[Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='pubs.acs.org/cm'),

Paragraph(id=None, references=[], text='Interplay of Molecular Orientation, Film Formation, and\nOptoelectronic Properties on Isoindigo- and Thienoisoindigo-Based\nCopolymers for Organic Field Eﬀect Transistor and Organic\nPhotovoltaic Applications\nChien Lu,\nand Pi-Tai Chou\*,#\n†\nDepartment of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan\n‡\nResearch Center for New Generation Photovoltaics, Graduate Institute of Energy Engineering, National Central University, Taoyuan\n320, Taiwan\n#Department of Chemistry, National Taiwan University, Taipei 106, Taiwan'),

Paragraph(id=None, references=[], text='Hsieh-Chih Chen,\*,‡,§'),

Paragraph(id=None, references=[], text='Wen-Chang Chen,\*,†'),

Paragraph(id=None, references=[], text='Wei-Ti Chuang,'),

Paragraph(id=None, references=[], text='Yen-Hao Hsu,'),

Paragraph(id=None, references=[], text='†,§'),

Paragraph(id=None, references=[], text='#'),

Paragraph(id=None, references=[], text='#'),

Paragraph(id=None, references=[], text='\*S Supporting Information'),

Paragraph(id=None, references=[], text='ABSTRACT: A systematic study on the eﬀects of heteroarenes\non the solid state structure and optoelectronic properties of\nisoindigo analogues, namely, PBDT-IIG and PBDT-TIIG, used\nin solution-processed organic ﬁeld eﬀect transistors (OFETs)\nand organic photovoltaics (OPVs) is reported. We discover that\nthe optical absorption, frontier orbitals, backbone coplanarity,\nmolecular orientation, solubility, ﬁlm morphology, charge carrier\nmobility, and solar cell performance are critically inﬂuenced by\nthe heteroarenes in the acceptor subunits. PBDT-IIG exhibits\ngood p-type OFET performance with mobility up to 1.03 × 10−1\ne = 2.81 × 10−4 cm2 V−1\ncm2 V−1 s−1, whereas PBDT-TIIG displays ambipolar mobilities of μ\ns−1. PBDT-IIG and PBDT-TIIG blended with [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) yield promising power\nconversion eﬃciencies (PCEs) of 5.86% and 2.55%, respectively. The excellent mobility of PBDT-IIG can be attributable to the\ngrowing fraction of edge-on packing by the interfacial surface treatment. Although PBDT-TIIG could construct a long-range face-\non packing alignment to meliorate its photocurrent in OPV applications, the low open-circuit voltage caused by its high-lying\nHOMO energy level and greater recombination demonstrates the trade-oﬀ between light absorption and solar cell performance.\nNevertheless, PBDT-TIIG with a PCE of 2.55% is the highest reported PCE to date for the TIIG-based systems.'),

Paragraph(id=None, references=[], text='h = 7.06 × 10−2 cm2 V−1 s−1 and μ'),

Paragraph(id=None, references=[], text='■ INTRODUCTION'),

Paragraph(id=None, references=[], text='Polymer-based organic ﬁeld eﬀect transistors (OFETs) and\norganic photovoltaics (OPVs) have gained considerable\nattention over the past few decades due to their potential for\nlightweight, solution processability and mechanical ﬂexibility,\nwhich possess huge commercial potential to be manufactured\nusing low-cost, high-throughput processes such as roll-to-roll\nprinting and inkjet printing. In order to improve the electronic\nπ-delocalization of conjugated polymers, the donor−acceptor\n(D−A) alternating copolymers has become an eﬃcient strategy\nfor obtaining low-bandgap conjugated polymers and modulat-\ning their optoelectronic properties because of the easy tuning of\ntheir bandgap, absorption spectra, and HOMO energy level by\nusing diﬀerent donor and acceptor units in the copolymers.1−10\nIt is believed that the intramolecular charge transfer (ICT) and\npolar interaction between the D−A moieties are able to\nimprove interchain packing and charge delocalization of\npolymer chains, which can further enhance the charge transport\nability. Thus, the development of low bandgap polymer donors\nhas meanwhile aided the boost of solar cell power conversion'),

Paragraph(id=None, references=[], text='eﬃciencies (PCEs) in excess of 8−10% for single junction solar\ncells.11−19 However,\nthere still have been few reports of\npolymers that perform well in both OTFTs and OPVs, due to\ntheir discrepancies in device architectures and charge transport\ndirections. The development of such versatile polymers could\nbe beneﬁcial for applications that incorporate both types of\ndevices.'),

Paragraph(id=None, references=[], text='irradiation,'),

Paragraph(id=None, references=[], text='To eﬃciently absorb solar'),

Paragraph(id=None, references=[], text='the conjugated\nbackbone in combination with bislactam-based quinoidal\nchromophoric moieties, such as diketopyrrolopyrrole (DPP),\nisoindigo (IIG), and thienoisoindigo (TIIG), has been evident\nfrom many recent studies of high-performance materials for\nOFET and OPV applications. Their planar structures were\npromoted by nonbonding Coulombic interactions (e.g., S···O\ninteractions for DPP and TIIG) in single moiety, which can\nreduce steric hindrance.20,21 The aromatic moieties or fused'),

Paragraph(id=None, references=[], text='Received: August 18, 2015\nRevised:\nSeptember 23, 2015\nPublished: September 23, 2015'),

Paragraph(id=None, references=[], text='© 2015 American Chemical Society'),

Paragraph(id=None, references=[], text='6837'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='Scheme 1. Synthesis and Structures of PBDT-IIG and PBDT-TIIG Copolymers'),

Paragraph(id=None, references=[], text='thiophene rings are favorable for the strong π-stacked structure\nleading to high crystallinity and high electrical performance.\nGiven the enormous combinations of diﬀerent conjugated\nmoieties, detailed knowledge of how speciﬁc chemical moieties\nand structures translate to material properties remains limited.\nThus, comprehending the inﬂuences of speciﬁc chemical\nmoieties on material and device properties is still essential to\nfacilitate the development of high performing materials.'),

Paragraph(id=None, references=[], text='show great potential'),

Paragraph(id=None, references=[], text='In this context, IIG analogues, including small molecules and\npolymers,\nfor OPV and OFET\napplications. Nevertheless, the structure of IIG was reported\nwith steric repulsion between the hydrogens on the phenyl\nrings and the oxygens of the oxindoles, contributing to its\nslightly twisted structure.22 To improve the planarity, the TIIG,\nin which the outer phenyl rings of IIG were replaced with\nthiophenes, was recently developed for incorporation with the\nstrong intramolecular S···O interactions as well as the quinoidal\nstructure to further enhance both the planarity and the charge\ndelocalization along the backbone,\nresulting in a better\nmolecular packing and higher charge carrier mobilities. The\nhighest hole mobility of TIIG-based conjugated polymers was\nrecorded over 14.4 cm2 V−1 s−1,23 which was controlled with\ndevice geometries and packing distributions in the thin ﬁlm.\nDespite its great progress in OFET application, very few\nexamples of TIIG-based D−A copolymers for OPVs have been\nreported. The high-lying HOMO energy levels of TIIG-based\nmaterials were not desirable for the high open circuit voltage\n(Voc) in OPV devices. Only few end-capped D−A small\nmolecules\nincoorperated with triphenylamine or phenyl-\ncarbazole were reported with power conversion eﬃciency up\nto 2.2% due to their deep low-lying HOMO energy levels,\ndespite their weak light harvesting propeties.24 However, the\nenhanced absorption characteristics and packing behaviors of\nTIIG-based materials allow for a more precise analysis of the\nstructure−function relationships compared to the original IIG-\nbased materials. Recently, a series of D−A copolymers\ncontaining benzodithiophene (BDT) and IIG moieties were\nalready reported to show potential performance in either OFET\nor OPV devices.24,25 These copolymers showed solar cell\neﬃciency in a range of 2.8−7.3%, contributed by diﬀerent'),

Paragraph(id=None, references=[], text='thiophene spacers between the D and A building blocks.26 On\nthe other hand, the improvement of absorption coeﬃcient and\neﬀective tuning of the HOMO energy level\nin BDT-based\nconjugated polymers suggest\nthat 4,8-bis(5-(2-ethylhexyl)-\nthiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (2D-BDT) moi-\nety is a promising building block for constructing conjugated\npolymers in OPV applications.27 As a result, on the basis of the\nreported performance of the IIG-based polymers, the TIIG unit\nshould be another promising building block to further compare\nthe coplanarity eﬀect on the molecular packing order and\noptoelectronics properties of polymers.'),

Paragraph(id=None, references=[], text='the optical absorption,'),

Paragraph(id=None, references=[], text='Herein, we report on the synthesis and characterization of\n2D-BDT-containing D−π−A copolymers (PBDT-IIG and\nPBDT-TIIG) coupled with either IIG or TIIG moieties as\nwell as the thiophenes π-spacers, which are the candidates for\nboth high performing OFETs and OPVs. The inserted\nthiophenes between D and A moieties can support the polymer\nbackbone to release the steric hindrance from adjacent building\nblocks, which could encourage us to scrutinize the eﬀects on\nthe IIG- and TIIG-copolymer backbones. The charge transport\ncharacteristics would be further addressed to compare the\npolymer orientations on surface-treated substrates. We found\nthat\nfrontier orbital energy levels,\ncoplanarity, crystallinity, solubility, ﬁlm morphology, charge\ncarrier mobility, and solar cell performance of\nthese two\ncopolymers are signiﬁcantly aﬀected by the plural heteroarenes\nin the A subunits. These results provide insight into the eﬀects\nof heteroarenes on the solid state structure and optoelectronic\nproperties of conjugated polymers used in solution-processed\nOFETs and OPVs. OFETs made from PBDT-IIG and PBDT-\nTIIG are shown here to exhibit hole carrier mobilities of 0.1\nand 0.07 cm2 V−1 s−1, respectively, while applied in solar cells,\nPBDT-IIG and PBDT-TIIG blended with [6,6]-phenyl-C71-\nbutyric acid methyl ester (PC71BM) have yielded promising\nPCEs of 5.86% and 2.55%, respectively. Our ﬁndings are able to\ndemonstrate clear methodology for molecular design toward\nOFET and OPV applications for the IIG analogues.'),

Paragraph(id=None, references=[], text='6838'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Table 1. Physicochemical Properties of the Study Polymers'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='Mn [kg mol−1]'),

Paragraph(id=None, references=[], text='polymer\nPBDT-IIG\nPBDT-TIIG\naHOMO and LUMO levels were estimated from the onset of the oxidation and reduction peaks of the cyclic voltammogram. bElectrochemical\nbandgap calculated from the cyclic voltammogram. cOptical bandgap estimated from the onset of the UV−vis spectrum of the ﬁlm.'),

Paragraph(id=None, references=[], text='PDI Tg [°C] Td [°C]\n2.6\n2.8'),

Paragraph(id=None, references=[], text='EC [eV]b Eg\n2.03\n1.67'),

Paragraph(id=None, references=[], text='HOMO [eV]a LUMO [eV]a Eg'),

Paragraph(id=None, references=[], text='367, 456, 631, 678\n466, 833,856'),

Paragraph(id=None, references=[], text='opt [eV]c\n1.59\n1.05'),

Paragraph(id=None, references=[], text='359, 446, 625\n463, 826,854'),

Paragraph(id=None, references=[], text='−3.35\n−3.29'),

Paragraph(id=None, references=[], text='−5.38\n−4.96'),

Paragraph(id=None, references=[], text='solution/λ'),

Paragraph(id=None, references=[], text='max [nm]'),

Paragraph(id=None, references=[], text='max [nm]'),

Paragraph(id=None, references=[], text='380\n411'),

Paragraph(id=None, references=[], text='ﬁlm/λ'),

Paragraph(id=None, references=[], text='21\n34'),

Paragraph(id=None, references=[], text='56\n76'),

Paragraph(id=None, references=[], text='Figure 1. UV−vis absorption spectra of PBDT-IIG and PBDT-TIIG in (a) DCB solution and (b) as thin ﬁlms.\n■ RESULTS AND DISCUSSION'),

