

Stable Postfullerene Solar Cells via Direct C–H Arylation Polymerization. Morphology-Performance Relationships

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ABSTRACT: The scope of the environmentally benign direct C–H arylation polymerization (DARP) process is validated and significantly extended in the synthesis of a high-performance benzodithiophene-based copolymer series, PBDT(Ar)-FTTE, with previously untested and systematically varied heteroaryl (Ar) substituents. Bulk-heterojunction polymer solar cells (PSCs) containing a high-performance nonfullerene acceptor (NFA), ITIC-Th, and DARP-derived donors are fabricated and evaluated, yielding PCEs as high as 8%. The relationships between Ar-sensitive copolymer structure, BHJ morphology, and PSC performance are elucidated through in-depth characterization of structural order, phase separation, and charge transport including SCLC, AFM, GIWAXS, R-SoXS, and NEXAFS measurements which conclusively demonstrate the important effects of Ar-tunable, dimensionally smaller and well-blended copolymer domains for maximum PSC performance. Smaller BHJ copolymer domains having greater ITIC-Th miscibility definitively correlate with enhanced J_{SC} , FF, and PCE metrics. Surprisingly regarding cell performance durability, while unencapsulated PBDTT-FTTE:ITIC-Th PSCs deliver the highest initial PCE, the unencapsulated PBDTTF-FTTE:ITIC-Th devices exhibit the optimum combination of high initial photovoltaic metrics and stability, retaining nearly 90% of the initial PCE after 51 days in ambient and 83% of initial PCE after 180 min simulated solar illumination. Importantly, for this PBDT(Ar)-FTTE:ITIC-Th series, PSC photovoltaic stability correlates with the presence of large pure BHJ domains, and moreover rivals or exceeds the stability of the analogous fullerene-based PSCs. Together these results argue that solar cells prepared with the environmentally DARP process and NFAs are promising for both greener and more stable solar energy generation.

INTRODUCTION

π -Conjugated organic semiconducting, alternating in-chain donor-acceptor copolymers are critical components of high-efficiency solution-processable polymer solar cells (PSCs).^{1–5} Recent advances in copolymer design and molecular mass control, as well as the emergence of indacenodithienothiophene (IDTT)-based nonfullerene acceptors (NFAs) have propelled single-junction PSC power conversion efficiencies (PCEs) to over 16%.^{6–10} Relative to previous-generation acceptors based on fullerenes^{2,3} and rylene diimides,^{8,11,12} IDTT-based NFAs such as the prototypical ITIC (2,2'-[6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-*d'*:2',3'-*d'*]-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,8-diyl]-bis[methyldiynyl]-bis[propanedinitrile]) have greater light absorption,⁹ lower internal reorganization energies,^{13,14} rapid hole transfer to polymeric donors,^{15,16} and superior operational stability,^{17–20} all of which are essential for practical high efficiency PSC technologies.²¹ Nevertheless, despite these attractions, the largely empirical optimization of donor and acceptor combinations as well as the reliance on environmentally unacceptable synthetic routes remain major obstacles to the promise of PSCs as a green, light-weight, and inexpensive renewable energy source.²²

Copolymers with the generic structure PBDT(Ar)-FTTE (Figure 1a), where Ar = benzodithiophene (BDT) heteroaryl substituent, are a PSC donor class that has traditionally been

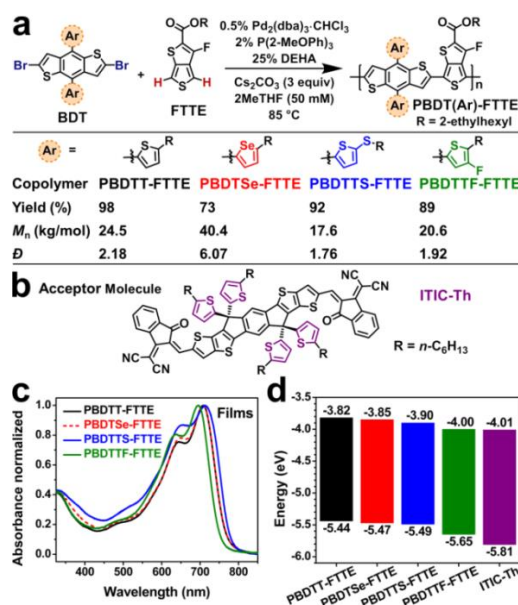


Figure 1. PBDT(Ar)-FTTE DARP synthesis and optoelectronic properties. (a) Conditions: BDT (0.1 mmol), FTTE (0.1 mmol), Pd₂(dba)₃·CHCl₃ (0.5 mol%), P(2-MeOPh)₃ (2 mol%), Cs₂CO₃ (3 equiv), and 2,2-diethylhexanoic acid (DEHA, 25 mol%) in 2MeTHF (2.00 mL) at 85 °C for 6–24 h. (b) Chemical structure of ITIC-Th. (c) Copolymer film optical absorption spectra. (d) CV-estimated frontier MO energetics.

