A Near-infrared Non-fullerene Acceptor with Thienopyrrole-expanded Benzo[1,2-b:4,5-b']dithiophene Core for Polymer Solar Cells

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INTRODUCTION

Bulk heterojunction (BHJ) organic solar cells (OSCs) have attracted much attention in both academic and industrial fields, and have been viewed as a promising solar energy conversion technology. Over the past few decades, one of the most significant progresses in OSCs is the development of non-fullerene acceptors (NFAs) which boosted the power conversion efficiency (PCE) of OSCs over 17% for both single-junction devices and tandem devices. Unlike the fullerene-based acceptors, NFAs have several distinct advantages, including easily tunable molecular structure and energy-level, strong and broad optical absorption to near-infrared region, and low energy loss, etc. For example, structural modification of the electron-donating fused-ring unit in NFAs is an efficient way of tuning the energy-level, absorption region of NFAs as well as the corresponding active layer morphology, which offer the OSCs great potential to obtain high power conversion efficiency.

In general, conjugation of the core unit in NFAs is critical for tuning the optical properties, which is closely related to the intramolecular charge transfer (ICT) effect. The conjugated system generally depends on the number of fused-ring. When the fused-ring is enlarged from five to seven or even to nine, the conjugated system will be gradually enhanced. Therefore, the fused-rings are commonly extended with aromatic ring such as C-substituted cyclopentadiene fragment, S-substituted thiophene ring or derivative, or N-substituted pyrrole ring. Compared with the sp3-hybridized C-substituted cyclopentadiene, sp2-hybridized N-substituted pyrrole ring possesses stronger electron-donating ability along the backbone, which allows the extension of delocalized n-electron system to contribute conjugation, resulting in enhanced ICT effect and narrowed absorption. However, extending the heterocyclic ring and improving the rigidity and coplanarity often lead to low solubility and strong aggregation of NFAs in both solution and blend film. To improve the solubility of these large coplanar n-systems, solubilizing side chains have been functionalized on NFAs. Among them, two side chains on the C-bridge of cyclopentadiene could provide NFAs with excellent solubility. However, the sp3-hybridized C atoms with two out-plane side chains are unfavorable for interchain π-π interaction and intermolecular charge transfer. In contrast, pyrrole ring with sp2-hybridized N atoms, of which only one in-plane side chain is attached.

**Electronic Supplementary Information**

**Abstract** A near-infrared non-fullerene acceptor (NFA) BDTIC, based on thienopyrrole-expanded benzo[1,2-b:4,5-b']dithiophene unit (heptacyclic S,N-heteroacene) as core, is designed and synthesized. The aromatic pyrrole ring with strong electron-donating ability in the core enhances the intramolecular charge transfer effect, finely tunes the optical bandgap and absorption profile of BDTIC, and thus results in a narrowed optical bandgap ($E_{opt}$) of 1.38 eV and a near-infrared absorption to 900 nm. When BDTIC is paired with donor polymer PBDB-T to fabricate organic solar cells, the optimized device achieves a best power conversion efficiency of 12.1% with a short-circuit current density of 20.0 mA·cm$^{-2}$ and an open-circuit voltage of 0.88 V. The photovoltaic performance benefits from the broad absorption, weak bimolecular recombination, efficient charge separation and collection, and favorable blend morphology. This work demonstrates that thienopyrrole-expanded benzo[1,2-b:4,5-b']dithiophene unit (heptacyclic S,N-heteroacene) is a promising building unit to construct high-performance NFAs by enhancing the intramolecular charge transfer effect, broadening absorption as well as maintaining good intermolecular stacking property.

**Keywords** Organic solar cells (OSCs); Non-fullerene acceptors (NFAs); Heptacyclic S,N-heteroacene

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shows great potential for building NFAs to enhance ICT effect, broaden absorption as well as balance the solubility and intermolecular stacking property.

