Macromolecules

An Indacenodithiophene–Quinoxaline Polymer Prepared by Direct **Arylation Polymerization for Organic Photovoltaics**

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Supporting Information

ABSTRACT: Seeking preparation of high-performance donor-acceptor (D-A) polymers based on bare thiophene units in a more environmentally friendly and faster way, we have carried out a direct arylation polymerization (DAP) of two starting β -unprotected thiophene-containing monomers (indacenodithiophene (IDT) and thiophene-quinoxaline-thiophene (TQ)). Through modulating DAP time and heating method, the resulting IDT-TQ polymer shows a relatively well-defined structure with low content of structural defects, as demonstrated by high temperature ¹H NMR, MALDI-TOF-MS, and elemental analysis. Integrating this polymer into bulk-heterojunction solar cells with PC71BM can induce an enhanced OPV performance compared to the other structural analogues that retain a certain amount of unwanted structural defects. However, the film morphology and crystallinity are negligibly influenced by the degree of the structural defects. Through a combination of detailed electrical measurements using light intensity dependence and net photocurrent, we are able to correlate the different



photovoltaic performances in structure-function relationships with the extent of the structural defects. Our study indicates that DAP is a promising asset for environmental production of many valuable thiophene-containing polymers for electroactive and photoactive applications.

INTRODUCTION

A rapid improvement in organic photovoltaic cells (OPVs) has been achieved with power conversion efficiencies (PCEs) exceeding 10%.¹⁻⁴ These great advances have been mainly driven by the development of donor-acceptor (D-A) π conjugated polymers with increasingly complex structures. 5-16 Such polymers have been prepared by using a classical and reliable transition-metal-catalyzed step-growth polycondensation method such as Stille- and Suzuki-type couplings.^{17,18} However, these methods generally involve time-consuming preparation of pure organomentallic monomers and formation of toxic byproducts.¹⁷ Given these financial and environmental costs associated with the materials synthesis, a direct arylation polymerization (DAP) as a C-H activation method is emerging as a highly promising alternative to the abovementioned traditional cross-couplings.¹⁹⁻³⁰ In this reaction, the preparation of organometallic intermediates is unnecessary; this contributes not only to reducing the additional synthetic steps and toxic wastes but also to minimizing the presence of difficult-to-remove byproducts that can have a negative impact on the devices.

Despite its manifold advantages, DAP still suffers from side reactions (i.e., branching, cross-linking, and homocouplings) during the coupling process, which leads to additional structural defects and alters polymers' electronic properties.³¹⁻³³ For those reasons, many important D-A conjugated polymers have not been sufficiently investigated by DAP. In particular, the DAP of two β -unprotected thiophene-containing monomers, enabling high selectivity of C–H bonds at α - and β -positions as well as restraining homocoupling regiodefects, is a big challenge.

To address this issue, we chose to work with indacenodithiophene (IDT) as a coplanar ladder-type donor unit fused by two outer thiophenes and thiophene-quinoxalinethiophene (TQ) as an acceptor counit for constructing a D-A model polymer with the following in mind: (i) Because the side chains introduced at both the cyclopentadienyl ring of the IDT and quinoxaline of TQ can guarantee solubility of the resulting polymer, it is unnecessary to have additional side

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Scheme 1. (a) Typical Design Motif Used by This Work, Where R_{sc} = Aliphatic Side Chains; (b) Synthesis of IDT Monomers M1 and M2; (c) Synthesis of IDT–TQ Polymer with DAP under Either Conventional or Microwave Heating as Well as Standard Stille Polymerization



chains on the outer thiophenes, which ensures the presence of α - and β -proton activations of the flanked thiophenes toward the central goal in this study. (ii) IDT–TQ-based D–A polymers have been proven to be one of the high-performance OPVs materials.^{34–39} Therefore, the optimized DAP for a class of such polymers should bring a valuable usability for the low-cost, large-scale, and commercially viable preparation of high-performance semiconducting materials.

Herein, we report an efficient DAP protocol based on simple time control along with proper heating mode toward a welldefined IDT-TQ polymer via two starting β -unprotected thiophene-containing monomers. We then compared their structural defects and properties, as well as OPV characteristics, with the polymer obtained from standard Stille polymerization. Compared to its Stille analogue, the OPVs based on P4 prepared by DAP under conventional heating exhibits an improved PCE of up to 5.1%, thanks to the relatively small amount of structural defects arising from unselective C-H activation and/or homocouplings within the polymer backbone.

