

# Nonfullerene Small Molecular Acceptors with a Three-Dimensional (3D) Structure for Organic Solar Cells

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**(5)** Supporting Information

**ABSTRACT:** Two spirobifluorene (SF)-functioned 3D nonfullerene electron acceptors—SF-OR and SF-ORCN—that use rhodanine and 2-(1,1-dicyanomethylene)rhodanine as the terminal units, respectively, were designed and synthesized. These new acceptor materials show reversible electrochemical reduction and a high optical absorption coefficient, which are critical in device operation. Electronic and structural characterizations reveal that the inclusion of cyano group on rhodanine improve the electron accepting ability at the sacrifice of structure order, since the conjugated backbone becomes less planar, which prohibits cofacial stacking. SF-OR and SF-ORCN show good photovoltaic performances when paired with a poly(3-hexylthiophene) (P3HT) donor, and the optimized devices give power conversion efficiencies of 4.66% and 4.48%, respectively. These values are higher than that of fullerene acceptor-based control devices (3.55%), which are



also among the best in small molecular nonfullerene acceptor organic solar cells based on P3HT.

## INTRODUCTION

Solution-processed bulk heterojunction organic solar cells (OSCs) have received tremendous attention in recent years, because of their advantages, such as low cost, light weight, and flexibility.<sup>1-5</sup> The past decade has witnessed the dramatic progress in this area, and a power conversion efficiency (PCE) of >10% has been achieved, because of the development of novel donor materials. $^{6-13}$  However, compared to donor materials, the development of acceptors lags relatively behind. Until now, fullerene derivatives ([6,6]-phenyl  $C_{61}/C_{71}$  butyric acid methyl ester ( $PC_{61}BM$  and  $PC_{71}BM$ )), because of the high electron affinity, high electron mobility, and isotropic charge transport, are still the dominating acceptor materials.<sup>14,15</sup> However, fullerene derivatives show intrinsic drawbacks, such as weak absorption in the visible region, high cost in synthesis and purification process, making them unideal in future industrialization. To address these issues, nonfullerene electron acceptor materials with good light absorption, facile synthesis, fine-tuned energy levels and low cost, are developed, which have drawn high attention in OSCs most recently.<sup>10</sup>

In the past few years, various small molecules such as PDI derivatives, molecules with electron push–pull structure, etc. have been used as acceptors in OSCs,<sup>17–22</sup> and PCEs over 9%

have been achieved.<sup>23–25</sup> Although there is no clear route to designing high-performance nonfullerene acceptors, some empirical clues have been observed in nonfullerene acceptor design. For small molecules with big planar structures, the strong cofacial  $\pi - \pi$  stacking would lead to large acceptor aggregations, which will exceed the ideal exciton diffusion length scale and deplete acceptor content in nearby regions to break the connectivity of acceptor domains. Meanwhile, a complete amorphous acceptor region can also be detrimental, since charge hopping would be abysmal. Thus, a subtle balance in molecules that show good electronic communication with moderate intermolecular interactions is highly desirable. In this track, the molecular geometry factor with a three-dimensional (3D) molecular geometry is employed to achieve such a goal. Some successful examples employing such a strategy have been reported.<sup>22,26</sup> For examples, series of building blocks, such as triphenylamine, <sup>27,28</sup> tetraphenyl methane (silane), <sup>29–31</sup> tetraphenylethylene, <sup>32</sup> and spirobifluorene (SF), <sup>33–36</sup> were used as centers to construct 3D nonfullerene acceptors. PCEs of >6%

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have been demonstrated.<sup>35,37–40</sup> Further improvement is expected when new building blocks are introduced.

In this work, we designed and synthesized two small molecule acceptors SF-OR and SF-ORCN, using spirobifluorene (SF) as the central unit to link four 3-octylrhodanine (OR) or 3-octyl-2-(1,1-dicyanomethylene)rhodanine (ORCN) arms. The end-capping rhodanine group and central fluorene core are connected by a thiophene unit. Both electron-withdrawing groups have successfully been applied in designing both small molecule donors and acceptors.<sup>41–45</sup> The specific chemical structures of two designed acceptors are depicted in Figure 1.



Figure 1. Chemical structures of 3D acceptors SF-OR and SF-ORCN.

