92, 686-714.
- 27 R. Pacios, A. J. Chatten, K. Kawano, J. R. Durrant, D. D. C. Bradley, J. Nelson, *Adv. Funct. Mater.*, 2006, **16**, 2117-2126.
- 28 I. A. Howard, R. Mauer, M. Meister, F. Laquai, J. Am. Chem. Soc., 2010, 132, 14866-14876.
- 29 Z. Xiao, Y. Yuan, B. Yang, J. VanDerslice, J. Chen, O. Dyck, G. Duscher, J. Huang, *Adv. Mater., 2014*, **26**, 3068-3075.
- 30 B. Meng, Z. Wang, W. Ma, Z. Xie, J. Liu, L. Wang, Adv. Funct. Mater., 2016, 26, 226-232.
- 31 M. A. Lampert, P. Mark, Current Injection in Solids, Academic, New York, 1970.
- 32 P. N. Murgatroyd , J. Phys. D., 1970, 3, 151-156.
- 33 C. H. Y. Ho, Q. Dong, H. Yin, W. W. K. Leung, Q. Yang, H. K. H. Lee, S. W. Tsang, S. K. So, Adv. Mater. Interfaces, 2015, 2, 1500166.
- 34 W. B. Jackson, N. M. Amer, A. C. Boccara, D. Fournier, Appl. Opt., 1981, 20, 1333-1344.
- 35 M. H. Chan, S. K. So, K. W. Cheah, J. App. Phy., 1996, 79, 3273-3275.
- 36 M. Kuik, J. Vandenbergh, L. Goris, E. J. Begemann, L. Lutsen, D. J. M. Vanderzande, J. V. Manca, P. W. M. Blom, *Appl. Phys. Lett.*, 2011, 99, 183305.
- 37 C. H. Y. Ho, S. H. Cheung, H.-W. Li, K. L. Chiu, Y. Cheng, H. Yin, M. H. Chan, F. So, S.-W.n Tsang, S. K. So, *Adv. Energy. Mater.*, 2017, 201602360.
- 38 M. H. Brodsky, Manuel Cardona, J. J. Cuomo, Phys. Rev. B, 1977, 16, 3556-3571.
- 39 F. Urbach, Phys. Rev., 1953, 92, 1324.
- 40 M. M. Mandoc, F. B. Kooistra, J. C. Hummelen, B. de Boer, P. W. M. Blom, *Appl. Phys. Lett.*, *2007*, **91**, 263505.
- 41 H. Yan, J. G. Manion, M. Yuan, F. P. García de Arquer, G. R. McKeown, S. Beaupré, M. Leclerc, E. H. Sargent, D. S. Seferos, Adv. Mater., 2016, 28, 6491-6496.
- 42 J. Mai, T.-K. Lau, J. Li, S.-H. Peng§, C.-S. Hsu, U-S. Jeng, J. Zeng, N. Zhao, X. Xiao, X. Lu, *Chem. Mater.*, 2016, 28, 6186–6195.
- 43 J. Mai, T.-K. Lau, T. Xiao, C.-J. Su, U-S. Jeng, N. Zhao, X. Xiao, X. Lu, RSC Adv., 2015, 5, 88500-88507.
- H.-C. Liao, C.-S. Tsao, Y.-T. Shao, S.-Y. Chang, Y.-C. Huang, C.-M. Chuang, T.-H. Lin, C.-Y. Chen, C.-J. Su, U-S. Jeng, Y.-F. Chen, W.-F. Su, *Energy Environ. Sci.*, 2013, 6, 1938-1948.
- 45 Y. Lei, P. Deng, J. Li, M. Lin, F. Zhu, T.-W. Ng, C.-S. Lee, B. S. Ong, *Sci. Rep., 2016*, **6**, 24476.
- 46 Y. Lei, P. Deng, M. Lin, X. Zheng, F. Zhu, B. S. Ong, Adv. Mater., 2016, 28, 6687-6694.

8 | J. Name., 2012, 00, 1-3

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Boosting Photovoltaic Thermal Stability of Fullerene Bulk Heterojunction Solar Cells through Charge Transfer Interactions

Carr Hoi Yi Ho, Huanyang Cao, Yong Lu, Tsz-Ki Lau, Sin Hang Cheung, Ho-Wa Li, Hang Yin, Ka Lok Chiu, Lik-Kuen Ma, Yuanhang Cheng, Sai-Wing Tsang, Xinhui Lu, Shu Kong So and Beng S. Ong

Table of contents:

Charge transfer interaction of donor polymer with an ultra-low concentration of an appositely functionalized 9-fluorenylidene malononitrile in the active layer leads to profoundly enhanced thermal stability of fullerene-based bulk heterojunction organic solar cells. This is attributable to the formation of a "frozen" 3-dimensional mesh-like donor polymer matrix which impedes fullerene aggregation.

