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Carboxylate-Substituted Polythiophenes for Efficient Fullerene-Free Polymer Solar Cells: The Effect of Chlorination on Their Properties

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ABSTRACT. Two new wide-bandgap polythiophenes, *i.e.*, poly[5,5'-bis(2-hexyldecyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-*alt*-5,5'-3-chloro-2,2'-bithiophene] (PDCBT-Cl) and poly[5,5'-bis(2-hexyldecyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-*alt*-5,5'-3,3'-dichloro-2,2'-bithiophene] (PDCBT-2Cl) comprising 3-chloro-2,2'-bithiophene and 3,3'-dichloro-2,2'-bithiophene moieties, respectively, were synthesized for fullerene-free polymer solar cells (PSCs). For comparison, three other polymers based on [2,2'-bithiophene]-4,4'-dicarboxylate (DCBT), *i.e.*, PDCBT, PDCBT-F and PDCBT-2F with 2,2'-bithiophene, 3-fluoro-2,2'-bithiophene and 3,3'-difluoro-2,2'-bithiophene as comonomers, respectively, were also prepared. PSC devices were fabricated with these polymers as donor materials and ITIC-Th1 as acceptor. The incorporation of chlorine (Cl) or fluorine (F) atoms into polymers both efficiently down-shifted the highest occupied molecular orbital (HOMO) energy levels, leading to higher open-circuit voltage (V_{oc}) in the PSCs. Owing to the proper phase-separated morphology with favorable molecular packing and miscibility, the device based on PDCBT-Cl:ITIC-Th1 exhibited efficient exciton dissociation and charge collection as well as weak charge recombination, and thereby displayed the best power conversion efficiency (PCE) up to 12.38%. The devices based on other polymers showed inferior PCEs (8.14% for PDCBT, 10.85% for PDCBT-F, 8.48% for PDCBT-2F and 6.94% for PDCBT-2Cl). The monomers that are used to make PDCBT-Cl can be synthesized in relatively large scale from commercial available chemicals. All these indicate that PDCBT-Cl is a promising donor material for the large area fabrication of high-performance fullerene-free PSCs.

INTRODUCTION

Polymer solar cells (PSCs) based on a blend of a semiconducting conjugated polymer donor and an electron acceptor have attracted enormous attention due to their advantages of low cost, flexibility, light weight and solution-based fabrication.¹⁻³ In the past few years, the power conversion efficiencies (PCEs) of PSCs have increased sharply owing to the rapid development of non-fullerene acceptors (NFAs).⁴⁻¹¹ Unlike fullerene derivatives and perylene diimide based electron acceptors, the acceptor-donor-acceptor (A-D-A)-type of fused-ring electron acceptors possess strong and broad absorption in visible region and the absorption spectra can be easily extended into the near-infrared (NIR) region via molecular design.¹²⁻²¹ To pursue maximized photon harvesting, wide bandgap (WBG) donor polymers that have complementary absorption with the medium- and low-bandgap acceptors are highly desired. Recently, the PCEs of single-junction PSCs have reached 14%-16%, attributed to the rational design of the WBG polymer donors and A-D-A-type fused-ring NFAs.^{19, 22-28} Along with the improvement of PSC performance, easy accessibility of the photoactive materials is of importance to meet the future commercial applications of PSCs.^{29, 30}

Polythiophenes (PTs) are one of the most important types of WBG donor materials. As a representative of PTs, regioregular poly(3-hexylthiophene) (P3HT) is featured by low cost and ease of synthesis, and plays an important role in the development of PSCs.³¹⁻³⁵ However, owing to the strongly electron-rich characteristics of the thiophene unit, P3HT has a high-lying highest occupied molecular orbital (HOMO) energy level of ~ -4.9 eV, and hence it is difficult to obtain a high open-circuit voltage (V_{oc}), because the V_{oc} of PSCs is directly related to the difference between the lowest unoccupied molecular orbital (LUMO) energy level of the acceptor and HOMO energy level of the donor. To address this issue, electron-withdrawing groups, such as

fluorine (F), carboxylate and cyano, have been introduced to PT conjugated backbones to lower the HOMO energy level.³⁶⁻⁴² For example, Hou et al. reported a poly(tetrathiophene), *i.e.*, PDCBT (Chart 1), which had two carboxylate substituents in each repeating unit. The HOMO energy level of this polymer was 0.36 eV lower than that of P3HT.³⁹ The fullerene-free PSCs based on PDCBT:ITIC with a high V_{oc} of 0.94 V and an excellent PCE of 10.16% were fabricated, while the device based on P3HT:ITIC showed a much lower V_{oc} of 0.52 V and a PCE of 1.25%.⁴³ In order to further enhance the V_{oc} , they attached F atoms to the backbone of PDCBT. The resulting polymer, PDCBT-2F (Chart 1), exhibited a deeper HOMO energy level of -5.56 eV, and a higher V_{oc} of 1.13 V with a PCE of 6.6% was achieved for PDCBT-2F:IT-M based device.⁴⁴ Using the IT-4F acceptor, which has a lower LUMO energy level than IT-M, the device showed a high PCE over 11% with a decreased V_{oc} of 0.92 V.⁴⁵

Fluorination has been a commonly-used method for lowering HOMO and LUMO energy levels of multifarious organic semiconductors, including polymers and small molecules, in the past decade.^{12, 46-51} The F atom with a large Pauling electronegativity of 3.98⁵² and a small Van der Waals radius of 1.35 Å, can lower the HOMO energy levels of polymers, and avoid inducing large steric effect. In addition, the molecular planarity could be improved through forming intramolecular F-S and F-H weak interactions. Compared to F, chlorine (Cl) is another electronegative halogen with smaller Pauling electronegativity (3.16).⁵² Nevertheless, chlorinated polymers displayed even deeper HOMO energy levels than those of fluorinated polymers,⁵³⁻⁵⁶ since the empty 3d-orbitals of the Cl atoms are available for π electron delocalization, leading to increased electron density over the Cl atoms relative to the F atoms.^{57, 58} More importantly, chlorinated polymers are much more accessible through convenient synthetic routes from commercial available chemicals in comparison to the corresponding

fluorinated ones.⁵⁶ There have been several successful examples of chlorinated donor-acceptor conjugated polymers being applied in organic optoelectronic devices,^{28, 53-55, 58-61} demonstrating that chlorination is a viable route toward developing high-performance materials.

Given that PTs have merits of ease synthesis and wide bandgap, the design, synthesis and understanding of chlorinated PTs are important for the development of low-cost and high-performance polymer donor materials. In the current paper, we incorporated the Cl atoms to the backbone of PDCBT, and designed and synthesized two chlorinated PTs with 3-chloro-2,2'-bithiophene (ClBT) and 3,3'-dichloro-2,2'-bithiophene (2ClBT) units, *i.e.*, PDCBT-Cl and PDCBT-2Cl, as shown in Chart 1. For comparison, three polymers, *i.e.*, PDCBT, PDCBT-F and PDCBT-2F (Chart 1), with 2,2'-bithiophene (BT), 3-fluoro-2,2'-bithiophene (FBT) and 3,3'-difluoro-2,2'-bithiophene (2FBT) units, respectively, were also synthesized and characterized. The effects of the Cl substitution on the photophysical properties, film morphology, photovoltaic properties and charge generation and recombination dynamics were investigated in detail. The PSC devices based on these polymers as donor materials and ITIC-Th1⁶² (Chart 1), which has absorption spectrum complementary to these polymers, as acceptor material, were fabricated. The PDCBT-Cl-based device yielded the highest PCE of 12.38% with a short-circuit current density (J_{sc}) of 18.50 mA cm⁻², a V_{oc} of 0.94 V and a fill factor (FF) of 71.2%, while the devices with PDCBT, PDCBT-F, PDCBT-2F and PDCBT-2Cl showed PCEs of 8.14%, 10.85%, 8.48% and 6.94%, respectively.

