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Benzo[1,2-*b*:4,5-*b'*]dithiophene-Pyrido[3,4-*b*]pyrazine Small-Molecule Donors for Bulk Heterojunction Solar Cells

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Supporting Information Placeholder

ABSTRACT: We report on the synthesis, material properties and bulk heterojunction (BHJ) solar cell characteristics of a set of π -conjugated small-molecule (SM) donors composed of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and pyrido[3,4-*b*]pyrazine (PP) units – examining the perspectives of *alkyl-substituted PP acceptor motifs* in SM designs. In these systems (**SM1-4**), both the type of side chains derived from the PP motifs and the presence of ring-substituents on BDT critically impact (i) molecular packing, and (ii) thin-film morphologies and charge transport in BHJ solar cells. With the appropriate side-chain pattern, the ring-substituted analogue **SM4** stands out: achieving efficiencies of ca. 6.5% with PC₇₁BM, and fine-scale morphologies comparable to those obtained with some of the best-performing polymer donors in BHJ solar cells. ¹H-¹H DQ-SQ NMR analyses are used to examine the distinct self-assembly pattern of **SM4**, expected to factor into the development of the BHJ morphology.

Introduction

Recent studies have shown that solution-processable π -conjugated small-molecule (SM) donors used in bulk heterojunction (BHJ) solar cells with fullerene acceptors can rival their polymer donor counterparts, yielding device efficiencies >6%¹⁻⁴ and as high as ca. 10%.⁵ Compared to polymers, SM systems have a well-defined, finite conjugation length and molecular weight, and they can be purified via conventional chromatography or recycling HPLC/SEC techniques – clear benefits that minimize batch-to-batch variations and lessen scalability issues. In parallel, solution-processed SMs can achieve higher short-range and mesoscale ordering than polymers,⁶⁻⁹ and since BHJ active layers with high carrier mobilities can yield improved figures of merit (*i.e.* short-circuit current, J_{sc} and fill-factor, FF),¹⁰⁻¹² these correlated material properties make SMs particularly attractive on the path to raising the *practical efficiency limits* of organic photovoltaics (OPVs).

Some of the best-performing SM systems in BHJ solar cells with fullerene acceptors rely on donor-acceptor dithieno[3,2-*b*:2',3'-*d'*]silole-benzo[*c*][1,2,5]thiadiazole building motifs^{1,4} and oligothiophene sequences capped with relatively electron-withdrawing units, such as rhodanine.¹³⁻¹⁵ As with polymer donors, the types and sequences of donor and acceptor motifs used along the

SM backbone impact their optical, electronic (*e.g.* ionization potential, bandgap, π -electron delocalization and orbital overlap)^{14,16-17} and self-assembling properties in thin films,¹⁸⁻¹⁹ in turn resulting in distinct efficiency patterns in BHJ solar cells. In addition, the set of solubilizing side chains appended to the SM backbone must allow for adequate solution-processability and mitigated aggregation, while preserving favorable packing effects that help promote self-assembly, π - π stacking, and in turn charge transport across the BHJ active layers. In parallel, the solution-processing conditions (*e.g.* use of additives,^{1,2,20} nucleating agents,²¹ solvent type,^{1,11}) and post-processing treatments (*e.g.* thermal^{22,22-23} and solvent annealing²⁴⁻²⁵) used in the optimization of SM-based BHJ solar cell performance induces important morphological effects that set the device efficiency baseline and help leverage optimal figures of merit.^{7,19,26} However, it is critical to note that most SM systems do not readily achieve power conversion efficiencies (PCEs) >6%, even upon careful, systematic BHJ device optimizations,^{22,27-30} and the molecular structure of SMs remains the determining factor directing material performance and BHJ solar cell efficiency.

