2D Outer Side Chain-Incorporated Y Acceptors for Highly Efficient Organic Solar Cells with Nonhalogenated Solvent and Annealing-Free Process

Jin Su Park, Cheng Sun, Yunghee Han, Geon-U Kim, Tan Ngoc-Lan Phan, Yun-Hi Kim,* and Bumjoon J. Kim*

To fabricate high-performance organic solar cells (OSCs) by green solvent processing, it is essential to control the aggregation behavior and processability of constituent small-molecule acceptors (SMAs). Herein, a series of SMAs (A1–A4) with enhanced aggregation behavior and processability is developed by replacing the linear alkyl outer side chains of BTP-eC9 with 2D functional groups. The PM6:A1 SMA blend exhibits appropriate crystallinity, favorable blend morphology, superior electrical properties, and affords an OSC with a high power conversion efficiency (PCE) of 16.8%. Importantly, the OSC is fabricated using a nonhalogenated solvent (ortho-xylene), annealing-free process. In contrast, the reference PM6:BTP-eC9-based OSC exhibits a lower PCE of 15.3%. Structural analyses reveal that the 2D outer side chains of A1 induce steric hindrance between its dithienothiophen[3,2-b]-pyrrolobenzothiadiazole (BTP) core and the 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile end groups, optimizing its molecular planarity and aggregation property. It is further found that the SMAs with chlorinated IC end groups afford OSCs with higher PCEs than SMAs with fluorinated end groups.

1. Introduction

Abundant spotlights of organic solar cells (OSCs) have been witnessed due to the development of small-molecule acceptors (SMAs) featuring strong light-absorption ability, suppressed energy loss, and excellent electrical properties.\[1] OSCs with power conversion efficiencies (PCEs) approaching 19% have been accomplished, ascribed to the development of Y-series SMAs based on the A-DA’D-A motif through the structural modification of their cores, electron-withdrawing end groups, and side chains extending from their fused backbones.\[2] The end-group halogenation of SMAs has been proven to be a facile strategy for fine tuning their crystallinity, thereby improving the performance of OSCs, as demonstrated by OSCs featuring different fluoride- or chlorine-containing SMAs.\[1c,1d,2d] However, to achieve optimal blend morphology and solubility, OSC active layers based on these Y-series SMAs are fabricated with toxic solvents containing chlorine atoms (i.e., chloroform [CF] or chlorobenzene [CB]), which are known to be extremely hazardous to the environment and humans.\[3] These processing conditions severely limit the commercial viability of OSCs, necessitating the development of similar high-performance materials that are processable using eco-friendly solvents. OSCs fabricated with nonhalogenated solvents show significantly lower photovoltaic performances, due to the poor processability of the active materials in the nonhalogenated solvents. This often prevents polymer donors from forming an appropriate aggregation structure in the solution, which is important for generating the crystalline network of the polymers in the blend. Accordingly, different polymer designs have been developed to improve the processability during OSC fabrication with halogen-free solvents.\[4]

Meanwhile, it is also reasonable to further explore the structural modification of Y-series SMAs to improve their processability in halogen-free solvents, without sacrificing the superior PCE of resulting OSCs.\[5] Side chain engineering of the SMAs can significantly tune their aggregation behavior, processability, and morphological properties.\[6] In particular, structural modification of the outer side chain pair attached at the thiieno[3,2-b]thiophene structures of the dithienothiophen[3,2-b]-pyrrolobenzothiadiazole (BTP)-based Y acceptor core provides an effective way to tailor their conformation, solution aggregation, and crystalline structures in the thin film. This strategy is feasible because the outer side chains of Y acceptors strongly affect the torsional angle between their core units and 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (IC)-based end groups. Therefore, outer side chain engineering...
can effectively tune the aggregation property of SMAs in the solution, as well as the relevant photovoltaic/electrical properties of the active layers. For example, the outer side chain engineering of SMAs, exemplified by Y-type derivatives of Y18, BTP-eC9, and L8-BO, has led to OSCs with improved PCE.\[2d,6a,6b\] Recently, our group investigated the influence of the 1D outer side chain length on the processability of YSe-based SMAs.\[6c\]

