Tunable Light-Harvesting Polymers Containing Embedded Dipolar Chromophores for Polymer Solar Cell Applications

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ABSTRACT: A series of light-harvesting conjugated polymers were designed and synthesized for polymer solar cells. These newly designed polymers comprise an unusual two-dimensional conjugated structure with an electron-rich thiophene-triphenylamine backbone and stable planar indacenodithiophene π -bridges terminated with tunable electron acceptors. It was found that the electron-withdrawing strength of the acceptor could be used to manipulate the energy level of the lowest unoccupied molecular orbital and bandgap (as much as 0.3 eV), generating derivatives with complementary absorbance in the visible spectrum. This approach provides

great flexibility in fine tuning the electronic and optical properties of the resultant polymers and facilitates the investigation of how these chemical modifications alter the subsequent photovoltaic properties of these materials. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1362–1373, 2012

KEYWORDS: bulk-heterojunction solar cells; charge transfer; conjugated polymers; D- π -A chromophore; low bandgap polymers; molecular modeling; organic solar cells; NLO; postpolymerization modification

INTRODUCTION Solar energy is the largest source of renewable energy in the world.¹ Solar cells can convert this energy to usable electricity, but commonly used inorganic solar cells are prohibitively expensive for widespread commercialization.² Thus, over the past decade, polymer solar cells (PSCs) based on the bulk heterojunction (BHJ) structure have emerged as a promising alternative to inorganic cells because of their potential for low-cost solution processability, light weight, flexibility, and large-scale printing.^{3,4} A significant amount of research has focused on the molecular engineering of linear donoracceptor (D–A) polymers to tune their bandgap (E_{g}) and energy levels to enhance PSC performance. Typically, these polymers consist of alternating electron-rich and electron-poor monomers. The characteristics of the monomers dictate the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the bandgap of the polymer.⁵ Although this method can theoretically be used to optimize the electronic attributes of light-harvesting polymers, it is difficult to systematically fine tune their energy levels because it requires parallel syntheses of modified donor and/or acceptor monomers and polymerization reactions. This leads to inconsistent electronic properties across different polymer batches.^{6,7}

To address this issue, several groups have explored the development of tunable $D-\pi$ -bridge-A polymers for PSC appli-

cations.⁷⁻¹⁴ The D– π -bridge–A motif is common to many second-order nonlinear optical (NLO) chromophores. This architecture exploits well-established knowledge of the structure/property relationships and charge transfer in NLO dyes, which can greatly decrease their bandgap.^{15–17} Unlike common D–A-based semiconducting polymers, the acceptors of these polymers terminate the electron-poor side chains, which are connected through a π -bridge to an electron-rich conjugated backbone.^{7–14}

Such tunable D- π -bridge-A polymers generally consist of an alternating D₁-D₂ backbone, with one of the donors connected to the electron acceptor through a π -bridge to form a push-pull chromophore incorporated into the polymer backbone. The π -bridge is terminated with a synthetic handle that can subsequently be functionalized with a range of acceptors after polymerization.⁷⁻¹⁴ Postfunctionalization represents a flexible and generally applicable method to easily tune the electronic and optical properties of the polymers and to probe structure/property relationships of the polymers. To date, most D- π -bridge-A polymers have utilized triphenylamine-styrylthiophene or thienylene-vinylene-based chromophores using indenofluorene,⁷ fluorene,⁸ silafluorene,⁹ cyclopentadithiophene,¹⁰ and carbazole¹¹⁻¹⁴ donors, though these materials have very similar properties and weaknesses.

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FIGURE 1 Structure of PThTPA-IDT polymer functionalized with DCN, TBA, and DCNIO acceptors.

Importantly, these polymers consistently show weak internal charge transfer (ICT) transition absorbance compared with linear D-A polymers, whose absorbance profile is typically dominated by their long wavelength ICT peak. In general, this is the result of poor spatial overlap between the HOMO orbitals on the polymer backbone and the LUMO orbitals on the side-chain acceptor. Limited electronic communication between the electron-rich backbone and pendant acceptors leads to weak ICT oscillator strength, thereby limiting the intensity of the ICT absorbance.¹⁸ This poor electronic communication could potentially be due to interrupted conjugation along the polymer backbone or between the backbone and side chain. For example, the phenyl-phenyl backbone linkages of such polymers are inherently problematic because these bonds experience severe twisting due to the steric hindrance between phenyl protons.¹⁹ In addition, benzene has a relatively high-aromatic stabilization energy and hence, has poor effective conjugation with its chemical environment.²⁰ Conversely, in the case of thienylene-vinylene side-chain polymers, it is possible that steric repulsion between the vinylene protons and backbone aromatic protons push the side chain out of plane with the backbone.²¹ In both cases, the electron-rich backbone is electronically isolated from the electron-poor side chain, which leads to a low-wavelength π - π ^{*} transition absorbance that is significantly more intense than the longer wavelength ICT peak.⁷⁻¹⁴ The resultant absorbance profile overlaps poorly with the solar spectrum, which decreases PSC performance.^{22,23} Moreover, most reported side-chain polymers for PSCs suffer from poor solubility in common organic solvents due to inadequate solubilizing groups on fluorene and carbazole moieties.⁷ This poor solubility complicates device processing and results in thin active layers with low optical densities. One recent report of an indenofluorene-based side-chain polymer exhibited improved processability, but still displayed a very intense low wavelength π - π * transition.⁷

To further investigate the structure–property relationships of $D-\pi$ -bridge–A polymers, a new class of $D-\pi$ -bridge–A polymer [PThTPA-indacenoditihophene (IDT)] was synthesized and functionalized with three acceptors (Fig. 1). These polymers consist of a thiophene–TPA backbone and a novel IDT

 π -bridge. We theorized that inclusion of thiophene in the polymer backbone would minimize steric repulsion, thereby increasing the planarity of the polymer backbone and the relative intensity of the ICT absorbance. In addition, recently reported conjugated copolymers based on the IDT donor have exhibited high PCE and mobilities $(10^{-1} \text{ to } 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ despite its bulky hexylbenzyl side chains, which hamper intermolecular π - π stacking.²⁴⁻²⁸ This suggests that the high hole mobilities of IDT-based D-A copolymers is the result of efficient intramolecular hole transport along their rigid, fused backbone. Thus, we hypothesized that incorporating the fused IDT unit as the polymer π -bridge could provide adequate carrier mobility and charge transfer properties, while also enhancing the polymer solubility through the peripheral hexylbenzyl groups.