paired with fullerenes^{23–27} or polymeric acceptors.^{28,29} One class member with alkylthiophene substituents, PBDTT-FTTE, is known to afford high-efficiency PSCs in BHJ blends with fullerenes,^{30,31} rylene diimides,^{8,11,16} and ITIC-variants including the well-known IDTT-based acceptor ITIC-Th (Figure 1b).^{16,32–36} The BDT Ar substituent is known to significantly influence the frontier MO (FMO) energetics, BHJ morphologies, and PSC efficiencies of many donor copolymers, including those of PBDT(Ar)-FTTE:fullerene blends.^{23–27} Therefore, it is noteworthy that there are few detailed, systematic studies of Ar substituent effects on PBDT(Ar)-FTTE blend morphology and PSC performance in blends with ITIC-type acceptors.

Irrespective of the copolymer, developing efficient and realistic synthetic processes remains a challenge for scaling up PSC technologies.³⁷ For example, the vast majority of PSC copolymers reported in the literature to date, including PBDTT-FTTE, have been prepared via Stille polycondensations.^{9,10,38,39} However, the toxic tin reagents used and the large quantities of toxic tin byproducts produced (1 equiv per C–C bond formed) in Stille processes raise serious cost and environmental concerns, seemingly incompatible with a green technology.^{22,40} In contrast, direct arylation polymerization (DARP) is an emerging, cost-effective, *tin-free* methodology for synthesizing the same Stille photovoltaic copolymers, but which circumvents many of the aforementioned Stille limitations.^{41–45} DARP uses one monomer with aryl C–H functional groups, affording enhanced atom economy, fewer synthetic steps, and minimized toxic reagents/byproducts.⁴⁶ Indeed, DARP is estimated to be 35% more cost-effective than a comparable Stille polymerization.⁴⁰ Nevertheless, there are few examples of DARP-derived copolymers yielding high PCEs,^{47–50} possibly due to unrecognized/unreported functional group tolerance issues or competing macromolecular defect formation.^{43,51} Despite the great advances in DARP optimization and ITIC NFAs, reports evaluating their compatibility are of great interest yet sparse.⁵²

Here, previously untested benzodithiophene-based comonomers with systematically varied heteroaryl (Ar) substituents (Figure 1a) are employed to evaluate the scope of a DARP protocol previously optimized for PBDTT-FTTE with photovoltaic performance equaling that of Stille PBDTT-FTTE.⁴⁷ The PBDT(Ar)-FTTE copolymers are first characterized by optical spectroscopy (UV-vis), cyclic voltammetry (CV), high-temperature gel permeation chromatography (GPC), and NMR spectroscopy. BHJ PSCs containing a high-performance NFA, ITIC-Th, and DARP-derived donors are then fabricated and evaluated, yielding PCEs as high as 8%. The relationships between Ar-sensitive copolymer structure, BHJ morphology, and PSC performance are then analyzed through in-depth characterization of structural order, phase separation, and charge transport using SCLC, AFM, GIWAXS, R-SoXS, and NEXAFS measurements, demonstrating the significant effects of the Ar-tunable, metrically smaller and well-blended BHJ copolymer domains for maximum PSC performance. It will be seen that smaller BHJ copolymer domains having greater ITIC-Th miscibility correlate with enhanced J_{SC} , FF, and PCE metrics. Regarding PSC performance durability, while unencapsulated PBDTT-FTTE:ITIC-Th PSCs provide the highest initial PCE, the unencapsulated PBDTTF-FTTE:ITIC-Th devices surprisingly provide the optimum combination of high initial photovoltaic metrics as well as stability, retaining an 90% of the initial PCE after

51 days in ambient and 83% of initial PCE after 180 min simulated solar illumination. Importantly, for this

PBDT(Ar)-FTTE:ITIC-Th series, it will be seen that solar cell photovoltaic stability correlates with the presence of large, pure BHJ domains, and rivals or exceeds the stability of the analogous fullerene-based devices. Together these results argue that PSCs prepared using an optimized DARP process and NFAs are promising for both more environmentally benign and more durable solar energy generation.

RESULTS AND DISCUSSION

We begin with the synthesis of the copolymer series, PBDT(Ar)-FTTE, and investigate the effects of the heteroaryl substituent on the optical absorption and electrochemical properties. The photovoltaic characteristics of the PBDT(Ar)-FTTE series are then evaluated in BHJ PSCs with the postfullerene acceptor ITIC-Th. The effects of copolymer backbone heteroaryl substituent on the BHJ morphology are characterized by AFM, GIWAXS, R-SoXS, and NEXAFS. The PSC performance stability is assessed as a function of exposure to both ambient conditions as well as simulated solar illumination, and is benchmarked against PSCs containing a traditional fullerene acceptor. Experimental details are reported in the Supporting Information (SI).

PBDT(Ar)-FTTE Synthesis and Characterization.