Paragraph(id=None, references=[], text='The chemical structures and synthetic routes of PBDT-IIG and\nPBDT-TIIG are shown in Scheme 1. The polymer structure\nincorporates 2D-BDT and IIG or TIIG with long, branched 2-\noctyldodecyl alkyl groups being used to ensure good solubility\nof\nthe polymer even at high molecular weight. Detailed\nexperimental procedures for the synthesis of the monomers and\npolymers are given in the Experimental Section and Supporting\nInformation. These two polymers were prepared by Stille cross-\ncoupling reactions with tris(dibenzylideneacetone)dipalladium\n(Pd2(dba)3) and tri(o-tolyl)phosphine (P(o-tol)3) as catalysts\nunder microwave heating conditions to obtain the PBDT-IIG\nand PBDT-TIIG copolymers. Crude polymers were puriﬁed by\nthe Soxhlet extraction with methanol, hexane, and chloroform,\nrespectively. The chloroform fraction was concentrated and\nprecipitated into methanol to obtain the target copolymers.\nThe number-average molecular weights (Mn) of the synthesized\nPBDT-IIG and PBDT-TIIG copolymers were determined by\ngel permeation chromatography (GPC) against polystyrene\nstandards in a THF eluent and were found to be 21 and 34\nkDa, with polydispersity indices of 2.6 and 2.8, respectively.\nThe thermal stability of these copolymers was investigated by\nthermal gravimetric analysis (TGA) under a nitrogen\natmosphere at a heating rate of 10 °C min−1. Table 1 lists\n5% weight\nthese copolymers\ndetermined from TGA curves (Figure S1). Both copolymers\nexhibit excellent thermally stability with a Td above 380 °C.\nThrough diﬀerential scanning calorimetry (DSC) measure-\nments, the glass transition temperatures (Tg) of PBDT-IIG and\nPBDT-TIIG were observed to be 56 and 76 °C, respectively.\nPBDT-TIIG copolymer shows a higher Tg probably because of\nthe higher chain rigidity of the polymer backbone.\nThe UV−vis absorption spectra of PBDT-IIG and PBDT-\nTIIG in DCB solution and as thin ﬁlms are shown in Figure 1,\nwhile Table 1 summarizes the relevant data. The two polymers\nexhibit well-deﬁned absorption bands in solution and as thin\nﬁlms, consisting of one at the high energy region and a broader\none at the low energy region. The short-wavelength absorption\nbands from 350 to 500 nm are assigned to the delocalized\nexcitonic π−π\* transition of the BDT moieties, while the long-\nwavelength absorption bands with well-resolved vibronic\nshoulders in the range of 600 to 1000 nm are reasonably'),

Paragraph(id=None, references=[], text='temperatures (Td) of'),

Paragraph(id=None, references=[], text='loss'),

Paragraph(id=None, references=[], text='ascribed to intramolecular charge transfer (ICT) interactions\nfrom the D to the A unit of the polymer backbone. It has been\nreported that the greater magnitude of this vibronic peak\nreveals a more ordered microstructure.28 The maxima\nabsorption coeﬃcients of PBDT-IIG and PBDT-TIIG thin\nﬁlms are 4.25 × 104 and 5.03 × 104 cm−1, respectively. Both\ncopolymers show slightly red-shifted absorption in the solid\nstate in comparison to that in solution, suggesting that the\npolymer thin ﬁlm has a more ordered molecular organization\nthan solution. Notably, the maximum absorption peak (λ\nmax) of\nPBDT-TIIG obviously appears in the longer wavelength region\nthan that of PBDT-IIG, indicating that the acceptor strength of\nTIIG is greater than that of IIG. This clearly demonstrates that\nthe replacement of benzene with thiophene in the A subunits\nresults in a reduction of the optical bandgap due to the increase\nof quinoid character in the polymer backbone. Support of this\nopt) deduced from\nviewpoint is given by the optical bandgaps (Eg\nthe absorption onsets of the ﬁlm spectra, which are in the order\nof PBDT-IIG (1.59 eV) > PBDT-TIIG (1.05 eV).'),

Paragraph(id=None, references=[], text='red − E1/2'),

Paragraph(id=None, references=[], text='ferrocene + 4.8] V; LUMO = −[Eonset'),

Paragraph(id=None, references=[], text='The electrochemical characteristics were then measured in\nacetonitrile with Ag/AgCl reference electrode at potential scan\nrate of 100 mV s−1 (Figure S2). The highest occupied\nmolecular orbital (HOMO) energy level, the lowest unoccu-\npied molecular orbital (LUMO) energy level, and the\nEC) were estimated from the\nelectrochemical bandgap (Eg\nox ) and onset reduction potential\nonset oxidation potential (Eonset\nred ), on the basis of the following equations: HOMO =\n(Eonset\nox − E1/2\n−[Eonset\nferrocene +\n4.8] V, where the potential is referred to an Ag/AgCl reference\nelectrode. Apparently,\nthese two polymers exhibit both\nreversible oxidation and reduction processes. The HOMO/\nLUMO energies for PBDT-IIG and PBDT-TIIG are −5.38/−\n3.35 eV and −4.96/−3.29 eV, respectively. Compared to\nPBDT-IIG, PBDT-TIIG shows higher-lying HOMO/LUMO\nenergy levels,\ninferring enhanced charge delocalization via a\nmore planar quinoidal structure of the TIIG fragment than that\nof the IIG unit.29 Since the open-circuit voltage (Voc) of OPVs\ncorrelates closely with the diﬀerence between the HOMO\nenergy level of the donor polymer and the LUMO energy level\nof the fullerene, a larger Voc for IIG-based PSCs is anticipated.\nThe LUMO energy levels of these two polymers are located at'),

Paragraph(id=None, references=[], text='6839'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials\n−3.35 to −3.29 eV, providing enough driving force for charge\nseparation and electron transfer without too much energy loss.\nTo gain more insight into the eﬀect of planarization on the\ntheoretical\nmolecular structures and electronic properties,\ncalculations by density functional theory (DFT) model at the\nB3LYP/6-31G\* level were performed on the molecules of IIG-\nBDT-IIG and TIIG-BDT-TIIG with methyl substituted alkyl\nchains for simplicity. The theoretical HOMO/LUMO energies\nfor PBDT-IIG and PBDT-TIIG are −4.94/−2.79 and −4.56/−\n2.70 eV, respectively (see Figure S3), which shows the similar\ntrend as the target polymers. As can be observed, the electron\ndensity in the HOMO wave function of PBDT-TIIG is more\nevenly delocalized along the whole polymer backbone than that\nof PBDT-IIG, resulting in the higher experimental HOMO\nenergy level of PBDT-TIIG. Conversely, the electron density\nassociated with the LUMO wave function of PBDT-IIG is fairly\nwell-localized at the electron acceptor site compared to that of\nPBDT-TIIG. Furthermore, the truncated PBDT-TIIG polymer\nrepresents excellent planarity through the entirety of\nthe\npolymer backbone (Figure 2), possibly enabling the higher\nHOMO energy level and lower bandgap in the isolated state,\ncontributed by its more eﬀective π-orbital conjugation.'),

Paragraph(id=None, references=[], text='Figure 2. Optimized backbone structure of (a) IIG-BDT-IIG and (b)\nTIIG-BDT-TIIG. The side chains were replaced with the methyl\ngroups to simplify the calculation.'),

Paragraph(id=None, references=[], text='Bottom-gate/top-contact OFETs of PBDT-IIG and PBDT-\nTIIG were fabricated with ODTS-treated silicon wafer. Figure 3\nshows the FET transfer characteristics of\nthe copolymer\n− Vt), Id can be\ndevices. In the saturation region (Vd > Vg\ndescribed by the following equation:'),

Paragraph(id=None, references=[], text='μ'),

Paragraph(id=None, references=[], text='='),

Paragraph(id=None, references=[], text='I\nds'),

Paragraph(id=None, references=[], text='WC\no\nL\n2'),

Paragraph(id=None, references=[], text='('),

Paragraph(id=None, references=[], text='V\ng'),

Paragraph(id=None, references=[], text='−'),

Paragraph(id=None, references=[], text='2\n)'),

Paragraph(id=None, references=[], text='V\nt'),

Paragraph(id=None, references=[], text='where W and L are channel width and length, respectively, Co is\nthe capacitance of gate insulator per unit area (SiO2, 300 nm,\nCo = 10 nF cm−2), μ is the hole mobility, and Vt is threshold\nvoltage. The saturation-region mobility of the polymers was\ncalculated from the transfer characteristics of FET involving\nplotting (Id)1/2 versus V. The copolymers were spin-coated\nfrom chlorobenzene solution (10 mg mL−1) and annealed at\n180 °C for 1 h before the deposition of gold. PBDT-IIG and\nPBDT-TIIG were measured by sweeping the gate voltage (Vg)\nunder a source-drain voltage (Vds) of −80 V and revealed\ntypical\ntransfer and output curves (Figure 3). The FET\nmobilities of the annealed PBDT-IIG and PBDT-TIIG thin\nﬁlms are (1.03 ± 0.20) × 10−1 and (7.06 ± 0.25) × 10−2 cm2\nV−1 s−1, which are both one order higher than the as-cast ﬁlms\n(see Table 2). The high mobility of the annealed PBDT-IIG\nand PBDT-TIIG thin ﬁlms on ODTS substrates could be\ncorrelated with their high crystallinity (vide infra). Intriguingly,\nPBDT-TIIG shows a slightly lower mobility than PBDT-IIG in'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='It'),

Paragraph(id=None, references=[], text='spite of its relatively higher crystallinity, which will be discussed\nlater.\nis worth noting that PBDT-TIIG is capable of\nexhibiting the n-type charge transport with mobility up to\n2.81 × 10−4 cm2 V−1 s−1 under Vds of 60 V, owing to its\nstronger electron-acceptor capability than PBDT-IIG.'),

Paragraph(id=None, references=[], text='To characterize the photovoltaic properties for PBDT-IIG\ninverted BHJ PSCs using ITO/ZnO (40\nand PBDT-TIIG,\nnm)/poly[(9,9-dioctyl-2,7-fuorene)-alt-(9,9-bis(3′-(N,N-\ndimethylamino)propyl)-2,7-fuorene)] (PFN) (5 nm)/poly-\nmer:PC71BM (80−110 nm)/MoO3 (6 nm)/Ag (100 nm)\ndevice conﬁguration were prepared and examined under\nsimulated 100 mW cm−2 AM 1.5G illumination. The\nincorporation of thin PFN cathode interlayer can construct\ninterfacial dipole, which could result in the reduced electron\ninjection barrier and enhanced built-in potential across the\ndevice.16 The optimized polymer to PC71BM ratios of PBDT-\nIIG and PBDT-TIIG used to form the active layers of the PSCs\nwere 1:2 and 1:4, respectively. The active layers of PBDT-IIG\nand PBDT-TIIG were prepared by spin-coating from a 4:1 (v/\nv) mixture of CB and DCB solutions with 2.5% and 2% (v/v)\n1,8-diiodooctane (DIO) additives,30 respectively. We optimized\nthe thickness of the active layers and found that 80−110 nm\nwas the best thickness for all devices. The J−V curves and\nincident photon-to-current eﬃciencies (IPCE) of solar cells are\npresented Figure 4. The detailed device performances are\nsummarized in Table 3. After post-thermal annealing at 120 °C\nfor 10 min, the optimized 1:2 PBDT-IIG:PC71BM device oﬀers\na high PCE of 5.86% with a Voc of 0.85 V, a Jsc of 10.48 mA\ncm−2, and a FF of 65.8%. Further increase of the fullerene ratio\nyielded a negative eﬀect in both Jsc and FF, which resulted in a\ndecreased PCE. As expected from the low-lying HOMO energy\nlevels of the polymers, the trend in Voc agrees well with the\nelectrochemical potentials. Conversely, the device based on\noptimized 1:4 PBDT-TIIG:PC71BM acquires a moderate PCE\nof 2.55%, with a Voc of 0.38 V, a Jsc of 11.74 mA cm−2, and a FF\nof 57.2%. To the best of our knowledge, this solar eﬃciency is\nhitherto among the highest in the TIIG-based materials with a\nPCE above 2.5%. In comparison with the optimized PBDT-\nIIG-based device,\nthe optimized PBDT-TIIG-based device\ndemonstrated a lower PCE owing to a signiﬁcantly lower Voc\nand FF. The relatively low Voc of the optimized PBDT-TIIG-\nbased device should be due to the high-lying HOMO energy\nlevel of PBDT-TIIG (vide supra). Notably, the HOMO energy\nlevel of PBDT-TIIG (−4.96 eV) is close to that of P3HT (−5.0\nto −5.1 eV), and yet, the Voc of P3HT:PCBM cells are typically\naround 0.6 V. Some explanations\nthe greater\nrecombination rate from ambipolar charge transport,31 the\ndiscrepancy in free energy for photoinduced charge transfer,32\nand the blend nanomorphology for enough interfacial area\nbetween D−A phases might also account for the signiﬁcant Voc\nloss of PBDT-TIIG-based devices. Additionally, the lower FF\nlimiting PCE can be ascribable to the fact\nthe high\ncrystallization tendency of the polymer leads to a much faster\ncrystallization than PC71BM during spin-coating. Further\ninvestigations of how to control the blend morphology via\nmixed solvent systems and the inﬂuence of polymer molecular\nweight are still in progress. Nevertheless, the advantage for the\nPBDT-TIIG is its relatively abundant absorption coverage at\nthe visible to near-infrared (NIR) region to achieve better\nsunlight harvesting and hence leads to a higher Jsc. In fact,\nregardless of the FF, the trade-oﬀ between light harvesting (Jsc)\nand Voc of low bandgap donor polymers in single-junction\nPSCs seems to act as a diﬃcult obstacle toward high solar'),

