

Full paper

High efficiency small molecular acceptors based on novel O-functionalized ladder-type dipyran building block

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ABSTRACT

Molecular electronic structure plays a vital role in the photovoltaic performances in nonfullerene polymer solar cells (PSCs) due to their influences on light-harvesting, charge carrier transfer, π - π stacking and morphology tuning etc. Oxygen as an electron donating atom, which has been incorporated into the nonfullerene acceptors (NFAs) system in the alkoxy forms at central, terminal or π bridged moieties, could effectively tune the electron donating ability, absorption spectra, energy levels of the highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO) etc. In this contribution, a novel centrosymmetric pyran based ladder-typed conjugated building block (**DTDP**) has been designed and synthesized via a facile route and it was applied as the donor (D) core in acceptor-donor-acceptor (A-D-A) type NFAs design to evaluate its potential usage in polymer solar cells. This incorporated-O in the conjugated backbones effectively elevated the electron donating ability for the D moiety and wide absorption behaviors are observed. Although slight bent appears at the central part of the **DTDP** block from the geometry quantum optimization, strong crystallinity are found for both molecules. Photovoltaic performances of the solar cell devices are systematically investigated with poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)-co-(1,3-bis(5-thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione)] (PBDB-T) as the polymer donor and a high power conversion efficiency (PCE) of 9.39% (V_{oc} = 0.80 V, J_{sc} = 16.82 mA/cm² and FF = 69.95%) could be afforded by **DTDP-MIC** after the preliminary optimization, demonstrating the great promise in PSCs. Meanwhile, the morphologies as well as the carrier mobilities of the blend films are gleaned to assist understanding the structure-property relationships. Overall, the study in this work not only provides a promise ladder-typed dipyran donor unit for NFAs PSCs, it also paves a new way to use oxygens in small molecule NFAs design.

1. Introduction

Polymer solar cells (PSCs) based on the bulk heterojunction (BHJ) of a conjugated polymer electron donor and an electron acceptor have attracted considerable attention in the past decades due to the relatively high efficiency, easy fabrication, low cost roll-to-roll process, and light weight. Very recently, PSCs based on fused nonfullerene acceptors (NFAs), have aroused intensive interests because of tunable energy levels, adjustable light absorption and regulated solid aggregation properties induced by the synthetic flexibility etc. [1–7]. 3,9-Bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d'*]-s-indaceno[1,2-*b*:5,6-*b'*]-

dithiophene (ITIC) as one of the star NFAs was firstly reported by Zhan et al. [8] and compatible power conversion efficiencies (PCEs) have been achieved in comparison with the fullerene based cells. Thus, various chemical modification methods have been applied on indaceno [1,2-*b*:5,6-*b'*]dithiophene (IDT) skeleton by extending the conjugation length [5,9], changing the substituted side chains [7,10,11], altering the bridging units [12] etc. In addition, attaching different 1,1-dicyanomethylene-3-indanone (IC) derivatives as the end-capping electron deficient units is another well utilized molecular design strategy and a variety of high efficiency NFAs have been produced [6,13]. Up to now, impressive PCEs have been achieved over 13% for single junction PSCs for these IC based NFAs PSCs [14].

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As known, complementary absorptions between donor and acceptor components, matched energy levels, balanced charge mobilities and favorable morphology are the key factors to realize high efficient PSCs. Among these encouraging results, it's obvious that the molecular engineering plays a vital role in the photovoltaic performance enhancement [5,6,10,12,15–17] and considerable efforts on the molecular design still need to be conducted. Generally, matched energy levels is the prerequisite for efficient charge separation with minimized energy loss (E_{loss} , defined as $E_{\text{gap}} - eV_{\text{oc}}$) [18,19], and E_{gap} of the low-band gap acceptor should be ideally reduced by elevating the HOMO level without sacrificing the energy gap between the HOMO level of the donor (HOMO_D) and the LUMO level of acceptor (LUMO_A). Meanwhile, a sufficient driving force for exciton dissociation, which is correlated with the HOMO levels of the donor and acceptor, should be kept at an appropriate level so as to minimize energy loss. In short, to achieve efficient NFAs in PSCs, it is crucial important to take the relationship between energy level tuning tendency and structures into account. Oxygen as an electron donating atom could effectively tune the electron donating ability, absorption spectra, HOMO & LUMO energy levels etc [11,20–23]. After comprehensive analysis of the current reports on the small-molecule NFAs, there are mainly three reported ways to utilize the oxygen atoms: **i)** modified lateral alkoxy chains at the π bridge blocks (Type-I) [11,20] (Chart 1), which may form planar conjugated structures via the supramolecular interaction locks according to the literature [20] and increase the NFAs' HOMO energy level without sacrificing the energy gap between HOMO_D and LUMO_A [11] as well; **ii)** introduction as lateral alkoxy chains at the central electron donating skeletons (Type-II) [21], which is conceived similar to the first way, i.e. enhance the electron donating ability and further reduce E_g by raising the HOMO level without sacrificing V_{oc} ; **iii)** introduction at the terminal electron deficient units (Type-III) [22,23], whose properties will be influenced by the O-functionalized positions and the alkoxy chain types. In summary, the oxygen modification methods are mainly about lateral or ending direction modification. They are not only good at assisting solubility and locking planar structure conformation, but also very effective at tuning HOMO energy levels and reducing E_g . However,

it's rare to see oxygen functionalized conjugated backbones in NFAs, not to mention the larger fused heterocyclic π -system containing oxygen atoms.

Pyran is a six-membered heterocyclic ring, featuring one oxygen atom and one saturated sp^3 -hybridized carbon atom, and has been widely used in dye-sensitized solar cells [24], fluorescence probe [25], nonlinear optical chromophores [26], organic light-emitting diode [27], ion detection [28], protein phototrigger [29], super-resolution imaging [30] etc. Very recently, Yang [31] and our group [32,33] have successfully developed the asymmetric pyran based building blocks with three fused rings i.e. dithienopyran (DTP) and dibenzopyran (DBP), respectively. The corresponding D-A polymer donors based on these pyran building blocks achieved excellent PCEs in polymer solar cells with single junction, which demonstrated that oxygen could not only serve as the molecular energy level adjusting and the electron donating roles, but also plays a part in solubility tuning via slightly reducing the rigidity of the skeleton in virtue of formation of flexible structures [34]. In addition, the intermolecular interactions for the resulting materials could be tuned via the incorporation of oxygen atoms and remarkable face-to-face π - π stacking could be formed, which is a favorable arrangement for organic electronics [35]. Whereas, the exploration of O-functionalized ladder-type molecule remains rare, although the intrinsic characteristics endow the pyran moiety great promise for the construction of advanced functional materials.

In this manuscript, a novel O-functionalized ladder-type dipyrans building block (DTDP) is designed, which is the combination of the DTP and DBP segments. Based on the previous discussion, it would be interesting to evaluate its potential usage as NFAs in PSCs, so two IC end-capped small molecule acceptors are designed based on the following considerations: **i)** introduction of the oxygen atoms into the conjugated backbones to broaden the absorption spectra and study the regulating effect on energy levels; **ii)** selection of octyl chains as the lateral modification so as to reduce the steric hindrance at lateral direction and increase molecular stacking aiming at higher charge mobility [36]; **iii)** comparative study of the compatibility with two different and widely used terminal IC units to provide a brief evaluation of

