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ABSTRACT. Since being introduced to the open literature in 2010, the isoindigo heterocycle has been extensively studied as a novel electron deficient building block for organic electronic materials in conjugated polymers, discrete length oligomers, and molecular systems, particularly targeting high charge mobility values and ambipolar transport in organic field effect transistors, along with high power conversion efficiencies in organic photovoltaic devices. This article introduces results obtained on copolymers of isoindigo with thiophene and alkylated terthiophenes to highlight fundamental characteristics in isoindigo-based polymers and the resulting organic field-effect transistors and photovoltaic devices. By comparing and contrasting the optoelectronic properties, thin film morphology, organic field-effect transistor (OFET) mobilities, and organic photovoltaic (OPV) performance to previously reported polymers, structure-processing-property relationships were uncovered. In particular, isoindigo-containing polymers with more rigid backbones and higher coherence lengths in thin-films lead to increased charge mobility in OFET devices. In OPV devices, efficiencies over 6% can be obtained by balancing high ionization potentials typically dictating the open-circuit voltage, and the charge transfer state energy and blend morphology impacting short-circuit currents. Furthermore, the impact of polymer structure on solubility and on phase separation in blends with PC$_{71}$BM is discussed, with isoindigo-based polymers exhibiting lower solubility possibly leading to more fiber-like morphologies due to both kinetic and thermodynamic effects, either stemming from
polymer dissolution in the casting solvent or from polymer self-assembly during film formation. This fiber-like polymer morphology remains unaffected by the presence of processing additives, such as 1,8-diiodooctane. These structure-property relationships developed for isoindigo-based polymers can also be discussed in the broader context of diketopyrrolopyrrole (DPP) and thienoisoiindigo (Til) as electron-deficient moieties that can also be doubly substituted on their amide functionality.

INTRODUCTION. π-Conjugated polymers have been successfully used in solution processed organic field-effect transistors (OFETs) and organic photovoltaic (OPV) devices, with FET measured hole mobilities\textsuperscript{1, 2} on the order of 10 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} and electron mobilities\textsuperscript{3, 4} ranging from 0.1 to 1.0 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1},\textsuperscript{5} while solar cells have attained AM 1.5 power conversion efficiencies (PCEs) in excess of 9.2%,\textsuperscript{6-11} and 10.5% in tandem cells.\textsuperscript{12} In examining this field of materials, similar polymer structures do not translate from one application to another, but rather need to be designed to fulfill application specific requirements. In materials designed for OFETs for instance, there is a need to combine (i) solution processability, (ii) high charge carrier transport, and (iii) ambient air stability. On the other hand, materials for OPVs may not require record-high carrier mobilities to perform well, but they also need (iv) broad optical absorption profiles and high extinction coefficients, as well as (v) appropriate energy levels for charge separation. Moreover, the solid state order in OFETs,\textsuperscript{13-16} and phase separation in OPVs are crucial components towards high performing devices.\textsuperscript{17}

Donor-acceptor (D-A) polymers have been developed using electron accepting units such as 1,3,2-benzothiadiazole (BTD), thienopyrrolodione (TPD) or diketopyrrolopyrrole (DPP) to yield
tunable optoelectronic properties. Recently, the electron deficient isoindigo (il) unit has shown promise as an electron acceptor in both OFETs and OPV materials, thanks to its high yielding synthetic access, two amide functionalities for dual substitution to ensure polymer solubility, large absorption coefficients and to the suitable electron affinity of the isoindigo polymers to be used in fullerene-based OPV devices.\textsuperscript{18} The il moiety was first reported in a CIBA patent,\textsuperscript{19} and subsequently introduced into the open literature by Reynolds \textit{et al.}\textsuperscript{20} Since then il-based polymers have demonstrated FET hole mobilities\textsuperscript{21, 22} up to 3 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} thanks to side-chain engineering using longer spacers to direct branching points away from the polymer backbone, as was also reported for other D-A polymers.\textsuperscript{23} In OPV devices, efficiencies\textsuperscript{24-27} of 7.0\% were reached using polymer structures based on thienylene-phenylene linkages by tuning the energy of the frontier molecular orbitals to achieve a balance between a deep electron affinity for efficient light absorption, charge transfer and charge separation for high short-circuit current ($J_{sc}$), and a deep ionization potential for a high open-circuit voltage ($V_{oc}$).\textsuperscript{28} Isoindigo is an attractive unit for organic electronics as it possesses two amide groups that can be functionalized, similar to DPP, but in contrast with BTD derivatives, which do not have similar groups for substitution, and TPD units, which only have one handle for substitution. The possibility of functionalizing the il core with solubilizing alkyl, oligoether or siloxane-terminated chains provides the opportunity to tune optoelectronic and morphological properties, as is the case for DPP or thienoisoiindigo (Til) units.\textsuperscript{23}

Based on previous literature on il-based polymers, six fundamental principles are made evident in these systems with the goal of understanding the correlation between polymer structure, solid-state morphology, and device properties. While this paper, and the analysis listed below, is
directed to the study of il-based polymers specifically, similar concepts can be drawn to other bi-
substituted acceptors like DPP and TiI:

- The electron affinity remains around 3.9 eV, as the electronic density in the LUMO is located on the isoindigo core, while the ionization potential can be tuned by the donor moiety.  

- Control of the ionization potential leads to tunable open-circuit voltages in OPV devices, ranging from 0.6 V to 0.9 V depending on the donor selected, correlating well with the effective band gap, i.e. excitation from the ground state of the donor to the excited state of the acceptor.

- The packing and orientation of the polymer chains can be influenced both by strong interchain interactions made possible by the rigidity of the isoindigo core compared to phenylene-flanked DPP, and by the side chain choice.

- Isoindigo-based polymers can lead to ambipolar transport, and high transport characteristics (up to 3.6 cm² V⁻¹ s⁻¹ hole mobility, and 0.7 cm² V⁻¹ s⁻¹ electron mobility in chlorinated isoindigo polymers). An increase in mobility values is not necessarily correlated to a decrease in π-stacking distances, and identical characteristic distances can lead to different mobilities if the morphology is different.

- Polymer solubility can be tuned through the side-chain density along the polymer backbone as well as through the nature of the side-chains. Furthermore, phase separation between polymer and fullerene in the solid-state is dictated by polymer solubility in the processing solvent, and phase separation is not as drastically modified by
the use of processing additives when polymers exhibit low solubility (<2 mg/mL in ortho-dichlorobenzene).

- In bulk heterojunctions with PCBM derivatives, polymer-rich domain sizes on the order of tens of nanometers surrounded by mixed regions of polymer and fullerene can be achieved through structural design and processing control.\textsuperscript{37} When coupled to low resistance in OPV devices this leads to high short-circuit currents and fill factors.

While these principles have been applied to different structures very rarely are they considered together. To illustrate these concepts, and in particular highlight the donor-acceptor effects on frontier energy levels and the impact of side-chains on polymer packing and morphology, we designed a family of three oligothiophene-isoindigo polymers with varying ratios of electron deficient il units along the backbone, and variations in the solubilizing side-chain as shown in Chart 1. The energy levels of the frontier molecular orbitals of an all-thiophene backbone are modulated by the content of isoindigo units along the conjugated backbone to shift the absorption to longer wavelengths going from P[T-il(HD)] to P[T3(C6)-il(HD)]. Furthermore, while keeping the conjugated repeat unit constant and following on the work of Bao and co-workers,\textsuperscript{22, 38} we designed P[T3(C6)-il(SiO)] to investigate the effect of the substitution pattern on solid state order, transport properties and phase separation.
In this contribution, three new isoindigo polymers are studied in OFET and OPV devices, and their behavior is compared and contrasted with previously published isoindigo-based polymers described in Chart 1. These comparative results are used to elucidate a set of guidelines for molecular design principles for isoindigo containing polymers in organic electronic applications. The structures discussed investigate the impact of electron-richness along the P[Tn-il] backbone on optoelectronic properties, as the electron-rich co-monomer is extended from P[T-il] (black), to P[T2-il] (orange), P[DTS-il] (brown), P[T3-il] (blue) and P[T6-il] (green). With the repeat unit kept constant, the side-chains on P[Tn(R)-il(R)] can also be modified to induce changes in
the polymer packing and optoelectronic properties. This study makes detailed comparison of optoelectronic structure-property relationships to work published on P[T-il(OD)] from Zhang et al., P[T-il(HD)], P[T3(C8)-il(HD)], and P[T6(C8)-il(HD)] from Ma, Wang et al. and Ho et al., P[T2-il(OD)] and P[T2-il(SiO)] from Mei, Kim et al., P[T-il(OD)], P[T2-il(OD)] and P[T2-il(4-DTd)] from Lei et al., and P[DTS(EH)-il(EH)] from Stalder et al. Grazing incidence wide angle X-ray scattering (GIWAXS) is used to emphasize the role of microscopic order and backbone orientation on charge transport in OFETs. Density functional theory (DFT) calculations, along with electrochemical results and charge-modulated electroabsorption spectroscopy (CMEAS) measurements, were used to understand the charge separation process and ultimately the open-circuit voltage in OPV devices. Furthermore, AFM and neutron reflectivity were used to study the lateral and vertical phase separation in the active layer blends with fullerene derivatives to explain variation in J_{sc} and fill factor (FF) in OPV devices.