Paragraph(id=None, references=[], text='such as'),

Paragraph(id=None, references=[], text='that'),

Paragraph(id=None, references=[], text='6840'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='Figure 3. p-type FET transfer characteristics of (a) PBDT-IIG and (b) PBDT-TIIG thin ﬁlms, (c) their n-type OFET transfer characteristics, and the\np-type output characteristics of (d) PBDT-IIG and (e) PBDT-IIG.'),

Paragraph(id=None, references=[], text='Table 2. OFET Device Parameters of the Study Polymers'),

Paragraph(id=None, references=[], text='polymer\nPBDT-IIG'),

Paragraph(id=None, references=[], text='PBDT-TIIG'),

Paragraph(id=None, references=[], text='TA'),

Paragraph(id=None, references=[], text='a [°C]\nn/a\n180\nn/a\n180'),

Paragraph(id=None, references=[], text='b [cm2 V−1 s−1]\nμ\nh\n(1.57 ± 0.45) × 10−3\n(1.03 ± 0.20) × 10−1\n(3.13 ± 0.39) × 10−3\n(7.06 ± 0.25) × 10−2'),

Paragraph(id=None, references=[], text='Vt,h'),

Paragraph(id=None, references=[], text='c [V]\n0.6\n0.97\n5.65\n7.52'),

Paragraph(id=None, references=[], text='d'),

Paragraph(id=None, references=[], text='Ion/Ioff\n5.26 × 104\n1.07 × 105\n6.13 × 102\n1.30 × 105'),

Paragraph(id=None, references=[], text='e [cm2 V−1 s−1]'),

Paragraph(id=None, references=[], text='μ\ne'),

Paragraph(id=None, references=[], text='Vt,e'),

Paragraph(id=None, references=[], text='f [V]'),

Paragraph(id=None, references=[], text='g\nIon/Ioff'),

Paragraph(id=None, references=[], text='(1.67 ± 0.13) × 10−5\n(2.81 ± 0.26) × 10−4'),

Paragraph(id=None, references=[], text='79.69\n83.62'),

Paragraph(id=None, references=[], text='7.22 × 101\n6.05 × 103'),

Paragraph(id=None, references=[], text='aAnnealing temperature during ﬁlm growth. bAverage hole mobilities. cThreshold voltages for p-type operation. dCurrent on/oﬀ ratio for p-type\noperation. eAverage electron mobilities. fThreshold voltages for n-type operation. gCurrent on/oﬀ ratio for n-type operation.'),

Paragraph(id=None, references=[], text='the photo J−V\neﬃciency.33 To verify the accuracy of\nmeasurements, the corresponding IPCE spectra of the devices\nelaborated above were measured under\nillumination of\nmonochromatic light shown in Figure 4b. Compared to the\nabsorption spectra of pristine polymers,\nthe substantially\nbroadened IPCE responses in the visible region can be\nattributed to both the intrinsic absorptions of the polymers\nand PC71BM. The integrated Jsc values from the IPCE spectra\nare 10.12 and 11.36 mA cm−2 for PBDT-IIG and PBDT-TIIG\ndevices, respectively. The Jsc values calculated from integration\nof the IPCE spectra are within 5% error, which conform well to\nthose obtained from the J−V measurements, supporting the\nreliability of the photovoltaic measurement.'),

Paragraph(id=None, references=[], text='To gain deeper insight into the connections with molecular\npacking charge transport properties and photovoltaic proper-\nties, synchrotron grazing incidence wide-angle X-ray scattering\n(GIWAXS) analysis was performed to examine the PBDT-IIG\nand PBDT-TIIG ﬁlms. The 2D GIWAXS patterns of the as-cast\nand annealed thin ﬁlms on bare substrates and on ODTS-\ntreated substrates are shown in Figures 5 and S5. The relevant\ndata are also summarized in Table S1. Additionally, their 1D\nproﬁles in both the out-of-plane and in-plane directions are\noutlined in Figure 6. The 2D GIWAXS pattern of the PBDT-\nIIG and PBDT-TIIG ﬁlms both show arcs and anisotropic ring\nscatterings. For the thin ﬁlms on bare substrates, the (100)\nreﬂection (q = 0.318 Å−1) in the in-plane direction and (010)'),

Paragraph(id=None, references=[], text='6841'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='in-plane direction, suggesting its almost extreme face-on\norientation. It is noteworthy that the intensity and fractions\nof face-on domains in both polymers were highly enhanced\nafter\nthermal annealing. The intrinsic molecular packing\ndiﬀractions of these two polymers are able to correlate with\nthe photovoltaic properties. Compared to PBDT-IIG,\nthe\nnearly drastic face-on scattering proﬁle and higher crystallinity\nof PBDT-TIIG allow better charge transport capability in the\nvertical direction. This arrangement is beneﬁcial\nfor charge\ntransport in the solar cells and has often correlated with high\nOPV performance. Additionally, the result correlated with the\nTEM image of the pristine PBDT-TIIG (Figure 7) that clearly\nreveals a crystalline ﬁbrillar interpenetrating network, possibly\nowing to the strong intermolecular π−π interactions.\nIn\nthe higher backbone\nagreement with DFT simulations,\nthe stronger π−π\ncoplanarity of PBDT-TIIG indicates\ninteractions and cofacial polymer packing, which displays a\npreference for the face-on packing,34 leading to a higher Jsc in\nthe solar cells. Contrarily,\nthe less planar PBDT-IIG\nsubsequently adopts the bimodal molecular packing orientation\nsince its intermolecular interactions dominate the alignment of\ncrystalline domains. Moreover, in assessing the eﬀect of these\nπ−π interactions on device performances, the full width at half-\nmaximum (fwhm) of (010) diﬀractions was calculated for\ncorrelating with the orientation distribution of the crystalline\ndomains. The fwhm of PBDT-IIG and PBDT-TIIG are 32.98°\nand 23.56°, respectively, indicating that PBDT-TIIG possesses\nlong-range and more ordered face-on packing than that of\nPBDT-IIG. Moreover, the GIWAXS patterns acquired from the\nthin ﬁlms on bare substrates (Figure 5) are remarkably diﬀerent\nfrom those on ODTS-treated substrates in virtue of\nthe\ncoplanarity of polymer backbone and introduction of branched\nalkyl side chains.35,36 First, the as-cast PBDT-IIG thin ﬁlm\nshows a face-on orientation rather than an edge-on orientation\non the bare substrate. Second, compared with the as-cast\nPBDT-IIG thin ﬁlm, the thermal-treatment PBDT-IIG ﬁlm\nappears as a stronger (100) peak (q = 0.319 Å−1) along the out-\nof-plane direction. The results can be attributed to the fact that\nthe original\nface-on packing gradually disappeared and the\nlamellar packing along the out-of-plane direction energetically\nappeared. This bimodal packing orientation of PBDT-IIG is\nable to promote the charge transport in the OFET application.\nIn contrast, the stronger intensity and sharper width of (010)\nreﬂection at q = 0.270 Å−1 appears in both as-cast and thermally\nannealed PBDT-TIIG thin ﬁlms,\nstill\nmaintains a highly ordered face-on packing on the ODTS-\ntreated substrates with relatively weak edge-on packing. After\nthermal annealing, the appearance of sharper (100) reﬂection\nand high-order (200) reﬂection of PBDT-TIIG at the in-plane\nthe more ordered face-on rich\ndirection also indicates\norientation than the edge-on orientation. However,\nin the\nOFETs with bottom-gate/top-contact architecture, the ideal\nmolecular alignment for improving mobility is thought to be\nedge-on packing where the charge transport is parallel to the\nπ−π stacking direction in the charge transport channel.37 As a\nresult, a slightly lower mobility of PBDT-TIIG might be\nattributable to its preferential\nface-on backbone orientation\ndespite its higher crystallinity, where the charge transport was\nthought\nto prefer the edge-on orientation for the charge\nhopping between polymer chains. In these cases, the molecular\npacking orientation of these two polymers was dominated by\ntheir backbone coplanarity and the eﬀect of thermal annealing\non the ﬁlm formation, which are able to correlate with the'),

Paragraph(id=None, references=[], text='suggesting that'),

Paragraph(id=None, references=[], text='it'),

Paragraph(id=None, references=[], text='6842'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='illumination and (b) the IPCE spectra of'),

Paragraph(id=None, references=[], text='Figure 4. (a) J−V curves of optimized devices based on 1:2 PBDT-\nIIG:PC71BM solar cells and 1:4 PBDT-TIIG:PC71BM solar cells under\nAM 1.5G solar\nthe\ncorresponding devices illuminated by monochromatic light. Legend:\norange circles (●) represent the PBDT-IIG device (Voc = 0.85 V, Jsc =\n−10.48 mA cm−2, FF = 65.8%, and PCE = 5.86%), and blue diamonds\n(⧫) represent the PBDT-TIIG device (Voc = 0.38 V, Jsc = −11.74 mA\ncm−2, FF = 57.2%, and PCE = 2.55%).'),

Paragraph(id=None, references=[], text='Table 3. Photovoltaic Parameters of Optimized Solar Cells'),

Paragraph(id=None, references=[], text='polymer:PC71BMa'),

Paragraph(id=None, references=[], text='1:1'),

Paragraph(id=None, references=[], text='1:2\n1:4\n1:1'),

Paragraph(id=None, references=[], text='Voc\n[V]\n0.80'),

Paragraph(id=None, references=[], text='0.85\n0.82\n0.36'),

Paragraph(id=None, references=[], text='Jsc'),

Paragraph(id=None, references=[], text='[mA cm−2]'),

Paragraph(id=None, references=[], text='9.51'),

Paragraph(id=None, references=[], text='10.48\n7.43\n8.64'),

Paragraph(id=None, references=[], text='FF\n[%]\n61.1'),

Paragraph(id=None, references=[], text='65.8\n57.6\n52.8'),

Paragraph(id=None, references=[], text='PCEb [%]\n4.65 (4.50)'),

Paragraph(id=None, references=[], text='5.86 (5.74)\n3.51 (3.30)\n1.64 (1.48)'),

Paragraph(id=None, references=[], text='polymer\nPBDT-'),

Paragraph(id=None, references=[], text='IIG'),

Paragraph(id=None, references=[], text='PBDT-\nTIIG'),

Paragraph(id=None, references=[], text='1:2\n1:4'),

Paragraph(id=None, references=[], text='2.07 (1.93)\n2.55 (2.43)\naInverted device conﬁguration of ITO/ZnO/PFN/polymer:PC71BM/\nMoO3/Ag. bAverage PCE of 10 optimized devices in parentheses.'),