While benzo[*c*][1,2,5]thiadiazole and its nitrogen- or fluorine-substituted analogues have frequently been used as acceptor motifs in the design of low-bandgap SM donors, these units lack synthetic modularity and solubilizing side chains cannot be easily derived.³¹⁻³³ In contrast,

quinoxaline³⁴⁻³⁷ and pyrido[3,4-*b*]pyrazine (PP) motifs are more synthetically tunable and can be made with alkyl side-chain substituents that can contribute towards solubility, yet PP units have seen only limited use thus far. Following the first account of PP units used in polymers for electrochromic applications,³⁸ a few studies have turned to PP motifs (or analogues) in the design of donor-acceptor polymers for BHJ solar cells.³⁹⁻⁴² Among those, fused bibenzo[*a,c*]phenazine units copolymerized with indacenodithiophene,⁴³ and a phenyl-substituted analogue copolymerized with thiophene,³⁹ have led to polymer donors with promising PCEs in the range of 3-4% in BHJ devices with fullerene acceptors. PP-based π -conjugated systems have occasionally been considered for dye sensitized solar cell (DSSC)^{3,44-46} or two-photon absorption⁴⁷ studies, but PP motifs remain practically unexplored in SM designs for BHJ solar cells.

In this contribution, we report on the synthesis, properties and BHJ solar cell characteristics of a set of four benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM donors with alkyl-substituted bithiophene end groups (**SM1-4**, Chart 1). In these systems, BDT and PP motifs replace their dithieno[3,2-*b*:2',3'-*d*]silole and (N- or F-substituted) benzo[*c*][1,2,5]thiadiazole analogues commonly used in prior SM studies,¹⁻² but the general donor-acceptor sequence remains analogous for direct comparisons. Importantly, we show that both the type of side-chain substituents on the PP motifs and the presence of ring-substituents on the BDT critically impact (i) molecular packing, and (ii) thin-film morphologies and charge transport in BHJ solar cells made with **SM1-4** and phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the fullerene acceptor. While device PCEs remain <3% with **SM1-3**, optimized BHJ solar cells made with the ring-substituted (BDT(T)) counterpart **SM4** achieve up to ca. 6.5% PCE, and fine-scale thin-film morphologies that are comparable to those obtained with some of the best-performing polymer donors used together with PC₇₁BM.⁴⁸⁻⁵⁰ ¹H-¹H double quantum-single quantum (DQ-SQ) NMR analyses are used to examine the distinct self-assembly pattern of **SM4**, which can be expected to factor into the development of the BHJ morphology with PC₇₁BM. In comparison with the low-bandgap dithieno[3,2-*b*:2',3'-*d*]silole-benzo[*c*][1,2,5]thiadiazole (N- or F-substituted) SM analogues ($E_{\text{opt}} \sim 1.5$ eV), benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM donors are wider-bandgap ($E_{\text{opt}} \sim 1.9$ eV; similar to that of P3HT⁵¹⁻⁵²) and promising systems for use in the high-bandgap cell of SM multi-junction devices with complementary absorbers.

Results and Discussion

Design and Synthesis

The convergent synthetic route described in Scheme 1 shows how solubilizing side chain permutations are made possible across the set of SM donors, **SM1-4**. The 2,3-dialkylpyrido[3,4-*b*]pyrazine acceptor motifs were synthesized from the 4-amino-3-nitropyridine precursor (**1**). Near-quantitative reduction (97%) of **1** to the diamine intermediate **2**, followed by regioselective bromination (60%) yields to intermediate **3**, which is then cyclized by

Chart 1. Benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM Donors, **SM1-4.**

condensation with alkyl diones to form the PP motifs **4a/b** in relatively high yields (86% and 72%, respectively). Stannylation of the alkyl-substituted bithiophene end groups **5a/b** (ca. 90%) leads to the coupling partners **6a/b**, which are then engaged in a microwave-assisted Stille-type Pd cross-coupling reaction with the PP motifs **4a/b** in toluene (see details in the Supporting Information, SI), yielding the intermediate building blocks **7a-c** (50-60%) with distinct patterns of alkyl side-chain substituents. Importantly, the regioselectivity of the Pd-mediated coupling between **4a/b** and **6a/b** is directed by the nitrogen heteroatoms in the unsymmetrical PP motifs, in consistency with the directing effects of nitrogen and fluorine discussed in prior reports on the low-bandgap dithieno[3,2-*b*:2',3'-*d*]silole-benzo[*c*][1,2,5]thiadiazole SM analogues.¹ Lastly, intermediate building blocks **7a-c** were coupled with the BDT or BDT(T) motifs **8a/b** by microwave-assisted Pd cross-coupling, producing **SM1-4** in satisfying yields (60-80%) after sequential purifications via column chromatography and recycling SEC (see details in SI). The regiochemistry of the Stille coupling reaction between **4a/b** and **6a/b** was confirmed by 2D-NOESY spectroscopy analyses carried out on **SM1-4**; Figure S43-46 in the SI emphasizes the aromatic regions of the NOESY spectra where the appropriate correlations are observed.