RESULTS AND DISCUSSION

Polymer synthesis. Isoindigo-based polymers have typically been synthesized using Suzuki and Stille polycondensations. The synthesis of P[T-il(HD)]-4 was previously reported, and P[T3(C6)-il(HD)]-2 and P[T3(C6)-il(SiO)] were synthesized by Stille polymerization as described in Scheme S1. We aimed to increase ordering of P[T3-il] polymers by using n-hexyl chains on the terthiophene unit rather than the n-octyl chains used previously to investigate the impact of alkyl side-chain length on polymer packing for OFET applications, along with examining the effect on phase separation with fullerenes in bulk heterojunction (BHJ) OPV
devices. By moving the branching point of the 2-hexyldecyl side chain further away from the backbone using siloxane side chains, as demonstrated by Mei et al., the impact of polymer orientation on its interaction with fullerenes can be determined. The number average molecular weight for these three polymers was estimated by gel permeation chromatography (GPC) in tetrahydrofuran (THF) and correlates with a degree of polymerization (DP) of 34, 16, and 25 (i.e. 102, 80, and 125 aromatic rings) for P[T-il(HD)]-4, P[T3(C6)-il(HD)]-2 and P[T3(C6)-il(SiO)], respectively (see Table 1: entries 6, 14 and 19, and SI). The three polymers also have comparable indices of polydispersity in THF (2.1, 3.7, and 2.2, respectively). Important for comparison, these macromolecules are similar in size and have reached a point where saturation of their optoelectronic properties is ensured. In particular, the use of branched side chains on the isoindigo unit for these polymers ensures solubility during polymerization, and prevents precipitation at lower molecular weights during polymerization. Furthermore, all three polymers structures were synthesized to have thienyl end-groups; however, the presence of controlled end-cappers was not confirmed experimentally.

**Theoretical Electronic and Structural Analysis.** Estrada et al. have previously demonstrated good correlation between HOMO and LUMO energy levels calculated by density functional theory (DFT) at the B3LYP/6-31G(d) level and electrochemically determined ionization potential and electron affinity. As such, DFT calculations at the B3LYP/6-31G(d) level were carried out on model structures of P[T-il] and P[T3-il] (where side chains have been replaced by methyl groups) to investigate shifts in the energy of the frontier molecular orbitals as a function of the electron-rich oligothiophene co-monomers. As expected, the less electron-rich T-il motif has a deeper calculated HOMO level at -4.72 eV compared to -4.97 eV for T3-il. This 0.25 eV difference in HOMO level energy is expected to be reflected in the open circuit voltage (Voc) of
OPV devices with polymers based on a T-il repeat unit having an increased $V_{oc}$ compared to T3-il polymers. In both T-il and T3-il, the HOMO is highly delocalized along the polymer chain, whereas the LUMO is mostly localized on the isoindigo unit as demonstrated by the T3-il dimer in Figure 1. The optimized ground state geometry in these model compounds shows a break in conjugation in the LUMO of P[T3-il], with electron density located over a single isoindigo unit and extending slightly over the neighboring thiophene rings. In P[T-il] systems, the electron density in the LUMO is spread continuously over two isoindigo cores bridged by a thiophene ring as seen in Figure S1, which would modify the intrachain transport of electrons and possibly their interchain hopping characteristics. Similar DFT results for T-il oligomers have been obtained by De Angelis et al., where the calculated HOMO and LUMO levels (in vacuum) are within 30 meV of those found in this work, despite a different conformation used for modeling of T-il oligomers.

![Figure 1](image)

**Figure 1.** Isodensity surfaces (0.04 e/bohr$^3$) of the frontier orbitals a T3-il dimer calculated at the B3LYP/6-31G(d) level: (a) LUMO and (b) HOMO (adapted from 49).

**Electrochemically Determined Energy Levels, and Optical Properties.** To verify the trends observed in the energy levels of the frontier molecular orbitals, electrochemical measurements of the oxidation and reduction potentials were conducted against a ferrocenium/ferrocene (Fc$^+$/Fc) standard to estimate the ionization potential and electron affinity of the polymers. Based on
measurements of the formal potential for $\text{Fc}^+/\text{Fc}$ at 0.4 V versus a saturated calomel electrode (SCE) in acetonitrile, and of -4.5 eV being equivalent to 0.0 V versus a normal hydrogen electrode (NHE) (with SCE at +0.2 V versus NHE). The formal potential of $\text{Fc}^+/\text{Fc}$ is taken to be -5.1 eV versus vacuum, which was highlighted by Cardona et al. Differential pulse voltammetry (DPV) measurements on polymer thin films on platinum electrodes in 0.1 M TBAPF$_6$ in acetonitrile estimated the electron affinity (EA) of the three polymers to be between 3.9 and 3.94 eV. The values match previous reports of the EA of donor-isoindigo-donor structures being around 3.7 eV and 3.8 eV, and are in agreement with the EA for other il copolymers listed in Table 1. The ionization potential (IP) of these structures was estimated from the onset of oxidation. The IP was calculated to be 5.59 eV, 5.57 eV and 5.43 eV for $\text{P[T-}\text{il(HD)}\text{-4}}, \text{P[T3(C6)-il(HD)]-2}$ and $\text{P[T3(C6)-il(SiO)]}$, respectively (entries 6, 14 and 20 in Table 1). Previously reported values for the HOMO energy level demonstrate that the measured IP varies with the technique used, with IP of $\text{P[T2-il(OD)]}$ (entry 9) measured at 5.5 eV using UV-PES and 6.0 eV using cyclic voltammetry with ferrocene oxidation at -5.1 eV against vacuum. In order to support the IP estimated from DPV measurements, UV-PES was also conducted on thin-films of $\text{P[T-il(HD)]-4}$ and $\text{P[T3(C6)-il(HD)]-2}$. The IP was found to be around 5.2 eV and 5.3 eV in films of $\text{P[T-il(HD)]-4}$ and $\text{P[T3(C6)-il(HD)]-2}$ respectively, again highlighting a 0.4-0.3 eV difference between the IP estimated by DPV relative to the IP measured by UV-PES. Furthermore, the electron affinity of these polymers is estimated to be between 3.8 eV and 4.1 eV as expected based on previous DFT calculations, where the calculated electron density in the LUMO was primarily localized on the il unit within model compounds. The IP fluctuated over a broader energy range (5.3 eV to 6.1 eV) based on the
electronic nature of the donor moiety, where il-based polymers with more electron-rich thiophene units tend to exhibit lower IP’s.

As observed in Figure 2, the absorption spectra of all three isoindigo polymers show a broad coverage of the visible region, from 400 to 800 nm with absorption maxima around 650 nm. There are only minor differences observed between the solution and solid-state spectra, where often times in conjugated polymers a substantial red-shift is observed in the solid state spectra compared to the spectra in solution. We attribute this to minimal changes in polymer conformation upon solidification, as both planarization of the polymer chains and interchain interactions in the solid state lead to a red-shift of the low energy absorption peak or to the appearance of a low energy shoulder in the UV-vis spectrum as discussed by Kim and Swager. Broader UV-vis spectra with a low energy aggregation shoulder are observed for films of P[T3(C6)-il(HD)]-2 and P[T3(C6)-il(SiO)] compared to solution, suggesting an increase in the intermolecular interactions between neighboring polymer chains in the solid state compared to solution state. This low energy shoulder is not observed in the case of P[T-il(HD)]-4 compared to solution, suggesting a more amorphous arrangement of the polymer backbones in thin films. This decrease in thin film order for P[T-il(HD)]-4 is hypothesized to be linked to the higher density of branched alkyl chains along the backbone, decreasing the extent of interchain interactions. This discussion based on UV-vis-NIR results is also supported by 2D-NMR spectroscopy and X-ray scattering data (vide infra). Making comparisons of the many il-based polymers reported, all of the entries in Table 1 have an onset of absorption between 1.50 eV and 1.62 eV, likely due to the similar electronic nature of the thiophene-based donors along the backbone, also described by Stalder et al. Figure 2 also highlights that the solution and solid-
state absorption of these oligothiophene-co-il polymers exhibit two main absorption bands, which span the visible region of the spectrum to yield blue-green colored polymers.