As predicted, the PThTPA-IDT polymers have a more intense ICT absorbance peak than π - π * transition peak and have higher absorbance coefficients than those reported for other D- π -bridge-A polymers. Also, IDT π -bridge imbued the polymers with enhanced solubility and processability. However, when relatively weak acceptors were used, the PThTPA-IDT polymers showed weaker ICT characteristics compared with polymers utilizing a vinylene π -bridge. This weaker ICT is due to the large stabilization energy of the fused IDT π bridge, which hinders effective charge transfer in the side chain. Interestingly, stronger acceptors facilitated efficient charge transfer and led to better ICT characteristics. Despite the high-hole mobility of IDT and TPA units, these copolymers showed moderate mobilities $(10^{-3} \text{ to } 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ s^{-1}) as measured by the organic field effect transistor (OFET) method. In addition, the BHJ active layer exhibited severe phase segregation for two of the three polymers. The resultant PSCs exhibited a depressed J_{sc} and FF, likely due to increased recombination rates caused by poor morphology and mobility. Although the PSCs have limited efficiencies, this approach provides a good system to study the effects of the fine tuning of the electronic and optical properties of $D-\pi$ -bridge-A polymers on PSC performance.

EXPERIMENTAL

Materials

Unless otherwise specified, all chemicals were purchased from Aldrich or TCI and used without further purification. 3-Bromo-4-iodothiophene,^{29,30} *N*,*N*-diphenyl-4-(trimethylstan-nyl)aniline,^{31,32} indacenodithiophene,³³ and 2,5-bis(trimethyl-stannyl)thiophene³⁴ were prepared as previously reported. Solvents for synthesis were purified by distillation. All chemical reactions were carried out in a nitrogen atmosphere.

Synthesis of Compound 1

IDT (1.51 g, 1.7 mmol) was dissolved in anhydrous DMF (40 mL) and the solution was cooled to 0 °C. $POCl_3$ (0.292 g, 1.9 mmol) was added to this dropwise. The solution was gradually warmed to room temperature, heated to 50 °C, and allowed to stir for 8 h. Then, saturated $NaC_2H_3O_2$ (60 mL) was added and the solution was stirred for a further 30 min. The mixture was extracted with dichloromethane and the combined organic layers were washed repeatedly with



saturated NaCl solution. Then, the organic fraction was dried with Na_2SO_4 , concentrated *in vacuo*, and the crude product was purified by column chromatography (1:1 dichloromethane:hexane) to yield compound **1**, a yellow solid (0.99 g). Yield: 64%.

¹H NMR (300 MHz, CDCl₃, ppm): 9.93 (s, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.59 (s, 1H), 7.43 (d, J = 6 Hz, 1H), 7.29 (m, 11H), 7.21 (d, J = 3 Hz, 2H), 7.18 (d, J = 3 Hz, 2H), 7.14 (d, J = 6 Hz, 2H), 2.69 (t, J = 6 Hz, 8H), 1.70 (m, 8H), 1.42 (m, 25H), 0.99 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): 183.02, 158.13, 154.81, 142.79, 142.15, 141.79, 135.91, 128.31, 128.25, 127.28, 123.90, 118.03, 62.87, 35.49, 31.78, 31.59, 29.50, 22.88, 14.33. HRMS calcd for C₆₅H₇₄OS₂ [M + H]⁺: 935.4192; found, 935.4190. Anal. calcd for C₆₅H₇₄OS₂: C, 83.53; H, 7.98. Found: C, 83.49; H, 7.96.

Synthesis of Compound 2

Compound **1** (0.95 g, 1.0 mmol) was dissolved in tetrahydrofuran (THF; 50 mL) and cooled to 0 °C. NBS (0.199 g, 1.1 mmol) was added in one portion, the solution was gradually warmed to room temperature and stirred overnight. The solution was poured into H_2O and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo* to yield compound **2**, a yellow solid (0.957 g). Yield: 93%.

¹H NMR (300 MHz, CDCl₃, ppm): 9.93 (s, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.59 (s, 1H), 7.29–7.13 (m, 17H), 2.69 (t, J = 6 Hz, 8H), 1.70 (m, 8H), 1.42 (m, 24H), 0.99 (t, J = 3 Hz, 12H).¹³C NMR (125 MHz, CDCl₃, ppm): 183.10, 158.08, 154.83, 142.84, 142.19, 141.80, 135.91, 128.29, 128.20, 127.29, 123.87, 117.99, 62.88, 35.49, 31.78, 31.59, 29.50, 22.88, 14.33. Anal. calcd for C₆₅H₇₃BrOS₂: C, 77.11; H, 7.26. Found: C, 77.08; H, 7.25.

Synthesis of Compound 5

Compound **2** (0.911 g, 0.9 mmol) was added to an ovendried flask and degassed three times. $Pd_2(dba)_3$ (4 mg) and $P(o-tol)_3$ (5 mg) were added to the flask and subsequently **4** (0.441 g, 0.1 mmol) dissolved in toluene (5 mL) was added, the solution was cooled to -78 °C and degassed three more times. The solution was stirred at 100 °C for 24 h. Then, the solution was concentrated, dissolved in dichloromethane and extracted with brine. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (1:1 dichloromethane:hexane) to yield compound **5**, a bright yellow solid (0.826 g). Yield: 78%.

