Article

Reassessing the Significance of Reduced Aggregation and Crystallinity of Naphthalene Diimide-Based Copolymer Acceptors in **All-Polymer Solar Cells**

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and effective strategy to control the aggregation and crystallinity of semiconducting polymers which has been exploited to improve the photovoltaic performance of all-polymer solar cells (all-PSCs). Applying this strategy to the well-studied electron-transporting polymer acceptor PNDI2OD-T2, different amounts of 3-octylthiophene (OT) are used to partially replace the bithiophene (T2) unit, resulting in three copolymer acceptors PNDI-OTx where x = 5, 10, or 15%. Another polymer, namely PNDI2OD-C8T2, consisting of naphthalene diimide (NDI) polymerized with 3-octyl-2,2'-bithiophene (C8T2) is also synthesized for comparison. It is found that the solution aggregation and thin-film crystallinity of PNDI-OTx are systematically tuned by varying x, evidenced by temperature-dependent UV-vis and grazing incidence wide-angle X-ray scattering measurements. PNDI2OD-C8T2 is also found to have reduced solution aggregation and



thin-film crystallinity relative to PNDI2OD-T2. However, the photovoltaic performance of all-PSCs based on J71:PNDI-OTx and J71:PNDI2OD-C8T2 blends are much lower than that of the reference J71:PNDI2OD-T2 system. Extensive morphological studies indicate that reduced aggregation and crystallinity do not guarantee a more favorable blend morphology, with coarser phase separation found in J71:PNDI-OTx and J71:PNDI2OD-C8T2 blends compared to J71:PNDI2OD-T2 blends. Furthermore, the OT-modified copolymers with reduced crystallinity are found to have reduced electron mobilities. The results here suggest that reduced aggregation and less crystallinity of random copolymer acceptors do not always produce favorable morphology in polymer/ polymer blends and do not guarantee for improvement in the photovoltaic performance.

KEYWORDS: *Il-polymer solar cells, copolymer acceptors, crystallinity, aggregation, miscibility*

INTRODUCTION

 π -Conjugated semiconducting materials are used to form the active layer of solution-processed polymer solar cells (PSCs).¹⁻³ Recent advances in the design and synthesis of new materials have propelled the single-junction power conversion efficiency (PCE) of PSCs toward 18% based on devices utilizing small molecular acceptors combined with semiconducting polymer donors.⁴⁻⁶ This achievement underscores the huge potential of PSCs for solution-processable, low-cost, and flexible solar energy.^{3,7} Besides, all-polymer solar cells (all-PSCs), in which the active layer is based on a blend of polymer donor and polymer acceptor, have also caught much attention due to their unique properties such as excellent thermal/light morphology stability and mechanical tolerance.⁸⁻¹⁰ Notwithstanding the recent development of polymerized small molecules acceptors,^{11,12} PNDI2OD-T2 is one of the most widely used polymer acceptors in all-PSCs due to its strong planarity, high crystallinity, and excellent mobility.^{8,9,13} However, the strong aggregation and poor compatibility of PNDI2OD-T2 with common donor polymers often results in a suboptimal morphology and poor photovoltaic performance.¹⁴ Thus, optimizing the crystallinity of naphthalene diimide (NDI)-based polymers is widely considered to be a versatile and powerful strategy for the design and synthesis of high-performing polymers in all-PSCs.^{9,15} As such, the copolymerization strategy has been introduced, in which a third monomer unit is incorporated into the backbone to regulate the aggregation and crystallinity of NDI-based polymer acceptors.^{8,16} Electron-donating or electron-accepting moieties can be partially introduced into the backbone to delicately control the crystallinity of the resulting polymers.¹⁷ The wide adaptation of the copolymerization method using three monomers in step growth polymerization has successfully produced a number of copolymers [often called terpolymers, contradicting the IUPAC recommendation that these polymers

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Figure 1.	Chemical	structure of	of the	polymer	donor	and fr	ve P	NDI	based	polymer	acceptors.
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Table 1	. Physical,	Thermal,	and Op	tical Pro	perties of	the P	olymer	Acceptors
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polymers	$M_{\rm n}~({\rm kDa})^a$	Đ	HOMO (eV) ^b	LUMO (eV) ^b	$T_{\rm m} [^{\circ}{\rm C}]^{c}$	$\Delta H_{\rm m} ({\rm J/g})^c$	$\lambda_{\mathrm{onset}}^{\mathrm{sol}}$ [nm]	$\lambda_{\mathrm{onset}}^{\mathrm{film}}$ [nm]	$\Delta\lambda \ [nm]^d$	$E_{g}^{opt} [eV]^{e}$
PNDI2OD-T2	44	2.8	-5.96	-3.90	308	6.68	801	807	6	1.54
PNDI-OT5	44	3.3	-5.95	-3.88	301	5.38	793	802	9	1.55
PNDI-OT10	52	2.9	-5.96	-3.90	297	3.66	788	807	19	1.54
PNDI-OT15	62	7.7	-5.96	-3.90	288	1.65	775	811	36	1.53
PNDI2OD-C8T2	32	6.1	-5.96	-3.89	246	3.71	715	820	105	1.51
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^{*a*}Determined by size exclusion chromatography. ^{*b*}Determined from electrochemical cyclic voltammetry. ^{*c*}Determined from the heating scan from DSC. ^{*d*} $\Delta\lambda$ is the difference between λ_{onset} of solution and thin-film states. ^{*e*}Determined by the formula $E_g = 1240/\lambda_{onset}^{film}$.

are made up of two implicit monomers (i.e., have two repeating units)]¹⁸ with tunable crystallinity that exhibit enhanced photovoltaic properties and/or improve mechanical stability.^{15,19-26} The employment of copolymerization also allows tuning of the aggregation tendency of copolymer acceptors, which has been found to greatly impact the electrical and photovoltaic properties of the resultant all-PSCs.^{24,27,28} Apart from tunable crystallinity and aggregation, enhancing the miscibility between the two components is another important parameter that has been taken into consideration when designing random copolymer acceptors for use in all-PSCs.²⁹⁻³¹ The better compatibility between the donor and acceptor usually implies a more favorable morphology, which in turn improves electrical and photovoltaic properties.^{19,23,29,30} However, it still remains unclear exactly what are the key parameters that determine whether a new acceptor polymer will lead to enhanced photovoltaic properties in all-PSCs. Resolving this question will clarify the design requirements for new materials that meet the requirements for the future commercialization of all-PSCs.

