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A Molecular Breakwater-Like Tetrapod for Organic Solar Cells

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We report the synthesis and characterization of a tetrapodal breakwater-like small molecule, **SO**, containing a tetraphenylsilane core and four cyanoester functionalized terthiophene arms. **SO** possesses a deep lying HOMO energy level of -5.2 eV and a narrow bandgap of 1.9 eV. Absorption, X-ray scattering and differential scanning calorimetry (DSC) measurements indicate crystalline nature of this compound but very slow crystallization kinetics. Solar cells employing **SO** and phenyl-C₆₁-butyric acid methyl ester (PCBM) were fabricated and evaluated. Relatively low performance was obtained mainly due to the lack of optimal phase separation under various processing conditions including thermal annealing, slow-cooling and solvent annealing. Addition of poly(thienylene vinylene) (PTV), poly(3-hexylthiophene) (P3HT) and a platinum-containing low bandgap conjugated polymer Pt-BODIPY, into the **SO**/PCBM blend was found to induce device favorable phase separation and the polymers were found to act as the primary hole conductor. Such ternary blend devices showed cooperatively improved performances over binary devices employing either **SO** or the individual conjugated polymer alone.

1. Introduction

Organic solar cells (OSCs) are considered a promising low-cost renewable energy source.¹⁻² Research efforts in OSCs have been exclusively focused on conjugated polymers (CPs) owing to the device favorable processability and thin film forming ability, as well as the versatility in structure/property variations through well-established chemical transformations.³⁻⁵ As a result, power conversion efficiencies (PCEs) of polymer solar cell (PSC) devices have been steadily improved to approach 10% in recent years.⁶⁻¹³ CPs are typically synthesized through cross-coupling reactions in step-growth fashions that unavoidably generate materials with large distributions of molecular weights and structural defects are frequently encountered. Control over this type of polymerization is poor, which commonly leads to batch-to-batch and lab-to-lab variations in polymer structures and properties. Most CPs applied in efficient PSCs have been found to be amorphous and thus possess relatively low charge mobilities. These aspects can potentially limit materials mass production and impede further device improvement. On the other hand, conjugated small molecules can be highly crystalline and thus have superior charge mobilities, and at the same time have discrete and reproducible molecular structures.¹⁴⁻²² These features have attracted increasing attention and bulk heterojunction (BHJ) OSC devices employing conjugated small molecules and fullerene derivatives have been constantly improved to rival their CP counterparts, showing great promises in solar cell research.²³⁻³⁰

Most small molecules applied in solar cells have linear structures containing multiple aromatic groups connected in series. These molecules are typically highly crystalline and conductive along the π -stacking direction. However, charge migration along both long and short molecular axes are relatively limited due to the one-dimensional (1-D) nature of these molecules. Unfavorable film forming ability and grain boundaries both originated from high crystallinity of linear molecules are also detrimental to device performances. As a result, significant attention has been paid to conjugated small molecules having conjugation extended in three dimensions (3-D).²² Such molecular design can increase absorption cross-sections and provide more extensively percolating pathways for charge transport. Among the many 3-D structures, breakwater-like tetrapods are especially interesting owing to their unique

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ability to mutually interlock, which prevents dislodging and provides high morphological stabilities. This concept has been frequently applied in inorganic nanocrystal synthesis and the size scales of resulting tetrapods are on the order of hundred nm.³¹⁻³³ On the other hand, organic molecular tetrapods are less common in OSC research.

Roncali et al. reported the synthesis of two tetrapodal molecules, each containing a silicon core and four terthiophene arms bearing alkyl and thioalkyl side chains, respectively.³⁴ The overall solar cell performances were significantly limited by the large bandgaps of these tetrapods, but still out-performed the devices employing corresponding linear counterparts having structures of one of the four arms. Köse et al. recently reported low bandgap tetrapodal molecules composed of a silicon core and four arms composed of thiophene and benzothiadiazole units.³⁵ Favorable impact of high dimensionality of these molecules on charge mobilities in disordered media was discovered. In both of these examples, the molecular tetrapods all contain silicon atoms as the cores that are connected to four thiophene rings. Owing to the electron rich character and relatively small sizes of thiophene rings, the silicon centers are more exposed and the silicon-thiophene bonds are relatively weak. This instability can potentially complicate compound synthesis and characterization, as well as reduce device operation lifetimes.³⁶

On the other hand, tetraphenylsilane is a commercially available compound and known to be robust under various reaction conditions, and is thus a better starting point to construct the molecular tetrapods. Herein, we report the synthesis, characterization and application in OSCs of a stable low bandgap breakwater-like tetrapod containing a tetraphenylsilane core and four cyanoester functionalized terthiophene arms.

2. Results and Discussion

2.1 Synthesis and Characterization.

Detailed synthetic procedures for the tetrapodal molecule SO, and a model compound **MO** that represents a single arm of the tetrapod, are shown in Scheme 1. Compound 1 was prepared from commercial 1,4-dibromobenzene through lithium halogen exchange followed by reaction with 0.20 equivalents of SiCl₄. Compound 1 can be conveniently applied as a common core for grafting with different arms toward 3-D tetrapodal molecules. After Stille coupling reaction with 10 followed by acetal deprotection, the tetra-aldehyde compound 11 was obtained. The aldehyde groups can be transformed to several strongly electron withdrawing substituents, e.g., dicyanovinyl and cyanoester groups. However, 11 was found to have very limited solubility in common OSC processing solvents including chlorobenzene and dichlorobenzene. We thus chose n-octyl cyanoacetate (12) to impart the electron deficient moiety as well as sufficient solubility. Indeed, after the simple Knoevenegal-type condensation reaction, compound SO was obtained in high yields and has good solubility in a wide range of organic solvents including CHCl₃, THF and chlorobenzene. All compounds are fully characterized by ¹H and ¹³C NMR spectroscopy, which agree well with proposed structures (Electronic Supplementary Information, ESI[†]). High resolution mass spectrometry (HR-MS) was attempted to confirm the tetra-arm structures of the newly synthesized compounds. Unfortunately, SO could not be ionized under current experimental conditions and no meaningful mass signals could be observed. Instead, HR-MS was performed on the precursor 11. The measured molar masses $(1768.3419 \text{ [M}^+\text{]})$ and 1791.3317 [M+Na⁺]) match perfectly with the calculated values (1768.3414 [M⁺] and 1791.3312 [M+Na⁺]), confirming the proposed tetrapodal structures of 11 and consequently of SO.



Scheme 1. Synthesis of SO and MO.

Journal Name



Figure 1. Normalized UV-vis absorption and emission spectra of (A) SO and (B) MO in chlorobenzene solutions (10^{-5} M, solid lines) and as thin films (dashed lines).