Based on the above considerations, a new heptacyclic S,N-heteroacene based NFA BDTIC with thiophyrrole-expanded benzo[1,2-b:4,5-6']dithiophene (BDT) unit as the core, and commonly employed electron-withdrawing unit 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile (IC) as the end groups was designed and synthesized. Compared to the NFA BT-IC, which incorporated cyclopentadiene-expanded BDT as the core and showed a low bandgap of 1.43 eV, BDTIC exhibited a narrowed optical bandgap ($E_{opt}$) of 1.38 eV and a strong near-infrared absorption to 900 nm. Moreover, BDTIC showed a decent solubility in commonly used solvents, enabling the fabrication of high-quality films. When PBDB-T was selected as a donor to fabricate OSCs, the optimized device achieved a PCE of 12.1% with an open-circuit voltage ($V_{oc}$) of 0.88 V, a short-circuit current ($I_{sc}$) of 20.0 mA·cm$^{-2}$ and a fill factor (FF) of 68%. The photovoltaic performance benefited from the broad absorption, weak bimolecular recombination, efficient charge separation and collection, and favorable blend morphology.

**EXPERIMENTAL**

**Materials**

$n$-BuLi (n-BuLi, 2.5 mol·L$^{-1}$ in n-hexane from ACROS), [1,1'-bis(diphenylphosphinopheno)ferrocene]dichloropalladium(II) complex with dichloromethane (Pd(dppf)Cl$_2$·DCM), bis(dibenzylidenediacetone)palladium(0) (Pd(dbazu$_2$), and 1,1'-ferrocenediyldiphenylphosphine) (dppf) were purchased from Sigma Aldrich. 2-(3-Oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC) was purchased from Sunatech. All solvents and materials were used without further purification unless specified. Compound 1 and compound 2 were synthesized following the procedure reported.$^{[31,32]}$ The synthetic route to BDTIC is depicted in Scheme 1.

**Synthesis of Compound 3**

$n$-BuLi in hexane (1.6 mol·L$^{-1}$, 3.94 mL, 6.3 mmol) was added dropwisely to a solution of 2,3-dibromothiophene (1.9 g, 7.86 mmol) in dry Et$_2$O (10 mL) at $-78$ °C. After stirring at $-78$ °C for 1 h, the solution was warmed up to room temperature. The resulting mixture was added to a ZnCl$_2$ solution in THF (1.071 g, 7.86 mmol) at $-78$ °C and then the mixture was warmed up to 0 °C and stirred for 1 h. Compound 2 (2.0 mg, 2.62 mmol) and Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (128 mg, 0.15 mmol) were added to the resulting mixture, which was stirred at 50 °C for 24 h. After the removal of the solvent under reduced pressure, the residue was extracted with ethyl acetate and washed with water. The collected organic layer was dried with MgSO$_4$ (magnesium sulfate) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to get product as yellow oil (0.97 g, 40%).$^{[33,34]}$$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$, ppm): 7.51 (d, $J$=5.7 Hz, 2H), 7.14 (d, $J$=5.4 Hz, 2H), 4.12 (d, $J$=6.6 Hz, 4H), 2.13–1.95

![Scheme 1 Synthetic route to BDTIC.](https://doi.org/10.1007/s10118-020-2440-8)
Synthesis of Compound 4
A solution of compound 3 (1.17 g 1.26 mmol), sodium tert-butoxide (1.94 g 20.2 mmol), Pd(dba)2 (72.4 mg 0.126 mmol), and dpff (280 mg 0.505 mmol) in toluene (15 mL) was stirred at room temperature for 30 min. Then, 2-ethyl-1-hexylamine (0.39 g 3.03 mmol) was added and the mixture was stirred at 110 °C overnight. After cooling to room temperature, the solution was poured into DCM (50 mL) and washed with H2O (3×100 mL). The organic phase was dried with MgSO4 and the solvent was removed under reduced pressure. Finally, the residue was purified by column chromatography on silica gel (petroleum ether) to get the product as yellow oil (0.61 g 56%). The crude BDTIC was further purified by flash column chromatography with the eluent of dichloromethane/hexanes (2/1) to get the product as red solid (415 mg 39%). The characterization of BDTIC was carried out on a SHIMADZU UV-3600 spectrophotometer. Cyclic voltammetry (CV) was carried out on a computer-controlled Keithley 2400 source measurement unit under 1 sun, AM 1.5G spectrum from solar simulator (Taiwan, Enlitech SS-FS) with physical mask of 0.04 cm2 effective area. The light intensity was calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech, China), giving a value of 100 mW·cm−2. The external quantum efficiency (EQE) spectra were measured on a commercial EQE measurement system (QE-R3011, Enlitech, China).

