

Unfused-ring Acceptors with Dithienobenzotriazole Core for Efficient Organic Solar Cells

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Electronic Supplementary Information

Abstract In recent years, non-fullerene acceptors (NFAs) with unfused-ring structure have received extensive attention due to their flexible combination of building blocks and relatively simple synthetic routes. In this work, three new A-D-C-D-A type unfused-ring acceptors (UFAs), named DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl, were designed and synthesized with dithienobenzotriazole (DTBTz) as the core. Through modification of alkyl chain on the DTBTz unit and change of halogen atoms on the cyanoindanone end groups, the differences in optoelectronic properties of these three small molecule acceptors were investigated. The results show that changes in alkyl chain and halogen atom endow UFAs with different features, including shift in absorption, changes in energy level and molecular packing. When blended with donor PBDB-T, the organic solar cell based on DTBTzMe-IC2Cl achieves the highest device efficiency of 12.3%, while DTBTzEH-IC2F-based device obtains 11.5% efficiency and DTBTzMe-IC2F-based device obtains 12.0% efficiency. The stability tests show that all the devices obtain good efficiency retention rates. These results demonstrate that the introduction of a rigid aromatic ring DTBTz as an intermediate core not only effectively results in highly planar A-D-C-D-A small molecules, but also provides a new reference for the design and development of UFAs in OSCs.

Keywords Organic solar cells; Non-fullerene acceptors; Unfused-ring acceptors; Dithienobenzotriazole; Stability

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INTRODUCTION

Organic solar cells (OSCs) have certain advantages in the construction of integrated photovoltaic glass, flexible solar panels, semitransparent devices, etc., due to their advantages of lightweight, flexibility, translucency and inkjet printing, so they have received extensive attention.^[1–4] As one of the important components of active layer, non-fullerene acceptors (NFAs) have achieved unprecedented high device efficiency, which triggered a new stage in research of OSCs.^[5–8] Generally, most high-performance non-fullerene acceptors have structure with a completely fused ring in the center, so they are called fused-ring acceptors (FRAs).^[9,10] The large planar molecular framework of FRAs is beneficial to enhance light absorption and improve charge transport.^[11,12] But ring-closure reaction of FRAs increases difficulty of synthesis to a certain extent.^[13] Correspondingly, small molecules with building blocks connected by C-C single bonds are called unfused-ring

acceptors (UFAs).^[14] Compared with FRAs, the synthetic route of UFAs is simpler. UFAs have potential to develop high efficiency organic solar cells through easy synthesizing.^[15–18]

Among UFAs, central core engineering and end-group engineering are effective strategies to diversify structures and properties of photovoltaic materials.^[19–21] Some UFAs with central cores, such as benzothiadiazole (BT),^[22,23] benzotriazole (BTz),^[24] thieno[3,4-c]pyrrole-4,6-dione (TPD),^[25,26] 2,2'-bithiophene-3,3'-dicarboximide (BTI),^[27] have been reported with impressive performances. For example, Chen *et al.* used benzothiadiazole as center core and adjusted halogenated end groups. Compared with F-substituted BCDT-4F, Cl-substituted BCDT-4Cl achieved better PCE of 12.10%.^[28] Huang *et al.* used dithienobenzothiadiazole as central core and changed end groups to synthesize three UFAs. As a result, halogenated DTBCIC-Cl and DTBCIC-F performed better than DTBCIC-H, especially the OSC based on DTBCIC-Cl obtained 12.71% PCE.^[29] Hou *et al.* applied simple 2,2'-bithiophene which connected a sterically hindered 2,4,6-tri-isopropyl-phenyl to enhance molecular planarity and obtained A4T-16 acceptor. PBDB-TF:A4T-16-based device achieved a high PCE of 15.2%, which is one of the highest efficiencies based on UFAs currently.^[30] It can be seen that the central core with a rigid aromatic ring plane will help to improve the overall planarity of molecules, which may broaden intramolecular conjugation and ameliorate intermolecular

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packing, ultimately obtaining good device efficiency.^[29,31]