The electronic properties of SO and MO were investigated by UV-vis absorption and fluorescence spectroscopies in both dilute solutions and as thin films. As shown in Figure 1, both **SO** and **MO** in chlorobenzene solutions (10^{-5} M) display nearly identical structureless absorption profiles with λ_{max} 's at ca. 470 nm. The solution fluorescence spectra of both compounds are also indistinguishable with λ_{em} 's at ca. 595 nm. Such similarity in absorption and emission spectra indicates that there is no electronic communication among the four conjugated arms of SO when intermolecular interactions are negligible in dilute solutions. This is understandable since these four arms are stretched out away from one another in a tetrahedral geometry. which are connected through a non-conjugated silicon core. However, owing to the differences in molecular geometries, SO and MO show very different spectra in thin films. The as-cast thin film of **SO** displays a λ_{max} at ca. 570 nm, which is redshifted from that of the solution profile by 100 nm. This redshift in absorption is commonly observed in conjugated systems due to structural planarization and intermolecular interactions in the solid state. The fluorescence of SO films is very weak, having a λ_{em} at ca. 625 nm when excited at the λ_{max} , which gives a relatively small Stoke's shift of 55 nm. On the contrary, the main absorption peak of MO is slightly blue-shifted to ca. 445 nm in thin films, indicating H-type aggregation of the molecules.³⁷ A low energy shoulder peak at ca. 530 nm is also observed, which is likely originated from new electronic species resulted from aggregation. Emission of MO films is expectedly quenched to a large extent and only a weak

fluorescence peaked at ca. 650 nm can be observed. From the absorption edges, the optical bandgaps of **SO** and **MO** are estimated to be both ca. 2.2 eV in solutions and 1.9 eV and 2.0 eV in thin films, respectively.

In order to quantify the frontier energy levels and bandgaps, cyclic voltammetry (CV) measurements were performed on SO and **MO** in dichloromethane solutions (1 mM). A glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt wire counter electrode were used. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) was used as the supporting electrolytes. The recorded CV curves were externally referenced to ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.80 eV below vacuum). Therefore, the HOMO and LUMO energy levels can be estimated using the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.80) \text{ eV}$ and $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} + 4.80) \text{ eV}$, respectively. As shown in Figure 2, both **SO** and MO displayed nearly identical redox behaviors. Two quasireversible oxidation peaks and one irreversible reduction peak, at onsets of ca. 0.4 V, 1.0 V and -1.5 V, respectively, were observed. As a result, the HOMO and LUMO levels of SO and MO were estimated to be -5.2 eV and -3.3 eV. This leads to an electrochemical bandgap of ca. 1.90 eV for both SO and MO, agreeing well with the results of optical measurements.



Figure 2. Cyclic voltammograms of MO and SO in CH_2Cl_2 solutions (1 mM) containing Bu_4NPF_6 as the supporting electrolytes (0.1 M). The voltages are referenced externally to ferrocene (Fc) redox couple. Scan rate: 100 mV/s.

Thermal properties of **SO** and **MO** were studied by using differential scanning calorimatry (DSC) measurements and the results are displayed in Figure 3. At a typical scanning rate of 10 °C/min, **SO** shows an exothermic crystallization transition peaked at 115 °C and two closely spaced melting transitions at 180 °C and 188 °C. No crystallization event is observed in the cooling curve. At a slower scanning rate of 1 °C/min, the crystallization transition is only observed during the cooling event at ca. 105 °C. Such behavior indicates slow crystallization kinetics of the compound. Similar behaviors were previously reported from a linear conjugated small molecule having two intentionally designed structural twists.³⁸ We originally thought that the tetrapodal structure of **SO**, which can be considered as having four structural twists in the molecule, is the leading cause for the slow crystallization

behavior. However, the same trend is observed for **MO**. At a scanning rate of 10 °C/min, **MO** displays both a crystallization (35 °C) and a melting transitions (68 °C) in the heating event while the crystallization transition (24 °C) is only observed upon cooling when the scanning rate is reduced to 1 °C/min. This indicates that the slow crystallization behavior of **SO** may be intrinsically resulted from the structure of each of its arms as demonstrated in the case of **MO**.



Figure 3. Differential scanning calorimetry (DSC) histograms of SO at a scanning rate of 10 °C/min (solid line) and at 1 °C/min (dashed line); and of MO at 10 °C/min (dotted line) and at 1 °C/min (dash dotted line). Second heating (lower segments) and cooling (upper segments) curves are shown.

In order to gain a deeper insight on the structural origin of these thermal behaviors, we performed density functional theory (DFT) calculations (B3LYP/6-31G*) on MO and the optimized geometries are shown in Figure S1[†]. The calculated minimum energy structure of MO is not completely planar. Dihedral angles of 26° and 15° are found between the phenyl and alkylthienyl groups and between the alkylthienyl and the adjacent thienyl groups, respectively. These structural twists are possibly responsible for inefficient molecular packing and thus slow crystallization kinetics. Also seen from the calculation results, the HOMO orbital of MO is delocalized throughout the entire conjugation and the LUMO orbital is positioned toward the cyanoester side. Electronic transitions from HOMO to LUMO thus possess charge transfer characteristics as expected. The HOMO level is calculated to be -5.3 eV, matching that from CV measurements, while the LUMO is over estimated to be -2.7 eV.

Hole mobilities in **SO** and **MO** films were estimated using space charge limited current (SCLC) method³⁹ in hole only devices having ITO/MoO₃ (10 nm)/organic/MoO₃ (10 nm)/Al (100 nm) geometries. The results are averaged from three devices with different organic layer thickness for each compound. The hole mobility of **SO** film is calculated to be ca. 1.8×10^{-4} cm²/Vs, which is more than 100 times higher than that found for the **MO** film at 1.1×10^{-6} cm²/Vs. The tetrahedral shape of **SO** likely leads to enhanced percolating pathways and thus improved charge mobilities, which is consistent with the previous report.³⁵

We have so far not been able to obtain high quality single crystals for SO in order for detailed X-ray analysis. DSC studies indicate certain crystallinity of the compound, which is further confirmed by thin film wide-angle X-ray scattering experiments as shown in Figure S2[†]. Multiple scattering peaks are observed at 20 values of ca. 4.0°, 5.7°, 8.1° and 12.3°, which correspond to d-spacings of ca. 2.2, 1.5, 1.1 and 0.7 nm, respectively. Assignments of these scattering peaks are still not certain at present. The SO thin films were further studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements, and the results are summarized in Figure S3[†]. Micron-sized ellipsoidal aggregates are randomly distributed throughout the film as seen in the TEM image. From the SAED image, only a few scattering rings can be observed and azimuthal integration of the major scattering ring gives a d-spacing of ca. 1.3 nm. The SAED pattern indicates that although there exists periodic structures in the SO films, the compound itself does not form conventional crystals ordered in three dimensions.