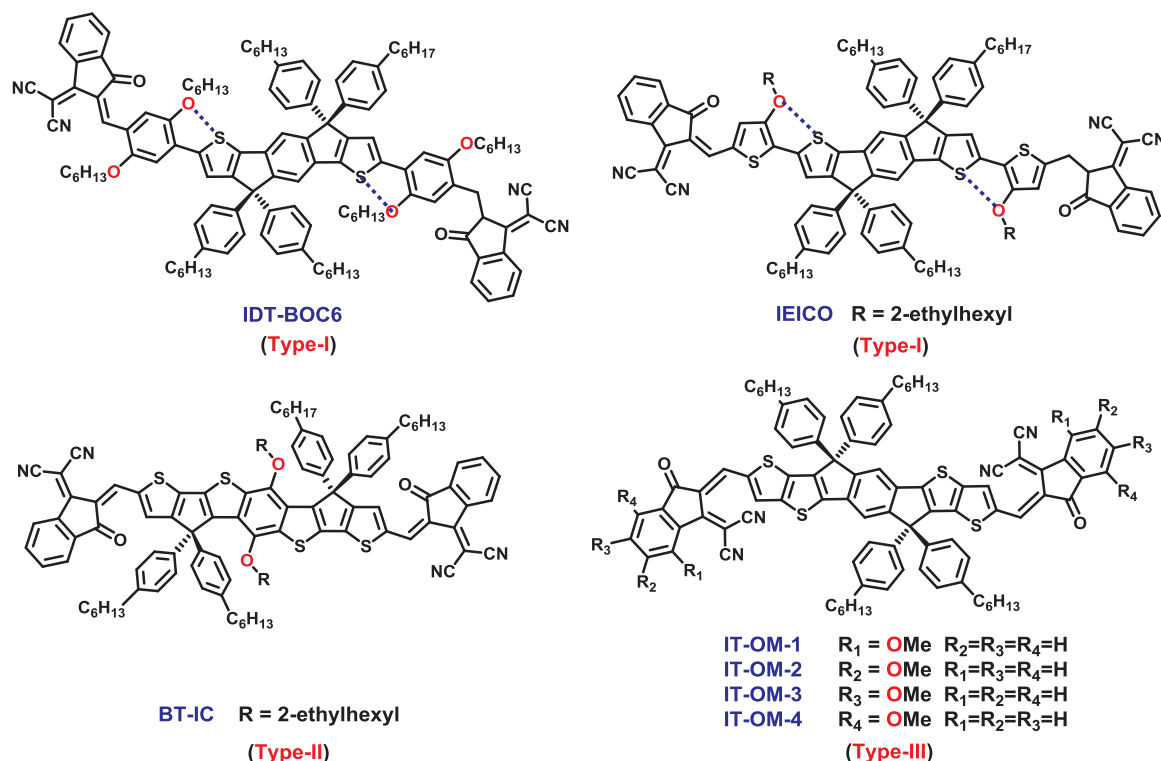


Chart 1. Examples for different ways of oxygen utilization in NFAs design.

this new donor segment.

Benefiting from the two incorporated oxygen atoms in **DTDP** units, the electron donating ability of the ladder core is elevated as expected and these **DTDP** based NFAs (**DTDP-IC** & **DTDP-MIC**) displayed broad and extended UV–vis absorption to 850 nm. The E_g are reduced to 1.4–1.5 eV and HOMO energy levels are enhanced without interference the LUMO energy levels (~ -3.95 eV) in comparison to the similar IDIC (LUMO of -3.91 eV) [17], which doesn't possess the incorporated oxygens. In addition, the theoretical calculation to predict the conformational properties has been systematically studied; the slight flexible configuration of the C–O moiety at the central **DTDP** core and the alkyl side chains in **DTDP** guarantee the good solubility for the final NFAs. Finally, with **PBDB-T** as the polymer donor, $PCEs$ of 8.88% and 9.39% are achieved for **DTDP-IC** and **DTDP-MIC**, respectively, which is the first example to put pyran unit in NFAs application. To this end, all results indicated that this new ladder-typed dipyrans building block is of great promise in NFAs design and more dipyrans derivatives could be prepared via the facile synthesis method, which will pave the new way to use oxygens in NFAs design. In addition, the E_{loss} for these **DTDP-IC** and **DTDP-MIC** are 0.73 and 0.75 eV, which is still relatively large compared to some other highly efficient blend systems [11], indicating there is still room for further enhancement of photovoltaic performance via energy level compatibility study.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes for the NFAs based on this novel ladder-type pyran-based block (**DTDP**) are depicted in Scheme 1. Starting from the crucial important ladder-type lactone (**1**), the four hydroxyl precursor (**2**) could be obtained when attacked by the octylmagnesium bromide in a yield of 46%. Through the subsequent dehydration reaction catalyzed under *p*-toluene sulfonic acid (PTSA), two pyran rings could be formed and the target **DTDP** molecule could be obtained in a yield of 90%. Finally, via bromination reaction of the **DTDP** in the presence of NBS, the dibromide monomer for **DTDP-Br** is generated as yellow solids. Through the Br/Li exchange reaction in the presence of *n*-BuLi, the **DTDP-CHO** could be afforded in a yield of 45% after quenching with DMF. Finally, the targeted A–D–A type molecules could be synthesized via the Knoevenagel condensation with the terminal electron deficient units (**IC** or **MIC**) in yields of 88% and 91%, respectively for **DTDP-IC** and **DTDP-MIC**. However, since the methyl substituted **MIC** block is composed of two isomers (methyl substituted at 5-position or 6-position) [6], there are three combinations for the terminal capping, resulting in three isomers of **DTDP-MIC**, which cannot be separated due

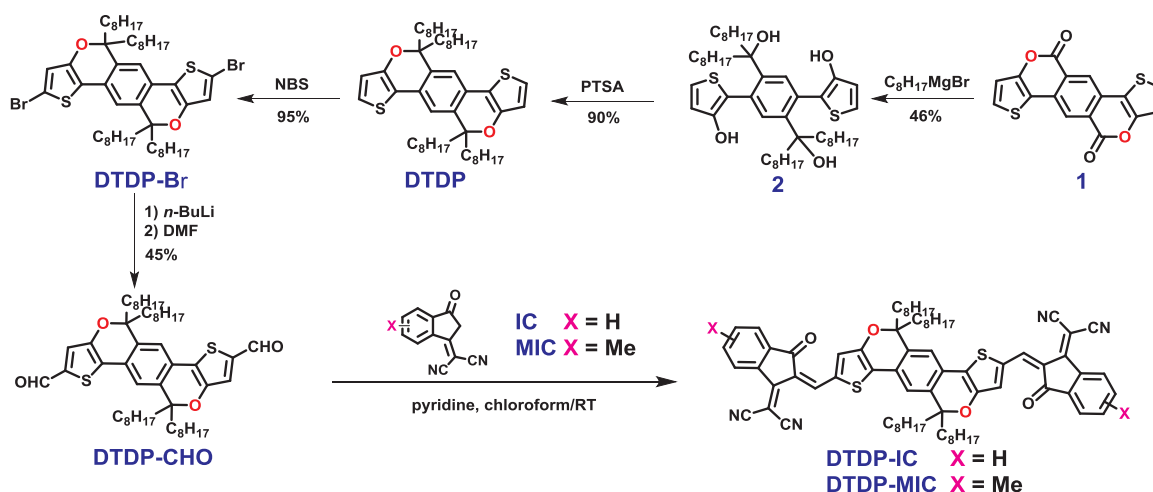
to the too similar chemical structures. The chemical structures of all new compounds are fully characterized by 1H NMR, ^{13}C NMR, and HRMS.