Table 1. Size exclusion chromatography (SEC), Redox, and Optical Properties of the Isoindigo Copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>SEC Mn (kDa)</th>
<th>PDI</th>
<th>$E_{\text{max}}$ (eV)</th>
<th>$E_{\text{max}}$ (eV)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P[T-il(OD)]-1</td>
<td>20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.0</td>
<td>1.76</td>
<td>1.76</td>
<td>1.55</td>
<td>6.1</td>
<td>4.10</td>
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</tr>
<tr>
<td>2</td>
<td>P[T-il(OD)]-2</td>
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<td>1.78</td>
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<td></td>
<td></td>
<td>5.72</td>
<td>4.00</td>
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<td>1.79</td>
<td>1.79</td>
<td>1.62</td>
<td>5.59/5.21</td>
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Reflecting on the spectroscopic properties of the full set of iI-based polymers in Table 1, it is seen that isoindigo P[Tn-iI] copolymers show an aggregation shoulder in thin films for n>3 although broadening of the absorption spectra is seen for all the isoindigo polymers listed. Even in P[T2-iI(SiO)] and P[T2-iI(4-DTd)] films, where the branching point on the side chain is moved away from the backbone, no aggregation shoulder is observed in the thin film absorption spectra. As such, based on the UV-vis spectra alone, it would seem that polymers with a lower density of branched side chains exhibit stronger interchain interactions, to be correlated to 2D-NMR and X-ray scattering results.

We recently reported the use of solid-state 2D-NMR spectroscopy to probe the correlation between branched side chain density and interchain interactions. The 2D 13C{1H} FSLG-HETCOR NMR correlation spectra of powder samples of P[T-ii(HD)]-4 and P[T3(C6)-ii(HD)]-1 were compared, effectively allowing us to visualize which protons of the branched side chains contacted strongly with which carbon of the neighboring polymer backbones. From the 2D solid-state NMR data alone, the higher branched side chain density for P[T-ii(HD)]-4 correlated with greater overlap of neighboring isoindigo units in the bulk compared to P[T3(C6)-ii(HD)]-1, for

<table>
<thead>
<tr>
<th></th>
<th>P[T6(C8)-iI(HD)]-1</th>
<th></th>
<th>P[T6(C8)-iI(HD)]-2</th>
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<tr>
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<tr>
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<td>67</td>
<td>1.52 5.44 3.91 1.53</td>
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<tr>
<td>21</td>
<td></td>
<td>35</td>
<td>1.8 2.00 1.96 1.57 5.37 3.80 1.57</td>
</tr>
</tbody>
</table>

Results from this work are highlighted in red. SEC performed in: \(^a\)THF, \(^b\)1,2,4-trichlorobenzene, \(^c\)oCB, all versus polystyrene standards, \(^d\)Absorption maxima in solution and thin film, \(^e\)ionization potential and electron affinity estimated from CV or DPV homogenized using \(E_{IP(EA)} = 5.1 + E^{onset_{ox(red)}} \text{vs} \text{Fc}^+/\text{Fc} \); \(^f\)HOMO determined by UV-PES. Values in italic obtained from spectra.
which the 2D NMR spectra suggested stronger intermixing of the isoindigo and terthiophene portions of the polymer backbone. Given the steric hindrance arising from side chain functionalization in conjugated polymers, this is consistent with a lower density of branched side chain affording greater interchain interaction, as seen from the UV-vis data in Figure 2.

**Figure 2.** Normalized UV-vis spectra of P[T-il(HD)]=4 (black), P[T3(C6)-il(HD)]-2 (red), and P[T3(C6)-il(SiO)] (blue) in chloroform solution (top) and thin film (bottom).

**Pristine Polymer Thin Film GIWAXS Characterization.** To investigate polymer packing and the interchain interactions mentioned above, grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed on thin films prepared by spin-coating from ortho-dichlorobenzene (oDCB) solutions onto silicon wafers with a layer of silicon oxide at the surface. The samples were measured both as-cast and dried at room temperature (GIWAXS measurements made approximately 7 days after preparation) and after annealing at 200 °C (see Figure 3). Indexing of the scattering peaks was related to the polymer packing structure, with (100) planes correlating to lamellar stacking and (010) planes to π-stacking. The interplane
distances were then calculated using the Bragg condition: \( d = \frac{2\pi}{Q_{hkl}} \). After integration over a quadrant of the detector, line shape analysis was conducted using Gaussian functions to fit the scattering peaks – the peak positions are attributed to the (hkl) scattering planes and the full widths at half maximum (FWHM) give indications on the coherence length (CL) calculated by Scherrer analysis.

Pristine polymer thin films exhibit varying \( \pi \)-stacking distances ranging from 3.6 Å for P[T3(C6)-il(SiO)] to 3.8 Å for P[T-il(HD)]-4, and P[T3(C6)-il(HD)]-2 has an ordered structure with a characteristic distance of 4.1 Å that cannot be attributed to \( \pi \)-stacking (Figure 3a-c). This corroborates what is observed from thin film absorbance measurements with P[T3(C6)-il(SiO)] showing the largest red shift among the three polymers. The lack of clear \( \pi \)-stacking scattering and the larger characteristic distance for P[T3(C6)-il(HD)]-2 can be explained by increased rotational freedom in the terthiophene unit containing alkyl chains, compared to a single thiophene unit in P[T-il(HD)]-4. The lamellar distance determined from the position of the (100) peak is similar in films of P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-2, around 18 Å, but increases to 25 Å in films of P[T3(C6)-il(SiO)], possibly due to the longer Si-O-Si distance compared to C-C-C distance (3.1 Å vs. 2.5 Å, respectively) leading to an overall side chain maximum length of around 11 Å and 13 Å in the case of 2-hexyldecyl and siloxane side chains respectively. These values for \( \pi \)-stacking and lamellar distances are close to previous results obtained on oligothiophene-isoindigo polymers. Prior to thermal annealing, the polymer films exhibit different backbone orientations relative to the substrate. P[T-il(HD)]-4 and P[T3(C6)-il(SiO)] both exhibit (100) lamellar peaks along the \( Q_{xy} \) axis (in-plane) and consequently a (010) \( \pi \)-stacking peak along the \( Q_z \) axis (polymer backbone mainly face-on relative to the substrate). By comparison, P[T3(C6)-il(HD)]-2 has its (100) peak along the \( Q_z \) axis, and a scattering peak at a
30° angle from the $Q_{xy}$ axis indicating the presence of scattering layers predominantly tilted towards, and not edge-on to, the substrate.

**Figure 3.** GIWAXS patterns of pristine (top) and thermally annealed (bottom) P[T-il(HD)]-4 (a,d), P[T3(C6)-il(HD)]-2 (b,e) and P[T3(C6)-il(SiO)] (c,f) thin films prepared from oDCB. Figures a-e use the same 5,000 intensity scale bar; for optimal data visualization. Figure f uses the 10,000 intensity scale bar to visualize lower intensity peaks before annealing, without saturating the scattering intensity after annealing.

