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Solvent Annealing Effects in Dithieno[3,2-*b*:2',3'-*d*]pyrrole-5,6-Difluorobenzo[*c*][1,2,5]thiadiazole Small Molecule Donors for BHJ Solar Cells

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ABSTRACT: Low-bandgap small molecule (SM) donors that can be solution-processed with fullerene acceptors (e.g. PC₆₁/71BM) are proving particularly promising in bulk-heterojunction (BHJ) solar cells. Compared to their π -conjugated polymer counterparts, SM donors are well defined (monodispersed) and more synthetically modular –with relatively wide ranges of bandgaps achievable in stepwise couplings of various donor and acceptor motifs. However, the optimization of SM-fullerene morphologies and BHJ device efficiencies relies more specifically on the use of processing additives, post-processing thermal or solvent vapor annealing (SVA) approaches, and achieving adequate interpenetrating networks and structural order in BHJ thin films can be challenging. In this report, we examine the correlated effects of molecular structure and post-processing SVA on the BHJ solar cell performance of a set of π -extended SM donors composed of dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) and 5,6-difluorobenzo[*c*][1,2,5]thiadiazole ([2F]BT) units. In these systems (SM1-3), the introduction of additional alkyl substituents and unsubstituted thiophene rings on the peripheral unit groups critically impacts the effects of SVA steps on BHJ solar cell efficiency. We show that the more π -extended and alkyl-substituted analogue SM3 stands out –with BHJ device efficiencies of ca. 6% obtained from SVA with CS₂– while SVA-treated SM3-based active layers also show the most favorable ordering and carrier mobility patterns. However, unlike numbers of SM donors reported in recent years, DTP–[2F]BT SM analogues are *in general* not prone to dramatic performance variations in BHJ thin films cast with processing additives. Our results indicate that the role of SVA steps is not independent of the molecular structure of the SM donors used in the BHJ solar cells.

Introduction

With recently reported power conversion efficiencies (PCEs) >9%,¹⁻³ solution-processed SM donors are very promising alternatives to their more studied polymer donor counterparts for BHJ solar cells with PCBM acceptors. Being well-defined, of finite conjugation length, and synthetically modular,⁴⁻⁵ SM donors with various combinations of electron-rich (donor, D) and electron-deficient (acceptor, A) motifs on their main chain achieve a broad range of optical bandgaps (E_{opt}), often reported in the range 1.5–2 eV.⁶⁻⁷ In single-cell BHJ devices, optimal E_{opt} values lie in the range 1.6–1.8 eV,⁸⁻⁹ while in multi-junction solar cells, π -conjugated systems with narrower E_{opt} values of 1.3–1.5 eV, or wider E_{opt} values of 1.9–2.1 eV, can be especially relevant for use in the low-bandgap or/and high-bandgap subcells, respectively.¹⁰⁻¹¹ A few recent studies indicate that SM-fullerene tandems can achieve PCEs >10%,¹²⁻¹³ and can therefore rival polymer-fullerene tandem¹⁴⁻¹⁵ and triple-junction¹⁶⁻¹⁷ devices. In turn, it is important to develop SM donor design approaches amenable to the synthesis of materials systems with complementary absorption (*i.e.* distinct E_{opt} values), and performance patterns comparable or better than those of their poly-

mer counterparts in BHJ solar cells (J_{sc} , V_{oc} , FF , and PCEs). In optimizing material properties and performance for single-cell and/or multi-junction BHJ solar cells, it should be noted that the maximum efficiency figures theoretically achievable with gap materials is not independent of the material's optical bandgap, E_{opt} .^{9,18-20}

In earlier reports detailing device optimization protocols for several low-bandgap SM donors,²¹⁻²⁵ the use of processing additives,^{22,26} post-processing thermal^{24,27} or solvent vapor annealing (SVA) approaches^{21,25,28} have been emphasized as determining steps in the optimization of SM-fullerene blend morphologies and BHJ device efficiencies. Compared to polymers, SM donors tend to be more prone to significant variations in thin-film device performance pattern when subjected to one or several of these morphology-directing protocols. For example, the use of processing additives with the low-bandgap dithieno[3,2-*b*:2',3'-*d*]silolebenzo[*c*][1,2,5]thiadiazole (N- or F-substituted) SM analogues (E_{opt} ~1.5 eV) has been shown to raise BHJ solar cell PCEs from a modest 1.8–4.5% for “*as-cast*” devices, to values as high as 8.3% in optimized solar cells.^{23,28} Likewise, SM donors composed of oligothiophene sequences (and other alternating sets of donor units)