2.2. Considerations for chemical structures by quantum calculations

Considering the potential usage of the novel **DTDP** moiety for high efficiency NFAs in organic photovoltaics, DFT calculation is first carried out at the B3LYP/6–31 G (d,p) level on the Gaussian 09 package to evaluate the optimal geometric configurations for the two **DTDP** molecules as shown in Fig. 1, in which the long alkyl chains are replaced by methyl ones to simplify the calculation. Due to the rigid aromatic structures of the ladder **DTDP** acceptors and positional isomerization of the methyl group at **MIC** unit, there are three types of rotamers in these two **DTDP** molecules. Relaxed potential energy scans (PES) for conformational preference of these segments have been studied (Fig. 1a and b) and the results indicate that the preferential configurations for all rotamers are similar with $\sim 0^\circ$ for φ and will not be influenced by the substituted methyl group or its positions. Based on the PES results, the geometric optimization for the **DTDP** molecules have been set up and the optimum backbones are as shown in Fig. 1c. All of the three isomers for **DTDP-MIC** have been studied, but only one example is depicted here to make a simple comparison and the results for the other two isomers are listed in supporting information (Fig. S20). Clearly, both **DTDP** molecules present nearly flat conformations and planar wings are formed by the thiophene segments and **IC** groups (Fig. 1d and e), which may facilitate the close mainchain packing and is preferred by charge transport, whereas slight bent are observed for the central **DTDP** segments due to flexible C–O moiety formed by the incorporated-O and the bridged sp^3 -carbon. The two **IC** arms in each molecule are paralleled with each other and the dihedral angles between the arms and the central benzene are 12.08° and 12.03° , respectively. Such flexible geometry may not hurt the molecular planarity and would achieve good solubility for the final NFAs.

2.3. Photophysical and electrochemical properties

Both **DTDP** based molecules have good solubility in common organic solvents such as chloroform and *o*-dichlorobenzene. The chloroform solutions of **DTDP-IC** and **DTDP-MIC** exhibit very similar absorption behavior (Fig. 2a) and two clear absorption bands are observed locating at 500–750 nm (Band I) and 250–450 nm (Band II), respectively. The weaker Band II at shorter wavelength may be attributed to $\pi \rightarrow \pi^*$ transitions, while the stronger absorption Band I located around longer wavelength region can be ascribed to the strong intramolecular charge transfer (ICT) interactions. In addition, clear



Scheme 1. Synthetic route for **DTDP-IC** and **DTDP-MIC**.

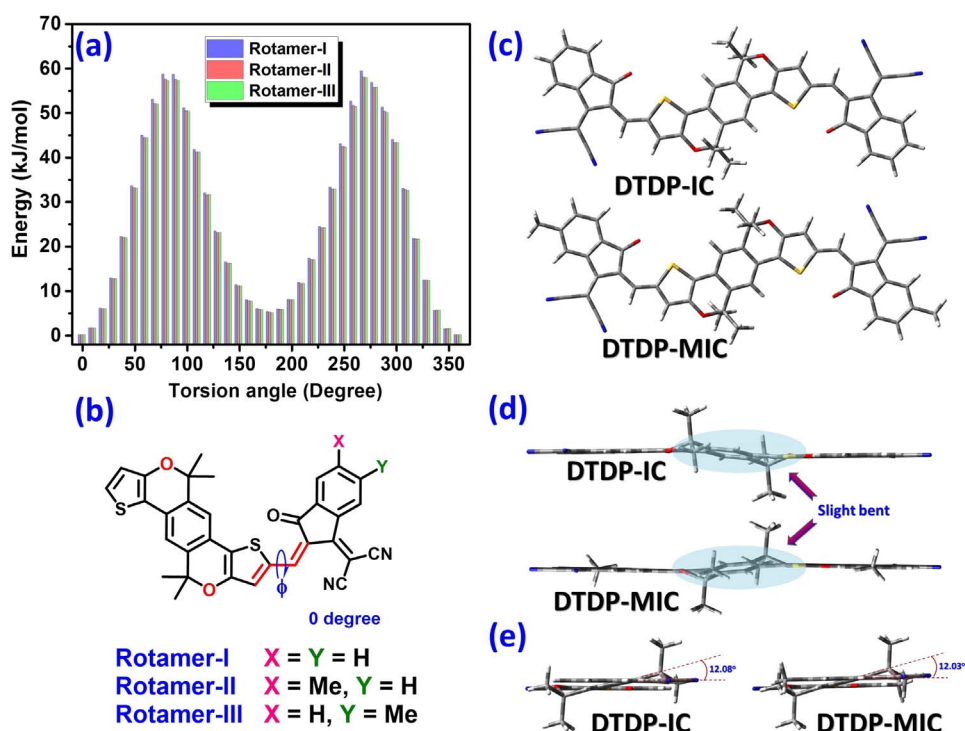


Fig. 1. (a) The total energy scan for the rotamers of the adjacent conjugated units in DTDP molecules (b) possible rotamers in the two DTDP molecules; DFT optimized conformations for the DTDP molecules: (c) top view, (d) front view and (e) side view.

shoulder peaks around 700 nm are observed for both DTDP molecules, indicating the molecular self-organization already formed in solutions. Whereas, due to the incorporation of the methyl group at the IC unit, DTDP-MIC presents very slightly blue-shifted absorption maximum and band-edge in relative to that of DTDP-IC, which may be produced by the weak electron-donating property of the methyl groups. As compared to the absorption spectra in chloroform, both DTDP molecules in thin films display remarkable red-shift (~ 50 nm) in maximum absorption and these significant bathochromic shifts in the solid state are correlating with its *J*-aggregates between the DTDP molecules. However, the absorption curves in solid state are greatly varied and DTDP-IC not only presents bathochromic absorption, it also has a broader light-harvesting region in relative to that of DTDP-MIC, which may result an elevated J_{sc} . The optical bandgaps of DTDP-IC and DTDP-MIC estimated from the absorption edge of the thin film are 1.49 and 1.55 eV, respectively (Table 1), which have been greatly reduced in comparison with the similar non-O-functionalized structure (i.e. IDIC and the E_g is of 1.78 eV) [17]. As shown in Fig. 2b, polymer PBDB-T and these DTDP based NFAs provide complementary absorption covering a wide absorption range from 450 to 850 nm, which should be desirable

for enhancing the harvest of sunlight.

To obtain further insight into the effect of molecular structure and electron distribution on the spectroscopic properties of the DTDP based molecules, quantum chemistry calculations were performed with Gaussian 09 suite by the TD-DFT/PCM approach at the 6–31 G (d,p) level to provide further insight on the transition contributions to the UV–vis spectra. As shown in Fig. S21, very similar absorption curves are obtained for both DTDP molecules in chloroform, which is in accordance with the experimental data. Due to the small structural variation, alike vertical excitation energies, oscillator strengths and transition contributions are produced and presented in Table S6. The significant absorption Band located around 600 nm is associated $S_0 \rightarrow S_1$ excitation mainly contributed by HOMO $\rightarrow$ LUMO transition. As for the Band located at the short wavelength, it is contributed by the combined excitations of $S_0 \rightarrow S_8$, $S_0 \rightarrow S_{10}$ and $S_0 \rightarrow S_{12}$ etc. related to mixed transitions as shown in Table S6.

Molecular frontier energy levels (HOMO & LUMO) are key factors to determine the compatibility for the acceptors and donors in PSCs, so the electrochemical properties of DTDP molecules are investigated by cyclic voltammetry (CV) with a standard three-electrode

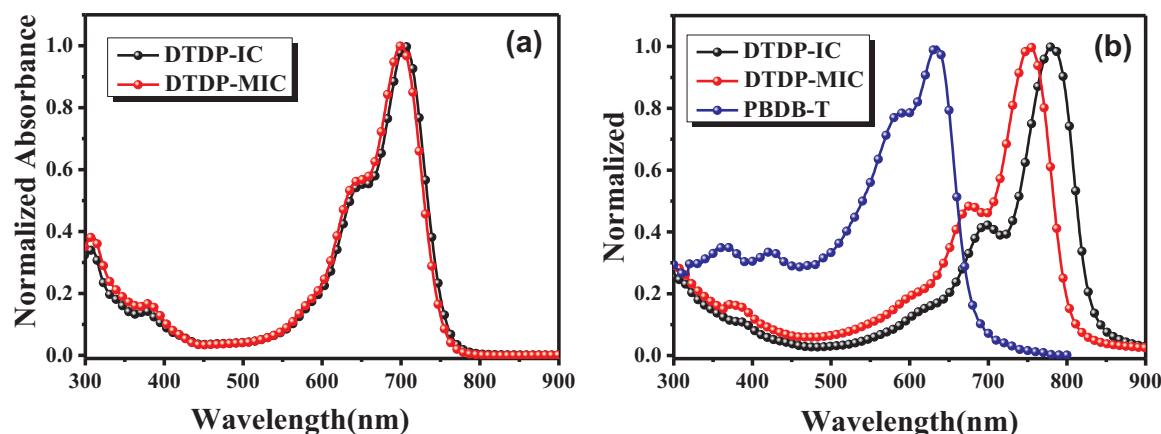


Fig. 2. Normalized UV–vis absorption spectra for the DTDP based molecules and PBDB-T polymer donor: (a) chloroform solution and (b) thin film.