The difference in orientation is made even more visible after thermal annealing at 200°C for 5 minutes as shown in Figure 3d-f. In particular in the case of P[T3(C6)-il(HD)]-2 films, the scattering peak at 30° off from the $Q_{xy}$ axis (Figure 3b, arrow) disappears, and two new peaks
appear along the \( Q_{xy} \) axis after thermal annealing (Figure 3e, arrow). The outermost peak is attributed to \( \pi \)-stacking of 3.7 Å indicating that the polymer backbones become primarily edge-on with regards to the substrate after thermal annealing (Table 2, entry 11). The second peak along the \( Q_{xy} \) axis corresponds to a spacing of 4.2 Å, possibly resulting from a rearrangement of the scattering of scattering peak at 30° off from the \( Q_{xy} \) axis. Furthermore, the \( \pi \)-stacking distance remains at 3.8 Å and 3.6 Å in \( \text{P[T-il(HD)]-4} \) and \( \text{P[T3(C6)-il(SiO)]} \) respectively (Table 2: entries 3 and 13 respectively). Thermal annealing also enables a higher degree of order to be reached in these systems as shown by the higher order scattering peaks in \( \text{P[T-il(HD)]-4} \) and \( \text{P[T3(C6)-il(HD)]-2} \), and the increase in scattering intensity in films of \( \text{P[T3(C6)-il(SiO)]} \) (Figures 3f uses a different intensity scale than 3e to prevent saturation of the scattering intensity in the figure). In order to quantify order in the \( \pi \)-stacking direction, Scherrer analysis was used to calculate CL based on the (010) peak. Interestingly, after thermal annealing the CL of the three polymers is comparable (around 9-10 nm), corresponding to approximately 20-30 polymer backbones involved in \( \pi \)-stacks. These numbers are on par with previously reported CL for (010) peaks for \( \text{P[T2-il(OD)]-2} \) (entry 5), and slightly lower than the length of \( \text{P[T2-il(SiO)]} \) (entry 8), which includes 38 backbones within a \( \pi \)-stack, and higher than \( \text{P[T3(C8)-il(HD)]-3} \) (entry 12), which includes 8 backbones within a \( \pi \)-stack.
Table 2. Summary of structural characteristics of thermally annealed thin film via GIWAXS, and OFET device data for the isoindigo polymer series.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Thin-Film Morphology</th>
<th>OFET Devices</th>
<th>Ref</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Lamellar Distance (Å)</td>
<td>π-Stacking (Å)</td>
<td>Backbone Orientation</td>
</tr>
<tr>
<td>1</td>
<td>P[T-il(OD)]-1</td>
<td>22, weak</td>
<td>Relatively Amorphous</td>
<td>BG/TC, OTS treated&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>P[T-il(HD)]-3</td>
<td>20</td>
<td>3.7</td>
<td>Face-on</td>
</tr>
<tr>
<td>3</td>
<td>P[T-il(HD)]-4</td>
<td>20</td>
<td>3.8</td>
<td>Face-on</td>
</tr>
<tr>
<td>4</td>
<td>P[T2-il(OD)]-1</td>
<td>20</td>
<td>3.8</td>
<td>Edge-on</td>
</tr>
<tr>
<td>5</td>
<td>P[T2-il(OD)]-2</td>
<td>20</td>
<td>3.8</td>
<td>Edge-on</td>
</tr>
<tr>
<td>6</td>
<td>P[T2-il(OD)]-3</td>
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</tr>
<tr>
<td>7</td>
<td>P[T2-il(4-DTd)]</td>
<td>25</td>
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<td>8</td>
<td>P[T2-il(SiO)]</td>
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<td>9</td>
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</tr>
<tr>
<td>11</td>
<td>P[T3(C6)-il(HD)]-2</td>
<td>18</td>
<td>3.7</td>
<td>Edge-on&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>OT-treated with OTS.
<sup>b</sup>Bulk deposited on the glass.
<sup>c</sup>HMDS treated.
<sup>d</sup>Bulk deposited on the glass.
<sup>e</sup>Treated with OTS.
<sup>f</sup>Face-on on BG/TC.
In developing a perspective on these results, trends can be established for this series of copolymers based on results detailed in Table 2. A first observation is the impact of processing conditions on the GIWAXS pattern of some polymers. Indeed films of P[T3(C6)-il(HD)] processed by drop-casting from a chloroform solution tend to exhibit a (100) lamellar peak along the Q\textsubscript{xy} axis (entry 10), whereas films spin coated from oDCB exhibit a (100) peak along the Q\textsubscript{z} axis (entry 11). By comparison, P[T-il(HD)]-4 exhibits a (100) along the Q\textsubscript{xy} axis, regardless of the processing conditions. As such, care needs to be made in comparing results between different studies where structural (repeat unit, degree of polymerization, dispersity, end group identity, branching, etc.), primary processing (solvent, temperature, substrate, time), and post-processing (solvent and thermal annealing, use of additives, etc.) all need to be carefully accounted for. Considering this, a second observation from these results is the lack of correlation between

<table>
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<th>Copolymer</th>
<th>Edge-on</th>
<th>Edge-on</th>
<th>BG/TC\textsuperscript{b}</th>
<th>3\times10^{-2}</th>
<th>5\times10^{-3}</th>
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<tr>
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<td>21</td>
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<td></td>
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<tr>
<td>13</td>
<td>P[T3(C6)-il(SiO)]</td>
<td>25</td>
<td>3.6</td>
<td>Face-on</td>
<td>BG/BC, HMDS treated\textsuperscript{c}</td>
<td>4\times10^{-3}</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>P[T6(C8)-il(HD)]</td>
<td>19</td>
<td>3.7</td>
<td>Edge-on</td>
<td>BG/TC\textsuperscript{b}</td>
<td>7\times10^{-3}</td>
<td>2\times10^{-4}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}spin coated from chloroform, annealed at 150°C for 20 min; \textsuperscript{b}spin coated from chloroform, annealed at 170°C for one hour; \textsuperscript{c}drop cast from chloroform, annealed at 150°C for one hour; \textsuperscript{d}spin coated from tetrachloroethane, annealed at 150°C for 30 min; \textsuperscript{e}spin coated from tetrachloroethane, annealed at 175°C for 30 min; \textsuperscript{f}spin coated from o-dichlorobenzene, annealed at 200°C for 5 min. All source/drain contacts are gold. BG: bottom-gate; TC: top-contact; BC: bottom-contact; CL: coherence length for (010) peak; NR: not reported.
molecular weight and packing in the case of P[T-il(HD)] and P[T2-il(OD)], where variations in molecular weight do not influence the π-stacking or lamellar distances (entries 2 and 3, and 4-6). In addition to molecular weight, polydispersity and the identity of end-capping groups are also expected to impact the scattering results as discussed by Koldemir et al.\textsuperscript{58} However, the challenges associated with characterization of the identity of the end-groups and the lack of reported data on the synthetic addition of end-cappers prevents a discussion on the effect of end-groups on polymer ordering in thin films in this article. A third observation is that interchain packing is not influenced by the number of thiophene rings in the backbone, but rather by the distance between the backbone and branching point on the solubilizing side-chain, with both siloxane-containing polymers P[T2-il(SiO)] and P[T3(C6)-il(SiO)] exhibiting a π-stacking distance of 3.6 Å (entries 8 and 13). Another noticeable change between the P[T3(C6)-il(HD)]-2 and P[T3(C6)-il(SiO)] thin film structures (Figure 3b and c) is their orientation relative to the substrate, which was also observed in the case of P[T2-il] by Bao et al.\textsuperscript{22, 38} Indeed, P[T3(C6)-il(SiO)] chains are mainly face-on ((010) π-stacking out-of-plane peak along Q\textsubscript{z} axis and (100) lamellar scattering in-plane peak along the Q\textsubscript{xy} axis), whereas after annealing the P[T3(C6)-il(HD)] backbones are predominantly edge-on with regards to the substrate. It was hypothesized by Chen et al.\textsuperscript{31} that highly soluble, planar isoindigo-like polymers lead to a majority of the chains being face-on ((100) lamellar in-plane scattering), which can explain why the more soluble, less sterically hindered P[T3(C6)-il(SiO)] shows predominantly face-on orientation compared to P[T3(C6)-il(HD)]-2. Another explanation for the face-on orientation of P[T3(C6)-il(SiO)] could be the amphiphilic-like effect of the siloxane and alkyl side-chains. As illustrated by Kim and Swager,\textsuperscript{55} it is possible that the siloxane side-chains on either side of the isoindigo units interact preferentially with the SiO\textsubscript{2} surface, while the alkyl side-chains on the terthiophene
units are elongated perpendicular to the substrate, leaving the polymer backbone to be face-on with regards to the substrate. This initial layer of face-on polymer backbone can further act as a template for the growth of subsequent polymer layers into a face-on arrangement. The different orientations are expected to affect the charge transport properties of the pristine polymers.

**Charge Transport.** Solid state structure of thin conjugated polymer films has been shown to have a large influence on transport properties as measured in field-effect transistors, but straightforward conclusions based on structure alone are difficult to obtain due to the sensitivity of measurements to processing conditions such as solvent effects (polymer-solvent interactions and film solidification rate) and to the device structure such as substrate choice, electrode material and contact resistance, and device architecture (bottom gate-bottom contact for e.g.). With so many variables, care must be taken in comparing these results with the relevant statistical analysis but general concepts can be extracted from comparing the structures described in Table 2. To test the influence of polymer packing on transport properties in these il-based polymers, bottom-gate, bottom-contact OFETs were fabricated based on P[T3(C6)-il(SiO)] and tested, and the results are included in Table 2, which summarizes results previously reported in the literature on similar isoindigo-based systems. In the approach used here, the active layer was drop cast at room temperature from a solution of the polymer (2 mg/mL) in chloroform, followed by drying at 150°C for one hour to reproduce the fabrication conditions of Stalder et al.32

Annealing of the polymer films at 150 °C and 200 °C leads to similar GIWAXS data so both processing conditions lead to similar observations of polymer packing and conclusions as to the relationship between film morphology and transport properties.