Paragraph(id=None, references=[], text='10.12\n11.74'),

Paragraph(id=None, references=[], text='53.9\n57.2'),

Paragraph(id=None, references=[], text='0.38\n0.38'),

Paragraph(id=None, references=[], text='peak (q = 0.289 Å−1) in the out-of-plane direction of PBDT-\nIIG became sharper and more intense than those of the as-cast\nﬁlm upon thermal annealing, suggesting that structures of the\nﬁlm became more ordered, and preferential face-on packing\ndomains after thermal annealing. In consequence, the annealed\nPBDT-IIG ﬁlm shows a bimodal molecular packing orientation\ndespite its relatively weak (100) reﬂection peak in the out-of-\nplane direction. In contrast, PBDT-TIIG as-cast ﬁlm exhibits a\ndistinctive (010) reﬂection peak (q = 1.736 Å−1) in the out-of-\nplane direction and (100) reﬂection peak (q = 0.271 Å−1) in the'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='Figure 5. 2D grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of annealed PBDT-IIG thin ﬁlms on (a) bare substrate and (b)\nODTS-treated substrate and annealed PBDT-TIIG thin ﬁlms on (c) bare substrate and (d) ODTS-treated substrate.'),

Paragraph(id=None, references=[], text='Figure 6. 1D GIWAXS proﬁles of (a) PBDT-IIG (out-of-plane), (b) PBDT-IIG (in-plane), (c) PBDT-TIIG (out-of-plane), and (d) PBDT-TIIG\n(in-plane).'),

Paragraph(id=None, references=[], text='charge transport characteristics in diﬀerent device architectures.\nNote that the feasibility of controlling the packing order in\nPBDT-IIG also demonstrates\nfurther\napplication into both OFET and OPV devices. On the\ncontrary,\nface-on packing orientation of\nPBDT-TIIG improves on the photocurrent but it is still not\nfavorable for the charge transport in OFET devices.'),

Paragraph(id=None, references=[], text='the preferential'),

Paragraph(id=None, references=[], text='its potential'),

Paragraph(id=None, references=[], text='for'),

Paragraph(id=None, references=[], text='The nanoscale morphology plays an important role in the\ndevice performance. Proper morphology is necessary for charge\ntransport to respective electrodes for eﬃcient collection.38−41'),

Paragraph(id=None, references=[], text='Therefore, the morphological structures of the neat PBDT-IIG\nand PBDT-TIIG ﬁlms were probed by transmission electron\nmicroscopy (TEM) and tapping mode atom force microscopy\n(TM-AFM) measurements. As revealed in Figure 7, PBDT-IIG\nand PBDT-TIIG display worm-like and nanoﬁbrillar textures,\nrespectively. Additionally, TM-AFM observations of the neat\nﬁlms are identical to those of TEM images shown in the insets\nof Figure 7. The pristine PBDT-TIIG ﬁlm exhibits a heavily\ndense ﬁbrillar nanostructure with a certain degree of long-range\norder,\nindicating the nanoscale self-assembly of PBDT and'),

Paragraph(id=None, references=[], text='6843'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Chemistry of Materials'),

Paragraph(id=None, references=[], text='Figure 7. TEM images of the pristine (a) PBDT-IIG and (b) PBDT-\nTIIG ﬁlm. Inset: Corresponding phase images of TM-AFM (scale bar:\n0.5 μm).'),

Paragraph(id=None, references=[], text='TIIG moieties (vide supra). The obvious spacing of\nthe\nnanostructures has a lateral dimension in the range of 15−25\nnm, which is nearly in the same magnitude as the exciton\ndiﬀusion length, and may eﬀectively support\nthe charge\ntransport prior to recombination. Furthermore, we scrutinized\nthe bulk-heterojunction nanostructures of the optimal polymer\nblends. The 1:2 PBDT-IIG:PC71BM blend ﬁlm (Figure 8a,c)'),

Paragraph(id=None, references=[], text='Article\nplatform to understand the structure−function relationships.\nOFETs made from PBDT-IIG and PBDT-TIIG exhibited hole\ncarrier mobilities of 0.1 and 0.07 cm2 V−1 s−1, respectively,\nwhile applied in OPVs, PBDT-IIG, and PBDT-TIIG blended\nwith PC71BM delivered promising PCEs of 5.86% and 2.55%,\nrespectively. The superior mobility of PBDT-IIG could be\nboosted by the growing portion of edge-on molecular packing\nvia the interfacial surface treatment. In spite of the long-range\nface-on packing alignment of PBDT-TIIG that could improve\nits Jsc in the OPV application, the low Voc arising from its high-\nlying HOMO energy level and greater recombination exhibited\nthe trade-oﬀ between light absorption and solar cell perform-\nance. Nonetheless, PBDT-TIIG, with a PCE of up to 2.55%,\nhas the highest reported value to date among the TIIG-based\nmaterials. We believe that these materials should have a high\npotential of targeting future optoelectronics with more ﬁne-\ntuning of the polymer structures. Our ﬁndings are able to\ndemonstrate clear methodology for molecular design for the\nIIG analogues toward new potential applications where dual\nOFET and OPV functions are required on a single substrate.'),

Paragraph(id=None, references=[], text='■ EXPERIMENTAL SECTION'),

Paragraph(id=None, references=[], text='Materials. Tri(o-tolyl)phosphin,'),

Paragraph(id=None, references=[], text='tris(dibenzylideneacetone)-\ndipalladium(0), trimethyl (thiophen-2-yl)stannane, and bromothio-\nphene were purchased from Aldrich (Missouri, USA) and used\nwithout further puriﬁcation. Common organic solvents for synthesis\nwere distilled to remain anhydrous or degassed by nitrogen 0.5 h\nbefore use. Ultra-anhydrous o-dichlorobenzene (DCB) for device\napplications was purchased from Aldrich (Missouri, USA). A surface\ntreatment agent of octadecyltrichlorosilane (ODTS) was purchased\nfrom Acros (Geel, Belgium) for ﬁeld-eﬀect transistor characterization.\n[6,6]-Phenyl-C71-butyric acid methyl ester (PC71BM) was purchased\nfrom Solenne BV (Groningen, The Netherlands) for photovoltaic cell\napplications.'),

Paragraph(id=None, references=[], text='General Procedures for Polymerization. The synthesis of all\nmonomers was described in the Supporting Information. The general\nprocedure of synthesizing PBDT-IIG and PBDT-TIIG is shown in\nScheme 1. (5,5′-(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-\nb:4,5-b′]dithiophene-2,6-diyl)bis(thiophene-5,2-diyl))bis-\n(trimethylstannane) (2D-BDT-ditin), (E)-6,6′-dibromo-1,1′-bis(2-oc-\ntyldodecyl)-[3,3′-biindolinylidene]-2,2′\n-dione or (E)-2,2′-dibromo-\n4,4′-bis(2-octyldodecyl)-[6,6′-bithieno[3,2-b]pyrrolylidene]-\n5,5′(4H,4′H)-dione, tri(o-tolyl)phosphine (16 mol % with respect to\nditin monomer), and tris(dibenzylideneacetone)dipalladium(0) (2\nmol % with respect\nto ditin monomer) were dissolved in\nchlorobenzene. Then, these copolymers were synthesized by Pd(0)-\ncatalyzed Stille coupling polymerization under microwave heating (150\n°C for 30 min). After being end-capped with trimethyl(thiophen-2-\nyl)stannane and bromothiophene (both 1.1 equiv. with respect to the\nmonomers and under microwave heating at 160 °C, 10 min for each\nend-capping), the mixture was cooled and poured into methanol to\naﬀord a crude solid. The crude polymer was puriﬁed by methanol,\nacetone, and hexane successively using a Soxhlet extraction to remove\nbyproducts, oligomers, and catalyst residues.'),

Paragraph(id=None, references=[], text='Characterization. Microwave reaction was carried out using a\nBiotage microwave reactor in sealed vessels. 1H NMR spectra were\nrecorded with a Bruker Avance DRX 400 MHz instrument. Gel\npermeation chromatographic (GPC) analysis was performed on a Lab\nAlliance RI2000 instrument (two column, MIXED-C and D from\nPolymer Laboratories) which was connected to one refractive index\ndetector\nfrom Schambeck SFD Gmbh. All GPC analyses were\nperformed on polymer/THF solution at 40 °C and calibrated with\npolystyrene standards. Thermogravimetric analysis (TGA) and\ndiﬀerential scanning calorimetry (DSC) measurements were per-\nformed under a nitrogen atmosphere at heating rates of 10 and 5 °C\nmin−1 using the TA Instruments Q-50 and Q-100, respectively. The\nthickness of the active ﬁlms was measured with a depth-proﬁle meter'),

Paragraph(id=None, references=[], text='6844'),

Paragraph(id=None, references=[], text='DOI: 10.1021/acs.chemmater.5b03197\nChem. Mater. 2015, 27, 6837−6847'),

Paragraph(id=None, references=[], text='Figure 8. Morphology characterization of TM-AFM topography\nimages (upper row) and phase images (lower row) of 1:2 PBDT-\nIIG:PC71BM blend ﬁlm with 2.5 vol % DIO (panels a and c) and 1:4\nPBDT-TIIG:PC71BM blend ﬁlm with 2 vol % DIO (panels b and d).\nThe imaging size is 2 μm × 2 μm for each panel.'),

Paragraph(id=None, references=[], text='reveals a considerable degree of ﬁne-grained texture with a root-\nmean-square (RMS) roughness of 2.1 nm, which is beneﬁcial to\nthe exciton dissociation and charge carriers transport. In stark\ncontrast, 1:4 PBDT-TIIG:PC71BM blend contains vast long\nnanoﬁbers that are around 15−25 nm in width, whereas the\nPC71BM-rich domains are well distributed in the polymer\nmatrix with a RMS roughness of 2.6 nm (Figure 8b,d). These\nnanoﬁbers construct an interpenetrating network surrounded\nby the PC71BM clusters and therefore maximize the interfacial\nD−A contact area for the exciton dissociation into free charge\ncarriers. Notably, the extremely dense ﬁbrillar nanostructure is\nstill conspicuous in the PC71BM-rich blends, suggesting that the\nhigh crystallinity nature of PBDT-TIIG is able to preserve the\nsame molecular arrangement when blended with fullerene. The\nintimately mixed and well-ordered domains within the matrix,\nalong with the high hole carrier mobility of the material, are\ncapable of eﬃcient charge separation and transport and could\nsupport the good performance of the cells.'),

Paragraph(id=None, references=[], text='■ CONCLUSION'),

Paragraph(id=None, references=[], text='In conclusion, we conducted a systematic study on the eﬀects\nof plural heteroarenes on the solid state structure and\noptoelectronic properties of PBDT-IIG and PBDT-TIIG used\nin solution-processed OFETs and OPVs to establish a useful'),

Paragraph(id=None, references=[], text='Chemistry of Materials\n(Veeco Dektak 150, USA). Five lines on a ﬁlm of 1 cm × 1 cm were\nmade by carefully scratching with a plastic tip, and the average height\nbetween the hills and valleys is used to represent the ﬁlm thickness.\nGrazing incidence wide-angle X-ray scattering (GIWAXS) patterns\nwere conducted on beamline BL13A1 in the National Synchrotron\nRadiation Research Center (NSRRC), Taiwan. The scattering patterns\nwere collected on a Mar165 CCD with a diameter of 40 mm. X-ray\ndiﬀraction (XRD) was performed by an X’Pert PRO X-ray\ndiﬀractometer (λ = 1.0219 Å). The scattering vector, q = 4π/λsin θ,\nalong with the scattering angles q in these patterns were calibrated\nusing silver behenate. The thin ﬁlms were mounted on a z-axis\ngoniometer. UV−vis absorption spectra were recorded using a Hitachi\nU-4100 spectrophotometer. Cyclic voltammetry (CV) was recorded\non a CHI 611B electrochemical analyzer using a three-electrode cell in\nwhich ITO (polymer ﬁlm areas were about 0.5 × 0.7 cm2) was used as\na working electrode. A platinum wire was used as an auxiliary\nelectrode. All cell potentials were taken with the use of a homemade\nAg/AgCl, KCl (sat.) reference electrode. The electrochemical\nproperties of the polymer ﬁlms were detected under 0.1 M anhydrous\nacetonitrile solution containing tetrabutylammonium perchlorate\n(TBAP) as electrolyte. The morphology of the polymer ﬁlm surface\nwas obtained with a Nanoscope 3D Controller atomic force\nmicrograph (AFM, Digital Instruments) operated in the tapping\nmode at room temperature. Transmission electron microscopy (TEM)\nimages were obtained with a JEOL JEM-1230 instrument operating at\na voltage of 100 kV with a Gatam dual vision CCD camera.'),