Table 1
Optical and electrochemical properties of the **DTDP** molecules.

Compound	Solution		Film		HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)	E_g^{opt} (eV)
	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)				
DTDP-IC	703	758	781	833	− 5.46	− 4.03	1.43	1.49
DTDP-MIC	700	749	753	802	− 5.54	− 3.95	1.59	1.55

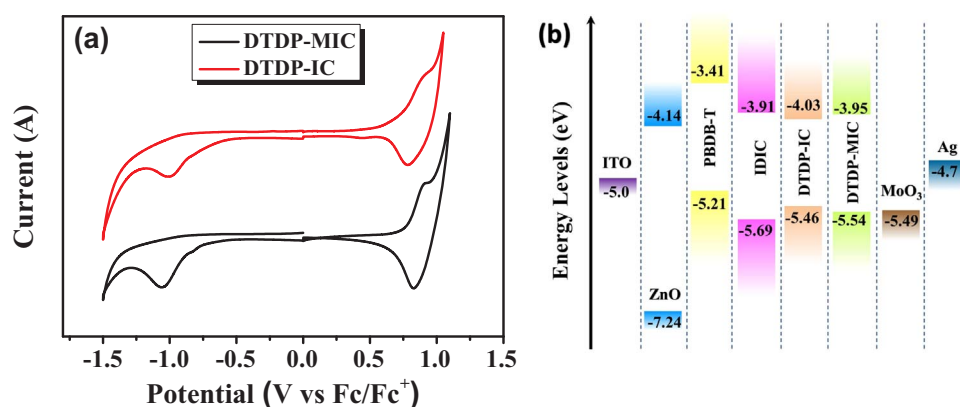


Fig. 3. (a) Cyclic voltammetry results and (b) energy level diagrams for PBDB-T polymer donor, **DTDP** molecules and the analogue IDIC acceptor in literature [17].

electrochemical cell in acetonitrile solution containing 0.1 M Bu_4NPF_6 at room temperature under nitrogen atmosphere with a scanning rate of 100 mV/s. $Ag/AgNO_3$ was used as the reference electrode with ferrocene/ferrocenium as the redox internal standard. The CV curves of **DTDP-IC** and **DTDP-MIC** are shown in Fig. 3. According to the following equations: $E_{HOMO} = -e[(E_{ox} - E_{(Fc/Fc^+)}) + 4.8]$ (eV) and $E_{LUMO} = -e[(E_{red} - E_{(Fc/Fc^+)}) + 4.8]$ (eV), their HOMO energy levels of **DTDP-IC** and **DTDP-MIC** are calculated to be − 5.46 and − 5.54 eV, respectively and LUMO energy levels are defined as − 4.03 and − 3.95 eV, respectively. Meanwhile, the energy gaps calculated by CV (E_g^{cv}) are well accordant with the optical E_g^{opt} , demonstrating the reliability and accuracy for the energy levels. From the energy level diagrams in Fig. 3, it's clear that the electron donating oxygen modified **DTDP-IC** could efficiently reduce the band gap to 1.43 eV and elevate the HOMO energy levels to − 5.46 eV without significantly influence the LUMO energy level, which is consequently reduced by 0.12 eV in comparison with its analogous IDIC and is not ideal for the high V_{oc} devices. When the methyl modified MIC block is utilized as the end-capping unit, the electron band gap is slightly enlarged by 0.16 eV and the LUMO level (− 3.95 eV) returns to the similar level of IDIC (− 3.91 eV) [17], which may be ascribed to the methyl substituted effect and is in favor of relative high V_{oc} . In addition, the simultaneously reduced HOMO level for **DTDP-MIC** may provide more sufficient driving force for the charge separation.

Meanwhile, visualized HOMO and LUMO orbitals for **DTDP** molecules and IDIC molecule are depicted by the DFT calculations to assist understanding the electronic wave-functions as shown in Fig. 4. All molecules present very similar electron distributions at LUMO states, but distinctive differences are shown at the HOMO states. In both **DTDP** molecules, the incorporated oxygen atoms contributed to the HOMO orbitals, however in the IDIC molecule, the bridged carbon doesn't take part in the HOMO formation. In addition, introduction of such electron donating oxygen atoms into the conjugated π system efficiently elevated the HOMO energy levels. When the molecules are excited under irradiation, it's clear that the electrons located at the oxygen atoms in the two **DTDP** molecules could flow to the electron deficient moieties efficiently, indicating good electron donating ability and favorable conjugation are formed with the neighbored thiophene rings.

2.4. GIWAXS characterization

With the grazing incidence wide angle X-ray scattering (GIWAXS) characterization, which is sensitive to the crystalline parts and allows for the determination of the crystal structure and the orientation of the crystalline regions with respect to the electrodes, the molecular arrangement of the material could be probed. So herein, it is employed for the investigation of the crystalline properties for the pure films of two **DTDP** acceptors and their blend films with PBDB-T. The GIWAXS results are shown in Fig. 5. It's clear that **DTDP-IC** and **DTDP-MIC** present very different scattering patterns (Fig. 5a and b). For **DTDP-IC**, a clear π - π stacking (010) diffraction peak is seen at $1.95 \text{ \AA}^{-1}$ with a d-spacing of $3.22 \text{ \AA}$ in out-of-plane (OOP) direction; in addition, a quite strong (100) lamellar diffraction peak is seen at $0.45 \text{ \AA}^{-1}$ with an interlamellar distance of $13.96 \text{ \AA}$ in in-plane (IP) direction. All the information demonstrates that **DTDP-IC** molecules in the neat film prefer to form the face-on orientation in relative to the substrate. Meanwhile, in comparison of the GIWAXS result for IDIC as shown in Fig. S22, it will found that the incorporation of oxygen at the conjugated skeleton will greatly increase the crystallization ability. However, as the methyl group introduced at the ending IC groups in **DTDP-MIC**, more scattering peaks are observed in Fig. 5b, which means **DTDP-MIC** adopts much different packing styles in comparison with **DTDP-IC**. It indicates that the introduction of the methyl groups would change the growth mode of the crystallites. Though minor structural change could lead to a completely different molecular ordering in the neat films for these two **DTDP** molecules, relative simple and very similar diffraction patterns are found in their corresponding blend films with PBDB-T. As for **DTDP-IC**:PBDB-T in Fig. 5c, a new (100) peak at $0.34 \text{ \AA}^{-1}$ with a lamellar d-spacing of $18.47 \text{ \AA}$ in IP direction appears, which is produced by the PBDB-T polymer. Interestingly, when the **DTDP-MIC** blended with PBDB-T, not only the (100) peak associated with PBDB-T polymer is observed at $0.34 \text{ \AA}^{-1}$ in Fig. 5d, a strong and sharp (100) peak belonging to the **DTDP-MIC** also shows up in the IP direction at $0.44 \text{ \AA}^{-1}$ corresponding to a lamellar d-spacing of $14.27 \text{ \AA}$. In addition, both blend films present a very similar (010) peaks at $1.91 \text{ \AA}^{-1}$ with a d-spacing of $3.29 \text{ \AA}$, which are corresponding to the π - π stacking. In short, both blend films present intensified (010) peaks at OOP direction and distinct (100) peaks at the IP direction, demonstrating that the molecular backbones incline to present face-on orientation to the substrate,