Previous OFET devices fabricated using these structures have shown ambipolar behavior for P[T-il(HD)] (entries 2 and 3), and some conflicting results for P(T3-il)-like polymers (entries 10
and 12). In the case of P[T3(C6)-il(HD)]-1, an OFET hole mobility of $5 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained, but no n-type behavior was observed. However, when the n-hexyl chains are replaced by n-octyl chains in P[T3(C8)-il(HD)]-3, the electron mobility is reported to be $5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with a hole mobility similar to that of P[T3(C6)-il(HD)]-1 as seen in entries 10 and 12 of Table 2.\textsuperscript{25} Ambipolar transport was measured in some isoindigo polymers (Table 2, entries 2, 3, 9, 12 and 14); however there is no clear correlation between electron mobility and isoindigo density in the backbone. This is due in part to the numerous parameters which come into play when measuring charge mobility in OFET devices. One example where device parameters are kept constant to focus on the effects of polymer structure on transport was conducted by Stalder et al. using 2D solid-state NMR to elucidate the interactions between polymer backbones. The authors conclude that P[T-il(HD)]-4 packing include slightly shifted isoindigo stacks, which maintain overlap of the isoindigo units over multiple polymer backbones, whereas P[T3(C6)-il(HD)]-1 packing favors mixed interactions of isoindigo and terthiophene across polymer backbones.\textsuperscript{32} These differences in molecular packing and orbital overlap between P[T-il] and P[T3-il] polymers account in part for the ambipolar charge transport in P[T-il] polymer, whereas P[T3-il] tend to be p-type polymers. This conclusion is backed up by the fact that the homopolymer of isoindigo, prepared via Suzuki coupling, exhibits only n-type transport ($\eta = 1 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) due the propensity of il interactions.\textsuperscript{32} In the case of P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-1, the differences in charge transport can thus be explained by considering intrachain transport at the molecular level, with breaks in conjugation observed for the LUMO of P[T3-il], and by interchain charge hopping through electronic coupling of adjacent il units, as was discussed in the case of poly(fluorene-alt-benzothiadiazole) F8BT.\textsuperscript{46,47}
Examining the results of Table 2, the isoindigo-based polymer films which exhibit \( \pi \)-stacking have \( \pi-\pi \) distances of 3.6 Å to 3.8 Å. While a short \( \pi \)-stacking distance may be a necessary condition for high interchain overlap and high mobilities, \( \text{P}[\text{T-ii(HD)}] \), \( \text{P}[\text{DTS(EH)-ii(HD)}] \), and \( \text{P}[\text{T3(C6)-ii(SiO)}] \) (entries 2-3, 9 and 13 respectively) demonstrate that it is not a sufficient characteristic in these polymers. Indeed, all three polymers have a \( \pi \)-stacking distance around 3.7 Å but two also have a face-on polymer orientation relative to the substrate, which sets the charge hopping direction perpendicular to the transport direction in OFETs, and explains in part their lower hole mobility compared to \( \text{P}[\text{T3(C6)-ii(HD)}]-1 \). Although orientation is not the only determining factor in some structures, the increase in mobility with edge-on orientation in isoindigo polymers seems to follow previous trends observed for DPP-containing polymers.\(^{16}\)

Coherence length (as discussed in the previous paragraph, also referred to as crystallite size) in the \( \pi \)-stacking direction also needs to be considered to explain the trends seen in the transport properties. For instance, \( \text{P}[\text{T2-ii(OD)}] \) (entries 4-6) shows similar packing to \( \text{P}[\text{T3(C8)-ii(HD)}]-3 \) (entry 12), but possesses a hole mobility that is an order of magnitude higher. This is explained by the fact that crystallinity is maintained over 3 nm (9 backbone segments) in the case of \( \text{P}[\text{T3(C8)-ii(HD)}]-3 \) and 8 nm (22 backbone segments) in the case of \( \text{P}[\text{T2-ii(OD)}]-2 \). The relationship between long-range order in crystallites and high mobility can be used to explain trends seen in isoindigo polymers, as discussed broadly for conjugated polymers in general in the recent work by Noriega et al.\(^{15}\) and Zhang et al.\(^{14}\) In one example, Zhang et al. found that both ordered aggregates and amorphous regions of a copolymer of indacenodithiophene and benzothiadiazole (IDT-BT) are uniformly oriented with respect to the substrate and both domains provide pathways for efficient intra- and interchain transport.\(^{14}\) In another publication, Noriega et al. showed that short-range order within polymer aggregates are connected through amorphous
regions by tie chains, which still allow for efficient interchain transport in the amorphous domains.\textsuperscript{15} As such, the work reported here on isoindigo-containing polymers does give some guidelines for the relationship between coherence length and charge carrier mobility, but our description is limited in the sense that only the short-range ordered regions were observed by GIWAXS and no data was obtained to include the impact of amorphous regions of the films on charge transport.

**Solar Cell Properties.** To determine the impact of the ground and excited state energy levels, along with the polymer’s solid state behavior, on photovoltaic properties, solar cells were fabricated and the processing conditions were optimized using a conventional device structure (indium tin oxide (ITO)/PEDOT:PSS/Isoindigo-based polymer:PC\textsubscript{71}BM/LiF/Al).
Table 3. Summary of optimized conventional OPV device characteristics.

<table>
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<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Processing</th>
<th>OPV Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Poly: PC₃BM Solvent/ Additive Thick. (nm)</td>
<td>J_{sc} (mA cm⁻²)</td>
</tr>
<tr>
<td>1</td>
<td>P[T-il(OD)]-2</td>
<td>1:2 PC₇₁BM CB</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>P[T-il(HD)]-1</td>
<td>1:2 PC₇₁BM oDCB/ 2.5% DIO</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1:1 PC₆₁BM oDCB/ 2.5% DIO</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>P[T-il(HD)]-2</td>
<td>1:1.5 PC₆₁BM oDCB/ 2.5% DIO</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>P[T-il(HD)]-3</td>
<td>1:1.5 PC₆₁BM oDCB/ 2.5% DIO</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>P[T-il(HD)]-4</td>
<td>1:1.5 PC₇₁BM oDCB/ 2.5% DIO</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
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<td>1:1 PC₇₁BM CF/ 4% DIO</td>
<td>170</td>
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<td>1:2 PC₇₁BM CF/ 0.5% DIO</td>
<td>150</td>
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<tr>
<td>9</td>
<td>P[DTS(EH)-il(EH)]</td>
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<td>13</td>
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<tr>
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<tr>
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<td>oDCB/2.5% DIO</td>
</tr>
<tr>
<td>16</td>
<td>P[T6(C8)-iI(HD)]-1</td>
<td>1:1.5</td>
<td>oDCB/2.5% DIO</td>
</tr>
<tr>
<td>17</td>
<td>P[T6(C8)-iI(HD)]-2</td>
<td>1:1.5</td>
<td>oDCB/3% CN</td>
</tr>
</tbody>
</table>

*Best device characteristics, all others are averages.*

The optimized device results are summarized in Table 3. As can be seen, the use of 1,8-diodooctane (DIO) as a processing additive proves to be beneficial to the PCE in these blends. In particular the drying time of the active layer was found to have a significant influence on device performance. When the P[T3(C6)-iI(HD)]-2:PC<sub>71</sub>BM film was placed under vacuum immediately after spin-coating the active layer, followed by LiF/Al deposition, the devices showed a V<sub>oc</sub> of 0.70±0.01 V, a J<sub>sc</sub> of 14.2±0.4 mA cm<sup>-2</sup>, and FF of 59 %. The PCE was therefore calculated to be 6.0±0.1 %. However, after drying the active layer overnight at room temperature in nitrogen atmosphere, the J<sub>sc</sub>, FF, and PCE increased to 15.2±0.1 mA cm<sup>-2</sup>, 62±1.0 %, and 6.6±0.1 %, respectively. These results indicate that an increase in J<sub>sc</sub> and FF is observed with the long evaporation time of the oDCB:DIO mixture. If the evaporation time of the solvent is short, there is insufficient time for self-organization of the polymer in the film as it solidifies. On the other hand, long evaporation times allow sufficient time for self-organization to occur. Indeed, Rogers et al. demonstrated little change in the assembly of poly(2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]-dithiophene-2,6-
diyl]) (PCPDTBT) polymer chains in films cast from chlorobenzene past 2 min after casting, whereas films cast with high boiling point 1,8-octanediethiol (ODT) as a processing additive showed structural evolution up to 78 min after casting. Furthermore, Ho et al.\textsuperscript{26} observed increased short-circuit currents and fill factors in isoindigo-based devices, where the active layer is processed with 1-chloronaphthalene (CN) as a processing additive. In their work, the active layer was left to dry overnight under inert atmosphere, which could indicate further rearrangement with longer drying times when CN is used as a processing additive. One question that arises is the possibility of the high boiling point additive remaining in the film after casting. The use of high vacuum ($10^{-6}$ torr) on the active layer prior to evaporation of the top electrode provides one mechanism for removal of the processing additive from the film. Previous reports have discussed the absence of thiol groups from ODT when observed in FTIR, Raman and XPS after drying the films under $10^{-3}$ torr.\textsuperscript{63} In this work, blends cast with DIO were analyzed by XPS, and showed no residual iodine peak in the top nanometer layer of the bulk heterojunction as seen in Table 5. However, complete removal of DIO from the active layer in the final device is still not fully proven.