RESULTS AND DISCUSSION
Characterization of BDTIC
The chemical structures of each compound were characterized by high-resolution mass spectrum (MALDI-TOF) and nuclear magnetic resonance (1H-NMR and 13C-NMR) as shown in Figs. S1–S3 (in the electronic supplementary information, ESI). BDTIC shows decent solubility in common organic solvents such as chloroform (CF), chlorobenzene (CB), and o-dichlorobenzene (ODCB) at room temperature, endowing good solution processability for solar cell fabrication. Besides, BDTIC exhibits good thermal stability with 5% weight loss (T5) at 242.4 °C as measured by thermogravimetric (TG) analysis in nitrogen (Fig. S4 in ESI). Density functional theory (DFT) calculations at the B3LYP/6-31G (d, p) level were carried out to study the molecular conformation of BDTIC. To simplify the calculation, 2-ethylhexyl side chains on nitrogen and oxygen atoms were replaced by methyl groups. As shown in Fig. 1, due to the weak steric hindrance on nitrogen atoms, the fused-ring core in simulated molecular configuration presents a planar and rigid confor-
mation, which is vital for molecular packing and crystallization. We can also observe that the electron density is well delocalized along the molecular backbone, rationalizing our design of using pyrrole ring to extend the conjugation of NFAs. In comparison, the electron densities on BT-IC HOMO are mainly localized at the central unit and two twisted side chains are attached on carbon atom.

The optical absorption of BDTIC in thin film and chloroform solution was measured by UV-Vis absorption spectra (Fig. 2a), and corresponding absorption data are listed in Table S1 (in ESI). BDTIC exhibits a strong absorption range from 300 nm to 800 nm in solution with a high molar extinction coefficient of $1.94 \times 10^5$ L·mol$^{-1}$·cm$^{-1}$. The absorption peaks in solution and thin film are located at 714 and 800 nm, respectively. The red-shifted absorption (~86 nm) of thin film in comparison with that of solution indicates strong aggregation of molecular backbone in the solid state, which is consistent with our expectation that one in-plane side chains in pyrrole ring can offer BDTIC strong packing ability. From absorption edges, $E_g$ of BDTIC is determined to be 1.38 eV. The narrowed $E_{\text{opt}}$ of BDTIC versus that of BT-IC suggests the $N$-substituted pyrrole ring offers strong electron-donating ability along the backbone, which allows the extension of the delocalized $n$-electron system to contribute conjugation, resulting in enhanced ICT effect and narrowed absorption. The electrochemical cyclic voltammetry (CV) method was employed to evaluate the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level of BDTIC (Fig. 2b). The onset oxidation and reduction potentials were calibrated using the Fc/Fc$^+$ redox couple of 0.39 eV as the reference. The HOMO and LUMO energy levels of BDTIC are estimated to be $-5.30$ and $-3.85$ eV.

![Simulated molecular conformations and frontier molecular orbital distributions of BDTIC.](image1.png)

Fig. 1  Simulated molecular conformations and frontier molecular orbital distributions of BDTIC.