Studies on the influence of bulkier 2D side chains have been recently performed.\[2b,2e,2i,7\] The 2D outer side chains are more likely to induce stronger steric hindrance along with the molecular structure compared with 1D side chains. Hence, they can more significantly control the aggregation properties and crystallinity, affecting the processability and device performance.\[8\] In particular, Yan et al. developed a Y6-based SMA series where the outer side chains of Y6 were replaced with n-undecyl (BTP-C11), 5-octylthienyl (BTP-Th), and 4-hexylphenyl (BTP-Ph).\[7d\] As the thioephene and benzene units at the outer positions induced significant steric hindrance, the crystallinity of the SMA series was decreased in the order of BTP-C11, BTP-Th, and BTP-Ph. An OSC featuring the PTQ10:BTP-Ph:BTP-Th ternary system achieved a high PCE of 17.6% using CF as processing solvent. In addition, the molecular planarity and intramolecular interaction of the SMAs can be precisely controlled by halogenation.\[7c,9\]

For example, He et al. prepared SMAs featuring thiienyl or chlorothienyl outer side chains and compared their 3D network structures.\[9c,9d\] The OSCs based on BTIC-4Cl-TCl-φ SMA achieved PCE of 15.7% owing to efficient electron transfer via the quasi-3D network formed by densely packed SMA molecules. Despite the effectiveness of 2D outer side chains of Y acceptors in manipulating molecular planarity and intramolecular interaction, to the best of our knowledge, the processing of these SMAs using nonhalogenated solvents has not been explored. In addition, it is important to elucidate the relationship between the structural properties of the SMAs, their processability, and OSC performance using nonhalogenated solvent process.

Herein, we design a series of SMAs based on the framework of representative Y-type SMA, BTP-eC9, by replacing its linear alkyl outer side chains with 2D-conjugated alkylthienyl groups to control the molecular rigidity of the SMA.\[28\] Accordingly, two functional groups, that is, 5-hexylthienyl-2-yl or 3-chloro-5-hexylthienyl-2-yl, are incorporated as outer side chains to produce 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (A1) and 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(3-chloro-5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (A2) acceptors, respectively. In addition, to understand the role of end group halogenations, we prepare 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (IC-Cl) and 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(3-chloro-5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (IC) and 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(3-chloro-5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (IC) and 2.2’-(12,13-bis(2-butyloctyl)-3,9-bis(3-chloro-5-hexylthien-2-yl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c:4,5]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]bipyridine[1,2,3-c]-dimalononitrile (IC).}

2. Results and Discussion

The chemical structures of the BTP-eC9-based SMAs developed in this study and earlier studies are shown in Figure 1. In this study, a representative Y acceptor, BTP-eC9, was structurally modified to produce a series of SMAs and investigate the effect of these structural modifications on its aggregation behavior and processability using nonhalogenated solvents. The linear n-undecyl outer side chains of BTP-eC9 were replaced with 2D hexylthienyl groups to obtain the first SMA in the series (A1), which resulted in more sterically hindered molecular backbone. The subsequent substitution of the H atoms at the β-positions of the thiienyl groups with Cl atoms, to tune the degree of the steric hindrance of A1, produced the second SMA in the series (A2). To investigate the role of end group halogen atoms, the Cl atoms attached to the IC end groups of A1 and A2 were substituted with F atoms to obtain the third and fourth SMAs in the series (A3 and A4, respectively). (Scheme S1, Supporting Information). The chemical structures were confirmed as shown in Figure S1–S5, Supporting Information. For convenience, BTP-eC9 and the four engineered SMAs are categorized into two groups: BTP-eC9, A1, and A2 are IC-Cl SMAs and A3 and A4 are IC-F SMAs.

The material properties of the synthesized SMAs were characterized. The thermal degradation temperatures (Tds) of the SMAs were determined by thermogravimetric analysis. The Tds of the IC-Cl SMAs are slightly higher (317–325 °C) than those of the IC-F SMAs (303–307 °C) (Figure S6, Supporting Information). Solubilities, optical, and electrochemical properties of the investigated materials are presented in Table 1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the materials were measured by cyclic voltammetry (Figure S7, Supporting Information). As shown in Figure 2a, the energy levels of all the SMAs align appropriately with those of PM6 to facilitate charge transfer. The LUMO energy level of A1 (−3.93 eV) is slightly upshifted from that of BTP-eC9, because hexylthienyl chains are stronger electron-donating units than hexyl chains.
The presence of Cl atoms on the outer side chains of A2 accounts for its comparatively lower LUMO energy level of $-4.14$ eV. The LUMO energy levels of A3 and A4 of $-3.90$ and $-4.07$ eV, respectively, are higher than those of their IC-Cl counterparts. The comparatively low LUMO energy levels of the IC-Cl SMAs indicate that the empty $3d$ orbitals of Cl atoms endow them with stronger electron-withdrawing ability.\[9a,9b\]