Solution-processed OSCs based on SF-OR and SF-ORCN blended with P3HT show maximum PCEs of 4.66% and 4.48%, respectively, which are higher than that of  $PC_{61}BM$ -based control devices.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthetic routes of SF-OR and SF-ORCN are depicted in Scheme 1, with details described in the Supporting Information. The target molecules were synthesized via three facile reactions. The intermediate

Scheme 1. Synthetic Routes of SF-OR and SF-ORCN

2,2',7,7'-tetrakis(4-octylthiophen-2-yl)-9,9'-spirobifluorene (2) was synthesized through Stille coupling reaction between 2,2',7,7'-tetrabromo-9,9'-spirobifluorene and tributyl(4-octylthiophen-2-yl)stannane (1). Compound 5,5',5",5"'-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrakis(3-octylthiophene-2-carbaldehyde) (3) was prepared by Vilsmeier—Haack reaction of intermediate 2 using POCl<sub>3</sub> and DMF as reagents. Subsequent Knoevenagel condensation between compound 3 and OR or ORCN afforded SF-OR and SF-ORCN. The chemical structures of SF-OR and SF-ORCN were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and MALDI-TOF MS (see Figures S5–S10 in the Supporting Information). Both molecules exhibit good solubility in common organic solvents, such as dichloromethane, chloroform, and *ortho*-dichlorobenzene at room temperature.

**Molecular Geometry.** In order to confirm their 3D structures of SF-OR and SF-ORCN, geometry optimizations based on density functional theory (DFT) at B3LYP/6-31G\* level were performed.<sup>46,47</sup> Frequency analysis was followed to ensure that the optimized geometries were stable states, and the octyl groups were replaced by ethyl ones, for the sake of simplification.

The two orthogonal fluorene units in spirobifluorene serve as a rigid central core, resulting in a high degree of D<sub>2</sub> point group symmetry. Dihedral angles of 22.5° and 22.3° were observed between the thiophene unit and the fluorene unit in SF-OR and SF-ORCN, respectively. (See Figure 2.) These dihedral angles were small and thus good electronic communication in each fluorene side was expected, which are consistent with the electron cloud distributions at frontier molecular orbitals (see Figure S1). Although the current SF-OR and SF-ORCN are quite simple in structure, it is very interesting to note the overall geometry is 90° twisted, thus leading to a 3D structure. The submolecule in each fluorene side is quite flat and fully extended, to accommodate intermolecular interactions. Thus, in this new system, we expect to see a good intermolecular interaction but with a short stacking coherence length in bulk heterojunction (BHJ) blends, which would be ideal in nonfullerene OSC applications.





Figure 2. Optimized molecular geometries of SF-OR and SF-ORCN at B3LYP/6-31G\*.

**Thermal Stability.** The thermal characteristics of these two molecules were studied by thermogravimetric analysis (TGA) (Figure 3) under nitrogen atmosphere. SF-OR and SF-ORCN



Figure 3. Thermogravimetric analysis (TGA) plots of SF-OR and SF-ORCN.

give weight losses of <5% up to 389 and 373 °C, respectively. The good thermal stabilities of both molecules meet the device fabrication requirements.

Optical and Electrochemical Properties. The ultraviolet-visible light (UV-vis) absorption spectra of both molecules in diluted chloroform and thin solid film are shown in Figures 4a and 4b, respectively. The corresponding data are summarized in Table 1. In solution, the absorption coefficients for both molecules were  $>10^5$  M<sup>-1</sup> cm<sup>-1</sup>, benefitting from the rhodanine-fluorene-rhodanine pushpull structure. SF-ORCN gives a bathochromic absorption band at 520 nm, compared with SF-OR (504 nm). Besides, SF-ORCN shows slightly higher light-absorbing capability than SF-OR, which was consistent with the prediction given by timedependent density functional theory (TDDFT) (see Figure S2 in the Supporting Information). In comparison with solution absorption, no significant changes in the positions of absorption peaks could be observed from thin-film absorption. In both molecules, a new absorption peak at ~540 nm appeared, indicating that intermolecular  $\pi - \pi$  interactions were obvious in the solid state. Also note that SF-OR showed a much more pronounced  $\pi - \pi$  stacking peak, which is due to a better-packed molecular structure.