end-capped with relatively electron-withdrawing units, such as rhodanine²⁹⁻³² and analogues,^{2,33} have been shown to undergo significant morphological changes in BHJ thin films subjected to thermal²⁹⁻³⁰ or SVA^{31,34} post-processing steps. In SVA treatments, the solvent vapors diffuse into the active layer, inducing a reorganization of the SM donor and/or fullerene acceptor across the bulk and, in some instances, significant changes in the extent of phase separation achieved between donor and acceptor components.^{3,34-35} These short-range and mesoscale morphological variations can result in substantial device performance improvements (or decays).^{3,34-35} When optimized protocols are employed, these SM systems can achieve BHJ solar cell PCEs as high as 9.6% with PCBM acceptors.³⁴ Overall, we note that achieving adequate interpenetrating networks and structural order in BHJ thin films can prove to be challenging and, in turn, extensive, systematic optimization protocols are often required to reach device PCE values that reflect the best performance pattern achievable with specific SM donors.⁵

In the design of *low*-bandgap material systems, the use of particularly electron-rich, “bridged or fused” building units yields reduced ionization potentials (IPs) and, concurrently, higher-lying HOMO energy levels that effectively narrow E_{opt} . For example, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDT) and dithieno[3,2-*b*:2',3'-*d*]silole (DTS) have often been used as monomers and central units in the synthesis of low-bandgap polymer³⁶⁻³⁸ and SM³⁹⁻⁴⁰ donors, respectively. Higher-HOMO systems can be achieved with dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) motifs,⁴¹⁻⁴³ and yet, interestingly, DTP-based SM donors have not received the same level of attention as their CDT and DTS counterparts. It is worth noting, however, that the pyrrole ring-forming step is relatively high yielding,⁴³⁻⁴⁴ and that a wide range of solubilizing side-chain substituents can be appended at the *N*-position, such as linear alkyl chains (*e.g.* hexyl, octyl) and/or branched substituents (*e.g.* 2-ethylhexyl, 2-hexyldecyl), conferring DTP-based polymer and SM donors with adequate solution-processability in common organic solvents.⁴³⁻⁴⁴

Surprisingly perhaps, earlier studies on DTP-based SMs examined in BHJ solar cells with PCBM acceptors have reported on relatively modest PCEs in the range 0.2–1.3%.⁴⁵⁻⁴⁷ In a different material design approach, DTP-based SM donors have, however, recently been shown to achieve PCEs of up to 6.1% upon systematic thin-film morphology and BHJ device optimizations,^{21,48} paving the way to further possible material performance improvements upon rational, systematic design developments. In this contribution, we report on the synthesis, properties and BHJ solar cell characteristics of a set of three dithieno[3,2-*b*:2',3'-*d*]pyrrole-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (DTP-[2F]BT) SM donors with alkyl-substituted thiophene end-groups and distinct solubilizing side-chain and chain length patterns (SM1-3, Chart 1). In SM1, the general donor-acceptor unit sequence remains analogous to that of the *low*-bandgap dithieno[3,2-*b*:2',3'-*d*]silolebenzo[*c*][1,2,5]thiadiazole (N- or F-substituted) SM analogues for direct comparisons with prior published work.^{22,24} Our systematic BHJ solar cell optimizations show that, in SM1-3, the introduction of additional alkyl substituents and unsubstituted thiophene rings on the peripheral unit groups critically impacts the effects of SVA steps on device efficiency, with PCEs ranging from *ca.* 2% (SM2; no SVA) to 6% (SM3; SVA with CS₂). Importantly, we emphasize the correlated effects of molecular structure and post-processing SVA on BHJ device performance in SM1-3, and note that SVA treatments can significantly improve the charge transport characteristics of SM donors in thin films.

Chart 1. Dithieno[3,2-*b*:2',3'-*d*]pyrrole-5,6-Difluorobenzo[*c*][1,2,5]thiadiazole SM Donors, SM1-3.