The UV–vis absorption spectra of the SMA solutions and films were investigated. To prevent any difference in solubility from affecting the results, CF was used as the solvent. Compared with BTP-eC9, A1, and A2 solutions, where the absorption maxima are centered at 746–747 nm, the absorption spectra of A3 and A4 solutions, centered at 731–732 nm, are slightly blueshifted (Figure S8, Supporting Information). All the solutions of A1–A4 with 2D outer side chains show significantly intensified absorption peaks located at 600–610 nm compared with that of BTP-eC9. The increased peak intensities observed from the A1–A4 solutions are attributed to the extended conjugation toward the thienyl outer side chains.\[7d\] The

![Figure 1. Molecular structures of BTP-eC9-based SMAs featured in this study and previous studies.](image-url)
peaks in the absorption spectra of SMA films are blueshifted by 70–80 nm with respect to the peaks in the absorption spectra of corresponding solutions (Figure 2b). As the preaggregation properties of the solutions are partly transferred to the films during the spin-coating process, the trends observed in the UV–vis absorbance of the SMA films are similar to those observed from the solutions. For example, absorption spectra of A1–A4 films display stronger shoulder peaks than those of BTP-eC9 in the range of 500–700 nm, owing to the abovementioned extended conjugation of the A1–A4 SMAs, where the backbone of A4 is more planar than that of A3 but its outer side chains are more twisted than those of A3. A similar trend is observed in the IC-F SMAs, where the backbone of A4 is more planar than that of A3 but its outer side chains are more twisted than those of A3.

Table 1. Solubilities, optical, and electrochemical properties of PM6 polymer donor, BTP-eC9, and A1–A4 SMAs used in this study.

| Material | Solubility in XY [mg mL⁻¹] | λmax, solution [nm] | λmax, film [nm] | εmax, film [×10⁴ cm⁻¹] | E_HOMO [eV] | E_LUMO [eV] |
|----------|---------------------------|---------------------|----------------|---------------------|----------|----------|
| PM6      | –                         | 580, 612            | 575, 606       | 6.5                 | -5.40    | -3.47    |
| BTP-eC9  | 8                         | 746                 | 820            | 11.3                | -5.57    | -3.99    |
| A1       | 51                        | 747                 | 823            | 9.9                 | -5.59    | -3.93    |
| A2       | 79                        | 746                 | 823            | 8.6                 | -5.74    | -4.14    |
| A3       | 47                        | 732                 | 809            | 9.2                 | -5.57    | -3.90    |
| A4       | 78                        | 731                 | 807            | 8.8                 | -5.73    | -4.07    |

a) Measured at room temperature; b) Determined from the UV–vis absorption onset of each thin film; c) Determined from corresponding CV curves.

To elucidate the effects of the 2D outer side chains on the structural conformations of the SMAs, computational simulations based on the DFT calculations were performed using B3LYP/6-31G* method. Three parameters were investigated to evaluate the molecular planarity of the SMAs: 1) the dihedral angle between the BTP core and IC groups (θ₁), 2) the dihedral angle between the BTP core and outer side chains (θ₂), and 3) the distance between the BTP core and outer side chains (D). The calculated parameters summarized in Table S1 (Supporting Information) are average values of the relevant positions. Figure 3 shows the molecular geometries of the IC-Cl SMAs estimated by DFT calculations. BTP-eC9 has an extremely planar backbone with the smallest θ₁ of 1.0° and D of 2.92 Å. Owing to its bulkier hexylthienyl side chains, the θ₁ and D of A1 are larger (8.3° and 3.06 Å, respectively), reducing molecular planarity. Owing to the Cl atoms on the 2D outer side chains of A2, the degree of distortion between its BTP core and outer side chains is increased. Consequently, the θ₁ of A2 (67.8°) significantly exceeds that of A1 (44.3°). Similarly, the D of A2 (3.88 Å) exceeds that of A1 (3.06 Å). Although the θ₁ of A2 (3.1°) is lower than that of A1 (8.3°), the difference in the angles is relatively small. Thus, the degree of steric hindrance increases in the order of BTP-eC9, A1, and A2, where the steric hindrance mainly originates from the outer side chains. A similar trend is observed in the IC-F SMAs, where the backbone of A4 is more planar than that of A3 but its outer side chains are more twisted than those of A3.