¹H NMR (300 MHz, CDCl₃, ppm): 9.82 (s, 1H), 7.67 (s, 1H), 7.58 (s, 1H), 7.47 (d, J = 6 Hz, 3H), 7.31–7.06 (m, 29H), 2.58 (t, J = 9 Hz, 8H), 1.62 (m, 8H), 1.33 (m, 25H), 0.90 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): 182.75, 158.01, 155.96, 154.93, 153.59, 151.64, 148.33, 147.40, 147.39, 145.10, 141.94, 141.72, 141.48, 141.08, 138.82, 138.17, 133.13, 129.37, 128.71, 128.65, 128.74, 127.88, 127.70, 126.21, 124.55, 123.58, 123.20, 118.82, 118.24, 117.27, 63.11, 62.88, 35.63, 31.79, 31.33, 29.19, 22.60, 14.13. HRMS calcd for C₈₃H₈₇NOS₂ [M + H]⁺: 1178.7233; found, 1178.7231. Anal.

calcd for $C_{83}H_{87}NOS_2\!\!:$ C, 84.57; H, 7.44. Found: C, 84.52; H, 7.40.

Synthesis of Compound 6

Compound **5** (0.810 g, 0.7 mmol) was dissolved in THF (50 mL) and cooled to 0 °C. NBS (0.269 g, 1.5 mmol) was added in one portion, the solution was allowed to gradually warm to room temperature and stirred overnight. The solution was poured into H_2O and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo* to yield compound **6**, a bright yellow solid (0.872 g). Yield: 95%.

¹H NMR (300 MHz, CDCl₃, ppm): 9.82 (s, 1H), 7.67 (s, 1H), 7.58 (s, 1H), 7.47 (m, 2H), 7.38 (d, J = 9 Hz, 3H), 7.22–7.09 (m, 20H), 7.04 (d, J = 9 Hz, 2 H), 6.97 (d, J = 9 Hz, 3 H), 2.60 (m, 8H), 1.61 (m, 8H), 1.33 (m, 25H), 0.90 (m, 12H).¹³C NMR (125 MHz, CDCl₃, ppm): 182.72, 158.11, 155.99, 154.90, 153.56, 151.61, 148.39, 147.32, 147.33, 145.12, 141.94, 141.76, 141.50, 141.07, 138.89, 138.20, 133.11, 129.37, 128.71, 128.69, 128.77, 127.86, 127.74, 126.20, 124.58, 123.60, 123.21, 118.84, 118.23, 117.28, 63.14, 62.88, 35.63, 31.79, 31.33, 29.19, 22.60, 14.13. Anal. calcd for $C_{83}H_{85}Br_2NOS_2$: C, 74.76; H, 6.43. Found: C, 84.36; H, 6.41.

Synthesis of PThTPA-IDT-CHO

Compound 12 (0.351 g, 0.26 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.108 g, 0.26 mmol) were added to an oven-dried flask and degassed three times. $Pd(PPh_3)_4$ (7 mg) was added to the flask and subsequently anhydrous toluene (4 mL) and DMF (0.5 mL) were added. The solution was stirred at 110 °C for 36 h. Bromobenzene (0.2 mL, 2 mmol) was added and the solution was stirred at 110 $^\circ C$ for 12 h. Trimethyl(phenyl)tin (0.35 mL, 2 mmol) was added and the solution was stirred at 110 °C for another 12 h. The solution was then cooled to rt, poured into MeOH (100 mL), the precipitate filtered through a Soxhlet thimble and purified by Soxhlet extraction for 12 h with acetone, 12 h with methanol, 12 h with hexanes and collected with CHCl₃. The CHCl₃ solution was concentrated and precipitated into MeOH. Filtration yielded PThTPA-IDT-CHO, a red solid (228 mg). Yield: 69%.

¹H NMR (300 MHz, CDCl₃, ppm): 9.79 (s, 1H), 7.63 (s, 1H), 7.52–7.37 (br, 10 H), 7.22–7.06 (br, 23H), 2.56 (m, 8H), 1.59 (m, 8H), 1.28 (m, 24H), 0.86 (m, 12H). GPC (THF, polystyrene standard): $M_{\rm w} = 43.1 \times 10^3$ g/mol; PDI = 1.94.

Synthesis of PThTPA-IDT-DCN

PThTPA-IDT-CHO (50 mg) was dissolved in THF (20 mL) and ethanol was added until the initial appearance of precipitate. Then, malononitrile (90 mg) was added. After 10 min, pyridine (0.05 mL) was added. The solution was warmed to 50 °C and stirred at that temperature for 16 h. The solution was concentrated *in vacuo*, dissolved in a small volume of dichloromethane, precipitated in methanol, and filtered to yield PThTPA-IDT-dicyanovinyl (DCN) as a deep red solid (47 mg). Yield: 91%.

¹H NMR (300 MHz, CDCl₃, ppm): 7.63–7.41 (br, 11H), 7.22– 7.06 (br, 24H), 2.55 (m, 8H), 1.28 (m, 25H), 0.86 (m, 12H).

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GPC (THF, polystyrene standard): $M_{\rm w} = 42.8 \times 10^3$ g/mol; PDI = 1.90.

Synthesis of PThTPA-IDT-TBA

PThTPA-IDT-CHO (50 mg) was dissolved in THF (20 mL) and ethanol was added until the initial appearance of precipitate. Then, 1,3-diethyl-2-thiobarbituric acid (TBA; 140 mg) was added. After 10 min, pyridine (0.05 mL) was added. The solution was warmed to 50 °C and stirred at that temperature for 16 h. The solution was concentrated *in vacuo*, dissolved in a small volume of dichloromethane, precipitated in methanol and filtered to yield PThTPA-IDT-TBA as a dark solid (53 mg). Yield: 93%.

