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Isomerizing Thieno[3,4-b]thiophene-Based Near-Infrared Nonfullerene Acceptors towards Efficient Organic Solar Cells

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Zeqi Zhang, Tong Shan, Yi Zhang, Lei Zhu, Lingwei Kong, Feng Liu and Hongliang Zhong*

With the rapid growth of the requirement for emerging photovoltaic technology like semitransparent solar cells applied for integrated smart windows, there is an urgent need to develop near-infrared (NIR) non-fullerene acceptors (NFAs). To address this issue, thieno[3,4-b]thiophene (TT), which has a stable quinoid structure to minify the energy difference between two resonance structures corresponding the band gap, is introduced into the push-pull molecular architecture as the bridge unit to narrow the band gap of derived acceptors. Due to the different linkage positions (4- or 6-position) of asymmetric TT, these acceptors are classified to two types of isomers, namely 4TIC, 4T4F, 6TIC and 6T4F, of which all have strong absorption in NIR range. By incorporation with polymer donor PTB7-Th, the devices based on 6-position isomers exhibit superior photovoltaic performance, wherein a champion device based on 6T4F is obtained with a power conversion efficiency of 10.74%. With detailed investigations on inherent optoelectronic properties as well as structural and morphological variation, this performance diversity induced by isomerism is determined by the evident difference in packing order which will impact the charge mobility and fill factor. This work presents a class of high-performance NIR acceptors in which the regioisomeric backbone will significantly impact the optoelectronic properties.

Introduction

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Recently, remarkable progresses have been achieved in the community of organic solar cells (OSCs) attributed to continuous advancements from both material and device approaches, in particular the innovation of non-fullerene acceptors (NFAs) which possess outstanding advantages, such as facile accessibility and structure flexibility, compared to fullerene derivatives.¹⁻⁶ The power conversion efficiencies (PCEs) over 16% have been achieved for single junction solar cells.⁷⁻¹⁰ Thus, some potential applications for OSCs in consumer market is emerging and might become mature in near future, e.g. building-integrated photovoltaics (BIPVs) in which traditional windows are replaced by transparent OSCs to provide an opportunity to supply additional energy with less effect on the origin functions of buildings. To ensure the visible transparency, it is essential to develop organic semiconductors mainly absorbing the near-infrared light with high extinction coefficient.11-30

It is an effective way to narrow the band gap to manipulate the absorption in near-infrared region by intramolecular charge transfer (ICT) between donor (D) and acceptor (A) moieties in push-pull conjugated molecules.^{21, 31-33} For example, a class of the most successful NFAs is based on an A-D-A configuration, such as middle band gap acceptors ITIC³⁴ and IDIC^{15, 35} with an electron-rich fused indacenodithienothiophene (IDTT) or indacenodithiophene (IDT) core and two strong electronwithdrawing 2-(3-oxo-2, 3-dihydro-1H-inden-1ylidene)malononitrile (IC) as the terminals, wherein fluorosubstituted IC terminal groups with a stronger electronwithdrawing ability are used to further enhance the ICT effect.^{36, 37} Another strategy to lower the band gap of an organic semiconductor is to construct a conjugated system wherein both the origin state and quinoid resonance structure possess aromatic rings.³⁸⁻⁴⁰ Consequently, the energy difference of varied resonance structures with varied aromatic states, as an indication of its band gap, is reduced. Therefore, we reasons that it might further minify synergistically the band gap by combining these two methods, to introduce a moiety with unique quinoid resonance structure into the push-pull conjugated molecules.