RESULTS AND DISCUSSION

Material Synthesis and Characterization. A typical design motif used by our research group and synthetic routes for the monomers are shown in Scheme 1. While TQ monomer was synthesized according to literature reports,⁴⁰ IDT monomer (M1) was synthesized from diethyl 2,5-dibromoterephthalate via several steps (Stille coupling, double nucleophilic addition, and intramolecular Friedel–Crafts cyclization). After lithiation of M1 followed by quenching with trimethyltin chloride, the corresponding bis-stannylated monomer M2 was obtained in a satisfying yield of 65%.

In addition to Stille polymerization of M2 with TQ for a reference polymer, we carried out the various DAPs by using M1 and TQ for the synthesis of IDT-TQ polymer. The resulting polymers were purified by Soxhlet extraction with

Table 1. Reaction	Conditions and	Characteristics	of the P	olymers	Obtained fr	om Stille	Polymerization	and DAP

entry	catalyst system [mol %]	salt [equiv]	solvent [mL]	heating/ T [°C]	reaction time [h]	insoluble material	M _n ^a [kDa]	PDI ^a	yield ^b [%]
P1	$Pd_{2}(dba)_{3}(2)/P(o-Tol)_{3}(10)$	_	toluene (5)	conventional/110	72	no	22.9	1.51	64
P2	$Pd(OAc)_2(2)$	$K_2CO_3(2.5)$	toluene (5)	conventional/100	6	no	_c	_ ^c	_c
P3	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	conventional/100	12	no	16.8	1.42	65
P4	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	conventional/100	24	no	27.3	1.62	71
P5	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	conventional/100	48	no	25.8	2.24	64
P6	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	microwave/100	1	no	9.9	1.48	40
P7	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	microwave/100	2	yes	21.9	1.9	59
P8	$Pd(OAc)_2(2)$	K_2CO_3 (2.5)	DMAc (5)	microwave/100	4	yes	d	d	d

^{*a*}Estimated by permeation chromatography (GPC) using THF as a solvent and calibrated on polystyrene standard. ^{*b*}Yield is based on the amount of chloroform fractions. ^{*c*}No polymerization occurred. ^{*d*}Gelation occurred. DMAc = N_iN -dimethylacetamide, M_n = number-average molecular weight, PDI = polydispersity index.



Figure 1. ¹H NMR spectra of P1, P4, and P7 in C₂D₂Cl₄ at 70 °C. The solvent peak was marked as an asterisk.

methanol, acetone, hexanes, and chloroform. All entries of IDT–TQ made via DAP (P2–P8) and Stille polymerization (P1) are compiled in Table 1. First, the Stille polymerization was performed essentially following the reported standard condition using $Pd_2(dba)_3/P(o-Tol)_3$ as a catalyst in a refluxing toluene for 72 h, which afforded a yield of 64% for the

chloroform-soluble fraction and molecular weight ($M_n = 22.9$ kDa) with polydispersity (PDI) of 1.51 (Table 1, entry P1).

On the basis of the literature data of DAP in terms of not only the simplicity but also unnecessary removal of phosphine compounds,⁸ the investigation into time-control DAP began under phosphine-free conditions using $Pd(OAc)_2$ (2 mol %) as



Figure 2. UV-vis absorption spectra of the polymers in (a) chloroform solution and (b) thin films. (c) CV curves of polymer films at a scan rate of 50 mV s⁻¹. (d) Ultraviolet photoelectron spectroscopy (UPS) spectra of polymer films.

a catalyst and K_2CO_3 (2.5 equiv) as a base in *N*,*N*-dimethylacetamide (DMAc, 0.2 M) at a mild reaction temperature of 100 °C. By employing the conventional heating, the DAP reaction for 12 h gave P2 with $M_n = 16.8$ kDa with a 65% yield. As the reaction time increased to 24 h, the obtained polymer (P4) showed higher M_n of 27.3 kDa, with an improved yield of 74%. However, the M_n value did not further increase when the reaction time was extended (48 h, P5), though a lower yield (chloroform-soluble fraction) was obtained due to the high content of insoluble fractions caused by the occurrence of cross-linking side reaction. Although toluene is a widely used solvent for the synthesis of most conjugated polymers, no polymeric solid (P2) was obtained from replacing DMAc with toluene, probably because of poor solubility of potassium carbonate in the less polar solvent.^{32,41}

In expansion of our studies, microwave-assisted DAP reaction was also investigated under the same conditions except for the reaction time (P6-P8). Under microwave heating for 4 h, a solvent-swollen gelation was observed, resulting in only insoluble product. By decreasing the reaction time to 2 h, P7 with $M_{\rm p}$ of 21.9 kDa (chloroform-soluble fraction) was obtained, though it still contained a lot of insoluble fractions in the Soxhlet thimble even after additional extraction with hot dichlorobenzene. For a shorter reaction time (1 h), P6 with a low $M_{\rm p}$ of 9.9 kDa was isolated without the insoluble fractions after chloroform extraction. These results indicate that the microwave-assisted DAP can indeed accelerate the reaction rate, yet simultaneously stimulating the β -H activation in the unsubstituted thiophene monomers, which causes the formation of cross-linking ill-defined structures.