2.2 Binary Blend Devices.

Solar cell devices were fabricated using conventional structures: ITO glass/MoO3 (10 nm)/active layer (100 nm)/Al (100 nm). Mixtures of SO or MO and phenyl-C₆₁-butyric acid methyl ester (PCBM, American Dye Source, Inc.) at various weight ratios in chlorobenzene were spun cast to form the active layer. Thermal annealing at various temperatures was employed to optimize the device performances. The best PCEs were found in as-cast devices employing SO/PCBM at a weight ratio of 1/3, and MO/PCBM at a weight ratio of 1/2. Devices employing SO generally out-performed those using MO. The current density-voltage (I-V) curves of the best performing devices are shown in Figure S4[†]. Both SO and MO devices show relatively high open circuit voltage ($V_{\rm OC}$) values at 0.84 V and 0.74 V, respectively, which is consistent with the deep lying HOMO levels of these molecules. However both devices suffer greatly from low short circuit current (J_{SC}) and fill factor (FF) values. For instance, the **MO** device gives a J_{SC} of 0.64 mA/cm^2 and a FF of 30%, leading to PCE of 0.14%. While the **SO** device displays a J_{SC} of 1.01 mA/cm², a FF of 26% and the PCE of 0.22%. Steep increases in current densities at reverse bias are observed for both devices under light, which indicates significant charge recombination at short circuit conditions. Similar behaviors were observed by Köse et al. for their tetrapodal molecules, which they ascribed to inferior blend morphologies.³⁵ We thus studied the thin film morphologies of SO, MO and corresponding PCBM blends at optimal weight ratios for device operation by using optical microscopy and the photographs are included in Figure 4. Micrographs of as-cast and annealed SO and MO thin films under cross-polarized light are included in Figure S5.

The as-cast **SO** thin films have smooth morphologies that are free of any visible aggregates or crystallites (Figure 4A). Annealing at 150 °C for 10 min leads to crystallization of **SO**, resulting in heavily textured morphology and dark crystallites as seen in Figure 4B. This observation is consistent with those from DSC studies and confirmed by cross-polarized light microscopy. As shown in Figure S5A, no features can be observed in the as-cast **SO** thin films while annealing leads to heavily textured morphologies with relatively small feature sizes (Figure S5B). However, thin films containing **SO**/PCBM mixture at a 1/3 weight ratio do not display any phase separation (Figure 4C) even after annealing at 150 °C for 10 min (Figure 4D). It is likely that PCBM molecules are

Journal Name

intercalated among the arms of SO, which effectively prevents crystallization of both SO and PCBM, and thus suppresses any appreciable phase separation within the blends. This lack of phase separation into pure domains of electron donors and acceptors can significantly limit charge transport and lead to large rates of charge recombination. On the other hand, MO thin films show slightly different behaviors. Clear and dense crystallites are observed in the as-cast films of **MO** (Figure 4E), which is not surprising since MO has a crystallization transition temperature around 25 °C. Annealing at 150 °C leads to still textured morphology with apparently less crystallites (Figure 4F). This trend is also confirmed by cross-polarized light microscopy. Crystals of MO can be cleared observed under cross-polarized light in as-cast films (Figure S5C), which become larger and less densely packed after thermal annealing (Figure S5D). As-cast thin films of MO/PCBM blends show overall smooth morphologies having a few sparsely located crystallites (Figure 4G) that become more populated in annealed films (Figure 4H). We suspect that these crystallites are those of PCBM molecules. In short summary, addition of PCBM seems to suppress crystallization of both MO and SO, while SO has a more pronounced effects on suppression of PCBM aggregation than MO does, owing to its tetapodal structure that can potential interact with PCBM molecules more strongly. On the other hand, because of the break-water like structure of SO, the molecularly mixed state seems to result in thermally robust morphologies, which is preferred for OSC operations.

Since DSC measurements showed slow crystallization behaviors of the SO compound, we attempted slow-cooling experiments on the SO/PCBM (1/3) devices in hope to induce phase separation of these two components and thus to improve device efficiencies. The typical procedure is to anneal the devices on a hotplate with preset temperatures for 10 min and the hotplate is turned off without removing the devices. The hotplate temperature then slowly drops to r.t. within 1.5 to 2 h and the devices are then tested. Four different preset hotplate temperatures at 100 °C, 150 °C, 200 °C and 250 °C were selected. However, the devices slow-cooled from 100 °C and 150 °C showed similar performances as the as-cast devices, while the devices slow-cooled from 200 °C and 250 °C displayed reduced PCE to ca. 0.04% and no photovoltaic behaviors, respectively. Optical micrographs of these slowcooled devices are shown in Figure S6[†]. When slow-cooled from 100 °C and 150 °C, identically smooth, aggregation free morphologies are observed (Figure S6A and S6B), indicating the ineffectiveness for inducing appreciable phase separation between SO and PCBM under these conditions. When the temperature was raised to 150 °C, dark needle like crystals of tens of microns in lengths emerged (Figure S6C), which became significantly bigger when slow-cooled from 250 °C (Figure S6D). Noticeably, there appear to be de-wetting processes taking place around these large crystallites, which possibly account for the reduced and eventually diminished device performances.



Figure 4. Optical micrographs ($400 \times$ magnificantion) of thin films of SO, MO and corresponding PCBM blends under different annealing conditions. Obvious artifacts are circled out in white. Scale bars in all: 20 μ m.

Alternatively, solvent annealing has been shown as an effective method for inducing phase separation in blend films.⁴⁰⁻⁴¹ We thus tested the SO/PCBM (1/3) devices under solvent annealing conditions by placing the devices in a sealed container saturated with chlorobenzene vapor for up to 20h. Devices were then tested after predetermined annealing times and subjected to optical microscopy measurements as summarized in Figure 5. No performance differences were observed for devices annealed up to 1 h, although spherulite-like crystals started to appear and became denser and bigger with time (Figures 5A to 5D). The devices annealed for 1.5 h, 3 h and 6 h all showed slightly improved PCE values to ca. 0.25-0.27%, which come from an improvement in FF to ca. 44% accompanied by a decrease in J_{SC} to ca. 0.62 mA/cm². However, devices annealed for 20 h lost almost all of the photovoltaic effects and no diode behaviors could be observed. As seen in Figures 5E to 5G, at longer annealing times, the spherulite-like crystals seem to grow and merge into large platelets having straight boundaries. These platelets have lighter smoother central regions and darker needle-like peripherals, accompanied by randomly dispersed black spheres. These two regions eventually became clearly differentiated after annealing for 20 h (Figure 5H). We suspect that the darker crystals are those of PCBM and the lighter regions consist of SO or SO/PCBM complexes. Such solvent

Page 6 of 13

annealing induced crystallization, phase separation and eventual macro-phase separation likely explain the initial device improvement and final breakdown as observed. The exact identity of the needle-like crystals and mechanisms of such phase separation are currently under more detailed investigation.



Figure 5. Optical micrographs ($100 \times$ magnificantion) of thin films of **SO** and PCBM (1/3, wt./wt.) blends after solvent annealing using chlorobenzene for various times. Scale bars in all: 100 µm.