Scheme 1. Syntheses of the SM Donors, SM1-4.

Figure 1. Representations of the HOMO and LUMO of **SM4** obtained by DFT at the B3LYP/6-31G(d,p) level of theory (see representation of **SM1-3** in SI; Fig. S1). The modeled frontier orbitals emphasize π -electron delocalization and localization effects across the SM donor.

First-level density functional theory (DFT) calculations show that the benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM donor structures are expected to be relatively planar and their π -system well delocalized in the ground state (see HOMO of **SM4** in Figure 1); DFT at the B3LYP/6-31G(d,p) level with Gaussian 09 (Revision C.01) (cf. details in SI). Although side chains play an important role in molecular self-assembly, it is commonly assumed that the electronic properties and backbone geometry of single isolated π -conjugated systems are well represented in gas phase calculations where side chains are swapped for methyl groups (to optimize computational time). From these calculations, we estimate dihedral angles of 15-16° between the BDT(T) and PP motifs; conformation in which the pyrazine moiety of PP is *syn* to the sulfur heteroatoms of adjacent thienyl motifs shown in Figure 1. The potential energy surfaces (PES) resulting from the rotation of the PP motifs with respect to BDT(T) and single-ring T units are represented in Figure S2 (cf. details in SI), showing that relative backbone planarity in **SM4** is achieved via statistical *syn* and *anti* conformations. The significant energetic barriers of ca. 3 kcal mol⁻¹ (Fig. S2a)

and 8 kcal mol⁻¹ (Fig. S2b) on going from *anti* to *syn* conformations parallels the idea that the backbone of **SM4** is expected to remain rather coplanar (*i.e.* disfavoring “out-of-plane” conformations); for reference, we note that *RT* at room temperature (298 K) is approximately 0.6 kcal mol⁻¹, and that the energetic barriers discussed above are expected to prohibit inter-conversion between *syn* and *anti* conformers at room temperature. While the HOMO of all systems was found to be well delocalized across the π -conjugated backbones, we note that some localization on PP motifs occurs in the LUMO (Figure 1), with significant quinoidal character induced across the structure as the aromaticity of the pyrazine moieties of the PP motifs competes with main chain conjugation. In these systems, the HOMO→LUMO transition is expected to possess at least partial charge transfer character because of the differences in localization patterns between HOMO and LUMO.

Material Properties

The solution and thin-film UV-vis absorption spectra of **SM1-4** are overlaid in Figure 2a-d. All four SM systems show comparable solution spectra, with near-equivalent molar absorptivity coefficients at their absorption peak: ca. 65400 L mol⁻¹ cm⁻¹ for **SM1**, ca. 61400 L mol⁻¹ cm⁻¹ for **SM2** and **SM3**, and ca. 58200 L mol⁻¹ cm⁻¹ for **SM4**. The absence of long-wavelength absorption shoulders in the solution spectra of all SM donors indicate that the molecules are not prone to π -aggregate formation at the concentration of this experiment (2 × 10⁻⁵ M). In thin films, the spectral absorption of all SMs shifts to longer wavelengths, with onsets shifting from ca. 615 nm in solution, to >650 nm in thin films (up to 685 nm for **SM3**). The spectral features of the main absorption band and the π -aggregation footprint visible at longer wavelengths mark the propensity of the SMs to self-assemble in thin films (molecular packing effects will be discussed further in the next sections). Expectedly, the optical bandgap (E_{opt}) values inferred from the onsets of thin-film absorption fall within the same range: 1.88 eV for **SM1**, 1.86 eV for **SM2**, 1.81 eV for **SM3**, and 1.87 eV for **SM4**. The ionization potentials (IPs) of **SM1-4** were determined via photoelectron spectroscopy in air (PESA): 5.02 eV for **SM1**, 5.09 eV for **SM2**, 5.05 eV for **SM3**, and 5.10 eV for **SM4**; expectedly

comparable IP values, slightly larger than the HOMO energy levels of ca. 4.7 eV inferred from our prior DFT calculations (predicted HOMO-LUMO gap of 2.2 eV).