![Normalized absorption spectra of BDTIC, PBDB-T, and PBDB-T:BDTIC blend; Cyclic voltammetry curves of Fc/Fc$^+$ and BDTIC; The chemical structures of PBDB-T and BDTIC; Energy diagrams of PBDB-T and BDTIC.](image2.png)

Fig. 2  (a) Normalized absorption spectra of BDTIC, PBDB-T, and PBDB-T:BDTIC blend; (b) Cyclic voltammetry curves of Fc/Fc$^+$ and BDTIC; (c) The chemical structures of PBDB-T and BDTIC; (d) Energy diagrams of PBDB-T and BDTIC.
Photovoltaic Performances of OSCs

Wide bandgap polymer PBDB-T\(^{[37]}\) was selected as an electron donor, for it exhibits a complementary absorption and favorable energy level with BDTIC. The chemical structures and energy level diagram of materials are presented in Figs. 2(c) and 2(d). Interestingly, compared with the BDTIC neat film, the absorption edge of PBDB-T:BDTIC blend film exhibits a ~50 nm blue-shift, which might be due to the good miscibility between PBDB-T and BDTIC, and thus the strong aggregation of BDTIC is partially diminished.\(^{[38]}\) It is reported that the good miscibility between donor and acceptor is favorable for achieving reasonable device sizes as well as improving the device stability.\(^{[39]}\)

The photovoltaic properties of BDTIC were evaluated by using a conventional device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS)/PBDB-T:BDTIC/poly(9,9-bis(3-(N,N-dimethyl)-N-ethylammonium-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)dibromide (PFN-Br)/Ag. PFN-Br was used as cathode interfacial material to facilitate electron collection.\(^{[40,41]}\) The device optimization including the weight ratio of donor/acceptor (D/A), thermal annealing, and solvent additive selection was carried out in detail and the corresponding device data can be found in Tables S2–S6 (in ESI). The current density-voltage (J-V) characteristics of as-cast device and optimized device measured under solar simulator with AM 1.5G spectrum at 100 mW·cm\(^{-2}\) are shown in Fig. 3(a) and the device parameters are listed in Table 1. As-cast device exhibits a best PCE of 9.9% (Avg. 9.8%) with a \(V_{oc}\) of 0.87 V, a \(J_{sc}\) of 18.6 mA·cm\(^{-2}\), and an FF of 61%. In comparison, the optimized device obtains a best PCE of 12.1% (Avg. 12.0%) with a \(V_{oc}\) of 0.88 V, a \(J_{sc}\) of 20.0 mA·cm\(^{-2}\), and an FF of 68%. It can be found that both \(J_{sc}\) and FF are significantly improved in the optimized device. The external quantum efficiency (EQE) spectra of as-cast device and optimized device are shown in Fig. 3(b). It can be found that both as-cast device and optimized device have broad responses covering the wavelength range from 300 nm to 860 nm. The optimized device shows EQE response over 70% in the wavelength region of 550–770 nm and has a maximum EQE response of 74% at ~670 nm, indicating efficient charge generation and collection. The integrated \(J_{sc}\) of as-cast and optimized devices from the EQE spectra is 18.2 and 19.5 mA·cm\(^{-2}\), respectively. These values match well with the J-V measurement with errors within 5%.

Charge Transport, Extraction, and Recombination in OSCs

To characterize the charge transport behavior of BDTIC, we employed the space charge-limited current (SCLC) method to evaluate the hole (\(\mu_h\)) and electron (\(\mu_e\)) mobilities with hole-dominant device ITO/PEDOT/PBDB-T:BDTIC/Ca/Ag and electron-dominant device ITO/ZnO/PBDB-T:BDTIC/Ca/Ag. \(\mu_h\) and \(\mu_e\) were determined by fitting the dark current to the model of single-carrier SCLC, which is described by the equation:\(^{[42]}\)

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_n \mu_e \frac{E^2}{L^3} \]
charge and \( I \) is the thickness of the active layer. The \( G_{\text{max}} \) value of the optimized device is figured to be 1.23 \( \times 10^{-7} \) m\(^2\)V\(^{-1}\)s\(^{-1}\), which is slightly higher than that of the as-cast device (1.13 \( \times 10^{-7} \) m\(^2\)V\(^{-1}\)s\(^{-1}\)). Under short-circuit condition, the exciton dissociation probability \( P(E,T) \) can be obtained by using the formula \( P(E,T) = J_{\text{ph}}/J_{\text{sat}} \). As-cast device and optimized device exhibit high \( P(E,T) \) value of 96.72% and 96.42%, respectively. The results of both \( G_{\text{max}} \) and \( P(E,T) \) values indicate that BDTIC based devices have efficient charge generation and separation processes.