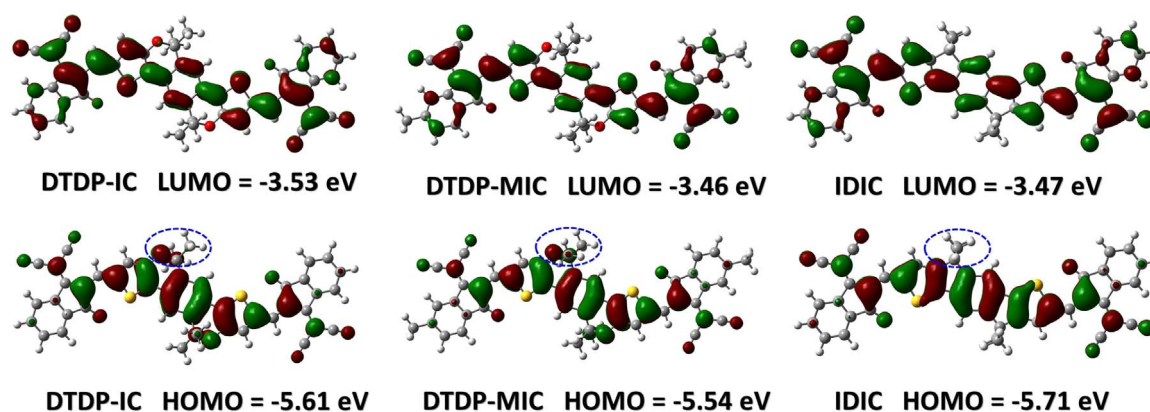


Fig. 4. Visualized HOMO, LUMO distributions and the calculated frontier orbital energies (B3LYP/6–31 G (d, p)) for the DTDP and IDIC molecules.

which is favorite by the OPV devices. According to the Scherrer equation [37], the information of crystalline size is related to the width of the diffraction peaks as coherence length ($CL = 2\pi K/\text{FWHM}$, where $K = 0.9$ is a shape factor (typically 0.8–1) and FWHM is the full width at half-maximum of a diffraction peak [38]). CL values of donor and acceptor in the blend system are calculated from the (100) peaks and slight variations for the crystalline sizes of the components in the active layers are as shown in Table S7.

2.5. Photovoltaic properties

Photovoltaic properties of these two molecules were investigated in an inverted device architecture of ITO/ZnO/photoactive layer/MoO₃/Ag, where the photoactive layers were blend of PBDB-T:DTDP acceptors in this work, and they are optimized by changing the weight ratios of polymer to NFAs, concentrations of blend solution and additive types. The *J*-*V* characteristics and the external quantum efficiency (*EQE*) spectra of the optimized devices are shown in Fig. 6 and the detailed optimization results are listed in Table S1. Coincidentally, both DTDP acceptors preferred the optimum ratio of polymer to NFAs at 1:1.2 (w/w) and *PCEs* of 8.15% and 8.81% achieved without additive, respectively. Obviously, introducing oxygen atoms into the conjugated ladder backbones could simply achieve high *J_{sc}* above 16.0 mA/cm², which may be attributed to the extended absorption, and the *V_{oc}* variations are ascribed to the methyl substitution at the IC terminal groups.

Subsequently, three type additives (1,8-diiodooctane (DIO), chloronaphthalene (CN) and *o*-chlorobenzaldehyde (CBA)) were utilized for further optimization of the device performance and 0.5% CBA seems to be the suitable additive for these NFAs system, which is advantageous for the *FF* improvement for both DTDP acceptors as shown in Table 2. Finally, the highest *PCE* of 9.39% (*V_{oc}* = 0.80 V, *J_{sc}* = 16.82 mA/cm² and *FF* = 69.95%) is achieved by DTDP-MIC. Generally, compatible energy levels of the donor and acceptor components are essential for highly efficiency PSCs, which can ensure efficient charge separation and minimize *E_{loss}*. [18,19,39] As shown in Fig. 3b, the ΔE_{LUMO} between the donor and acceptor in the PBDB-T:DTDP acceptor blends are 0.62 and 0.54 eV for DTDP-IC and DTDP-MIC, respectively; while the ΔE_{HOMO} are 0.25 and 0.33 eV for DTDP-IC and DTDP-MIC, respectively, which should be sufficient for exciton dissociation and charge transfer between the donor and acceptor. However, the *E_{loss}* for these DTDP-IC and DTDP-MIC are 0.73 and 0.75 eV, which is still relatively large compared to some other highly efficient blend systems [39], indicating there is still room for further enhancement of photovoltaic performance via fine-tuning the energy level compatibility.

In addition, the *EQE* curves in Fig. 6b showed a broad response from 300 to 850 nm and a maximum *EQE* value of 76.6% was achieved by DTDP-MIC at 730 nm, indicating efficient photoharvesting and charge collection. The calculated *J_{sc}* values from the integration of the *EQE* curves are in good agreement with the observed *J_{sc}* values in the *J*-*V* measurement and the deviations are within 5%.

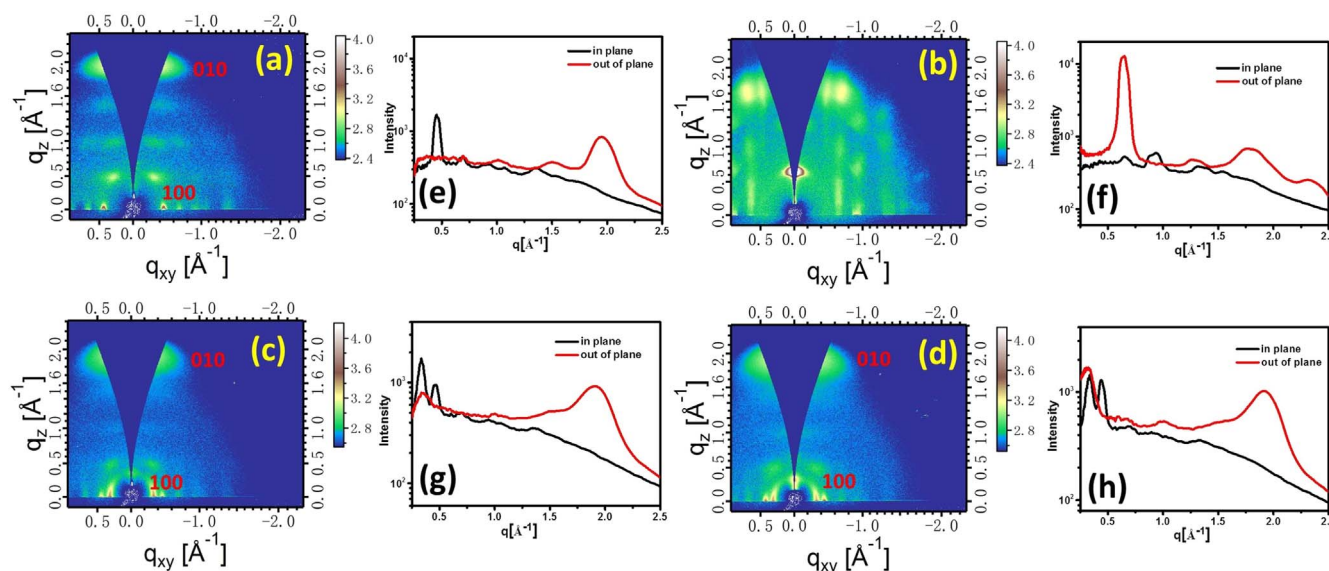


Fig. 5. GIWAXS 2D patterns for (a) pure DTDP-IC, (b) pure DTDP-MIC, (c) PBDB-T:DTDP-IC blend, (d) PBDB-T:DTDP-MIC blend and 1D line-cuts for the corresponding films (e–h).