Chart 1. Chemical structures of PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl, PDCBT-2Cl and ITIC-Th1

RESULTS AND DISCUSSION

Materials synthesis and characterization

Scheme 1. Synthetic routes to the monomer DCBT-2Br and the polymers^a

^aReagents and conditions: i) 2-hexyl-1-decanol, DCC, DMAP, CH_2Cl_2 , RT; ii) bis(pinacolato)diboron, $\text{Pd}_2(\text{dba})_3$, HPCy_3BF_4 , CsF, dioxane, 80°C ; iii) NBS, $\text{CHCl}_3/\text{CF}_3\text{COOH}$, RT; iv) $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, AgNO_3 , KF, DMSO, 60°C ; v) TsOH, methanol, reflux; vi) 2-hexyl-1-decanol, $\text{Ti}(\text{acac})_2$, toluene, reflux; vii) $\text{Pd}(\text{PPh}_3)_4$, chlorobenzene, 135°C . DCC: *N,N'*-dicyclohexylcarbodiimide; DMAP: 4-dimethylaminopyridine.

The synthesis of bis(2-hexyldecyl) 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (DCBT-2Br) monomer and the polymers is depicted in Scheme 1, and the details of the synthesis are described in the Supporting Information. Fluorinated and chlorinated thiophene monomers were prepared following the procedure reported in the literatures.^{47, 60} The synthetic routes of chlorinated thiophene monomers delivered high reaction yields and are much shorter than those of fluorinated thiophene monomers. To realize the efficient preparation of the polymers, the synthesis of monomer DCBT-2Br was studied in detail. Route 1 was developed by Hou et al., and the monomer was obtained in three steps from the compound **1**.³⁹ We found that the small amount of unknown impurities with polarity similar to the monomer always presented in the bromination step. Consequently, the repeated column chromatography purification was required to obtain the pure monomer. Since DCBT-2Br is a liquid, other purification technique such as recrystallization cannot be used. These problems make the large-scale preparation of DCBT-2Br difficult. Then route 2 was developed. It is more efficient and only two steps, including esterification and direct arylation reaction, required from the compound **4**, affording the monomer in a two-step yield of 64%. The route 3 developed by Janssen et al. was also re-investigated,⁶³ and the modified reaction conditions suitable to large-scale preparation were proposed. Via a typical esterification using methanol as reactant and solvent, the solid compound **6** was synthesized in a yield of 88% after recrystallization. Pd-catalyzed coupling of **6** afforded **7** in a yield of 85% after column chromatography and recrystallization. Since **8** is also a solid, trace amount of impurities produced in bromination could be easily removed by recrystallization, giving the compound **8** in a high yield (91%). Finally, the monomer DCBT-2Br was obtained via a transesterification. Since the reaction is clean and efficient (yield > 90%), pure DCBT-2Br can be easily prepared in several grams scale. However, this route is the longest among all three

routes. Obviously, the route 2 is the shortest and should be more suitable to the preparation of the monomer in large scale. All polymers were synthesized by typical Stille polycondensation in yields of 86%-95%. The chemical structures of the intermediates and the polymers were verified by NMR spectra (Figure S1-S9) and elemental analysis.

Table 1 Number-average molecular weights (M_n), molar mass dispersities ($\mathcal{D}$), and photophysical and electrochemical parameters of the polymers

Polymer	M_n [kDa]/ $\mathcal{D}$	$T_{d,5\%}$ [°C]	λ_{max} [nm]		$E_g^{opt\ a}$ [eV]	$E_{LUMO}^{b}/E_{onset}^{re}$ [eV]	$E_{HOMO}^{b}/E_{onset}^{ox}$ [eV]
			solution	film			
PDCBT	28.0/1.92	360	483	560/600	1.90	-2.90/-1.90	-5.20/0.40
PDCBT-F	24.7/2.13	392	501	533/594	1.93	-2.98/-1.82	-5.32/0.52
PDCBT-2F	22.4/2.20	372	501	511/592	1.92	-3.03/-1.77	-5.40/0.60
PDCBT-Cl	24.8/1.74	370	491	555/599	1.91	-3.01/-1.79	-5.34/0.54
PDCBT-2Cl	21.2/1.93	370	486	485/585	1.95	-3.00/-1.80	-5.44/0.64

^a The optical bandgap E_g^{opt} was calculated from the film absorption onset; ^b The HOMO and LUMO energy levels were calculated according to $E_{HOMO} = - (4.80 + E_{onset}^{ox})$ eV and $E_{LUMO} = - (4.80 + E_{onset}^{re})$ eV, in which E_{onset}^{ox} and E_{onset}^{re} represent oxidation and reduction onset potentials, respectively, versus the half potential of Fc/Fc⁺.

All the polymers exhibited good solubility in common chlorinated solvents, such as chloroform, chlorobenzene and dichlorobenzene. The molecular weights of the polymers were determined by high temperature gel permeation chromatography (GPC) at 150 °C using polystyrene as standard. The number-average molecular weights (M_n) of PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl were 28.0, 24.7, 22.4, 24.8 and 21.2 kDa with corresponding molar mass dispersities ($\mathcal{D}$) of 1.92, 2.13, 2.20, 1.74 and 1.93, respectively (Table 1). Similar molecular weights allow the fair comparison of the properties of the polymers. All

five polymers exhibited good thermal stability with decomposition temperatures (T_d , 5% weight loss) exceeding 360 °C, as confirmed by thermogravimetric analysis (TGA) (Figure S10).

Density functional theory calculations

Figure 1. DFT optimized molecular geometries of the methyl-substituted trimers of the polymers.

Figure 1 depicts the optimized geometries of the trimers of the polymers by using the density functional theory (DFT) calculations at the B3LYP/6-31g(d) level. There was little difference of torsion angles (13-18°) between carboxylate substituted thiophene units and their adjacent thiophene units for these polymers. The torsion angles between the two thiophene rings in FBT (1.7°) and 2FBT (0.6°) units were much smaller than that in BT (12.0°) unit. The improved coplanarity of the polymer backbones was induced by the presence of weak intramolecular F-S interaction, as revealed by the smaller calculated F-S distances (2.94 Å for PDCBT-F and 2.92 Å

for PDCBT-2F) than the sum of Van der Waals radii of F and S atoms (3.27 Å). Different from the F atom, the Cl atom causes a less planar structure. The torsion angle between two thiophene units in ClBT (15.2°) was slightly higher than that in BT unit, whereas the torsion angle in 2ClBT unit with two Cl atoms sharply increased to 42.8°. The highly twisted conjugated backbone of PDCBT-2Cl could be detrimental for molecular packing. The calculated distribution of the frontier molecular orbitals of the trimers is shown in Figure S11. These polymers showed similar electron density distribution with HOMO and LUMO being delocalized over the whole conjugated backbone. The calculated HOMO/LUMO energy levels were -4.91/-2.59 eV for PDCBT-F, -5.10/-2.66 eV for PDCBT-2F, -5.00/-2.61 eV for PDCBT-Cl and -5.32/-2.59 eV for PDCBT-2Cl, which are lower than those (-4.87/-2.52 eV) of PDCBT, because of the introduction of electron-withdrawing F and Cl atoms. Moreover, the F and Cl atoms preferentially stabilize the HOMO, resulting in the greater down-shift of the HOMO energy levels than that of the LUMO energy levels.

Photophysical and electrochemical properties

Figure 2. Solution (a, 10^{-5} mol/L in chloroform) and film (b) absorption spectra and schematic energy levels (c) of the polymers, and the relative dielectric constants of the polymers at different frequencies (d).

The solution and film absorption spectra of the polymers are shown in Figure 2, and the corresponding data are summarized in Table 1. In solution, the five polymers showed similarly shaped absorption spectra with maxima at 483 to 501 nm (Figure 2a), and similar molar extinction coefficients, ranging from 4.5×10^4 to 5.5×10^4 $L mol^{-1} cm^{-1}$ at maximum absorption peaks. From solution to film, the maximum absorption peaks were red-shifted by 77, 32, 10 and 64 nm for PDCBT, PDCBT-F, PDCBT-2F and PDCBT-Cl, respectively, whereas PDCBT-2Cl showed almost unchanged absorption maximum at 485 nm. In addition, a vibronic absorption shoulder peak appeared for all the five polymers at 585 - 600 nm, caused by intermolecular interactions in solid state. After thermal annealing at 150 °C, the shoulder peaks increased and

became more pronounced for the polymers except PDCBT-2Cl whose shoulder was still weak with no obvious change (Figure S12). These results indicate the less effective intermolecular interaction of PDCBT-2Cl, which could be ascribed to the highly twisted conjugated backbones as predicted by DFT. The optical bandgaps of the polymers calculated from the film absorption onsets are 1.90, 1.93, 1.92, 1.91 and 1.95 eV for PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl, respectively.