Paragraph(id=None, references=[], text='Computational Methodology. Theoretical molecular simulation\nof the studied polymers was calculated through a Gaussian 03 program\npackage. The density functional theory (DFT) method, using Becke’s\nthree-parameter functional with the Lee, Yang, and Parr correlation\nfunctional method (B3LYP) with 6-31G\*, was used for\nthe\noptimization of ground-state molecular geometry.42'),

Paragraph(id=None, references=[], text='Fabrication and Characterization of Field Eﬀect Transistors.\nHighly doped n-type Si (100) wafers, with 300 nm SiO2 layer\n(capacitance per unit area Co = 10 nF cm−2) as a gate dielectric, were\nused as substrates. The cleaned Si wafers were then modiﬁed with an\noctadecyltrichlorosilane (ODTS) self-assembled monolayer according\nto the reported method.43 FET devices were deposited by spin-coating\nfrom chlorobenzene (10 mg mL−1) at a spin rate of 1000 rpm for 60 s\nand annealing at 180 °C for 60 min and thermally evaporated with 100\nnm-thick gold electrode (channel length (L) and width (W) were 50\nand 1000 μm). FET transfer and output characteristics were recorded\nin a N2-ﬁlled glovebox by using a Keithley 4200 semiconductor\nparametric analyzer.'),

Paragraph(id=None, references=[], text='Fabrication and Characterization of Polymer Photovoltaic\nCells. The inverted solar cells were fabricated with the device\narchitecture of ITO/ZnO (40 nm)/poly[(9,9-dioctyl-2,7-ﬂuorene)-alt-\n(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-ﬂuorene)] (PFN) (5\nnm)/polymer:PC71BM (80−110 nm)/MoO3 (6 nm)/Ag (100 nm).\nPrior to use, patterned ITO-coated glass substrates (10 Ω/square)\nwere successively cleaned according to the reported literature.7,11,19\nThe ZnO precursor was prepared using zinc acetate dehydrate\n·2H2O, Aldrich, 99.999%) as starting material and 2-\n(Zn(CH3COO)2\nethoxyethanol and monoethanolamine (MEA, Aldrich, 99.7%) as the\nnontoxic solvent and stabilizer under vigorous stirring for 12 h for the\nhydrolysis reaction in air. The respective solutions were spin-coated on\nITO-coated glass substrates at 5000 rpm for 30 s and preheated at 180\n°C for 30 min in air to remove residual organic materials and then\ntransferred into an inert N2-ﬁlled glovebox (<0.1 ppm of O2 and\nH2O). Subsequently, the PFN interfacial layer was spin-coated onto\nthe active layer according to a similar method described in the\nliterature.16 Blend solutions were prepared by dissolving the target\npolymer (PBDT-IIG or PBDT-TIIG) and PC71BM in mixed CB:DCB\n(4:1, v/v) solution in the blend ratios of 1:1, 1:2, and 1:4 with a\npolymer concentration of 10 mg mL−1 and were heated to 100 °C and\nstirred for 8 h for complete dissolution. Afterward, the blend solution\nwas spin-coated after adding 2.5% and 2% (v/v) 1,8-diiodooctane\n(DIO) for PBDT-IIG and PBDT-TIIG-based systems. The wet ﬁlm\nwas slowly dried in a covered Petri dish for 3 h in the glovebox and\nthen annealed at 120 °C for 10 min. Thereupon, methanol was'),

Paragraph(id=None, references=[], text='Article'),

Paragraph(id=None, references=[], text='dropped onto the active layer with a spin-coating rate of 2000 rpm for\n60 s, and subsequently, the coated substrates were transferred to a\nthermal evaporator and evacuated to ≤5 × 10−6 Torr. Molybdenum\noxide was thermally deposited on top of the active layer with an\nevaporation rate of 0.1 Å s−1. Ultimately, 100 nm silver ﬁlm was\ndeposited on top of the molybdenum oxide layer through a shade\nmask. The J−V curves were measured using a Keithley 4200 source-\nmeasuring unit. A calibrated solar simulator (Oriel) with a 100 mW\ncm−2 power density was used as the light source. An IPCE (QE-\nR3011) characterization platform supplied by Enlitech Inc. was used\nfor data acquirement. All IPCE spectra were recorded using a lock-in\ntechnique at a chopping frequency of 100 Hz.'),

Paragraph(id=None, references=[], text='■ ASSOCIATED CONTENT\n\*S Supporting Information\nThe Supporting Information is available free of charge on the\nACS Publications website at DOI: 10.1021/acs.chemma-\nter.5b03197.'),

Paragraph(id=None, references=[], text='Experimental details, syntheses of monomers, complete\ncharacterization of materials and devices. (PDF)'),

Paragraph(id=None, references=[], text='■ AUTHOR INFORMATION\nCorresponding Authors\n\*E-mail: austinchen@ncu.edu.tw (H.-C.C.).\n\*E-mail: chenwc@ntu.edu.tw (W.-C.C.).\n\*E-mail: chop@ntu.edu.tw (P.-T.C.).\nAuthor Contributions\n§\nC.L. and H.-C.C. contributed equally.\nNotes\nThe authors declare no competing ﬁnancial interest.'),

Paragraph(id=None, references=[], text='■ ACKNOWLEDGMENTS'),

Paragraph(id=None, references=[], text='This work was ﬁnancially supported by the Ministry of Science\nand Technology of Taiwan (MOST 103-2113-M-008-010-\nMY2). The solar cell device fabrication was carried out in the\nAdvanced Laboratory of Accommodation and Research for\nOrganic Photovoltaics, Ministry of Science and Technology of\nTaiwan.'),

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Article

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Interplay of Molecular Orientation, Film Formation, and Optoelectronic Properties on Isoindigo- and Thienoisoindigo-Based Copolymers for Organic Field Eﬀect Transistor and Organic Photovoltaic Applications Chien Lu, and Pi-Tai Chou\*,# † Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan ‡ Research Center for New Generation Photovoltaics, Graduate Institute of Energy Engineering, National Central University, Taoyuan 320, Taiwan #Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

Hsieh-Chih Chen,\*,‡,§

Wen-Chang Chen,\*,†

Wei-Ti Chuang,

Yen-Hao Hsu,

†,§

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\*S Supporting Information

ABSTRACT: A systematic study on the eﬀects of heteroarenes on the solid state structure and optoelectronic properties of isoindigo analogues, namely, PBDT-IIG and PBDT-TIIG, used in solution-processed organic ﬁeld eﬀect transistors (OFETs) and organic photovoltaics (OPVs) is reported. We discover that the optical absorption, frontier orbitals, backbone coplanarity, molecular orientation, solubility, ﬁlm morphology, charge carrier mobility, and solar cell performance are critically inﬂuenced by the heteroarenes in the acceptor subunits. PBDT-IIG exhibits good p-type OFET performance with mobility up to 1.03 × 10−1 e = 2.81 × 10−4 cm2 V−1 cm2 V−1 s−1, whereas PBDT-TIIG displays ambipolar mobilities of μ s−1. PBDT-IIG and PBDT-TIIG blended with [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) yield promising power conversion eﬃciencies (PCEs) of 5.86% and 2.55%, respectively. The excellent mobility of PBDT-IIG can be attributable to the growing fraction of edge-on packing by the interfacial surface treatment. Although PBDT-TIIG could construct a long-range face- on packing alignment to meliorate its photocurrent in OPV applications, the low open-circuit voltage caused by its high-lying HOMO energy level and greater recombination demonstrates the trade-oﬀ between light absorption and solar cell performance. Nevertheless, PBDT-TIIG with a PCE of 2.55% is the highest reported PCE to date for the TIIG-based systems.

h = 7.06 × 10−2 cm2 V−1 s−1 and μ

■ INTRODUCTION

Polymer-based organic ﬁeld eﬀect transistors (OFETs) and organic photovoltaics (OPVs) have gained considerable attention over the past few decades due to their potential for lightweight, solution processability and mechanical ﬂexibility, which possess huge commercial potential to be manufactured using low-cost, high-throughput processes such as roll-to-roll printing and inkjet printing. In order to improve the electronic π-delocalization of conjugated polymers, the donor−acceptor (D−A) alternating copolymers has become an eﬃcient strategy for obtaining low-bandgap conjugated polymers and modulat- ing their optoelectronic properties because of the easy tuning of their bandgap, absorption spectra, and HOMO energy level by using diﬀerent donor and acceptor units in the copolymers.1−10 It is believed that the intramolecular charge transfer (ICT) and polar interaction between the D−A moieties are able to improve interchain packing and charge delocalization of polymer chains, which can further enhance the charge transport ability. Thus, the development of low bandgap polymer donors has meanwhile aided the boost of solar cell power conversion

eﬃciencies (PCEs) in excess of 8−10% for single junction solar cells.11−19 However, there still have been few reports of polymers that perform well in both OTFTs and OPVs, due to their discrepancies in device architectures and charge transport directions. The development of such versatile polymers could be beneﬁcial for applications that incorporate both types of devices.

irradiation,

To eﬃciently absorb solar

the conjugated backbone in combination with bislactam-based quinoidal chromophoric moieties, such as diketopyrrolopyrrole (DPP), isoindigo (IIG), and thienoisoindigo (TIIG), has been evident from many recent studies of high-performance materials for OFET and OPV applications. Their planar structures were promoted by nonbonding Coulombic interactions (e.g., S···O interactions for DPP and TIIG) in single moiety, which can reduce steric hindrance.20,21 The aromatic moieties or fused

Received: August 18, 2015 Revised: September 23, 2015 Published: September 23, 2015

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

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Scheme 1. Synthesis and Structures of PBDT-IIG and PBDT-TIIG Copolymers

thiophene rings are favorable for the strong π-stacked structure leading to high crystallinity and high electrical performance. Given the enormous combinations of diﬀerent conjugated moieties, detailed knowledge of how speciﬁc chemical moieties and structures translate to material properties remains limited. Thus, comprehending the inﬂuences of speciﬁc chemical moieties on material and device properties is still essential to facilitate the development of high performing materials.

show great potential

In this context, IIG analogues, including small molecules and polymers, for OPV and OFET applications. Nevertheless, the structure of IIG was reported with steric repulsion between the hydrogens on the phenyl rings and the oxygens of the oxindoles, contributing to its slightly twisted structure.22 To improve the planarity, the TIIG, in which the outer phenyl rings of IIG were replaced with thiophenes, was recently developed for incorporation with the strong intramolecular S···O interactions as well as the quinoidal structure to further enhance both the planarity and the charge delocalization along the backbone, resulting in a better molecular packing and higher charge carrier mobilities. The highest hole mobility of TIIG-based conjugated polymers was recorded over 14.4 cm2 V−1 s−1,23 which was controlled with device geometries and packing distributions in the thin ﬁlm. Despite its great progress in OFET application, very few examples of TIIG-based D−A copolymers for OPVs have been reported. The high-lying HOMO energy levels of TIIG-based materials were not desirable for the high open circuit voltage (Voc) in OPV devices. Only few end-capped D−A small molecules incoorperated with triphenylamine or phenyl- carbazole were reported with power conversion eﬃciency up to 2.2% due to their deep low-lying HOMO energy levels, despite their weak light harvesting propeties.24 However, the enhanced absorption characteristics and packing behaviors of TIIG-based materials allow for a more precise analysis of the structure−function relationships compared to the original IIG- based materials. Recently, a series of D−A copolymers containing benzodithiophene (BDT) and IIG moieties were already reported to show potential performance in either OFET or OPV devices.24,25 These copolymers showed solar cell eﬃciency in a range of 2.8−7.3%, contributed by diﬀerent

thiophene spacers between the D and A building blocks.26 On the other hand, the improvement of absorption coeﬃcient and eﬀective tuning of the HOMO energy level in BDT-based conjugated polymers suggest that 4,8-bis(5-(2-ethylhexyl)- thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (2D-BDT) moi- ety is a promising building block for constructing conjugated polymers in OPV applications.27 As a result, on the basis of the reported performance of the IIG-based polymers, the TIIG unit should be another promising building block to further compare the coplanarity eﬀect on the molecular packing order and optoelectronics properties of polymers.