Figure 2. Superimposed solution (given in molar absorptivity; dotted line) and thin-film (normalized; straight line) UV-Vis absorption spectra of (a) **SM1**, (b) **SM2**, (c) **SM3** and (d) **SM4**. Solution spectra for concentrations of 2×10^{-5} M in CHCl_3 .

The thermogravimetric analyses (TGA) given in Figure S3 show that the SM donors **SM1-3** are thermally stable in nitrogen atmosphere until ca. 300 °C (ca. 5% weight loss observed at 335 °C; ca. 17% weight loss at ca. 400 °C). The onset of decomposition of **SM1-3** can be assigned to the loss of the BDT alkoxy side chains, while the ring-substituted counterpart **SM4** involving BDT(T) motifs shows significantly improved thermal stability, with an onset of decomposition at ca. 400 °C (ca. 5% weight loss observed at 432 °C). The differential scanning calorimetry (DSC) analyses and polarized optical microscopy (POM) images shown in Figures 3, S4 and S5 show complex characteristic phase transition behaviors, with sharp melting transitions on the heating scans in a wide range of temperatures (197 °C for **SM1**, 234 °C for **SM2**, 173 °C for **SM3**, and 154 °C for **SM4**), indicating that the side-chain substitution patterns critically impact the physical properties of the SM donors. While the delayed crystallization transition of **SM4** is observed at 76 °C in Figure 3a, the solidification/crystallization transitions are not always obvious from the cooling scans (cf. details in SI, including 1st and 2nd cycles), despite our effort to carefully characterize those systems using various conditions and scan rates. Figures 3b-d show the transition from highly crystalline films of **SM4** to the isotropic melt state (the morphology depicted in Fig. 3c suggests that a mesophase may be achieved within range of the melting transition; cf. additional details in SI, including 1st and 2nd DSC cycles). In parallel, we note that **SM3** showed more apparent liquid-crystal characteristics (in the range 100-170 °C, cf. details in SI).

Figure 3. (a) Differential scanning calorimetry (DSC) trace of **SM4** measured at a scan rate of 10 K min^{-1} . The first heating (bottom, endo scan) and cooling (top, exo scan) cycle is shown; the SM sample was prepared under freeze-dry conditions (cf. details on the DSC analyses in SI). (b-d) Polarized optical microscopy (POM) images of **SM4** on going from highly crystalline films to the isotropic melt state (through apparent mesophase); analyses performed with crossed-polarizers: (b) rt. – 155 °C, (c) 156 – 159 °C, and (d) >160 °C.

Device Testing and Characterizations

Thin-film BHJ solar cells with the conventional device structure ITO/ MoO_3 /SM:PC₇₁BM/Ca/Al (device area: 0.1 cm^2) were fabricated and tested under AM1.5G solar illumination (100 mW/cm^2). The cells with optimized SM:PC₇₁BM blend ratios (1:1, wt/wt) were cast from chlorobenzene (CB) (cf. details in SI, film thicknesses in the range of 75-85 nm). As shown in Table 1 (device statistics provided in the SI, Table S2), “as-cast” devices made from **SM1** did not show any significant promise (Avg. PCE = 0.5%), yielding concurrently low J_{sc} (2.2 mA/cm^2) and FF (36%) values. In these devices, the V_{oc} of ca. 0.6 V is substantially lower than the expected figure of ca. 0.8 V based on the PESA-estimated IP of **SM1** (ca. 5.0 eV), suggesting serious morphological limitations in the bulk of the active layer and/or at the contact interfaces. Optimized devices made from blends containing 1% (v/v) of the processing additive 1,8-diiodooctane (DIO), showed improved V_{oc} (0.75 V) in better agreement with the IP of **SM1**, higher J_{sc} (6.7 mA/cm^2) and FF (42%), and reached PCEs of 2.5% (Max.). Small-molecule additives, such as DIO and 1-chloronaphthalene (CN), have been shown to improve the blend morphologies of SM-fullerene BHJ solar cells, and in turn device PCEs^{2,15} – although, we note that those improvements are not systematic and remain SM system-dependent. Considering solubility limitations and excess aggregation as possible grounds for the low efficiencies measured with **SM1**, we turned to the **SM2** counterpart with branched 2-ethylhexyl-substituted bi-thiophene end groups (as opposed to linear *n*-hexyl). However, as shown in Table 1, optimized BHJ devices made with the slightly more soluble derivative **SM2** did not outperform those made with **SM1**, yielding reduced