Next, in order to compare the degree of the structural defects and optoelectronic properties, as well as OPVs performance, with the same IDT-TQ (P1) synthesized via Stille polymerization, we chose each P4 and P7 sample made by DAP under different heating tools. Note that all the polymers (P1, P4, and P7) have similar M_n and PDI values ($M_n = 21.9-27.3$ kDa and PDI = 1.51-1.90), which can rule out the molecular-weight-dependent properties as a complicating variable.⁴²⁻⁴⁷

To characterize the structural differences between the three polymers, high temperature ¹H NMR spectroscopy was performed in $C_2D_2Cl_4$ at 70 °C and compared in Figure 1. In addition to the distinct 12 peaks arising from the backbone repeating unit in the aromatic regions and two peaks in the 4.01–3.83 ppm due to the OCH₂ protons of the alkoxy side chains on each IDT and TQ, extra peaks a and b with low intensity were observed in all cases. To determine such extra peaks in the ¹H NMR spectra, PIDT and PTQ homopolymers were prepared by DAP under conventional heating, respectively, and the corresponding ¹H NMR spectra are provided in the Supporting Information (Figures S1 and S2). Referring to the ¹H NMR spectra of the monomers (TQ and Br-TQ-Br) (Figure S2), the peaks **b** at around 7.54 and 7.24 ppm can be speculated to different end groups. It is noteworthy that P7 exhibits the broad, split resonances in the 8.25-8.15 ppm range, implying a certain amount of structural defects.

A closer look at the NMR spectra of the homopolymers (PIDT and PTQ) and IDT-TQ polymers (P1, P4, and P7) reveals that the peaks a at 7.65 and 4.07 ppm, related to the backbone signals of the homopolymer PTQ (see Figure S2), are visible in both P1 and P7, but fail for P4, which indicates that P4 is a relatively well-defined structure with low content of the structural defects.

To further validate their structural features, the polymers were also analyzed via MALDI-TOF-MS spectrum and elemental analysis (Figures S3–S5). In the measurable molecular weight range, linking to our findings from ¹H NMR spectra, MALDI-TOF-MS of P4 showed a series of IDT–TQ alternating peaks except for an lesser extent containing TQ–TQ sequences, while the peaks corresponding

to TQ-TQ segments can be clearly detected in P1 and P7. In particular, P7 exhibited large quantities of TQ-TQ sequences, suggesting the presence of severe homocoupling or even branching defects, as a result of a negative side effect from the enhanced reactivity system induced by microwave heating. Surprisingly, other nonalternating IDT-IDT fragments that are expected to form accompanying with the occurrence of TQ-TO homocouplings have not been detected yet. A possible reason for the result is that the directly positioned bulky side chains close to the IDT unit render large steric hindrance, suppressing these nonalternating IDT-IDT structures. Compared to those of both P1 and P7, the elemental analysis for the composition of C, H, N, and S for P4 matched well with the values calculated from the composition of the repeating unit (Table S1). This also supports a relatively higher purity of P4. On the basis of all the data above, one can conclude that in the case of DAP between two unprotected thiophene-containing monomers P4 made by the carefully time-controlled DAP under conventional heating has less homocoupling compared to P1 and P7.

Optical and Electrochemical Properties. The optical properties of the three polymers (P1, P4, and P7) were investigated by UV-vis spectroscopy in dilute chloroform solution and solid state (Figure 2a,b). In chloroform solution, the absorption spectra of P1 and P4 were almost identical, each exhibiting absorption maxima at 570 nm (low-energy band) and 440 nm (high-energy band). In contrast, for P7 solution, the low-energy absorption maximum was blue-shifted (λ_{max} = 551 nm), and a broad high-energy band with indefinable feature was exhibited. Transitioning from solution to solid state, all absorption spectra of P1, P4, and P7 were found to be slightly red-shifted compared to the corresponding ones observed from the solution, and the optical bandgaps were determined to be 1.84, 1.84, and 1.81 eV from the onsets in their films, respectively. The different optical features of P7 are presumably due to the above-mentioned high content of nonalternating and/or branching structures.