Thin film cyclic voltammograms (CV, see Figure S13) were measured to study the electrochemical properties of the five polymers. The HOMO and LUMO energy levels of the polymers were calculated from the redox onset potentials. As shown in Figure 2c and Table 1, the HOMO and LUMO energy levels are -5.20 and -2.90 eV for PDCBT, -5.32 and -2.98 eV for PDCBT-F, -5.40 and -3.03 eV for PDCBT-2F, -5.34 and -3.01 eV for PDCBT-Cl, and -5.44 and -3.00 eV for PDCBT-2Cl, respectively. Clearly, fluorination and chlorination endow the polymers with down-shifted HOMO and LUMO energy levels, which is consistent with the DFT calculation results. In addition, the introduction of Cl atoms is more effective in terms of lowering HOMO energy levels of the polymers. This phenomenon is consistent with He's studies on donor-acceptor conjugated polymers.^{54, 55}

Dielectric constant

The relative dielectric constants (ϵ_r) of the polymer neat films were determined by capacitance-voltage (C - V) measurements with a device architecture of ITO (indium tin oxide)/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, ~30 nm)/polymer film (~100 nm)/PDINO (10 nm, Figure S14)/Al (100 nm), where PDINO is an efficient cathode interlayer.⁶⁴ The relative dielectric constants were calculated by the equation of $\epsilon_r = Cd/\epsilon_0A$, where C is the capacitance, d is the thickness of the polymer film, ϵ_0 is the vacuum dielectric constant, and A is

the device area. The relative dielectric constants of the polymers as a function of frequency are shown in Figure 2d. The ϵ_r values at 10^4 Hz were 3.67, 4.01, 4.66, 4.52 and 4.99 for PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl, respectively. Clearly, both fluorination and chlorination result in the enhanced ϵ_r , and the chlorinated polymers showed higher ϵ_r than their fluorinated counterparts. This is related to the polarity of the polymer backbones.⁶⁵⁻⁶⁷ In PSCs, excitons should overcome the binding energy of CT state (E_B^{CT}) to dissociate into free holes and electrons within the lifetime.^{67, 68} According to the equation of $E_B^{CT} = q^2/(4\pi\epsilon_0\epsilon_r r_0)$,⁶⁹ where q is the elementary charge, and r_0 is the electron and hole separation distance, higher relative dielectric constants of the fluorinated and chlorinated polymers (PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl) would be beneficial for charge separation in PSCs.

Molecular packing and hole transport properties

Two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) was used to investigate the molecular packing and orientation of the polymers in neat films. The GIWAXS patterns and the corresponding profiles of the polymers are shown in Figure S15. PDCBT neat films showed a pronounced (100) diffraction peak at $0.29 \text{ \AA}^{-1}$ in the out-of-plane (q_z) direction, corresponding to a d -spacing of $21.7 \text{ \AA}$, and a (010) diffraction located at $\sim 1.72 \text{ \AA}^{-1}$ in the in-plane (q_{xy}) direction stronger than that in q_z direction, corresponding to a π - π stacking distance of $\sim 3.65 \text{ \AA}$. The PDCBT-F, PDCBT-2F and PDCBT-Cl neat films presented clear (100) diffractions in both q_{xy} and q_z directions, with lamellar packing d -spacing of 23.4 - $26.1 \text{ \AA}$. In addition, PDCBT-F, PDCBT-2F and PDCBT-Cl films exhibited more intense (010) diffraction peaks relative to that of PDCBT. The π - π stacking peaks located at $\sim 1.72 \text{ \AA}^{-1}$ in q_z direction with d -spacings of $\sim 3.65 \text{ \AA}$, identical to that of PDCBT, while no discernible (010) diffraction was observed in q_{xy} direction. These results indicate that PDCBT backbones tend to form an edge-on

orientation, but PDCBT-F, PDCBT-2F and PDCBT-Cl exhibit more preferential face-on molecular packing. The ordered face-on backbone packing is desirable for photovoltaic devices, which is favorable to the charge transport in vertical sandwich device architecture. For PDCBT-2Cl neat film, (100) and (200) diffraction peaks existed in q_z direction with a lamellar d -spacing of 24.4 Å, and extremely weak (010) diffraction peaks were observed in q_{xy} and q_z directions with a d -spacing of ~3.74 Å larger than those of other four polymers (~3.65 Å). The poor intermolecular π - π stacking and the large π - π stacking distance of PDCBT-2Cl could be ascribed to the severe distortion of the backbones. Compared with PDCBT (lamellar d -spacing: ~21.7 Å), PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl displayed slightly larger lamellar d -spacings (23.4~26.1 Å), which could be attributed to the larger radii of F and Cl atoms relative to that of H atom and therefore larger space for the interdigitation of side chains. The microstructure of ITIC-Th1 neat film was also characterized by in-plane and out-of-plane XRD. As shown in Figure S16, ITIC-Th1 backbones are prone to form face-on orientation. The obvious (100) and (010) diffraction peaks at $2\theta = 6.5^\circ$ and $2\theta = 25.8^\circ$, corresponding to d -spacings of 13.6 and 3.5 Å, respectively, were observed in the out-of-plane direction, while there was no obvious peak in the in-plane direction.

The hole transport property of the polymers was investigated by the space-charge limited current (SCLC) method with a device architecture of ITO/PEDOT:PSS (~30 nm)/polymer film (~100 nm)/Au (100 nm), as shown in Figure S17 and Table S1. Compared to PDCBT with hole mobility (μ_h) of $0.65 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, PDCBT-F, PDCBT-Cl and PDCBT-2F exhibited somewhat higher μ_h of 0.82×10^{-4} , 0.84×10^{-4} , and $0.79 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, benefiting from the ordered face-on backbone packing in the films. Owing to the poor molecular π - π stacking, PDCBT-2Cl showed the lowest μ_h of $0.49 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Photovoltaic properties

Figure 3. Current density-voltage (J - V) characteristics (a) and the external quantum efficiency (EQE) curves (b) of the PSCs under the optimized conditions.

Table 2. Photovoltaic performance of the PSCs based on the polymers under different conditions

Polymer	Treatment ^a	J_{sc} (mA/cm^2) ^b	V_{oc} (V) ^b	FF (%) ^b	PCE (%) ^b
PDCBT	As cast	13.02 $\pm$ 0.25 (13.33)	0.91 $\pm$ 0.01 (0.92)	44.2 $\pm$ 1.0 (45.8)	6.23 $\pm$ 0.17 (6.44)
	TA	15.65 $\pm$ 0.20 (15.92)	0.90 $\pm$ 0.01 (0.90)	47.6 $\pm$ 1.0 (49.2)	6.79 $\pm$ 0.21 (7.06)
	SVA	16.35 $\pm$ 0.21 (16.60)	0.88 $\pm$ 0.01 (0.89)	53.8 $\pm$ 0.9 (55.2)	7.86 $\pm$ 0.22 (8.14)
PDCBT-F	As cast	13.96 $\pm$ 0.15 (14.15)	0.95 $\pm$ 0.01 (0.95)	60.1 $\pm$ 1.2 (61.8)	8.06 $\pm$ 0.25 (8.37)
	TA	16.51 $\pm$ 0.19 (16.75)	0.94 $\pm$ 0.01 (0.94)	60.7 $\pm$ 0.8 (62.0)	9.47 $\pm$ 0.22 (9.76)
	SVA	17.27 $\pm$ 0.20 (17.52)	0.93 $\pm$ 0.01 (0.93)	64.9 $\pm$ 1.0 (66.2)	10.54 $\pm$ 0.23 (10.85)
PDCBT-2F	As cast	13.49 $\pm$ 0.20 (13.73)	0.98 $\pm$ 0.01 (0.99)	52.0 $\pm$ 1.2 (53.8)	7.03 $\pm$ 0.24 (7.32)
	TA	14.13 $\pm$ 0.25 (14.44)	0.97 $\pm$ 0.01 (0.98)	52.5 $\pm$ 0.9 (54.0)	7.35 $\pm$ 0.20 (7.63)
	SVA	15.03 $\pm$ 0.23 (15.32)	0.98 $\pm$ 0.01 (0.98)	55.1 $\pm$ 1.1 (56.5)	8.23 $\pm$ 0.18 (8.48)
PDCBT-Cl	As cast	14.05 $\pm$ 0.21 (14.34)	0.94 $\pm$ 0.01 (0.95)	57.9 $\pm$ 0.8 (59.1)	7.79 $\pm$ 0.20 (8.05)
	TA	17.15 $\pm$ 0.19 (17.40)	0.93 $\pm$ 0.01 (0.94)	60.1 $\pm$ 1.3 (62.1)	9.87 $\pm$ 0.22 (10.16)
	SVA	18.28 $\pm$ 0.18 (18.50)	0.93 $\pm$ 0.01 (0.94)	69.6 $\pm$ 1.1 (71.2)	12.11 $\pm$ 0.19 (12.38)
PDCBT-2Cl	As cast	12.84 $\pm$ 0.17 (13.06)	1.00 $\pm$ 0.01 (1.00)	44.1 $\pm$ 0.9 (45.5)	5.64 $\pm$ 0.23 (5.94)
	TA	13.08 $\pm$ 0.20 (13.35)	0.98 $\pm$ 0.01 (0.99)	46.7 $\pm$ 1.1 (48.5)	6.13 $\pm$ 0.20 (6.41)
	SVA	13.26 $\pm$ 0.22 (13.54)	0.98 $\pm$ 0.01 (0.99)	50.2 $\pm$ 1.0 (51.8)	6.65 $\pm$ 0.21 (6.94)