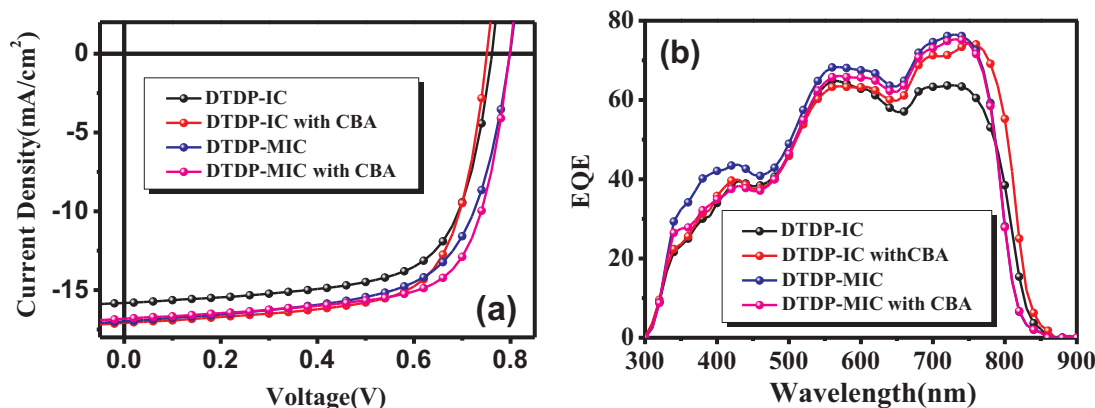


Fig. 6. (a) *J-V* curves and (b) EQE curves of OSCs fabricated based on the device structure of ITO/ZnO/PBDB-T:DTDP acceptor/MoO₃/Ag.

2.6. Charge carrier mobilities

Charge transport mobility plays an important role on photovoltaic performances for the final materials. High mobility values and balanced hole (μ_h)/electron (μ_e) are desired for high performance devices. Therefore, the μ_h and μ_e of the PBDB-T:DTDP acceptor blends were investigated via the space charge limited current (SCLC) method in typical device structures of ITO/PEDOT:PSS/PBDB-T:DTDP acceptor/Au and ITO/ZnO/PBDB-T:DTDP acceptor/LiF/Al, respectively. The averaged μ_h and μ_e are listed in Table 3 and the corresponding $J^{1/2}$ -*V* curves are shown in Fig. 7. In comparison with blend films prepared without additive, both devices prepared with 0.5% CBA displayed relative balanced μ_h/μ_e ratios, which is in favor of reducing charge recombination and increasing the J_{sc} and *FF*, hence resulting in better photovoltaic performance. Clearly, the most balanced charge transport ($\mu_h/\mu_e = 1.11$) among these blends was achieved by PBDB-T:DTDP-MIC blend with 0.5% CBA, which demonstrated the photo-generated charge carriers could be efficiently collected at the electrode.

2.7. Morphological properties

Morphology of blend films can largely affect the charge separation and transport. In order to get further insight into the relationships between molecular structures and the device performances, morphologies of blend films were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements for more details at surface or in-depth levels as shown in Fig. 8. Due to the strong crystallization properties of the two molecules, morphologies with obvious aggregation for sole polymer donor or the NFAs in the blend films are observed. Since the polymer PBDB-T tends to form fibrillar aggregates, [22] the irregular aggregates observed here are referred to aggregations of DTDP acceptors. In the height images for the blend films without additive (Fig. 8a and c), DTDP-IC presents a large root-mean-square (RMS) roughness of 4.85 nm (Fig. 8a) and obvious aggregation of DTDP-IC and PBDB-T are observed on the surface of the blend film. Though a smaller RMS of 2.64 nm is found for DTDP-MIC (Fig. 8c), clear separation of the two components still exists. When 0.5% CBA is applied as additive to the polymer: NFAs blend in Fig. 8b

Table 2
Performances of PSCs based on ITO/ZnO/PBDB-T:DTDP acceptors/MoO₃/Ag.

Active layer	Additive	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA/cm ²)	<i>FF</i> (%)	<i>PCE</i> (%)
PBDB-T:DTDP-IC = 1:1.2	no	0.76 (0.75 ± 0.007)	15.82 (16.10 ± 0.36)	67.63 (65.46 ± 1.46)	8.15 (7.93 ± 0.14)
PBDB-T:DTDP-IC = 1:1.2	0.5% CBA	0.75 (0.75 ± 0.007)	17.08 (16.96 ± 0.32)	69.24 (67.82 ± 1.22)	8.88 (8.67 ± 0.12)
PBDB-T:DTDP-MIC = 1:1.2	no	0.80 (0.80 ± 0.008)	16.99 (16.62 ± 0.22)	64.94 (65.12 ± 0.48)	8.81 (8.65 ± 0.099)
PBDB-T:DTDP-MIC = 1:1.2	0.5% CBA	0.80 (0.80 ± 0.005)	16.82 (16.77 ± 0.22)	69.95 (69.49 ± 1.00)	9.39 (9.25 ± 0.12)

*The values in the parentheses are the statistical data from eight independent cells.

Table 3
Charge transport properties of PBDB-T:DTDP acceptors blended films measured by SCLC method.

Active layer	additive	μ_h [cm ² V ⁻¹ S ⁻¹]	μ_e [cm ² V ⁻¹ S ⁻¹]	μ_h/μ_e	<i>d</i> (nm)
PBDB-T:DTDP-IC	–	6.59×10^{-6}	1.68×10^{-6}	3.92	93
PBDB-T:DTDP-IC	0.5% CBA	7.81×10^{-6}	3.29×10^{-6}	2.37	101
PBDB-T:DTDP-MIC	–	7.36×10^{-6}	3.36×10^{-6}	2.19	97
PBDB-T:DTDP-MIC	0.5% CBA	1.64×10^{-5}	1.48×10^{-5}	1.11	105

and d, the fibrillar aggregates of PBDB-T became less distinct and the self-aggregation phenomenon for the DTDP-IC has been restricted at the surface of the blend films, since larger aggregates disappeared in the blend film of PBDB-T:DTDP-IC with a reduced RMS of 2.80 nm. As for DTDP-MIC, CBA also improved the miscibility between donor and acceptor, but the RMS didn't change so much. Phase images as shown in Fig. 8e-h presented consistent results to their corresponding height images. TEM offered in-depth morphology for the compositions in active layers (in Fig. 8i-l), it's clear that all blend films presented bi-continuous polymer/acceptor interpenetrating networks and the PBDB-T fibers are distributed all over the substrates with varied sizes and thicknesses. It's quite consistent with the AFM results at the changes of the fibrillar structures and self-aggregation of the NFAs acceptors. In short, the photovoltaic improvements for these PSCs devices are ascribed to the miscibility improvement for polymer donor and NFAs acceptors.