The electrochemical properties of both molecules were investigated by cyclic voltammetry (CV) experiments (Figure 4c). The energy levels were calculated from the oxidation and reduction wave in CV spectra. Measurement is referenced by the energy level of  $Fc/Fc^+$  (-4.8 eV below vacuum).<sup>48</sup> The oxidation and reduction potentials of SF-OR were estimated to



**Figure 4.** (a) Ultraviolet–visible light (UV-vis) absorption spectra of SF-OR and SF-ORCN in diluted chloroform solutions; (b) UV-vis absorption spectra of SF-OR and SF-ORCN as cast films; (c) cyclic voltammograms of SF-OR and SF-ORCN dichloromethane solutions with 0.1 mol  $L^{-1}$  *n*-Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>.

be 0.70 V and -1.55 V (vs Fc/Fc<sup>+</sup>), and 0.75 V and -1.51 V for SF-ORCN, respectively. The electrochemical and calculated results are summarized in Table 1. In CV traces, reversible reduction peaks were observed; thus, these materials would be stable during electron-accepting and carrier transport processes

#### Table 1. Optical, Electrochemical and Calculation Data of SF-OR and SF-ORCN

	UV-vis			CV			DFT			
molecule	$\lambda_{\max}^{\mathrm{sol}}$ (nm)	$\varepsilon_{\rm max}~({ m M}^{-1}~{ m cm}^{-1})$	$\lambda_{\max}^{\mathrm{film}}$ (nm)	$E_{\rm g}^{\rm opt} ({\rm eV})^a$	HOMO (eV)	LUMO (eV)	$E_{\rm g}^{\rm cv}~({\rm eV})$	HOMO (eV)	LUMO (eV)	$E_{\rm g}^{\rm cal}~({\rm eV})$
SF-OR	504	$1.49 \times 10^{5}$	504, 538	2.15	-5.50	-3.25	2.25	-5.56	-2.94	2.62
SF-ORCN	520	$1.55 \times 10^{5}$	515, 543	2.08	-5.55	-3.29	2.26	-5.86	-3.26	2.60
<sup>4</sup> Optical bandgap was obtained from the onset wavelength of the film.										

Table 2. Photovoltaic Performance of OSCs Based on P3HT Measured at Simulated 100 mW cm<sup>-2</sup> AM 1.5G Illumination

		$J_{\rm sc}$ (mA cr				
acceptor	$V_{\rm oc}~({ m V})$	expt	calc	FF (%)	PCE (%)	PCE <sub>max</sub> (%)
SF-OR	$0.965 \pm 0.005$	$7.30 \pm 0.20$	7.045	$62.9 \pm 1.8$	$4.46 \pm 0.20$	4.66
SF-ORCN	$0.912 \pm 0.003$	$7.58 \pm 0.16$	7.260	$63.3 \pm 1.7$	$4.42 \pm 0.07$	4.48
PC <sub>61</sub> BM	$0.608 \pm 0.004$	$9.43 \pm 0.17$	9.341	$60.6 \pm 1.3$	$3.47 \pm 0.15$	3.55

during solar cell operation. The lowest unoccupied molecular orbital (LUMO) energy levels of these two acceptors were not deep enough, which lead us to choose P3HT as the donor polymer. The LUMO offsets between SF-OR/SF-ORCN and P3HT (-2.74 eV) were >0.5 eV, which was large enough to provide the driving force for exciton dissociation.<sup>36,49</sup> The higher LUMOs of these molecules would give rise to larger open circuit voltages ( $V_{oc}$ ) in devices.