The crystalline properties of the SMAs in thin films were investigated by grazing-incidence X-ray scattering (GIXS) measurements. SMA thin film samples were spin-coated from the CF solutions and subsequently annealed at 150 °C for 30 min. The 2D GIXS patterns and the linecut profiles in the in-plane (IP) and the out-of-plane (OOP) directions of the SMAs and the PM6 polymer donor are depicted in Figure S10–11 (Supporting Information). The results of GIXS analysis of PM6 are consistent with those of previous studies. The OOP linecut profiles of all five SMAs exhibit distinct π–π stacking peaks, suggesting predominant face-on molecular orientations in the pristine films. Among the SMAs, BTP-eC9 has the shortest π–π stacking distance (d_{π-π} = 2π/λ) of 3.57 Å, which indicates the densest molecular packing (Table S2, Supporting Information). In comparison, A1–A4 SMAs possess larger d_{π-π}s in the range of...
3.65–3.70 Å. The degree of crystallinity of each SMA was evaluated in terms of its crystal coherence length ($L_c$), calculated using the Scherrer equation. BTP-eC9 exhibits the strongest crystallinity with an $L_c$ of 26.2 Å. Among the SMAs with 2D outer side chains, A1 has relatively strong crystallinity with an $L_c$ of 21.7 Å compared with A2 ($L_c = 19.5$ Å), A3 ($L_c = 19.8$ Å), and A4 ($L_c = 17.9$ Å). The trend in crystallinity of the pristine SMA films agrees with that observed in their electron mobilities ($\mu_e$), determined using the space-charge-limited current (SCLC) method (Table S3, Supporting Information). BTP-eC9 exhibits the highest $\mu_e$ of 7.0 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ owing to its strong crystallinity. A1 and A3, containing hexylthienyl outer side chains, exhibit slightly lower $\mu_e$ values of 4.8 $\times$ $10^{-4}$ and 4.3 $\times$ $10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. A2 and A4 exhibit order lower $\mu_e$s of 6.4 $\times$ $10^{-5}$ and 8.9 $\times$ $10^{-5}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, due to their chlorinated hexylthienyl outer side chains. Overall, these trends correlate well with those observed in the optical properties and structural conformations of the SMAs and confirm that the 2D outer side chains of the SMAs effectively control their molecular planarity and crystallinity.

To investigate the photovoltaic properties of PM6:SMA-based OSCs, conventional OSC devices with an architecture of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/poly(3,7-bis[2-ethylhexyl-1,2,3,6,7,8-hexahydro-1,3,6,8-tetraoxobenzol[n]phenanthrolin-4,9-diyl]-2,5-thiophenediyl][9,9-bis[3'((N,N-dimethyl)-N-ethylammonium)]-propyl]-9H-fluorene-2,7-diyl]-2,5-thiophenediyl] (F3N-Br)/Ag were fabricated. PM6 was employed as a donor material in the active layers. XY, a well-known, nonhalogenated solvent for organic conducting materials, was selected as the processing solvent since its high boiling point (i.e., 144 °C) could provide a sufficient interval for obtaining desirable film morphologies during the spin-coating process. The device fabrication processes are detailed in the Experimental Section (Supporting Information). The A1–A4 blends dissolve easily in XY, whereas the BTP-eC9 blend dissolves only at high temperatures above 80 °C (Figure S12, Supporting Information). Specifically, the PM6:BTP-eC9-based OSCs processed using XY at temperatures below 60 °C exhibit very poor photovoltaic performance owing to the formation of large aggregates on the active layer surfaces. These aggregates do not form when the processing temperature is higher than 80 °C. Accordingly, the performance of PM6:BTP-eC9 OSCs strongly depends on their processing temperature, and the PM6:BTP-eC9 OSC achieving the highest PCE of 15.3% is processed at 80 °C (Table S4, Supporting Information). In contrast, all the A1–A4-based OSCs are processable using XY over a wide temperature range and show negligible variations in device performance.