Thieno[3,4-b]thiophene (TT) is a building block with exactly required properties since the fused thiophene ring can stabilize its quinoid resonance structure (conductive state).^{41, 42} In addition, thieno[3,4-b]thiophene derivatives substituted by ester or carbonyl groups are commonly used as electron-deficient acceptor in organic semiconductors.^{12, 43-46} However, it is notable the asymmetric configuration of TT raises an issue of isomerism to complicate structural definition. Our previous study has revealed there are two different repeat units in PTB7-Th, as one of many successful donor polymers, due to the asymmetry of fluoro-substituted TT (FTT), while the ratio of these two units plays a key role in determining the material properties and device performance.^{47, 48} Zhu *et al.* have reported a series of small molecules and oligomers containing TT units wherein the regioregularity significantly affects the

School of Chemistry and Chemical Engineering, Shanghai Key Lab of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, P. R. China. Email: hlzhong@sjtu.edu.cn

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charge mobility and photovoltaic property.^{42, 44, 49, 50} In the meanwhile of this work is carrying out, Li *et al.* have synthesize a family of isomers with FTT as bridge unit and revealed the impact of the fluorine orientation in derived OSCs.⁵¹ Hence, it is still challenging to develop new near-infrared NFAs involving of TT which causes the isomerism of relevant materials.

Herein, we introduce TT into A-D-A molecules as conjugated bridge to form A-TT-D-TT-A configuration to obtain four acceptors 4TIC, 4T4F, 6TIC and 6T4F. The four compounds comprise a fused IDT core and two strong electron-withdrawing IC(2F) bridged by quinoidal ester-substituted TT (Scheme. 1), wherein the asymmetry of TT creates two types of derivatives, 4-position isomers 4TIC and 4T4F, and 6-position isomers 6TIC and 6T4F. With the help of a strong push-pull effect and the unique resonance structure of TT, these acceptors show extended absorption in near-infrared region wherein the absorption edge of 4TIF and 6TIF with fluorinated terminal group is over 1000 nm. More importantly, the choice of linkage position in TT unit play a key role in affecting the optoelectronic properties and crystallinity, and consequently determining the photovoltaic performance. The champion device based on 6T4F shows the best PCE of 10.74% with a high short circuit current $(J_{\rm SC})$ of 25.79 mA cm⁻², an open-circuit voltage ($V_{\rm OC}$) of 0.60 V, and a fill factor (FF) of 69.4%, but 4T4F-based device shows a much lower PCE of 6.58%. The detailed study reveals the superior performance of 6-position is ascribed to their higher packing order when blended with PTB7-Th, which enhances the charge mobility, and thus improving the fill factors. This work is one of few examples wherein NIR acceptors with absorption edge exceeding 1000 nm can achieve a PCE over 10%.

Results and discussion

Synthesis and characterization

The synthetic routes of the four NFAs are shown in Scheme. 1 and Scheme S1. The precursors 1a and 1b are prepared by Stille cross-coupling involving of two regioisomers, 2-ethylhexyl 4bromo-6-formylthieno[3,4-b]thiophene-2-carboxylate and 2-6-bromo-4-formylthieno[3,4-b]thiophene-2ethylhexyl carboxylate, respectively. Then the final products are obtained by Knoevenagel reaction of 1a (1b) and IC (IC-2F). According to the linking position between IDT core and TT, these acceptors are classified to two types: 4-position isomers 4TIC and 4T4F, and 6-position isomers 6TIC and 6T4F. The four NFAs are able to be dissolved in common organic solvents such as chloroform (CF), chlorobenzene (CB) and 1, 2-dichlorobenzene (DCB), which favors the solution processability. Their chemical structures have been confirmed by ¹H NMR, ¹³C NMR, and mass spectra which are shown in Electronic Supplementary Information (ESI).