Dithienobenzotriazole (DTBTz), as a weak electron-withdrawing unit, was initially used in dye-sensitized solar cells. Despite potential of DTBTz unit in photovoltaics, so far, there are few studies and reports in the area of organic solar cells. Yang *et al.* copolymerized DTBTz unit with BDT unit to obtain polymer donor PY1, finally obtained excellent hole mobility and photovoltaic parameters.^[32] Afterward, our group connected thiophene π -bridges on both sides of DTBTz unit and adjusted alkyl chain length on the triazole to synthesize polymer donor pBDT-DTBTz-Me, which achieved higher device efficiency than control device.^[33] In addition, we also applied DTBTz unit to preparation of FRAs and obtained dodeca-fused aromatic ring acceptors MS-4F and MS-4Cl. The corresponding devices achieved PCE close to 12% and good single-carrier mobility.^[34] The large rigid conjugated plane of DTBTz unit is crucial for enhancing molecular stacking and maintaining high charge mobility. In addition, the active site on N-2 position of its triazole unit provides possibility to modify chemical structure, adjust material properties and optimize morphology of blend film. Therefore, the materials based on DTBTz unit still have huge room for exploration in photovoltaic field.

In this work, we designed and synthesized three A-D-C-D-A type UFAs with DTBTz unit as central core, named DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl, respectively. Here, A-D-C-D-A stands for the configuration of Acceptor-Donor-Central core-Donor-Acceptor. The D unit in small molecules is 4,4-bis(2-butyloctyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen, which acts as an excellent electron donating unit with

branched alkyl chain to effectively ensure solubility of small molecules. After modulation of the alkyl chain on DTBTz unit and change of the halogen atoms on end groups of cyanoindanone, the differences in optoelectronic properties of these three UFAs were investigated. Experimental results show that Cl substitution is better than F substitution in intramolecular electron delocalization, and short alkyl chain substitution is better than long alkyl chain substitution in optimization of blend film morphology. When polymer donor PBDB-T were blended with these UFAs, the OSC based on DTBTzMe-IC2Cl achieves the best PCE of 12.3%, V_{OC} of 0.82 V, J_{SC} of 20.50 mA·cm⁻² and FF of 73.2%, which is greater than the devices based on DTBTzEH-IC2F and DTBTzMe-IC2F. These results show that the introduction of a rigid aromatic ring as an intermediate core not only effectively results in highly planar A-D-C-D-A small molecules, but also provides a new reference for the design and development of UFAs in OSCs.

EXPERIMENTAL

Experimental section is applied in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Characterization of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl

The molecular structures of DTBTzEH-IC2F, DTBTzMe-IC2F, DTBTzMe-IC2Cl and PBDB-T can be found in Figs. 1(a) and 1(b).