Results and Discussion

Design, Synthesis and Material Properties

In the design of solution-processable SM donors used as alternatives to their polymer counterparts in BHJ solar cells with PCBM acceptors, the sequence of donor and acceptor units incorporated in the SM main-chain sets the optical and electronic properties of the chromophore (*i.e.* spectral absorption, optical bandgap, IPs, EAs, etc.), while the alkyl side-chain pattern should provide sufficient solubility in common organic solvents. The stepwise (“unit-by-unit”) substitution of the various motifs can proceed via convergent⁷ or divergent⁶ synthetic protocols, yielding well-defined π -extended molecular systems amenable to large-scale reactions and purifications via conventional and/or automated chromatography techniques.^{5,49-51} It should be noted that polymer donors do not benefit from the same level of synthetic modularity because of the symmetry requirements on the monomers used in the Pd-mediated cross-coupling polycondensation reactions.^{8,52} Scheme 1 lays out the convergent protocol used for the synthesis of the DTP-[2F]BT SM donors, SM1-3; detailed experimental procedures are provided in the Supporting Information (SI). Extending the π -conjugated main chain of SM1 yields the analogue SM3 whose solution-processability can be raised by the substitution of additional alkyl side chains (2-ethylhexyl, see Chart 1); for consistency in our systematic study, SM2 includes the same additional branched side-chain substituents as SM3, while being consistent with SM1 in terms of chain length. In brief, the alkyl-substituted bithiophene and terthiophene peripheral segments 4, 5 and 7 were prepared by successive (microwave-assisted) Stille coupling, lithiation, and

Scheme 1. Synthesis of the DTP-[2F]BT SM Donors, SM1-3.

stannylation steps. Next, the asymmetric cross-couplings between intermediate 4, 5 and 7, and [2F]BT (8) in similar Pd-mediated Stille conditions yielded intermediates 9a-c in *ca.* 30-45% yields. Lastly, symmetrical cross-couplings between the DTP precursor 10 and intermediates 9a-c led to the SM donors SM1-3 in 55-60% yields after sequential purifications via column chromatography and recycling SEC (see details in SI). We note that the 1,4-octylthiophene-substituted DTP unit was synthesized according to established procedures.⁵³ The ^1H , ^{13}C , and ^{19}F NMR spectra, and the high-resolution mass spectrometry (HRMS) analyses pertaining to all key intermediates and SM1-3 are provided in the SI. All three SM donors were found soluble in common organic solvents such as dichloromethane, chloroform, and 1,2-dichlorobenzene; the differences in self-assembly patterns for SM1-3 on going from solution to thin films will be discussed in later sections in the report.

The thin-film UV-vis absorption spectra of SM1-3 are superimposed in Figure 1a, and the solution (in CHCl_3) and thin-film spectra for each SM system are overlaid in Figure S1a-c. In solution (Fig. S1a-c), all three SM systems show comparable two-band absorption spectra, with a shorter-wavelength absorption band (300–450 nm) attributed to electronic transitions arising from the more electron-rich (thiophene-based) segments in the SM donors,^{21,43-44} and a longer-wavelength absorption band (450–700 nm) characteristic of HOMO→LUMO transitions localized on the

[2F]BT acceptor motifs.^{25,54-55} The absence of long-wavelength absorption shoulders in the solution spectra of SM1-3 indicates that the molecules are not subject to π -aggregation at the concentration of this experiment (1×10^{-5} M). In thin films (Fig. 1a), the absorption spectra of SM1-3 shift to longer wavelengths, with onsets shifting from *ca.* 675 nm in solution, to >750 nm in thin films. The prominent aggregation footprints convoluted with the main absorption band at longer wavelengths mark the propensity of the SM donors to self-assemble in thin films (ordering effects and aggregation patterns in thin films will be discussed further in the next sections of the report). Some differences in relative intensity between long-wavelength absorption and aggregation peaks suggest that the SM donors have different ordering propensities. Expectedly, comparable E_{opt} values can be inferred from the onsets of thin-film absorption: 1.59 eV for SM1, 1.63 eV for SM2, and 1.58 eV for SM3. The ionization potentials (IPs) of SM1-3 were determined via photoelectron spectroscopy in air (PESA): 5.03 eV for SM1, 5.07 eV for SM2, and 5.05 eV for SM3; IP values expectedly comparable across the set of SM donors. Those figures are summarized in Table 1, along with extrapolated electron affinity (EA) values inferred by subtracting IP and E_{opt} values.