^a The TA treatment was conducted at 100 °C for 10 min and the SVA treatment was conducted with CS₂ for 120s; ^b Statistical and optimal results are listed outside of parentheses and in parentheses, respectively. The average values are obtained from over 15 devices. TA: thermal annealing; SVA: solvent vapor annealing.

To evaluate the photovoltaic performance of these polymers, PSC devices with an architecture of ITO/PEDOT:PSS (~30 nm)/polymer:ITIC-Th1/PDINO (~10 nm)/Al (100 nm) were fabricated. The typical current density-voltage (J - V) curves are displayed in Figure 3a, and the corresponding device parameters are summarized in Table 2. The device fabrication conditions of the PSCs were systematically screened by varying the D/A ratios, active layer thickness and post treatments (see Table S2-S5). The optimized devices were fabricated by using chloroform as the processing solvent with a donor/acceptor weight ratio of 1:1 and an active-layer thickness of ~110 nm. Without any post-treatment, PSCs based on PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl showed PCEs of 6.44%, 8.37%, 7.32%, 8.05% and 5.94%, respectively. The V_{oc} s of these devices follow the order of PDCBT < PDCBT-F, PDCBT-Cl < PDCBT-2F, PDCBT-2Cl, which is consistent with the lower HOMO energy levels induced by fluorination and chlorination in PDCBT series. In addition, the PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl based devices displayed reduced E_{loss} with the values of 0.60, 0.56, 0.60 and 0.55 eV, respectively, compared with PDCBT based device ($E_{loss} = 0.66$ eV). The J_{sc} s and FFs were improved after thermal annealing (TA) and solvent vapor annealing (SVA) for all polymers. With 100 °C TA treatment, the PCEs of the PSCs based on PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl were enhanced to 7.06%, 9.76%, 7.63%, 10.16% and 6.41%, respectively. Upon SVA treatment with carbon disulfide (CS₂) for 120 s, all polymers achieved the best device performance with higher J_{sc} s and FFs relative to their counterparts with TA treatment. The device based on PDCBT showed a PCE of 8.14% with V_{oc} of 0.89 V, J_{sc} of 16.60 mA cm⁻² and FF of 55.2%. The devices based on PDCBT-F and PDCBT-Cl exhibited superior V_{oc} s, J_{sc} s and FFs, thus high PCEs exceeding 10%. A PCE of 12.38% with a V_{oc} of 0.94 V, an J_{sc} of 18.50 mA cm⁻² and a FF of 71.2%, was achieved for PDCBT-Cl, which is the best

photovoltaic performance for polythiophene derivatives reported so far. The PDCBT-2F and PDCBT-2Cl based devices afforded significantly elevated V_{oc} s, but relatively low J_{sc} s and FFs, leading to inferior PCEs of 8.48% and 6.94%, respectively, relative to their monosubstituted counterparts. Figure 3b shows the external quantum efficiency (EQE) curves of the optimized devices. All the PSC devices displayed broad response from 300 to 820 nm. Compared with the devices based on PDCBT, PDCBT-F and PDCBT-2F, the PDCBT-Cl based device gave much higher EQE exceeding 70% in a broad wavelength range from 450 to 700 nm, while the PDCBT-2Cl based device showed relatively lower EQE. The calculated J_{sc} obtained from EQE curves were in accordance with those extracted from J - V curves within an acceptable deviation of 5%. The charge transport properties of the blend films were examined using the SCLC method, and the corresponding data are shown in Figure S18 and Table S6. The μ_h and electron mobility (μ_e) all the blend films with TA and SVA treatments were higher than their counterparts without any post treatment, and the highest charge mobility was obtained by SVA treatment for all the blends. With SVA treatment, μ_h and μ_e were 0.95×10^{-4} and $0.31 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PDCBT:ITIC-Th1, 1.15×10^{-4} and $0.47 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PDCBT-F:ITIC-Th1, 0.96×10^{-4} and $0.35 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PDCBT-2F:ITIC-Th1, 1.53×10^{-4} and $0.71 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PDCBT-Cl:ITIC-Th1, and 0.63×10^{-4} and $0.20 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PDCBT-2Cl:ITIC-Th1, respectively. The PDCBT-2Cl:ITIC-Th1 blend film exhibited the inferior charge mobility, which could be ascribed to the weak π - π stacking of PDCBT-2Cl backbones and the unfavorable morphology as discussed below. The high hole and electron mobilities of PDCBT-Cl:ITIC-Th1 blend film are the key factors for the high J_{sc} and FF of the PSCs.

Figure 4. The photocurrent density versus effective voltage (J_{ph} - V_{eff}) characteristics (a), transient photocurrent (b) and transient photovoltage (c) measurements for the PSCs under the optimized conditions.

To investigate charge generation and extraction involved in the PSC devices, the effective voltage (V_{eff}) dependent photocurrent density (J_{ph}) was measured (Figure 4a). As shown in Figure 4a, J_{ph} for all devices increased with V_{eff} , and reached a saturated value (saturation current density, J_{sat}) at high V_{eff} . The overall exciton dissociation probability can be estimated from the ratio of J_{ph}/J_{sat} . At the short-circuit conditions, the ratios of J_{ph}/J_{sat} were 90%, 93%, 91%, 96% and 88% for the devices based on PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl, respectively. At the maximal power output conditions, the ratios for PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl based devices were 83%, 90%, 86%, 92% and 79%, respectively. The high J_{ph}/J_{sat} ratios of PDCBT-Cl based device are indicative of efficient process of exciton dissociation and charge collection. This could be resulted from the ordered molecular packing and the desirable blend film morphology as discussed below, and the high relative dielectric constant of PDCBT-Cl might also contribute to the efficient exciton dissociation.^{66, 70} In contrast, the device based on PDCBT-2Cl presented the lowest J_{ph}/J_{sat} ratios, which is correlated to its poor photovoltaic performance. Figure 4b and 4c showed transient photocurrent and photovoltage decay kinetics of the optimized devices based on the polymers.