Table 1. PV Performance of the SM Donors SM1-4 in Direct BHJ Devices with PC₇₁BM.^{a,b}

SM	DIO %(v/v)	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	Avg. PCE [%]	Max. PCE [%]
SM1	0	2.2	0.62	36	0.5	0.7
SM1 ^c	1.0	6.7	0.75	42	2.1	2.5
SM2	0	1.6	0.65	33	0.3	0.5
SM2 ^c	0.5	3.6	0.71	37	0.9	1.0
SM3	0	2.1	0.66	36	0.5	0.7
SM3 ^c	0.5	5.7	0.81	49	2.3	2.5
SM4	0	7.0	0.95	36	2.4	2.6
SM4 ^c	0.2	10.5	0.90	67	6.3	6.5

^aDevices with optimized SM:PC₇₁BM ratio of 1:1 (wt/wt) solution-cast from chlorobenzene (CB). ^bAdditional device statistics, including standard deviations, are provided in the SI (Fig. S4). ^cOptimized device conditions.

J_{sc} (3.6 mA/cm²), FF (37%) and PCEs of 1.0% (Max.). Swapping linear side chains⁵³⁻⁵⁵ for branched ones to impart more solubility influences molecular packing and can sometimes be detrimental to material performance. In an alternative effort to impart greater solubility to the SM donors, in **SM3**, the ethyl side chains on the PP motifs were swapped for the longer *n*-butyl substituents. As shown in Table 1, optimized BHJ devices made with **SM3** showed significantly improved V_{oc} (0.81 V) and FF (49%), yet modest J_{sc} (5.7 mA/cm²) and, in turn, PCEs of 2.5% (Max.) equivalent to those achievable with **SM1**. The BHJ morphologies of “as-cast” and optimized devices made from **SM3** were inspected by bright-field electron transmission microscopy (TEM; cf. details in SI). Significant differences in phase separation patterns are known to impact SM-fullerene BHJ solar cell performance.⁵⁶⁻⁵⁷ Here, the TEM images in Figure 5a and 5b show a net degree of phase separation on ca. 100 nm (Avg.) length scales (especially pronounced in “as-cast” devices). In bright-field TEM, the darker areas are attributed to the fullerene-rich regions, here interconnected via a network of SM-rich boundaries. The coarse phase separation seen in the “as-cast” blend films of **SM3** and PC₇₁BM is likely to limit the efficiency of exciton diffusion to the SM-fullerene interfaces, in turn yielding low device photocurrents and poor BHJ solar cell efficiencies. While the use of 0.5% DIO (v/v) appears to mitigate the phase-segregated pattern in optimized BHJ devices, distinct SM- and PC₇₁BM-rich domains subsist, and the J_{sc} (5.7 mA/cm²) and PCEs (Max. 2.5%) remain modest.

Our effort to further improve SM solubility and miscibility between our benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM donors and PC₇₁BM led to **SM4**, in which the central BDT unit bears alkyl-derived ring substituents (referred to earlier as BDT(T) motifs). In recent work, we showed that ring-substituted BDTs can help mediate the development of the BHJ morphologies between polymer donors and fullerene acceptors in BHJ solar cells.⁵⁸ Turning to **SM4**, Table 1 shows that “as-cast”

Figure 4. (a) Characteristic J - V curves of optimized BHJ solar cells fabricated from **SM1-4** (cast from CB, processing conditions detailed in Table 1); AM1.5G solar illumination (100 mW/cm²). (b) EQE spectra of the devices fabricated from **SM1-4** under optimized conditions. Integrated EQEs are in agreement (± 0.4 mA/cm²) with the J_{sc} values reported in Table 1.

Figure 5. Bright-field TEM images of the BHJ thin-film morphologies of **SM3** and **SM4**. (a) **SM3** cast from CB, no DIO additive; (b) **SM3** cast from CB, 0.5% DIO (v/v); (c) **SM4** cast from CB, no DIO; (d) **SM4** cast from CB, 0.2% DIO (v/v).

