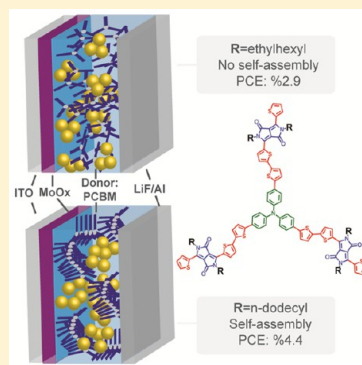


Self-Assembling Tripodal Small-Molecule Donors for Bulk Heterojunction Solar Cells

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Supporting Information

ABSTRACT: The power conversion efficiency of organic solar cells (OSCs) could benefit from systematic studies to improve bulk heterojunction (BHJ) morphology by modifying donor compounds. Supramolecular self-assembly is an attractive strategy to combine the beneficial properties of polymeric donors, such as a well-controlled morphology, with the homogeneous composition of small molecule donors for OSCs. We report here on two tripodal “star-shaped” small-molecule donor compounds based on diketopyrrolopyrrole (DPP) side chains for solution-processed BHJ OSCs. The tripod molecules were found not to aggregate in solution or form crystalline domains in thin films when a branched alkyl chain (2-ethylhexyl) substituent was used, whereas linear (dodecyl) alkyl chains promote the formation of one-dimensional (1D) nanowires and more crystalline domains in the solid state. We demonstrate that the 1D self-assembly of these tripods enhances the performance of the corresponding solution-processed OSCs by 50%, which is attributed to the significant increase in the fill factor of devices resulting from a reduction of trap states.



INTRODUCTION

Solution-processed bulk heterojunction (BHJ) organic photovoltaic (OPV) materials remain under intensive investigation after almost 2 decades of fundamental research driven by their potential to bring low-cost, lightweight, flexible solar-to-electric energy conversion devices to market.^{1–4} OPV power conversion efficiencies (PCEs) have been rising steadily, now exceeding 9%.⁵ The active layer of a BHJ OSC typically utilizes a fullerene-based acceptor (n-type) material in a phase-separated blend with polymeric or small-molecule organic donor (p-type) material.^{6,7} The morphological elements of the active layer's p–n heterojunction include the topology of its percolation network, domain sizes, distribution of trap sites, and spatial orientation of molecules. These features collectively play a critical role in the physical phenomena that ultimately lead to charge extraction.⁸ Research efforts to increase OPV PCEs often involve controlling BHJ morphology through covalent modification of the donor compounds⁹ or optimization of processing conditions,¹⁰ (e.g., thermal annealing,¹¹ solvent vapor annealing,^{12,13} solvent additives¹⁴). These two factors influence the process of spinodal decomposition during formation of the active layer. An alternative strategy for controlling active layer morphology is the use of programmed self-assembly in an attempt to control molecular organization within the active layer at specific length scales.^{15,16} There have been several strategies used to promote self-assembly of donor

molecules in solution, including discotic liquid crystals,^{17,18} nematic liquid crystals,¹⁹ liquid crystalline polymers,²⁰ nanostructured block copolymers,²¹ bimolecular crystals,²² hydrogen bonded networks,²³ and one-dimensional (1D) nanostructures.²⁴ Our group has focused recently on the use of small molecule donors that assemble into 1D nanofibers for OSCs in order to form high interfacial area percolated networks when blended with fullerenes.^{25–27}

Small molecules with linear architecture have been used to create devices with efficiencies of 6%–9%.^{28–33} Several “star-shaped” donors with more complex architectures (C-3 symmetric or tripodal) have also been reported, with efficiencies that have now surpassed 4%.^{34–38} We envisioned that the increased π – π stacking interactions of these disc-like molecules would promote fiber assembly when appended with alkyl side chains for solubility. We chose diketopyrrolopyrrole (DPP) units flanked by thiophene groups to serve as the chromophoric “arms” of our tripods because of DPP's favorable optoelectronic properties and well-established use in efficient OPVs.^{27,32,39} We designed tripodal donor molecules T_{EH} (with 2-ethylhexyl) and T_{C12} (with dodecyl) (Figure 1a) in which an electron-donating triphenylamine (TPA) unit serves as the

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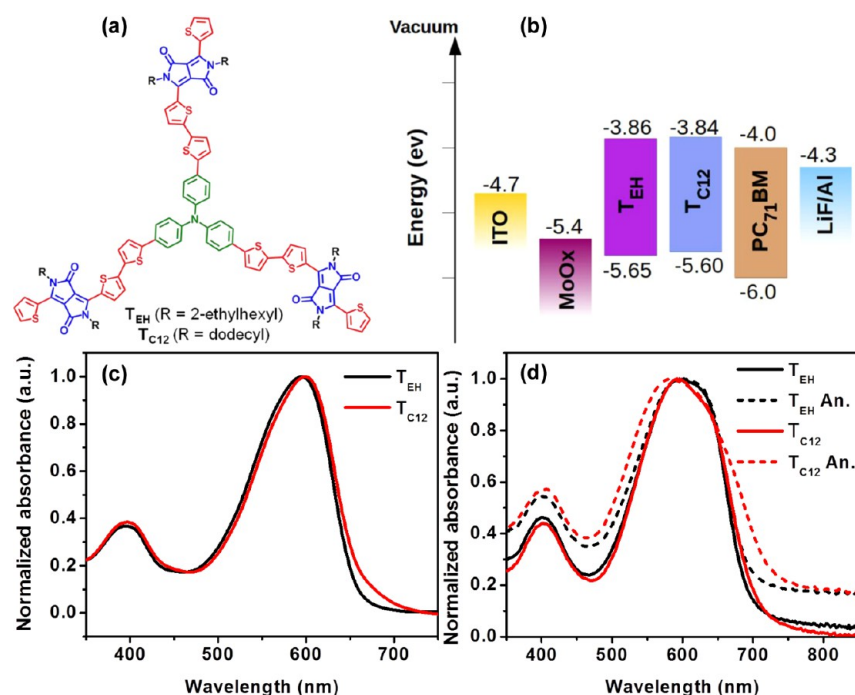