To investigate the charge recombination behavior, we measured the light intensity dependence of \( J_{\text{sc}} \) with the function of \( J_{\text{sc}} \propto P_{\text{light}}^\alpha \) where the fitted value \( \alpha \) close to 1 means negligible bimolecular recombination in the device.\(^{[44,45]}\) The \( \alpha \) value of the optimized device and as-cast device is calculated to be 0.991 and 0.986, respectively, suggesting low bimolecular recombination in these devices and the bimolecular recombination in the optimized device is further suppressed (Fig. 3c). The transient photovoltage (TPV) and transient photocurrent (TPC) were measured to characterize the carrier lifetime and charge extraction time in these devices (Fig. S7 in ESI and Fig. 3d). The carrier lifetime is calculated to be 13 \( \mu \)s for the optimized device, which is far longer than 8.67 \( \mu \)s of the as-cast device. The charge extraction time of the as-cast device is calculated to be 0.41 \( \mu \)s, which is reduced to 0.32 \( \mu \)s in optimized device, indicating the charges can be extracted more rapidly in the optimized device. These results indicate weaker charge recombination and more efficient charge extraction in the optimized device, which are responsible for higher \( J_{\text{sc}} \) and FF.

**Morphologies of the Blended Films**

To further characterize the molecular packing of blend films, the microstructure of both as-cast device and optimized device was studied by grazing-incidence wide-angle X-ray scattering (GIWAXS) (Fig. 4a).\(^{[46]}\) The 2D GIWAXS patterns and intensity profiles of devices are shown in Fig. 4b. The neat PBDB-T film exhibits a lamellar peak at \(-0.37 \text{ Å}^{-1}\) and \( n-n \) stacking peak at

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**Table 1**: Photovoltaic parameters of as-cast and optimized devices.

|                  | \( V_{\text{oc}} (V) \) | \( J_{\text{sc}} \) (mA cm\(^{-2}\)) | FF (%) | PCE (%) |
|------------------|------------------------|----------------------------------|-------|---------|
| As-cast          | 0.87                   | 18.6                             | 61    | 9.9 (9.8) |
| Optimized        | 0.88                   | 20.0                             | 68    | 12.1 (12.0) |

\(^{a}\) Statistical data obtained from 8 independent devices.

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu V^2 \]

where \( J \) is the current density, \( \mu \) is the zero-field mobility, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the relative permittivity of the material, \( d \) is the thickness of the active layers, and \( V \) is the effective voltage (\( V_{\text{appl}} - V_{\text{bi}} - V_{\text{sh}} \)). \( \mu_h \) and \( \mu_e \) can be calculated from the slope of the \( J^{1/2} - V \) curves (Fig. 55 in ESI). Compared to the as-cast device with \( \mu_h \) of 1.23 \( \times 10^{-4} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) and \( \mu_e \) of 9.67 \( \times 10^{-5} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\), the optimized device shows higher \( \mu_h \) of 2.92 \( \times 10^{-4} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) and \( \mu_e \) of 2.33 \( \times 10^{-4} \) cm\(^2\)V\(^{-1}\)s\(^{-1}\), respectively. Both devices exhibit balanced charge mobilities with \( \mu_h/\mu_e \) ratios of 1.27 for as-cast device and 1.25 for optimized device. These results indicate that the optimized device presents higher charge mobilities, which is ascribed to the more ordered molecular packing as verified by the later morphology characterizations.