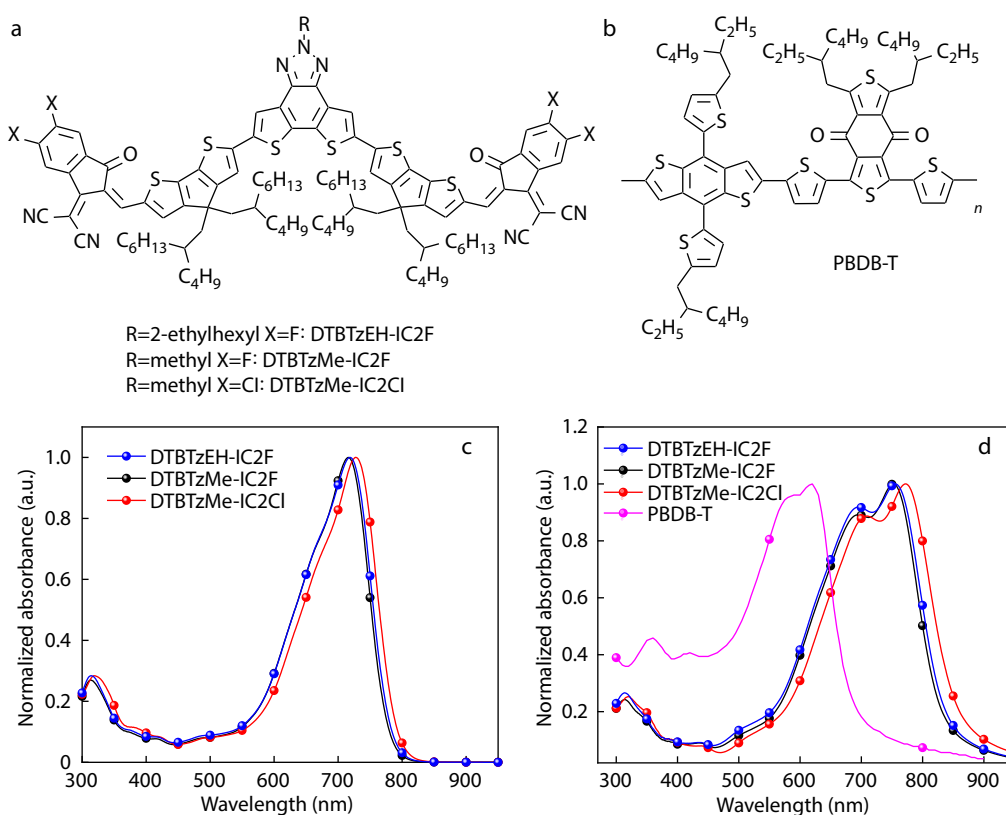


Fig. 1 The chemical structures of (a) target acceptors and (b) PBDB-T; UV-Vis absorption spectra of (c) target acceptors in solutions and (d) target acceptors and PBDB-T in films.

Detailed synthesis procedures and characterization methods are shown in ESI. The chemical structures of corresponding compounds were characterized by nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) as shown in Figs. S1–S12 (in ESI). The three UFAs exhibit good thermal stability in thermogravimetric analysis (TGA) measurement. The corresponding decomposition temperatures are 352, 358 and 356 °C for DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl when the mass loss is 5%. (Fig. S13 in ESI). In addition, DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl show good solubility in common solvents, such as chloroform (CF) and chlorobenzene (CB), ensuring their solution processability.

Density functional theory (DFT) calculations were carried out at B3LYP/6-31G (D, P) level with Gaussian 09 program to study molecular geometry and frontier orbital energy levels. For the sake of simplifying calculation, all long alkyl chains were replaced by methyl as shown in Fig. S14 (in ESI). For fluorine-substituted UFA, dihedral angles of cyanoindanone-cyclopentylthiophene and cyclopentylthiophene-DTBTz units (from left to right: θ_1 , θ_2 , θ_3 and θ_4) are 0°, 3.6°, 4.0° and 0° respectively, which are the same as chlorine-substituted UFA. These results demonstrate that these acceptors with whether Cl substitution or F substitution has a nearly planar and linear configuration, which can promote intermolecular packing and enhance carrier transport.^[35] Furthermore, the highest occupied molecular orbitals (HOMOs) are mostly distributed on conjugated electron-rich nuclei, and the lowest unoccupied molecular orbitals (LUMOs) are delocalized on π -conjugated system of molecules. Calculated LUMO/HOMO energy

levels of F substitution and Cl substitution are $-3.76/-5.64$ and $-3.77/-5.64$ eV respectively.

The optical absorption of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl in chloroform solutions, pure films and blend films were measured by UV-Vis absorption spectra (as shown in Figs. 1c and 1d and Fig. S15 in ESI). Relevant optical parameters are summarized in Table S1 (in ESI). Acceptors in solutions have strong absorption band in the range of 600–800 nm, the absorption peaks of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl are 718, 716 and 727 nm, respectively. Compared with DTBTzEH-IC2F and DTBTzMe-IC2F, DTBTzMe-IC2Cl shows an obvious red shift. This may be related to the stronger intramolecular electron delocalization in DTBTzMe-IC2Cl.^[36] The similar absorption curves of DTBTzEH-IC2F and DTBTzMe-IC2F show that change of alkyl chain in DTBTz unit has no obvious effect on its absorption. The molar extinction coefficient of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl are 2.30×10^5 , 2.39×10^5 and 2.48×10^5 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, respectively. Compared with that in solutions, absorption spectra of the three acceptors in pure films are significantly red-shifted by 38, 36 and 46 nm, respectively, indicating that the existence of intermolecular aggregation in film state.^[37] The calculated optical bandgaps (E_g^{opt}) of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl from the film absorption onsets are 1.47, 1.47 and 1.44 eV, respectively.