Figure 1. (a) Chemical structure of T_{EH} and T_{C12} molecules. (b) Energy levels of T_{EH} and T_{C12} molecules with the energy levels of other device layers. (c) Absorption spectra of T_{EH} and T_{C12} in chloroform solution and (d) in solid film cast from chloroform before and after annealing.

central trifurcated core.⁴⁰ A recent study by Giuseppone and co-workers has shown that TPA exhibits a remarkable propensity to form fibers and conduct charge carriers via the generation and sharing of free radicals upon photoexcitation.⁴¹ While several tripodal molecules incorporating similar TPA–DPP designs have been reported for OPVs,^{42,43} there was no indication that they self-assemble into well-defined nanostructures. A similar set of tripodal molecules with the 2-ethylhexyl groups and differing number of thiophenes was recently reported and yielded devices with PCEs as high as 2.95%.⁴⁴ The true potential of tripodal chromophore solar cells will not be realized until the role of self-assembly in determining the morphology and performance is understood. In this work we investigate the influence of side chains on molecular packing of TPA–DPP tripods and therefore solar cell performance. As a complement to T_{EH} , we study a related new tripod molecule, T_{C12} , with straight side chains that will not interfere with molecular packing. The dodecyl (C12) side chain is used because shorter straight chains were not able to solubilize the molecule enough to form homogeneous thin films and working devices.

EXPERIMENTAL SECTION

Materials and Methods. $DPPC_{12}$ and $N(PhTSnBu_3)_3$ were prepared according to published literature procedures.⁴⁴ All solvents and reagents were purchased from commercial suppliers (Aldrich, Matrix Scientific) and used without further purification, with the exceptions of *N*-Bromosuccinimide (NBS), which was recrystallized from water. All reactions were carried out under an inert atmosphere of N_2 . Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-F₂₅₄ (Merck 5554). Flash column chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase.

Experimental Details. NMR spectra were recorded on a Bruker Avance III 500 spectrometer with working frequencies

of 500 MHz for 1H and 125 MHz for ^{13}C . Chemical shifts are reported in ppm and referenced to the residual nondeuterated solvent frequencies ($CDCl_3$: δ 7.27 ppm for 1H , δ 77.0 ppm for ^{13}C). Mass spectra were obtained on a Bruker Autoflex III MALDI mass spectrometer. Ultraviolet–visible (UV–vis) spectra were recorded on a PerkinElmer LAMBDA 1050 spectrophotometer. Photovoltaic measurements were recorded while the devices were illuminated by an Oriel Xe solar simulator equipped with an Oriel 130 monochromator and a Keithley 2400 source meter. Filters were used to cut off grating overtones. The solar spectrum was simulated using an AM 1.5 filter with $100\text{ mW}\cdot\text{cm}^{-2}$ power density. A calibrated silicon reference solar cell with a KG5 filter certified by the National Renewable Energy Laboratory was used to confirm the measurement conditions. AFM characterization was performed using a Bruker Dimension ICON atomic force microscope (Bruker Co.) at ambient conditions. Tapping mode was utilized with single-beam silicon cantilevers with a nominal oscillation frequency of 300 kHz. GIXD measurements were performed at Beamline 8ID-E of the Advanced Photon Source at Argonne National Laboratory. An X-ray wavelength of $\lambda = 1.6868\text{ \AA}$ was used and data were collected using a 1–2 s exposure at a sample–detector distance of 204 mm with a Pilatus photodiode array. Impedance spectroscopy measurements were carried out on an AUTOLAB [PGSTAT128N with the FRA32 module for EIS] electrochemical system.

Synthesis and Characterization. $TDPP_{C12}\text{-Br}$. Protected from light, NBS (558 mg, 3.14 mmol) in $CHCl_3$ (50 mL) was added to a solution of $TDPP_{C12}$ (2.5 g, 3.9 mmol) in $CHCl_3$ (100 mL) at $0\text{ }^\circ\text{C}$. The reaction was stirred at ambient temperature overnight and the solvent was removed under reduced pressure using rotary evaporator. The residue was subjected to flash column chromatography on SiO_2 (hexanes–DCM, 2:1) to afford the title compound as a purple solid (625 mg, 22%). 1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.94 (d, J = 3.9 Hz, 1H), 8.68 (d, J = 4.1 Hz, 1H), 7.66 (d, J = 4.9 Hz,

1H), 7.29 (dd, $J = 4.7, 4.2$ Hz, 1H), 7.25 (d, $J = 4.3$ Hz, 2H), 4.07 (t, $J = 7.9$ Hz, 2H), 4.00 (t, $J = 7.6$ Hz, 2H), 1.79–1.68 (m, 6H), 1.47–1.37 (m, 6H), 1.37–1.21 (m, 36H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): $\delta = 161.3, 161.1, 140.5, 138.5, 135.5, 135.1, 131.5, 131.2, 131.0, 129.7, 128.7, 118.8, 107.9, 107.6, 42.3, 42.2, 31.9, 30.0, 30.0, 29.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.2, 26.9, 26.8, 22.7, 14.1$. MS (MALDI) m/z , with no matrix: calcd for $\text{C}_{38}\text{H}_{55}\text{BrN}_2\text{O}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$, 716.890; found, 716.955.