BHJ solar cells achieve significantly higher PCEs of 2.4% (Avg.) compared to **SM1-3**-based “as-cast” devices, combining a large V_{oc} of 0.95 V in agreement with the PESA-estimated IP of **SM4** (ca. 5.1 eV), and an increase of over three-fold in J_{sc} (7.0 mA/cm²). Here, devices made with

DIO (0.2%, v/v) achieved PCEs of up to ca. 6.5% (Max.), correlated to a net increase in J_{sc} (10.5 mA/cm²) and FF (ca. 67%). The high J_{sc} values achieved with **SM4**-based BHJ solar cells (Fig. 4a) are consistent with the external quantum efficiency (EQE) spectra (Fig. 4b); with **SM4**-based devices showing EQE values higher by >20% in the range 350-600 nm (peaking at 70%), while the EQE responses of **SM1-3**-based devices remains under 50% in the same range, in agreement with the modest J_{sc} values of 3.6-6.7 mA/cm² estimated from the J - V plots (Fig. 4a). Integrated EQEs are in agreement (± 0.4 mA/cm²) with the J_{sc} values reported in Table 1. The BHJ morphologies of “as-cast” and optimized devices made from **SM4** were inspected by bright-field TEM and compared to those obtained for **SM3**-based devices; TEM images shown in Figure 5c and 5d. Here, the thin-film morphologies of

SM4-based devices are well mixed compared to those discussed earlier for **SM3**, indicating that the ring-substituted BDT(T) motifs play a critical role in mediating the development of the BHJ morphologies. These observations are in agreement with the high J_{SC} values achieved with **SM4**-based devices (Table 1 and Fig. 4a), and the near-complete photoluminescence (PL) quenching of the **SM4** analogue in the presence of PC₇₁BM (quenching efficiency of ca. 99.2%; Fig. S9) – indicating that morphological aspects are not limiting the diffusion of photogenerated excitons to the SM- and PC₇₁BM-rich domain interfaces.

Important morphological differences between BHJ thin films often correlate with distinct charge transport patterns, impacting the figures of merit of OPV devices.^{53,59} To probe carrier effects, we measured the hole mobilities of **SM3** and **SM4** in optimized BHJ thin films; values inferred from the space charge limited current (SCLC) model (cf. details in SI). Figure 6 shows the dark current densities of the optimized BHJ thin films in hole-only diodes (ITO/MoO₃/SM:PC₇₁BM/MoO₃/Ag) as a function of applied effective field (fits for various BHJ thicknesses in Fig. S10). Our analyses indicate that the zero-field hole mobilities of **SM4**-based BHJs are one order of magnitude larger than those of the **SM3**-based counterparts: $1.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. $1.5 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively; results consistent with the marked PCE differences in **SM4**- and **SM3**-based optimized BHJ solar cells: 6.3% (Avg.; Max. 6.5%) vs. 2.3% (Avg.; Max. 2.5%).

Figure 6. Dark J - V curves for hole-only diodes made with optimized BHJ thin films with **SM3** (square) and **SM4** (circle) as SM donors; diode configuration: ITO/MoO₃/SM:PC₇₁BM/MoO₃/Ag (film thickness: 80 nm). Data obtained for different film thicknesses are provided in SI (Fig. S10). The experimental data is fitted using the single-carrier SCLC model (solid lines; cf. details in SI).

Beyond morphological considerations, charge transport also critically depends on how π -conjugated SM systems self-assemble and pack in thin films.⁶⁰ In parallel, packing effects can factor into the development of the BHJ morphology. To examine those effects and determine if BDT(T) motifs in **SM4** affect molecular packing, we turned to ¹H-¹H double quantum-single quantum (DQ-SQ) solid-state NMR analyses (cf. details in SI). The

Figure 7. ¹H-¹H DQ-SQ NMR spectra of the SM donors (a) **SM3** and (b) **SM4**; samples prepared from thin films (cf. details in SI). The color-coded assignment of the protons in the chemical structures of the SM donors is shown in insets. The red contours depict the same spectra recorded at an intensity level that is one-step lower than that used for the black contours; lower intensity levels correlating with lower proton-proton interactions. The arrows near the markers indicate key differences between the spectra (detailed in the manuscript text).