Optical, electrochemical properties and theory calculation

The optical property of these NFAs has been characterized by UV–vis–NIR absorption. The spectra of the NFAs in chloroform solution and film are shown in **Fig. 1** and detailed parameters are summarized in **Table 1**. All of these new acceptors show broad absorption in near-infrared region. Compared to 4-position isomers 4TIC (818 nm) and 4T4F (833 nm), the maximum absorption of 6-position isomers 6TIC (798 nm) and 6T4F (813 nm) in solution shows hypsochromic shifts approximate 20 nm, respectively, indicating the linkage position has significantly impacted on the push-pull structure. Compared to the solution, the absorption of films exhibits evident bathochromical shifts with the edge extending to over 1000 nm,

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Fig. 1 The normalized UV-vis absorption of the four acceptors in solution (a) and film (b). Cyclic voltammetry curves (c) and energy levels (d) of 4TIC, 4T4F, 6TIC and 6T4F.

implying the strong aggregation in solid state, in particular for 6T4F which shows a red-shift of 106 nm. In addition, the fluorosubstituent in the IC terminal group is helpful to prompt the electron-withdrawing ability to result in the red-shift in relevant absorption spectra. The optical band-gap (E_g) of 6T4F and 4T4F estimated from the absorption edge of corresponding films are 1.23 and 1.22 eV, which are slightly lower than E_g of 6TIC (1.30 eV) and 4TIC (1.26 eV), respectively.

To study the electrochemical property, the cyclic voltammetry measurement has been conducted. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of 4TIC 4T4F, 6TIC and 6T4F are estimated to be -5.36/-4.11 eV, -5.38/-4.13 eV, -5.31/-3.96 eV and -5.45/-4.00 eV, respectively from the onset potentials (**Fig. 1c**). The corresponding energy level diagram and data are listed in **Fig. 1d** and **Table 1**. It is obvious that different linkage positions affect energy levels of the four isomers. Compared to 6TIC and 6T4F, 4TIC and 4T4F have downshifted LUMOs, respectively. With introducing fluorine into IC terminals, the LUMOs show apparent downshifts attributed to the strong electron-withdrawing ability of fluorine. The electrochemical band gaps are consistent with the optical band gap except 6T4F (1.45 vs 1.25 eV), since the films are prepared by different methods for cyclic voltammetry (drop casting) and absorption (spin casting), while 6T4F shows a strong tendency to aggregate wherein the packing mode is significantly impacted by the processing condition.

Mator	$arepsilon_{max}^{sol.}$ [M ⁻¹ cm ⁻¹]	λ _{max} ^{sol.} [nm]	λ _{max} ^{film} [nm]	E ^{g opt a)} [eV]	Е _{номо} ь) [eV]	E _{LUMO} ^{b)} [eV]	E ^{cv b)} [eV]
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4TIC	1.91 × 10⁵	818	881	1.26	-5.36	-4.11	1.25
4T4F	2.20 × 10 ⁵	833	920	1.22	-5.38	-4.13	1.25
6TIC	1.85 × 10⁵	798	853	1.30	-5.31	-3.96	1.35
6T4F	2.09 × 10⁵	813	919	1.23	-5.45	-4.00	1.45

a) Estimated from the absorption. b) Estimated from the electrochemical measurement.

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Fig. 2 (a) J-V curves and (b) corresponding EQE spectra of the optimal PTB7-Th:acceptors devices.

Photovoltaic properties.

In order to investigate the photovoltaic properties of the four acceptors, bulk heterojunction (BHJ) OSCs were fabricated with an inverted device architecture of ITO(indium tin oxide)/ZnO /PTB7-Th:acceptor/MoO₃/Al. The active layers were prepared by using chloroform as solvent. The optimized weight ratio of PTB7-Th:acceptors is 1:1.3 and the temperature of thermal annealing (TA) is 110 °C. Fig. 2a shows the current densityvoltage (J-V) curves of PTB7-Th:acceptors solar cells under the optimized conditions and the detailed device parameters are listed in Table 2. Interestingly, 6-position isomers outperform 4position isomers in photovoltaic performance. 4TIC based device shows the lowest PCE of 5.26% with a $V_{\rm oc}$ of 0.70 V, a $J_{\rm sc}$ of 14.58 mA/cm² and a FF of 48.7%, while changing the linkage position dramatically prompts all parameters leading to a higher PCE of 8.13%. Meanwhile, fluorine substitution on IC group decreases the $V_{\rm oc}$ around 0.1 V which is consistent with the tendency of lowering LUMO levels in relevant acceptors, but significantly enhances the J_{sc} and FF, and then synergistically realizing the best PCE of 10.74% with a J_{sc} of 25.79 mA/cm⁻², a $V_{\rm oc}$ of 0.60 V and a FF of 69.4% in the champion device PTB7-Th:6T4F. The external quantum efficiency (EQE) curves are shown in Fig. 2b. The 6T4F-based device exhibits a higher EQE