$\text{T}_{\text{C}_{12}}$. Dry toluene (10 mL) and dry DMF (5 mL) were added to $\text{N}(\text{PhTSSnBu}_3)_3$ and $\text{TDPP}_{\text{C}_{12}}\text{-Br}$ (175 mg, 0.245 mmol) and degassed with N_2 . $\text{Pd}(\text{PPh}_3)_4$ (10.0 mg, 8.66 μmol) was added and the reaction was heated to 120 $^\circ\text{C}$ and stirred for 24 h. The reaction mixture was poured into MeOH (150 mL), and the resulting precipitate was collected by vacuum filtration and chromatography was carried on SiO_2 (PhMe-CHCl_3 , gradient from 50:50 to 0:100). The blue solid was recrystallized by slow vapor diffusion of EtOAc into CHCl_3 to afford the title compound as a shiny, blue solid (83 mg, 14%). ^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 8.96$ (d, $J = 4.2$ Hz, 3H), 8.93 (d, $J = 3.9$ Hz, 3H), 7.64 (d, $J = 5.1$ Hz, 3H), 7.56 (d, $J = 8.6$ Hz, 6H), 7.36 (d, $J = 4.1$ Hz, 3H), 7.33 (d, $J = 3.7$ Hz, 3H), 7.29 (dd, $J = 4.48$ Hz, 4.10 Hz, 3H), 7.25 (d, $J = 3.9$ Hz, 3H), 7.20 (d, $J = 9.1$ Hz, 6H), 4.10 (t, $J = 7.5$ Hz, 12H), 1.84–1.73 (m, 12H), 1.5–1.2, (m, 108H), 0.87 (t, $J = 6.8$ Hz, 9H), 0.85 (t, $J = 6.8$ Hz, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): $\delta = 161.4, 161.2, 146.8, 143.1, 139.6, 139.4, 136.7, 135.1, 134.7, 130.6, 129.8, 128.7, 128.6, 127.8, 126.7, 126.3, 124.7, 124.5, 123.6, 116.4, 107.9, 107.9, 42.3, 42.2, 31.9, 29.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.2, 26.8, 22.7, 14.1$. MS (MALDI) m/z , with dithranol matrix: calcd for $\text{C}_{144}\text{H}_{183}\text{N}_7\text{O}_6\text{S}_9\text{H}$ [$\text{M} + \text{H}$] $^+$, 2397.658; found, 2397.636

Device Fabrication. Experimental conditions for active layer deposition such as solvent, concentration and solvent composition were optimized. Prepatterned indium-doped tin oxide (ITO) on glass was used as the transparent bottom electrode. The ITO was scrubbed with soapy water and cleaned by ultrasonically in hexanes, soapy water, water, and a 1:1:1 solution of acetone/methanol/2-propanol. The electrode was then blown dry in a N_2 stream and transferred into a N_2 glovebox (O_2 and $\text{H}_2\text{O} < 0.1$ ppm). Before active layer coating, MoO_x (10 nm) was thermally evaporated on ITO surface as the interfacial layer. Bulk heterojunction photovoltaic devices were fabricated from blends of donor small molecule and acceptor phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM). In the optimized conditions, the donor/acceptor ratio is fixed at 1:2 for the $\text{T}_{\text{C}_{12}}$ molecules and 1:3 for T_{EH} , with a total solution concentration of 13.5 mg/mL for $\text{T}_{\text{C}_{12}}$ and 16 mg/mL for T_{EH} in chloroform. Films were cast by spin-coating at 1500 rpm for $\text{T}_{\text{C}_{12}}$ and 4000 rpm for T_{EH} in the glovebox for 60 s with no thermal annealing for $\text{T}_{\text{C}_{12}}$ and 5 min of annealing on a hot plate at 100 $^\circ\text{C}$ for T_{EH} . Total organic layer thickness ranged from 90 to 100 nm as determined by AFM. Devices were completed by thermally evaporating 1 nm of LiF then 100 nm of Al through a shadow mask at 1×10^{-6} mbar to yield devices of 4 mm 2 in area and sealed with a UV-curable epoxy if needed. The devices for space-charge-limited-current (SCLC) measurements were fabricated with a similar procedure. The top electrode was replaced with Au (50 nm) rather than LiF/Al in order to suppress electron injection.

RESULTS AND DISCUSSION

Synthesis and Characterization. The tripodal donors were synthesized by Stille cross coupling of tris(4-(5-(tributylstannyl)thiophen-2-yl)phenyl)amine and monobrominated thiophene-flanked DPP compounds (BrTDPP) with 2-ethylhexyl (EH) or dodecyl (C_{12}) side-chains to afford T_{EH} and $\text{T}_{\text{C}_{12}}$, respectively. Detailed synthetic procedures can be found in the [experimental section](#). Variations with hexyl (C6) and octyl (C8) side chains were made as well, but were found to be unsuitable for device work due to poor solubility.

In order to study the impact of self-assembly on solar device performance, two homologous molecules, T_{EH} and $\text{T}_{\text{C}_{12}}$ (see [Figure 1a](#)), were synthesized. These were found to have similar electronic and optical properties. The highest occupied molecular orbital (HOMO) levels were calculated by ultraviolet photoelectron spectroscopy (UPS) (see the [Supporting Information](#) for details), and the band gaps were calculated from the onset of thin film UV–vis absorption spectra. T_{EH} has a HOMO of -5.65 eV relative to vacuum level, and $\text{T}_{\text{C}_{12}}$ has a similar one of -5.60 eV. The HOMO levels of both compounds show slight offsets from MoO_x , which is favorable for hole transport out of the active layer. The band gaps of T_{EH} and $\text{T}_{\text{C}_{12}}$ are 1.79 and 1.76 eV, respectively. The compounds show offsets from the lowest unoccupied molecular orbital (LUMO) of PC_{71}BM of 0.16 and 0.14 eV. As can be seen in [Figure 1b](#), the energy levels of the two compounds are comparable, and their small offsets to PC_{71}BM are favorable for effective exciton splitting. The UV–vis absorption spectra of T_{EH} and $\text{T}_{\text{C}_{12}}$ in CHCl_3 ([Figure 1c](#)) confirm that the optical properties between the two molecules are analogous (both with extinction coefficients higher than $10^5 \text{ M}^{-1}\text{cm}^{-1}$). T_{EH} shows an absorption maximum at 595 nm and $\text{T}_{\text{C}_{12}}$ at 598 nm, and they both absorb up to wavelengths of approximately 700 nm. We also observed some differences in the absorption spectra of the two tripods as thin films spin coated from CHCl_3 ([Figure 1d](#)). The absorption maximum of the T_{EH} film is red-shifted, while that of $\text{T}_{\text{C}_{12}}$ is blue-shifted relative to the solution spectra. Both of these shifts are magnified upon annealing. The red-shift in the case of T_{EH} indicates the formation of J -aggregates involving the stacking of T_{EH} molecules in an end-to-end manner. Similarly, the blue-shift can be attributed to the formation of H -aggregates, providing evidence for the cofacial stacking of $\text{T}_{\text{C}_{12}}$ molecules in the film. Additionally, a shoulder in the $\text{T}_{\text{C}_{12}}$ film at 670 nm most likely arises from J -aggregate formation involved in nanowire bundling. The optical properties of the compounds are summarized in [Table 1](#).