Figure 3. Molecular structures of BTP-eC9, A1, A2, A3, and A4 simulated based on DFT calculations using the B3LYP/6-31G* method.
The optimized device performances of XY-processed OSCs are described in Figure 4 and Table 2. The PM6:A1 OSC shows the highest PCE of 16.8% with an open-circuit voltage \( V_{oc} \), a short-circuit current density \( J_{sc} \), and a fill factor (FF) of 0.86 V, 24.5 mA cm\(^{-2}\) and 76.5%, respectively. The high PCE of the PM6:A1 OSC is mainly attributed to its high \( J_{sc} \) and FF. While the A3-based OSC achieves a comparable PCE of 15.7%, the PCEs of the A2- and A4-based devices are considerably lower, that is, 13.9% and 13.1%, respectively. It is noted that the optimized PM6:A1 OSC is fabricated using a simple spin-coating process at 60 °C. To investigate the effect of processing solvent on the device performance, we also prepared the OSCs using CF as the processing solvent (Table S5, Supporting Information). The BTP-eC9-based OSC from CF processing exhibits a higher PCE of 16.7% than the XY-processed OSC (15.3%). However, the 2D outer side chain-incorporated SMAs produce the OSCs with high PCE value when they are processed with XY. For example, CF-processed A1-based OSC yields a PCE

**Table 2.** Photovoltaic parameters of PM6:SMA-based OSCs fabricated with XY.

| Acceptor     | \( V_{oc} \) [V] | \( J_{sc} \) [mA cm\(^{-2}\)] | \( J_{cal} \) [mA cm\(^{-2}\)] | FF [%]       | \( PCE_{avg} \) [%] \((PCE_{max})\) | \( \mu_e \) [cm\(^2\) V\(^{-1}\) s\(^{-1}\)] | \( \mu_h \) [cm\(^2\) V\(^{-1}\) s\(^{-1}\)] |
|--------------|------------------|--------------------------|-----------------|-------------|---------------------------------|------------------|------------------|
| BTP-eC9\(^a\) | 0.86 ± 0.00      | 24.4 ± 0.4               | 23.46           | 71.1 ± 3.3  | 14.9 ± 0.4 (15.3)               | 1.3 × 10\(^{-4}\) | 4.6 × 10\(^{-4}\) |
| A1\(^a\)     | 0.86 ± 0.01      | 24.5 ± 0.4               | 24.46           | 76.5 ± 0.6  | 16.1 ± 0.4 (16.8)               | 4.0 × 10\(^{-4}\) | 2.9 × 10\(^{-4}\) |
| A2\(^a\)     | 0.80 ± 0.01      | 21.5 ± 1.0               | 21.29           | 73.5 ± 2.3  | 12.7 ± 1.0 (13.9)               | 7.0 × 10\(^{-5}\) | 2.5 × 10\(^{-4}\) |
| A3\(^a\)     | 0.87 ± 0.01      | 23.2 ± 1.0               | 23.24           | 74.5 ± 1.4  | 15.0 ± 0.4 (15.7)               | 2.7 × 10\(^{-4}\) | 1.3 × 10\(^{-4}\) |
| A4\(^a\)     | 0.82 ± 0.00      | 20.9 ± 0.9               | 20.95           | 73.4 ± 1.9  | 12.6 ± 0.3 (13.1)               | 4.7 × 10\(^{-5}\) | 1.6 × 10\(^{-4}\) |

\(^a\) Calculated by integrating the corresponding EQE spectrum; \(^b\) Average value obtained for each OSC system from at least 15 devices; \(^c\) The active layers were processed at 80 °C; \(^d\) The active layers were processed at 60 °C.

**Figure 4.** a) \( J-V \) curves, b) PCE distribution, c) EQE spectra, and d) \( J_{ph}-V_{eff} \) curves of the OSCs based on PM6:SMA blends.
of 14.9%, which is lower than that of the XY-processed PM6:A1 OSC (16.8%).