As observed in comparing previous reported results summarized in Table 3 to the new results reported here, we show that the number of thiophenes in the backbone has an influence on the device performance.\textsuperscript{25, 26} In the case of P[T-il(HD)]-4 (entry 6) which has one backbone thiophene, $V_{oc}$ is 0.9 V while the $V_{oc}$ of P[T3(C6)-il(HD)]-2 (entry 10) with three backbone thiophenes is 0.7 V. However, P[T3(C6)-il(HD)]-2 shows higher PCEs compared to P[T-il(HD)]-4 due to higher $J_{sc}$ and FF. The morphology investigated by atomic force microscopy as shown in Figure 4 gives some insight as to the cause for this increase in $J_{sc}$. As seen in Figures 4b and d, P[T3(C6)-il(HD)]-2:PC$_{71}$BM exhibits finer phase separated microstructure compared
to P[T-il(HD)]-4:PC$_7$BM blends, which is one possible explanation to the higher J$_{sc}$ in P[T3(C6)-il(HD)]-2 devices than P[T-il(HD)]-4 devices.

Preliminary analysis of Table 3 highlights some discrepancies in J$_{sc}$ trends between P[T3-il] device and P[T6-il] device as shown by entries 13-14 and 16-17. In work by Ho et al.,$^{26}$ CN was used as a solvent additive instead of 1,8-diiodooctane (DIO) that was used by Ma et al.$^{25}$ in P[T6(C8)-il(HD)]:PC$_7$BM blend, leading to an improvement in J$_{sc}$ from 10.5 mA cm$^{-2}$ to 15.7 mA cm$^{-2}$. As summarized in Table 3, almost all reported devices based on isoindigo-containing polymers required the use of processing additives to achieve optimized OPV performance. As such, the effect of processing additives on the morphology and device characteristics of P[T-il(HD)]-4, P[T3(C6)-il(HD)]-2 and P[T3(C6)-il(SiO)]-based films will be discussed in the following paragraph.

**Effect of DIO as a Processing Additive.** DIO has been successfully used to control phase separation in BHJ devices constructed using isoindigo-based polymers blended with fullerenes, inducing a fine structure, which enhances cell performance.$^{40,44}$ As illustrated by the results in Table 4 for the polymers studied in this work, adding DIO into isoindigo polymer:PC$_7$BM blends yields an enhancement in J$_{sc}$ and FF, which in turn leads to higher PCE for all three polymer systems studied. The largest increase in J$_{sc}$ with DIO is observed in blends based on P[T3(C6)-il(SiO)], with the use of DIO leading to an over five-fold enhancement in J$_{sc}$ to 8.6 mA cm$^{-2}$ compared to 1.6 mA cm$^{-2}$ without DIO. The J$_{sc}$ is also increased from 2.3 mA cm$^{-2}$ to 5.8 mA cm$^{-2}$ and from 12.5 mA cm$^{-2}$ to 15.2 mA cm$^{-2}$ with DIO in blends based on P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-2 respectively. Interestingly, the V$_{oc}$ decreases ($< 10\%$) for all devices cast with DIO compared to devices fabricated without DIO. This was also observed in blends
containing P[DTS(EH)-iI(HD)], where the $V_{oc}$ dropped to 0.76 V with DIO from 0.86 V without DIO.$^{44}$

Table 4. Effect of DIO concentration in oDCB on conventional OPV device characteristics

<table>
<thead>
<tr>
<th>Polymer:PC$_{71}$BM</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[T-il(HD)]-4</td>
<td>2.3±0.1</td>
<td>0.97±0.01</td>
<td>52±2</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>P[T-il(HD)]-4, 2.5% DIO</td>
<td>5.8±0.1</td>
<td>0.90±0.01</td>
<td>55±1</td>
<td>2.9±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(HD)]-2</td>
<td>12.5±0.5</td>
<td>0.72±0.01</td>
<td>56±1</td>
<td>5.0±0.2</td>
</tr>
<tr>
<td>P[T3(C6)-iI(HD)]-2, 2.5% DIO</td>
<td>15.2±0.1</td>
<td>0.70±0.01</td>
<td>62±1</td>
<td>6.6±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(SiO)]</td>
<td>1.6±0.3</td>
<td>0.69±0.01</td>
<td>37±1</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(SiO)], 2.5% DIO</td>
<td>8.6±0.2</td>
<td>0.66±0.01</td>
<td>49±1</td>
<td>2.8±0.1</td>
</tr>
</tbody>
</table>

Although both P[T3(C6)-iI(HD)]-2 and P[T3(C6)-iI(SiO)] have the same conjugated backbone structure, they express very different OPV device efficiencies.$^{38}$ These differences in efficiencies can be partly explained by the variations in lateral phase structure that cause differences in charge generation and transport, leading to differences in $J_{sc}$ and FF. Atomic force microscopy (AFM) was used to investigate the change in surface morphology as a function of DIO content as shown in Figure 4. It can be seen that DIO has a large effect on the topology in the case of P[T-il(HD)]-4, but little influence on blends with P[T3(C6)-iI(HD)]-2. The finer feature size in the P[T-il(HD)]-4 and P[T3(C6)-iI(SiO)] films formed with DIO are consistent with an increase in $J_{sc}$ compared to films processed without this additive. Comparing these results, it appears that DIO as a processing additive has little visible effect on the microscopic phase separation in the case of materials with low solubility in the processing solvent, such as P[T3(C6)-iI(HD)]-2, when compared to the more soluble polymers P[T-il(HD)]-4, P[T3(C6)-iI(SiO)], or P[DTS(EH)-iI(HD)].$^{44}$ However, the use of DIO does impact surface roughness in all three polymer films. To
a certain extent, a rougher surface of the active layer in OPV can improve light harvesting and charge collection. Surface roughness can also be used as an indicator of crystallite formation in thin films. The increase in surface roughness can explain in part the increase in FF and \( J_{sc} \), both leading to higher power conversion efficiency in the devices processed with DIO, although the correlation between increased surface thickness and increased FF and \( J_{sc} \) remains unclear for these three systems.

**Figure 4.** AFM images of blends of PC\(_{71}\)BM with (a,b) P[T-il(HD)]-4, (c,d) P[T3(C6)-il(HD)]-2, and (e,f) P[T3(C6)-il(SiO)] without (top) and with 2.5%v DIO (bottom). The root-mean-square roughness is indicated at the bottom right corner. All images are 1×1 µm\(^2\) with a 30 nm height scale.

The mechanism by which processing additives modify the blend morphology is complex,\(^{64, 65}\) however, some preliminary work has shown that DIO has an impact on the size of PC\(_{71}\)BM aggregates.\(^{66}\) Without DIO present, fullerene derivatives tend to aggregate into large fullerene rich domains as the film dries. In comparison, DIO serves as a better solvent for the fullerene than chlorobenzene or oDCB, and reduces PC\(_{71}\)BM aggregation, allowing fullerene to mix more
homogeneously with the polymer in the amorphous phases. In contrast to this hypothesis for DIO, Schmidt et al. have postulated that CN helps form polymer lamellar crystallites within polymer aggregates in solution, which in turn leads to smaller and more ordered polymer domains in the dried thin film. Gao et al. also demonstrated the variations in film forming mechanisms when aliphatic additives (e.g. DIO) are used as opposed to aromatic additives (e.g. oDCB). In the latter case, polymer aggregates with some degree of ordering are formed in solution as observed with UV-visible absorption. Yan et al. have also discussed the impact of polymer self-assembly on the choice of processing additive for optimal device performance. CN was shown to increase Jsc compared to DIO in blends where the polymer exhibited a propensity to form polymers fibrils, and addition of DIO leads to an increase in Jsc in blends where the polymer forms less crystalline, irregular particles. This variation in film formation mechanism could explain the difference in OPV device parameters in the case of P[T6(C8)-il(HD)] devices as measured by Ma et al. and Ho et al. where Jsc of 10.5 mA cm$^{-2}$ and 15.7 mA cm$^{-2}$ are measured in blends cast with DIO and CN respectively (entries 16 and 17). In this case, differences in self-assembly of P[T3(C8)-il(HD)] and P[T6(C8)-il(HD)] chains could explain the difference in choice of processing additive between DIO and CN for optimized device performance.