correlations produced by these experiments reflect the spatial connectivity of locally proximate (<4 Å) protons, which provides important insights into the molecular packing within π -conjugated stacks.⁵⁰ Figure 7 shows the ¹H-¹H DQ-SQ NMR spectra of **SM3** and **SM4**; the color-coded assignment of the protons in the chemical structures of the SM donors is shown in insets. As shown in the single quantum axes, peaks from the SM backbones are relatively well resolved while the alkyl chains (labelled black) on the different motifs merge into a single broad

peak. Expectedly, the ^1H peak of the PP motif (labeled blue) shows as the most downfield chemical shift in both SM spectra. Since the PP protons are distant by $>4\text{\AA}$ from their direct (intramolecular) neighbors in adjacent PP motifs, any double quantum signal on the plot diagonal at that chemical shift indicates the presence of an intermolecular interaction with a cofacially packed SM neighbor. As shown in Figure 7a, the PP proton in **SM3** shows a stronger correlation with the side-chain protons (black-blue; emphasized by arrows) and a weaker correlation with backbone-appended protons (indicated by the blue dotted circle). In contrast, as shown in Figure 7b, the PP proton in **SM4** shows a significantly more pronounced correlation with backbone-appended protons (blue-green, blue-blue; emphasized by arrows), and a weaker correlation with the side chain protons (indicated by the black dotted circle). In parallel, we note that ^1H - ^1H intermolecular backbone interactions in **SM4** are comparatively more prominent than in **SM3** (cf. details in Fig. 7 caption), suggesting close packing driven by π - π interactions in thin films of **SM4**. These differences in molecular packing patterns between **SM3** and **SM4** are schematically illustrated in Figure 8.

Figure 8. Schematic representation of the variations in molecular packing inferred from the ^1H - ^1H DQ-SQ NMR spectra of **SM3** and **SM4**; subset (a) shows the general structure of the SM donors. Subset (b) depicts the lesser backbone-correlated extent of packing in **SM3**-based thin films, and subset (c) emphasizes the close molecular packing in **SM4**-based thin films.

Overall, these analyses indicate that **SM3** and **SM4** adopt distinct self-assembly patterns, implying that BDT(T) motifs in **SM4** impact molecular packing. The distinct self-assembly patterns and packing effects in **SM3** and **SM4** can be expected to contribute to the BHJ morphology and charge transport differences discussed earlier. Lastly, we note that the extent and composition of the mixed SM-fullerene phase in SM-based BHJs can be considered as a morphological effect,⁶²⁻⁶⁴ and may also affect

the J_{SC} and FF values of the optimized devices, however these detailed analyses are beyond the scope of this study.

Conclusions

In summary, we have shown that in benzo[1,2-*b*:4,5-*b'*]dithiophene-pyrido[3,4-*b*]pyrazine SM donors (**SM1-4**), ring-substituted BDT(T) core units are critical to achieving efficient material and BHJ solar cell characteristics. While practically unexplored in SM designs, *alkyl-substituted PP acceptor motifs* can contribute to improving SM solubility and film-forming properties. In these systems, the pattern of substituents appended to the π -conjugated main chain critically impacts (i) molecular packing, and (ii) thin-film morphologies and charge transport in BHJ solar cells. We found that, with the appropriate side-chain pattern, the ring-substituted analogue **SM4** stands out: achieving efficiencies of ca. 6.5% with PC₇₁BM, and fine-scale morphologies comparable to those obtained with some of the best-performing polymer donors in BHJ solar cells. ^1H - ^1H DQ-SQ NMR analyses show a distinct self-assembly pattern for **SM4**, expected to factor into the development of the BHJ morphology.

In parallel, we note that – in comparison with the low-bandgap dithieno[3,2-*b*:2',3'-*d'*]silole-benzo[*c*][1,2,5]thiadiazole (N- or F-substituted) SM analogues ($E_{\text{opt}} \sim 1.5$ eV) – benzo[1,2-*b*:4,5-*b'*]di-thiophene-pyrido[3,4-*b*]pyrazine SM donors are wider-bandgap ($E_{\text{opt}} \sim 1.9$ eV; similar to that of P3HT) and promising systems for use in the high-bandgap 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: $0.1\ \text{cm}^2$). 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 and PL instrumentation, and carrier mobility measurements are developed in the SI.

ASSOCIATED CONTENT

Supporting Information

Detailed 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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