The HOMO and LUMO energy levels of the three acceptors were evaluated by electrochemical cyclic voltammetry (CV) method (Fig. 2a). Energy level diagrams can be found in Fig. 2(b). Using the Fc/Fc^+ redox couple of 0.37 eV calibrated on-

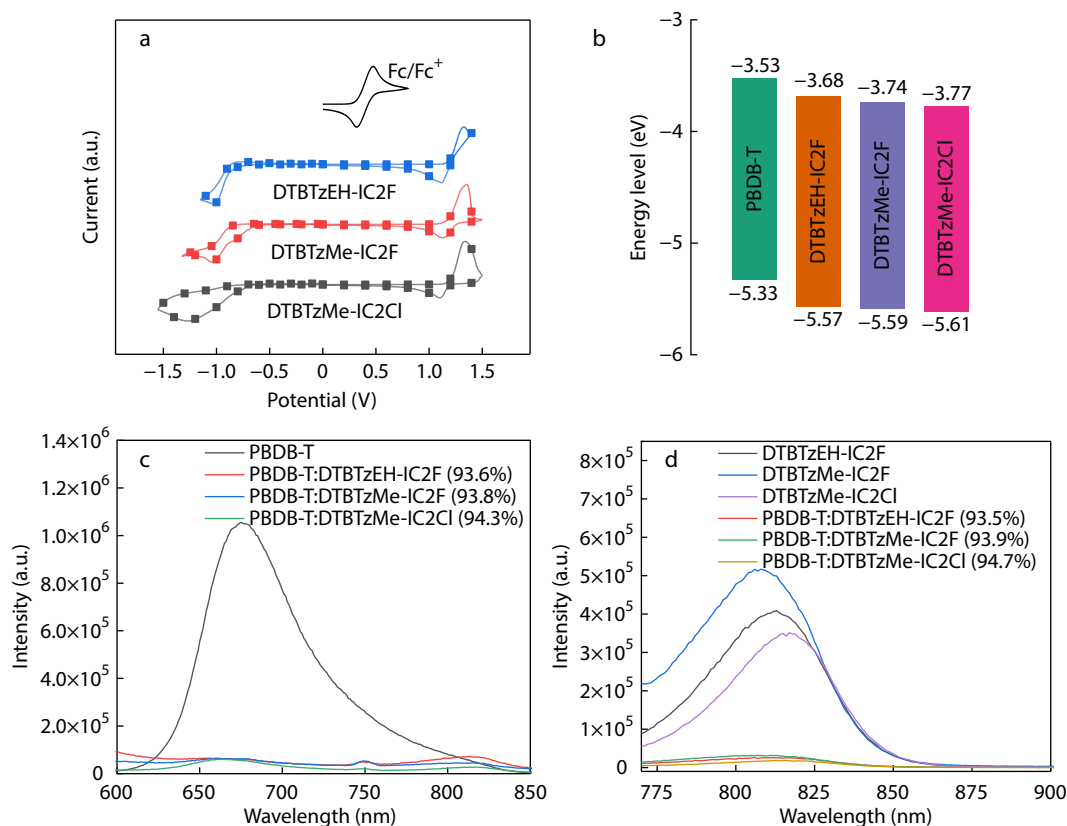


Fig. 2 (a) Cyclic voltammograms for target acceptors; (b) Energy level diagrams of PBDB-T and target acceptors; Photoluminescence spectra of (c) PBDB-T pure film and blend films excited at 500 nm and (d) target acceptors pure films and blend films excited at 750 nm.

Table 1 Photovoltaic parameters of the optimal OSCs.

Devices	V_{OC} (V)	J_{SC} (mA·cm ⁻²)	Cal. J_{SC} (mA·cm ⁻²)	FF (%)	PCE _{max} (%)	PCE ^a (%)
PBDB-T:DTBTzEH-IC2F	0.87	18.75	18.57	70.5	11.5	11.35±0.13
PBDB-T:DTBTzMe-IC2F	0.83	19.52	18.94	73.9	12.0	11.72±0.14
PBDB-T:DTBTzMe-IC2Cl	0.82	20.50	19.80	73.2	12.3	12.07±0.12

^a Average of 20 devices.

set oxidation and reduction potentials. The HOMO energy levels of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl are estimated to be −5.57, −5.59 and −5.61 eV, respectively. The LUMO energy levels are estimated to be −3.68, −3.74 and −3.77 eV, respectively (Table S1 in ESI). Energy levels trend is consistent with DFT calculation results.

Before photovoltaic performances test, charge-transfer efficiencies between these acceptors and selected polymer donor PBDB-T were tested by photoluminescence (PL) spectra. As shown in Figs. 2(c) and 2(d), the lights with wavelength of 500 and 750 nm were used to selectively excite donor and acceptors, respectively. It can be found that in blend films, D/A quenching among DTBTzEH-IC2F-, DTBTzMe-IC2F- and DTBTzMe-IC2Cl-based devices are all efficient, giving D/A quenching efficiencies of 93.6%/93.5%, 93.8%/93.9% and 94.3%/94.7%, respectively.