the optical absorption,

Herein, we report on the synthesis and characterization of 2D-BDT-containing D−π−A copolymers (PBDT-IIG and PBDT-TIIG) coupled with either IIG or TIIG moieties as well as the thiophenes π-spacers, which are the candidates for both high performing OFETs and OPVs. The inserted thiophenes between D and A moieties can support the polymer backbone to release the steric hindrance from adjacent building blocks, which could encourage us to scrutinize the eﬀects on the IIG- and TIIG-copolymer backbones. The charge transport characteristics would be further addressed to compare the polymer orientations on surface-treated substrates. We found that frontier orbital energy levels, coplanarity, crystallinity, solubility, ﬁlm morphology, charge carrier mobility, and solar cell performance of these two copolymers are signiﬁcantly aﬀected by the plural heteroarenes in the A subunits. These results provide insight into the eﬀects of heteroarenes on the solid state structure and optoelectronic properties of conjugated polymers used in solution-processed OFETs and OPVs. OFETs made from PBDT-IIG and PBDT- TIIG are shown here to exhibit hole carrier mobilities of 0.1 and 0.07 cm2 V−1 s−1, respectively, while applied in solar cells, PBDT-IIG and PBDT-TIIG blended with [6,6]-phenyl-C71- butyric acid methyl ester (PC71BM) have yielded promising PCEs of 5.86% and 2.55%, respectively. Our ﬁndings are able to demonstrate clear methodology for molecular design toward OFET and OPV applications for the IIG analogues.

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

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Table 1. Physicochemical Properties of the Study Polymers

Article

Mn [kg mol−1]

polymer PBDT-IIG PBDT-TIIG aHOMO and LUMO levels were estimated from the onset of the oxidation and reduction peaks of the cyclic voltammogram. bElectrochemical bandgap calculated from the cyclic voltammogram. cOptical bandgap estimated from the onset of the UV−vis spectrum of the ﬁlm.

PDI Tg [°C] Td [°C] 2.6 2.8

EC [eV]b Eg 2.03 1.67

HOMO [eV]a LUMO [eV]a Eg

367, 456, 631, 678 466, 833,856

opt [eV]c 1.59 1.05

359, 446, 625 463, 826,854

−3.35 −3.29

−5.38 −4.96

solution/λ

max [nm]

max [nm]

380 411

ﬁlm/λ

21 34

56 76

Figure 1. UV−vis absorption spectra of PBDT-IIG and PBDT-TIIG in (a) DCB solution and (b) as thin ﬁlms. ■ RESULTS AND DISCUSSION

The chemical structures and synthetic routes of PBDT-IIG and PBDT-TIIG are shown in Scheme 1. The polymer structure incorporates 2D-BDT and IIG or TIIG with long, branched 2- octyldodecyl alkyl groups being used to ensure good solubility of the polymer even at high molecular weight. Detailed experimental procedures for the synthesis of the monomers and polymers are given in the Experimental Section and Supporting Information. These two polymers were prepared by Stille cross- coupling reactions with tris(dibenzylideneacetone)dipalladium (Pd2(dba)3) and tri(o-tolyl)phosphine (P(o-tol)3) as catalysts under microwave heating conditions to obtain the PBDT-IIG and PBDT-TIIG copolymers. Crude polymers were puriﬁed by the Soxhlet extraction with methanol, hexane, and chloroform, respectively. The chloroform fraction was concentrated and precipitated into methanol to obtain the target copolymers. The number-average molecular weights (Mn) of the synthesized PBDT-IIG and PBDT-TIIG copolymers were determined by gel permeation chromatography (GPC) against polystyrene standards in a THF eluent and were found to be 21 and 34 kDa, with polydispersity indices of 2.6 and 2.8, respectively. The thermal stability of these copolymers was investigated by thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C min−1. Table 1 lists 5% weight these copolymers determined from TGA curves (Figure S1). Both copolymers exhibit excellent thermally stability with a Td above 380 °C. Through diﬀerential scanning calorimetry (DSC) measure- ments, the glass transition temperatures (Tg) of PBDT-IIG and PBDT-TIIG were observed to be 56 and 76 °C, respectively. PBDT-TIIG copolymer shows a higher Tg probably because of the higher chain rigidity of the polymer backbone. The UV−vis absorption spectra of PBDT-IIG and PBDT- TIIG in DCB solution and as thin ﬁlms are shown in Figure 1, while Table 1 summarizes the relevant data. The two polymers exhibit well-deﬁned absorption bands in solution and as thin ﬁlms, consisting of one at the high energy region and a broader one at the low energy region. The short-wavelength absorption bands from 350 to 500 nm are assigned to the delocalized excitonic π−π\* transition of the BDT moieties, while the long- wavelength absorption bands with well-resolved vibronic shoulders in the range of 600 to 1000 nm are reasonably

temperatures (Td) of

loss

ascribed to intramolecular charge transfer (ICT) interactions from the D to the A unit of the polymer backbone. It has been reported that the greater magnitude of this vibronic peak reveals a more ordered microstructure.28 The maxima absorption coeﬃcients of PBDT-IIG and PBDT-TIIG thin ﬁlms are 4.25 × 104 and 5.03 × 104 cm−1, respectively. Both copolymers show slightly red-shifted absorption in the solid state in comparison to that in solution, suggesting that the polymer thin ﬁlm has a more ordered molecular organization than solution. Notably, the maximum absorption peak (λ max) of PBDT-TIIG obviously appears in the longer wavelength region than that of PBDT-IIG, indicating that the acceptor strength of TIIG is greater than that of IIG. This clearly demonstrates that the replacement of benzene with thiophene in the A subunits results in a reduction of the optical bandgap due to the increase of quinoid character in the polymer backbone. Support of this opt) deduced from viewpoint is given by the optical bandgaps (Eg the absorption onsets of the ﬁlm spectra, which are in the order of PBDT-IIG (1.59 eV) > PBDT-TIIG (1.05 eV).

red − E1/2

ferrocene + 4.8] V; LUMO = −[Eonset

The electrochemical characteristics were then measured in acetonitrile with Ag/AgCl reference electrode at potential scan rate of 100 mV s−1 (Figure S2). The highest occupied molecular orbital (HOMO) energy level, the lowest unoccu- pied molecular orbital (LUMO) energy level, and the EC) were estimated from the electrochemical bandgap (Eg ox ) and onset reduction potential onset oxidation potential (Eonset red ), on the basis of the following equations: HOMO = (Eonset ox − E1/2 −[Eonset ferrocene + 4.8] V, where the potential is referred to an Ag/AgCl reference electrode. Apparently, these two polymers exhibit both reversible oxidation and reduction processes. The HOMO/ LUMO energies for PBDT-IIG and PBDT-TIIG are −5.38/− 3.35 eV and −4.96/−3.29 eV, respectively. Compared to PBDT-IIG, PBDT-TIIG shows higher-lying HOMO/LUMO energy levels, inferring enhanced charge delocalization via a more planar quinoidal structure of the TIIG fragment than that of the IIG unit.29 Since the open-circuit voltage (Voc) of OPVs correlates closely with the diﬀerence between the HOMO energy level of the donor polymer and the LUMO energy level of the fullerene, a larger Voc for IIG-based PSCs is anticipated. The LUMO energy levels of these two polymers are located at

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

Chemistry of Materials −3.35 to −3.29 eV, providing enough driving force for charge separation and electron transfer without too much energy loss. To gain more insight into the eﬀect of planarization on the theoretical molecular structures and electronic properties, calculations by density functional theory (DFT) model at the B3LYP/6-31G\* level were performed on the molecules of IIG- BDT-IIG and TIIG-BDT-TIIG with methyl substituted alkyl chains for simplicity. The theoretical HOMO/LUMO energies for PBDT-IIG and PBDT-TIIG are −4.94/−2.79 and −4.56/− 2.70 eV, respectively (see Figure S3), which shows the similar trend as the target polymers. As can be observed, the electron density in the HOMO wave function of PBDT-TIIG is more evenly delocalized along the whole polymer backbone than that of PBDT-IIG, resulting in the higher experimental HOMO energy level of PBDT-TIIG. Conversely, the electron density associated with the LUMO wave function of PBDT-IIG is fairly well-localized at the electron acceptor site compared to that of PBDT-TIIG. Furthermore, the truncated PBDT-TIIG polymer represents excellent planarity through the entirety of the polymer backbone (Figure 2), possibly enabling the higher HOMO energy level and lower bandgap in the isolated state, contributed by its more eﬀective π-orbital conjugation.

Figure 2. Optimized backbone structure of (a) IIG-BDT-IIG and (b) TIIG-BDT-TIIG. The side chains were replaced with the methyl groups to simplify the calculation.

Bottom-gate/top-contact OFETs of PBDT-IIG and PBDT- TIIG were fabricated with ODTS-treated silicon wafer. Figure 3 shows the FET transfer characteristics of the copolymer − Vt), Id can be devices. In the saturation region (Vd > Vg described by the following equation:

μ

=

I ds

WC o L 2

(

V g

−

2 )

V t

where W and L are channel width and length, respectively, Co is the capacitance of gate insulator per unit area (SiO2, 300 nm, Co = 10 nF cm−2), μ is the hole mobility, and Vt is threshold voltage. The saturation-region mobility of the polymers was calculated from the transfer characteristics of FET involving plotting (Id)1/2 versus V. The copolymers were spin-coated from chlorobenzene solution (10 mg mL−1) and annealed at 180 °C for 1 h before the deposition of gold. PBDT-IIG and PBDT-TIIG were measured by sweeping the gate voltage (Vg) under a source-drain voltage (Vds) of −80 V and revealed typical transfer and output curves (Figure 3). The FET mobilities of the annealed PBDT-IIG and PBDT-TIIG thin ﬁlms are (1.03 ± 0.20) × 10−1 and (7.06 ± 0.25) × 10−2 cm2 V−1 s−1, which are both one order higher than the as-cast ﬁlms (see Table 2). The high mobility of the annealed PBDT-IIG and PBDT-TIIG thin ﬁlms on ODTS substrates could be correlated with their high crystallinity (vide infra). Intriguingly, PBDT-TIIG shows a slightly lower mobility than PBDT-IIG in

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spite of its relatively higher crystallinity, which will be discussed later. is worth noting that PBDT-TIIG is capable of exhibiting the n-type charge transport with mobility up to 2.81 × 10−4 cm2 V−1 s−1 under Vds of 60 V, owing to its stronger electron-acceptor capability than PBDT-IIG.