First, to assess the versatility of the DARP methodology, dibrominated BDT monomers with varied heteroaryl substituents (Schemes S1–S3) and the “C–H monomer” (2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTTE) were copolymerized using the pre-catalyst components $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{P}(2\text{-MeOPh})_3$, 2,2-diethylhexanoic acid (DEHA), and Cs_2CO_3 with 2-methyltetrahydrofuran (2MeTHF) as the solvent (Figure 1a).⁴⁷ Note that the PBDT(Ar)-FTTE copolymers are likely not regioregular, as depicted in Figure 1a, because of the unsymmetrical nature of the FTTE monomer, which may align in either direction along the copolymer backbone. Following purification by Soxhlet extraction, the PBDTT-FTTE, PBDTTS-FTTE, and PBDTTF-FTTE yields are $\geq 89\%$ while that of PBDTSe-FTTE is slightly lower (73%) due to insoluble coproduct formation. GPC-derived copolymer number-average molecular mass (M_n) and dispersity ($\mathcal{D}$) values are shown in Figure 1a. The PBDT(Ar)-FTTE are obtained with $M_n > 17$ kg/mol and that of PBDTSe-FTTE (40 kg/mol) is nearly twice that of PBDTT-FTTE (25 kg/mol). These M_n differences likely reflect the respective copolymer solubilities in 2MeTHF. While high-temperature ^1H and ^{19}F solution NMR reveals no obvious copolymer defects (see SI), low intensity features in the PBDTTS-FTTE ^1H spectrum may be attributable to end-groups, in accord with the lower M_n .⁸

Copolymer optical absorption properties were investigated in dilute 1,2-dichlorobenzene (DCB) solutions and in DCB-cast films (Figure 1c). All of the PBDT(Ar)-FTTE solutions exhibit a strong absorbance with $\lambda_{\text{max}} \approx 707$ nm and a higher energy shoulder at ≈ 641 nm (Figure S1). The copolymer film absorbance spectra are similar to those of the respective solutions, which suggests folding and/or aggregation in solution (Table S1).^{53,54} The PBDTT-FTTE and PBDTSe-FTTE film spectra are similar, with an optical bandgap (E_g^{opt}) of 1.62 eV. In comparison, PBDTTS-FTTE films exhibit slightly red-shifted absorption and a lower E_g^{opt} of 1.59 eV, whereas PBDTTF-FTTE films exhibit blue-shifted absorption and a higher E_g^{opt} of 1.65 eV. The copolymer and ITIC-Th FMO energies were estimated by CV (Figure 1d, Table S2).

Table 1. PSC and SCLC Diode Metrics of the DARP Copolymer:ITIC-Th Blends

Blend	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	FF (%) ^a	PCE (%) ^a	$\mu_h \times 10^4$ (cm ² V ⁻¹ s ⁻¹) ^b	$\mu_e \times 10^4$ (cm ² V ⁻¹ s ⁻¹) ^b
PBDTT-FTTE	0.805 ± 0.006 (0.806)	14.8 ± 0.5 (15.5)	64.2 ± 0.7 (64.1)	7.62 ± 0.28 (8.02)	8.3 ± 3.2	2.2 ± 0.9
PBDTSe-FTTE	0.785 ± 0.005 (0.783)	15.6 ± 0.3 (15.7)	59.4 ± 1.1 (60.3)	7.26 ± 0.10 (7.42)	8.8 ± 4.5	5.3 ± 4.5
PBDTTS-FTTE	0.860 ± 0.008 (0.860)	12.1 ± 0.6 (12.6)	53.4 ± 1.7 (55.0)	5.57 ± 0.33 (5.95)	0.5 ± 0.3	0.8 ± 0.6
PBDTTF-FTTE	0.995 ± 0.009 (0.993)	13.1 ± 0.4 (14.0)	57.1 ± 0.8 (56.9)	7.44 ± 0.18 (7.90)	0.4 ± 0.3	0.4 ± 0.2

^a Average of ≥ 5 devices. Value in parentheses is for the champion PSC. ^b Average of ≥ 3 devices.

PBDTT-FTTE, PBDTSe-FTTE, and PBDTTS-FTTE exhibit similar HOMO energies (−5.44, −5.47, and −5.49 eV, respectively).^{23,24,55} The PBDTTF-FTTE HOMO is deeper, −5.65 eV, consistent with electron-withdrawing fluorination effects.⁵⁶ ITIC-Th exhibits an even deeper HOMO (−5.81 eV), which should ensure efficient hole transfer to the donors.^{15,32}