The thermogravimetric analyses (TGA) given in Figure S2 indicate that the SM donors SM1-3 are thermally stable in nitrogen atmosphere until *ca.* 380 °C (*ca.* 5% weight loss observed at 410 °C). The differential scanning calorimetry (DSC) analyses shown

Figure 1. (a) Superimposed thin-film UV-vis optical absorption spectra of SM1-3 (normalized). (b) Representations of the HOMO and LUMO of SM3 obtained by DFT at the B3LYP/6-31G(d,p) level of theory (see representations for SM1 and SM2 in SI; Fig. S6). The modeled frontier orbitals emphasize ground state-electron delocalization and localization effects due to the presence of [2F]BT acceptor motifs.

in Figures S3 (2nd heating and cooling scans) show characteristic phase transition behaviors on the heating scans at ca. 100 °C for SM1 and SM3, and 125 °C for SM2, indicating that the side-chain substitution pattern (SM1 vs. SM2) and the substitution with additional single-ring thiophenes (SM1 vs. SM3) impact the physical properties of the SM donors. The solidification transitions are observed from the cooling scans at ca. 55 °C for SM1 and SM3, and 75 °C for SM2. The relative ratio of alkyl side-chain vs. aromatic content in π -conjugated systems has been found to influence the occurrence of characteristic phase transitions in prior studies.^{49,56}

As shown in Figures 1b and S4-6, first-level density functional theory (DFT) calculations show that the DTP-[2F]BT SM donor structures are expected to be near-planar and their π -system well delocalized in the ground state (see HOMO of SM3 in Fig. 1b); DFT at the B3LYP/6-31G(d,p) level with Gaussian 09 (Revision C.01) (cf. details in SI). Here, we note that side chains were swapped for methyl groups to optimize computational time; acknowledging that the electronic properties and backbone geometry

of single isolated π -conjugated systems are appropriately described in gas phase calculations without additional constraints on the presence of fully developed alkyl side chains.⁵⁷⁻⁵⁸ The potential energy surfaces (PES) produced by rotation of the single-ring thiophene (T) and DTP motifs with respect to the [2F]BT acceptor unit are shown in Figure S4 (cf. details in SI; all geometric parameters were allowed to relax except for the fixed torsion angles), indicating that the most energetically favorable conformational pattern for the SM donors is achieved when the donor motifs adjacent to the [2F]BT acceptor unit have the sulfur heteroatoms point towards to fluorine substituents of [2F]BT. The corresponding T-[2F]BT-DTP segments are near-planar, with estimated dihedral angles of ca. 179.5° and 179.8° between [2F]BT, and T and DTP motifs, respectively. The significant energetic barriers of ca. 4-6 kcal mol⁻¹ (Fig. S4) on going from *anti* to *syn* conformations suggest that the SM donor main chains are expected to remain rather coplanar (*i.e.* “out-of-plane” conformations are unlikely); for comparison, RT(298 K) amounts to ca. 0.6 kcal mol⁻¹ and, in turn, energetic barriers of ca. 4-6 kcal mol⁻¹ are expected to prohibit inter-conversion between *syn* and *anti* conformers at room temperature. We note that planarization effects linked to the presence of fluorine substituents on the main chain have been discussed in several other studies.⁵⁹⁻⁶¹ Figure 1b emphasizes the conformation in which the fluorine moieties of [2F]BT are *syn* to the sulfur heteroatoms of adjacent thienyl motifs. From Figure S5, it is worth noting that the presence of β alkyl side-chain substituents in SM2 and SM3 induces only modest dihedral angle increments and, overall, Figures 1b and S6 show that the HOMO of all SM donors is well delocalized along the π -extended main chains. Some significant degree of localization on [2F]BT motifs occurs in the LUMO, and we note that significant quinoidal character is induced in DTP as the aromaticity of the thiadiazole moieties of the [2F]BT motifs competes with main-chain conjugation. In SM1-3, the HOMO→LUMO transitions are expected to possess substantial charge transfer character in light of the differences in localization patterns between HOMO and LUMO. DFT-estimated HOMO and LUMO energy levels, and HOMO-LUMO gaps are summarized in Table 1. The calculated HOMO energies in the range 4.65-4.75eV for SM1-3 are only slightly lower than the PESA-estimated IPs of ca. 5eV discussed earlier.

Device Testing and Characterizations

Thin-film BHJ solar cells with the direct device structure ITO/PEDOT:PSS/SM:PC₇₁BM/Ca/Al (device area: 0.1 cm²) were fabricated and tested under AM1.5G solar illumination (100 mW/cm²). The cells with optimized SM:PC₇₁BM blend ratios (1:1, wt/wt) were cast from chloroform (CHCl₃), resulting in active layer thicknesses in the range 85–95 nm; see detailed experimental section in the SI. Table 2 summarizes the figures of merit of optimized BHJ devices made from blends of SM1-3 and PC₇₁BM;

Table 1. Summary of Optical and Electronic Parameters for the DTP-[2F]BT SM Donors, SM1-3.