Herein, a series of newly synthesized acceptor semiconducting polymers with controlled aggregation and crystallinity are prepared and employed in all-PSCs. To tune the properties of the polymer PNDI2OD-T2, a certain amount of the 3-octylthiophene (OT) moiety is partially incorporated to replace the T2 (bithiophene) unit, affording three copolymer acceptors PNDI-OTx where x represents the fraction of the OT unit (x = 5, 10, and 15%). A fourth polymer, PNDI2OD-C8T2, is also prepared where the bithiophene unit is completely replaced with 3-octyl-2,2'-bithiophene to separately study the effect of n-octyl substitution. The solution aggregation and solid-state crystallinity of these polymers are found to be lower than that of PNDI2OD-T2 and furthermore are found to systematically decrease with increasing OT fraction, evidenced from temperature-dependent UV-vis, differential scanning calorimetry (DSC), and grazing incidence

wide-angle X-ray scattering (GIWAXS) measurements. All-PSCs are prepared and characterized by pairing these acceptor polymers with the donor polymer J71.³² Though the family of PNDI-OTx polymers possesses tunable aggregation and crystallinity, solar cells based on blends of J71 with PNDI-OTx are found to exhibit reduced photovoltaic performance compared to those based on blends of J71 with the reference PNDI2OD-T2 acceptor. Furthermore, J71:PNDI2OD-C8T2 blends also show a decrease in photovoltaic performance relative to J71:PNDI2OD-T2. Extensive morphological characterization with GIWAXS, atomic force microscopy (AFM), and resonant soft X-ray scattering (R-SoXS) demonstrates that the modification of PNDI2OD-T2 with OT units results in acceptor polymers that drive strong phase separation in blends with J71. This suboptimal phase separation is likely to limit the fraction of excitons that are dissociated at donor/acceptor interfaces ultimately exacerbating the photovoltaic performance. The current results demonstrate that the employment of random copolymer acceptors with reduced crystallinity and tunable aggregation is not always needed to optimize the morphology of the blends, specifically in this case when blending the polymer J71. Copolymer acceptors need to retain good electron-transporting properties and produce an optimum phase-separated blend in combination with the donor polymer in order to ensure the improved photovoltaic performance in all-PSCs.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization. The chemical structures of the polymers investigated in this work are shown in Figure 1. The polymers were synthesized by direct aryl heteroatom polymerization (DAHP), which has been previously employed for the synthesis of PNDI2OD-T2.^{33,34} All polymerization reactions show relatively good reaction yields, ranging from 80 to 95%. The DAHP method provides an alternative to conventional polymerization reactions



Figure 2. Normalized UV-vis absorption spectra of the five polymer acceptors: (a) solution state at 30 $^{\circ}$ C in CB, (b) solution state at 80 $^{\circ}$ C in CB; (c) thin-film state at room temperature in CB. (d) DSC of the second cycle.

involving a more cost-effective polymerization reaction and use of less toxic monomers.^{33,35} The detailed synthetic procedures are described in the Supporting Information. All polymers were characterized by NMR (Figure S1), and molar masses were measured using size exclusion chromatography with trichlorobenzene as the eluent. The random copolymers tend to have higher number average molar mass (M_n) with higher fraction of OT unit in the polymer backbone (Table 1). The dispersities of PNDI-OT15 and PNDI2OD-C8T2 are notably higher than that of the other polymers, the OT-containing acceptors, which could be due to different reaction rates between the comonomer units with bulky side chains compared to T2 units in the direct arylation reaction protocol. The larger dispersities of PNDI-OT15 and PNDI2OD-C8T2 could have a detrimental effect on the solar cell performance,³⁰ though it is noted that good efficiencies were achieved in PTB7-Th:PNDI-T10 blends with a dispersity of 5.0 for the PNDI-T10 acceptor.²² In any case, the batches of PNDI-OT5 and PNDI-OT10 have similar dispersities to the batch of PNDI2OD-T2 used.

Solution-State Aggregation and Thin-Film Optical and Electrochemical Properties. The presence of the hydrophobic *n*-octyl side chain is expected to affect the solution phase aggregation behavior. Temperature-dependent UV-vis spectroscopy was performed on solutions of PNDI2OD-T2, PNDI-OT*x*, and PNDI2OD-C8T2 in chlorobenzene (CB) over a temperature range of 30-130 °C (Figures 2 and S2). At the highest temperature of 130 °C, all five polymers are completely dissolved and disaggregated (see Figure S2), evidenced by a lack of aggregation features in the charge-transfer (CT) absorption band at 600 nm. With a decrease in solution temperature, a gradual transition from disaggregated to aggregated is seen, evidenced by the emergence of new absorption features associated with chain aggregation.²⁴ In particular, at 80 °C (Figure 2b), the reference polymer PNDI2OD-T2 shows a weak shoulder at 720 nm, which is absent in the cases of PNDI-OT15 and PNDI2OD-C8T2. With cooling of solutions to 30 °C (Figure 2a), there is a dramatic red-shift in the absorption profiles. The reference PNDI2OD-T2 shows the strongest degree of aggregation with the highest absorption intensity at 720 nm, whereas the polymer PNDI2OD-C8T2 still shows an apparent lack of aggregation. With an increase in the fraction of OT unit in the backbone, the intensity of the peak at 720 nm decreases systematically, implying reduced aggregation in the copolymers due to the influence of the *n*-octyl side change that frustrates planarization of these random copolymers is consistent with previous studies and has been associated with improved photovoltaic performance in various cases.^{24,27,28}

The UV-vis absorption spectra of thin films of all five polymers cast from CB have also been measured, Figure 2c. In general, all five acceptors show quite similar light absorption profiles with estimated optical band gaps of 1.51-1.55 eV. All polymers exhibit two absorption bands, one at 350-450 nm belonging to the $\pi - \pi^*$ transition and the other at 500-800 nm belonging to the CT transition.³⁷ Comparing the solution and thin-film absorption profiles, PNDI2OD-T2 has a similar absorption edge of approximately 800 nm in thin film and in solution at 30 °C, suggesting strong pre-aggregation of PNDI2OD-T2 in solution due to strong $\pi - \pi$ stacking interactions and more delocalized excitonic states.³⁸ The extent of pre-aggregation is suppressed with increased loading of the OT unit in the backbone, characterized by an increasing bathochromic shift going from solution to film (Table 1). Intriguingly, a bathochromic shift of approximately 105 nm of the absorption edge is seen for the case of PNDI2OD-C8T2, demonstrating a lack of pre-aggregation in the solution state. Overall, the incorporation of OT units here systematically tunes the aggregation of the resulting copolymers, with



Figure 3. 1D scattering profiles of five polymer acceptor neat films: (a) IP direction, (b) OOP direction; (c) coherence length of the (100) peak from IP direction; (d) $\pi - \pi$ distance of the (010) peak extracted from the OOP direction [the graphs (a,b) are vertically shifted for clarity].

complete substitution of the T2 unit for the C8T2 able to suppress aggregation completely. Molar absorptivity (solution) and absorption coefficient (film) data can be found in Supporting Information, Figure S3.