2.3 Ternary Blend Devices.

As discussed above, SO molecules tend to molecularly mix with PCBM molecules and thermal annealing is ineffective to drive appreciable phase separation. Slow-cooling from high temperatures and solvent annealing do induce macroscopic phase separation but are not able to improve the device performances significantly. We suspect that addition of a third component, which has stronger interactions with either SO or PCBM, can potentially break up the SO/PCBM interactions and lead to one of the components to crystallize and phase separate into domains better for charge separation and extraction. To test this hypothesis, we chose poly(thienylene vinylene) (PTV) to be the third component. PTVs are a well-known class of conjugated polymers possessing narrow bandgaps and high crystallinity.⁴²⁻⁴⁵ The π - π interactions among aromatic rings may lead to stronger SO/PTV interactions and the absorption windows of SO and PTV are complementary to each other,





The binary P3DTV/PCBM devices were first fabricated and optimized, from which a weight ratio of 1/1 and a thermal annealing temperature of 80 °C for 10 min were found to be optimal, leading to a *PCE* of 0.49%. This relatively low efficiency is comparable to previously reported examples and is possibly caused by the short lifetimes of excitons in PTVs.⁴⁷⁻⁴⁸ Thus, in the ternary blends, we kept the weight ratios of **SO**/PCBM and P3DTV/PCBM to be consistent at 1/3 and 1/1, respectively. Thermal annealing was found to slightly enhance ternary device performance and the optimal temperature was found to be 80 °C, beyond which device deterioration occurred. Table 1 summarizes detailed device parameters involving binary and ternary blends at different weight ratios and the corresponding I-V curves are included in Figure 6.

Table 1. Binary and Ternary Device	Performances. ⁴
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SO/P3DTV/PCBM ^b	$V_{\rm OC}\left({\rm V}\right)$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	PCE (%)
A. 2.5 / 0.0 / 7.5 ^c	0.84	1.01	26	0.22
B. 2.5 / 0.5 / 8.0	0.55	2.17	37	0.44
C. 2.5 / 1.5 / 9.0	0.52	3.67	52	1.00
D. 2.5 / 2.5 /10.0	0.52	4.34	54	1.22
E. 2.0 / 2.5 / 8.5	0.52	5.18	54	1.45
F. 1.5 / 2.5 / 7.0	0.52	5.52	54	1.54
G. 1.0 / 2.5 / 5.5	0.51	4.27	55	1.19
H. 0.5 / 2.5 / 4.0	0.48	3.48	52	0.87
I. 0.0 / 2.5 / 2.5	0.45	2.22	49	0.49

^a All devices are thermally annealed at 80 °C for 10 min; results are reported as averages of five individual cells. ^b All ratios by weight. ^c As-cast device.

Journal Name



Figure 6. Current density-voltage (I-V) curves of devices employing **SO**, P3DTV and PCBM at various weight ratios under simulated white light (100 mW/cm²).

Several trends are clearly observed going from binary blends to ternary blends. The $V_{\rm OC}$ values of ternary devices are all between those of the binary devices employing P3DTV and **SO.** These values decrease with increasing P3DTV contents and are all much closer to the side of P3DTV. For instance, in devices B (Table 1), addition of only 20 wt.% P3DTV (relative to **SO**) reduces the V_{OC} from 0.84 V in device A to 0.55 V. It is known that the V_{OC} of a BHJ solar cell is closely related to the energy difference between the HOMO level of electron donor and the LUMO level of the electron acceptor.49 Owing to the high lying HOMO level of P3DTV at ca. -4.9 eV (from CV measurements), devices containing P3DTV are expected to have reduced V_{OC} values. Interestingly, previous examples showed close to linear relationships between $V_{\rm OC}$ and composition changes.⁵⁰⁻⁵¹ In our case, we plot the $V_{\rm OC}$ values against P3DTV contents in the donor blends (Figure S7[†]) and find that the relationship is far from linearity. All devices containing P3DTV display comparable V_{OC} values that are significantly smaller than that of the SO only device. This implies that in our ternary devices, P3DTV is the primary hole conducting material despite of its contents, which is likely caused by high crystallinity and long-chain structures of the polymer.



Figure 7. Tapping-mode atomic force microscopy (AFM) height images (left column) and phase images (right column) of binary device A (**SO**/PCBM 1/3; A and B), binary device I (P3DTV/PCBM 1/1; C and D) and ternary device F (**SO**/P3DTV/PCBM 1.5/2.5/7.0; E and F). All images are $2 \times 2 \mu m$ in size. (G) Transmission electron microscopy (TEM) image of device F; scale bar: 50 nm.

Another obvious trend is the enhancement of J_{sc} in the ternary blend devices that all, except B, show higher J_{sc} values than the binary devices. Device D can be considered a linear combination of the contents of binary devices A and I, but gives a higher J_{sc} of 4.34 mA/cm² than the sum of J_{sc} values of devices A and I (3.23 mA/cm²). This indicates that there are cooperative effects on photocurrent generation by mixing **SO** and P3DTV, which enhance charge extraction within the ternary blends. The best device tested is F that displays the highest J_{sc} of 5.52 mA/cm² and a *PCE* of 1.54%, which is ca. 3 and 7 times higher than those of binary devices employing P3DTV and **SO** alone, respectively.

Noticeably, all ternary devices show significantly higher FFs than the **SO** binary device, which can be related to improved morphologies by adding P3DTV. Thus, we have studied the best ternary device F by optical microscopy (Figure S8†), atomic force microscopy (AFM) and transmission electron

microscopy. The binary devices are also studied by AFM for comparison and all AFM and TEM images are included in Figure 7. As shown in Figure S8, the ternary film under both as-cast and annealing at 80 °C conditions do not display any appreciable aggregation or crystallization. However, when annealed at 150 °C for 10 min, large needle like PCBM crystallites are observed. This macro-phase separation indicates the effectiveness of adding P3DTV on reducing the strong SO/PCBM interactions. The AFM measurements probe the thin film morphologies on the nanometer scale. As displayed in Figure 7A and 7B, the SO/PCBM binary blends show very smooth morphologies that lack appreciable phase separation, confirming the intermixed nature of these blends. On the other hand, much rougher topography is observed in the P3DTV/PCBM binary blends and larger aggregates are clearly present (Figure 7C and 7D). As a result, the SO/P3DTV/PCBM ternary blends display morphologies somewhat in between those of the binary blends (Figure 7E and 7F). The nanometer scale phase separation observed in device F by AFM is further confirmed by TEM. As shown in Figure 7G, inter-penetrating brighter (SO and P3DTV rich) and darker (PCBM rich) phases are observed, corresponding to domain sizes on the order of 10 nm. Such more pronounced phase separation on the nanometer scale creates more pure donor and acceptor domains that lead to better charge separation and collection, and enhanced performance of the ternary devices over that of the binary devices.