SM Donor	$\lambda_{\text{abs}}/\text{sol}$ (nm) (log ϵ)	$\lambda_{\text{abs}}/\text{film}$ (nm)	E_{opt}^a (eV)	IP ^b (eV)	EA ^c (eV)	HOMO ^d (eV)	LUMO ^d (eV)	HL _{gap} ^d (eV)
SM1	382,602 (5.18)	395,623,688	1.59	5.03	3.44	4.75	2.87	1.88
SM2	380,597 (5.20)	394,616,673	1.63	5.07	3.44	4.72	2.84	1.88
SM3	387,607 (5.34)	412,618,695	1.58	5.05	3.47	4.67	2.89	1.78

^aOptical bandgaps estimated from the onset of the UV-vis absorption spectra (films). ^bEstimated by photoelectron spectroscopy (PESA). ^cInferred from PESA-estimated IPs and E_{opt} values. ^dDFT-calculated HOMO and LUMO energy levels (absolute values), and HOMO→LUMO gaps (HL_{gap}); obtained at the B3LYP/6-31G(d,p) level.

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Figure 2. Characteristic *J-V* curves for “as-cast” and SVA-treated BHJ solar cells fabricated from (a) SM1, (b) SM2 and (c) SM3 (cast from CB, post-processing experimental details in Table 2); AM1.5G solar illumination (100 mW/cm²). EQE spectra of the devices fabricated from (d) SM1, (e) SM2 and (f) SM3 under optimized conditions. Integrated EQEs are in agreement (± 0.4 mA/cm²) with the *J*_{sc} values reported in Table 2.

Table 2. PV Performance of the DTP-[2F]BT SM Donors SM1-3 in Direct BHJ Devices with PC₇₁BM.^{a,b}

SM	SVA [s]	<i>J</i> _{sc} [mA cm ⁻²]	<i>V</i> _{oc} [V]	FF [%]	Avg. PCE [%]	Max. PCE [%]
SM1	0	8.0±0.1	0.75±0.01	38.5±0.3	2.31±0.02	2.52
SM1 ^c	30	8.8±0.1	0.72±0.01	39.5±0.9	2.48±0.09	2.64
SM1 ^d	5	8.8±0.2	0.74±0.01	39.2±1.1	2.55±0.15	2.71
SM2	0	6.9±0.1	0.85±0.03	31±0.3	1.83±0.04	1.89
SM2 ^c	40	10.9±0.1	0.81±0.01	55.2±0.3	4.85±0.07	4.96
SM2 ^d	5	10.8±0.2	0.80±0.02	60.5±0.2	5.19±0.22	5.28
SM3	0	9.8±0.2	0.74±0.03	41.4±1.0	3.0±0.15	3.22
SM3 ^c	10	12.4±0.2	0.65±0.01	61.3±0.9	4.91±0.07	5.05
SM3 ^d	3	12.8±0.6	0.67±0.03	62.1±0.8	5.72±0.07	5.84

^aDevices with optimized SM:PC₇₁BM ratio of 1:1 (wt/wt) solution-cast from chlorobenzene (CB). ^bAverage values calculated from >10 devices with standard deviation for the measurements, additional device statistics, are provided in the SI (Fig. S4). ^cSVA-treated with DCM, ^dSVA-treated with CS₂.

Tables S1-S4 in the SI provide optimization details (including device statistics) relative to the use of processing additive (1,8-diiodooctane, DIO) and post-processing solvent vapor annealing (SVA) treatments (DCM and CS₂). As discussed earlier in this report (cf. introduction section), the use of processing additives, post-processing thermal or SVA approaches can – *in some instances* – be determining steps in the optimization protocols of SM-fullerene blend morphologies, in turn significantly improving BHJ solar cell efficiencies. We note that, in general, achieving adequate interpenetrating networks and domain sizes in BHJ thin films with SM donors and PCBM tends to be more challenging than what is seen with polymer-based BHJ solar cells; morphological variations induced by additives, thermal annealing and SVA protocols can also result in reduced performance figures^{22,62} and the outcome of

those tentative optimization steps vary from one SM donor system to another.