3. Conclusion

In conclusion, a novel pyran based ladder-typed conjugated building block (DTDP) has been designed and prepared through a facile route. Via the Knoevenagel condensation with two terminal electron deficient indanone derivatives, two A-D-A type NFAs are efficient prepared. Theoretical optimization predictions presented near flat structures for the two DTDP based molecules, although slight bent with dihedral angles of about 12° appear at the central part of DTDP blocks. XRD

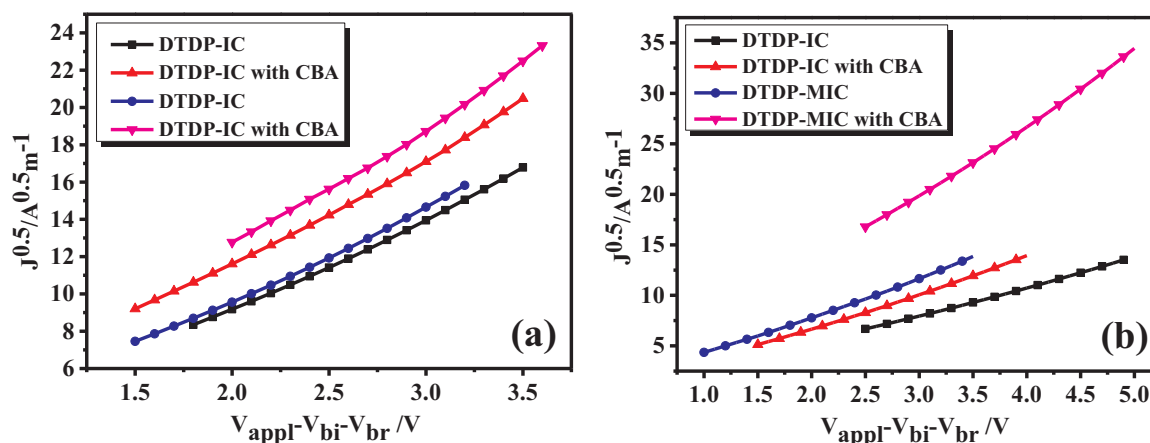


Fig. 7. $J^{1/2}$ - V curves for blended films with PBDB-T and DTDP acceptors: a) hole-only devices with the structure of ITO/PEDOT:PSS/polymer or actively layer/Au, and b) the electron-only devices with the structure of ITO/ZnO/actively layer/LiF/Al according to the SCLC model.

results confirmed this observation and strong crystallinity are found for both molecules with sharp peaks. Functionalized-O at the conjugated backbone could serve for molecular energy level adjusting and the HOMO energy levels are elevated to ~ -5.5 eV without sacrificing the LUMO energy and V_{oc} in comparison to the counterpart in literature. Due to the strong crystallization properties of the DTDP molecules and the PBDB-T polymers, clearly self-aggregations are observed by morphology study and the miscibility of the two components has been improved by adding 0.5% CBA. Finally, these pyran based NFAs are applied in the OPV device fabrication and the highest PCE of 9.39% with quite balanced hole/electron mobility is achieved by DTDP-MIC. In addition, the high J_{sc} of about 17.0 mA/cm² for both molecules are attributed to the elevation of the electron donating ability and broadened absorption induced by O-incorporating. Overall, this is the first

example to put pyran into NFAs designs and all results demonstrated the ladder-typed DTDP is a promising building block for high efficiency NFAs based PSCs. Though the E_{loss} for the devices are relatively large in comparison with highly efficient NFAs systems, it also provides room for further enhancement of photovoltaic performance via polymer compatibility selection. In summary, this work not only contributes a promise ladder-typed dipyrans unit for conjugated material exploration, it also it paves a new way to use oxygens in NFAs design.

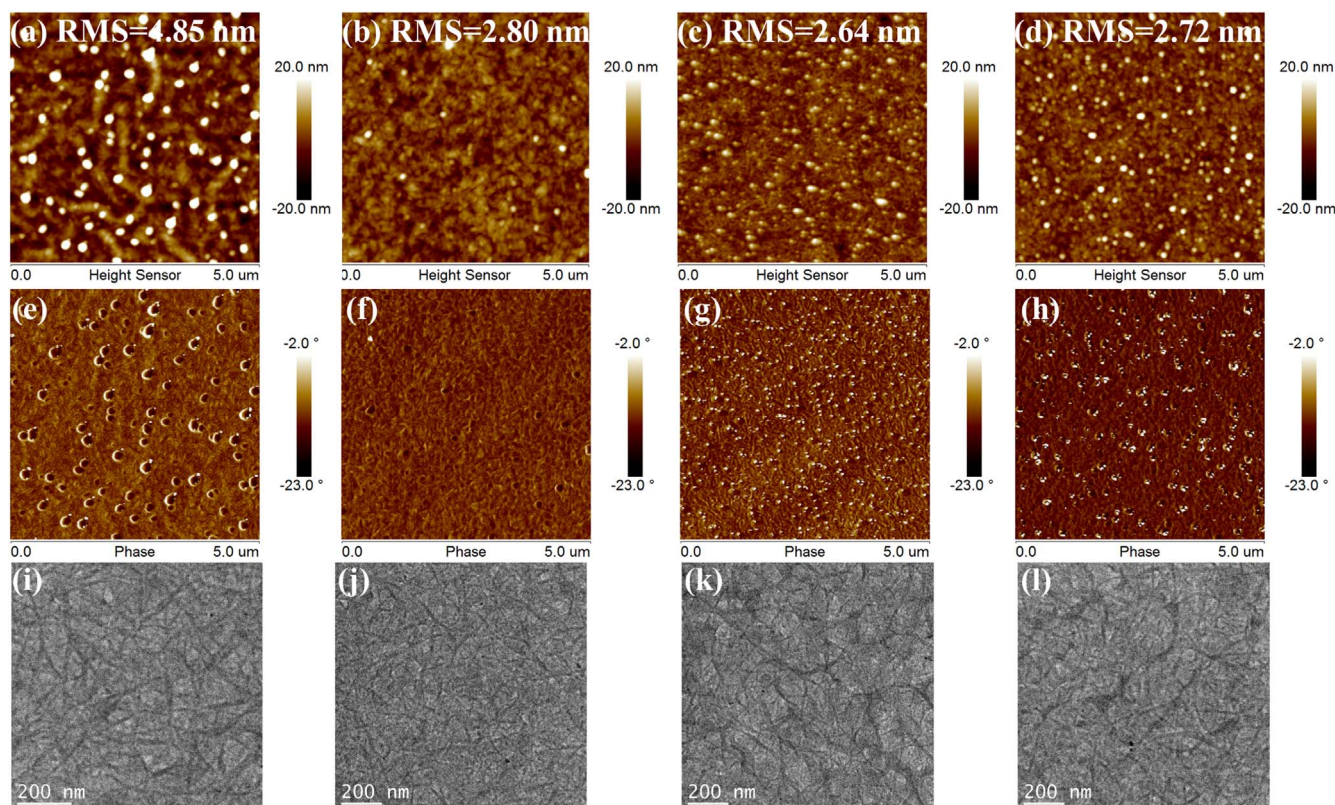


Fig. 8. AFM (height and phase, 5 $\mu\text{m} \times 5 \mu\text{m}$) and TEM images for blend films of PBDB-T and the DTDP molecules: (a, e, i) PBDB-T:DTDP-IC; (b, f, j) PBDB-T:DTDP-IC with 0.5% CBA; (c, g, k) PBDB-T:DTDP-MIC; (d, h, l) PBDB-T:DTDP-MIC with 0.5% CBA.

4. Experimental

4.1. Materials synthesis

4.1.1. Synthesis of compound 2

To a solution of **1** (0.94 g, 2.88 mmol) in dry tetrahydrofuran (100 mL) was added the fresh-made *n*-octylmagnesium bromide (15.0 mL, 20.18 mmol) dropwise at -78°C and stirred for 1 h, then the reaction mixture was slowly warmed up to ambient temperature overnight. The reaction was quenched with aq. NH_4Cl solution (5 mL), extracted with ethyl acetate (20×2 mL), and then washed with saturated NaHCO_3 (2×20 mL) and H_2O (20 mL). After the organic phase was dried over anhydrous MgSO_4 , the solvent was removed under reduced pressure, and the residue was purified by column chromatography with 5:1 (v/v) hexane/ethyl acetate as the eluent to afford compound **2** as white solids (1.04 g, 46%). M.p. = $125\text{--}126^{\circ}\text{C}$, ^1H NMR (300 MHz, acetone- d_6) δ 7.50 (s, 2 H), 7.26 (d, $J = 5.4$ Hz, 2 H), 6.71 (d, $J = 5.4$ Hz, 2 H), 3.31 (s, 4 H), 2.01–1.81 (m, 4 H), 1.81–1.63 (m, 4 H), 1.37–1.07 (m, 48 H), 0.84 (t, 12 H). ^{13}C NMR (75 MHz, acetone- d_6) δ 150.30, 143.65, 134.40, 129.15, 122.26, 119.71, 117.95, 76.58, 40.71, 31.57, 29.74, 29.29, 28.98, 28.09, 23.53, 22.26, 13.36. HRMS (DART/Positive): m/z $[\text{M}]^+$ Calcd for $[\text{C}_{48}\text{H}_{78}\text{O}_4\text{S}_2]$ 782.5336, Found 782.5330.