The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of the polymer donor and acceptors were measured by cyclic voltammetry, for investigating the impact of the OT unit on the electronic energy level and the energy alignments between donor and acceptor polymers (Figure S4). J71 has LUMO/ HOMO levels of -3.09/-5.42, which is very close to that reported in the literature.³² By replacing the bithiophene moiety with different amounts of OT unit, the energy levels remain unchanged compared to those of PNDI2OD-T2 (Table 1). The HOMO/HOMO offset between J71 and acceptor polymers is larger than 0.3 eV, which is sufficient for efficient hole transfer across the interfaces.³⁹ This means the structural modification with OT unit is likely to have no impact on the electronic energy level and ensure sufficient driving force for exciton dissociation.

Solid-State Crystallinity and Backbone Orientation of Neat Films. DSC is used to probe the thermal transitions of the as-synthesized polymers, with the second heating and cooling measured DSC traces, as shown in Figure 2d. The reference polymer PNDI2OD-T2 shows a relatively high melting point (T_m) at 308 °C, whereas PNDI2OD-C8T2 has a much lower T_m of 246 °C. The inclusion of additional *n*-octyl side chains in the backbone is likely to weaken alkyl stacking and induce backbone disorder, with a systematic decrease in $T_{\rm m}$ observed with the increasing loading of OT in the copolymer acceptors. Specifically, the $T_{\rm m}$ of PNDI-OT5, PNDI-OT10, and PNDI-OT15 is determined as 301, 297, and 288 °C, respectively. Furthermore, the melting enthalpy $(\Delta H_{\rm m})$ of those polymers, which strongly correlates with the crystallinity, is determined by calculating the area of melting peaks.^{40,41} Intriguingly, PNDI2OD-T2 and PNDI2OD-C8T2 show high $\Delta H_{\rm m}$ values of 6.68 and 3.71 J/g, respectively. There is then a gradual drop in $\Delta H_{\rm m}$ with the incorporation of

OT units into the backbone (Table 1). The variation in $T_{\rm m}$ and $\Delta H_{\rm m}$ of copolymer acceptors indicates a gradual decrease in crystallinity with increasing OT loading in the backbone.⁴² The higher $\Delta H_{\rm m}$ of PNDI2OD-C8T2 compared to PNDI-OT*x* suggests disorder associated with the random nature of the OT substitution and/or the shorter length of the OT unit along the backbone compared to the C8T2 unit, also affecting the degree of crystallinity.

To further characterize the influence of OT substitution and C8T2 substitution on solid-state crystallinity and crystallite orientation of those polymers, GIWAXS experiments have been carried out on neat films. The 2D GIWAXS images are presented in Figure S5 with the reduced 1D scattering profiles, as shown in Figure 3a,b. PNDI2OD-T2 shows a strong face-on orientation, featuring up to three orders of lamellar stacking peaks (h00) with d_{100} at ≈ 24.3 Å in the in-plane (IP) direction.⁴³ Backbone stacking peaks are also observed in the plane, with the (001) peak appearing at ≈ 0.46 Å⁻¹ that overlaps with the second-order lamellar stacking peak, (200). Higher order backbone stacking peaks are also seen, labelled as (002) and (004). PNDI2OD-C8T2 exhibits similar crystallographic features but with reduced crystallinity reflected by broader peaks and the fact that only two orders of lamellar stacking peaks are seen. It is interesting that the incorporation of *n*-octyl alkyl chains only seems to have a subtle influence on the molecular packing judging by the position of the peaks with the lamellar distance gradually decreasing from 24.3 Å for PNDI2OD-T2 to 23.9 Å for PNDI-OT10 and to 23.3 Å for PNDI2OD-C8T2. In addition, a π - π stacking peak is found in the out-of-plane (OOP) direction in all five pristine films, corroborating the face-on orientation of all polymers. The $\pi - \pi$ stacking distance determined for PNDI2OD-T2 is 3.96 Å, which increases with incorporation of OT into the backbone to a value of 4.02 Å for PNDI-OT15 and with a value of 4.08 Å for PNDI2OD-C8T2 (Figure 3d). The increase in $\pi - \pi$ stacking distance with n-octyl substitution may have an influence on the electrical properties of the corresponding polymers. Furthermore, peak fitting performed on the (100)



Figure 4. Extracted tilt angles of the polymer backbone: (a) PEY and (b) TEY.



Figure 5. (a) J-V curves of solar cells based on J71:PNDI-based acceptors and (b) the corresponding EQE spectra.

lamellar stacking peak was used to evaluate the crystal coherence length (CCL), as determined by the Scherrer equation, with the results depicted in Figure 3c. PNDI2OD-T2 shows the largest CCL of 110 Å. With increasing OT fraction, the CCL of the corresponding copolymers systematically decreases, indicating a decrease in the crystal size and/or increase in disorder. PNDI2OD-C8T2 is found to have a similar, even slightly higher CCL compared to PNDI-OT15. The reduction in CCL with increasing OT content is consistent with the observations from the DSC measurement, which inferred a decrease in crystallinity with increasing OT content. A reduced crystallinity of the copolymer acceptors is in agreement with previous reports and can be ascribed to suppressed intermolecular interaction when introducing a third monomer unit via copolymerization.^{15,19–25,44} For comparison, the donor polymer J71 shows broader features in its neat GIWAXS pattern characteristic of a less ordered polymer (Figure S6). The GIWAXS pattern of J71 is characterized by a single and broad lamellar stacking (100) peak located IP at q_{xy} ≈ 0.28 Å⁻¹, corresponding to a *d*-spacing of $d_{100} = 22.6$ Å, and $\pi - \pi$ stacking peak located OOP at $q_z \approx 1.68$ Å⁻¹, corresponding to a $\pi - \pi$ stacking distance of 3.74 Å. The CCL extracted from the (100) peak of J71 is about 35 Å, which is significantly lower than that of the pristine polymer acceptors.