Using cyclic voltammetry (CV) of polymer films (Figure 2c), the HOMO/LUMO values of P1, P4, and P7 were estimated to be -5.21/-3.35 eV, -5.20/-3.35 eV, and -5.25/-3.45 eV, respectively. These results indicate that the energy levels are somewhat sensitive to the extent of structural defects in even the identical repeating backbone. The bandgaps determined from CV are in perfect agreement with the measured optical bandgaps above. Ultraviolet photoelectron spectroscopy (UPS) was also used to measure the ionization potential (IP) levels of the three polymers (Figure 2d). Despite the slight discrepancy between the IP and HOMO values, the IPs (5.04, 5.02, and 5.11 eV for P1, P4, and P7, respectively) showed the same trends as the HOMO values obtained from CV.

Theoretical Calculation. To demonstrate the optimal molecular geometry and electronic properties, theoretical calculations were performed by using density functional theory (DFT) B3LYP with 6-31G* basis set. All of the alkoxy side chains were replaced by methoxy groups to simplify the calculation. As shown in Figure 3a, the HOMO wave functions are distributed entirely over the planar conjugated backbone, which improved gain of high hole mobility, while its LUMO wave functions are mainly localized on the acceptor moiety (TQ). We found that the alkoxy phenyl side chains on IDT units extended mostly perpendicular to the conjugated plane of the polymer backbone, while a rotation of the phenyl side chains on TQ by only about 0.03° with respect to the plane of



Figure 3. (a) Optimized frontier orbitals and (b) top and side views of a single repeating unit of IDT–TQ at the level of the B3LYP/6-31 G* basis set.

the main backbone took place. Therefore, we propose that the IDT-based polymer investigated here remains largely disordered in the solid state (see the following GIWAXS data below).

OPV Performance. For evaluating the impact of the synthetic methods on the characteristics of the OPV materials, bulk-heterojunction (BHJ) solar cells were fabricated using a conventional structure of ITO/PEDOT:PSS/active layer/Al and measured under 100 mW cm⁻², AM 1.5G solar illumination. It was found that unannealed as-spun films from *o*-dichlorobenzene (*o*-DCB) with a 1:3 polymer:PC₇₁BM ratio gave the best performance. Figure 4a shows the representative current density–voltage (J-V) curves of the three polymers, and the detailed photovoltaic parameters are summarized in Table 2. The OPV cells with an active layer of P1:PC₇₁BM afforded performance with an open-circuit voltage (V_{OC}) of 0.89 V, a short-circuit current density (J_{SC}) of 10.42 mA cm⁻²,



Figure 4. (a) J-V curves of IDT-TQ-based OPVs under 100 mW cm⁻², AM1.5G solar illumination. (b) The corresponding EQE spectra.

Table 2.	OPVs	Performance	of the	Polymers
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polymer	blend ratio [polymer:PC ₇₁ BM]	$J_{\rm SC} [{\rm mA}~{\rm cm}^{-2}]$	$V_{\rm OC}$ [V]	FF [%]	PCE [%] max/av ^a	EQE	$\mu_{\rm h}^{\ b} \left[{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1} \right]$
P1	1:3	10.42	0.89	52.10	4.82/4.77	9.35	1.50×10^{-3}
P4	1:3	10.75	0.89	53.40	5.10/5.05	9.40	4.09×10^{-3}
P7	1:3	9.23	0.84	43.10	3.35/3.28	8.41	1.23×10^{-4}
a					1.1.		

^aAverage values at least six runs. ^bSpace-charge-limited current (SCLC) measured hole mobilities.



Figure 5. AFM images of blend films of polymer/PC₇₁BM; the size of the image is 5 μ m × 5 μ m.



Figure 6. GIWAXD images of (a-c) neat P1, P4 and P7 polymer films and (d-f) as-cast blend films of P1:PC71BM, P4:PC71BM, and P7:PC71BM.

and a fill factor (FF) of 0.52, resulting in a PCE of 4.8%. Very interestingly, without the solvent additives or postprocessing techniques, P4:PC₇₁BM-based devices exhibited an enhanced PCE of 5.1% with a J_{SC} of 10.75 mA cm⁻², FF of 0.53, and an identical V_{OC} of 0.89 V. On the other hand, with even the same conditions, a decent PCE of 3.35% with the decreased every parameter (J_{SC} = 9.23 mA cm⁻², FF = 0.43, V_{OC} = 0.83 V) was obtained from the devices based on P7 having the higher content of the nonalternating structures. Recently, other groups have also reported a similar reduction in OPVs when the abundance of the homocouplings was present.^{48–50} Consequently, we attribute the improved performance of P4 to the increased alternating D–A structures with higher regioregularity.