value over 70% in the region from 600 to 900 nm with the maximum value reaching 73.7%, indicating both polymer donor and acceptor make a considerable and complementary contribution to the whole J_{sc} values. The J_{sc} values calculated from the EQE curves are 14.93, 16.97, 19.14, and 24.28 mA/cm⁻² for the 4TIC, 4T4F, 6TIC, and 6T4F based devices, respectively. All the integrated J_{sc} values are within about 5% errors compared to those values obtained from J-V curves, indicating that the measurements are reliable for the PCEs. The EQE response of devices based on 6-position isomers is much higher than that of 4-isomers. To rationalize this, the absorption of various blend films are measured (Fig.S1). However, the absorption spectra show approximate intensity for the analogues. Furthermore, photoluminescence (PL) experiments have been carried out to probe the origin of the varied performance as shown in Fig. S2. For the four blend films, the PL emissions of PTB7-Th (excited at 685 nm) are completely quenched by acceptors respectively, indicating efficient charge transfer from polymer donor PTB7-Th to electron acceptors. The PL emissions of 4TIC, 4T4F, 6TIC and 6T4F were efficiently quenched in blend films with quenching efficiencies of 72.6%, 79.8%, 87.4%, and 93.9%, suggesting better charge transfer between 6-position isomers and PTB7-Th, thus leading to higher photocurrent.

Acceptors ^{a)}	V _{oc} (V)	J _{sc} (mA/cm²)	J _{cal} ^{b)} (mA/cm²)	FF (%)	PCE ^{c)} (%)	μ _{hole} (cm² V ⁻¹ s ⁻¹)	$\mu_{ ext{electron}}$ (cm ² V ⁻¹ s ⁻¹)
4TIC	0.70±0.00	14.58±0.53	14.93	48.7±0.5	5.26 (5.00±0.25)	7.97×10 ⁻⁴	4.36×10 ⁻⁴
4T4F	0.60±0.00	17.32±0.60	16.97	60.0±0.6	6.58 (6.26±0.30)	1.13×10 ⁻³	4.76×10 ⁻⁴
6TIC	0.74±0.00	19.22±0.67	19.14	54.1±0.5	8.13 (7.74±0.38)	1.35×10 ⁻³	9.76×10 ⁻⁴
6T4F	0.60±0.00	24.87±0.70	24.28	68.6±0.6	10.74 (10.22±0.50)	1.41×10 ⁻³	1.27×10 ⁻³

a) The donor:acceptor weight ratio is 1:1.3 with 1% CN as additive and thermal annealed at 110 °C; b) The integral J_{sc} calculated from the EQE curves; c) The average values and standard deviations in parentheses are statistical data from ten independent cells

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Fig. 3 (a) J_{Ph} - V_{eff} characteristics and (b) light intensity dependence of J_{sc} for the optimal PTB7-Th:acceptors devices.

Charge transport, exciton dissociation and charge recombination

The charge transport properties of the PTB7-Th:acceptors films are evaluated for hole-only devices ITO/PEDOT:PSS/PTB7-Th:acceptors/MoO₃/Al and electron-only devices ITO/ZnO/ PTB7-Th:acceptors /ZnO/Al by the space-charge limited current (SCLC) method (Fig. S4 and Table 2). The blend films based on 6-postion acceptors shows higher mobilities, in particular for the electron which typically transports along the pathway formed by acceptor. Furthermore, 6-position isomers exhibit more balanced charge transport than 4-position isomers. In addition, the fluorination in terminal groups is able to enhance both hole and electron mobilities. Consequently, the hole and electron mobilities for the PTB7-Th:6T4F film are calculated to be 1.41×10⁻³ and 1.27×10⁻³ cm² V⁻¹ s⁻¹, respectively. This enhanced and more balanced mobility leads to the champion device performance with the best FF and J_{sc} . The diversity of charge mobility is interrelated with morphology and microstructure which will be discussed in following section.