4.1.2. Synthesis of DTDP

To a solution of compound **2** (270.4 mg, 0.35 mmol) in toluene (50 mL), *p*-toluenesulfonic acid monohydrate (50 mg, 0.29 mmol) was added under argon. Then, the mixture was heated to reflux and stirred for about 24 h. The solution was cooled down to room temperature and extracted with DCM. After the organic phase was dried over MgSO_4 , the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane as an eluent to afford yellow solids (231.9 mg, 90%). M.p. = $85\text{--}86^{\circ}\text{C}$, ^1H NMR (300 MHz, CDCl_3) δ 7.04 (d, $J = 5.3$ Hz, 2 H), 6.77 (s, 2 H), 6.69 (d, $J = 5.3$ Hz, 2 H), 2.04–1.78 (m, 8 H), 1.49–1.12 (m, 48 H), 0.85 (t, 12 H). ^{13}C NMR (75 MHz, CDCl_3) δ 151.99, 132.88, 126.87, 122.13, 119.55, 117.37, 114.59, 85.61, 39.32, 31.99, 30.05, 29.56, 29.40, 23.83, 22.80, 14.26. HRMS (DART/Positive): m/z $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{48}\text{H}_{75}\text{O}_2\text{S}_2]$ 747.5206, Found 747.5203.

4.1.3. Synthesis of DTDP-Br

N-Bromosuccinimide (NBS) (103.3 mg, 0.58 mmol) was added in portions into a mixture of **DTDP** (211.5 mg, 0.28 mmol) and chloroform (10 mL) at 0°C , then the reaction mixture was slowly warmed up to ambient temperature for 3 h. The reaction was quenched with water, extracted with dichloromethane, and then washed with saturated NaHCO_3 (2×20 mL) and H_2O (20 mL). After the organic phase was dried over anhydrous MgSO_4 , the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane as the eluent to afford compound **DTDP-Br** as yellow solids (424.4 mg, 95%). M.p. = $74\text{--}75^{\circ}\text{C}$, ^1H NMR (300 MHz, CDCl_3) δ 6.67 (s, 2 H), 6.59 (s, 2 H), 2.00–1.77 (m, 8 H), 1.48–1.15 (b, 48 H), 0.86 (t, 12 H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.94, 132.82, 126.26, 122.65, 117.09, 116.01, 110.45, 85.87, 39.20, 32.00, 29.98, 29.54, 29.39, 23.77, 22.81, 14.26. HRMS (DART/Positive): m/z $[\text{M}]^+$ Calcd for $[\text{C}_{48}\text{H}_{75}\text{Br}_2\text{O}_2\text{S}_2]$ 902.3335, Found 902.3309.

4.1.4. Synthesis of DTDP-CHO

To a solution of **DTDP-Br** (390 mg, 0.43 mmol) in dry tetrahydrofuran (40 mL), *n*-BuLi (2.46 M in hexane, 1.51 mmol) was added dropwise at -78°C . After the temperature was maintained at -78°C for 2 h, anhydrous DMF (0.12 mL, 1.51 mmol) was added dropwise. The reactant was warmed to room temperature and stirred overnight. Then, the reaction was quenched with methanol at -78°C , extracted with CH_2Cl_2 (3×20 mL), and then washed with water (2×20 mL). After the organic layer dried over MgSO_4 , the solvent was removed

under vacuum. The residue was purified by column chromatography on silica gel with a mixture of hexane/DCM as the eluent to afford compound **DTDP-CHO** as orange solids (155.7 mg, 45%). ^1H NMR (CDCl_3 , 400 MHz) δ 9.82 (s, 2 H), 6.94 (s, 2 H), 2.03–1.84 (m, 8 H), 1.46–1.16 (m, 48 H), 0.84 (t, 12 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 182.20, 152.65, 138.64, 134.77, 124.82, 118.65, 86.03, 77.01, 76.69, 39.48, 31.79, 29.77, 29.36, 29.19, 23.68, 22.62, 14.05. HRMS (ESI): m/z Calcd for $\text{C}_{50}\text{H}_{75}\text{O}_4\text{S}_2^+ [\text{M} + \text{H}]^+$ 803.5101, Found 803.5101.

4.1.5. Synthesis of DTDP-IC

To a schlenk flask were added **DTDP-CHO** (41.7 mg, 0.05 mmol), IC (50.4 mg, 0.26 mmol). Pyridine (0.1 mL) and chloroform (10 mL) was added under argon after it was degassed for 30 min. Subsequently, the mixture was stirred for 12 h and then it was poured into methanol (200 mL). The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:1, v/v) as eluent yielding dark solids (53 mg, 88%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.79 (s, 2 H), 8.74–8.68 (m, 2 H), 7.98–7.92 (m, 2 H), 7.84–7.73 (m, 4 H), 7.47 (s, 2 H), 7.15 (s, 2 H), 2.10–1.89 (m, 8 H), 1.48–1.14 (m, 48 H), 0.83 (t, 12 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.47, 154.05, 140.12, 137.25, 136.91, 136.33, 135.34, 134.60, 134.15, 132.64, 132.28, 128.45, 125.42, 123.75, 123.40, 119.43, 114.49, 114.39, 86.21, 70.03, 40.33, 31.81, 29.78, 29.41, 29.23, 23.70, 22.64, 14.09. HRMS (ESI) m/z Calcd for $\text{C}_{74}\text{H}_{82}\text{N}_4\text{O}_4\text{S}_2^+ [\text{M}]^+$ 1154.5772, Found 1154.5753.

4.1.6. Synthesis of DTDP-MIC

To a schlenk flask were added **DTDP-CHO** (44 mg, 0.05 mmol), IC-M (57 mg, 0.27 mmol). Pyridine (0.1 mL) and chloroform (10 mL) was added under argon after it was degassed for 30 min. Subsequently, the mixture was stirred for 12 h and then it was poured into methanol (200 mL). The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:2, v/v) as eluent yielding dark solid (59.2 mg, 91%). ^1H NMR (400 MHz, CDCl_3): δ 8.75 (s, 2 H), 8.60–8.56 (d, $J = 8.0$ Hz, 0.72 H), 8.49 (s, 1.28 H), 7.87–7.80 (d, $J = 8.0$ Hz, 1.28 H), 7.73 (s, 0.72 H), 7.61–7.55 (m, 2 H), 7.47–7.42 (m, 2 H), 7.13 (s, 0.72 H), 2.62–2.52 (m, 6 H), 2.07–1.86 (m, 8 H), 1.48–1.14 (m, 48 H), 0.83 (t, 12 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.56, 188.18, 160.21, 153.93, 147.01, 146.40, 140.52, 136.84, 136.22, 135.62, 134.81, 134.11, 132.42, 131.90, 128.40, 125.72, 125.34, 124.04, 123.95, 123.64, 119.34, 114.55, 114.44, 86.16, 69.75, 69.17, 40.31, 31.80, 29.79, 29.40, 29.22, 23.69, 22.63, 22.57, 22.09, 14.07. HRMS (ESI) m/z Calcd for $\text{C}_{76}\text{H}_{86}\text{N}_4\text{O}_4\text{S}_2^+ [\text{M}]^+$ 1182.6085, Found 1182.6073.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2017.12.030>.

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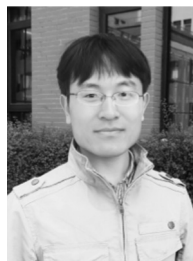
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