As shown in Figure 4b, the external quantum efficiency (EQE) as a function of wavelength of the OPVs based on the polymers is measured under illumination of monochromatic

light. P1 and P4 devices showed a similar photoresponse from 300 to 800 nm with a maximum EQE value of 67.8% at 410 nm, while the device based on P7 exhibited a decreased photoresponse intensity in the whole wavelength range, with a maximum EQE value of 59.7% at 410 nm. The results are concordant with the lower $J_{\rm SC}$ of P7 device compared to those of P1 and P4 devices, revealing the limited photocurrent generation when a large amount of structural defects was remained. The current density ($J_{\rm SC}$) values calculated from integration of the EQEs of P1, P4, and P7 devices are 9.35, 9.40, and 8.41 mA cm⁻², respectively, which agree well with the $J_{\rm SC}$ values obtained from J-V measurements (within 10% mismatch).

To investigate charge transport characteristics, space-chargelimited current (SCLC) models were used to determine the hole mobilities of each optimized polymer film (Table 2). The detailed fabrication and analysis are described in the



Figure 7. (a) Light intensity dependence of J_{SC} . (b) Light intensity dependence of V_{OC} . (c) J-V curves of IDT-TQ-based OPVs in the dark. (d) Photocurrent density versus effective voltage characteristics.

Experimental Section. The hole mobilities of P1, P4, and P7 are 1.50×10^{-3} , 4.09×10^{-3} , and 1.23×10^{-4} cm² V⁻¹ s⁻¹, respectively. There does seem to be strong correlation between the mobilities and relative abundance of structural defects. Moreover, the observed higher mobility of P4 compared to the other samples is one important reason that can contribute to the enhanced J_{SC} and FF values, though this cannot be solely the result of the changes seen in PCEs.

Morphological Properties. The morphology of the polymer: $PC_{71}BM$ blend films with the optimized weight ratio (1:3) was investigated by tapping-mode atomic force microscopy (AFM) (Figure 5). All the blend films show fairly homogeneous surfaces in size and feature. No distinct difference was observed in the three AFM images with a similar root-mean-square (rms) roughness of 0.411–0.482 nm for the blend films of P1, P4, or P7 with PC₇₁BM. We were unable to see clear polymer–PC₇₁BM domains, and there was no evidence of ordered nanostructures in the films, presumably due to the rather amorphous nature of the IDT-based polymers. These results seem to be directly linked to the above-observed independency of PCEs on the application of various processing techniques, such as addition of additives, solvent annealing, and thermal annealing.

For further investigation into the relevant structural features, grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements of neat polymers and blends with PC₇₁BM were performed, and detailed crystallographic parameters are summarized in Table S2. As shown in Figure 6, the neat films of all three polymers showed very similar scattering patterns in GIWAXD analysis; along the out-of-plane (q_z) axis, all films exhibited (100) lamellar packing reflections at 0.271–0.277 Å⁻¹ (corresponding to *d*-spacing distances of 23.1, 22.7, and 23.1 Å, for P1, P4, and P7, respectively) and almost identical (010) $\pi-\pi$ stacking reflections at ~1.37 Å⁻¹ (corresponding to *d*-spacings of ~4.6 Å), while the reflections along in-plane (q_{xy}) axis did not appear, suggesting preferential self-assembly into

face-on orientation relative to the substrate surface. In addition, the calculated coherence lengths of the three polymers were also nearly equal at around 9 Å. Even though the lamellar packing distances are slightly shortened from P7 to P1 to P4, at this point, the impact on molecular packing of the neat films remained unclear as a function of the structure defects content in the polymer backbone.

When each polymer was then blended with $PC_{71}BM$, the emergence of a new isotropic ring at 1.3–1.4 Å⁻¹ was assigned to $PC_{71}BM$. However, both the lamellar packing and π – π stacking peaks in the films were faded, suggesting a lack of the ordered structures induced by π -stacking, which coincides with the observations from the AFM images. When the findings from AFM and GIWAXD were considered, we were unable to clearly point out the exact reason why P4-based devices showed better performance since there was no obvious variation in morphology and microstructural order of the three polymers. This means there must be some other cause for the difference in OPVs performance (*vide infra*).

Charge Recombination and Transport Properties. To assess the effects of the structure defects on the charge recombination properties in OPVs, the light-intensity-dependent J-V characteristics of the three polymers were measured. Figure 7a shows a log–log plot of J_{SC} as a function of the light intensity (I). This study could give a clue for answering the above question. A power-law relationship is found, given by I_{SC} $\propto I^{\alpha}$, where α would be unity ($\alpha = 1$), when the bimolecular recombination can be negligible under short circuit condition.⁵¹ The calculated α values for the devices of P1, P4, and P7 were 0.88, 0.90, and 0.85, respectively, suggesting that the bimolecular recombination can function as the content of structural defects within the identical repeating backbone. As a result, P4:PC₇₁BM-based devices having the highest α value could lead to relatively better performance via the reduced bimolecular recombination.