Solar Cell Performance. PSC devices were fabricated with “inverted” device architecture, ITO/ZnO/BHJ/MoO₃/Ag, using copolymer:ITIC-Th BHJ active layers spin-coated from DCB (see SI). Photovoltaic device metrics are summarized in Table 1 and the champion current density–voltage (J – V) response for each blend is shown in Figure 2a. The open-circuit voltage (V_{oc}) values follow the trend PBDTTF-FTTE > PBDTTS-FTTE > PBDTT-FTTE ≈ PBDTSe-FTTE, consistent with the copolymer HOMO energies estimated by CV (Figure 1d).⁵⁷ The PBDTT-FTTE and PBDTSe-FTTE PSC blend short-circuit current density (J_{sc}) and fill factor (FF) values of exceed those of PBDTTS-FTTE and PBDTTF-FTTE blends. Consequently, the PCEs are highest for PSCs based on PBDTT-FTTE (8.02%) and PBDTTF-FTTE (7.90%), while the PBDTTS-FTTE devices deliver modest performance (5.95%). Note that the average DARP-derived PBDTT-FTTE:ITIC-Th PCE (7.6%) rivals that reported for similarly processed *Stille*-derived PBDTT-FTTE:ITIC-Th blends (7.5%).³² The external quantum efficiency (EQE) spectra of the optimized PSCs (Figure 2b) show broad photo-response between 300–800 nm, with the integrated EQEs in good agreement with the J_{sc} values (Table S3).

Charge Transport Characterization. Next, single carrier diodes were fabricated to probe vertical charge transport in the BHJ blends. Hole (μ_h) and electron (μ_e) mobilities were then extracted in the SCLC regime (Figure S7).⁵⁸ The PBDTT-FTTE:ITIC-Th and PBDTSe-FTTE:ITIC-Th blend μ_h s are similar $\sim 8 \times 10^{-4}$ cm²V⁻¹s⁻¹ and $\sim 10\times$ greater than those of the corresponding PBDTTS-FTTE and PBDTTF-FTTE blends which are $\sim 5 \times 10^{-5}$ cm²V⁻¹s⁻¹ (Table 1). The former two blends also exhibit μ_e s $\sim 2\text{--}5 \times 10^{-4}$ cm²V⁻¹s⁻¹, comparable in magnitude to those for previously reported similar blends,^{15,31} and exceeding those for the latter two blends $\sim 4\text{--}8 \times 10^{-5}$ cm²V⁻¹s⁻¹. The simultaneously greater μ_h s and μ_e s of the PBDTT-FTTE:ITIC-Th and PBDTSe-FTTE:ITIC-Th blends likely underlie more efficient charge carrier extraction as well as the higher J_{sc} and FF metrics.^{2,59}

Active Layer Morphology. The blend surfaces were first probed by tapping mode AFM. The height images of the PBDTTF-FTTE:ITIC-Th, PBDTT-FTTE:ITIC-Th, and PBDTSe-FTTE:ITIC-Th blends exhibit fine continuous

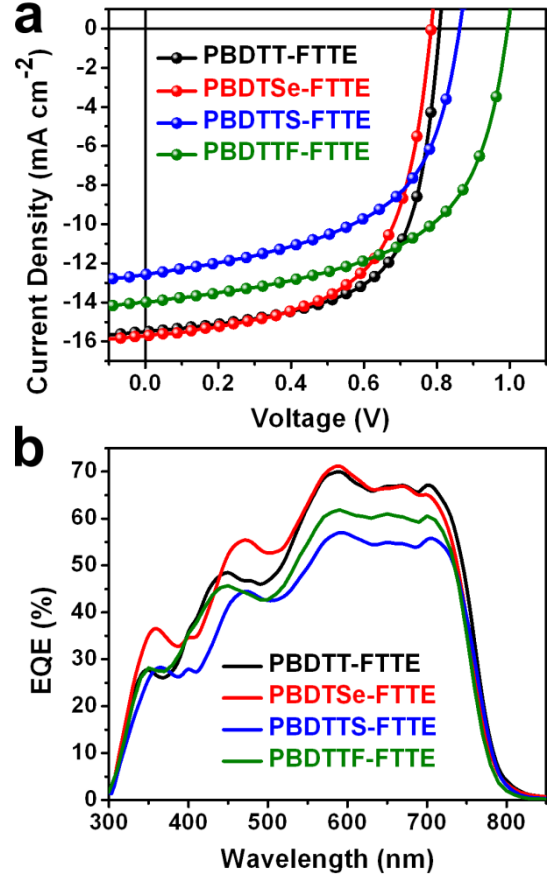


Figure 2. Photovoltaic responses of the DARP copolymer PBDT(Ar)-FTTE:ITIC-Th PSCs. (a) J – V responses and (b) EQE spectra of the champion PBDT(Ar)-FTTE:ITIC-Th PSCs.

networks and roughness $\sim 1\text{--}2$ nm (Figure S6). In contrast the PBDTTS-FTTE:ITIC-Th blend exhibits increased roughness (~ 5 nm), suggesting coarser phase separation (*vide infra*). Next, the packing characteristics of the neat copolymers and blends were analyzed by GIWAXS. The blend 2D scattering patterns and 1D line cuts obtained from in-plane (IP) and out-of-plane (OoP) sector slices are shown in Figure 3. The OoP π – π spacings and coherence lengths (CLs) are summarized in Table S5. All blends exhibit IP lamellar packing (100) peaks at ~ 0.25 Å⁻¹ and ~ 0.45 Å⁻¹ for the copolymer and ITIC-Th, respectively, and a weak OoP π – π stacking peak. Note that the PBDTTS-FTTE OoP π – π stacking (010) distance (3.90 Å) is shorter than those of the other copolymers (~ 4.15 Å) and