In order to understand the mechanisms of exciton dissociation and charge extraction in the devices based on varied acceptors, the variation of photocurrent density (J_{ph}) with effective voltage (V_{eff}) is employed and shown in **Fig. 3a**. J_{ph} is defined as $J_{ph} = J_L - J_D$, where J_L and J_D are the current densities under illumination and in dark, respectively. $V_{\rm eff}$ is described as $V_{\rm eff}$ = $V_{\rm o}$ - $V_{\rm bias}$, where $V_{\rm 0}$ is the voltage at which $J_{\rm ph}$ is zero and V_{bias} is the applied external voltage bias. In general, it is assumed that at high $V_{\rm eff}$, photogenerated excitons can be dissociated into free charge carriers and collected by the individual electrodes efficiently. Herein, for these four devices, the $J_{\rm ph}$ reaches the saturation current density (J_{sat}) at high V_{eff} (> 2V). The exciton dissociation probability (P_{diss}) and collection probability (P_{coll}) were estimated by the ratio of J_{ph}/J_{sat} in which $J_{\rm ph}$ is obtained under short circuit and maximal power output conditions, respectively. The P_{diss}/P_{coll} are 78.2%/67.7%, 92.6%/73.4%, 89.9%/67.6% and 94.5%/82.1% for 4TIC, 4T4F,

6TIC and 6T4F based devices, respectively. These results imply that 6-position linkage and fluoro-substituent are able to improve the P_{diss}/P_{coll} in relevant devices. Thus, the 6T4F based device exhibits the most efficient exciton dissociation and charge collection process and this contributes to its enhanced values of J_{sc} and FF.

The charge carrier recombination mechanism was further examined by measuring the correlation between V_{oc} or J_{sc} and light intensity (P_{light}) as shown in Fig. S3 and Fig. 3b. The slope of $V_{\rm oc}$ versus light intensity can help to verify the main recombination mechanism in the OSCs. When the slope is kT/q where k is the Boltzmann constant, T is the temperature and q is the elementary charge, bimolecular recombination is the primary mechanism. A slope of 2 kT/q implies that the trapassisted or Shockley-Read Hall (SRH) recombination is dominant, The values of slopes for 4TIC, 4T4F, 6TIC and 6T4Fbased devices are about 1.09 kT/q, 1.24 kT/q, 1.11 kT/q and 1.37 kT/q (Fig. S3), respectively, indicating that the trap-assisted recombination is suppressed and bimolecular recombination is domain in all fabricated devices. The dependence of J_{sc} with P_{light} can be described as $J_{sc} \propto (P_{\text{light}})^{\alpha}$. In general, when the value of α is close to unity, bimolecular recombination of charge carriers is negligible. The values of α for 4TIC, 4T4F, 6TIC and 6T4F based devices are 0.934, 0.936, 0.911 and 0.975, respectively, which manifests that bimolecular recombination is more suppressed in the 6T4F based device compared to another three devices.