The charge sweep-out time at short-circuit condition was 0.58 μs for PDCBT based device, 0.42 μs for PDCBT-F based device, 0.62 μs for PDCBT-2F based device, 0.35 μs for PDCBT-Cl based device and 0.72 μs for PDCBT-2Cl based device. The difference in the sweep out time can be correlated to the charge mobility in the blend films. For example, the higher charge mobility in PDCBT-Cl:ITIC-Th1 blend film is responsible for the shorter charge extraction time. The carrier lifetimes calculated from the traces of transient photovoltage (TPV) measurements were 57, 62, 51, 83 and 35 μs for the devices based on PDCBT, PDCBT-F, PDCBT-2F, PDCBT-Cl, and PDCBT-2Cl, respectively.^{71, 72} The lifetime of carriers at open-circuit voltage is dominated by recombination. The much longer carrier lifetime in PDCBT-Cl based device may indicate less recombination, which is consistent to the superior J_{sc} and FF. Nevertheless, the long charge extraction time and short carrier lifetime for PDCBT-2Cl based device agree with its low photovoltaic performance.

Film microstructures and morphology

Figure 5. 2D-GIWAXS patterns for PDCBT:ITIC-Th1 (a), PDCBT-F:ITIC-Th1 (b), PDCBT-2F:ITIC-Th1 (c), PDCBT-Cl:ITIC-Th1 (d) and PDCBT-2Cl:ITIC-Th1 (e) blend films with SVA

treatment, and the out-of-plane and in-plane GIWAXS profiles for the blend films (f) derived from (a)-(e).

The molecular packing in the blend films with different treatments was studied by 2D-GIWAXS. Compared to the untreated blend films (Figure S21), the blend films with TA (Figure S22) or SVA (Figure 5) treatment showed improved crystallinity, as indicated by the stronger diffraction peaks in both q_{xy} and q_z directions. In the blend films with SVA treatment, the (100) diffraction peaks arising from lamellar packing of the polymers, were observed in q_{xy} and q_z directions at $0.30 \text{ \AA}^{-1}$ for PDCBT:ITIC-Th1 and $0.25\text{-}0.27 \text{ \AA}^{-1}$ for the other four blend films, corresponding to d -spacings of 20.9 and 25.1-23.3 $\text{\AA}$, respectively. The larger lamellar d -spacing of PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl than that of PDCBT in the blend films is in accordance with the 2D-GIWAXS data in the neat polymer films. The (100) peaks at $\sim 0.45 \text{ \AA}^{-1}$ with a d -spacing of $\sim 13.9 \text{ \AA}$ coming from ITIC-Th1 existed in all the blend films, and the (100) peaks along q_{xy} and q_z in PDCBT-2Cl:ITIC-Th1 blend film were weaker than those in the other films, implying the poor lamellar packing of ITIC-Th1. All the blend films showed more intense (010) diffraction peaks at $\sim 1.76 \text{ \AA}^{-1}$ in q_z direction than those in q_{xy} direction. The broad (010) peaks could be ascribed to the overlapped diffractions of the polymers and ITIC-Th1. The (010) diffraction peaks in PDCBT-Cl:ITIC-Th1 and PDCBT-F:ITIC-Th1 blend films were more intense, indicative of more ordered π - π stacking in the films, which is a benefit for charge transport in the PSCs. The PDCBT-2Cl:ITIC-Th1 blend film presented the relatively weak (010) diffraction peak in comparison to other blend films. This indicates poor π - π stacking between the molecules, resulting in the low charge carrier mobility.

Figure 6. AFM height (a-e) and phase (f-j) images, and TEM images (l-p) of polymer:ITIC-Th1 blend films with SVA treatment.

To comprehensively understand the different device performance of these polymers, the morphology of the blend films was investigated by atomic force microscope (AFM) and transmission electron microscope (TEM). The AFM images of the blend films with different treatments are shown in Figure S19, S20 and Figure 6a-6j, and all blend films were smooth and uniform. Without any post treatment, the blend films showed root-mean-square (RMS) roughness from 0.61 to 1.55 nm. After TA or SVA treatment, the RMS roughness slightly increased to 1 - 3 nm. From AFM phase images, all blend films exhibited more pronounced phase separation after TA and SVA treatments. The TEM images of the blend films with SVA treatment are displayed in Figure 6l-6p. The nano-scale phase separation with different domain sizes were observed for all blend films, in accordance with AFM results. There was no obvious phase separation of the donor and the acceptor in the PDCBT:ITIC-Th1 blend film, which could obstruct charge transport. In contrast, the blend films based on fluorinated and chlorinated polymers exhibited more pronounced phase separation, likely due to the reduced miscibility

between the fluorinated/chlorinated polymers and ITIC-Th1, as discussed below. Nevertheless, relatively large aggregates were observed in PDCBT-2Cl:ITIC-Th1 blend film, which could induce unfavorable exciton recombination and hence reduced charge generation. The PDCBT-Cl:ITIC-Th1 blend film exhibited more desirable morphology with polymer-rich fibrils of hundreds nanometers in length and several nanometers in width close to the exciton diffusion length in organic materials. The well-percolated bicontinuous network of the PDCBT-Cl:ITIC-Th1 blend film is highly favorable for charge generation and transport, consistent with the aforementioned device results.

Table 3. Contact angle, surface tension of individual materials and $(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ values

Organic layer X	Contact angle [water] (deg)	Contact angle [GL] (deg)	γ^d (mN/m)	γ^p (mN/m)	Surface tension (mN/m)	$(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$
ITIC-Th1	100.39	85.80	22.36	4.20	26.56	-
PDCBT	104.87	91.30	20.50	3.15	23.65	0.07
PDCBT-F	105.24	91.98	19.91	3.20	23.11	0.11
PDCBT-2F	106.19	93.51	18.83	3.21	22.04	0.20
PDCBT-Cl	105.80	93.89	17.04	4.23	21.27	0.27
PDCBT-2Cl	105.33	94.17	16.12	4.48	20.60	0.35

The miscibility of the donor and acceptor materials has a great influence on the blend film morphology. To further understand the molecular miscibility between these polymer donors and ITIC-Th1, we measured the contact angles of the neat films based on the polymers and ITIC-Th1, and calculated their surface tension (γ) (Figure S22 and Table 3). The surface tensions of all polymer films (20.60 - 23.65 mN/m) are lower than that (26.56 mN/m) of ITIC-Th1 film. In addition, the polymers with F or Cl substituents, *i.e.* PDCBT-F, PDCBT-2F, PDCBT-Cl and PDCBT-2Cl showed reduced surface tension with values of 23.11, 22.04, 21.27 and 20.60 mN/m, respectively, compared to that (23.65 mN/m) of PDCBT; the chlorinated polymers (PDCBT-Cl

and PDCBT-2Cl) showed lower surface tension than those of the fluorinated polymers (PDCBT-F and PDCBT-2F). The molecular interaction parameter $\chi \propto (\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ suggested by Moons and co-workers in which χ is the Flory–Huggins interaction parameter, was used to compare the miscibility of the polymer donor and acceptor materials in blend.^{26, 73 74} The smaller χ or $(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ values imply a higher degree of molecular miscibility between the two materials. According to the $(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ values in Table 3, the molecular miscibility of the polymers and ITIC-Th1 follows the order of PDCBT > PDCBT-F > PDCBT-2F > PDCBT-Cl > PDCBT-2Cl. The lack of obvious phase separation in the PDCBT:ITIC-Th1 blend film could be caused by the high molecular intermixing between PDCBT and ITIC-Th1. The poor miscibility of PDCBT-2Cl and ITIC-Th1 should be a reason for the severe phase separation of the polymer donor and the acceptor in the blend film. The suitable molecular miscibility of PDCBT-F:ITIC-Th1, PDCBT-2F:ITIC-Th1 and PDCBT-Cl:ITIC-Th1 systems contributes to the more appropriate phase separation in the blend films.