To characterize the photovoltaic properties for PBDT-IIG inverted BHJ PSCs using ITO/ZnO (40 and PBDT-TIIG, nm)/poly[(9,9-dioctyl-2,7-fuorene)-alt-(9,9-bis(3′-(N,N- dimethylamino)propyl)-2,7-fuorene)] (PFN) (5 nm)/poly- mer:PC71BM (80−110 nm)/MoO3 (6 nm)/Ag (100 nm) device conﬁguration were prepared and examined under simulated 100 mW cm−2 AM 1.5G illumination. The incorporation of thin PFN cathode interlayer can construct interfacial dipole, which could result in the reduced electron injection barrier and enhanced built-in potential across the device.16 The optimized polymer to PC71BM ratios of PBDT- IIG and PBDT-TIIG used to form the active layers of the PSCs were 1:2 and 1:4, respectively. The active layers of PBDT-IIG and PBDT-TIIG were prepared by spin-coating from a 4:1 (v/ v) mixture of CB and DCB solutions with 2.5% and 2% (v/v) 1,8-diiodooctane (DIO) additives,30 respectively. We optimized the thickness of the active layers and found that 80−110 nm was the best thickness for all devices. The J−V curves and incident photon-to-current eﬃciencies (IPCE) of solar cells are presented Figure 4. The detailed device performances are summarized in Table 3. After post-thermal annealing at 120 °C for 10 min, the optimized 1:2 PBDT-IIG:PC71BM device oﬀers a high PCE of 5.86% with a Voc of 0.85 V, a Jsc of 10.48 mA cm−2, and a FF of 65.8%. Further increase of the fullerene ratio yielded a negative eﬀect in both Jsc and FF, which resulted in a decreased PCE. As expected from the low-lying HOMO energy levels of the polymers, the trend in Voc agrees well with the electrochemical potentials. Conversely, the device based on optimized 1:4 PBDT-TIIG:PC71BM acquires a moderate PCE of 2.55%, with a Voc of 0.38 V, a Jsc of 11.74 mA cm−2, and a FF of 57.2%. To the best of our knowledge, this solar eﬃciency is hitherto among the highest in the TIIG-based materials with a PCE above 2.5%. In comparison with the optimized PBDT- IIG-based device, the optimized PBDT-TIIG-based device demonstrated a lower PCE owing to a signiﬁcantly lower Voc and FF. The relatively low Voc of the optimized PBDT-TIIG- based device should be due to the high-lying HOMO energy level of PBDT-TIIG (vide supra). Notably, the HOMO energy level of PBDT-TIIG (−4.96 eV) is close to that of P3HT (−5.0 to −5.1 eV), and yet, the Voc of P3HT:PCBM cells are typically around 0.6 V. Some explanations the greater recombination rate from ambipolar charge transport,31 the discrepancy in free energy for photoinduced charge transfer,32 and the blend nanomorphology for enough interfacial area between D−A phases might also account for the signiﬁcant Voc loss of PBDT-TIIG-based devices. Additionally, the lower FF limiting PCE can be ascribable to the fact the high crystallization tendency of the polymer leads to a much faster crystallization than PC71BM during spin-coating. Further investigations of how to control the blend morphology via mixed solvent systems and the inﬂuence of polymer molecular weight are still in progress. Nevertheless, the advantage for the PBDT-TIIG is its relatively abundant absorption coverage at the visible to near-infrared (NIR) region to achieve better sunlight harvesting and hence leads to a higher Jsc. In fact, regardless of the FF, the trade-oﬀ between light harvesting (Jsc) and Voc of low bandgap donor polymers in single-junction PSCs seems to act as a diﬃcult obstacle toward high solar

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

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Figure 3. p-type FET transfer characteristics of (a) PBDT-IIG and (b) PBDT-TIIG thin ﬁlms, (c) their n-type OFET transfer characteristics, and the p-type output characteristics of (d) PBDT-IIG and (e) PBDT-IIG.

Table 2. OFET Device Parameters of the Study Polymers

polymer PBDT-IIG

PBDT-TIIG

TA

a [°C] n/a 180 n/a 180

b [cm2 V−1 s−1] μ h (1.57 ± 0.45) × 10−3 (1.03 ± 0.20) × 10−1 (3.13 ± 0.39) × 10−3 (7.06 ± 0.25) × 10−2

Vt,h

c [V] 0.6 0.97 5.65 7.52

d

Ion/Ioff 5.26 × 104 1.07 × 105 6.13 × 102 1.30 × 105

e [cm2 V−1 s−1]

μ e

Vt,e

f [V]

g Ion/Ioff

(1.67 ± 0.13) × 10−5 (2.81 ± 0.26) × 10−4

79.69 83.62

7.22 × 101 6.05 × 103

aAnnealing temperature during ﬁlm growth. bAverage hole mobilities. cThreshold voltages for p-type operation. dCurrent on/oﬀ ratio for p-type operation. eAverage electron mobilities. fThreshold voltages for n-type operation. gCurrent on/oﬀ ratio for n-type operation.

the photo J−V eﬃciency.33 To verify the accuracy of measurements, the corresponding IPCE spectra of the devices elaborated above were measured under illumination of monochromatic light shown in Figure 4b. Compared to the absorption spectra of pristine polymers, the substantially broadened IPCE responses in the visible region can be attributed to both the intrinsic absorptions of the polymers and PC71BM. The integrated Jsc values from the IPCE spectra are 10.12 and 11.36 mA cm−2 for PBDT-IIG and PBDT-TIIG devices, respectively. The Jsc values calculated from integration of the IPCE spectra are within 5% error, which conform well to those obtained from the J−V measurements, supporting the reliability of the photovoltaic measurement.

To gain deeper insight into the connections with molecular packing charge transport properties and photovoltaic proper- ties, synchrotron grazing incidence wide-angle X-ray scattering (GIWAXS) analysis was performed to examine the PBDT-IIG and PBDT-TIIG ﬁlms. The 2D GIWAXS patterns of the as-cast and annealed thin ﬁlms on bare substrates and on ODTS- treated substrates are shown in Figures 5 and S5. The relevant data are also summarized in Table S1. Additionally, their 1D proﬁles in both the out-of-plane and in-plane directions are outlined in Figure 6. The 2D GIWAXS pattern of the PBDT- IIG and PBDT-TIIG ﬁlms both show arcs and anisotropic ring scatterings. For the thin ﬁlms on bare substrates, the (100) reﬂection (q = 0.318 Å−1) in the in-plane direction and (010)

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

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in-plane direction, suggesting its almost extreme face-on orientation. It is noteworthy that the intensity and fractions of face-on domains in both polymers were highly enhanced after thermal annealing. The intrinsic molecular packing diﬀractions of these two polymers are able to correlate with the photovoltaic properties. Compared to PBDT-IIG, the nearly drastic face-on scattering proﬁle and higher crystallinity of PBDT-TIIG allow better charge transport capability in the vertical direction. This arrangement is beneﬁcial for charge transport in the solar cells and has often correlated with high OPV performance. Additionally, the result correlated with the TEM image of the pristine PBDT-TIIG (Figure 7) that clearly reveals a crystalline ﬁbrillar interpenetrating network, possibly owing to the strong intermolecular π−π interactions. In the higher backbone agreement with DFT simulations, the stronger π−π coplanarity of PBDT-TIIG indicates interactions and cofacial polymer packing, which displays a preference for the face-on packing,34 leading to a higher Jsc in the solar cells. Contrarily, the less planar PBDT-IIG subsequently adopts the bimodal molecular packing orientation since its intermolecular interactions dominate the alignment of crystalline domains. Moreover, in assessing the eﬀect of these π−π interactions on device performances, the full width at half- maximum (fwhm) of (010) diﬀractions was calculated for correlating with the orientation distribution of the crystalline domains. The fwhm of PBDT-IIG and PBDT-TIIG are 32.98° and 23.56°, respectively, indicating that PBDT-TIIG possesses long-range and more ordered face-on packing than that of PBDT-IIG. Moreover, the GIWAXS patterns acquired from the thin ﬁlms on bare substrates (Figure 5) are remarkably diﬀerent from those on ODTS-treated substrates in virtue of the coplanarity of polymer backbone and introduction of branched alkyl side chains.35,36 First, the as-cast PBDT-IIG thin ﬁlm shows a face-on orientation rather than an edge-on orientation on the bare substrate. Second, compared with the as-cast PBDT-IIG thin ﬁlm, the thermal-treatment PBDT-IIG ﬁlm appears as a stronger (100) peak (q = 0.319 Å−1) along the out- of-plane direction. The results can be attributed to the fact that the original face-on packing gradually disappeared and the lamellar packing along the out-of-plane direction energetically appeared. This bimodal packing orientation of PBDT-IIG is able to promote the charge transport in the OFET application. In contrast, the stronger intensity and sharper width of (010) reﬂection at q = 0.270 Å−1 appears in both as-cast and thermally annealed PBDT-TIIG thin ﬁlms, still maintains a highly ordered face-on packing on the ODTS- treated substrates with relatively weak edge-on packing. After thermal annealing, the appearance of sharper (100) reﬂection and high-order (200) reﬂection of PBDT-TIIG at the in-plane the more ordered face-on rich direction also indicates orientation than the edge-on orientation. However, in the OFETs with bottom-gate/top-contact architecture, the ideal molecular alignment for improving mobility is thought to be edge-on packing where the charge transport is parallel to the π−π stacking direction in the charge transport channel.37 As a result, a slightly lower mobility of PBDT-TIIG might be attributable to its preferential face-on backbone orientation despite its higher crystallinity, where the charge transport was thought to prefer the edge-on orientation for the charge hopping between polymer chains. In these cases, the molecular packing orientation of these two polymers was dominated by their backbone coplanarity and the eﬀect of thermal annealing on the ﬁlm formation, which are able to correlate with the

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

illumination and (b) the IPCE spectra of

Figure 4. (a) J−V curves of optimized devices based on 1:2 PBDT- IIG:PC71BM solar cells and 1:4 PBDT-TIIG:PC71BM solar cells under AM 1.5G solar the corresponding devices illuminated by monochromatic light. Legend: orange circles (●) represent the PBDT-IIG device (Voc = 0.85 V, Jsc = −10.48 mA cm−2, FF = 65.8%, and PCE = 5.86%), and blue diamonds (⧫) represent the PBDT-TIIG device (Voc = 0.38 V, Jsc = −11.74 mA cm−2, FF = 57.2%, and PCE = 2.55%).

Table 3. Photovoltaic Parameters of Optimized Solar Cells

polymer:PC71BMa

1:1

1:2 1:4 1:1

Voc [V] 0.80

0.85 0.82 0.36

Jsc

[mA cm−2]

9.51

10.48 7.43 8.64

FF [%] 61.1

65.8 57.6 52.8

PCEb [%] 4.65 (4.50)

5.86 (5.74) 3.51 (3.30) 1.64 (1.48)

polymer PBDT-

IIG

PBDT- TIIG

1:2 1:4

2.07 (1.93) 2.55 (2.43) aInverted device conﬁguration of ITO/ZnO/PFN/polymer:PC71BM/ MoO3/Ag. bAverage PCE of 10 optimized devices in parentheses.

10.12 11.74

53.9 57.2

0.38 0.38

peak (q = 0.289 Å−1) in the out-of-plane direction of PBDT- IIG became sharper and more intense than those of the as-cast ﬁlm upon thermal annealing, suggesting that structures of the ﬁlm became more ordered, and preferential face-on packing domains after thermal annealing. In consequence, the annealed PBDT-IIG ﬁlm shows a bimodal molecular packing orientation despite its relatively weak (100) reﬂection peak in the out-of- plane direction. In contrast, PBDT-TIIG as-cast ﬁlm exhibits a distinctive (010) reﬂection peak (q = 1.736 Å−1) in the out-of- plane direction and (100) reﬂection peak (q = 0.271 Å−1) in the

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Figure 5. 2D grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of annealed PBDT-IIG thin ﬁlms on (a) bare substrate and (b) ODTS-treated substrate and annealed PBDT-TIIG thin ﬁlms on (c) bare substrate and (d) ODTS-treated substrate.

Figure 6. 1D GIWAXS proﬁles of (a) PBDT-IIG (out-of-plane), (b) PBDT-IIG (in-plane), (c) PBDT-TIIG (out-of-plane), and (d) PBDT-TIIG (in-plane).

charge transport characteristics in diﬀerent device architectures. Note that the feasibility of controlling the packing order in PBDT-IIG also demonstrates further application into both OFET and OPV devices. On the contrary, face-on packing orientation of PBDT-TIIG improves on the photocurrent but it is still not favorable for the charge transport in OFET devices.

the preferential

its potential

for

The nanoscale morphology plays an important role in the device performance. Proper morphology is necessary for charge transport to respective electrodes for eﬃcient collection.38−41

Therefore, the morphological structures of the neat PBDT-IIG and PBDT-TIIG ﬁlms were probed by transmission electron microscopy (TEM) and tapping mode atom force microscopy (TM-AFM) measurements. As revealed in Figure 7, PBDT-IIG and PBDT-TIIG display worm-like and nanoﬁbrillar textures, respectively. Additionally, TM-AFM observations of the neat ﬁlms are identical to those of TEM images shown in the insets of Figure 7. The pristine PBDT-TIIG ﬁlm exhibits a heavily dense ﬁbrillar nanostructure with a certain degree of long-range order, indicating the nanoscale self-assembly of PBDT and

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

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Figure 7. TEM images of the pristine (a) PBDT-IIG and (b) PBDT- TIIG ﬁlm. Inset: Corresponding phase images of TM-AFM (scale bar: 0.5 μm).