¹H NMR (300 MHz, CDCl₃, ppm): 8.64 (s, 1H), 7.73–7.65 (m, 3H), 7.58–7.44 (br, 10H), 7.22–7.06 (br, 21H), 4.58 (m, 4H), 2.56 (m, 8H), 1.28 (m, 30H), 0.86 (m, 12H). GPC (THF, polystyrene standard): $M_{\rm w} = 42.1 \times 10^3$ g/mol; PDI = 1.87.

Synthesis of ThTPA-IDT-DCNIO

PThTPA-IDT-CHO (50 mg) was dissolved in THF (20 mL) and ethanol was added until the initial appearance of precipitate. Then, 3-dicyanomethylene-1-indanone (DCNIO; 135 mg) was added. After 10 min, pyridine (0.05 mL) was added. The solution was warmed to 50 °C and stirred at that temperature for 16 h. The solution was concentrated *in vacuo*, dissolved in a small volume of dichloromethane, precipitated in methanol, and filtered to yield PThTPA-IDT-DCNIO as a dark solid (51 mg). Yield: 90%.

¹H NMR (300 MHz, CDCl₃, ppm): 8.87 (d, 1H), 8.65 (d, 1H), 7.88 (m, 2H), 7.72–7.61 (m, 4H), 7.54–7.43 (m, 9H), 7.23– 7.07 (m, 22H), 2.56 (m, 8H), 1.28 (m, 25H), 0.86 (m, 12H). GPC (THF, polystyrene standard): $M_{\rm w} = 42.2 \times 10^3$ g/mol; PDI = 1.91.

Quantum Mechanical Calculations

All density functional theory (DFT) calculations were performed using Gaussian $09(A.02)^{35}$ employing the hybride B3LYP^{36,37} exchange-correlation functional with a split valence 6-31G^{*38} basis set. Alkyl substituents were replaced by methyl groups for computational simplicity as their replacement with shorter chains does not significantly affect optimized geometry or predicted energy levels of the polymers.

General Measurement and Characterization

UV-vis spectra were tested using a Perkin-Elmer Lambda-9 spectrophotometer. ¹H NMR and ¹³C NMR spectra were collected on a Bruker AV 300 or 500 spectrometers operating at 300 or 125 MHz in deuterated chloroform solution with TMS as reference. Elemental analysis was conducted using a ThermoFisher Scientific Thermo Finnigan EA 1112 Flash Elemental Analyzer. HRMS spectra were recorded on an Applied Biosystems QTOF QStar XL Mass Spectrometer. Polymer molecular weights were measured by a Waters 1515 gel permeation chromatograph (GPC) with a refractive index detector at room temperature (THF as the eluent). Cyclic voltammetries (CVs) of polymer films were conducted on a BAS CV-50W voltammetric system with a three-electrode cell in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) using a scan rate of 50 mV s⁻¹. ITO, Ag/

AgCl, and Pt mesh were used as working electrode, reference electrode, and counter electrode, respectively. The differential scanning calorimetry (DSC) was performed using DSC2010 (TA instruments) under a heating rate of $10 \,^{\circ}$ C min⁻¹ and a nitrogen flow of 50 mL min⁻¹. The AFM images under tapping mode were taken from the actual devices fabricated for photovoltaic measurement on a Veeco multimode AFM with a Nanoscope III controller. All spectra were plotted using OriginPro 8.

Fabrication and Characterization of OFET and PSC Devices

The field effect transistors were fabricated with a bottomgate, top-contact configuration. The heavily n-doped silicon substrates with a 300-nm thick thermally grown SiO₂ dielectric (from Montco Silicon Technologies) were first cleaned by sonication in acetone and isopropanol and exposed to air plasma. The cleaned substrates were then treated with hexamethyldisilazane (HMDS) through vapor phase deposition in a vacuum oven (200 mTorr, 100 °C, 3 h). Subsequently, the semiconductor polymer films were spin-coated in a glove box from their 10 mg mL⁻¹ chloroform:*o*-dichlorobenzene (1:1, v/v) solutions, which were stired overnight and filtered with $0.2-\mu m$ PTFE filter. Interdigitated source and drain electrodes ($W = 1000 \ \mu m$, $L = 12 \ \mu m$) were deposited by evaporating a 50-nm thick gold film and defined with a shadow mask. The transfer and output characteristics were measured in glove box using an Agilent 4155B semiconductor parameteranalyzer. The saturation field-effect mobility (μ) was calculated from the following equation:

$$I_{\rm ds} = \mu (W/2L)C_{\rm i}(V_{\rm gs} - V_{\rm th})^2$$

where *W* and *L* are the channel width and length, respectively. C_i is the capacitance of insulating SiO₂ layer per unit, $V_{\rm gs}$ and $V_{\rm th}$ are the gate voltage and the threshold voltage, respectively. $V_{\rm th}$ was obtained as the \times intercept of the linear section of the plot of $(I_{\rm ds})_{1/2}$ versus $V_{\rm gs}$. The subthreshold swing was estimated by taking the inverse of the slope of $I_{\rm ds}$ versus $V_{\rm gs}$ in the region of exponential current increase.