To determine the molecular orientation of the polymer backbone at the surface of these neat films, angle-resolved near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy has been performed, with the results shown in Figures S7 and S8. Four peaks located at between 283 and 287 eV are seen, which correspond to $1s-\pi^*$ transitions on the conjugated backbone. By observing the change in peak intensity with variation of the angle of incidence of the polarized X-ray beam, the average tilt angle $\langle \alpha \rangle$ of the transition dipole moment can be determined, which is indicative of the molecular orientation of the backbone (with $\langle \alpha \rangle = 90^\circ$ corresponding to a perfect

edge-on orientation of planar aromatic units and $\langle \alpha \rangle = 0^{\circ}$ corresponding to a perfect face-on orientation of planar aromatic units).^{45–47} Note that although PNDI2OD-T2 has a highly planar backbone, there is a pronounced torsional angle between the T2 and NDI units, which is calculated to be 46.05° and 47.17° for two different conformers.⁴⁸ Unfortunately, NEXAFS cannot individually determine whether local absorption is assigned to T2 or NDI units, and thus, $\langle \alpha \rangle$ is assumed to be an average of the contributions from both T2 and NDI moieties. For spin-coated films, which lack long-range IP alignment, the "magic angle" is 54.7°; this means that it is impossible to discern between a preferential molecular orientation that gives a value of $\langle \alpha \rangle$ and a random orientation of transition dipole moments.⁴⁹ The extracted tilt angles for the neat films are shown in Figure 4, with values for the partial electron yield (PEY) measurement shown in Figure 4a and values for total electron yield (TEY) measurement shown in Figure 4b. For the PEY measurements, the average tilt angles $\langle \alpha \rangle$ of all five polymers are close to the magic angle of 54.7°, which could suggest a random orientation and/or amorphous state. When switching to TEY measurements, a clear trend with smaller tilt angles is observed across the five films for the π^* regions. These angles—which are significantly below the magic angle-indicate a preferential orientation rather than a random orientation. The systematic decrease in average tilt angle from PEY to TEY can be understood in terms of the different probing depths of the two techniques, which is $\approx (1 - 1)^{-1}$ 3) nm for PEY and \approx (3–5) nm for TEY.⁴⁸ Furthermore, it is known that PNDI2OD-T2 exhibits a distinct edge-on surface layer on top of face-on orientation in the bulk.⁵⁰ Comparing the tilt angles of PNDI2OD-T2 with PNDI2OD-C8T2, very similar values of $\langle \alpha \rangle$ are seen, whereas for PNDI-OT*x*, a subtle yet systematic decrease in tilt angle is observed with increasing OT content. These observations suggest that OT substitution and C8T2 substitution have different effects on molecular orientation. These differences could also be due to differences

Table 2. Photovoltaic Properties of	Five Systems	Processed from	CB Solvent	Taken from	at Least Five	e Individual	Cells with
Uncertainties from Variations betwee	een Cells						

Systems	$V_{\rm OC}$ [V]	$J_{\rm SC} \left[{\rm mA/cm^2} \right]$	FF [%]	PCE [%]
J71:PNDI2OD-T2	0.93 ± 0.01	10.2 ± 0.1	54.4 ± 0.5	5.2 ± 0.1
J71:PNDI-OT5	0.93 ± 0.01	8.1 ± 0.2	52.5 ± 0.5	4.0 ± 0.1
J71:PNDI-OT10	0.93 ± 0.01	6.2 ± 0.2	52.2 ± 0.8	3.0 ± 0.1
J71:PNDI-OT15	0.94 ± 0.01	4.9 ± 0.2	50.4 ± 1.0	2.3 ± 0.1
J71:PNDI2OD-C8T2	0.94 ± 0.01	5.5 ± 0.2	50.8 ± 1.1	2.6 ± 0.2



Figure 6. 1D scattering profiles of blend films: (a) IP direction, (b) OOP direction; (c) coherence length of the (100) peak from the IP direction [the graphs (a,b) are vertically shifted for clarity].

in the dihedral angle between NDI and thiophene units caused by n-octyl substitution since NEXAFS provides an averaged measurement of the tilt of the aromatic units in the backbone. In general, however the changes in tilt angle are relatively minor, indicating that the incorporation of the third monomer unit into the backbone does not significantly impact backbone orientation.

All-Polymer BHJ Solar Cells. The photovoltaic properties of these polymers have been evaluated in BHJ all-PSCs using an inverted device configuration of ITO/ZnO/PEIE/active layer/MoO_x/Ag, Figure 5, Table 2. The reference J71:PNDI2OD-T2 cell displays a relatively high open-circuit voltage (V_{OC}) of 0.93 V, a short-circuit density (J_{SC}) of 10.2 mA/cm^2 , and a fill factor (FF) of 54.4%, corresponding to a PCE of 5.2%, which is comparable to values reported in the literature.⁵¹ The J71:PNDI2OD-C8T2 cell shows a similar V_{OC} of 0.94 V but much lower J_{SC} and FF, leading to an inferior PCE of 2.6%. For the J71:PNDI-OTx cells, incorporation of OT again has a negligible effect on $V_{\rm OC}$ but leads to a systematic deterioration of device efficiency. Compared to J71:PNDI2OD-T2, the performance of J71:PNDI-OT5 is slightly lower with a PCE of 4.0%, J_{SC} of 8.1 mA/cm² and FF of 52.5%. Further increase in the OT loading deteriorates the electrical and photovoltaic properties due to further reductions in both J_{SC} and FF. Cells based on blend films of J71:PNDI-OT10 and J71:PNDI-OT15 show a J_{SC} of 6.2 and 4.9 mA/cm², respectively, corresponding to PCEs of 3.0 and 2.3%, respectively. The external quantum efficiency (EQE) spectra of the all-PSCs are depicted in Figure 5b, which show a broad photoresponse over the visible spectral region of 350-800 nm, which is consistent with the UV-vis absorption spectra of the films. The EQE spectra show distinct features characteristic of photocurrent generation following absorption by both donor and acceptors. The EQE peak at around 700 nm is characteristic of the acceptor polymers with photocurrent generation proceeding via hole transfer from the NDI-based acceptor to J71, while the EQE region at 500-600 nm is associated with absorption by J71 with photocurrent

generation proceeding via electron transfer from J71 to the polymer acceptors.