Besides, the trap-assisted recombination process was also investigated via measuring the dependence of $V_{\rm OC}$ on the light intensity. Normally, when bimolecular recombination dominates in OPVs, the slope of $V_{\rm OC}$ versus light intensity should equal kT/q, while when trap-assisted recombination predominates the loss of charge carriers, a stronger dependence of $V_{\rm OC}$ on light intensity with a slope larger than kT/q is observed.⁵² As shown in Figure 7b, compared to slopes of 1.40 kT/q and 1.50 kT/q for each device made by P1-and P7-based blends, the calculated slope of 1.32 kT/q for P4:PC₇₁BM indicated the weakest dependence of $V_{\rm OC}$ on the light intensity. These results demonstrated that increasing structural defects leads to more trapping centers during charge transport, consequently reducing the FF and $J_{\rm SC}$ parameters in OPVs.

To further probe the charge dissociation and collection process, the photocurrent density $(J_{\rm ph})$ as a function of effective applied voltage (V_{eff}) were examined for the three polymer devices. The J_{ph} is defined as $J_{light} - J_{dark}$, where J_{light} and J_{dark} are the current densities under illumination and in the dark, respectively, and the $V_{\rm eff}$ is defined as $V_0 - V$, where V_0 is the compensation voltage at $J_{\rm ph} = 0$ and V is the applied bias.^{52,53} As shown in Figure 7d, J_{ph} reaches saturation (J_{sat}) at a sufficiently large reverse voltage (i.e., $V_{\text{eff}} > 2.0$ V). Thus, the charge dissociation efficiency can be evaluated by using $J_{\rm ph}/J_{\rm sat}$ ratio. At the short-circuit condition, assuming J_{sat} at 2.5 V_{eff} P4based blends exhibited a higher $J_{\rm ph}/J_{\rm sat}$ value of 81% than those of the other samples (78% and 77% for P1 and P7, respectively), indicating a higher charge-dissociation efficiency. More interestingly, under the maximum power output condition, P4 devices again show a slightly higher $J_{\rm ph}/J_{\rm sat}$ value of 79%, compared to both P1 and P7 devices (74% and 76%), implying that alternating structures with relatively higher purity can improve the charge extraction and collection as well. Not only do all the results observed above demonstrate that the charge recombination and transport characteristics are very sensitive to relative amount of the structural defects within polymer distribution, but they are also consistent with the trends in performance of the tested polymer-based devices (vide supra).

CONCLUSIONS

In summary, we have demonstrated a well-defined IDT-TQ model polymer with satisfied and controllable molar mass synthesized by DAP of two β -unprotected thiophenecontaining monomers. The resulting polymer (P4) made by DAP under conventional heating is a well-definded structure with low content of structural defects, as proven by ¹H NMR, MALDI-TOF-MS, and elemental analysis data. Even though there are no obvious changes in their morphology and packing orientation as the amount of the embedded structural defects into the backbone, P4-based OPVs show slightly higher PCEs (up to 5.1%) than the Stille analogue-based ones (4.7%). By using experimental photocurrent measurement in combination with light intensity dependence, the performance enhancement is clarified as the corresponding charge recombination and transport characteristics affected by the structural defects content in the polymer backbone. The presented study brings a simple and efficient synthetic method, which paves the way for the preparation of various bare thiophene-containing D-A polymers via DAP for organic photovolatics.

EXPERIMENTAL SECTION

General Measurement and Characterization. ¹H NMR were recorded on a Varian VNRS 400 MHz (Varian, USA) spectrophotometer using CDCl₃ as solvent and tetramethylsilane (TMS) as a reference as well as Varian VNRS 600 MHz (Varian, USA) spectrophotometer using $C_2D_2Cl_4$ as solvent. UV-vis absorption spectra were recorded on Cary 5000 (Varian USA) spectrophotometer. The number-average (M_n) , weight-average (M_w) molecular weights, and polydispersity index (PDI) of the polymers were determined by GPC with Agilent 1200 HPLC and miniDAWN TREOS using polystyrene as a standard in THF (HPLC grade). Cyclic voltammetry (CV) were measured on Solartron electrochemical station (METEK, Versa STAT3) equipped with a three-electrode cell in tetra-n-butylammonium hexafluorophosphate solution in acetonitrile (0.1 M) at a scan rate of 50 mV s⁻¹ under an argon atmosphere at room temperature. Ag/Ag^+ electrode, a platinum wire, and a glass carbon disk were used as the reference electrode, counter electrode, and working electrode, respectively. The HOMO energy levels were obtained from the equation HOMO (eV) = $-(E_{(ox)})^{onset}$ $E_{(\text{ferrocene})}^{\text{onset}}$ + 4.8) (S1). The LUMO levels of polymers were obtained from the equation LOMO (eV) = $-(E_{(red)}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ (S2). MALDI-TOF-MS were conducted from Ultraflex (Bruker, Germany). Elemental analyses were performed with Flash 2000 (Thermo Scientific, Netherlands).