Fabrication of Photovoltaic and Hole Only Devices

To fabricate conventional configuration solar cells, ITOcoated glass substrates (15 Ω /sq.) were first cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. Subsequently, PEDOT:PSS (Baytron[®] PVP AI 4083, filtered at 0.45 μ m) layer (~45 nm) was spin-coated (5000 rpm) on the cleaned ITO-coated glass substrates and then annealed at 120 $^\circ\text{C}$ for 30 min under ambient conditions. After that, the substrates were loaded into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated (2000 rpm) onto the PEDOT:PSS layer from a homogeneous blending solution of polymer:PC71BM. The solution was prepared by dissolving the polymer and $PC_{71}BM$ with a particular blending weight ratio in chloroform:o-dichlorobenzene (o-DCB) overnight and filtered with a $0.2-\mu m$ PTFE filter. Finally, the substrates were transferred into the evaporator with shadow masks to define the active area of the devices (10.08 mm²) and pumped under high vacuum ($< 2 \times 10^{-7}$ Torr). Then calcium





SCHEME 1 Synthesis of PThTPA-IDT polymers. (i) POCI3, DMF, 0 °C to rt; (ii) *N*-bromosuccinimide, THF, 12 h, rt; (iii) *N*-bromosuccinimide, THF, 12 h, 0 °C; (iv) (a) *n*-BuLi, THF, -78 °C, 1 h, (b) CISnMe₃, hexane, rt, 12 h; (v) Pd₂(dba)₃, P(o-tol)₃, THF, reflux, 16 h; (vi) *N*-bromosuccinimide, THF, 12 h, rt; (vii) 2,5-bis(trimethylstannyl)thiophene, Pd(PPh₃)₄, toluene, DMF, 110 °C, 48 h; (viii) malononitrile, CHCl₃, pyridine, 50 °C, 16 h; (ix) TBA, CHCl₃, pyridine, 50 °C, 16 h; (x) 3-dicyanomethylene-1-indanone, CHCl₃, pyridine, 50 °C, 16 h.

(30 nm) and aluminum (100 nm) were thermally evaporated onto the active layer sequentially. The unencapsulated solar cells were measured in glove box conditions using a Keithley 2400 SMU source measurement unit and an Oriel Xenon lamp (450 W) with an AM1.5 filter as the solar simulator. A reference silicon solar cell with a KG5 filter, which has been previously standardized by the National Renewable Energy Laboratory (NREL), was used to calibrate the light intensity to 100 mW cm⁻². To fabricate the hole only device, the same procedure to the photovoltaic device was followed except that MoO₃ was used to relace the calcium.

RESULTS AND DISCUSSION

Synthesis

General synthesis of the TPA-IDT monomer and PThTPA-IDT are shown in Scheme 1. The IDT unit was prepared as reported previously.³³ The IDT molecule was then monoformylated in moderate yield via the Vilsmeier–Haack reaction and then brominated with NBS to give **2**. Concurrently, triphenylamine was monobrominated with NBS to yield **3**, which was lithiated and quenched with trimethyltin chloride to generate **4**. Then, **2** and **4** were coupled via a Stille reaction to yield **5**, which was then dibrominated with NBS. Copolymer PThTPA-IDT-CHO was synthesized by Stille crosscoupling between and 2,5-bis(trimethylstannyl)thiophene, using tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) as a catalyst in toluene/DMF solution. The polymerization was carried out at 110 °C under nitrogen atmosphere for 48 h. The resulting polymers were collected by precipitating the reaction solution in methanol followed by filtration. After Soxhlet extraction with acetone, hexane and methanol for 12 h each, the final polymer was collected by extraction with CHCl₃ and the resultant solution was precipitated in methanol. This polymer was then functionalized with malononitrile (DCN), TBA, and DCNIO acceptors via a Knoevenagel condensation to yield their respective polymers.

Polymer Characterization

The polymers all have good solubility in a wide range of organic solvents including THF, dichloromethane, chlorobenzene, and dichlorobenzene. The molecular weights of the polymers were measured by GPC with polystyrene as standard and THF as eluent. The number-average molecular weights (M_n) of PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO are 22.0, 21.7, and 22.1 kDa with polydispersity indices (PDI) of 1.90, 1.87, and 1.91, respectively. Because of the improved solubility of PThTPA-IDT, M_n is higher than those reported for many reported D– π -bridge–A polymers.⁷⁻¹⁴ This improved solubility is attributed to the solubilizing IDT unit.

The thermal properties of these polymers were evaluated using DSC. All three PThTPA-IDT polymers exhibit two



FIGURE 2 DSC spectra for PThTPA-IDT-DCN (solid line), PThTPA-IDT-TBA (dotted line), and PThTPA-IDT-DCN (dashed line).

identical glass transition temperatures ($T_{\rm g}$) around 70 and 100 °C (Fig. 2), which correspond to $T_{\rm g}$ for the solubilizing alkyl chains and the polymer backbone, respectively. This amorphous behavior is expected based on the propellor-like twist of the triphenylamine moiety, which inhibits intermolecular π - π packing.⁵

The UV-vis absorption spectra of the polymers in CHCl₃ solutions and thin films are shown in Figure 3 and the summarized data is listed in Table 1. The absorption maxima in chloroform solution were observed at 445, 581, and 639 nm for PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO, respectively. The peaks of the thin film absorption are slightly broadened compared with the solution peaks, but otherwise are identical. As expected for amorphous materials, the spectra show no evidence of strong intermolecular packing. The absorption coefficients were calculated from the solid state absorbance and are 1.11×10^5 cm⁻¹, 0.87 $\times 10^5$ cm⁻¹, and 0.86 $\times 10^5$ cm⁻¹ for PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO, respectively.