Nonfullerene Organic Solar Cells. Solar cells using a conventional configuration of indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PE-DOT:PSS)/active layer/zinc oxide nanoparticles (ZnO NPs)/ Al were fabricated and tested under simulated 100 mW cm<sup>-2</sup> AM 1.5G illumination. The active layers were prepared by spincoating the P3HT:SF-OR or P3HT:SF-ORCN blend solution onto PEDOT:PSS-coated substrates. Control devices based on P3HT:PC<sub>61</sub>BM were also fabricated. The device performances were summarized in Table 2, and the corresponding J-Vcharacteristics are shown in Figure 5a. More-detailed device parameters are provided in the Supporting Information (Table S1 and S2). As a benefit from their high-lying LUMO energy levels, OSCs based on these two acceptors provided a rather high  $V_{0c}$  of over 1.10 V in as-cast devices. The  $V_{0c}$  value under optimized conditions was still >0.90 V, which presented the main advantage comparing to devices based on PC<sub>61</sub>BM. Because of the improved light absorption, the short-circuit current density  $(J_{sc})$  for OSCs based on SF-ORCN (7.58 mA cm<sup>-2</sup>) was slightly larger than that in SF-OR-based devices  $(7.30 \text{ mA cm}^{-2})$ . The fill factors (FF) for devices based on SF-OR and SF-ORCN can be as high as 0.646 and 0.652, respectively, indicating the weak charge recombination in the optimized devices, which was further confirmed by the photocurrent behavior analysis (Figure 5b). The exciton dissociation efficiencies for devices based on SF-OR and SF-ORCN were as high as 95.97% and 95.77%, respectively, which were comparable to the best-performing fullerene-based devices. Based on these results, the maximum PCEs for the two acceptors reached 4.66% and 4.48%, respectively. These PCE values were higher than that of control devices based on P3HT:PC<sub>61</sub>BM, and were among the highest values ever reported for P3HT and nonfullerene acceptor solar cells.<sup>36,50,51</sup>

The external quantum efficiency (EQE) was measured to explore the spectral response of the optimized devices. The results are shown in Figure 5c. The slightly higher  $J_{sc}$  obtained from SF-ORCN-based devices can be attributed to its stronger response in the wavelength region of 520–600 nm. The maximum EQE values for these two acceptor-based devices are



**Figure 5.** (a) Current density–voltage (J-V) characteristics and (b) photocurrent–effective voltage curves of nonfullerene OSCs under optimized conditions; (c) EQE spectra of OSCs based on SF-OR and SF-ORCN under optimized conditions.

Table 3. Carrier Mobilities of P3HT:SF-OR and P3HT:SF-ORCN Blend Films before and after Thermal Annealing

	Hole Mobility (	$cm^2 V^{-1} s^{-1}$ )	Electron Mobility ( $cm^2 V^{-1} s^{-1}$ )		
blend film	without thermal annealing	with thermal annealing	without thermal annealing	with thermal annealing	
P3HT:SF-OR P3HT:SF-ORCN	$2.29 \times 10^{-5}$ $5.04 \times 10^{-5}$	$8.49 \times 10^{-5}$ $1.55 \times 10^{-4}$	$5.19 \times 10^{-6}$ $3.71 \times 10^{-5}$	$6.71 \times 10^{-6}$ $1.01 \times 10^{-4}$	

~60%. The calculated  $J_{\rm sc}$  obtained by integration of the EQE curves are 7.045 mA cm<sup>-2</sup> and 7.260 mA cm<sup>-2</sup>, respectively, whose mismatch are within 3%–5% compared to the  $J_{\rm sc}$  values obtained from their J-V curves.

Carrier Mobility. It is known that good hole and electron transport properties are a key factor for high-performance devices. The hole and electron mobilities of the active layer blend films were measured by the space-charge limit current (SCLC) method with device structures of ITO/PEDOT:PSS/ P3HT:acceptor/Au and Al/P3HT:acceptor/Al for hole and electron, respectively. In addition, the experimental results are summarized in Table 3 and the Supporting Information (Figures S3 and S4 in the Supporting Information). Before thermal annealing, the hole mobilities of the blend films were calculated to be  $2.29\times 10^{-5}$  and  $5.04\times 10^{-5}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$  for P3HT:SF-OR and P3HT:SF-ORCN, respectively. These two values are enhanced to  $8.49 \times 10^{-5}$  and  $1.55 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$ , respectively, after thermal annealing. Similar improvements were observed in electron mobilities. Therefore, thermal annealing could promote the structural ordering in BHJ blending for both donor and acceptor materials, leading to improved morphology, charge transport, and power conversion efficiency.

**Morphology Analysis.** The morphology of BHJ blends was thoroughly studied using microscopy and scattering methods. The surface morphology of the active layer was investigated by tapping-mode atomic force microscopy (AFM). Figure 6 showed the topographical images for P3HT:SF-OR and P3HT:SF-ORCN blend films. Very smooth films could be obtained in as-cast thin films, showing root-mean-square (RMS) roughness values of 0.515 and 0.306 nm, respectively. After thermal annealing, the film surface became rougher, with roughnesses of 0.917 and 0.610 nm, respectively. Thus, thermal



**Figure 6.** Atomic force microscopy (AFM) topographical images of (a, c) P3HT:SF-OR and (b, d) P3HT:SF-ORCN blend films: (a, b) ascast (panels a and b) and thermal annealing (panels c and d).

annealing can be very effective in changing the crystallization and phase separation in the BHJ blends.