In addition to P3DTV, which is a low bandgap, crystalline and less efficient polymer, we have started investigating ternary solar cells containing **SO**/PCBM and other types of conjugated polymers including regio-regular poly(3-hexylthiophene) (P3HT) and a platinum containing polymer (Pt-BODIPY) made in-house,⁵² as shown in Scheme 2. Compared with P3DTV, P3HT possesses similarly high crystallinity and comparable HOMO energy level, but a slightly larger bandgap at ca. 1.9 eV, and is one of the most studied high performing conjugated polymers in OSC research. On the other hand, the Pt-BODIPY polymer has a small bandgap at ca. 1.7 eV, a deep lying HOMO level at ca. -5.3 eV and is an amorphous material. Table 2 summarizes performance parameters of ternary devices employing these materials at various weight ratios.

Table 2. Ternary Devices Involving P3HT and Pt-BODIPY. ^a						
SO/P3HT/PCBM ^b	V _{OC} (V)	$J_{\rm SC}$ (mA/cm ²)	FF (%)	PCE (%)		
J. 0.0 / 5.0 / 5.0	0.57	10.70	59	3.63		
K. 1.0 / 5.0 / 5.0	0.59	10.31	69	4.22		
L. 2.5 / 2.5 / 7.5	0.62	4.23	62	1.63		
M. 4.0 / 1.0 /12.0	0.71	2.46	48	0.83		
SO/Pt-BODIPY/PCBM ^c						
N. 0.0 / 2.5 / 7.5	0.86	2.23	48	0.91		
O. 0.5 / 2.5 / 7.5	0.91	3.39	45	1.39		
P. 2.5 / 2.5 / 7.5	0.93	2.49	33	0.77		
Q. 2.5 / 0.5 / 7.5	0.86	2.05	38	0.68		

 $^{\rm a}$ Results are reported as averages of five individual cells; All ratios by weight. $^{\rm b}$ All devices are thermally annealed at 150 °C for 10 min. $^{\rm c}$ As-cast devices.

Consistently, cooperative effects are observed in both types of ternary devices, as both devices K and O outperform the corresponding optimized binary devices. In device K, addition of 20 wt.% **SO** increases the optimized P3HT/PCBM binary device efficiency from 3.63% to 4.22%, which mainly comes from the enhancement in FF up to 69%. This indicates

improved morphologies in this ternary blend over the well studied P3HT/PCBM binary blends, which implies an effective wav to optimize conjugated polymer/fullerene blend morphologies and is currently under more detailed studies. Not surprisingly, the highly crystalline P3HT acts as the major hole conductor in the ternary blends similar to the case for P3DTV, since the addition of a minority amount of P3HT drastically decreases the $V_{\rm OC}$ values. On the other hand in device O, addition of 20 wt.% SO into the Pt-BODIPY/PCBM binary device also improves the performance, which is however resulted from an increase in J_{SC} . Since Pt-BODIPY has a lower bandgap than SO, such increase in J_{SC} is likely a result of complementary absorption. The relatively small FFs in all ternary devices are supposedly explained by the amorphous nature of both SO and Pt-BODIPY, mixtures of which are thus expected to result in hardly improved morphologies. Both compounds have similar deep lying HOMO levels, leading to high $V_{\rm OC}$ values in all ternary devices. Interestingly, devices O and P have V_{OC} values slightly higher than those of corresponding binary devices, the reasons for which are currently under investigation.

3. Conclusions

We have successfully prepared a molecular tetrapod possessing a tetraphenylsilance core. The molecule has a relatively small bandgap and a deep lying HOMO energy level. The tetrapod was also found to be very hard to crystallize, which led to molecularly mixed blends with PCBM and poor solar cell device performances. This inferior morphology could be improved by adding a conjugated polymer that can induce appreciable phase separation in the ternary blends and result in much enhanced device efficiencies, the effects of which depend on the conjugated polymers' bandgaps, HOMO levels and crystallinity. Our findings can give useful insights on the structure-property relationships of such 3-D small molecules and provide a unique way to control device morphologies by using ternary blends employing both a 3-D small molecule and a linear conjugated polymer. We are currently investigating the possibilities of increasing the crystallization kinetics of the tetrapods and of controlling the phase separations in multicomponent blend films by variations of the molecular structures and processing conditions.

4. Experimental Section

4.1 Materials and General Methods.

All reagents and solvents were used as received from Sigma-Aldrich or Alfa Aesar unless otherwise noted. THF was distilled from Na/benzophenone prior to use. 2-**(3**),⁵³ Tributylstannylthiophene 2,2'-bithiophene-5-**(4)**,⁵⁴ carbaldehyde 5'-bromo-(2,2'-bithiophene)-5carbaldehyde (5),⁵⁴ 2-bromo-3-hexylthiophene (6),⁵⁵ 3-hexyl-2trimethylstannylthiophene (7)⁵⁶ were prepared according to literature procedures. 300.13 MHz ¹H and 75.48 MHz ^{13}C NMR spectra were recorded on a Bruker Avance III Solution 300 spectrometer. All solution ¹H and ¹³C NMR spectra were referenced internally to solvent signals. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-2401 PC spectrometer over a wavelength range of 240–900 nm.

Cary Eclipse fluorimeter. Time-of-flight mass spectrometry (TOF MS) was performed on a Waters/Micromass LCT Premier system operating under atmospheric pressure photoionization (APPI+) mode. Cyclic voltammetry was performed at 25 °C on a CH Instrument CHI604xD electrochemical analyzer using a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode calibrated using ferrocene redox couple (4.8 eV below vacuum). Optical Micrographs were taken on a Carl Zesis Axio Imager 2 microscope at 400X or 100X magnification. Optical micrographs under cross polarized light were obtained on a LEICA DM EP microscope at 400X magnification. Atomic force microscopy (AFM) measurements were performed on an Asylum MFP3D AFM instrument operated under tapping mode. Powder X-ray diffraction measurements were performed on a Rigaku SmartLab Differential scanning calorimetry instrument. (DSC) measurements were performed on a Mettler Toledo DSC STAR^e system with ca. 10 mg sample and at scan rates of 10 °C / min and 1 °C / min. Thin film thickness was measured using a KLA-Tencor AlphaStep D-100 profiler. Electron scattering experiments were carried out on a JEOL JEM-2010 transmission electron microscope (TEM) in a transmission geometry through the thickness of the **SO** film (perpendicular to the surface). The accelerating voltage of the TEM was maintained at 200 keV. Reported images were recorded at a nominal camera length of 300 mm on a Gatan Orius CCD camera (1336 x 2004 pixels). TEM specimens were produced by first spin coating a solution of SO compound onto an ITO slide coated with PEDOT: PSS supporting layer (ca. 30 nm). The **SO** films were then floated in DI water and transferred onto carbon coated TEM grids.