CONCLUSIONS

In summary, we have synthesized five polythiophene derivatives, *i.e.*, PDCBT, PDCBT-F, PDCBT-Cl, PDCBT-2F and PDCBT-2Cl with wide optical bandgaps of 1.90~1.95 eV. The effect of the chlorination on photophysical and charge transport properties, molecular packing, and film microstructures, were studied comprehensively in comparison to the fluorination. The chlorinated and fluorinated polymers possess deeper HOMO and LUMO energy levels and higher dielectric constants than their unsubstituted counterpart PDCBT. As expected from the deep HOMO energy levels, PDCBT-F and PDCBT-Cl based PSCs showed enhanced V_{oc} of 0.93 V, and the V_{oc} of PDCBT-2F and PDCBT-2Cl based PSCs reached 0.98 V, higher than that of PDCBT based PSCs ($V_{oc} = 0.89$ V). Compared to PDCBT and the fluorinated polymers

(PDCBT-F and PDCBT-2F), PDCBT-Cl with monochlorinated BT unit had higher hole mobility, while PDCBT-2Cl with dichlorinated BT displayed lower hole mobility due to the poor intermolecular π - π stacking derived from the highly twisted backbone. The PDCBT-Cl:ITIC-Th1 blend film showed a proper phase-separated morphology with favorable molecular packing and miscibility, resulting in the efficient exciton dissociation and charge collection as well as weak recombination in the PSC device. Consequently, the PDCBT-Cl:ITIC-Th1 based PSCs achieved the highest PCE of 12.38% with a V_{oc} of 0.94 V, a J_{sc} of 18.50 mA cm⁻² and a FF of 71.2%, which is the best photovoltaic performance for polythiophene derivatives reported so far. Owing to the structural simplicity and synthetic accessibility of the monomers, the high-performance chlorinated polythiophene PDCBT-Cl is promising for future PSC commercialization.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Details of synthesis of monomers and polymers, instruments, device fabrication and characterization, SCLC measurements, 2D-GIWAXS data, AFM and TEM images, and other data. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) He, Z.; Xiao, B.; Liu, F.; Wu, H.; Yang, Y.; Xiao, S.; Wang, C.; Russell, T. P.; Cao, Y. Single-junction polymer solar cells with high efficiency and photovoltage. *Nat. Photon.* **2015**, 9, 174-179.
- (2) Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photon.* **2012**, 6, 153-161.

- (3) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. J. S. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, *270*, 1789-1791.
- (4) Cheng, P.; Li, G.; Zhan, X.; Yang, Y. Next-generation organic photovoltaics based on non-fullerene acceptors. *Nat. Photon.* **2018**, *12*, 131-142.
- (5) Gao, G.; Liang, N.; Geng, H.; Jiang, W.; Fu, H.; Feng, J.; Hou, J.; Feng, X.; Wang, Z. Spiro-Fused Perylene Diimide Arrays. *J. Am. Chem. Soc.* **2017**, *139*, 15914-15920.
- (6) Gao, L.; Zhang, Z. G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y. All-Polymer Solar Cells Based on Absorption-Complementary Polymer Donor and Acceptor with High Power Conversion Efficiency of 8.27%. *Adv. Mater.* **2016**, *28*, 1884-1890.
- (7) Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic solar cells based on non-fullerene acceptors. *Nat. Mater.* **2018**, *17*, 119-128.
- (8) Lin, Y.; Wang, J.; Zhang, Z. G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An electron acceptor challenging fullerenes for efficient polymer solar cells. *Adv. Mater.* **2015**, *27*, 1170-1174.
- (9) Meng, D.; Sun, D.; Zhong, C.; Liu, T.; Fan, B.; Huo, L.; Li, Y.; Jiang, W.; Choi, H.; Kim, T.; Kim, J. Y.; Sun, Y.; Wang, Z.; Heeger, A. J. High-Performance Solution-Processed Non-Fullerene Organic Solar Cells Based on Selenophene-Containing Perylene Bisimide Acceptor. *J. Am. Chem. Soc.* **2016**, *138*, 375-380.
- (10) Yan, C.; Barlow, S.; Wang, Z.; Yan, H.; Jen, A. K. Y.; Marder, S. R.; Zhan, X. Non-fullerene acceptors for organic solar cells. *Nat. Rev. Mater.* **2018**, *3*, 18003.

- (11) Yuan, J.; Huang, T.; Cheng, P.; Zou, Y.; Zhang, H.; Yang, J. L.; Chang, S. Y.; Zhang, Z.; Huang, W.; Wang, R.; Meng, D.; Gao, F.; Yang, Y. Enabling low voltage losses and high photocurrent in fullerene-free organic photovoltaics. *Nat. Commun.* **2019**, *10*, 570-578.
- (12) Cui, Y.; Yang, C.; Yao, H.; Zhu, J.; Wang, Y.; Jia, G.; Gao, F.; Hou, J. Efficient Semitransparent Organic Solar Cells with Tunable Color enabled by an Ultralow-Bandgap Nonfullerene Acceptor. *Adv. Mater.* **2017**, *29*, 1703080.
- (13) Li, T.; Dai, S.; Ke, Z.; Yang, L.; Wang, J.; Yan, C.; Ma, W.; Zhan, X. Fused Tris(thienothiophene)-Based Electron Acceptor with Strong Near-Infrared Absorption for High-Performance As-Cast Solar Cells. *Adv. Mater.* **2018**, *30*, 1705969.
- (14) Li, Y.; Zhong, L.; Gautam, B.; Bin, H.-J.; Lin, J.-D.; Wu, F.-P.; Zhang, Z.; Jiang, Z.-Q.; Zhang, Z.-G.; Gundogdu, K.; Li, Y.; Liao, L.-S. A near-infrared non-fullerene electron acceptor for high performance polymer solar cells. *Energy Environ. Sci.* **2017**, *10*, 1610-1620.
- (15) Liu, F.; Zhou, Z.; Zhang, C.; Zhang, J.; Hu, Q.; Vergote, T.; Liu, F.; Russell, T. P.; Zhu, X. Efficient Semitransparent Solar Cells with High NIR Responsiveness Enabled by a Small-Bandgap Electron Acceptor. *Adv. Mater.* **2017**, *29*, 1606574.
- (16) Shi, X.; Liao, X.; Gao, K.; Zuo, L.; Chen, J.; Zhao, J.; Liu, F.; Chen, Y.; Jen, A. K. Y. An Electron Acceptor with Broad Visible-NIR Absorption and Unique Solid State Packing for As-Cast High Performance Binary Organic Solar Cells. *Adv. Funct. Mater.* **2018**, *28*, 1802324.
- (17) Shi, X.; Zuo, L.; Jo, S. B.; Gao, K.; Lin, F.; Liu, F.; Jen, A. K. Y. Design of a Highly Crystalline Low-Band Gap Fused-Ring Electron Acceptor for High-Efficiency Solar Cells with Low Energy Loss. *Chem. Mater.* **2017**, *29*, 8369-8376.

- (18) Wang, W.; Yan, C.; Lau, T. K.; Wang, J.; Liu, K.; Fan, Y.; Lu, X.; Zhan, X. Fused Hexacyclic Nonfullerene Acceptor with Strong Near-Infrared Absorption for Semitransparent Organic Solar Cells with 9.77% Efficiency. *Adv. Mater.* **2017**, *29*, 1701308.
- (19) Xiao, Z.; Jia, X.; Ding, L. Ternary organic solar cells offer 14% power conversion efficiency. *Sci. Bull.* **2017**, *62*, 1562-1564.
- (20) Yao, H.; Cui, Y.; Yu, R.; Gao, B.; Zhang, H.; Hou, J. Design, Synthesis, and Photovoltaic Characterization of a Small Molecular Acceptor with an Ultra-Narrow Band Gap. *Angew. Chem. Int. Ed.* **2017**, *56*, 3045-3049.
- (21) Liang, Z.; Li, M.; Zhang, X.; Wang, Q.; Jiang, Y.; Tian, H.; Geng, Y. Near-infrared absorbing non-fullerene acceptors with selenophene as π bridges for efficient organic solar cells. *J. Mater. Chem. A* **2018**, *6*, 8059-8067.
- (22) Cui, Y.; Yao, H.; Hong, L.; Zhang, T.; Xu, Y.; Xian, K.; Gao, B.; Qin, J.; Zhang, J.; Wei, Z.; Hou, J. Achieving Over 15% Efficiency in Organic Photovoltaic Cells via Copolymer Design. *Adv. Mater.* **2019**, *31*, 1808356.
- (23) Fan, B.; Zhang, D.; Li, M.; Zhong, W.; Zeng, Z.; Ying, L.; Huang, F.; Cao, Y. Achieving over 16% efficiency for single-junction organic solar cells. *Sci. China: Chem.* **2019**, *62*, <https://doi.org/10.1007/s11426-019-9457-5>.
- (24) Geng, R.; Song, X.; Feng, H.; Yu, J.; Zhang, M.; Gasparini, N.; Zhang, Z.; Liu, F.; Baran, D.; Tang, W. Nonfullerene Acceptor for Organic Solar Cells with Chlorination on Dithieno[3,2-b:2',3'-d]pyrrol Fused-Ring. *ACS Energy Lett.* **2019**, *4*, 763-770.