Structure order of P3HT and acceptor small molecules were investigated using grazing-incidence X-ray diffraction (GIXD) measurement. Figure 7 shows two-dimensional (2D) GIXD diffraction patterns and line-cut profiles. We first looked into the SF-OR/SF-ORCN pure thin films. As seen from Figure 7a (left column), the as-cast SF-OR thin film showed an obvious (100) diffraction peak in the out-of-plane direction at 0.36 Å<sup>-1</sup>. A corresponding  $\pi - \pi$  stacking was located at ~1.6 Å<sup>-1</sup> with a quite broad angle spreading. An amorphous halo was seen in  $\sim$ 1.2 Å<sup>-1</sup>. Thermal annealing led to very strong enhancement in crystallization, as seen from the reduced amorphous scattering ring and enhanced scattering peaks. Note that, upon thermal treatment, SF-OR crystals adopted an edge-on orientation, indicated from a largely reduced angle spreading of  $\pi - \pi$  scattering peak. Details of crystalline information could be tracked in the line-cut profiles (Figure 7b). The (100) crystal size (crystal coherence length) in the out-of-plane direction was estimated to be 13.2 nm using the Scherrer equation. The corresponding  $\pi - \pi$  stacking crystal size in the in-plane direction was estimated to be 7.9 nm. SF-OR is a twisted molecule with two planar molecular fragments perpendicular to each other. Thus, in molecule crystals, the  $\pi - \pi$  stacking should have originated from the submolecule fragments interaction and the (100) stacking should have originated from the alkylalkyl interaction from the submolecule fragments. Thus, as expected, SF-OR molecule could form good structure order, but the overall crystal packing would be reduced, since molecular twisting could reduce the strong cofacial stacking.

SF-ORCN showed less-ordered crystalline packing in both as-cast and annealed thin films. In both as-cast and annealed thin films of SF-ORCN, no strong diffraction peak could be observed and the scattering was dominated by the amorphous halo. These results actually supported the augmentation of SF-OR solid-state order. The substitution of dicyano group onto rhodanine units could disturb the cofacial stacking of the submolecule conjugated plan, as cyano group in molecule would stretch out in the conjugated plan. The disappearance of the intermolecular cofacial interaction drastically led to a decrease in crystalline order, both in  $\pi$ - $\pi$  stacking and (100) stacking directions.

When these acceptor molecules were blended with P3HT, the morphology became complicated. As seen from the diffraction patterns, P3HT formed face-on crystallites in ascast BHJ blends. The (100) peak located at  $0.37 \text{ Å}^{-1}$ , which was similar to that in SF-OR. The (020) peak located at  $1.67 \text{ Å}^{-1}$ , which was slightly tighter than SF-OR. When film is thermally annealing, the crystallization from P3HT and SF-OR was both enhanced. If assuming P3HT was dominantly face-on and SF-OR was dominantly edge-on (admittedly this was a rough estimation), the (100) crystal sizes for P3HT and SF-OR were 13.3 and 9.6 nm, respectively. Thus, in the BHJ blends, both donor crystallites and acceptor crystallites existed, giving rise to a phase-separated morphology. In P3HT:SF-ORCN blends, ascast thin film GIXD was dominated by the face-on



Figure 7. (a) Two-dimensional (2D) grazing-incidence X-ray diffraction (GIXD) patterns of SF-OR and SF-ORCN pure films and blend films; (b) 1D line-cut profiles extracted from GIXD for SF-OR and SF-ORCN pure films; (c) 1D line-cut profiles extracted from GIXD for blend films (solid line represents the out-of-plane line cut; dotted line represents the in-plane line cut).

crystallization of P3HT. When thermal annealing was used, strong enhancement in crystalline feature was observed. We saw, in the pristine thin film, that SF-ORCN was reluctant to order during thermal annealing process; therefore, in annealed BHJ blends, we ascribe the crystalline feature to P3HT. It was not surprised that thermal annealing could drastically enhance the structure order of P3HT. However, to our surprise, the crystallization orientation of P3HT changed upon thermal treatment. Strong highly ordered reflections could be seen in the out-of-plane direction, indicating the edge-on crystallization. The overall spreading of the (100) and (020) peaks was quite broad, thus crystallites assumed all directional orientations. The crystal size from in-plane (100) peak and out-of-plane (020) peaks were 20.9 and 5.1 nm, respectively.