Two obvious absorption bands are observed for the polymers in films and solutions. The shorter wavelength absorbance can be assigned to the backbone π - π * transition while

the longer-wavelength absorption band is attributed to ICT from the electron-rich backbone through the π -bridge to the electron-deficient side-chain acceptors.⁸ Similar to reported D- π -bridge-A polymers, stronger electron acceptors decrease $E_{\rm g}$ and redshift the ICT absorption peak by increasing the polymer LUMO level.⁷⁻¹⁴

Interestingly, PThTPA-IDT-DCN exhibits a very weak ICT shoulder on the main π - π * transition peak instead of the full ICT peak as displayed by PThTPA-IDT-TBA and PThTPA-IDT-DCNIO. This unusual phenomenon suggests that the DCN acceptor is not strong enough to pull electron density away from the polymer backbone through the π -bridge and form a stable ICT state. This is attributed to the high-aromatic stabilization energy of the IDT unit, making the formation of an ICT state with a weak acceptor energetically unfavorable. The absorbance profile suggests that there is a threshold acceptor strength that is sufficient to funnel charge through the IDT π -bridge by stabilizing the ICT state; the DCN acceptor does not possess this threshold electron-withdrawing strength. In contrast, both TBA and DCNIO have sufficient electron withdrawing strength to stabilize the ICT state of the IDT π -bridge. In addition, both the TBA and DCNIO acceptors blueshift the π - π^* transition peak by \sim 25 nm, while the DCN acceptor does not cause a similar hypsochromic shift. This $\pi - \pi^*$ peak shift also does not occur in any existing D- π -bridge-A polymers. Although this shift is not fully understood, it is attributed to the fact that these acceptors pull electron density away from the electron-rich backbone via the IDT π -bridge to form a CT state. This CT state stabilizes the polymer HOMO, effectively increasing the π - π^* transition energy. If this is accurate, the shift is not seen in other D- π -bridge-A polymers because there is very poor electronic communication between the polymer backbone and the side chain and thus, regardless of its electron-withdrawing strength, the acceptor is unable to pull electrons away from the electron-rich backbone.

Encouragingly, the ratio of the low-energy π - π * ICT peak intensity to the high-energy backbone π - π * transition peak intensity of PThTPA-IDT-TBA and PThTPA-IDT-DCNIO



FIGURE 3 (a) Solution absorbance (CHCl₃) and (b) thin film absorbance for PThTPA-IDT-CHO (dotted-dashed line), PThTPA-IDT-DCN (solid line), and PThTPA-IDT-TBA (dotted line) and PThTPA-IDT-DCN (dashed line).

					CHCl ₃ Solution		Thin Film			
Polymer	<i>M</i> w (kDa)	<i>M</i> n (kDa)	PDI	λ _{max} (nm)	E ^g _{opt} (eV)	λ _{max} (nm)	E ^g opt (eV)	α ^a	HOMO ^b (ev)	LUMO ^c (eV)
PThTPA-IDT-DCN	22.0	41.8	1.90	439	2.05	439	2.05	1.11	-5.18	-3.13
PThTPA-IDT-TBA	21.7	40.5	1.87	581	1.86	581	1.86	0.87	-5.14	-3.28
PThTPA-IDT-DCNIO	22.1	42.2	1.91	639	1.69	639	1.69	0.86	-5.13	-3.44

TABLE 1 PThTPA-IDT Characteristics

^a Absorption coefficient of thin films at λ_{max} (×10⁵ cm⁻¹).

^b HOMO calculated from the oxidation onset of the CV curve.

(~1.2:1) is much larger than that of previous D- π -bridge-A polymers ($\sim 0.5:1$),⁷⁻¹⁴ which leads to better overlap with the solar spectrum. In addition, the absorption coefficients of thin films of the three polymers are much higher than those reported for indenofluorene-TPA side-chain polymers (7 imes 10^4 cm⁻¹ at π - π * peak; 3 × 10⁴ cm⁻¹ at ICT peak)⁷ and carbazole thienylene-vinylene side-chain polymers ($\sim 5 \times 10^4$ cm^{-1} at $\lambda_{\text{max}}).^{14}$ This increase in relative ICT intensity and optical density is attributed to the inclusion of thiophene in the polymer backbone. It is known that phenyl-thiophene linkages are more planar than phenyl-phenyl bonds due to the minimized steric hindrance between adjacent aromatic protons.³⁹ In addition, thiophene has a lower aromatic stabilization energy than benzene,¹⁹ which should improve the electron delocalization along the backbone and the electronic communication between the polymer backbone and sidechain acceptor. The increase in ICT intensity could also be due to the inclusion of the IDT π -bridge. However, due to the high resonance stabilization energy and resultant poor charge transfer character of the IDT unit compared with vinylene-based π -bridges, we think it is unlikely that the IDT π -bridge is enhancing the ICT absorbance.

^c LUMO calculated from HOMO and optical bandgap.

This hypothesis was corroborated by DFT^{35,40,41} calculations at the B3LYP/6-31G* level (Fig. 4).³⁶⁻³⁸ Although DFT often overestimates theoretical energy levels, the B3LYP/6-31G* method has been found to be an accurate formalism for predicting the optical and geometrical properties of conjugated polymers.⁴² The optimized geometry shows that the dihedral angle between the thiophene monomer and the TPA phenyl rings is $\sim 22^{\circ}$. Conversely, the phenyl-phenyl linkages of related fluorene-TPA side-chain polymers exhibit a dihedral angle of $\sim 36^{\circ}$. It is known that twists in the backbone of conjugated polymers breaks their π -conjugation and shortens the delocalization length of the polymer.⁴³ As a result, DFT models predict that fluorene-TPA polymers have a relatively short effective conjugation length. This is seen in the HOMO wave function, which is interrupted by the fluorene unit. In contrast, since the thiophene-TPA linkage is relatively planar, the HOMO wave function delocalizes along the polymer backbone and enhances the effective polymer conjugation length.

Contrary to the differences in the polymer HOMO wave functions, the LUMO wave functions are quite similar. In both cases, the LUMO is almost entirely localized on the side



FIGURE 4 Density functional theory models of HOMO and LUMO orbitals for PThTPA-IDT-DCN and PFTPA-DCN.