Table 1. Optical Properties of Solutions and Films of Tripod Molecules

	solution λ_{max} (nm)	film λ_{max} (nm)	film annealed λ_{max} (nm)	E_g (eV) ^a	ϵ at $\lambda_{\text{max}} \times 10^5$ ($\text{M}^{-1}\text{cm}^{-1}$)
T_{EH}	595	596	600	1.79	1.7
$\text{T}_{\text{C}_{12}}$	598	592	584	1.76	1.3

^aMeasured from the onset of the absorbance of the film.

Supramolecular Self-Assembly of Tripodal Molecules.

The assembly of the tripodal molecules was further characterized by atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD). AFM topography and phase images in [Figure 2a](#) and [Figure 2d](#) show that T_{EH} forms featureless films when cast from chloroform, even after annealing for 5 min at 120 $^\circ\text{C}$. Conversely, [Figure 2b](#) and

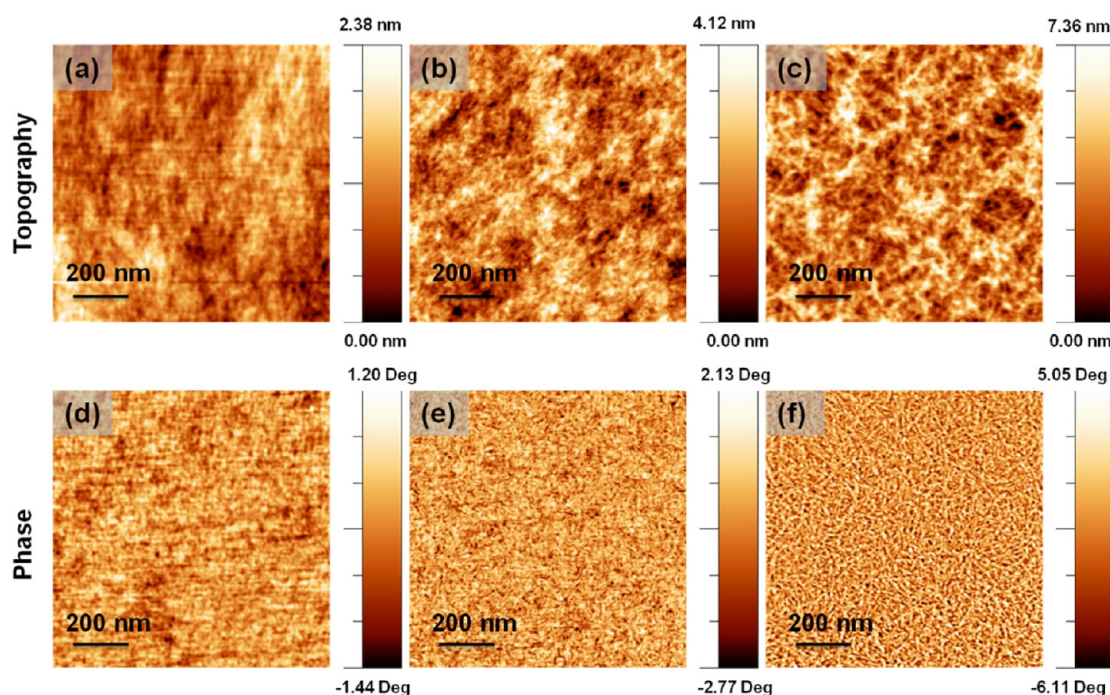


Figure 2. AFM topography images of T_{EH} cast from chloroform (a), T_{C12} cast from chloroform (b), and T_{C12} cast from chlorobenzene (c), with the corresponding phase images (d–f), respectively.

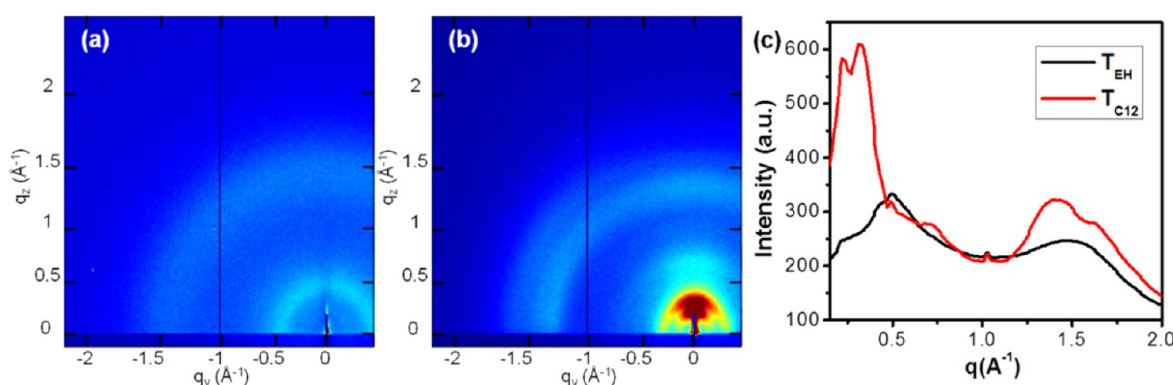


Figure 3. GIXD of T_{EH} (a) and T_{C12} (b) drop cast from chloroform. (c) Line profiles of GIXD data for T_{EH} and T_{C12} .

Figure 2e show that T_{C12} forms short nanowires when cast under same conditions. When a T_{C12} solution is cast from chlorobenzene, the self-assembly of the nanowire morphology is further enhanced, as shown in Figure 2c and Figure 2f. The height of the nanowires in Figure 2c is around 2.5–3 nm, which scales with the molecular diameter of T_{C12} molecules. On the other hand, there was no such morphology change for T_{EH} when it was cast from chlorobenzene (Figure S6).