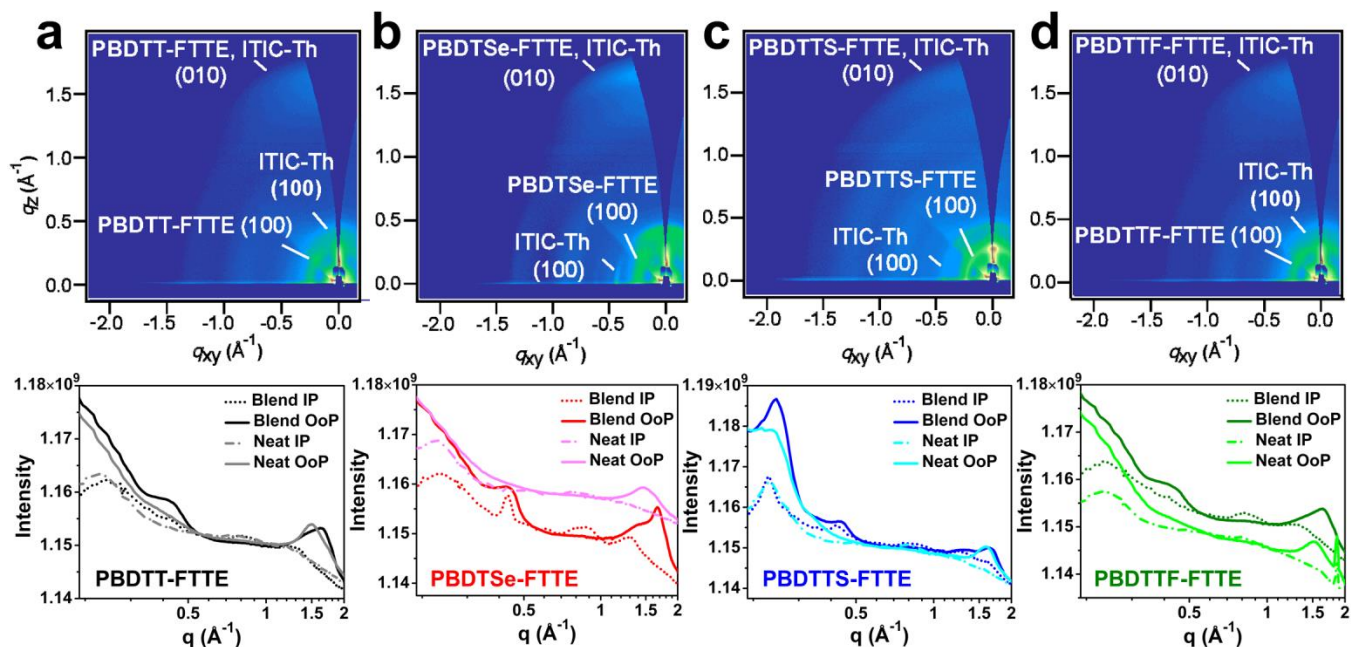


Figure 3. 2D GIWAXS patterns of ITIC-Th blend films with (a) PBDTT-FTTE, (b) PBDTSe-FTTE, (c) PBDTTS-FTTE, and (d) PBDTTF-FTTE. Bottom: 1D line cuts were obtained from in-plane (IP) and out-of-plane (OoP) sector slices of 2D scattering patterns from blend and neat copolymer films.

may reflect reduced steric repulsion of the 2-ethylhexyl substituent as sulfur incorporation shifts the branching point further from the backbone, also in agreement with the lower copolymer solubility and M_n (*vide supra*).²⁶

Diffraction strength (DS) values were next calculated by integrating the lamellar peak pole plots for the neat and blend films. The magnitude and trend of copolymer DS values are similar in both the neat and blend films, indicating little influence of ITIC-Th on copolymer ordering. The copolymer DS values are relatively low and independent of the BDT Ar substituent (Figure S8), with the notable exception being that the PBDTTS-FTTE DS is roughly twice that of the other copolymers, potentially reflecting greater order and/or crystallographic structure factor.⁶⁰ The paracrystallinity parameter, g , estimated from the copolymer IP lamellar peak in the blend films is $>15\%$ ($g = 12\%$ for amorphous SiO_2 glass) suggesting that domains of these copolymers are significantly disordered,^{61,62} consistent with the low DS. While ITIC-Th incorporation does not significantly impact the copolymer DS, note however that the copolymer Ar substituent has a marked impact on the ITIC-Th ordering in blends. Specifically, a sharper and more pronounced ITIC-Th IP lamellar (100) peak³² and an OoP π - π (010) peak are evident in the PBDTSe-FTTE blend (Figure 3b), indicating increased ITIC-Th ordering with greater π -face-on orientation versus the more isotropic ordering in the PBDTTS-FTTE blend or weak edge-on ITIC-Th ordering in the other blends. The higher degree of ITIC-Th π -face-on ordering together with a somewhat greater π - π CL is consistent with the higher μ_e of the PBDTSe-FTTE blend (Table 1). Note however that this ordering does not appear essential for achieving high PSC performance since the ITIC-Th DS in the PBDTT-FTTE blend is lower despite the higher PCE (Table 1, Figure S8). Overall, copolymer ordering is found to be far more important in optimizing PSC performance because the copolymer DS is found to correlate more strongly, albeit negatively, with PSC performance than does the ITIC-Th DS.