TIIG moieties (vide supra). The obvious spacing of the nanostructures has a lateral dimension in the range of 15−25 nm, which is nearly in the same magnitude as the exciton diﬀusion length, and may eﬀectively support the charge transport prior to recombination. Furthermore, we scrutinized the bulk-heterojunction nanostructures of the optimal polymer blends. The 1:2 PBDT-IIG:PC71BM blend ﬁlm (Figure 8a,c)

Article platform to understand the structure−function relationships. OFETs made from PBDT-IIG and PBDT-TIIG exhibited hole carrier mobilities of 0.1 and 0.07 cm2 V−1 s−1, respectively, while applied in OPVs, PBDT-IIG, and PBDT-TIIG blended with PC71BM delivered promising PCEs of 5.86% and 2.55%, respectively. The superior mobility of PBDT-IIG could be boosted by the growing portion of edge-on molecular packing via the interfacial surface treatment. In spite of the long-range face-on packing alignment of PBDT-TIIG that could improve its Jsc in the OPV application, the low Voc arising from its high- lying HOMO energy level and greater recombination exhibited the trade-oﬀ between light absorption and solar cell perform- ance. Nonetheless, PBDT-TIIG, with a PCE of up to 2.55%, has the highest reported value to date among the TIIG-based materials. We believe that these materials should have a high potential of targeting future optoelectronics with more ﬁne- tuning of the polymer structures. Our ﬁndings are able to demonstrate clear methodology for molecular design for the IIG analogues toward new potential applications where dual OFET and OPV functions are required on a single substrate.

■ EXPERIMENTAL SECTION

Materials. Tri(o-tolyl)phosphin,

tris(dibenzylideneacetone)- dipalladium(0), trimethyl (thiophen-2-yl)stannane, and bromothio- phene were purchased from Aldrich (Missouri, USA) and used without further puriﬁcation. Common organic solvents for synthesis were distilled to remain anhydrous or degassed by nitrogen 0.5 h before use. Ultra-anhydrous o-dichlorobenzene (DCB) for device applications was purchased from Aldrich (Missouri, USA). A surface treatment agent of octadecyltrichlorosilane (ODTS) was purchased from Acros (Geel, Belgium) for ﬁeld-eﬀect transistor characterization. [6,6]-Phenyl-C71-butyric acid methyl ester (PC71BM) was purchased from Solenne BV (Groningen, The Netherlands) for photovoltaic cell applications.

General Procedures for Polymerization. The synthesis of all monomers was described in the Supporting Information. The general procedure of synthesizing PBDT-IIG and PBDT-TIIG is shown in Scheme 1. (5,5′-(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2- b:4,5-b′]dithiophene-2,6-diyl)bis(thiophene-5,2-diyl))bis- (trimethylstannane) (2D-BDT-ditin), (E)-6,6′-dibromo-1,1′-bis(2-oc- tyldodecyl)-[3,3′-biindolinylidene]-2,2′ -dione or (E)-2,2′-dibromo- 4,4′-bis(2-octyldodecyl)-[6,6′-bithieno[3,2-b]pyrrolylidene]- 5,5′(4H,4′H)-dione, tri(o-tolyl)phosphine (16 mol % with respect to ditin monomer), and tris(dibenzylideneacetone)dipalladium(0) (2 mol % with respect to ditin monomer) were dissolved in chlorobenzene. Then, these copolymers were synthesized by Pd(0)- catalyzed Stille coupling polymerization under microwave heating (150 °C for 30 min). After being end-capped with trimethyl(thiophen-2- yl)stannane and bromothiophene (both 1.1 equiv. with respect to the monomers and under microwave heating at 160 °C, 10 min for each end-capping), the mixture was cooled and poured into methanol to aﬀord a crude solid. The crude polymer was puriﬁed by methanol, acetone, and hexane successively using a Soxhlet extraction to remove byproducts, oligomers, and catalyst residues.

Characterization. Microwave reaction was carried out using a Biotage microwave reactor in sealed vessels. 1H NMR spectra were recorded with a Bruker Avance DRX 400 MHz instrument. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) which was connected to one refractive index detector from Schambeck SFD Gmbh. All GPC analyses were performed on polymer/THF solution at 40 °C and calibrated with polystyrene standards. Thermogravimetric analysis (TGA) and diﬀerential scanning calorimetry (DSC) measurements were per- formed under a nitrogen atmosphere at heating rates of 10 and 5 °C min−1 using the TA Instruments Q-50 and Q-100, respectively. The thickness of the active ﬁlms was measured with a depth-proﬁle meter

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DOI: 10.1021/acs.chemmater.5b03197 Chem. Mater. 2015, 27, 6837−6847

Figure 8. Morphology characterization of TM-AFM topography images (upper row) and phase images (lower row) of 1:2 PBDT- IIG:PC71BM blend ﬁlm with 2.5 vol % DIO (panels a and c) and 1:4 PBDT-TIIG:PC71BM blend ﬁlm with 2 vol % DIO (panels b and d). The imaging size is 2 μm × 2 μm for each panel.

reveals a considerable degree of ﬁne-grained texture with a root- mean-square (RMS) roughness of 2.1 nm, which is beneﬁcial to the exciton dissociation and charge carriers transport. In stark contrast, 1:4 PBDT-TIIG:PC71BM blend contains vast long nanoﬁbers that are around 15−25 nm in width, whereas the PC71BM-rich domains are well distributed in the polymer matrix with a RMS roughness of 2.6 nm (Figure 8b,d). These nanoﬁbers construct an interpenetrating network surrounded by the PC71BM clusters and therefore maximize the interfacial D−A contact area for the exciton dissociation into free charge carriers. Notably, the extremely dense ﬁbrillar nanostructure is still conspicuous in the PC71BM-rich blends, suggesting that the high crystallinity nature of PBDT-TIIG is able to preserve the same molecular arrangement when blended with fullerene. The intimately mixed and well-ordered domains within the matrix, along with the high hole carrier mobility of the material, are capable of eﬃcient charge separation and transport and could support the good performance of the cells.

■ CONCLUSION

In conclusion, we conducted a systematic study on the eﬀects of plural heteroarenes on the solid state structure and optoelectronic properties of PBDT-IIG and PBDT-TIIG used in solution-processed OFETs and OPVs to establish a useful

Chemistry of Materials (Veeco Dektak 150, USA). Five lines on a ﬁlm of 1 cm × 1 cm were made by carefully scratching with a plastic tip, and the average height between the hills and valleys is used to represent the ﬁlm thickness. Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were conducted on beamline BL13A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The scattering patterns were collected on a Mar165 CCD with a diameter of 40 mm. X-ray diﬀraction (XRD) was performed by an X’Pert PRO X-ray diﬀractometer (λ = 1.0219 Å). The scattering vector, q = 4π/λsin θ, along with the scattering angles q in these patterns were calibrated using silver behenate. The thin ﬁlms were mounted on a z-axis goniometer. UV−vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. Cyclic voltammetry (CV) was recorded on a CHI 611B electrochemical analyzer using a three-electrode cell in which ITO (polymer ﬁlm areas were about 0.5 × 0.7 cm2) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. The electrochemical properties of the polymer ﬁlms were detected under 0.1 M anhydrous acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) as electrolyte. The morphology of the polymer ﬁlm surface was obtained with a Nanoscope 3D Controller atomic force micrograph (AFM, Digital Instruments) operated in the tapping mode at room temperature. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1230 instrument operating at a voltage of 100 kV with a Gatam dual vision CCD camera.

Computational Methodology. Theoretical molecular simulation of the studied polymers was calculated through a Gaussian 03 program package. The density functional theory (DFT) method, using Becke’s three-parameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) with 6-31G\*, was used for the optimization of ground-state molecular geometry.42

Fabrication and Characterization of Field Eﬀect Transistors. Highly doped n-type Si (100) wafers, with 300 nm SiO2 layer (capacitance per unit area Co = 10 nF cm−2) as a gate dielectric, were used as substrates. The cleaned Si wafers were then modiﬁed with an octadecyltrichlorosilane (ODTS) self-assembled monolayer according to the reported method.43 FET devices were deposited by spin-coating from chlorobenzene (10 mg mL−1) at a spin rate of 1000 rpm for 60 s and annealing at 180 °C for 60 min and thermally evaporated with 100 nm-thick gold electrode (channel length (L) and width (W) were 50 and 1000 μm). FET transfer and output characteristics were recorded in a N2-ﬁlled glovebox by using a Keithley 4200 semiconductor parametric analyzer.

Fabrication and Characterization of Polymer Photovoltaic Cells. The inverted solar cells were fabricated with the device architecture of ITO/ZnO (40 nm)/poly[(9,9-dioctyl-2,7-ﬂuorene)-alt- (9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-ﬂuorene)] (PFN) (5 nm)/polymer:PC71BM (80−110 nm)/MoO3 (6 nm)/Ag (100 nm). Prior to use, patterned ITO-coated glass substrates (10 Ω/square) were successively cleaned according to the reported literature.7,11,19 The ZnO precursor was prepared using zinc acetate dehydrate ·2H2O, Aldrich, 99.999%) as starting material and 2- (Zn(CH3COO)2 ethoxyethanol and monoethanolamine (MEA, Aldrich, 99.7%) as the nontoxic solvent and stabilizer under vigorous stirring for 12 h for the hydrolysis reaction in air. The respective solutions were spin-coated on ITO-coated glass substrates at 5000 rpm for 30 s and preheated at 180 °C for 30 min in air to remove residual organic materials and then transferred into an inert N2-ﬁlled glovebox (<0.1 ppm of O2 and H2O). Subsequently, the PFN interfacial layer was spin-coated onto the active layer according to a similar method described in the literature.16 Blend solutions were prepared by dissolving the target polymer (PBDT-IIG or PBDT-TIIG) and PC71BM in mixed CB:DCB (4:1, v/v) solution in the blend ratios of 1:1, 1:2, and 1:4 with a polymer concentration of 10 mg mL−1 and were heated to 100 °C and stirred for 8 h for complete dissolution. Afterward, the blend solution was spin-coated after adding 2.5% and 2% (v/v) 1,8-diiodooctane (DIO) for PBDT-IIG and PBDT-TIIG-based systems. The wet ﬁlm was slowly dried in a covered Petri dish for 3 h in the glovebox and then annealed at 120 °C for 10 min. Thereupon, methanol was

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dropped onto the active layer with a spin-coating rate of 2000 rpm for 60 s, and subsequently, the coated substrates were transferred to a thermal evaporator and evacuated to ≤5 × 10−6 Torr. Molybdenum oxide was thermally deposited on top of the active layer with an evaporation rate of 0.1 Å s−1. Ultimately, 100 nm silver ﬁlm was deposited on top of the molybdenum oxide layer through a shade mask. The J−V curves were measured using a Keithley 4200 source- measuring unit. A calibrated solar simulator (Oriel) with a 100 mW cm−2 power density was used as the light source. An IPCE (QE- R3011) characterization platform supplied by Enlitech Inc. was used for data acquirement. All IPCE spectra were recorded using a lock-in technique at a chopping frequency of 100 Hz.

■ ASSOCIATED CONTENT \*S Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma- ter.5b03197.

Experimental details, syntheses of monomers, complete characterization of materials and devices. (PDF)

■ AUTHOR INFORMATION Corresponding Authors \*E-mail: austinchen@ncu.edu.tw (H.-C.C.). \*E-mail: chenwc@ntu.edu.tw (W.-C.C.). \*E-mail: chop@ntu.edu.tw (P.-T.C.). Author Contributions § C.L. and H.-C.C. contributed equally. Notes The authors declare no competing ﬁnancial interest.

■ ACKNOWLEDGMENTS

This work was ﬁnancially supported by the Ministry of Science and Technology of Taiwan (MOST 103-2113-M-008-010- MY2). The solar cell device fabrication was carried out in the Advanced Laboratory of Accommodation and Research for Organic Photovoltaics, Ministry of Science and Technology of Taiwan.

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