2D GIXD data collected from films of the tripodal molecules are shown in Figure 3. A T_{EH} film drop cast from chloroform and slowly dried produces diffuse and weak diffraction rings (Figure 3a). The ring around $0.5 \text{ \AA}^{-1}$ corresponds to a 1.3 nm distance, which can be attributed to the center-to-center distance when one arm of each molecule overlaps. The ring around $1.47 \text{ \AA}^{-1}$ corresponds to 0.43 nm, which can arise from the cofacial packing of each arm of adjacent molecules in a stack. This spacing is greater than what is expected for π – π stacking distances ($\sim 0.37 \text{ nm}$) in conjugated small molecules. In addition, neither of the diffuse rings have a directional preference with respect to the substrate. We conclude that the

T_{EH} molecules do not self-organize with a significant order parameter. On the other hand, T_{C12} films prepared under similar conditions exhibit diffraction rings with much higher intensities (Figure 3b). Two distinct rings at $0.22 \text{ \AA}^{-1}$ (2.9 nm) and $0.31 \text{ \AA}^{-1}$ (2.0 nm) appear in the low q region (Figure 3c). The 2.9 nm distance can be attributed to the center-to-center spacing between two adjacent nanowires, in agreement with AFM observations. The ring around $1.4 \text{ \AA}^{-1}$ (0.45 nm) is similar to T_{EH} but in this case there is a small hump in the line profile around $1.6 \text{ \AA}^{-1}$ (0.38 nm) which is very close to conventional π – π stacking distances. In summary, GIXD results show that T_{C12} molecules tend to organize with cofacial stacking to a greater extent than T_{EH} molecules, which is consistent with the “nanowire” morphologies observed by AFM.

To support this hypothesis, a classical molecular dynamics (MD) simulation was performed with Groningen machine for chemical structures (GROMACS) package.^{45,46} The objective of the simulation was to compare the relative ordering capacity in solution of the two donor molecules investigated here. We

carried this out using explicit solvent molecules since interaction potentials for MD are parametrized against solvent environments. In vacuum, we would expect to predict an overly packed structure.^{47,48} The simulations were therefore done in water and chloroform.

The final supramolecular structures predicted by the simulations of the two molecules are shown in Figure 4a and

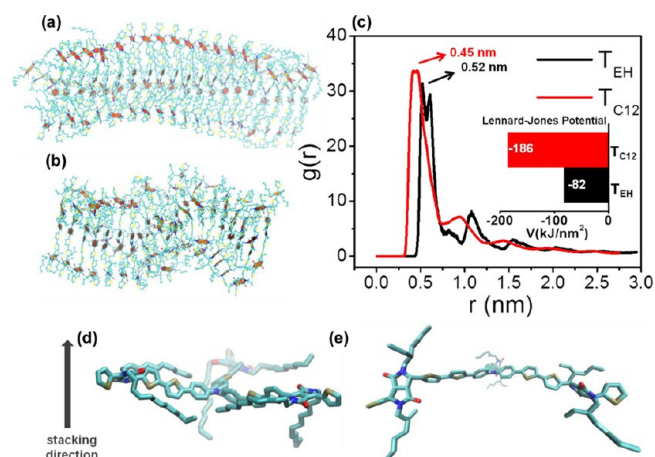


Figure 4. MD simulation of stacked (a) T_{C12} and (b) T_{EH} and (c) radial distribution function of the molecules with an inset of Lennard-Jones potential values. Single molecules from the MD stacking simulation for (d) T_{C12} and (e) T_{EH} .

Figure 4b. T_{C12} shows ordering and alignment of molecules in the assembly, while T_{EH} exhibits a significant degree of disorder. Moreover, T_{C12} molecules appear from the simulation to be much less challenged by sterics along the stacking direction (Figure 4d) relative to T_{EH} molecules (Figure 4e). We

have quantified further the ordering stability in both supramolecular systems using the intermolecular radial distribution functions (RDF) shown in Figure 4c. The RDF of T_{C12} assemblies contains sharper and more intense peaks than that of the T_{EH} system indicating a higher local density of π - π stacking. The peaks of the T_{C12} compound yield an intermolecular spacing of 0.45 nm compared to 0.52 nm for T_{EH} . One might expect that the larger spacing between molecules predicted by the simulation relative to GIXD data can be attributed to the explicit use of a solvent environment. Also, a degree of periodicity can be observed in the peaks of T_{C12} , which provides further evidence of the stronger interactions T_{C12} relative to T_{EH} . The Lennard-Jones energy calculations are shown in the inset in Figure 4c, quantifying the relative strengths of noncovalent interactions in the two systems, -186 kJ/nm² for T_{C12} and -82 kJ/nm² for T_{EH} .

Morphology of the Active Layer. AFM was utilized to evaluate the morphology of active layer films containing donor molecules and PC₇₁BM as the electron acceptor. Chloroform was used as the solvent for devices because the limited solubility of T_{C12} in chlorobenzene resulted in devices with lower efficiencies. As shown in Figure 5, parts a and d, T_{EH} :PC₇₁BM cast from chloroform without any additives forms predominantly flat, featureless films. Two solvent additives were used in this study, 1,8-diiodooctane (DIO) and *m*-cresol (MC). DIO is a high boiling point solvent additive that is known to solubilize PC₇₁BM, and therefore allows the film to reach a more crystalline morphology by slowing the precipitation of the fullerene phase.⁴⁹ MC was used to increase the solubility of the donor molecule. Upon the addition of DIO, the root-mean-square (RMS) roughness of the film increases from 0.3 to 1.2 nm (Figure 5b), but the phase image (Figure 5e) indicates that the film remains homogeneous without any obvious sign of textures resulting from supramolecular self-assembly. The