A more complete picture of blend morphology, including the domain size distributions and relative average phase purities over length scales spanning 10–1000 nm, is obtained with R-SoXS.^{63,64} The azimuthally averaged 1D scattering profiles obtained from the blend 2D scattering data are shown in Figure 4a. The integrated scattering intensity (ISI) is affected by both the phase contrast and the volume fraction of each phase.⁶⁵ Analyzing the resulting characteristic size scales (Figure 4b) and relative average phase purities (Figure 4c) provides insight into the morphological origins of PBDT(Ar)-FTTE:ITIC-Th PSC performance.^{66–68} All of the blends exhibit broad scattering profiles indicating the presence of multiple length scales. The PBDTSe-FTTE:ITIC-Th blend exhibits no distinct scattering feature indicating an especially broad distribution of length scales, including low- q scattering that may be due to the larger ITIC-Th crystallites detected by GIWAXS (Figure 3b). In contrast, the PBDTT-FTTE, PBDTTF-FTTE, and PBDTTS-FTTE blends with ITIC-Th exhibit a clear correlation peak, with that of the PBDTTS-FTTE blend having the largest characteristic size scale (108 nm). This is far greater than typical exciton diffusion lengths ~ 10 –20 nm,⁴ and is consistent with the GIWAXS and AFM measurements, where PBDTTS-FTTE ordering was also found to be greatest (*vide supra*). In comparison, the characteristic size scales for the PBDTT-FTTE (48 nm) and PBDTTF-FTTE (67 nm) blends are smaller. Not surprisingly, the characteristic size scale is found to correlate inversely with the PSC J_{sc} and FF values (Figure S11).^{2,3} The R-SoXS estimated relative average phase purity in the present blends varies as shown in Figure 4c and follows the trend PBDTTS-FTTE (1.00) > PBDTTF-FTTE (0.70) > PBDTT-FTTE (0.65) > PBDTSe-FTTE (0.58). Interestingly, the FF values trend downward as both relative average phase purity and characteristic size scale increase (Figure S11), in marked contrast to previous reports where increased relative average phase purity generally correlates with higher FF.^{67,68}

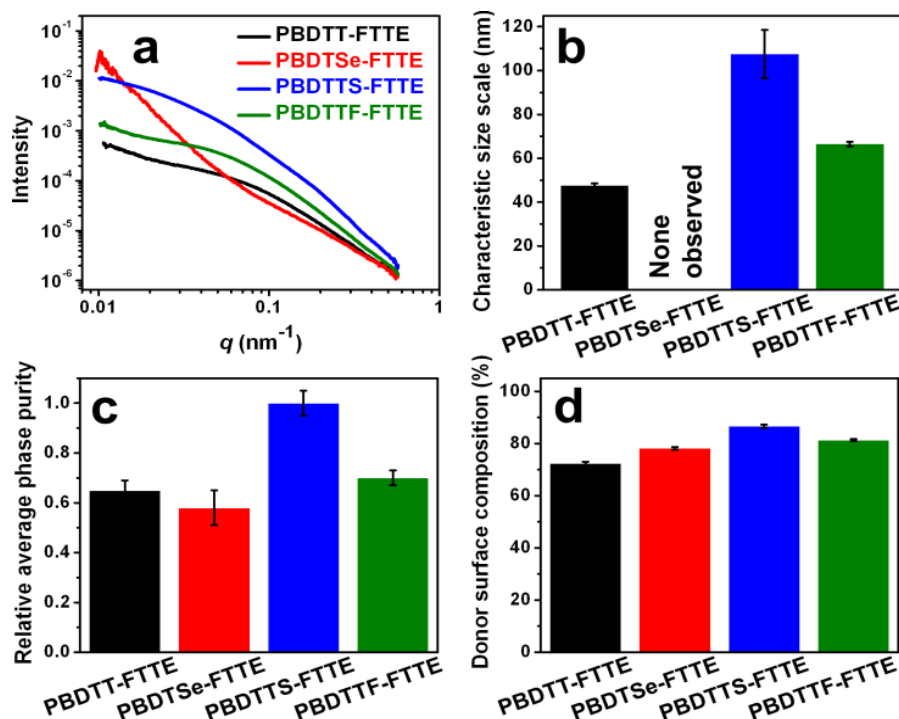


Figure 4. (a) R-SoXS profiles acquired at the maximum copolymer:ITIC-Th contrast energy (284 eV). (b) Characteristic size scale and (c) relative average phase purities obtained from the R-SoXS profiles. The size scale for the PBDTSe-FTTE blend was not evaluated due to the absence of a clear scattering peak. (d) Copolymer composition at the top of the BHJ blend surface.