Phase separation in BHJ blends was investigated using resonant soft X-ray scattering (RSoXS) measurement. Figure 8



Figure 8. RSoXS profiles for SF-OR:P3HT and SF-ORCN:P3HT films before and after thermal annealing.

shows RSoXS scattering profiles, using a photon energy of 286.8 eV. It can be seen, in the as-cast thin films, that both blends did not form obvious phase separation. Thus, these acceptor molecules could mix quite well with P3HT. The scattering profile for P3HT:SF-OR blends showed a slightly enhanced scattering hump (~0.01 Å<sup>-1</sup>), in comparison to P3HT:SF-ORCN blends. This could be due to the fact that, in blends, there were SF-OR crystallites, and the scattering gave an average distance of crystalline contents. In thermally treated thin films, RSoXS scattering changed largely. For P3HT:SF-OR blends, a very broad scattering peak, from 0.01 to 0.03  $Å^{-1}$ , was observed. We ascribe this feature to the results of SF-OR and P3HT crystallization. In addition, the broad scattering hump came from a continuous landscape of intercrystal distances. In annealed P3HT:SF-ORCN blends, a clear phase separation at 0.0165 Å<sup>-1</sup> was seen, corresponding to a distance of  $\sim$ 38 nm. In these BHJ blends, SF-ORCN did not crystallize, and thus the driving force of phase separation was ascribed to P3HT crystallization. The (100) crystal size in in-plane direction was estimated to be 20.9 nm, which matched well with phase separation length scale. Thus, the final BHJ was constituted of P3HT crystalline species and P3HT:SF-ORCN mixed domains.

When the morphology results were correlated with device performances, important conclusions could be obtained. As we can see from device results, the major drawback for SF-ORCN was the inferior  $V_{\rm oc}$  compared to that for SF-OR, which is an electronic structure issue that is related to the chemical structure. Morphologically, SF-ORCN blends are superior, forming better-defined phase-separated domains. Although the crystalline of the acceptor phase is weak, the high crystallinity of P3HT leads to an acceptor domain with good phase purity, which could effective transport electrons, as we saw in SCLC results. SF-OR molecules are more readily to crystallize under thermal annealing. The electron mobility in BHJ thin films is much poorer, compared to SF-ORCN blends. This can be that SF-OR is less effective to transport electrons molecularly (for example, smaller transfer integrals). It can also be observed that, in the acceptor domain, the high tendency of SF-OR crystallization would lead to disruption of the domain continuity, since crystallization would deplete SF-OR concentration in local regions and thus electrons would suffer from some harder hopping sites (similar to the observations made by McGehee and coworkers on PBDTTPD polymers).<sup>52</sup>

### CONCLUSION

In summary, we designed and synthesized two new nonfullerene acceptors with a three-dimensional (3D) structure: SF-OR and SF-ORCN. It is quite encouraging that such an easy material design and chemical process could lead to acceptor materials with good thermal stability, strong absorption, and appropriate energy levels. The introduction of 3D conformation can prevent overaggregation in acceptor phases, contributing to the formation of favorable interpenetrating network with a suitable degree of phase separation in the blend film of the active layer. In our investigation, we see that a less crystalline acceptor material with a good phase separation is beneficial for electron transport and works well in organic solar cells. With regard to solar cell performance, SF-OR and SF-ORCN give high device efficiencies of 4.66% and 4.48%, respectively, which are higher than that of the control device based on PC<sub>61</sub>BM. These results indicate that new acceptor can be more favorable than the conventional fullerene-based species, especially at the cost of chemistry.

#### EXPERIMENTAL SECTION

**Materials.** All reactions and manipulations were carried under an argon atmosphere with the use of standard Schlenk techniques. The solvents were purified and dried according to standard procedures. The commercially available products were purchased from Alfa Aesar and Sigma–Aldrich. Donor P3HT polymer was purchased from Rieke Metals.  $PC_{61}BM$  was purchased from American Dye Source. The synthetic routes of SF-OR and SF-ORCN are shown in Scheme 1, with details described in the Supporting Information. Tributyl(4-octylthiophen-2-yl)stannane (1) was synthesized according to the reported procedure.<sup>53</sup>

Measurements and Instruments. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained by using a Bruker AV400 spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer in dichloromethane solutions. All measurements were carried out at room temperature with a conventional three-electrode configuration, employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (n-Bu4NPF6, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s<sup>-1</sup>. Atomic force microscopy (AFM) investigation was performed using Bruker MultiMode 8 in tapping mode. DFT calculations were carried out using Gaussian 09 package (see the Supporting Information for the full citation).