Photovoltaic Performances of OSCs

In order to study photovoltaic properties of the three acceptor materials, OSCs with structure of ITO/PEDOT:PSS/PBDB-T:Acceptors/PFN-Br/Ag were prepared. The other experimental details can be found in ESI. Device optimization was performed in detail as shown in Tables S2–S4 (in ESI), including donor/acceptor weight ratio (D/A), thermal annealing and solvent additive. The corresponding optimal device data can be found in Table 1. Current density-voltage (J - V) plots are shown in Fig. 3(a). When DTBTzEH-IC2F with long chain and F substitution is used as acceptor, the best device based on that achieves a J_{SC} of 18.75 mA·cm⁻², a V_{OC} of 0.87 V, an FF of 70.5%, so a PCE of 11.5%. When methyl- and F-substituted DTBTzMe-IC2F is used, the best device achieves a PCE of 12.0%, with a J_{SC} of 19.52 mA·cm⁻², V_{OC} of 0.83 V, FF of 73.9%. When methyl- and Cl- substituted in the side chain, the device based on PBDB-T:DTBTzMe-IC2Cl achieves the best of PCE of 12.3%, with a J_{SC} of 20.50 mA·cm⁻², a V_{OC} of 0.82 V and an FF of 73.2%. Furthermore, to confirm the accuracy of J_{SC} , external quantum efficiency (EQE) measurement was then performed (Fig. 3b). We find that devices based on DTBTzEH-IC2F and DTBTzMe-IC2F have similar light response range from 300 nm to 850 nm, while device based on DTBTzMe-IC2Cl has a broader light response range from 300 nm to 870 nm. DTBTzEH-IC2F-, DTBTzMe-IC2F- and DTBTzMe-IC2Cl-based devices demonstrate EQE response over 70% in the wavelength regions of 560–760 nm, 560–780 nm and 550–790 nm, respectively. Higher and broader optical response of DTBTzMe-IC2Cl-based OSC results in a high integrated current density to 19.80 mA·cm⁻², while the OSCs based on DTBTzEH-IC2F and DTBTzMe-IC2F show lower values of 18.57 and 18.94 mA·cm⁻², respectively. Comprehensive J_{SC} values from EQE spectra are listed in Table 1. Compared to the J_{SC} values obtained from J - V curves, these J_{SC} values agree well with J - V measurement with mismatch within 5%.

Charge Transport, Extraction, and Recombination in OSCs

To understand charge transport properties of blend films,

space-charge-limited current (SCLC) method was used to evaluating mobilities (μ_h and μ_e) of devices prepared under optimal conditions. We applied structure of ITO/PEDOT:PSS/PBDB-T:Acceptors/MoO₃/Ag for hole-only devices and structure of ITO/ZnO/PBDB-T:Acceptors/PFN-Br/Ag for electron-only devices. As can be seen from $J^{1/2}$ - V curves and related data (Fig. S16 and Table S5 in ESI), PBDB-T:DTBTzEH-IC2F blend film exhibits a μ_h of 2.83×10^{-4} cm²·V⁻¹·s⁻¹ and a μ_e of 1.66×10^{-4} cm²·V⁻¹·s⁻¹, PBDB-T:DTBTzMe-IC2F film exhibits a μ_h of 2.73×10^{-4} cm²·V⁻¹·s⁻¹ and a μ_e of 2.39×10^{-4} cm²·V⁻¹·s⁻¹, PBDB-T:DTBTzMe-IC2Cl film exhibits a μ_h of 2.57×10^{-4} cm²·V⁻¹·s⁻¹ and a μ_e of 2.50×10^{-4} cm²·V⁻¹·s⁻¹. Therefore, compared with PBDB-T:DTBTzEH-IC2F film ($\mu_h/\mu_e=1.70$), PBDB-T:DTBTzMe-IC2F film ($\mu_h/\mu_e=1.14$) and PBDB-T:DTBTzMe-IC2Cl film ($\mu_h/\mu_e=1.03$) show more balanced charge carrier transport. The varied electron mobilities in these devices should be mainly ascribed to molecular packing properties as demonstrated in morphology study (will be discussed later). Balanced values of μ_h and μ_e are beneficial to inhibit accumulation and recombination of charge.^[38]