As shown in Table 2, “as-cast” devices made from SM1 yield high short-circuit current densities (*J*_{sc}) of *ca.* 8.0 mA/cm², open-circuit voltages (*V*_{oc}) of 0.75 V, but modest fill-factor (*FF*) values of *ca.* 40%, resulting in only modest PCEs of up to 2.5% (max.). Interestingly, Tables 2, S1 and S2 show that additions of DIO in the blend solutions and SVA protocols have only negligible (or detrimental) effects on these figures of merit and, overall, all SM1-based BHJ device efficiencies remain limited by low *FF* values of less than 50%. In contrast, Table 2 shows that SVA-treated devices made from SM2 (analogous to SM1, but including additional branched alkyls symmetrically substituted on the main chain, see Chart 1) achieve PCEs of up to 5.3% (max.), appreciably higher

than those made with **SM1** (by *ca.* 2 $\times$). The optimization protocols by SVA using DCM and CS₂ are detailed in Table S3; while Table S1 indicates that the use of DIO is not conducive to the same level of PCE improvements, with only 3.9% (max.) reached when using 0.4% DIO (v/v). DCM and CS₂ have proven to be effective solvents for SVA protocols in several prior studies.^{25,34,54} Optimizations via SVA approaches rely on the relative solubility of the donor and acceptor components in the BHJ active layer, and SVA treatments with CS₂ impart solubility to both SM donor and PC₇₁BM.^{25,35} In brief, and while “*as-cast*” devices made from **SM2** yield modest

PCEs of less than 2% (Table 2), relatively short exposure times of 10–40 s for DCM and 3–10 s for CS₂ significantly improve the device J_{sc} and FF to values in ranges of *ca.* 10–11 mA/cm² and 45–60%, respectively. In particular, Table 2 shows that FF values of up to 61% can be obtained upon 5 s exposure to CS₂, yielding average PCEs of 5.2%, and suggesting that favorable morphological effects are occurring in the BHJ active layer. The shorter exposure times required to achieve high-performing, optimized BHJ devices with CS₂ compared to DCM may stem from the greater propensity of

Figure 3. GIXS patterns of (a) **SM1**, (b) **SM2** and (c) **SM3** in “*as-cast*” BHJ thin films prepared from CHCl₃ (no SVA), and GIXS patterns of SVA-treated BHJ thin films (CS₂ treatment as described in Table 2) with (d) **SM1**, (e) **SM2** and (f) **SM3** cast from CHCl₃.

CS₂ to diffuse across the active layer and solvate the donor and acceptor components. The slightly higher V_{oc} of 0.80 V obtained for optimized **SM2**-based BHJ devices (compared to 0.75 V with **SM1**) is in agreement with the PESA-estimated IP of **SM2** (*ca.* 5.07 eV), considering commonly reported EA values of 4.2–4.3 eV for PC₇₁BM. We note that slight IP and V_{oc} variations seemingly linked to distinct side-chain pattern effects have been observed in several other polymer and SM donor systems.^{63–64} Turning to **SM3** (analogous to **SM2**, but including additional single-ring thiophenes on the main chain, see Chart 1), “*as-cast*” devices achieve higher J_{sc} values than those of their counterparts made with **SM2** and **SM3** (*ca.* 10 mA/cm² vs. 7–8 mA/cm², respectively) and, as a result, slightly improved PCEs of 3.0% (avg.). As shown in Table 2, SVA-treated devices made from **SM3** afford PCEs of up to 5.8% (max.; exposure time: 3 s), with drastically increased J_{sc} (12.8 mA/cm²) and FF (62%) compared to the values obtained for **SM3**-based “*as-cast*” devices. The optimization protocols with DIO (Table S1), and by SVA using DCM and CS₂ (Table S4), show that SVA-treated devices with CS₂ can achieve concurrently high J_{sc} and FF values (*ca.* 11–13.5 mA/cm² and 61–65%, respectively) and, in turn, higher device PCEs compared with those treated with DCM (cf. solubility parameters for **SM1**–**3** in Table S5, and related discussions in the SI). Meanwhile, BHJ active layers cast from blend solutions containing DIO can yield up to 5% PCE, but generally do not combine high J_{sc} and FF . It is worth noting that higher PCEs can be reached with **SM3**-based BHJ solar cells, in spite of their slightly reduced V_{oc} of 0.70 V (compared to *ca.* 0.80 V with **SM2**).