Both the hole mobility and electron mobility were measured using the space-charge limited current (SCLC) method, employing a diode configuration of ITO/PEDOT:PSS/active layer/Au for hole and glass/Al/active layer/Al for electron by taking the dark current density in the range of 0-8 V and fitting the results to a space-charge limited form, where SCLC is described by

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu V^2}{8L^3}$$

where J is the current density, L the film thickness of the active layer,  $\mu$  the hole or electron mobility,  $\varepsilon_{\rm r}$  the relative dielectric constant of the transport medium,  $\varepsilon_0$  the permittivity of free space (8.85 × 10<sup>-12</sup> F m<sup>-1</sup>), V the internal voltage in the device ( $V = V_{\rm appl} - V_{\rm bi}$ , where  $V_{\rm appl}$  is the applied voltage to the device and  $V_{\rm bi}$  is the built-in voltage due to the relative work function difference of the two electrodes).

The current density–voltage (J-V) characteristics of photovoltaic devices were obtained using a Keithley 2400 sourcemeasure unit. The photocurrent was measured under illumination simulated 100 mW cm<sup>-2</sup> AM1.5G irradiation using a xenon-lamp-based solar simulator [Oriel 96000 (AM1.5G)] in an argon-filled glovebox. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode. External quantum efficiency (EQE) values of the encapsulated devices were obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and photon flux was determined by a calibrated silicon photodiode.

Fabrication and Characterization of Nonfullerene OSCs. The conventional photovoltaic devices were fabricated with the structure of glass/ITO/PEDOT:PSS/active layer/ ZnO nanoparticles (NPs)/Al. Patterned ITO-coated substrates with a sheet resistance of ~15  $\Omega/\Box$  were cleaned using a detergent scrub and subsequently subjected to ultrasonic treatment in soap water, deionized water, acetone, and isopropyl alcohol for 15 min in each step. After drying using a nitrogen flow, the ITO substrates were subjected to ultraviolet-ozone treatment for 20 min. A thin layer (ca. 35 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45  $\mu$ m) was then spin-coated onto ITO substrates. After baking at 150 °C for 20 min under ambient conditions, the substrates were transferred into an argon-filled glovebox. Subsequently, a P3HT:SF-OR or P3HT:SF-ORCN blend solution in chloroform (1:0.5 w/w, 7 mg mL $^{-1}$  for donor component) was spincoated onto the PEDOT:PSS substrate to form an ~100 nm active layer, followed by thermal annealing for 10 min on a digitally controlled hot plate. The optimized annealing temperatures are 150 °C for P3HT:SF-OR and 120 °C for P3HT:SF-ORCN. The thickness of the active layer was measured by AFM. The ZnO NPs solution (in n-BuOH, filtered at 0.22  $\mu$ m) was spin-coated onto the active layer. ZnO NPs were prepared using the techniques reported by Beek et al.<sup>54</sup> Finally, an 80-nm-thick Al layer was evaporated under high vacuum ( $<2 \times 10^{-4}$  Pa). The effective areas of cells were 4 mm<sup>2</sup>, defined by metal masks. For the P3HT:PC<sub>61</sub>BM control device, the only difference is the preparation of the active layer. A P3HT: PC<sub>61</sub>BM blend solution in ortho-dichlorobenzene (1:1 w/w, 40 mg mL<sup>-1</sup> in total, filtered at 0.22  $\mu$ m) was spincast for 20 s onto the PEDOT:PSS layer, followed by solvent annealing for above 2 h to fully remove residual solvent. Thermal annealing at 100 °C for 10 min was performed before spin-coating the ZnO NPs. The thickness of P3HT:PC $_{61}$ BM blend film is ~250 nm.

#### ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b03323.

Detailed synthetic procedures and characterization data for the new compounds and additional experimental results (PDF)

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#### Notes

The authors declare no competing financial interest.

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