In order to study charge extraction efficiencies of these three devices, the dependence of photocurrent density (J_{ph}) on effective voltage (V_{eff}) was tested. Here, J_{ph} is defined as $J_{ph} = J_{Light} - J_{Dark}$, where J_{Light} and J_{Dark} are the current densities under light and dark conditions, respectively. V_{eff} is defined as $V_{eff} = V_0 - V_{Bias}$, where V_0 is the voltage at which J_{ph} is zero and V_{bias} is the applied voltage bias. Relevant calculation parameters are listed in Table S6 (in ESI), and J_{ph} versus V_{eff} curves are shown in Fig. S17 (in ESI). It can be observed that when V_{eff} is higher than 1 V, J_{ph} becomes saturated (J_{sat}), and all photogenerated excitons are dissociated into free charge carriers and collected by the corresponding electrodes.^[39] The maximum exciton generation rate (G_{max}) can be estimated as $G_{max} = J_{sat}/qL$, where q is the elementary charge and L is the thickness of active layer.^[40] Increasing trend of G_{max} from PBDB-T:DTBTzEH-IC2F to PBDB-T:DTBTzMe-IC2F and then to PBDB-T:DTBTzMe-IC2Cl is 1.22×10^{27} , 1.24×10^{27} and 1.32×10^{27} m⁻³·s⁻¹, respectively. In addition, the P(E, T) ($P(E, T) = J_{ph}/J_{sat}$) charge dissociation probability values of these three devices under short-circuit condition are 95.86%, 97.34% and 97.65%, respectively. The results of P(E, T) show that compared with DTBTzEH-IC2F, the devices based on DTBTzMe-IC2F and DTBTzMe-IC2Cl have more efficient charge generation and separation process.

Charge recombination process of different devices was studied by measuring the characteristics of J_{SC} versus light intensity (P_{light}) and V_{OC} versus P_{light} . In general, the relationship between J_{SC} and P_{light} should follow a power-law relationship, namely $J_{SC} \propto P_{light}^a$. If a equals to 1, which means that bimolecular recombination is very weak.^[41] Results are plotted in Fig. 3(c). The a values of the devices based on DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl are 0.98, 0.99 and

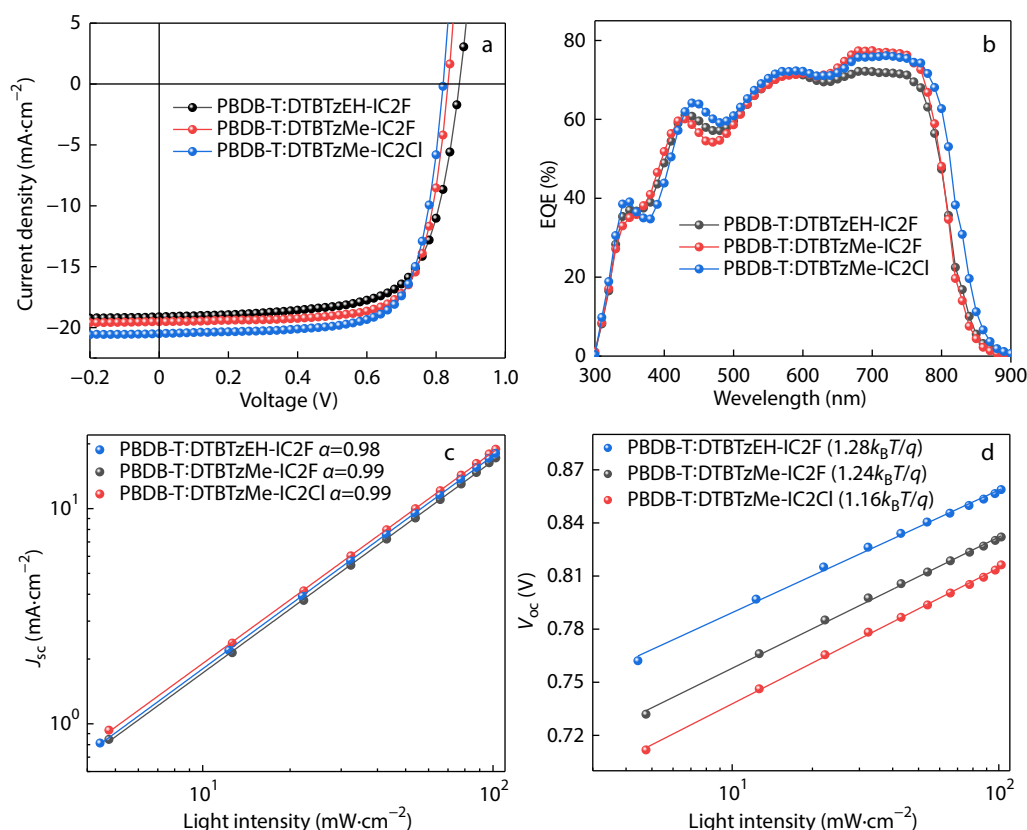


Fig. 3 (a) J - V and (b) EQE curves of corresponding OSCs; (c) J_{sc} and (d) V_{oc} versus light intensity characteristics of corresponding OSCs.