In addition to AFM, GIWAXS was conducted on blends of P[T3(C6)-il(HD)] and P[T3(C6)-il(SiO)] with PC$_{71}$BM to check for a correlation between molecular ordering and device parameters (Figures S4 and S5), as discussed in the previous paragraph for other polymer systems. Based on the GIWAXS results on both polymer:PC$_{71}$BM blends, slight changes are observed in the molecular orientation and crystalline packing of the polymers in films spun cast with and without DIO. In Figure S4, an increase in the scattering intensity is seen in both
polymer blends when DIO is used, suggesting an increase in crystallinity. This is also supported by the increase in intensity of the higher order (200) peak in blends based on P[T3(C6)-il(SiO)] with DIO (Figures S4d and S5c). Another difference observed is a slight broadening of the (100) peak around the Q_z axis when DIO is used (Figure S5, b and d) for both polymers. As such, the GIWAXS results on polymer crystallites do not indicate a strong dependence of the molecular morphology of P[T3(C6)-il(HD)]-2 or P[T3(C6)-il(SiO)] on the presence of DIO during processing, but small variations are seen, which can offer a partial explanation for the increase in FF and J_sc through increased crystallinity when DIO is used.

Beyond lateral phase separation, processing additives can also affect vertical phase separation as reported by Shao et al. in blends based on a copolymer of benzo[1,2-b:4,5-b']dithiophene and thieno[3,4-b]thiophene (PBDTTT-C-T). Depending on the vertical phase separation in the blends, charge collection can be improved at those electrodes by minimizing leakage currents. However, in the case of P3HT:PCBM blends, it has been demonstrated that even an interface made up of only 3% PCBM at the cathode enables low-resistance electron collection. In order to determine the surface composition of the active layer at the PEDOT:PSS and LiF/Al interfaces, XPS was used on the device active layer to determine the carbon, nitrogen, oxygen and sulfur content in the top few nanometers of the bulk heterojunction. The relative atomic content were then related back to the material concentration at the surface using the chemical formula of the two components in order to quantify the ratio of polymer to fullerene at the LiF/Al interface of conventional cells, as detailed in the supporting information. As seen in Table 5, there is an increase of the fraction of PCBM at the surface, near the LiF/Al cathode, with added DIO.
**Table 5.** XPS data showing elemental composition and calculated material concentrations at the film surface as a function of processing conditions.

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Polymer (%)</th>
<th>PC$_{71}$BM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No DIO</td>
<td>92.0</td>
<td>2.3</td>
<td>2.8</td>
<td>2.8</td>
<td>83±12</td>
<td>16±10</td>
</tr>
<tr>
<td>2.5% DIO</td>
<td>92.5</td>
<td>1.5</td>
<td>3.0</td>
<td>3.0</td>
<td>69±13</td>
<td>30±10</td>
</tr>
</tbody>
</table>

The vertical phase composition was subsequently fully probed using neutron reflectivity (NR) in order to observe a possible impact of DIO on the vertical composition profile of the active layer. Figure 5 shows the fits to the experimental data that are used to extract the vertical scattering length density (SLD) profile for the P[T3(C6)-iI(HD)] blends cast with and without DIO. The SLD profiles were analyzed in terms of the vertical composition profile of P[T3(C6)-iI(HD)] and PC$_{71}$BM, which have calculated SLD values of $7.29 \times 10^{-7}$ Å$^{-2}$ and $4.3 \times 10^{-6}$ Å$^{-2}$ respectively. A homogeneous blend of these two materials with a 1:1.5 (or 40:60) ratio has a SLD of $2.87 \times 10^{-6}$ Å$^{-2}$ for the active layer, so the NR fits were also tested to meet this requirement to ensure accuracy of the fit parameters. Furthermore, the NR fits shown in Figure 5b and c estimate that the thickness of the bulk heterojunction active layer beneath the aluminum (Al) electrode is around 125 nm and 100 nm for the blends processed without and with DIO respectively. Profilometry on the active layer of OPV devices gave active layer thicknesses of 130±3 nm and 120±3 nm for the films processed without and with DIO respectively, which correlates well with the values obtained from fits to the NR measurements.

In terms of vertical composition in the active layer, (Figure 5b and c) the NR fits indicate that the active layer has a non-uniform distribution of the polymer and fullerene through the film.
thickness. Without added DIO, the surface of the active layer is slightly PC$_{71}$BM-rich, with a composition of 52% of PC$_{71}$BM, and the buried interface at the PEDOT:PSS is polymer-rich, with a composition of 74% P[T3(C6)-il(HD)]-2 (decreased SLD) (Table S3). When DIO is used in the casting solution, the polymer-rich phase at the PEDOT:PSS interface becomes even more polymer-rich (composition of the layer is 91% P[T3(C6)-il(HD)]-2) but also becomes thinner (20 nm to a couple nanometers without and with DIO respectively). Based on these NR fits, it is shown that DIO not only has an impact on lateral phase separation, but also on vertical composition. However, these NR fits exhibit a different trend from XPS. XPS showed an increase of the concentration of PC$_{71}$BM at the LiF/Al interface with DIO, whereas NR fits indicate a PC$_{71}$BM-rich interface without DIO. An explanation for this discrepancy is that capping of the active layer with the cathode material could have an effect on the composition at that interface. Moreover, the difference in the size of the area analyzed by each technique (4 cm$^2$ in the case of NR, and less than 0.5 mm$^2$ in the case of XPS) could account for variations between NR and XPS results. Indeed, as seen in Figure S3 and Table S2 of the supporting information, there is a variation of the surface composition as the measurement is taken closer to the electrode, where the fraction of polymer drops from 83 % to 70 % closer to the Al layer.

Figure 5. Neutron reflectivity data and fits (a) leading to scattering length density (SLD) profiles of P[T3(C6)-il(HD)]-2 devices spun cast without (b) and with 2.5%v DIO (c).
**Balance between $V_{oc}$ and $J_{sc}$.** Interestingly, devices based on P[T-il(HD)]-4 exhibit high open-circuit voltages, but low short-circuit currents, while the opposite is true for P[T3(C6)-il(HD)]-2. In general, as described in Table 3, high $V_{oc}$ values of up to 0.91 V are obtained with blends containing less electron-rich polymer donors (Table 3, entries 1-8), where the high $V_{oc}$ without sacrificing $J_{sc}$ leads to 4.5% power conversion efficiency (Table 3, entry 3).\(^{25}\) On the other hand, in a device containing more electron-rich isoindigo polymer (Table 3, entries 9-17) the $V_{oc}$ was lowered to 0.7 V while $J_{sc}$ reached 15.7 mA cm\(^{-2}\), yielding higher PCEs of 7.1 % when CN is used as a processing additive (Table 3, entry 17).\(^{26}\)

As described in previous work,\(^ {28}\) device results show a substantial 0.2 V difference in $V_{oc}$ between P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-2 or P[T3(C8)-il(HD)] devices. Because of the unstable electrochemical oxidation of the polymers, the understanding of this difference in $V_{oc}$ based solely on the ionization potential of the polymers is challenging. Moreover, the UV-PES results show a 0.1 eV difference in the IP of P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-2, which does not explain the 0.25 V difference in the $V_{oc}$ of blends cast without DIO. Vandewal *et al.*\(^ {28}\) have discussed this difference in the $V_{oc}$ by measuring the energy difference between the excited state of the donor and the charge transfer state (CT) by Fourier-transform photoelectron spectroscopy and electroluminescence.\(^ {28}\) They find that P[T-il(HD)]-2:PC\(_{61}\)BM blends exhibit a lower energy offset between the polymer excited state and the CT state (close to 0 eV) compared to P[T3(C8)-il(HD)]:PC\(_{71}\)BM blends, along with low radiative charge transfer state recombination. This leads to low voltage losses in P[T-il(HD)]-2 cells, resulting in a high $V_{oc}$ of 0.9 V in the case of P[T-il(HD)]:PC\(_{61}\)BM blends. Furthermore, field-dependent photoluminescence quenching indicates that this low energy difference between excited and CT states in P[T-il(HD)]-2:PC\(_{61}\)BM blends
is responsible for the low $J_{sc}$ due to repopulation of the exciton from the CT state, rather than charge separation.