Fluorescence emission spectra were obtained using a Varian

4.2 Solar Cell Fabrication and Testing.

A conventional structure of ITO/MoO₃ (10 nm)/active laver (100 nm)/Al (100 nm) was adopted for the solar cells studied. Devices were fabricated according to the following procedures. SO and PCBM (American Dye Source, Inc.) at predetermined weight ratios were dissolved in chlorobenzene (CB) and stirred at 80 °C for 10 h in a nitrogen glovebox (Innovative Technology, model PL-He-2GB, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). ITO-coated glass substrates (China Shenzhen Southern Glass Display. Ltd, 8 Ω/\Box) were cleaned by ultrasonication sequentially in detergent, DI water, acetone and isopropyl alcohol, each for 15 min. These ITO-coated glass substrates were further treated by UV-ozone (PSD Series, Novascan) for 45 min before transferred into a nitrogen glovebox (Innovative Technology, model PL-He-4GB-1800, $O_2 < 0.1$ ppm, $H_2O <$ 0.1 ppm) for MoO₃ deposition. MoO₃ (10 nm) was deposited using an Angstrom Engineering Åmod deposition system at a base vacuum level $< 7 \times 10^{-8}$ Torr. The blend solution was first filtered through a 0.45 µm PTFE filter and spin-coated on top of the MoO₃ layer at preset speeds for 30s. Typical thickness of organic layers was ca. 100 nm. Al (100 nm) was finally thermally evaporated through patterned shadow masks as anodes. Current-voltage (I-V) characteristics were measured by a Keithley 2400 source-measuring unit under simulated AM1.5G irradiation (100 mW/cm²) generated by a Xe arc-lamp based Newport 67005 150-W solar simulator equipped with an AM1.5G filter. The light intensity was calibrated by using a Newport thermopile detector (model 818P-010-12) equipped with a Newport 1916-C Optical Power Meter.

4.3 Synthetic Details.

1. 1,4-Dibromobenzene (5.00 g, 21.2 mmol) was weighed into a dry 100 mL Schlenk flask and 50 mL anhydrous THF was added through cannular. The flask was cooled to -78 °C and 8.1 mL ⁿBuLi (2.5 M in THF, 20.2 mmol) solution was added dropwise. The reaction mixture was stirred at -78 °C for 2 hours and a 5 mL THF solution of SiCl₄ (0.742 g, 4.36 mmol) was added dropwise through syringe. The reaction mixture was first kept stirring at -78 °C for 1 hour and then warmed up to room temperature and stirred overnight. The reaction mixture was extracted by ethyl ether, followed by washing with DI H₂O and saturated brine solution. After the organic layer was dried with anhydrous Na2SO4, the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography using hexanes to yield compound 1 as a white powder (2.24 g, 78.9%). ¹H NMR (300.13 MHz, CDCl₃): δ $(ppm) = 7.33 (Ph-H, d, 8H, J^{3}_{HH} = 8.4 Hz), 7.53 (Ph-H, d, 8H,)$ $J_{\rm HH}^3 = 8.1$ Hz). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 125.4, 131.4, 131.5, 137.6.

2. 2-Bromothiophene (21.6 mL, 0.223 mol) was injected via syringe into a 1 L 3-neck round bottom flask equipped with an addition funnel and a stir bar under positive N2 pressure. Anhydrous THF (ca. 400 mL) was transferred into the flask through cannular. Lithium diisopropylamide solution (2M in THF/heptane/ethylbenzene, 123.0 mL, 0.246 mol) was transferred into the addition funnel and added dropwise at -78 °C. The reaction mixture was kept stirring at -78 °C for 30 min and then warmed up to room temperature. Anhydrous N,Ndimethylformamide (25.8 mL, 0.335 mol) was added slowly through a degassed syringe. The reaction mixture was further stirred at room temperature overnight. After standard aqueous workup, compound 2 was obtained as a colorless liquid by vacuum distillation. (37.0 g, 86.8%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 7.19 (*Th-H*, d, 1H, J^{3}_{HH} = 3.9 Hz), 7.52 (*Th-H*, d, 1H, $J_{HH}^3 = 4.2$ Hz), 9.78 (-*CHO*, s, 1H).

8. Compound 7 (1.09 g, 4.00 mmol) and compound 5 (1.59 g, 4.80 mmol) were dissolved in 30 mL anhydrous DMF in a pressure vessel containing a magnetic stir bar inside an argon filled glovebox. Pd(PPh₃)₄ (69.3 mg, 1.5 mol%) was then added to the reaction mixture. The pressure vessel was sealed and taken out of the glovebox. The reaction was carried out at 80 °C for 24 hours and then cooled to room temperature. After standard aqueous workup, compound 8 was further purified by silica gel chromatography with hexane/ethyl acetate (1.28 g, 88.9%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.89 (-*CH*₃, t, 3H, $J_{HH}^{2} = 6.9$ Hz), 1.28-1.41 (-*CH*₂-, m, 6H), 1.65 (-*CH*₂-, m, 2H), 2.78 (-*CH*₂-, t, 2H, J^{3}_{HH} = 7.8 Hz), 6.96 (*Th*-*H*, d, 1H, $J_{\rm HH}^3 = 6.6$ Hz), 7.07 (*Th-H*, d, 1H, $J_{\rm HH}^3 = 3.6$ Hz), 7.22 (*Th-H*, d, 1H, J^{3}_{HH} = 4.8 Hz), 7.25 (*Th-H*, d, 1H, J^{3}_{HH} = 4.2 Hz), 7.32 (*Th-H*, d, 1H, $J_{HH}^3 = 3.6$ Hz), 7.68 (*Th-H*, d, 1H, $J_{HH}^3 = 3.9$ Hz), 9.87 (-CHO, s, 1H). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 13.9, 22.4, 29.0, 29.1, 30.2, 31.4, 123.6, 124.2, 126.2,126.3, 129.5, 130.0, 134.9, 137.1, 138.0, 140.1, 141.2, 146.5, 182.0

9. Compound **8** (1.28 g, 3.55 mmol), ethylene glycol (2.0 mL, 35.8 mmol) and a catalytic amount of *p*-toluenesulfonic acid were dissolved in 50 mL benzene in a 100 mL round bottom flask equipped with a Dean-Stark apparatus. The reaction mixture was refluxed at 150 °C for 24 hours. The resulted reaction mixture was extracted by ethyl ether and followed by washing with saturated NaHCO₃, DI H₂O and saturated brine solution. After the organic layer was dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The crude compound was further dried under vacuum and used for

next step without further purification (1.24 g, 86.4%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.88 (-*CH*₃, t, 3H, J^{3}_{HH} = 6.6 Hz), 1.26-1.39 (-*CH*₂-, m, 6H), 1.64 (-*CH*₂-, m, 2H), 2.76 (-*CH*₂-, t, 2H, J^{3}_{HH} = 7.8 Hz), 4.04 (-*OCH*₂-, m, 2H), 4.14 (-*OCH*₂-, m, 2H), 6.09 (-*OCHO*-, s, 1H), 6.93 (*Th*-H, d, 1H, J^{3}_{HH} = 5.1 Hz), 7.01 (*Th*-H, d, 1H, J^{3}_{HH} = 3.6 Hz), 7.05 (*Th*-H, d, 1H, J^{3}_{HH} = 3.6 Hz), 7.07 (*Th*-H, d, 1H, J^{3}_{HH} = 3.6 Hz), 7.11 (*Th*-H, d, 1H, J^{3}_{HH} = 3.6 Hz), 7.17 (*Th*-H, d, 1H, J^{3}_{HH} = 5.1 Hz). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 14.1, 22.6, 29.2, 29.3, 30.6, 31.6, 65.2, 100.2, 123.0, 123.9, 124.2, 126.4, 127.0, 130.1, 130.2, 135.6, 136.8, 138.2, 139.9, 140.6.