0.99, respectively, which demonstrate weak bimolecular recombination in three types of OSCs. And the slightly higher α values of devices based on DTBTzMe-IC2F and DTBTzMe-IC2Cl ensure better J_{sc} . Properties of V_{oc} versus $\ln(P_{light})$ are plotted in Fig. 3(d). Slope of the curves is fitted linearly to $nk_B T/q$, where n is between 1 and 2 (where k_B is the Boltzmann constant, q is the elementary charge, and T is the temperature).^[42] Value of $n=1$ indicates that bimolecular recombination dominates, and $n=2$ means more monomolecular or trap-assisted recombination. It can be observed that slope of the curves is gradually decreasing from PBDB-T:DTBTzEH-IC2F to PBDB-T:DTBTzMe-IC2F and then to PBDB-T:DTBTzMe-IC2Cl. Corresponding data are $1.28k_B T/q$, $1.24k_B T/q$ and $1.16k_B T/q$ respectively, implying monomolecular or trap-assisted recombination is reduced in PBDB-T:DTBTzMe-IC2Cl, matching well with its excellent performance.

Morphologies of the Blended Films

To study the morphology of blend films, atomic force microscopy (AFM) measurement was performed (Fig. S18 in ESI). As shown in AFM height images, all three blend films exhibit uniform and smooth surface morphology. Roughness values of the three blend films are relatively small and similar, among PBDB-T:DTBTzEH-IC2F, PBDB-T:DTBTzMe-IC2F and PBDB-T:DTBTzMe-IC2Cl blend films are 1.65, 1.77 and 1.30 nm, respectively, demonstrating proper phase separation.

Through grazing-incidence wide-angle X-ray scattering (GIWAXS), we further understand molecular orientation and crystallinity characteristics of blend films. As shown in Fig. 4,

corresponding two-dimensional diffraction patterns and one-dimensional integral curves are displayed. It can be seen that diffraction pattern of the blend film based on PBDB-T:DTBTzEH-IC2F shows (100) diffraction peak at $\sim 0.39 \text{ \AA}^{-1}$ in the out-of-plane (OOP) direction which stronger than the other two blend films, implying edge-on orientation in corresponding blend film. Blend film based on PBDB-T:DTBTzMe-IC2F shows weak face-on orientation, demonstrated by the weak (010) π - π stacking peak at $\sim 1.60 \text{ \AA}^{-1}$ in the OOP direction. According to Bragg equation, the π - π stacking distance is 3.92 $\text{\AA}$. And according to Scherrer equation, the crystal coherence length (CCL) is 17.35 $\text{\AA}$.^[43] The strong π - π stacking (010) peak $\sim 1.68 \text{ \AA}^{-1}$ appearing at the OOP direction indicates blend film based on PBDB-T:DTBTzMe-IC2Cl has face-on orientation, which is obviously stronger than the former two. The π - π stacking distance is calculated to be 3.74 $\text{\AA}$. The smaller stacking distance indicates that molecules are packed more tightly, and the stronger π orbital overlap will be beneficial to charge transfer.^[44] In addition, the CCL of PBDB-T:DTBTzMe-IC2Cl blend film is 28.69 $\text{\AA}$, which indicates that this blend film has strong crystallinity. That is helpful to improve charge transport characteristics of the device.^[45]

Stability of OSCs

Photostability of three devices was characterized. The devices were encapsulated with epoxy glue and illuminated under a white light emitting diodes array. Evolution of PCE during continuous illumination is shown in Fig. S19(a) (in ESI). After more than 1200 h of continuous illumination, the devices based on PBDB-T:DTBTzEH-IC2F, PBDB-T:DTBTzMe-IC2F and PBDB-