Additionally, surface-sensitive NEXAFS spectroscopy was employed to quantify the composition of the BHJ top surface (Figures 4d and S12).^{69–73} The PBDTTS-FTTE blend exhibits the greatest donor copolymer top surface composition (87%), and the those for the PBDTTF-FTTE (81%), PBDTSe-FTTE (78%), and PBDTT-FTTE (72%) blends are lower. The top surface PBDTT-FTTE enrichment in the ITIC-Th blend is slightly greater than that recently reported for a PBDTT-FTTE:PC₇₁BM blend (~64%), but less than that reported for a P3HT:PC₆₁BM blend (~90%).^{74,75} Donor material enrichment at the top surface of inverted architecture PSCs has previously been linked to increased photovoltaic performance.^{72,74} However higher donor surface enrichment in the PBDT(Ar)-FTTE:ITIC-Th blends correlates with lower performance, suggesting that sufficient copolymer composition at the BHJ top surface for efficient hole extraction to the electrode has been achieved in all of the present blends. The trend in surface composition also indicates that PBDTTS-FTTE has the lowest, and that PBDTSe-FTTE and PBDTT-FTTE have the highest miscibility with ITIC-Th, in accord with the R-SoXS results (*vide supra*). Note that, the lower phase miscibility in the PBDTTS-FTTE and PBDTTF-FTTE blends may reflect less favorable interactions between the respective heteroaryl substituents and ITIC-Th and/or the lower copolymer M_n s, which can increase copolymer ordering and alter PSC metrics.^{8,76–78}

Solar Cell Performance Stability. Operational stability is a critical factor affecting the practicality of PSC technologies.^{37,79} Consequently, the stability of the present PBDT(Ar)-FTTE PSCs was evaluated using protocols established by the International Summits on OPV Stability.^{79–81} Specifically, PSC photovoltaic stability was assessed as a function of exposure to ambient conditions as well as to simulated solar illumination. In the ambient stability evaluations, unencapsulated

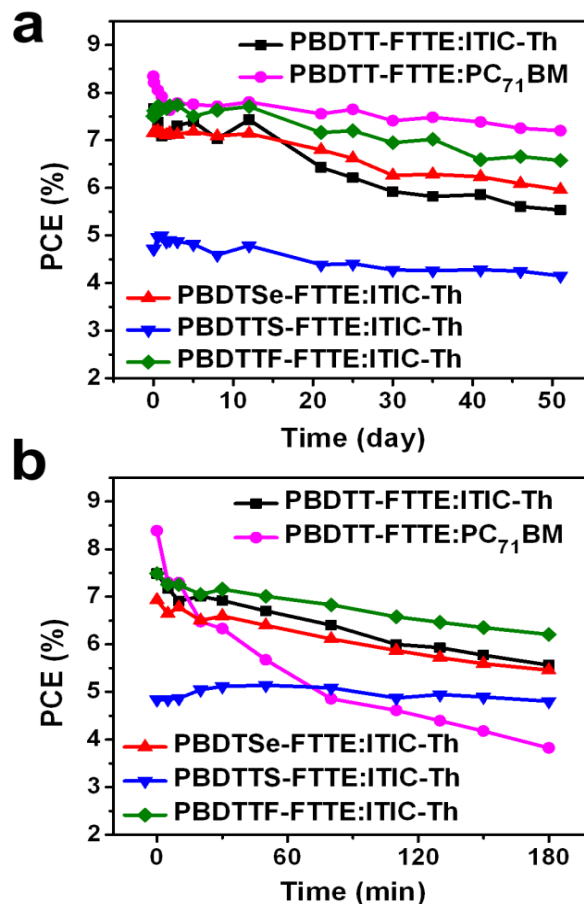


Figure 5. Photovoltaic stability of the PBDT(Ar)-FTTE:ITIC-Th PSCs. (a) Ambient stability of the PSCs. (b) PSC stability under AM 1.5G illumination (100 mW cm⁻²).