FIGURE 5 CV curves for PThTPA-IDT-DCN (solid line), PThTPA-IDT-TBA (dotted line), and PThTPA-IDT-DCN (dashed line).

chain and acceptor. There is negligible overlap of the HOMO and LUMO wave functions. This poor wave function overlap in the PThTPA-IDT polymers indicates that any change in the electronic nature of the acceptor will have a large effect on the polymer LUMO and a very minimal effect on the polymer HOMO. This poor spatial overlap also likely leads to a weak ICT oscillator strength and could explain why the ICT transition is less intense compared with typical linear D-A polymers.¹⁸

The HOMO and LUMO levels of the PThTPA-IDT polymers were investigated using CV of polymer films on indium tin oxide (ITO) substrates in a 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 50 mV s⁻¹ using ITO, Ag/AgCl and Pt mesh as the working electrode, reference electrode and counter electrode, respectively. The CV curves are shown in Figure 5 and the data is summarized in Table 1. All three polymers exhibit two quasi-reversible oxidation processes. The first is attributed to the oxidation of the triphenylamine unit and the second may be due to the oxidation of the fused IDT moiety, which can delocalize and stabilize the resultant charge. The HOMO was calculated from the equation

$$E_{\text{HOMO}}(\text{eV}) = -e(E_{\text{ox}} - E_{1/2}(\text{ferrocene}) + 4.8\text{V})$$

where E_{ox} is the onset oxidation potential of the polymers versus Ag/Ag⁺. Conversely, the reductive curves were entirely irreversible and changed drastically upon repeated cycles. Therefore, the LUMO was calculated from the optical bandedge and HOMO energy level from the equation

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\sigma}^{\rm opt}$$

where $E_{\rm g}^{\rm opt}$ denotes the optical bandgaps of the polymers. PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO have HOMO levels of -5.18, -5.14, and -5.13 eV and LUMO levels of -3.13, -3.28, and -3.44 eV, respectively. The strength of the acceptor has minimal effect on polymer HOMO, but a significant effect on the LUMO and $E_{\rm g}$, in agreement with the DFT predictions. Stronger acceptors stabilize the LUMO to a greater extent, which thereby lowers $E_{\rm g}$.

Field Effect Transistor and Photovoltaic Properties

Finally, the PThTPA-IDT behavior and device performance were evaluated. The device parameters are summarized in Table 2. Top contact OFET devices were fabricated to test the lateral hole mobility of the PThTPA-IDT polymers. Polymer thin films were spin-coated on Si/SiO₂ substrates coated with an HMDS self-assembled monolayer (SAM) and gold was used for the source and drain electrodes. Figure 6 depicts the resultant I–V transfer and output OFET characteristics obtained by sweeping $V_{\rm gs}$ from -100 to 10 V under a $V_{\rm ds}$ of -100 V. The OFET devices displayed typical p-channel characteristics. The hole mobilities of PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO were 2.63×10^{-4} , 1.28×10^{-3} , and 5.30×10^{-4} cm² V⁻¹ s⁻¹, respectively.

The space charge limited current (SCLC) model was also employed to investigate the vertical hole mobilities. The mobilities were extracted by modeling the dark current in the SCLC region. The calculated vertical hole mobility of PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO BHJ films were 6.76×10^{-5} , 1.15×10^{-4} , and 1.66×10^{-4} cm² V⁻¹ s⁻¹, respectively. The vertical mobilities are roughly one order of magnitude lower than the horizontal mobilities. This small discrepancy suggests that these polymers exhibit nearly isotropic charge transport characteristics, which can be attributed to the hyperbranched amorphous nature of the polymers.

The hole mobilities were largely insensitive to annealing, as expected for amorphous polymers. These mobility values are very similar to the previously reported hole mobilities of other D– π -bridge–A polymers.⁷⁻¹⁴ Although these mobilities are reasonable for PSC applications, they are lower than those reported for IDT-containing linear D–A polymers,^{24–28} which might lead to increased charge recombination and inefficient charge transfer. It is likely that the mobilities are limited by poor intermolecular charge transport due to weak intermolecular interactions.

The photovoltaic properties of the PThTPA-IDT polymers were tested using $PC_{71}BM$ as the acceptor in the conventional device configuration of ITO/PEDOT:PSS (40 nm)/polymer:PC_{71}BM/Ca (30 nm)/Al (100 nm). PC_{71}BM, which

Polymer	$\mu_{FET} \ (cm^2 \ V^{-1} \ s^{-1})$	μ_{SCLC} (cm ² V ⁻¹ s ⁻¹)	$V_{ m oc}$ (V)	$J_{ m SC}$ (mA cm ⁻²)	FF	PCE (%)
PThTPA-IDT-DCN	$\textbf{2.63}\times\textbf{10}^{-4}$	6.76×10^{-5}	0.83	3.42	0.43	1.23
PThTPA-IDT-TBA	1.28×10^{-3}	1.15×10^{-4}	0.87	5.19	0.44	1.97
PThTPA-IDT-DCNIO	5.30×10^{-4}	1.66×10^{-4}	0.86	5.17	0.45	1.98

TABLE 2 PThTPA-IDT Device Characteristics





FIGURE 6 Output (a,c,e) and transfer (b,d,f) characteristics of PThTPA-IDT-DCN (a,b), PThTPA-IDT-TBA (c,d) and PThTPA-IDT-DCNIO (e,f) OFETs on HMDS-modified SiO₂ as a function of V_{gs} ($W = 1000 \ \mu m$ and $L = 12 \ \mu m$).

absorbs more visible light than $PC_{61}BM$,⁴⁴ was utilized as the n-type acceptor to efficiently harvest solar output. The BHJ active layer was prepared by spin coating a chloroform: chlorobenzene (1:1, v/v) solution of polymer:PC₇₁BM on the PEDOT:PSS layer. All the devices were heated at 150 °C for 10 min prior to electrode deposition. The device parameters are summarized in Table 2. Thermal annealing improved the device performance marginally compared with unannealed devices (data not shown). This insensitivity to thermal annealing is expected for noncrystalline polymers. Solvent annealing with dichlorobenzene vapor was also explored, but resulted in unfavorable morphologies and poor device performance. In addition, different polymer:PCBM ratios were tested, but the best device performances were obtained with a 1:4 blending ratio. This unfavorable optimal blending ratio is likely due to the hyperbranched nature of the polymers,