The electron-only mobilities of blends were investigated via the space charge limited current (SCLC) method with the results, as shown in Figure S9 and mobility values, as tabulated in Table S4. The J71:PNDI2OD-T2 blend shows the highest electron mobility (μ_e) of 1.3×10^{-4} cm² V⁻¹ s⁻¹, whereas the J71:PNDI2OD-C8T2 blend displays the lowest $\mu_{\rm e}$ of 2.0 \times 10^{-5} cm² V⁻¹ s⁻¹. The swapping of 5% of T2 units for OT units results in a significant drop in μ_e to 4.1×10^{-5} cm² V⁻¹ s⁻¹. μ_e further drops to $\approx 2 \times 10^{-5}$ cm² V⁻¹ s⁻¹ for the J71:PNDI-OT10 and J71:PNDI-OT15 blends, corresponding to a nearly six-fold decrease in μ_e compared to J71:PNDI2OD-T2. Because all polymer acceptors here possess quite similar molar mass, the discrepancy in mobility is attributed to differences in molecular packing and crystallinity of polymer acceptors. The incorporation of hydrophobic n-octyl chains in the backbone disrupts the packing leading to larger $\pi - \pi$ stacking distances and increased disorder, which significantly reduces $\mu_{\rm e}$. The hole-only mobilities ($\mu_{\rm h}$) for all blends in comparison are similar at $\approx 2.0 \times 10^{-4}$ to 2.7×10^{-4} cm² V⁻¹ s⁻¹. Thus, only the electron mobility is significantly affected, with the hole mobility of J71 unaffected. The strong reduction in $\mu_{\rm e}$ of the OT-containing acceptors results in more severe $\mu_{\rm h}/$ μ_{e} imbalance, which increases from 2.1 for J71:PNDI2OD-T2 to 12.5 for J71:PNDI-OT10 (with values of over 10 for J71:PNDI-OT15 and J71:PNDI2OD-C8T2). This increase in the mobility ratio is likely to increase bimolecular recombination and reduce J_{SC} and FF due to the fact there is a smaller fraction of charge carriers being able to escape from the bulk and be collected at the corresponding electrodes.^{43,52,53}

Morphology of Blend Films. GIWAXS experiments were employed to probe the microstructure and texture of the blend films. All five blends show similar 2D GIWAXS patterns (Figure S11) with two orders of lamellar stacking along the IP direction and a strong $\pi-\pi$ stacking peak in the OOP direction, indicating a preferential face-on orientation of polymers, which is beneficial for charge transport through

	TEY		PI	EY
blends, top	% donor	% acceptor	% donor	% acceptor
J71:PNDI2OD-T2	19.1 ± 0.4	80.9 ± 0.4	8.7 ± 0.4	91.3 ± 0.4
J71:PNDI-OT5	17.2 ± 0.7	82.8 ± 0.8	11.1 ± 0.4	88.9 ± 0.4
J71:PNDI-OT10	16.9 ± 0.4	83.1 ± 0.4	8.2 ± 0.4	91.8 ± 0.3
J71:PNDI-OT15	18.4 ± 0.4	81.6 ± 0.4	12.1 ± 0.3	87.9 ± 0.3
J71:PNDI2OD-C8T2	19.0 ± 0.3	81.0 ± 0.4	11.2 ± 0.3	88.8 ± 0.3
blends, bottom				
J71:PNDI2OD-T2	36.9 ± 0.5	63.1 ± 0.6	40.9 ± 0.6	59.1 ± 0.6
J71:PNDI-OT5	35.0 ± 0.6	65.0 ± 0.6	42.1 ± 0.8	57.9 ± 0.8
J71:PNDI-OT10	15.0 ± 0.9	85.0 ± 0.9	18.5 ± 0.9	81.5 ± 0.9
J71:PNDI-OT15	35.3 ± 0.6	64.7 ± 0.4	45.2 ± 0.8	54.8 ± 0.8
J71:PNDI2OD-C8T2	6.3 ± 0.8	93.7 ± 0.8	5.3 ± 1.0	94.7 ± 1.0

Table 3. Composition Distribution of Donor and Acceptors at the Top and Bottom Surfaces Extracted from NEXAFS Peak Fit and Fit Uncertainties of Blend Films via TEY and PEY

the vertical direction. Figure 6 shows the 1D line profiles. The (100) alkyl stacking peaks of J71 and the acceptor polymers overlap make it hard to separate the contributions from donor and acceptors. Figure 6c plots values of CCL for the composite (100) peak fitted with a single peak with values ranging from 40 to 45 Å. Given that the CCL of neat J71 is \approx 35 Å, it is likely that the broadness of the composite (100) peak in the blend is due to the presence of J71. An attempt has been made to fit the composite (100) peak by fitting two peaks corresponding to the donor and acceptor. This has been carried out by fixing the peak positions based on the peak values found from the neat films with the fitting parameters, as presented in Table S3. While the peak position of the PNDI2OD-T2 (100) peak at q_{xy} = 0.259 Å⁻¹ is sufficiently removed from that of J71 at q_{xy} = 0.278 \AA^{-1} to enable a reliable separation, the position of the acceptor peak gets closer to that of J71 with increasing OT content and with C8T2 substitution, making the fits less reliable. In particular, the (100) peak of PNDI2OD-C8T2 is at $q_{xv} = 0.270$ Å⁻¹ bringing it very close to that of J71 at $q_{xy} =$ 0.278 Å⁻¹. For J71:PNDI2OD-T2, the fitted CCLs for the donor and acceptor are \approx 41 and 108 Å respectively, indicating that the donor and acceptor crystallites have similar properties in the blend compared to in the neat films. For all other blends, the CCL of the J71 component is \approx 38–41 Å, consistent with what was observed for the neat film. The CCL of the acceptor components is similar to that seen in the neat films, or if anything slightly higher. For J71:PNDI2OD-C8T2, the CCL of the fitted PNDI2OD-C8T2 component is unrealistically low, suggesting that a reliable separation of J71 and PNDI2OD-C8T2 peaks was not possible.