PSC devices were stored under ambient temperature and humidity in the dark. Under these conditions, all of the present PSCs exhibit decay of performance metrics with continued exposure (Figures 5a and S4). After 51 days, the PBDTSe-FTTE:ITIC-Th, PBDTTS-FTTE:ITIC-Th, and PBDTTF-FTTE:ITIC-Th PSCs retain between 83–88% of the initial PCE. In comparison, the PBDTT-FTTE:ITIC-Th PSCs exhibit the greatest decrease, retaining only 73% of their initial PCE. These results rival or exceed the stabilities exhibited by similar PSC blends containing IDTT-related acceptors under similar stress conditions.^{82,83}

Additionally, PBDTT-FTTE:PC₇₁BM PSCs were fabricated as previously reported and assessed for ambient storage stability (see SI).⁴⁷ Interestingly, these PC₇₁BM-based PSCs are more stable than the corresponding ITIC-Th-based ones and retain 86% of the initial PCE after 51 days, in contrast to previous reports where decay is far more dramatic.¹⁷ In all of the present ITIC-Th- and PC₇₁BM-based PSCs, the PCE losses are mainly due to FF decline (Figures S4).⁸⁴

Finally, photostability was evaluated by subjecting the PSCs to continuous AM 1.5G illumination (100 mW cm⁻²) under ambient conditions with periodic performance evaluation. The PBDTT-FTTE:ITIC-Th, PBDTSe-FTTE:ITIC-Th and PBDTTF-FTTE:ITIC-Th PSCs exhibit linear PCE decay with no obvious “burn-in” period, and retain 74–83% of the initial PCE after 180 min illumination (Figure 5b). Similar to previous reports,^{20,82} these decreases reflect simultaneously diminished V_{OC} , J_{SC} , and FF (Figure S5). In marked contrast, the PBDTTS-FTTE:ITIC-Th PSC performance is virtually unchanged after 180 min. One known morphological photodegradation mechanism of PBDTT-FTTE PSCs is small molecule acceptor diffusion to the BHJ top surface,²⁰ which presumably degrades inverted architecture PSC performance by impeding hole extraction.^{85,86} In other studies, organic semiconductor crystallinity is correlated with greater resilience to photobleaching.^{87,88} Thus, we speculate that the enhanced PBDTTS-FTTE:ITIC-Th PSC photostability reflects the increased copolymer ordering (Figure 3c), larger characteristic size scales (Figure 4b), and greater copolymer top surface enrichment (Figure 4d), all of which may help minimize active layer morphological degradation and photobleaching.⁷⁹

Unlike in the above ambient stability experiments where the PBDTT-FTTE:PC₇₁BM PSCs are quite robust, these fullerene-based PSCs exhibit the poorest photostability, retaining <50% of the initial PCE after only 180 min exposure to illumination, in line with previous reports.^{20,89} The most likely origin of which is the presence of iodinated film processing additives, which are required to achieve optimal PBDTT-FTTE:PC₇₁BM PSCs performance initially,^{30,31,47,74} but are well-known degrade performance on prolonged light exposure.^{90,91} Consequently, the absence of iodinated processing additives employed in the fabrication of the present ITIC-Th-based PSCs may partly explain their superior photostability.

CONCLUSIONS

A series of alternating in-chain donor-acceptor π -conjugated semiconducting copolymers, PBDT(Ar)-FTTE, with high molecular masses and selected heteroaryl BDT substituents was prepared by an environmentally benign DARP protocol, extending the scope of DARP for PSC copolymers. For the first time, BHJ PSCs containing a nonfullerene acceptor, ITIC-Th, and a DARP-derived donor are fabricated and evaluated. Three PSC blends deliver >7% PCE and PBDTT-FTTE devices

achieve >8% PCE, rivalling the record for DARP copolymer:fullerene PSCs and broadening the applicability of this green synthetic methodology. Next, the relationships between Ar-sensitive copolymer structure, BHJ morphology, and PSC performance are evaluated by in-depth characterization of phase separation, structural order, and carrier mobility using AFM, GIWAXS, R-SoXS, NEXAFS, and SCLC measurements. The resulting data convincingly highlight the important effects of Ar-related, smaller and well-blended copolymer domains for maximum PSC performance. Smaller BHJ copolymer domains having greater ITIC-Th miscibility correlate with enhanced J_{SC} , FF, and PCE metrics. Surprisingly regarding cell performance durability, while unencapsulated PBDTT-FTTE:ITIC-Th PSCs deliver the highest initial PCE, the unencapsulated PBDTTF-FTTE:ITIC-Th devices exhibit the optimum combination of high initial photovoltaic metrics and stability, retaining nearly 90% of the initial PCE after 51 days in ambient air and 83% of initial PCE after 180 min exposure to simulated solar illumination. Noteworthy for this PBDT(Ar)-FTTE:ITIC-Th series, PSC photovoltaic stability correlates with the presence of dimensionally large and compositionally purer BHJ domains, and moreover is comparable to or exceeds the stability of the analogous fullerene-based PSCs. Together these results argue that BHJ solar cells fabricated with DARP-derived donors and nonfullerene acceptors are promising for greener, more stable solar energy generation.

ASSOCIATED CONTENT

Supporting Information

Monomer and copolymer synthesis and characterization, UV-vis and NMR spectra, CV, PSC device fabrication, AFM, SCLC, GIWAXS, R-SoXS, and NEXAFS measurements are available in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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