The significantly higher J_{sc} values achieved with optimized (SVA-treated) **SM2**- and **SM3**-based BHJ solar cells compared to

those obtained with **SM1** (Fig. 2a–c) translate into larger external quantum efficiency (EQE) values across the UV-visible spectral range (Fig. 2d–f). In particular, optimized **SM3**-based devices (5.8% PCE) attain EQE values greater than those achieved with **SM1** by >15% across the range 350–700 nm (peaking at *ca.* 68%; reflecting an EQE increase of *ca.* 40%). Meanwhile the EQE responses of **SM1**-based devices remain under 55% across the same range, an observation consistent with the more modest J_{sc} values of 8–9 mA/cm² measured from the J - V plots (Fig. 2a). Integrated EQEs are in agreement (± 0.4 mA/cm²) with the J_{sc} values discussed above and reported in Table 2. Importantly, the determining role of SVA treatments in the optimization protocol of **SM2**- and **SM3**-based BHJ solar cells is also largely apparent from the EQE spectra, with notable increases in EQE suggesting that favorable morphological changes are occurring as the solvent vapors diffuse across the BHJ thin films. In Figure S7, the subtle changes in spectral absorption for optimized BHJ active layers subjected to SVA treatments are worth noting; including slight variations in relative peak intensities on the main absorption band pertaining to the SM donor contribution (Fig. S7b and S7c). These subtle changes could originate from local molecular reorganizations and/or improved nanostructural order (these effects will be discussed later in the report).

Significant differences in phase separation length scales between donor and acceptor components are known to impact BHJ solar cell efficiency.^{65–68} We examined the BHJ morphologies of “*as-cast*” and SVA-treated films of **SM1**–**3** (CS₂ treatment) by bright-field electron transmission microscopy (TEM); experimental protocol and TEM images are provided in the SI. Despite observable ramifi-

cations related to the processing conditions (contrast differences are linked to thickness variations), all thin film morphologies shown in Figure S8 appear relatively well mixed with donor- (bright) and acceptor-rich (dark) domains homogeneously distributed within sub-100 nm length scales. The prevalence of fine-scale morphologies in SVA-treated films (Fig. S8b, S8d and S8f) is also consistent with the high J_{sc} values outlined in Table 2 for SM1-3 (8–13.5 mA/cm²) and the EQE responses shown in Figure 2d–f. It is interesting to note that the ramifications observed, more pronounced for “*as-cast*” films, are somewhat mitigated after the post-processing SVA step.

As stated earlier, SVA treatments may induce subtle local molecular reorganizations and/or improved nanostructural order in BHJ thin films. To probe those effects, we turned to grazing incidence X-ray scattering (GIXS) analyses, comparing “*as-cast*” and SVA-treated BHJ thin films of SM1-3 with PC₇₁BM (CS₂ treatment); see experimental details in SI, neat films of SM1-3 are also shown in Figure S9. Examining the scattering patterns shown in Figure 3a–f, the relatively isotropic lamellar reflections in the q range 0.3–0.4 Å^{−1}, and the lack of higher-order lamellar reflections and π -stacking scattering intensities at larger q values (~ 1.7 Å^{−1}), indicate that aggregates formed in “*as-cast*” (Fig. 3a,b) and SVA-treated (Fig. 3d,e) BHJ thin films of SM1 and SM2 are misoriented and uncorrelated along the π -stacking direction; the absence of pronounced scattering intensity suggests only modest propensities to form SM donor aggregates in the presence of PC₇₁BM. In parallel, SVA-treated active layers with SM3 (Fig. 3f) show more anisotropy than SM1 and SM2-based films (Fig. 3a,b), and a higher scattering intensity for the lamellar reflection in the q_z axis direction (out-of-plane) compared to “*as-cast*” SM3-based active layers, indicating a more substantial extent of aggregation. In particular, we note that the higher-intensity lamellar reflection in SVA-treated SM3-based BHJ thin films points to an increase in structural ordering. These results show that the concurrent symmetrical substitution of branched alkyl side chains and the π -extension of the SM main-chain by addition of single-ring thiophenes impact the propensity of the DTP-[2F]BT SM donors to rearrange when subjected to post-processing SVA steps.

As local packing improves across the active layer, one may expect a correlated improvement in charge transport characteristics in the BHJ solar cells. To prove those effect, we measured the hole and electron mobilities of SM1-3 in “*as-cast*” and SVA-treated (CS₂) BHJ thin films (as per the conditions defined in Table 2); estimates inferred from the space charge limited current (SCLC) model (cf. details in SI). The dark current density-voltage characteristics of the BHJ active layers in hole-only diodes (ITO/MoO₃/SM:PC₇₁BM/MoO₃/Ag) are shown in Figure 4, and the carrier mobility estimates (electrons and holes) are detailed in Table S6 and S7; fits for various BHJ thicknesses provided in the SI (Fig. S10). These examinations indicate that hole mobilities tend to improve upon post-processing SVA steps, with particularly notable increases (by approx. one order of magnitude) in BHJ thin films made with SM2 and SM3. The zero-field hole mobility in SM2-based active layers increases from 3.2×10^{-6} cm² V^{−1} s^{−1} to 2.7×10^{-5} cm² V^{−1} s^{−1} upon SVA treatment with CS₂, and a comparably substantial increase from 1.2×10^{-5} cm² V^{−1} s^{−1} to 1.2×10^{-4} cm² V^{−1} s^{−1} is observed for CS₂-treated SM3-based active layers. In contrast, the zero-field hole mobility of *ca.* 1×10^{-4} cm² V^{−1} s^{−1} in SM1-based active layers remains relatively unchanged upon SVA treatment. As shown in Table 2, SM2 and SM3 are also the most responsive to SVA treatments in terms of BHJ solar cell performance. These