As well as enabling measurement of surface molecular orientation, NEXAFS spectroscopy can also be used to determine the surface composition. Each material has a distinct NEXAFS spectrum, which can be used as a fingerprint for chemical composition determination of the polymer blend by fitting the spectrum of the blend film with a linear combination of neat spectra.^{54,55} All samples had an overall donor/acceptor weight ratio of 2:1 donor/acceptor, giving an expected acceptor concentration of 33% by mass for a homogeneously distributed film. Compositional analysis was performed using spectra acquired at the "magic angle" to negate any orientational effects. The NEXAFS fits (Figures S12–S15) show that there is strong vertical phase separation in the blends, with the results tabulated in Table 3. Using the PEY mode, the top surface is determined to have an acceptor composition of $\approx 90\%$ by mass for all blends, which is much

larger than the expected concentration of 33% by mass. Using the TEY mode, which probes slightly further into the bulk, gives an acceptor concentration of $\approx 80\%$ by mass. This analysis of the top surface demonstrates that there is a depletion of J71 at the top of the film, which may hinder the collection of holes at the top electrode. On other hand, the composition of the substrate/film interface (exposed via delamination) indicates that there is less severe phase segregation as compared to the top surface. On an average, a value of \approx 55% by mass to 60% by the mass acceptor is determined for most blends, with the exception of J71:PNDI-OT10 and J71:PNDI2OD-C8T2. These two blends show higher values of 82% by mass and 95% by mass, respectively, which seem to be out of character with the other samples; however, this could be due to issues associated with clean floating off the films rather than an actual difference in the surface energy of the materials and degree of phase segregation. Overall, all five systems show a similar level of phase separation across the films with the acceptors accumulating near both the cathode and anode sides. Thus, the modification of acceptor structures here is unlikely to result in significant change in the distribution of donor/acceptor sites across the film. In other words, the reduced performance with copolymer acceptors here could not be ascribed to differences in vertical phase segregation.

To investigate the impact of different amounts of the OT unit on surface energy and the interactions between donor and acceptor polymers, contact angle measurements were performed with relevant images, as shown in Figure S16, and the corresponding parameters, as displayed in Table S5. Distilled water and ethylene glycol were used as liquid probes, and the surface energies of these materials were calculated based on the Owen-Wendt method.⁵⁶ The experiments were triplicated, and average contact angles were taken. The OT-containing acceptors generally show smaller contact angles in both solvents. The Flory-Huggins interaction parameters, χ , were then calculated based on the solubility parameters. χ parameterizes the interaction between the polymer donor and acceptor, with a larger value of χ representing a stronger tendency to phase separate.¹⁴ The J71:PNDI2OD-T2 blend showed a slightly smaller γ than that of the blends with OTcontaining acceptors; however, the differences in χ across the five blends is subtle, with a difference of 10% between the value of χ calculated for J71:PNDI2OD-T2 and that calculated for J71:PNDI-OT15. Having larger χ for the blends with OTcontaining acceptors does suggest a poorer miscibility with J71,



Figure 7. (a-e) AFM height images of J71:PNDI2OD-T2, J71:PNDI-OT5, J71:PNDI-OT10, J71:PNDI-OT15, and J71:PNDI2OD-C8T2, respectively, and (f) R-SoXS profiles of blend films.

but it is not clear whether this is enough in itself to produce the strong differences in the phase-separated morphology observed.

To understand the impact of structural modification on morphological evolution, the blend films were further characterized with AFM. The height and phase images of AFM for the five blends are displayed in Figures 7a-e and S17, respectively. The reference J71:PNDI2OD-T2 shows a relatively smooth surface with an average root-mean-square (RMS) roughness of 0.97 nm. With the increasing OT content in the PNDI-OTx copolymers, there is a coarsening of the surface morphology, evidenced by an increase in RMS roughness to 1.19, 1.32, and 2.77 nm corresponding to the J71:PNDI-OT5, J71:PNDI-OT10, and J71:PNDI-OT15 samples, respectively. There is also an apparent coarsening in the lateral length scale of the surface features, as seen with AFM. Intriguingly, the J71:PNDI2OD-C8T2 film exhibited a smaller surface RMS roughness of 2.04 nm and finer lateral features compared to that of J71:PNDI-OT15.

To provide a probe of bulk mesoscale morphology, R-SoXS was utilized to understand the impact of the hydrophobic side chain OT unit on morphology evolution.⁵⁷⁻⁶⁰ R-SoXS experiments were performed as a function of photon energy across the carbon K-edge, with an energy of 286 eV found to maximize scattering intensity and contrast between materials. The R-SoXS profiles are shown in Figure 7f, which plots the measured scattering intensity (rather than the Lorentzcorrected scattering intensity, as shown in Figure S18) as a function of scattering vector, q. The J71:PNDI2OD-T2 shows a relatively featureless scattering profile with a slight bump at q \approx 0.025 nm⁻¹, corresponding to a spatial fluctuation wavelength of ≈250 nm. The J71:PNDI2OD-T2 film is likely to have a large distribution of domain sizes with little evidence for the existence of large-scale phase separation. More welldefined peaks are seen for J71:PNDI-OT5 and J71:PNDI-

OT10, suggesting more pronounced bulk phase separation. From the position of the peaks in these two blends, spatial fluctuation wavelengths of 280 nm (J71:PNDI-OT5) and 370 nm (J71:PNDI-OT10) are evident. This apparent coarsening of the bulk morphology is consistent with what was seen with AFM. For the J71:PNDI-OT15 system, a dramatic coarsening of the morphology is seen with strong scattering at low q, consistent with spatial fluctuations on the length scale of 500 nm to 1 μ m, again consistent with the much larger lateral features seen for this blend with AFM. The J71:PNDI-OT5 and J71:PNDI-OT10. In general, there is good consistency between the R-SoXS and AFM measurements, meaning that the surface features imaged by AFM are likely to be representative of the underlying bulk morphology.