10. Compound 9 (0.505 g, 1.25 mmol) was weighed into a dry 100 mL Schlenk flask under nitrogen, and 50 mL anhydrous THF was transferred through a cannular. The flask was cooled to -78 °C and 0.55 mL ⁿBuLi (2.5 M in THF, 1.37 mmol) solution was added dropwise through a degassed syringe. The reaction mixture was stirred at -78 °C for 30 min and warmed up to room temperature. A Me₃SnCl solution (1 M in THF, 1.5 mL, 1.5 mmol) was then added dropwise. The reaction mixture was kept stirring at room temperature overnight. The resulting reaction mixture was extracted by ethyl ether, followed by washing with DI H₂O and saturated brine solution. After the organic layer was dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The crude compound was further dried under high vacuum and used for next step without further purification (0.709 g, 100%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.38 (-*CH*₃, s, 9H), 0.87 (-*CH*₃, t, 3H, J^{3}_{HH} = 6.9 Hz), 1.26-1.39 (-CH₂-, m, 6H), 1.64 (-CH₂-, m, 2H), 2.78 (- CH_{2} -, t, 2H, $J_{HH}^{3} = 7.8$ Hz), 4.02 (- OCH_{2} -, m, 2H), 4.15 (-OCH2-, m, 2H), 6.08 (-OCHO-, s, 1H), 6.99 (Th-H, d, 1H, J³HH = 3.9 Hz), 7.00 (*Th-H*, s, 1H), 7.04 (*Th-H*, d, 1H, J_{HH}^3 = 3.6 Hz), 7.06 (*Th-H*, d, 1H, J^{3}_{HH} = 3.9 Hz), 7.10 (*Th-H*, d, 1H, J^{3}_{HH} = 3.6 Hz). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = -8.2, 14.1, 22.6, 29.2, 29.3, 30.7, 31.6, 65.2, 100.2, 122.9, 124.2, 126.0, 127.0, 135.9, 136.0, 136.5, 136.8, 138.3, 138.4, 140.4, 141.0

11. Compound 1 (0.170 g, 0.26 mmol), compound 10 (0.709 g, 1.25 mmol) and Pd(PPh₃)₄ (9 mg, 3 mol%) were dissolved in 20 mL anhydrous DMF in a pressure vessel containing a magnetic stir bar under argon. The pressure vessel was sealed and stirred at 90 °C for 24 hours. After cooling to room temperature, the reaction mixture was extracted with CHCl₃, followed by washing with 1 M HCl, saturated NaHCO₃, DI H₂O and brine. After the organic layer was dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The crude product was further purified by silica gel chromatography with dichloromethane/ethyl acetate to yield 11 as a brown solid (200 mg, 43.3%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.90 (-*CH*₃, t, 12H, J^3_{HH} = 6.9 Hz), 1.32-1.43 (-CH2-, m, 24H), 1.71 (-CH2-, m, 8H), 2.81 (-CH2-, t, 8H, $J^{3}_{HH} = 4.8$ Hz), 7.13 (*Th-H*, d, 4H, $J^{3}_{HH} = 3.6$ Hz), 7.24 (*Th-H*, s, 4H), 7.27(*Th-H*, d, 4H, J^{3}_{HH} = 3.6 Hz), 7.33 (*Th-H*, d, 4H, $J^{3}_{HH} = 3.9 \text{ Hz}$, 7.64(*Ph-H*, m, 16H), 7.68 (*Th-H*, d, 4H, $J^{3}_{HH} =$ 3.9 Hz), 9.87 (-CHO, s, 4H). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 14.1, 22.6, 29.2, 29.7, 30.4, 31.6, 124.0, 125.0, 126.5, 126.6, 126.8, 129.9, 133.1, 135.1, 135.3, 136.9, 137.4, 138.1, 141.5, 141.6, 142.2, 146.8, 182.4. TOF MS (APPI⁺): Calcd. for SiC₁₀₀H₉₂O₄S₁₂N: 1768.3414 [M⁺], 1791.3312 [M+Na⁺]; found: 1768.3419 [M⁺], 1791.3317 [M+Na⁺].

12. Cyanoacetic acid (5.00 g, 58.8 mmol), octanol (9.8 mL, 61.8 mmol) and a catalytic amount of p-toluenesulfonic acid were dissolved in 30 mL benzene into a 100 mL round bottom flask equipped with a Dean-Stark apparatus. The reaction mixture was refluxed at 120 °C for 24 hours. After solvent

removal under vacuum, **12** was purified by vacuum distillation as a colorless liquid (9.40 g, 81.1%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.89 (-*CH*₃, t, 3H, J^{3}_{HH} = 6.9 Hz), 1.28-1.38 (-*CH*₂-, m, 10H), 1.68 (-*CH*₂-, m, 2H), 3.45 (-*CH*₂-, s, 1H), 4.20 (-*OCH*₂-, t, 2H, J^{3}_{HH} = 6.9 Hz). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 14.0, 22.6, 24.7, 25.7, 28.3, 29.1, 31.7, 67.1, 113.0, 162.9.

13. Compound 8 (0.600 g, 1.66 mmol) was dissolved in 25 mL DMF in a 50 mL round bottom flask and immersed in an ice bath. N-bromosuccinimide (NBS, 0.356 g, 2.00 mmol) powder was added with vigorous stirring. The reaction was warmed up to room temperature and stirred for overnight. The resulting reaction mixture was first extracted with CHCl₃, followed by washing with saturated Na₂SO₃, 1 M HCl solution, DI H₂O and brine solution. Solvents were removed under reduced pressure and the resulted crude product was further purified by column chromatography to get 13 as a yellow solid (0.655 g, 89.5%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.89 (-*CH*₃, t, 3H, $J_{\rm HH}^3 = 6.9$ Hz), 1.28-1.41 (-*CH*₂-, m, 6H), 1.62 (-*CH*₂-, m, 2H), 2.71 (-*CH*₂-, t, 2H, J^{3}_{HH} = 7.8 Hz), 6.92 (*Th*-*H*, s, 1H), 7.01 (*Th*-*H*, d, 1H, $J_{HH}^3 = 3.9$ Hz), 7.25 (*Th-H*, d, 1H, $J_{HH}^3 = 4.8$ Hz), 7.30 (*Th-H*, d, 1H, $J_{HH}^3 = 3.6$ Hz), 7.68 (*Th-H*, d, 1H, $J_{HH}^3 =$ 4.2 Hz), 9.87 (-*CHO*, s, 1H). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 13.9, 22.4, 28.9, 29.1, 30.1, 31.4, 111.1, 123.9, 126.2, 126.7, 131.0, 132.7, 135.5, 136.5, 137.1, 140.7, 141.5, 146.2, 182.1.