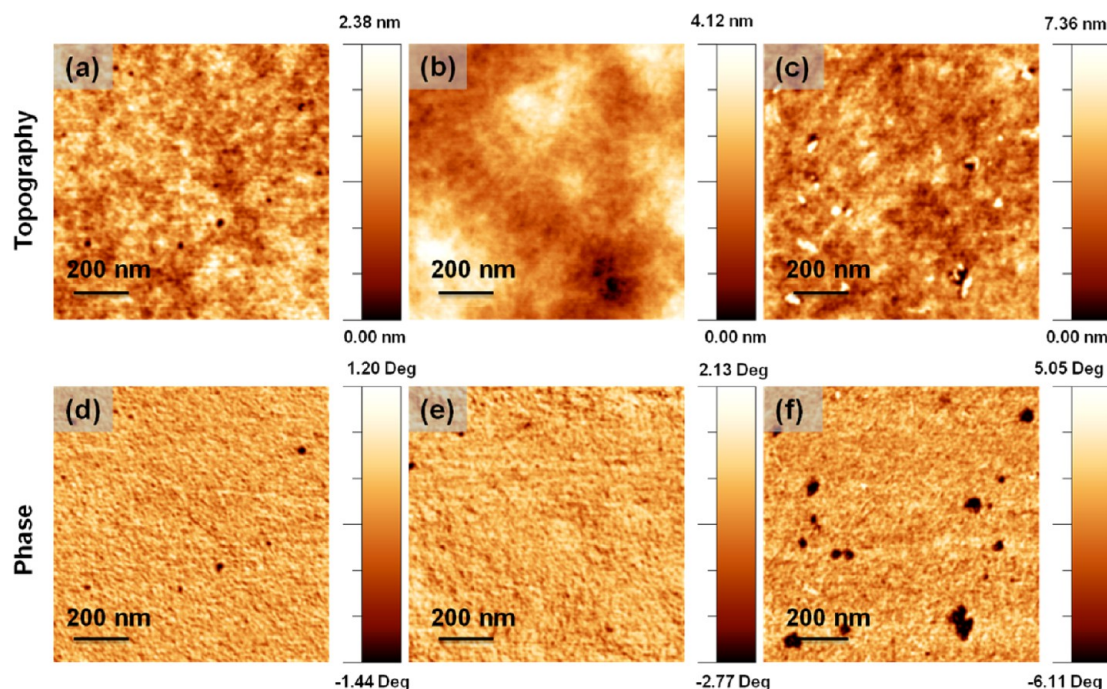


Figure 5. AFM topography and phase images of films created with the T_{EH} donor. Parts a and d are, respectively, the height and phase image of the material without any solvent additives, parts b and e have 0.8 volume percent DIO, and parts c and f contain both the same amount of DIO and 1.0 volume percent *m*-cresol.

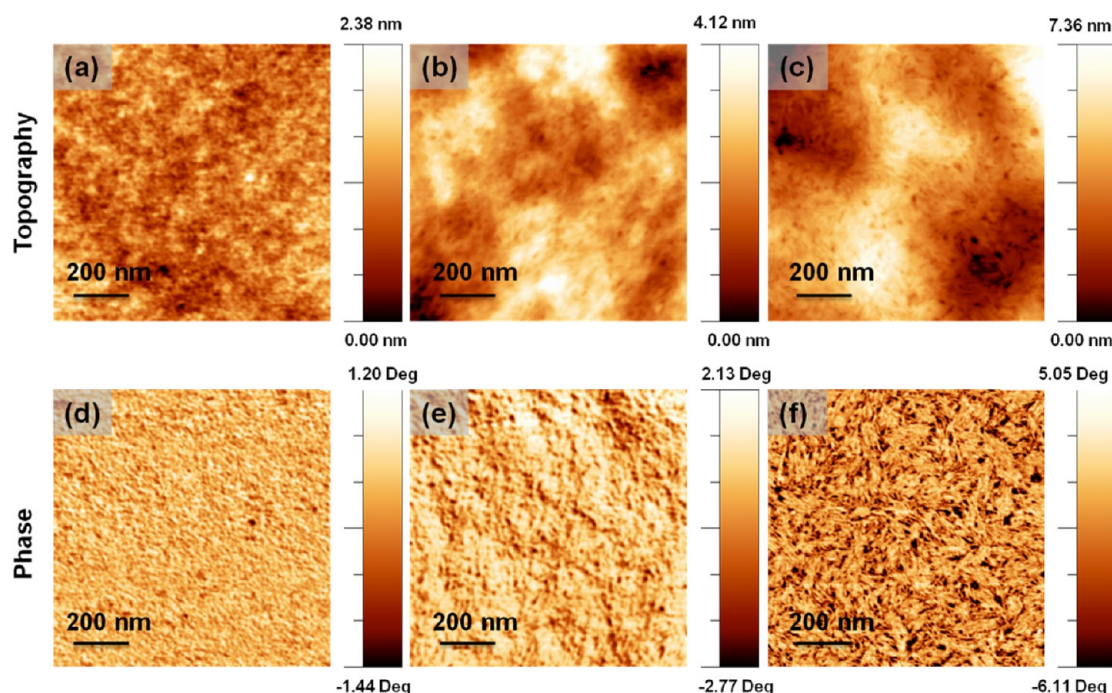


Figure 6. AFM topography and phase images of films created with the T_{C12} donor. Parts a and d are, respectively, the height and phase image of the material without any solvent additives, parts b and e, have 0.8 volume percent DIO, and parts c and f contain both the same amount of DIO and 1.0 volume percent *m*-cresol.

Table 2. Optimized Solar Cell Results of Tripod Molecules with $PC_{71}BM$

sample	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	R_{sh} (Ω·cm ²)	R_s (Ω·cm ²)
T_{EH} : $PC_{71}BM$	7.78	0.89	35	2.41 (2.34) ^a	212	30
T_{EH} : $PC_{71}BM$ with DIO	8.61	0.87	37	2.75 (2.63)	167	22
T_{EH} : $PC_{71}BM$ with DIO + MC	8.95	0.89	36	2.91 (2.82)	200	27
T_{C12} : $PC_{71}BM$	4.92	0.83	32	1.29 (1.23)	230	57
T_{C12} : $PC_{71}BM$ with DIO	10.10	0.73	57	4.19 (4.04)	322	8
T_{C12} : $PC_{71}BM$ with DIO + MC	10.17	0.75	58	4.39 (4.26)	390	9

^aAverage PCE of four devices.