DISCUSSION

The results presented above demonstrate that the incorporation of OT units via copolymerization realizes three new copolymers PNDI-OT5, PNDI-OT10, and PNDI-OT15 with reduced solution aggregation and reduced thin-film crystallinity compared to the reference PNDI2OD-T2. However, this reduced solution aggregation tendency and thin-film crystallinity do not result in improved photovoltaic efficiency in comparison to the reference PNDI2OD-T2. All blends studied exhibited similar degrees of vertical phase segregation, with all films exhibiting enrichment of the acceptor polymer at both top and bottom surfaces, and differences in vertical phase separation can be then ruled out as being an influencing factor. Other characteristics that are likely to contribute to the reduced photovoltaic performance of the J71:PNDI-OTx blends are the lower electron mobilities of the PNDI-OTx polymers and the coarser phase separation of the J71:PNDI-OTx blends. While both charge transport and morphological

factors are likely to influence the lower efficiencies observed, it seems that morphology is playing a particularly important role.

When considering the various factors that influence the degree of phase separation that results, equilibrium and nonequilibrium considerations can be made. From the perspective of equilibrium considerations, Flory-Huggins theory can be applied to predict whether a blend will be stable to phase separation or not. The Flory interaction parameter χ and the molar masses of the polymers are the key parameters determining whether the mixed or demixed state will be the equilibrium state. Polymers that are stable to phase separation are then said to be miscible with a very fine intermixing of donor and acceptor polymers. The morphological studies deduced from AFM and R-SoXS indicate the introduction of OT unit into the backbone induces large-scale phase separation in all-PSCs. The stronger phase separation exhibited by the J71:PNDI-OTx blends suggests a larger "driving force" for phase separation, which was reflected by a larger value of χ for these blends relative to the reference J71:PNDI2OD-T2 system with χ determined from contact angle measurements.

Alternatively, from a kinetic perspective, the spin-coating of semiconductor blends results in non-equilibrium structures due to the rapid evaporation of the solvent, and one should not necessarily expect equilibrium considerations to account for the observed morphology in spin-coating films. The resulting morphology that forms after spin-coating corresponds to the structure that is frozen in when the solvent fully evaporates. The degree of phase separation that results can therefore reflect the time afforded for phase separation to proceed, which is initiated when sufficient solvent has evaporated causing polymer chains to interact, and terminated when sufficient solvent has evaporated such that chains are no longer mobile. Aggregated chains in solution will generally have a smaller radius of gyration, meaning that phase separation will be initiated later in the spin-coating process. Unaggregated chains will have a larger radius of gyration as they adopt a more open coil conformation, meaning that phase separation will be initiated earlier. Thus, for the PNDI-OTx polymers studied here, the systematic increase in the degree of phase separation in blends with J71 may reflect an earlier onset of phase separation during spin-coating due to PNDI-OTx chains becoming less aggregated with increasing x. Such a mechanism is consistent with the previous observation that larger molar mass chains with larger radius of gyration drive coarser phase separation.⁶¹ In any case, the alteration of the backbone to reduce crystallinity was found to inadvertently impact the resulting morphology in a negative way.

Apart from the influence of morphology, the estimated mobilities from the SCLC measurement indicate that the low μ_e of the PNDI-OTx and PNDI2OD-C8T2 polymers is another reason for the poor PCE of cells based on these acceptors. Imbalanced charge carrier mobilities drive bimolecular recombination, meaning that separated charges are unlikely to be collected at the electrodes. The combination of suboptimal morphology with low μ_e will further reduce the efficiency of charge transportation and extraction. Studies reporting enhancement in the photovoltaic performance with copolymer acceptors in all-PSCs demonstrate that though having slightly reduced crystallinity, copolymer acceptors still retain relatively good electron mobility.^{15,19,20,22} Therefore, it is critical to control the molecular packing and crystallinity to tuning miscibility without sacrificing transport properties, thus

achieving an enhanced performance. Thus, effective copolymer acceptors need to preserve a good electron mobility to facilitate the charge transport to mitigate carrier recombination. From a design perspective, incorporation of a third monomer into the backbone must mediate the negative effects of large crystallites while retaining good local charge transport properties. The OT and C8T2 comonomers used here have bulky side chains, with the large steric hindrance expected to negatively impact backbone planarity. In contrast, PNDI-T10, which replaces T2 units with a single thiophene unit without bulky side chains, results in the improved photovoltaic performance. Using thiophene comonomers with varied sidechain lengths could thus be an effective way to fine-tune these effects.

The work presented here highlights the importance of selecting a third monomer unit in random copolymer acceptors that facilitates a favorable degree of mixing between donors and acceptors. Tailoring the domain size of polymer blends to be comparable to exciton diffusion length is therefore a prerequisite for achieving an enhanced performance. Furthermore, though having reduced crystallinity, copolymer acceptors are required to maintain high absorption coefficient and good electron-transporting properties. While the slightly distorted planarity of the OT unit is effective for tuning aggregation and crystallinity, it also had the negative effect of reducing carrier mobility which negatively impacted the device performance. The ability of a copolymer acceptor to affect a favorable morphology while maintaining a good electron mobility are thus key factors identified here for improving the photovoltaic properties.

CONCLUSIONS

In conclusion, a series of four new NDI-based polymer acceptors featuring OT units have been designed and synthesized by DHAP with their photovoltaic properties in all-PSCs investigated. Though having reduced aggregation and crystallinity in comparison to PNDI2OD-T2, the acceptor polymers PNDI-OTx showed worse photovoltaic performance in blends with J71. Morphology characterization revealed that the modification of PNDI2OD-T2 with the OT moiety resulted in coarser phase separation between J71 and PNDI-OTx, as evidenced by larger-scale features observed with both AFM and R-SoXS and higher interaction parameter with J71. Thus, the lower aggregation and crystallinity of the PNDI-OTxacceptor polymers did not help to realize a more favorable morphology. Furthermore, addition of OT units was found to significantly reduce the electron mobility of the resulting polymers, with PNDI-OT15 having an electron mobility six times lower than that of PNDI2OD-T2. The combination of low mobility and inappropriate domain size was identified as being responsible for the decrease in J_{SC} and hence PCE in cells based on the OT-based polymer acceptors. An effective copolymer acceptor thus needs to exhibit enhanced compatibility with the donor polymer to promote a favorable morphology while maintaining a good electron mobility for efficient charge extraction and collection. The insights into the relationship between chemical structure, solution aggregation, and morphology disclosed here will be useful for the future design and synthesis of high-performance all-PSCs toward commercialization of PSCs.