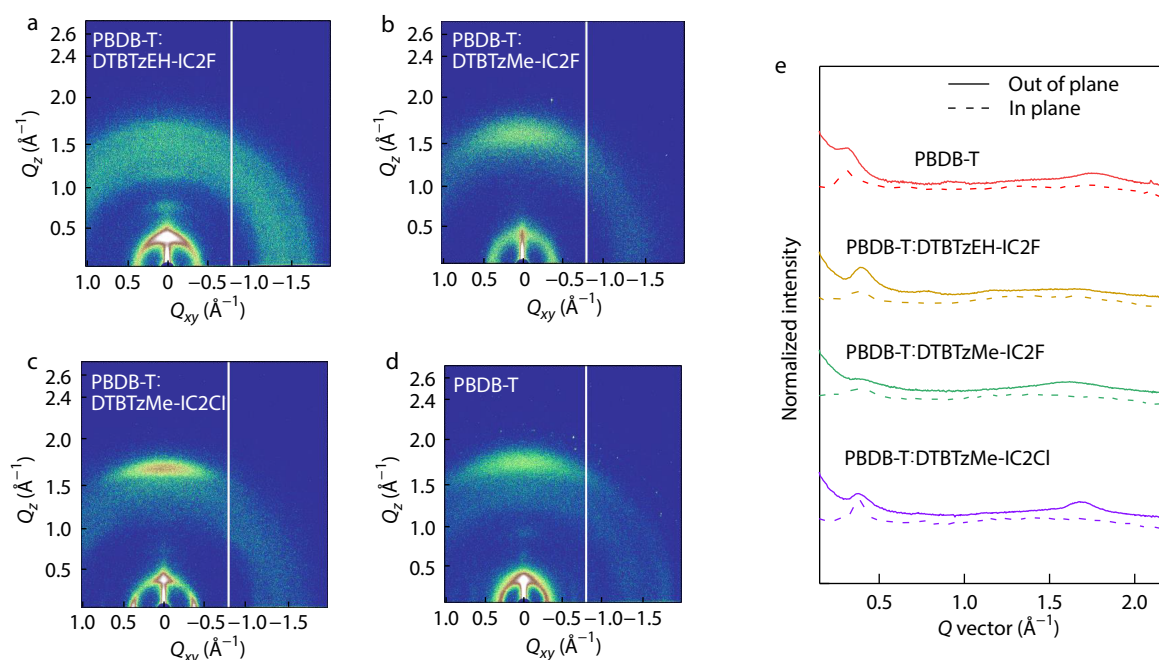


Fig. 4 (a–d) 2D GIWAXS diffraction patterns of corresponding films; (e) Intensity profiles of corresponding films along in-plane (dotted line) and out-of-plane (solid line) directions.

T:DTBTzMe-IC2Cl maintain around 60% of the initial efficiency. In terms of storing in nitrogen atmosphere more than 1000 h, the efficiency retention rates are all above 90%, indicating that the devices prepared based on these three UFAs have good storage stability. Relative plot can be found in Fig. S19(b) (in ESI). Moreover, when annealed at 85 °C for more than 100 h, the efficiency of all devices remains over 60% of their original efficiencies (Fig. S19c in ESI).

CONCLUSIONS

In this work, we designed and synthesized three small molecule unfused-ring acceptors, named DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl, by changing length of alkyl chain on DTBTz unit and halogen-substitution atoms of cyanoindene terminal groups. The three acceptors exhibit strong and broad light absorption between 600–850 nm in thin film state due to strong intramolecular charge transfer effect favored by DTBTz core. When DTBTzMe-IC2Cl is paired with polymer donor PBDB-T to prepare organic solar cell, the optimized device achieves the best PCE of 12.3%, with J_{sc} of 20.50 mA·cm⁻², V_{oc} of 0.82 V and FF of 73.2%. DTBTzEH-IC2F-based device obtains 11.5% efficiency, and DTBTzMe-IC2F-based device obtains 12.0% efficiency. More in-deep researches show that Cl substitution is better than F substitution in intramolecular electron delocalization, and short alkyl chain substitution is better than long alkyl chain substitution in optimization of blend film morphology. The photostability, storage stability and thermal stability of three devices were also tested. After more than 1200 h of continuous illumination, the efficiency retention rates of DTBTzEH-IC2F, DTBTzMe-IC2F and DTBTzMe-IC2Cl are around 60%. After being stored for more than 1000 h in nitrogen atmosphere, the efficiency retention rates are all above 90%. After being annealed at 85 °C for more than 100 hours, the

efficiency retention rates are all over 60%.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2825-y>.

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