- (25) Kan, B.; Feng, H.; Yao, H.; Chang, M.; Wan, X.; Li, C.; Hou, J.; Chen, Y. A chlorinated low-bandgap small-molecule acceptor for organic solar cells with 14.1% efficiency and low energy loss. *Sci. China: Chem.* **2018**, *61*, 1307-1313.
- (26) Li, S.; Ye, L.; Zhao, W.; Yan, H.; Yang, B.; Liu, D.; Li, W.; Ade, H.; Hou, J. A Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2% Efficiency in Polymer Solar Cells. *J. Am. Chem. Soc.* **2018**, *140*, 7159-7167.
- (27) Yuan, J.; Zhang, Y.; Zhou, L.; Zhang, G.; Yip, H.-L. Lau, T.-K.; Lu, X.; Zhu, C.; Peng, H.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y.; Zou, Y. Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **2019**, *3*, 1-12.
- (28) Zhang, S.; Qin, Y.; Zhu, J.; Hou, J. Over 14% Efficiency in Polymer Solar Cells Enabled by a Chlorinated Polymer Donor. *Adv. Mater.* **2018**, *30*, 1800868.
- (29) Li, X.; Pan, F.; Sun, C.; Zhang, M.; Wang, Z.; Du, J.; Wang, J.; Xiao, M.; Xue, L.; Zhang, Z. G.; Zhang, C.; Liu, F.; Li, Y. Simplified synthetic routes for low cost and high photovoltaic performance n-type organic semiconductor acceptors. *Nat. Commun.* **2019**, *10*, 519.
- (30) Sun, C.; Pan, F.; Bin, H.; Zhang, J.; Xue, L.; Qiu, B.; Wei, Z.; Zhang, Z. G.; Li, Y. A low cost and high performance polymer donor material for polymer solar cells. *Nat. Commun.* **2018**, *9*, 743.
- (31) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de

Leeuw, D. M. Two-dimensional charge transport in self-organized, high-mobility conjugated polymers. *Science* **1998**, 280, 1741-1744.

(32) Guo, X.; Cui, C.; Zhang, M.; Huo, L.; Huang, Y.; Hou, J.; Li, Y. High efficiency polymer solar cells based on poly(3-hexylthiophene)/indene-C70 bisadduct with solvent additive. *Energy Environ. Sci.* **2012**, 5, 7943-7949.

(33) Holliday, S.; Ashraf, R. S.; Wadsworth, A.; Baran, D.; Yousaf, S. A.; Nielsen, C. B.; Tan, C. H.; Dimitrov, S. D.; Shang, Z.; Gasparini, N.; Alamoudi, M.; Laquai, F.; Brabec, C. J.; Salleo, A.; Durrant, J. R.; McCulloch, I. High-efficiency and air-stable P3HT-based polymer solar cells with a new non-fullerene acceptor. *Nat. Commun.* **2016**, 7, 11585.

(34) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* **2005**, 15, 1617-1622.

(35) Zhao, G.; He, Y.; Li, Y. 6.5% Efficiency of polymer solar cells based on poly(3-hexylthiophene) and indene-C(60) bisadduct by device optimization. *Adv. Mater.* **2010**, 22, 4355-4358.

(36) Greve, D. R.; Apperloo, J. J.; Janssen, R. A. J. Synthesis and Characterisation of Novel Regioregular Polythiophenes-Tuning the Redox Properties. *Eur. J. Org. Chem.* **2001**, 3437-3443.

(37) Huo, L.; Chen, T. L.; Zhou, Y.; Hou, J.; Chen, H.-Y.; Yang, Y.; Li, Y. Improvement of Photoluminescent and Photovoltaic Properties of Poly(thienylene vinylene) by Carboxylate Substitution. *Macromolecules* **2009**, 42, 4377-4380.

- (38) Jo, J. W.; Jung, J. W.; Wang, H.-W.; Kim, P.; Russell, T. P.; Jo, W. H. Fluorination of Polythiophene Derivatives for High Performance Organic Photovoltaics. *Chem. Mater.* **2014**, *26*, 4214-4220.
- (39) Zhang, M.; Guo, X.; Ma, W.; Ade, H.; Hou, J. A polythiophene derivative with superior properties for practical application in polymer solar cells. *Adv. Mater.* **2014**, *26*, 5880-5885.
- (40) Zhang, M.; Guo, X.; Yang, Y.; Zhang, J.; Zhang, Z.-G.; Li, Y. Downwards tuning the HOMO level of polythiophene by carboxylate substitution for high open-circuit-voltage polymer solar cells. *Polym. Chem.* **2011**, *2*, 2900-2906.
- (41) Blaskovits, J. T.; Bura, T.; Beaupré, S.; Lopez, S. A.; Roy, C.; de Goes Soares, J.; Oh, A.; Quinn, J.; Li, Y.; Aspuru-Guzik, A.; Leclerc, M. A Study of the Degree of Fluorination in Regioregular Poly(3-hexylthiophene). *Macromolecules* **2016**, *50*, 162-174.
- (42) Homyak, P. D.; Liu, Y.; Harris, J. D.; Liu, F.; Carter, K. R.; Russell, T. P.; Coughlin, E. B. Systematic Fluorination of P3HT: Synthesis of P(3HT-co-3H4FT)s by Direct Arylation Polymerization, Characterization, and Device Performance in OPVs. *Macromolecules* **2016**, *49*, 3028-3037.
- (43) Qin, Y.; Uddin, M. A.; Chen, Y.; Jang, B.; Zhao, K.; Zheng, Z.; Yu, R.; Shin, T. J.; Woo, H. Y.; Hou, J. Highly Efficient Fullerene-Free Polymer Solar Cells Fabricated with Polythiophene Derivative. *Adv. Mater.* **2016**, *28*, 9416-9422.
- (44) Zhang, H.; Li, S.; Xu, B.; Yao, H.; Yang, B.; Hou, J. Fullerene-free polymer solar cell based on a polythiophene derivative with an unprecedented energy loss of less than 0.5 eV. *J. Mater. Chem. A* **2016**, *4*, 18043-18049.

- (45) Yao, H.; Qian, D.; Zhang, H.; Qin, Y.; Xu, B.; Cui, Y.; Yu, R.; Gao, F.; Hou, J. Critical Role of Molecular Electrostatic Potential on Charge Generation in Organic Solar Cells. *China J. Chem.* **2018**, *36*, 491-494.
- (46) Gao, Y.; Zhang, X.; Tian, H.; Zhang, J.; Yan, D.; Geng, Y.; Wang, F. High Mobility Ambipolar Diketopyrrolopyrrole-Based Conjugated Polymer Synthesized Via Direct Arylation Polycondensation. *Adv. Mater.* **2015**, *27*, 6753-6759.
- (47) Kawashima, K.; Fukuhara, T.; Suda, Y.; Suzuki, Y.; Koganezawa, T.; Yoshida, H.; Ohkita, H.; Osaka, I.; Takimiya, K., Implication of Fluorine Atom on Electronic Properties, Ordering Structures, and Photovoltaic Performance in Naphthobisthiadiazole-Based Semiconducting Polymers. *J. Am. Chem. Soc.* **2016**, *138*, 10265-10275.
- (48) Li, Z.; Jiang, K.; Yang, G.; Lai, J. Y.; Ma, T.; Zhao, J.; Ma, W.; Yan, H. Donor polymer design enables efficient non-fullerene organic solar cells. *Nat. Commun.* **2016**, *7*, 13094.
- (49) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 7148-7151.
- (50) Uddin, M. A.; Kim, Y.; Younts, R.; Lee, W.; Gautam, B.; Choi, J.; Wang, C.; Gundogdu, K.; Kim, B. J.; Woo, H. Y. Controlling Energy Levels and Blend Morphology for All-Polymer Solar Cells via Fluorination of a Naphthalene Diimide-Based Copolymer Acceptor. *Macromolecules* **2016**, *49*, 6374-6383.