Then, we studied the charge generation and separation in devices by testing the photocurrent density (\( J_{\text{ph}} \)) versus effective voltage (\( V_{\text{eff}} \)).\(^{[43]}\) \( J_{\text{ph}} \) is defined from the equation of \( I_{\text{ph}} = I_{\text{light}} - I_{\text{dark}} \), where \( I_{\text{light}} \) and \( I_{\text{dark}} \) are the current densities under illumination and in the dark condition, respectively. \( V_{\text{eff}} \) is calculated from \( V_{\text{eff}} = V_{\text{oc}} - V_{\text{bi}} \), whereas \( V_{\text{oc}} \) is defined as the voltage when \( J_{\text{ph}} \) is zero and \( V_{\text{bi}} \) is the applied external voltage. The relevant calculated parameters are listed in Table S7 (in ESI) and \( J_{\text{ph}} \) versus \( V_{\text{oc}} \) characteristic is shown in Fig. S6 (in ESI). Herein, by applying a 2 V reverse bias to the as-cast device and optimized device, \( J_{\text{ph}} \) becomes saturated (\( J_{\text{sat}} \)), at which all photogenerated excitons are dissociated into free charge carriers and collected by the corresponding electrodes. The maximum charge generation rate \( G_{\text{max}} \) is evaluated by the formula \( G_{\text{max}} = J_{\text{sat}}/qI \), where \( q \) is elementary charge.

**Fig. 4** (a) 2D GIWAXS pattern and (b) GIWAXS intensity profiles along the in-plane (dashed lines) and out-of-plane (solid line) directions.

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~1.74 Å⁻¹ in out-of-plane (OOP) direction. Meanwhile, a relatively weak lamellar peak at 0.30 Å⁻¹ can also be observed in neat PBDB-T film in the in-plane (IP) direction, indicating the coexistence of face-on and edge-on molecular orientation, but preferably face-on orientation of neat PBDB-T film. Neat BDTIC film exhibits a strong lamellar peak at 0.46 Å⁻¹ and a weak n-n stacking peak at 1.80 Å⁻¹ in the OOP direction, while a weak n-n stacking peak in the IP direction at 1.80 Å⁻¹, demonstrating an edge-on dominant structure. When blending BDTIC with PBDB-T, the patterns of both devices maintain the scattering features of PBDB-T, indicating the molecular packing of PBDB-T is preserved but the orientation of BDTIC is partially diminished, which is consistent with the UV-absorption spectrum of PBDB-T:BDTIC where the absorption was blue-shifted compared with BDTIC. Further, the optimized blend film shows sharper lamellar diffraction peaks at ~0.3 Å⁻¹ (belong to the diffraction of PBDB-T) in both OPP direction and IP direction, indicative of stronger packing, which is beneficial to charge transport as verified by SCLC measurements.

The morphologies were further verified by atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Fig. S8 in ESI). As shown in AFM images, the optimized device film exhibits uniform and smooth surface morphology with a relatively small root-mean-square roughness of 1.75 nm compared with the as-cast device of 3.93 nm. In the AFM phase images, the optimized device film presents a uniform and appropriate phase separation while the as-cast device film shows a rough surface with large domains. In the TEM images, the as-cast device also exhibits excessive phase separation in the thin film. In contrast, the optimized device displays a distinct phase separation with more reasonable domain size, which may be due to the more closely packed molecular as demonstrated in GIWAXS measurement.

CONCLUSIONS

In this work, we designed and synthesized a heptacyclic S,N-heteroacene based NFA BDTIC. Compared to the BT-IC incorporating cyclopentadiene with sp³-hybridized C as extended fused-ring, BDTIC exhibits narrowed optical bandgap (geff) of 1.38 eV and strong near-infrared absorption to 900 nm, which is attributed to the extension of the delocalized π-electron system. When blended with polymer donor PBDB-T, PCE of the optimized device reached 12.1% with a short-circuit current density of 20.0 mA cm⁻², an open-circuit voltage of 0.88 V, and a fill factor of 68%. The photovoltaic performance results from the broad absorption, weak bimolecular recombination, efficient charge separation and collection, and favorable blend morphology. Our results demonstrate that thienopyrrole-expanded benzo[1,2-b:4,5-d]thiophene unit (heptacyclic S,N-heteroacene) is a promising building unit to construct high-performance NFAs by enhancing the intramolecular charge transfer effect, broadening absorption band as well as maintaining good intermolecular stacking property.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2440-8.

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