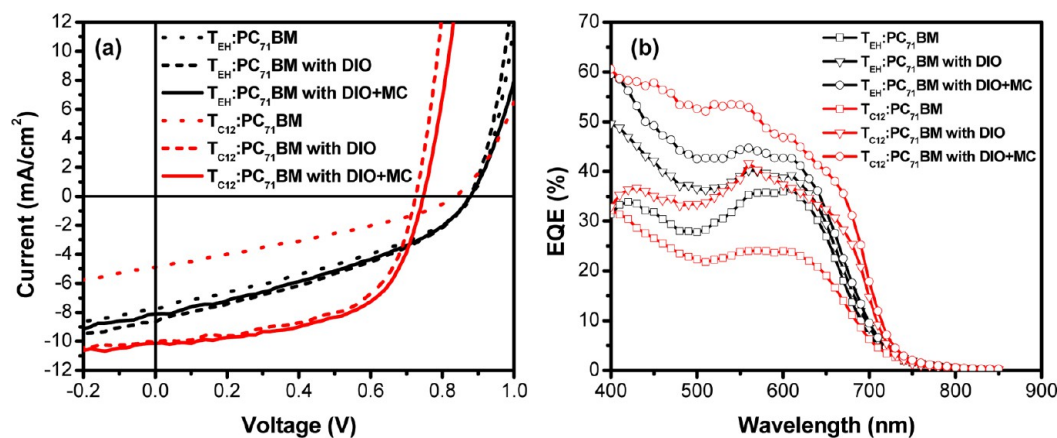


Figure 7. (a) J - V characteristics of optimized organic solar cells of tripod molecules with $PC_{71}BM$ under illumination (AM 1.5). (b) External quantum efficiency (EQE) of the same devices.

incorporation of MC as a solvent additive flattens the film (Figure 5c), returning the roughness to 0.3 nm, but does not induce any obvious nanoscale organization (Figure 5f). T_{C12} : $PC_{71}BM$ films (Figure 6a) are equally featureless in the absence of any solvent additives. Although T_{C12} forms small nanowires in chloroform, it forms featureless films after

blending with $PC_{71}BM$ (Figure 6d). One of the reasons for this could be that $PC_{71}BM$ disrupts the stacking of tripod molecules. Another reason could be that chloroform leaves the film quickly during the spin coating process and does not provide enough time for T_{C12} molecules to stack effectively. However, the incorporation of DIO increases both the

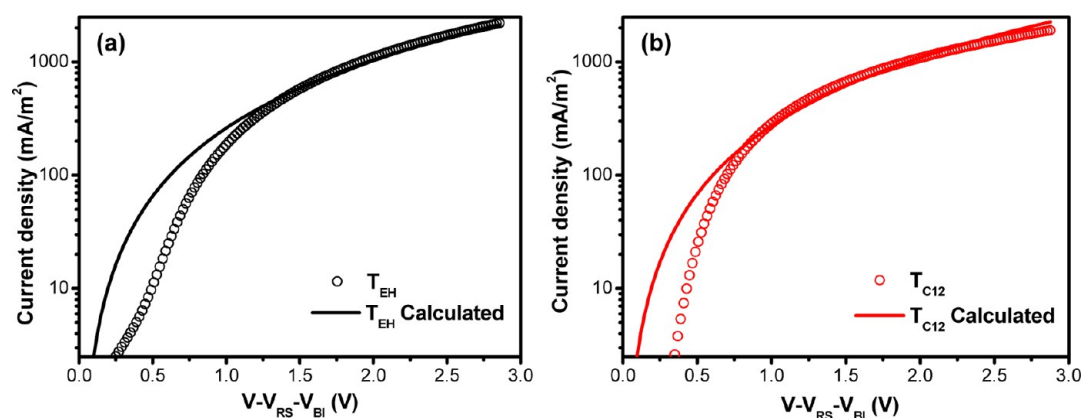


Figure 8. Experimental dark-current densities measured at room temperature in a hole-only device configuration (open circles) superimposed with curves calculated from SCLC theory (solid lines) for (a) T_{EH} :PC₇₁BM with DIO + MC and (b) T_{C12} :PC₇₁BM with DIO + MC.

roughness of the film from 0.3 to 2.6 nm (Figure 6b) and creates large, seemingly amorphous features in the phase image (Figure 6e). The aggregates that appear in the phase image are potentially bundled nanowires that are too dense to be clearly resolved by AFM. In the third set of images, it is apparent that the combination of MC and DIO promotes assembly of T_{C12} into a well-dispersed network of nanowires. Instead of lowering the roughness of the film as in the case of T_{EH} , the nanowires that form in the presence of MC and DIO additives raise the RMS roughness to 3.5 nm (Figure 6c). The nanowires visible in Figure 6f are likely well-dispersed but otherwise identical to the bundles present in Figure 6e, since the UV–vis spectra of the two active layer films show the same features with minimal spectral shift (see Figure S7). GIXD characterization was also performed on the active layer blends, but few features could be resolved, indicating that the stacking of tripodal donors is disrupted by PC₇₁BM during spin-casting (Figure S8).

Photovoltaic Properties of Tripodal Molecules. Solar cells containing T_{C12} and T_{EH} were fabricated using optimized weight ratios of donor:PC₇₁BM of 1:2 and 1:3, respectively. Each blend used chloroform as the primary solvent. Annealing conditions for T_{EH} and T_{C12} devices were optimized separately. For T_{EH} , annealing at 100 °C for 5 min resulted in the best performing devices. By contrast, the T_{C12} devices performed best when not annealed. The results of optimized devices are summarized in Table 2 and Figure 7, parts a and b, and further information on the fabricated devices can be found in the Supporting Information. Without any solvent additives, devices based on T_{EH} show higher performance than those of T_{C12} , with PCEs of 2.41% and 1.29%, respectively. T_{C12} exhibits slightly lower open circuit voltage (V_{oc}) and significantly lower short circuit current (J_{sc}) than T_{EH} . The drop in V_{oc} matches the difference in HOMO levels between the two donors, and the change in J_{sc} can be attributed to a lower solubility of the T_{C12} donor and its longer, electrically insulating alkyl tails. The addition of 0.8 volume percent DIO, however, greatly increases the performance of both donors. As demonstrated by the AFM images (Figures 5 and 6), DIO induces the formation of molecular nanowires in the active layer for T_{C12} , which can explain the significant increase in fill factor (FF) from 0.32 to 0.54, and J_{sc} from 7.78 to 10.19 mA·cm^{−2}. Moreover, the series resistance of T_{C12} decreases significantly from 57 to 8 Ω·cm², while T_{EH} had a much smaller decrease from 30 to 22 Ω·cm². Interestingly, the V_{oc} of T_{C12} devices was further depressed by the addition of DIO. This decrease can be attributed to the

assembly of the nanowires with long alkyl tails further impeding the donor–fullerene interactions and to a narrowing of the band gap and increase in the donor HOMO level on account of π – π stacking. Since the two molecules show very similar optical properties, we believe the difference in performance is due to the self-assembly of T_{C12} into a supramolecular nanostructure. T_{EH} does not form nanowires in the film, and exhibits inferior performance compared to T_{C12} after DIO is added. The performance of the solar cells was further improved by the addition of 1.0 volume percent MC as a solvent additive, which most likely functions as a dispersant. The addition of MC increased the shunt resistance of the T_{EH} active layer from 167 to 200 Ω·cm², while T_{C12} active layers rose from 322 to 389 Ω·cm². The fully optimized devices have a PCE of 4.39% for T_{C12} and 2.91% for T_{EH} . Our optimized results for T_{EH} are in agreement with what has been reported previously.⁴⁴ We conclude that the use of linear alkyl tails rather than branched ones promotes supramolecular self-assembly in these tripodal molecules, imparting a 50% improvement in device performance while minimally affecting the optoelectronic properties of the molecules.