In this current work, charge modulated electroabsorption spectroscopy (CMEAS) is used to understand the change in $V_{oc}$ between P[T-iI(HD)]=4 and P[T3(C6)-iI(HD)]=2. CMEAS is a technique that detects the changes in optical absorption below the polymer bandgap by modulating the electric field to directly measure the effective band gap in a bulk heterojunction solar cell. This novel technique allows detection of the CT states which have been correlated with $V_{oc}$. CMEAS provides higher signal-to-noise resolution compared to linear optical absorption techniques, and takes into account interfacial effects between the two compounds in contrast to electrochemical measurements.

The results obtained by Lai et al. using CMEAS show that the effective energy gap in P[T-iI(HD)]=4:PC$_{71}$BM blends is measured to be 1.3 eV compared to 1.0 eV in P[T3(C6)-iI(HD)]=2:PC$_{71}$BM blends. The 0.3 eV difference between these two blends is in agreement with the variations observed for the $V_{oc}$ of the OPV devices. The CMEAS results indicate that, while polymers may have similar onsets of oxidation, the CT states formed at the donor/acceptor interface can have different energy levels. This difference in CT energy can be explained by the differences in electronic coupling at the interface between polymer and fullerene in blends of P[T-iI(HD)]=4:PC$_{71}$BM and P[T3(C6)-iI(HD)]=2:PC$_{71}$BM respectively, as described for other systems by Graham et al., which affects the effective energy gap. The difference between CT state energy and $V_{oc}$ is further explained by energy losses to reach charge separated states from the CT state. Furthermore, higher dissociation efficiency is observed as a result of the more delocalized CT states in P[T3(C6)-iI(HD)]=2:PC$_{71}$BM blends than P[T-iI(HD)]=4:PC$_{71}$BM blends, resulting in a higher $J_{sc}$ in solar cells. This underlines the role played by dielectric
constants in isoindigo-based blends, which could also explain why the low energy offset between excited and CT states still leads to high internal quantum efficiencies (IQE) in the case of P[T3(C6)-il(HD)] or P[T3(C8)-il(HD)].

**Inverted Device Architecture.** The effect of device architecture on device properties was further investigated in inverted devices, more amenable to roll-to-roll fabrication. Inverted bulk-heterojunction solar cells with a structure of ITO glass/ZnO–PVP nanocomposite/isoindigo-based polymer:PC_{71}BM/MoOx/Ag was fabricated using the three focus polymers in this work: P[T-il(HD)]-4, P[T3(C6)-il(HD)]-2, and P[T3(C6)-il(SiO)]. We previously reported ZnO–poly(vinyl pyrrolidone) (PVP) composite sol–gel film as the ETL. On top of the ZnO–PVP composites, the active layer in inverted devices was deposited using the same conditions as in conventional devices. The inverted device results are summarized in Figure 6 and Table 6. For both P[T-il(HD)]-4 and P[T3(C6)-il(HD)]-2, the conventional and inverted devices showed similar device performances. On the other hand, inverted devices based on P[T3(C6)-il(SiO)] showed higher device performance, such as higher J_{sc} and FF in spite of having a lower V_{oc}, compared to conventional devices. The increase in device efficiency in P[T3(C6)-il(SiO)]:PC_{71}BM inverted OPV devices could not only result from a difference in electrode work function, but also from variations in the blend morphology and carrier recombination dynamics.77
Figure 6. J-V curves of conventional and inverted solar cells based on P[T-iI(HD)]-4, P[T3(C6)-iI(HD)]-2, and P[T3(C6)-iI(SiO)] polymer:PC71BM blends.

Table 6. Conventional and inverted device characteristics.

<table>
<thead>
<tr>
<th>Device</th>
<th>J_sc (mA cm⁻²)</th>
<th>V_oc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[T-iI(HD)]-4 conventional</td>
<td>5.8±0.1</td>
<td>0.90±0.01</td>
<td>55±1</td>
<td>2.9±0.1</td>
</tr>
<tr>
<td>P[T-iI(HD)]-4 inverted</td>
<td>5.6±0.1</td>
<td>0.81±0.01</td>
<td>52±1</td>
<td>2.4±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(HD)]-2 conventional</td>
<td>15.2±0.1</td>
<td>0.70±0.01</td>
<td>62±1</td>
<td>6.6±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(HD)]-2 inverted</td>
<td>15.2±0.3</td>
<td>0.68±0.01</td>
<td>63±1</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td>P[T3(C6)-iI(SiO)] conventional</td>
<td>8.6±0.2</td>
<td>0.66±0.01</td>
<td>49±1</td>
<td>2.8±0.1</td>
</tr>
<tr>
<td>P[T3(C6)-iI(SiO)] inverted</td>
<td>9.5±0.1</td>
<td>0.64±0.01</td>
<td>63±1</td>
<td>3.8±0.1</td>
</tr>
</tbody>
</table>

SUMMARY AND PERSPECTIVE
In summary, we have synthesized and characterized a series of new isoindigo polymers to highlight structure-processing-property relationships which can lead others in further developing this family of polymers. Facile access to isoindigo in bulk syntheses suggests these systems are worth optimization and bulk preparation for further practical development of OPV’s. These polymers were designed to include one or three thiophene units as electron-rich moieties, and to study the impact of side-chain branching on the electronic properties of the resulting polymer and on the solid-state morphology. In terms of electronic and geometric considerations, the strong electron accepting character of isoindigo localizes the electron density in the LUMO and sets the electron affinity around 3.9 eV. The impact of side-chains on these interchain interactions was discussed using UV-Vis absorption, 2D NMR and GIWAXS data, where increasing the density of branched side-chains along the backbone tends to decrease interchain interactions. These interchain interactions are particularly important for reaching high mobility values in OFETs, where charge transport was shown to be consistently improved by increasing the order of the isoindigo-containing polymer in thin-films, as quantified here by the coherence length. This can be achieved by promoting backbone interactions through reducing steric hindrance by moving the side chain branching point away from the backbone as shown in this article by the P[T2-il] family, and in other literature reports.\textsuperscript{78, 79} Orientation of polymer chains in the bulk of thin films can be dictated by the chemical nature and density of the side chains, with alkylated side chains mainly leading to edge-on orientations compared to siloxane side chains, which yield some face-on orientation. This leads to increased transport in OFETs when the il-containing polymer backbones are preferentially oriented perpendicular to the substrate, and the charge carrier mobility depends on the coherence length rather than on the $\pi$-stacking distance in these isoindigo-based systems. Furthermore, the interchain interactions are crucial to the type of
charge carrier transport and to the magnitude of the charge carrier mobility, where 2D NMR was used to correlate the il-il interchain interactions in P[T-il] polymers to ambipolar charge transport, whereas T3-il interactions were prevalent in P[T3-il] polymers leading to p-type charge transport.

In OPV devices, high $V_{oc}$ can be achieved thanks to high ionization potentials of the isoindigo-based polymers, which needs to be balanced with a high density of charge transfer states to achieve high $J_{sc}$, and thus optimal PCE. The morphology in isoindigo-based blends can be tuned by using solvent additives such as DIO or CN; however, in the case of P[T3(C6)-il(HD)]-2 the use of DIO does not lead to a large change in phase separation as is the case for P[T-il(HD)]-4 or P[T3(C6)-il(SiO)] as investigated by AFM. The increased solubility of P[T-il(HD)]-4 and P[T3(C6)-il(SiO)] in oDCB compared to P[T3(C6)-il(HD)] is one explanation for the more visible change in morphology when a poor solvent for the polymer, such as DIO, is used. These observations point to the impact of the state of the polymer chains in solution prior to film formation on the resulting thin-film morphology, in addition to the impact of residual of high boiling point solvents in the film to allow for polymer chain rearrangement or fullerene aggregation. This work, along with previous reports,25, 26, 40 also highlights the balance in OPV performance, with PCEs over 6% in both conventional and inverted devices with il-based polymers, and the synthetic accessibility of isoindigo-containing polymers.

Overall, this work establishes some structure-processing-property relationships that could lead to the design of novel high performance isoindigo-based polymers. Furthermore, this work can be extended to other dually substituted acceptors such as DPP or TiI, where most of the differences between these three units stem from their electronic characteristics, where il-based polymers tend to exhibit the highest ionization potential and electron affinity.
ASSOCIATED CONTENT

Supporting Information. Experimental details, electrochemical details and square-wave voltamograms, description, OFET and OPV device fabrication, XPS sample preparation and analysis, additional data from DFT calculation, monomer and polymer synthesis and gel permeation chromatograms are supplied as 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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Structure-Property Relationships Directing Transport and Charge Separation in Isoindigo Polymers

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