Materials. All starting materials were purchased from Acros or Aldrich and used without further purification. 4-Bromo-1-(2-ethylhexyl)oxy)-2-fluorobenzene and 5,8-bis(5-bromothiophen-2-yl)-2,3bis(3-(octyloxy)phenyl)quinoxaline (TQ) were prepared according to previous reports.⁴⁰

Synthesis of Compound 1. To a solution of 2-(tributylstannyl)thiophene (9.0 g, 24 mmol) and diethyl 2,5-dibromoterephthalate (3.70 g, 10 mmol) in anhydrous toluene (50 mL), Pd(PPh₃)₄ (0.58g, 0.5 mmol) was added under nitrogen. The resulting mixture was kept at 110 °C for 24 h and then quenched with water and extracted with diethyl ether. The diethyl ether solution was dried over MgSO₄. After removing the solvent, the crude compound 1 was purified by silica gel chromatography using a mixture of dichloromethane and hexane (1:1) as the eluent to afford a colorless solid (3.3 g, 82%). ¹H NMR (400 MHz, CDCl₃, δ): 7.80 (s, 2H), 7.39 (dd, 2H), 7.11 (m, 4H), 4.21 (d, 4H), 1.15 (t, 6H).

Synthesis of 4-Bromo-1-(2-ethylhexyl)oxy)-2-fluorobenzene. To a solution of 4-bromo-2-fluorophenol (10.0 g, 52.5 mmol) and K₂CO₃ (8.5 g, 62.8 mmol) in DMF (50 mL), 1-bromo-2-ethylhexane (10.0 g, 52.4 mmol) was added, and the stirred mixture was kept at 130 °C for 12 h, then cooled to room temperature, and extracted with ethyl acetate. The combined organic phase was dried over MgSO₄. After removing the solvent, the resulting crude compound was purified by silica gel chromatography using hexane as the eluent to afford a colorless oil (13.0 g, 81%). ¹H NMR (400 MHz, CDCl₃, δ): 7.24 (dd, 1H), 7.16 (d, 1H), 6.88 (t, 1H), 3.92 (d, 2H), 1.78 (m, 1H), 1.59–1.32 (m, 8H), 0.92–0.86 (m, 6H).

Synthesis of Compound M1. To a solution of 4-bromo-1-(2ethylhexyl)oxy)-2-fluorobenzene (3.0 g, 12.5 mmol) in THF (25 mL) at -78 °C was added *n*-BuLi (5.5 mL, 2.5 M in hexane, 13.75 mmol); the mixture was kept at -78 °C for 1 h, and then a solution of compound 1 (0.8 g, 2.1 mmol) in THF (15 mL) was added slowly. After the addition, the mixture was stirred at room temperature overnight and then quenched with water and extracted with ethyl acetate. The combined organic phase was dried over MgSO4. After removing the solvent, the crude product was directly dissolved in acetic acid (100 mL) and concentrated H_2SO_4 (2 mL) was added. The mixture was refluxed for 4 h and cooled to room temperature. After pouring into water, the mixture was extracted with ethyl acetate and dried over MgSO₄. The resulting crude compound was purified by silica gel chromatography using a mixture of hexane/dichloromethane (5:1) as the eluent to afford a yellow solid (1.6 g, 68%). ¹H NMR (400 MHz, CDCl₃, δ): 7.36 (s, 2H), 7.29–7.28 (d, 2H), 6.97–6.94 (m, 6H), 6.93-6.89 (d, 4H), 6.88-6.79 (m, 4H), 3.86-3.84 (m, 8H), 1.75-1.52 (m, 4H), 1.46-1.27 (m, 34H), 0.92-0.86 (m, 24H). ¹³C

NMR (100 MHz, CDCl₃, δ): 155.1, 153.5, 153.1, 151.1, 146.4, 141.2, 136.8, 135.0, 128.1, 123.3, 122.6, 117.2, 116.0, 114.3, 71.8, 39.3, 30.3, 28.9, 23.7, 23.0, 14.0. Anal. Calcd for C₇₂H₈₆F₄O₄S₂: C 74.83, H 7.50, O 5.54, S 5.55. Found: C 74.65, H 7.61, O 5.64, S 5.60.