Among the XY-processed OSCs, the $V_{OC}$ of PM6:A3 OSC (0.87 V) is slightly higher than that of PM6:A1 OSC (0.86 V), while the $V_{OC}$s of the PM6:A2 (0.80 V) and PM6:A4 (0.82 V) OSCs are lower. Thus, the trend in $V_{OC}$s correlates well with the LUMO energy levels of the SMAs.[16] To support the $J_{SC}$ trend, the external quantum efficiencies (EQEs) of the OSC devices were also examined (Figure 4c). The PM6:A1 OSC exhibits the highest EQE across investigated wavelength range, with a maximum EQE of 82% at 640 nm. The calculated current densities ($J_{calc}$) of the PM6:SMA OSCs, determined from their corresponding EQE spectra, are consistent with their $J_{SC}$s within 4% error. Next, the photocurrent density ($J_{ph}$)–effective voltage ($V_{eff}$) relationship of the OSCs was analyzed (Figure 4d). The exciton dissociation probability ($P(E,T)$), that is, the ratio between the $J_{ph}$s under short-circuit condition and saturated voltage condition (i.e., $V_{eff} = 3$ V), of each device was calculated. The PM6:A1 and PM6:BTP-eC9 OSCs exhibit the highest (94%) and lowest (86%) $P(E,T)$s, respectively. The high $P(E,T)$ achieved in the PM6:A1 OSC indicates that its charge collection process is the most efficient, which contributes to its high $J_{SC}$ and FF.[17]
Next, the light intensity ($P_{\text{light}}$)-dependent $V_{\text{oc}}$ and $J_{\text{sc}}$ of each device were measured to compare their recombination properties (Figure 5). The slope ($S$) of the $V_{\text{oc}}$ versus $\ln(P)$ plot with units of $k_B T q^{-1}$ (where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $q$ is the elementary charge) represents the degree of monomolecular or trap-assisted Shockley–Read–Hall recombination in the system.\cite{17b,18} Among the PM6:SMA OSCs, the $S$ value associated with the PM6:A1 OSC (1.07) is the lowest, indicating effectively suppressed recombination, while the $S$ values associated with the other OSCs are in the range of 1.13–1.24. In addition, the slope ($\alpha$) of the $\ln(J_{\text{sc}})$ versus $\ln(P)$ plot represents the degree of bimolecular recombination in the system.\cite{18,19} Among the PM6:SMA OSCs, the $\alpha$ values of the PM6:A1 (0.95) and PM6:A3 (0.95) OSCs are the closest to the unity, while the $\alpha$ values of the other OSCs are slightly lower in the range of 0.92–0.94. These results indicate that recombination is suppressed in the PM6:A1 OSC, resulting in its high FF.

The charge transport ability of the blend film is another influential factor that affects the photovoltaic performance of an OSC. Accordingly, the charge carrier mobility of each blend film was measured using the SCLC method, where the device architectures of hole- and electron-only devices were ITO/ PEDOT:PSS/active layer/Au and ITO/zinc oxide (ZnO)/active layer/poly(9,9-bis(3'-N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene-alt-2,7-(9,9-dioctylfluorene)) dibromide (PFN-Br)/Al, respectively (Table 2). The PM6:A1 blend shows the highest electron mobility ($\mu_e$) of $4.0 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the PM6:A3 blend shows a slightly lower $\mu_e$ of $2.7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The PM6:A2 and PM6:A4 blends present an order lower $\mu_e$ of $7.0 \times 10^{-5}$ and $4.7 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Furthermore, the balance between $\mu_e$ and hole mobility ($\mu_h$) of each blend was calculated to correlate with the FF of the corresponding OSC. The PM6:A1 blend exhibits a significantly better $\mu_e/\mu_h$ (1.39) than the PM6:A3 blend (2.14). As the $\mu_s$ of the BTP-eC9, A2, and A4-based blends are lower than their $\mu_h$s, their mobility balances are less than unity, that is, 0.28, 0.27, and 0.30, respectively. The best mobility balance of the PM6:A1 blend minimizes the accumulation of either hole or electron within the active layer, thus contributing to the high FF of the corresponding OSCs.\cite{13,20} Meanwhile, the $\mu_e$ of the PM6:BTP-eC9 blend of $1.3 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ is lower than the $\mu_e$ of the BTP-eC9 pristine film ($7.0 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$). This is probably due to the poor processability of BTP-eC9 in the XY processing solvent. Overall, the superior charge transport properties of the

![Figure 7](image-url)  
Figure 7. a) 2D GIXS patterns of PM6:SMA blend films. b) Linecut profiles in the IP (left) and the OOP (right) directions.
PM6:A1 blend contribute to the high $J_{sc}$ and FF of the corresponding OSC.