14. Compound 13 (0.655 g, 1.50 mmol) and trimethylstannylbenzene (0.542 g, 2.25 mmol) were dissolved in 30 mL anhydrous DMF in a pressure vessel containing a magnetic stir bar under argon. Pd(PPh₃)₄ (43.4 mg, 2.5 mol%), CuI (28.5 mg, 10.0 mol%) and CsF (0.342 g, 2.25 mmol) were added to the pressure vessel in an argon filled glovebox. The pressure vessel was sealed and taken out of the glovebox. The reaction was stirred at 80 °C for 24 hours. After cooling to room temperature, the reaction mixture was first extracted with CHCl3 and followed by washing with 1 M HCl solution, saturated NaHCO₃, DI H₂O and brine solution. Solvents were removed under reduced pressure and the crude product was further purified by silica gel column chromatography with hexane/ethyl acetate (0.46 g, 70.7%) ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.90 (-*CH*₃, t, 3H, J^{3}_{HH} = 6.9 Hz), 1.30-1.42 $(-CH_{2}-, m, 6H), 1.62 (-CH_{2}-, m, 2H), 2.79 (-CH_{2}-, t, 2H, J^{3}_{HH} =$ 7.8 Hz), 7.11 (*Th-H*, d, 1H, $J_{HH}^3 = 3.9$ Hz), 7.17 (*Th-H*, s, 1H), 7.25 (*Th-H*, d, 1H, $J_{HH}^3 = 3.6$ Hz), 7.30 (*Ph-H*, d, 1H, $J_{HH}^3 =$ 6.6 Hz), 7.32 (*Th-H*, d, 1H, $J_{HH}^3 = 3.6$ Hz), 7.39 (*Ph-H-*, m, 2H), 7.60 (*Ph-H-*, d, 2H, $J^{3}_{HH} = 8.4$ Hz), 7.67 (*Th-H*, d, 1H, $J_{\rm HH}^3 = 3.9$ Hz), 9.87 (-*CHO*, s, 1H). ¹³C NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 14.1, 22.6, 29.2, 29.7, 30.4, 31.6, 123.9, 125.6, 126.2, 126.4, 126.5, 127.8, 128.9, 129.2, 133.8, 135.1, 137.3, 138.3, 141.4, 141.5, 142.8, 146.9, 182.3.

MO. Compounds 14 (0.131 g, 0.300 mmol) and 12 (0.118 g, 0.60 mmol) were dissolved 15 mL CHCl₃ containing 0.5 mL triethylamine. The reaction mixture was first bubbled with N₂ for 30 min and stirred at room temperature for 2 days. Solvents were removed under reduced pressure and MO was purified by column chromatography with silica gel hexane/dichloromethane and by precipitation into methanol as a dark red solid (160 mg, 86.7%) ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.90 (-*CH*₃, t, 3H, J^3_{HH} = 6.9 Hz), 1.33-1.42 $(-CH_2-, m, 16H), 1.74 (-CH_2-, m, 4H), 2.81 (-CH_2-, t, 2H, J^3_{HH})$ = 7.8 Hz), 4.30 (-*CH*₂-, t, 2H, J^{3}_{HH} = 6.9 Hz) 7.13 (*Th*-*H*, d, 1H, $J_{HH}^{3} = 4.2$ Hz), 7.18 (*Th-H*, s, 1H), 7.26 (*Th-H*, d, 1H, $J_{HH}^{2} = 3.6$ Hz), 7.31 (*Ph-H*, d, 1H, $J_{HH}^{3} = 7.2$ Hz), 7.37 (*Th-H*, d, 1H), $J_{HH}^{3} = 7.2$ Hz), 7.37 (*Th-H*, d), 7.31 (*Th-H*, $J_{\rm HH}^3 = 3.9$ Hz), 7.39 (*Ph-H-*, m, 2H), 7.61 (*Ph-H-*, d, 2H, $J_{\rm HH}^3 =$

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7.8 Hz), 7.68 (*Th-H*, d, 1H, $J_{HH}^3 = 4.2$ Hz), 8.26 (-*CH=C*-, s, 1H). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 14.1, 22.6, 25.6, 28.5, 29.1, 29.7, 30.4, 31.7, 31.8, 66.6, 97.6, 116.0, 124.1, 125.6, 126.3, 126.6, 126.9, 127.8, 128.9, 129.3, 133.7, 134.2, 134.8, 138.7, 139.1, 141.6, 142.9, 146.0, 147.2, 163.0.

SO. Compound 11 (88 mg, 0.05 mmol), compound 12 (98.5 mg, 0.50 mmol) and 1 mL triethylamine were dissolved in 30 mL CHCl₃. The reaction mixture was purged with N_2 for 30 min and then stirred at room temperature for 48 h. After solvent removal under vacuum, SO was purified by silica gel chromatography with hexane/dichloromethane and then precipitation into methanol as a dark red solid (105 mg, 84.5%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.89-0.90 (-*CH*₃, t, 24H), 1.31-1.34 (-CH₂-, m, 64H), 1.69-1.77 (-CH₂-, m, 16H), 2.82 (-*CH*₂-, t, 8H, J^{3}_{HH} = 7.8 Hz), 4.29 (-*OCH*₂-, t, 8H, J^{3}_{HH} = 6.9 Hz), 7.14 (*Th-H*, d, 4H, $J_{HH}^3 = 3.9$ Hz), 7.25 (*Th-H*, d, 4H, $J_{\rm HH}^{3} = 3.9$ Hz), 7.27 (*Th-H*, s, 4H), 7.37 (*Th-H*, d, 4H, $J_{\rm HH}^{3} =$ 3.9 Hz), 7.64 (*Ph-H*, m, 16H), 7.67 (*Th-H*, d, 4H, $J^{3}_{HH} = 4.2$ Hz), 8.26 (-CH=C, s, 4H). ¹³C NMR (75.48 MHz, CDCl₃): δ (ppm) = 14.1, 22.6, 25.8, 28.6, 29.2, 29.7, 30.4, 31.7, 31.8,66.6, 97.7, 116.0, 124.2, 125.0, 126.7, 126.8, 126.9, 129.9, 133.2, 134.3, 135.0, 135.1, 136.9, 138.6, 139.1, 141.7, 142.4, 146.1, 147.1, 163.0.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: DFT calculations, X-ray scattering profile of **SO** films, TEM and SAED images, J-V curves, optical micrographs under cross polarized light, optical micrographs of the **SO**/PCBM devices under slow-cooling conditions, relation plot of $V_{\rm OC}$ vs. P3DTV contents, optical micrographs of the ternary blends and NMR spectra of all synthesized compounds. See DOI: 10.1039/b000000x/

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Graphical Abstract

The tetrahedral geometry of the conjugated small molecule displays unique thermal properties that lead to distinct behaviors in binary and ternary blend organic solar cells.