- (51) Kranthiraja, K.; Long, D. X.; Sree, V. G.; Cho, W.; Cho, Y.-R.; Zaheer, A.; Lee, J.-C.; Noh, Y.-Y.; Jin, S.-H. Sequential Fluorination on Naphthaleneamide-Based Conjugated Polymers and Their Impact on Charge Transport Properties. *Macromolecules* **2018**, *51*, 5530-5536.
- (52) Tang, M. L.; Oh, J. H.; Reichardt, A. D.; Bao, Z. Chlorination: A General Route toward Electron Transport in Organic Semiconductors. *J. Am. Chem. Soc.* **2009**, *131*, 3733–3740.
- (53) Hiszpanski, A. M.; Saathoff, J. D.; Shaw, L.; Wang, H.; Kraya, L.; Lüttich, F.; Brady, M. A.; Chabinyk, M. L.; Kahn, A.; Clancy, P.; Loo, Y.-L. Halogenation of a Nonplanar Molecular Semiconductor to Tune Energy Levels and Bandgaps for Electron Transport. *Chem. Mater.* **2015**, *27*, 1892-1900.
- (54) Qu, S.; Wang, H.; Mo, D.; Chao, P.; Yang, Z.; Li, L.; Tian, L.; Chen, W.; He, F. Fine Tuning of Open-Circuit Voltage by Chlorination in Thieno[3,4-b]thiophene–Benzodithiophene Terpolymers toward Enhanced Solar Energy Conversion. *Macromolecules* **2017**, *50*, 4962-4971.
- (55) Wang, H.; Chao, P.; Chen, H.; Mu, Z.; Chen, W.; He, F. Simultaneous Increase in Open-Circuit Voltage and Efficiency of Fullerene-Free Solar Cells through Chlorinated Thieno[3,4-b]thiophene Polymer Donor. *ACS Energy Lett.* **2017**, *2*, 1971-1977.
- (56) Zhang, Y.; Yao, H.; Zhang, S.; Qin, Y.; Zhang, J.; Yang, L.; Li, W.; Wei, Z.; Gao, F.; Hou, J. Fluorination vs. chlorination: a case study on high performance organic photovoltaic materials. *Sci. China: Chem.* **2018**, *61*, 1328-1337.
- (57) Lee, W.-Y.; Oh, J. H.; Suraru, S.-L.; Chen, W.-C.; Würthner, F.; Bao, Z. High-Mobility Air-Stable Solution-Shear-Processed n-Channel Organic Transistors Based on Core-Chlorinated Naphthalene Diimides. *Adv. Funct. Mater.* **2011**, *21*, 4173-4181.

- (58) Wu, Y.; An, C.; Shi, L.; Yang, L.; Qin, Y.; Liang, N.; He, C.; Wang, Z.; Hou, J. The Crucial Role of Chlorinated Thiophene Orientation in Conjugated Polymers for Photovoltaic Devices. *Angew. Chem. Int. Ed.* **2018**, *57*, 12911-12915.
- (59) Tang, M. L.; Oh, J. H.; Reichardt, A. D.; Bao Z. Chlorination: A General Route toward Electron Transport in Organic Semiconductors. *J. Am. Chem. Soc.* **2009**, *131*, 3733-3740
- (60) Chen, H.; Hu, Z.; Wang, H.; Liu, L.; Chao, P.; Qu, J.; Chen, W.; Liu, A.; He, F. A Chlorinated π -Conjugated Polymer Donor for Efficient Organic Solar Cells. *Joule* **2018**, *2*, 1623-1634.
- (61) Lei, T.; Dou, J.-H.; Ma, Z.-J.; Liu, C.-J.; Wang, J.-Y.; Pei, J. Chlorination as a useful method to modulate conjugated polymers: balanced and ambient-stable ambipolar high-performance field-effect transistors and inverters based on chlorinated isoindigo polymers. *Chem. Sci.* **2013**, *4*, 2447-2452.
- (62) Zhao, F.; Dai, S.; Wu, Y.; Zhang, Q.; Wang, J.; Jiang, L.; Ling, Q.; Wei, Z.; Ma, W.; You, W.; Wang, C.; Zhan, X. Single-Junction Binary-Blend Nonfullerene Polymer Solar Cells with 12.1% Efficiency. *Adv. Mater.* **2017**, *29*, 1700144.
- (63) Heuvel, R.; Colberts, F. J. M.; Wienk, M. M.; Janssen, R. A. J., Thermal behaviour of dicarboxylic ester bithiophene polymers exhibiting a high open-circuit voltage. *J. Mater. Chem. C* **2018**, *6*, 3731-3762.
- (64) Zhang, Z.-G.; Qi, B.; Jin, Z.; Chi, D.; Qi, Z.; Li, Y.; Wang, J., Perylene diimides: a thickness-insensitive cathode interlayer for high performance polymer solar cells. *Energy Environ. Sci.* **2014**, *7*, 1966-1973.

- (65) Carsten, B.; Szarko, J. M.; Son, H. J.; Wang, W.; Lu, L.; He, F.; Rolczynski, B. S.; Lou, S. J.; Chen, L. X.; Yu, L. Examining the effect of the dipole moment on charge separation in donor-acceptor polymers for organic photovoltaic applications. *J. Am. Chem. Soc.* **2011**, *133*, 20468-20475.
- (66) Xu, X.; Li, Z.; Wang, J.; Lin, B.; Ma, W.; Xia, Y.; Andersson, M. R.; Janssen, R. A. J.; Wang, E. High-performance all-polymer solar cells based on fluorinated naphthalene diimide acceptor polymers with fine-tuned crystallinity and enhanced dielectric constants. *Nano Energy* **2018**, *45*, 368-379.
- (67) Yang, P.; Yuan, M.; Zeigler, D. F.; Watkins, S. E.; Lee, J. A.; Luscombe, C. K. Influence of fluorine substituents on the film dielectric constant and open-circuit voltage in organic photovoltaics. *J. Mater. Chem. C* **2014**, *2*, 3278-3284.
- (68) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110*, 6736-6767
- (69) Koster, L. J. A.; Shaheen, S. E.; Hummelen, J. C. Pathways to a New Efficiency Regime for Organic Solar Cells. *Adv. Energy Mater.* **2012**, *2*, 1246-1253.
- (70) Liu, X.; Xie, B.; Duan, C.; Wang, Z.; Fan, B.; Zhang, K.; Lin, B.; Colberts, F. J. M.; Ma, W.; Janssen, R. A. J.; Huang, F.; Cao, Y. A high dielectric constant non-fullerene acceptor for efficient bulk-heterojunction organic solar cells. *J. Mater. Chem. A* **2018**, *6*, 395-403.
- (71) Baumann, A.; Lorrmann, J.; Rauh, D.; Deibel, C.; Dyakonov, V. A new approach for probing the mobility and lifetime of photogenerated charge carriers in organic solar cells under real operating conditions. *Adv. Mater.* **2012**, *24*, 4381-4386.

(72) Nilsson, S.; Bernasik, A.; Budkowski, A.; Moons, E.; Morphology and Phase Segregation of Spin-Casted Films of Polyfluorene/PCBM Blends. *Macromolecules* **2007**, *40*, 8291-8301.

(73) Feng, H.; Yi, Y. Q. Q.; Ke, X.; Yan, J.; Zhang, Y.; Wan, X.; Li, C.; Zheng, N.; Xie, Z.; Chen, Y. New Anthracene-Fused Nonfullerene Acceptors for High-Efficiency Organic Solar Cells: Energy Level Modulations Enabling Match of Donor and Acceptor. *Adv. Energy Mater.* **2019**, *9*, 1803541.

(74) Ye, L.; Hu, H.; Ghasemi, M.; Wang, T.; Collins, B. A.; Kim, J. H.; Jiang, K.; Carpenter, J. H.; Li, H.; Li, Z.; McAfee, T.; Zhao, J.; Chen, X.; Lai, J. L. Y.; Ma, T.; Bredas, J. L.; Yan, H.; Ade, H. Quantitative relations between interaction parameter, miscibility and function in organic solar cells. *Nat. Mater.* **2018**, *17*, 253-260.

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