Hole Mobility and Impedance Spectroscopy of Tripodal Solar Cells. To explain the relative increase in FF for the T_{C12} devices with additives, we performed hole mobility measurements and impedance spectroscopy on active layers cast from solutions containing both solvent additives (DIO + MC). It has been shown that increases in FF are correlated with increases in hole mobility and reduction of trap states.⁵⁰ The hole mobilities of the active layers were measured for hole-only devices fabricated with gold top electrodes and using the space-charge limited current (SCLC) method.⁵¹ The SCLC regime occurs at higher voltages, and so the hole mobilities were extracted from a fit of those data points, as shown in Figure 8a and Figure 8b. The hole mobility values for the T_{EH} device (5.2×10^{-5} cm²·V^{−1}·s^{−1}) and the T_{C12} device (4.0×10^{-5} cm²·V^{−1}·s^{−1}) are very similar. Thus, changes in hole mobility do not explain the improved FF in the T_{C12} device. Furthermore, the device mobilities measured cannot be used to draw conclusions about differences in mobilities corresponding to the two molecules used, since this property in the device is influenced by other factors including molecular packing and alignment, nanoscale morphology, the presence of PC₇₁BM, interfaces, and trap states.

In order to study the recombination kinetics of our system, impedance spectroscopy was carried out on devices under open

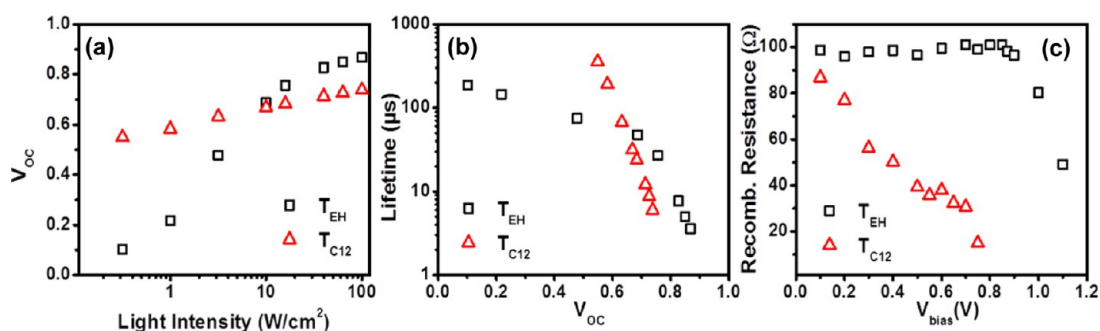


Figure 9. (a) V_{OC} versus light intensity, (b) lifetime versus V_{OC} , (c) and recombination resistance versus applied bias (V_{bias}) of the optimized T_{EH} and T_{C12} devices.

circuit conditions. Upon varying the illumination, the photovoltage of the T_{C12} film scales linearly, with $dV_{OC}/d(\ln(\Phi)) = 1.3k_B T/q$, reasonably close to the expected value of unity for a system experiencing bimolecular recombination.⁵² However, the photovoltage of the T_{EH} film is far more sensitive to light intensity, its slope changing from 2.4 at higher light intensities to 6.8 at lower light intensities, indicating the presence of an additional recombination mechanism (Figure 9a). Furthermore, while the carrier lifetime in the T_{C12} film shows the predicted dependence on V_{OC} , the carrier lifetime in the T_{EH} film is nonlinear, trending toward a smaller slope at low illumination intensities (Figure 9b), which suggests that trap-mediated recombination is far more prevalent in the T_{EH} film than in the T_{C12} film.⁵³

The device with a larger degree of trap recombination would be expected to have a higher series resistance. When the bias is swept (Figure 9c) the series resistance of the T_{EH} film is nearly unchanged until it dramatically decreases as the V_{OC} is approached, implying that the traps lie deep in the energy landscape of the system. In contrast, the series resistance of the T_{C12} film decreases gradually as the bias is swept, suggesting that that device's trap states are shallow and easily surmounted. On the basis of these impedance spectroscopy experiments, we conclude that trap states in the T_{EH} active layer are more numerous and deeper seated than those in the T_{C12} active layer. Therefore, the supramolecular self-assembly of T_{C12} molecules creates ordered domains, while steric effects prevent T_{EH} molecules from stacking thus forming amorphous domains with more structural defects that may lead to electronic trap states.

CONCLUSIONS

Two homologous tripodal small molecule electron donors with triphenylamine cores and diketopyrrolopyrrole chromophoric arms were synthesized and used to study the impact of supramolecular self-assembly on OPV performance. We found that branched alkyl solubilizing chains inhibit the self-assembly of these tripodal molecules, while linear side chains promote the self-assembly of bundled one-dimensional nanowires. The two molecules have comparable optoelectronic properties in solution and neat films, but respond differently to the addition of solvent additives. This in turn generates significantly different film morphologies and device performances. The compound with linear side chains (T_{C12}) assembles into nanowires, and also shows a 50% increase in PCE relative to its branched counterpart (T_{EH}) owing to a significant gain in FF. We attribute the improvement in performance to the nanowires reducing trap states in the active layer, which is supported by

impedance spectroscopy. This work demonstrates that creating supramolecular structures via self-assembly is a useful strategy for improving the photovoltaic performance of small molecules by helping to control morphology across length scales.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b10064.

Circuit model used for fitting, impedance spectroscopy, ultraviolet photoelectron spectroscopy, solar cell results, grazing incidence X-ray diffraction, and simulation results (PDF)

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Notes

The authors declare no competing financial interest

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