Figure 4. Experimental dark current densities as a function of effective electric field for hole-only diodes (ITO/MoO₃/SM:PC₇₁BM/MoO₃/Ag); here, $V_{bi} = 0$ (flat band pattern formed by MoO₃-MoO₃). Dark currents are reported for “*as-cast*” (circles) and SVA-treated devices (squares) made with BHJ active layers of similar thickness (indicated in the legends). The experimental data is fitted using the single-carrier SCLC model (solid lines; cf. details in the Supporting Information). Carrier mobilities obtained for various film thicknesses, including statistics, are given in Tables S6 and S7.

results further emphasize the determining role of molecular structure on the optimization protocols applied to DTP-[2F]BT SM donors. Our combined GIXS and SCLC analyses indicate that the effect of post-processing SVA steps on morphologies and BHJ solar cell performance is not independent of the molecular structure of the SM donors used in the BHJ solar cells. We also note that the extent and composition of the mixed SM-fullerene phase, and the relative composition and size of SM- and fullerene-rich domains in the BHJ thin films may influence carrier transport and mobility figures.^{54,69} While these detailed analyses are beyond the scope of this report, such examinations will be the topic of future, separate studies.

Conclusions

In summary, we have shown that dithieno[3,2-*b*:2',3'-*d'*]pyrrole-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (DTP-[2F]BT) SM donors (SM1-3) with distinct peripheral unit groups (including branched alkyls, and/or added unsubstituted thiophenes) yield different BHJ solar cell efficiency patterns with PC₇₁BM. Our concurrent GIXS and SCLC analyses indicate that adding branched alkyls and extending the main chain in DTP-[2F]BT impact the propensity of the SM donors to rearrange when subjected to post-processing SVA steps (using DCM, CS₂), improving local packing and nanostructural order in SM3-based BHJ thin films. In parallel, the more favorable carrier transport characteristics (hole and electron mobilities, carrier balance) of the BHJ active layers contribute to the high J_{sc} (12.8 mA/cm²) and *FF* (62%) achieved in optimized BHJ solar cells with SM3, which yield PCEs of *ca.* 6%. In contrast, its shorter counterpart SM1 lacking branched alkyls is not

prone to undergo the same favorable morphological changes on SVA treatments and achieves only modest BHJ device PCEs of *ca.* 2.5%. Our results indicate that the role of post-processing SVA steps is not independent of the molecular structure of the SM donors used in the BHJ solar cells. Low-bandgap DTP-[2F]BT SM donors ($E_{\text{opt}} \sim 1.6$ eV) are promising systems for use in the back cell of SM multi-junction solar cells with complementary absorbers.

Experimental Section

Material Characterizations. All compounds were characterized by NMR spectroscopy on Bruker Avance III Ultrashield Plus instruments using a 400, 500, 600 or 700 MHz proton frequency. High-resolution mass spectrometry (HRMS) data was recorded using a Thermo Scientific - LTQ Velos Orbitrap MS. Information on materials, synthetic methods and protocols for the syntheses of SM1-4 are detailed in the Supporting Information (SI). Further details on PESA, UV-vis, TGA, DSC, and solid-state NMR instrumentation and experimental conditions are developed in the SI.

Computational Analyses. All density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory with the Gaussian 09 (Revision C.01) software. B3LYP functional was chosen for the potential energy surface (PES) scans in order to maintain consistency with the small-molecule orbital density calculations. Additional details and references can be found in the SI.

Device Testing Protocols. The solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, $15 \Omega \text{ sq}^{-1}$) patterned on the surface (device area: 0.1 cm^2). Information on substrate preparation, active layer and contact depositions are detailed in the SI. Solar cell *J-V* measurements were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G, with a KG-5 silicon reference cell certified by Newport. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST. Additional details on various active layer deposition conditions, TEM instrumentation, and carrier mobility measurements are developed in the SI.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, characterization, and additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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