Synthesis of Compound M2. To a solution of M1 (1.1 g, 1.0 mmol) in THF (20 mL) at -78 °C was added *n*-BuLi (1 mL, 2.5 M, 2.5 mmol). After addition, the mixture was kept at -78 °C for another 1 h, and then trimethyltin chloride (1.0 M, 4.0 mmol) was added. The resulting mixture was stirred overnight at room temperature overnight and then quenched with water and extracted with diethyl ether. The diethyl ether solution was dried over MgSO₄. Recrystallization from methanol afford a yellow solid (0.9 g, 65%). ¹H NMR (400 MHz, CDCl₃, δ): 7.35 (s, 2H), 7.25–6.98 (m, 6H), 6.97–6.89 (d, 4H), 6.84–6.80 (m, 4H), 3.89–3.83 (m, 8H), 1.80–1.56 (m, 4H), 1.45–1.23 (m, 38H), 0.99–0.88 (m, 27H), 0.44–0.30 (t, 18H). ¹³C NMR (100 MHz, CDCl₃, δ): 156.8, 153.5, 153.3, 151.0, 146.3, 142.2, 137.3, 134.7, 129.9, 123.4, 117.5, 116.2, 114.3, 71.8, 39.3, 30.3, 29.7, 23.7, 23.0, 14.0, –8.0. Anal. Calcd for C₇₈H₁₀₂F₄O₄S₂Sn₂: C 63.25, H 6.94, O 4.32, S 4.33. Found: C 64.69, H 7.46, O 4.24, S 4.11.

Stille-Coupling Polymerization. The compound M2 (150.0 mg, 0.112 mmol), TQ (95.9 mg, 0.112 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.002 mmol), and P(o-Tol)3 (3.4 mg, 0.010 mmol) were put into a Schlenk flask and purged with argon for 10 min. Then 5 mL of anhydrous toluene was added, and the mixture was heated at 110 °C for 72 h. After cooling to room temperature, the mixture was poured into methanol. The crude product was collected by filtration and washed by Soxhlet extraction in methanol, acetone, and hexane. Finally, chloroform-soluble fraction was reprecipitated in methanol to afford a dark purple solid.

DAP. The compound M1 (100.0 mg, 0.069 mmol), TQ (74.5 mg, 0.069 mmol), Pd(OAc)₂ (0.3 mg, 0.002 mmol), and K₂CO₃ (23.9 mg, 0.173 mmol) were put into a microwave vessel and purged with argon for 10 min. Then 5 mL of anhydrous DMAc was added, and the mixture was heated at 100 °C by using either conventional or microwave tool for each reaction time noticed in Table 1. After cooling to room temperature, the mixture was poured into methanol. The crude product was collected by filtration and washed by Soxhlet extraction in methanol, acetone, and hexane. Finally, chloroform-soluble fraction was reprecipitated in methanol to afford a dark purple solid.

Fabrication and Characterization of Solar Cells. The structure of the all the polymer solar cells was glass/ITO/PEDOT: PSS/active layer/Al. PEDOT:PSS (Bayer Baytron 4083) was spin-coated at 4000 rpm onto ITO substrate, followed by annealing at 150 °C for 15 min to remove water completely. The active layer was spin-coated from *o*dichlorobenzene solution of polymers and PC₇₁BM (10 mg mL⁻¹) onto the PEDOT:PSS layer. Finally, 80 nm aluminum was thermally evaporated under vacuum ($<5.0 \times 10^{-5}$ Pa). The active area of each sample was 5.0 mm². The current density–voltage (*J*–*V*) characteristics were measured on a Keithley 2400 source under illumination of an AM1.5G solar simulator with an intensity of 100 mW cm⁻². EQE measurements were conducted in ambient air using an EQE system (Model QEX7) by PV measurements Inc. (Boulder, CO). The hole mobilities were measured via the space-charge-limited current (SCLC) method with the structure of ITO/PEDOT:PSS/active layer/Au.

AFM Characterization. An Agilent 5500 scanning probe microscope (SPM) running with a Nanoscope V controller was used to obtain AFM images of polymer thin films. AFM images were recorded in high-resolution tapping mode under ambient conditions. Premium silicon cantilevers (TESP-V2) were used with a rotated tip to provide more symmetric representation of features over 200 nm.

GIWAXS Characterization. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength $\lambda = 1.109$ 94 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) × 60 (V) μ m² in fwhm at sample position) using K-B type mirrors. The GIWAXS sample stage was equipped with a 7-axis motorized stage for the fine alignment of sample, and the incidence angle of X-ray beam was set to

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ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ acs.macromol.5b02324.

7.7624 Å, $\beta = 102.938^{\circ}$), and the sample-to-detector distance was

Figures S1-S5; Tables S1 and S2 (PDF)

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Notes

~231 mm.

The authors declare no competing financial interest.

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