To better understand the relationship between SMA processability and device performance, the spin-coating process and resulting film morphologies were further analyzed. First, the in situ UV–vis absorptions of BTP-eC9- and A1-based blends were monitored during the spin-coating process performed at their respective optimal processing temperatures of 80 and 60 °C, respectively. As shown in Figure 6, two stages are distinguishable during the spin-coating process. In the first stage, most of the solvent is removed from the substrate by centrifugal force, in which the measured absorbance is decreased, but the positions of the solution absorption peaks are maintained. In the second stage, the active materials crystallize, resulting in a shift in the observed absorption peaks and eventually reaching their saturation points. The saturation times ($t_{sats}$) of the PM6:A1 blend exceed those of the PM6:BTP-eC9 blend at the $\lambda_{max}$ of both PM6 (623–624 nm) and the SMAs (811–820 nm). For example, at $\lambda = 623–624$ nm, the $\lambda_{max}$ of PM6, the $t_{sats}$ of the BTP-eC9 and A1 blends are 9.2 and 10.4 s, respectively. Moreover, at $\lambda = 811–820$ nm, the $\lambda_{max}$ of the SMAs, the $t_{sats}$ is significantly increased from 9.4 s for the PM6:BTP-eC9 blend to 11.5 s for the PM6:A1 blend. These results suggest that the PM6:A1 blend has sufficient time to develop a favorable blend morphology and molecular packing structure during the spin-coating process. In contrast, because of the stronger aggregation of BTP-eC9 in XY, PM6:BTP-eC9 precipitates significantly faster than PM6:A1 to form a more kinetically trapped blend morphology.

The surfaces of the blend films were imaged using atomic force microscopy (AFM) (Figure S13, Supporting Information). While all the XY-processed PM6:SMA blend films have smooth surfaces with a comparable root-mean-square roughness of 1.0–1.6 nm, the PM6:A1 blend exhibits the most developed fibril structures, indicative of a favorable blend morphology for charge transport. Next, their crystalline properties were evaluated by GIXS measurements. Each blend film was prepared using the same process as that used for the fabrication of the corresponding optimized device. As shown in Figure 7, the OOP GIXS linecut profiles of all of the PM6:A1–A4 blends show clear $\pi-\pi$ stacking peaks, indicating that face-on molecular orientations dominate in the blend films. The $d_{\pi-\pi}$ of the PM6:A1 and PM6:A2 blend films of 3.70 Å is shorter than that of the PM6:A3 and PM6:A4 blend films ($d_{\pi-\pi} = 3.74$ Å). Thus, the blends containing the IC-Cl SMAs have denser packing than those containing the IC-F SMAs. Moreover, IP GIXS linecut profile of the PM6:A1 blend film exhibits the most distinct shoulder peaks near $q_{in} \approx 0.4$ Å$^{-1}$. These peaks indicate the presence of the additional charge transport pathways toward the electrodes.$^{[1c, 8d, 9d]}$ The OOP GIXS linecut profile of the BTP-eC9-based blend film also shows $\pi-\pi$ stacking peak; however, the shape of the peak is less regular. Moreover, the $d_{\pi-\pi}$ of the PM6:BTP-eC9 blend film of 3.79 Å is larger than that of the PM6:A1 blend film. The OOP GIXS linecut profile of the PM6:BTP-eC9 blend film shows an additional intense peak located at $q_{out} \approx 0.58$ Å$^{-1}$, which is often observed when a film contains excess aggregates of the Y-series SMAs.$^{[6c, 21]}$ These results support that the limited processability of BTP-eC9 in XY causes excessive aggregation, resulting in poor blend morphology and modest device performance.

3. Conclusion

In this study, we developed a series of SMAs, to realize high-performance OSCs that are processable using nonhalogenated solvents, by structurally modifying BTP-eC9, that is, replacing its linear alkyl chains with 2D alkylthienyl chains. The selective halogenation effect was also investigated with IC-F and IC-Cl variations of the SMAs. The incorporation of the 2D outer side chains induces sufficient steric hindrance between the core structure and IC end groups of the SMA to optimize its molecular planarity and aggregation behavior for halogen-free solvent processing. In particular, the A1 SMA with hexylthienyl outer side chains and IC-Cl end groups affords an OSC with a significant PCE of 16.8%; importantly, the OSC is processed using a nonhalogenated XY solution without any post-treatment process. In short, we demonstrated that the molecular planarity of an SMA can be effectively controlled by the appropriate design of 2D outer side chains, which affects its processability using halogen-free solvent and impacts the OSC device performance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ecofriendly processing, high performances, organic solar cells, small-molecule acceptors, 2D side chains

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