Morphology characterization

To investigate the impact of isomerism on the morphology of devices, 6T4F, 6TIC, 4T4F and 4TIC neat films as well as blend films were characterized by atomic force microscopy (AFM). The neat films of 6TIC and 6T4F show greater root mean square (RMS) roughness with values of 2.66 nm and 10.8 nm respectively, compared with 4TIC (0.49 nm) and 4T4F (0.90 nm) (**Fig. S5**), indicating stronger aggregation. From the AFM height images (**Fig. 4**), we observed uniform surfaces for all four blend films. The PTB7-Th:4TIC and PTB7-Th:4T4F blend films show

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Fig.5. 2D GIWAX patterns of (a) PTB7-Th:4TIC, (b) PTB7-Th:4T4F, (c) PTB7-Th:6TIC, (d) PTB7-Th:6T4F. (e) Corresponding 1D line-cut profiles.

relatively small root mean square (RMS) roughness with values of 1.68 and 1.25 nm, respectively. No large phase separation appears for both films, indicating the excessive miscibility between polymer donor and 4-position acceptors. It can be deduced that the extremely low crystallization in the blend films is unfavorable for efficient charge separation and transportation, and consequently limiting device performance especially J_{sc} and FF. As for PTB7-Th:6TIC and PTB7-Th:6T4F blend films, the aggregate becomes evident and the RMS is increased up to 2.30 and 3.15 nm, respectively, indicating the existence of phase separation induced by 6TIC or 6T4F with improved crystallinity.

To get a deep insight into the molecular packing structures, the four blend films are studied by grazing incidence wide-angle X-ray scattering (GIWAXS), as shown in **Fig. 5**. The key

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parameters calculated from the GIWAXS line-cut profiles for the packing behavior of these films are displayed in Table S1. It is well known PTB7-Th tends to pack with face-on orientation, leading to a lamellar packing (100) peak at around 0.27 Å⁻¹ in the in-plane (IP) direction and a π - π stacking (010) diffraction peaks at 1.57 Å⁻¹ in the out-of-plane (OOP) direction,⁴⁷ both of which are observed in Fig. 5 with relatively weak intensity. Compared to the peaks for PTB7-Th, much stronger diffraction peaks resulted from acceptors are evident at approximate 0.34 Å⁻¹ in IP and 1.86 Å⁻¹ in OOP direction in all four blend films, corresponding to lamellar packing and π - π stacking. The π - π distances are calculated to 3.39 Å (4TIC), 3.36 Å (4T4F), 3.38 Å (6TIC) and 3.36 Å (6T4F), respectively. Such exceptionally tight π - π stacking implies a very strong intermolecular interaction in these NFAs which may be resulted from their rigid planar skeletons. Notably, the blend film based on 6-position isomers show stronger and sharp scattering peaks, compared to those of 4-position isomers. As depicted in Table S1, the coherence lengths evaluated form full width at half maximum (FWHM) of 6-position isomers are bigger, indicating 6-position isomers possess higher packing order even in blend film. This feature is believed to be beneficial for constructing a well-organized active layer, and thus helping 6T4F to achieve high efficiency.

Conclusions

In summary, four near-infrared NFAs were designed and synthesized through tailoring the A-TT-D-TT-A molecular backbones, in which an asymmetrical ester-substituted thieno[3,4-b]thiophene with a stable quinoid structure is employed as bridge to further minify the bandgap. Due to different linkage positions of asymmetrical TT, these acceptors are classified to two types: 4-position isomers (4TIC and 4TIF) and 6-position isomers (6TIC and 6T4F). The four molecules show strong absorption in near-infrared range, wherein the absorption of 4T4F and 6T4F is exceeding 1000 nm since the fluorinated terminals enhance the intramolecular charge transfer. Noted that the 6-position isomers show superior photovoltaic performance compared to 4-position isomers. A champion device based on 6T4F is obtained with a PCE of 10.74% with a better J_{sc} (25.79 mA cm⁻²) and FF (69.4%). This interesting result can be deduced that higher packing order demonstrated by UV-vis absorption in solid state and GIWAXS facilitates the exciton dissociation and charge transporting, leading to enhanced charge mobility and FF. This work provides a solution for designing NIR high-performance organic semiconductors by the incorporation of quinoid unit, and reveals the relationship between isomeric structure and photoelectric properties, eventually leading to a bright future of near-infrared OSCs in emerging applications.

Conflicts of interest

The authors declare no competing financial interest.

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