FIGURE 7 Current voltage curve for PThTPA-IDT-DCN (solid line), PThTPA-IDT-TBA (dotted line), and PThTPA-IDT-DCN (dashed line).

which introduces large interstitial spaces around the polymer chain. PCBM molecules initially intercalate into these voids before PCBM forms continuous pure-phase domains in the BHJ and thereby generates balanced electron-hole charge transport and reduced charge recombination.⁴⁵



FIGURE 8 External quantum efficiency plot for PThTPA-IDT-DCN (solid line), PThTPA-IDT-TBA (dotted line), and PThTPA-IDT-DCN (dashed line).

Photovoltaic devices fabricated from PThTPA-IDT-DCN showed a PCE up to 1.23% with a $V_{\rm oc}$ of 0.83 V, a FF of 0.43, and a $J_{\rm sc}$ of 3.42 mA cm⁻². Comparatively, PThTPA-IDT-TBA and PThTPA-IDT-DCNIO showed nearly identical FF (0.44 and 0.45), $V_{\rm oc}$ (0.87 and 0.86 V), $J_{\rm sc}$ (5.19 and 5.17 mA



FIGURE 9 Tapping mode atomic force microscopy topography (a–c) and phase images (d–f) of polymer:PC₇₁BM (1:4) blends of (a,d) PThTPA-IDT-DCN, (b,e) PThTPA-IDT-TBA, and (c,f) PThTPA-IDT-DCNIO.



cm⁻²), and PCE (1.97 and 1.98%). Representative currentvoltage curves for the three polymers measured under standard illumination conditions (100 mW cm⁻², AM 1.5G) are plotted in Figure 7. Since the V_{oc} is largely governed by the difference between the polymer HOMO level and PCBM LUMO and the polymers have nearly identical HOMO levels as measured by CV, the $V_{\rm oc}$ values are expected to be very similar for all the PThTPA-IDT polymers. These $V_{\rm oc}$ values are reasonably high for PSC devices. The FF values of the three polymers are nearly identical as well, suggesting similar loss mechanisms for each polymer. However, despite the improved absorbance profile compared with existing $D-\pi$ bridge-A polymers, each of the PThTPA-IDT devices has comparatively low J_{sc} values, which results in low PCE values. We speculate that the low J_{sc} and FF values are due to the limited external quantum efficiency (EQE) of the polymers (Fig. 8). All three polymers have EQE values below 30%, which is lower than many high-efficiency D-A polymers.

These limited EQE values could be due to several factors. First, the polymers exhibit relatively small absorption coefficients compared with D-A polymers. Second, based on the limited hole mobilities, geminate recombination is likely a major loss pathway. This is supported by the relatively thin optimized BHJ thicknesses (70-80 nm). Finally, higher recombination rates could be due to the undesirable morphology of the polymers (Fig. 9). Both PThTPA-IDT-DCN and PThTPA-IDT-DCNIO exhibit severe phase segregation with PC₇₁BM, which could contribute to exciton recombination before the excitons are able to diffuse to polymer/fullerene interfaces. Conversely, PThTPA-IDT-TBA shows no significant polymer or fullerene domains, which may contribute to increased geminate recombination. The reasons for these striking morphological differences between the three polymers are not known and are currently under investigation.

Interestingly, the device parameters of PThTPA-IDT-TBA and PThTPA-IDT-DCNIO are nearly identical despite the significant differences in their electronic properties and film morphologies. The EQE for PThTPA-IDT-TBA approaches 30% from 400 to 625 nm, while the EQE for PThTPA-IDT-DCNIO for the same range never surpasses 25%. The maximum EQE for PThTPA-IDT-TBA is slightly higher than that of PThTPA-IDT-DCNIO probably because PThTPA-IDT-TBA possesses a marginally higher hole mobility. However, the photoresponse of PThTPA-IDT-DCNIO is extended to longer wavelengths because of its smaller bandgap. As a result, both polymers have very similar aggregate EQEs over the visible spectrum. Moreover, the morphology of PThTPA-IDT-TBA/ PCBM films shows no uninterrupted polymer or PCBM networks, which likely contributes to a high rate of geminate recombination. Conversely, the PThTPA-IDT-DCNIO/PCBM films exhibit severe phase segregation, suggesting that excitonic recombination is the major loss pathway. Thus, the higher mobility and geminate recombination rates of PThTPA-IDT-TBA are very nearly balanced with the redshifted absorbance and excitonic recombination rates of PThTPA-IDT-DCNIO. Since J_{sc} and FF are intimately related to absorbance, mobility, recombination rates and EQE, this

explains why the device parameters are nearly identical for these two polymers, despite their inherent chemical, electronic, and morphological differences.

CONCLUSIONS

In summary, a new class of tunable light-harvesting polymer (PThTPA-IDT) with dipolar chromophores embedded in the conjugated backbone was designed and synthesized. This precursor polymer was functionalized with three electronaccepting moieties via a Knoevenagel condensation reaction. The thiophene-triphenylamine backbone contributed to enhanced conjugation length and improved ICT characteristics, as seen in the absorbance spectra. The photovoltaic properties of these polymers were investigated and the highest achieved PCE for PThTPA-IDT-DCN, PThTPA-IDT-TBA, and PThTPA-IDT-DCNIO were 1.23, 1.97, and 1.98%, respectively. The PCE was limited by the low J_{sc} and FF of this polymer system, which are attributed to poor morphology and relatively low hole mobilities. The undesirable morphology and low mobilities could contribute to decreased charge separation efficiency and increased recombination rates in the active layer.

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