EXPERIMENT METHODS

Device Fabrication. All-PSCs were fabricated with an inverted device geometry with structure of ITO/ZnO/PEIE/active layer/ MoO₃/Ag. Pre-patterned ITO glass slides were cleaned in an ultrasonic bath with acetone and isopropanol consecutively for 10 min, followed by oxygen plasma treatment for another 10 min. After that, the ZnO (0.1 M) precursor was spin-coated onto the cleaned ITO glass substrates at 3000 rpm for 30 s and then annealed at 200 °C for 30 min. PEIE (polyethylenimine ethoxylated) in 2methoxyethanol (0.4% v/v) solution was subsequently deposited on the ZnO layer followed by thermal annealing at 110 °C for 15 min to form a cross-linked hole-blocking layer. The active layer blend solutions were prepared by dissolving J71 and polymer acceptors with the optimized D/A ratio of 2:1 (w/w). The total concentration of (D + A) in CB was 15 mg/mL. No processing additive was used. The active layers were spin-coated on top of the ZnO/PEIE-modified substrates. The final film thickness of cells processed from CB was 90-100 nm. Then, MoO₃ (12 nm) and Ag (100 nm) were thermally deposited on the active layer under high vacuum. The device area was defined as 4.5 mm² via a shadow mask. All devices were encapsulated with glass cover slides using epoxy resin before testing the device performance.

Photovoltaic Characterization. The J-V characteristics of all-PSCs were measured under a solar simulator with 100 mW/cm² irradiance from Photo Emission Tech using a Keithley 2635 source meter. The intensity of simulated sunlight was calibrated with a silicon reference cell with KG3 glass filter. The EQE was measured as a function of wavelength to cross-check the current density. The EQE was measured using light from a tungsten halogen lamp (Newport 250 W QTH) dispersed through a monochromator (Oriel Cornerstone 130). A spot size smaller than the active area was used. The system was calibrated with a reference photodiode prior to the measurement.

SCLC Measurement. Electron-only devices were made with a device configuration of ITO/PEDOT:PSS/Al/active layer/Ca/Al, whereas hole-only devices were made with an architecture of ITO/PEDOT:PSS/active layer/Au. The mobilities were fitted with the Murgatroyd equation⁶²

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp\left(0.89\beta \sqrt{V - \frac{V_{\rm bi}}{d}}\right) \frac{V^2}{d^3} \tag{1}$$

in which J is the current density in the dark, μ_0 is the zero-field carrier mobility, ε_0 is the permittivity of free space, ε_r is the permittivity of the active materials (ε_r was assumed to be 3.5 for all polymers in this work), β is the field activation factor, d is the film thickness, V is the applied bias, and $V_{\rm bi}$ is the build-in potential. Values for μ_0 and β were extracted from the fit.

Temperature-Dependent UV–vis Measurement. UV–vis solution spectra were recorded using a Deuterium-Halogen DH-2000-CAL light source (Ocean Optics) and a USB4000 spectrometer (Flame-S-VIS-NIR-ES from Ocean Optics). The temperature of the cuvette was controlled with a Quantum Northwest qpod in combination with a TC1 temperature controller. The solution temperature was adjusted from 30 to 130 °C for CB. Before each measurement, the solution temperature was held for 2 min at targeted temperature to reach the thermal equilibrium.

AFM Measurement. Films were prepared under optimized conditions with active layers deposited on top of PEIE-modified glass substrates. AFM experiments were performed on a PicoPlus atomic force microscope (Agilent 5500 SPM) at the Melbourne Centre for Nanofabrication.

Grazing Incidence Wide-Angle X-ray Scattering. GIWAXS measurements were conducted at the SAXS/WAXS beamline at the Australia Synchrotron.⁶³ 15 keV photons were incident at a grazing angle of $0.8-0.15^{\circ}$ with images taken at the critical angle identified by the angle which maximized the scattering intensity from samples. X-ray scattering was recorded using an in-vacuum Dectris Pilatus 2 M detector. The sample-to-detector distance was calibrated with a silver behenate sample. The data were analyzed using a modified Nika

software package in IgorPro 8.38.⁶⁴ Lorentzian multi-peak fitting was used to calculate the peak positions and full width at half-maximum (Δq) . CCL was calculated from the following formula where K is a shape factor (K was set to 0.9 in this work)⁶⁵

$$CCL = \frac{2\pi K}{\Delta q}$$
(2)

NEXAFS Spectroscopy. NEXAFS measurements were performed at the soft X-ray spectroscopy beamline at the Australia Synchrotron.⁶⁶ All samples were spin-coated on pre-cleaned Si wafer substrates. Average tilt angles were determined by measuring angledependent NEXAFS spectra and fitting to the following equation⁴⁹

$$I = \frac{1}{3} \left[1 + \frac{1}{2} 3(\cos^2 \theta - 1)(3(\cos^2 \alpha - 1)) \right]$$
(3)

where I is the resonance intensity, θ is the X-ray incidence angle, and $\langle \alpha \rangle$ is the average tilt angle of the C 1s to π^* transition dipole moment. Data were analyzed with the assistance of QANT software.⁶⁷

Resonant Soft X-ray Scattering. The R-SoXS transmission measurements were performed at the National Institute of Standards and Technology Spectroscopy Soft and Tender (SST-1) beamline of the National Synchrotron Light Source II.⁶⁸ Samples were prepared on PEIE-modified Si substrates using the same conditions as those used for device fabrication. Samples were floated off in deionized water and transferred to 1.5 mm × 1.5 mm silicon nitride membranes supported by a 5 mm × 5 mm Si frame (Norcada, Inc.). Samples were measured under vacuum with scattering recorded on a 2D CCD camera (Greateyes). The 2D R-SoXS patterns were reduced to 1D line profiles using a customized Nika package implemented in IgorPro 8.38. Scattering was measured at two sample-to-detector positions, with the low-q (SAXS region) and high-q data (WAXS).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c01822.

Synthetic procedure of monomers and polymers; ¹H and ¹³C NMR spectra; temperature-dependent UV-vis spectra; cyclic voltammetry; GIWAXS measurements and analysis; angle-resolved NEXAFS spectra of neat films and NEXAFS spectra fit of blends; contact angle measurements; charge carrier mobility measurements; AFM phase images; and Lorentz-corrected R-SoXS profiles (PDF)

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Notes

The authors declare no competing financial interest.

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