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Novel wide-bandgap non-fullerene acceptors for efficient tandem organic solar cells†

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The power conversion efficiency (PCE) of tandem organic photovoltaics (OPVs) is currently limited by the lack of suitable wide-bandgap materials for the front-cell. Here, two new acceptor molecules, namely IDTA and IDTTA, with optical bandgaps (E_g^{opt}) of 1.90 and 1.75 eV, respectively, are synthesized and studied for application in OPVs. When PBDB-T is used as the donor polymer, single-junction cells with PCE of 7.4%, for IDTA, and 10.8%, for IDTTA, are demonstrated. The latter value is the highest PCE reported to date for wide-bandgap ($E_g^{\text{opt}} \geq 1.7$ eV) bulk-heterojunction OPV cells. The higher carrier mobility in IDTTA-based cells leads to improved charge extraction and higher fill-factor than IDTA-based devices. Moreover, IDTTA-based OPVs show significantly improved shelf-lifetime and thermal stability, both critical for any practical applications. With the aid of optical-electrical device modelling, we combined PBDB-T:IDTTA, as the front-cell, with PTB7-Th:IEICO-4F, as the back-cell, to realize tandem OPVs with open circuit voltage of 1.66 V, short circuit current of 13.6 mA cm⁻² and a PCE of 15%; in excellent agreement with our theoretical predictions. The work highlights IDTTA as a promising wide-bandgap acceptor for high-performance tandem OPVs.

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Although initial attempts to commercialize organic photovoltaics (OPVs) were frustrated due to the power conversion efficiency (PCE) being lower than the estimated market viability of 15%,¹ recent years have witnessed a rapid increase in reported PCE values, primarily due to the advent of new non-fullerene acceptor (NFA) molecules.² Unlike fullerene-based bulk-heterojunctions (BHJs), NFAs combine improved optical absorption characteristics with optimal energetic pairing with a broad range of existing donor polymers, both of which have helped to push the PCE of single junction cells to 17%.^{3–6}

One way to improve the cell's PCE even further is by using multi-junction architectures (*i.e.*, tandem cells) where multiple

sub-cells with complementary optical absorption spectra are stacked on top of each other in order to harness photons from a wider range of the solar spectrum. To this end, in a recent study we predicted that carefully engineered tandem cells may achieve PCE values of over 25%.⁷ However, to reach these values, development of highly-efficient front-cells with a wide optical bandgap ($E_g^{\text{opt}} \approx 1.8\text{--}2.0$ eV) is urgently required.⁷ To this end, recent developments in the field of NFAs have focused almost exclusively on low bandgap materials (<1.5 eV),^{3,8–11} with wide-bandgap acceptors that work well with wide-bandgap polymer donors receiving significantly less attention.^{12,13} Thus, to exploit the additional opportunities offered by the tandem OPV architecture, high performance wide-bandgap NFAs are needed.

Here we report the development of two new wide-bandgap NFAs and their application in single-junction and tandem OPVs. Our synthetic strategy is based on the so-called acceptor-donor-acceptor (A–D–A) strategy,¹⁴ in which two electron-deficient groups are attached to an electron-rich core. The approach has been used previously for the synthesis of high performance, low-bandgap NFAs, as exemplified by the popular NFA, ITIC.^{2,15} Here, two strong 1,1-dicyanomethylene-3-indanone (IC) acceptors flank an electron-donating core of indacenodithienothiophene (IDTT) resulting in a relatively low bandgap material (1.59 eV). To this end, we have recently shown that substitution of the bulky phenylalkyl solubilizing groups at

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the bridgehead positions of the ITIC core with linear alkyl groups resulted in an NFA (C8-ITIC) with significantly improved device efficiency, primarily due to increased crystallinity and enhanced optical absorption.¹⁶ By replacing the strong IC acceptor end groups of C8-ITIC with the weaker acceptor 3-diethyl-2-thiobarbituric acid,^{17,18} we obtain the IDTTA (Fig. 1a) that exhibits a significant widening of the optical bandgap. Additionally, we examine the impact of the central donor unit on the performance by employing a shorter indacenodithiophene core (IDTA). When blended with the known wide-bandgap polymer, poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b'*]dithiophene))-*alt*-(5,5-(1',3'-di-2-thienyl-5',7' bis(2-ethylhexyl)benzo[1',2'-*c*:4',5'-*c'*]dithiophene-4,8-dione))] (PBDB-T),¹⁹ IDTA and IDTTA-based OPVs show PCEs of 7.4% and 10.8%, respectively. The latter value represents the highest reported PCE to date for wide-bandgap ($E_g^{\text{opt}} \geq 1.7$ eV) OPVs and is significantly higher than previously published NFA analogues.²⁰ Finally, with the aid of optical and electrical modelling, we were able to design and develop tandem OPVs with a PCE of 15% – a value 44% higher to that obtained from single-junction cells based on IDTTA. The work demonstrates how the availability of novel wide-bandgap materials can lead to tandem OPVs with improved performance characteristics.

The synthesis of C8IDTA and C8IDTTA (hereafter called IDTA and IDTTA, respectively) is shown in Scheme 1. In brief, the starting materials 4,4,9,9-tetraoctyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-dicarbaldehyde (C8IDT-CHO)²¹ and 6,6,12,12-tetraoctyl-6,12-dihydrothieno[3,2-*b*]thieno[2'',3'':4',5']thieno[2',3':5,6]-*s*-indaceno[2,1-*d*]thiophene-2,8-dicarbaldehyde (C8IDTT-CHO)¹⁶ were synthesized following previously reported methods.^{16,21} Conversion to the final acceptors IDTA and IDTTA was achieved by the Knoevenagel

condensation reaction between C8IDT-CHO or C8IDTT-CHO and 1,3-diethyl-2-thiobarbituric acid in good yield (see ESI†).

The chemical structures of IDTA, IDTTA and PBDB-T are shown in Fig. 1a, while the UV-vis absorption spectra of their solutions and solid films are presented in Fig. 1b. Importantly, the donor and acceptor materials exhibit overlap absorption across the visible-wavelength range (300–700 nm). Comparing IDTA to IDTTA, the extended core results in a modest red-shift of the absorption in chlorobenzene (CB), with absorption maxima at 600 and 621 nm, respectively. Critically, the molar attenuation coefficient (ϵ) in solution was increased from 2.04 to $2.58 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for the extended core. The absorption spectra of both materials red-shifted in thin-film, indicative of enhanced intermolecular interactions. IDTTA exhibits a red-shift of ≈ 33 nm, which is larger than that of IDTA (≈ 18 nm). The optical bandgap (E_g^{opt}), as measured by the onset of absorption, was 1.90 and 1.75 eV for IDTA and IDTTA, respectively (Fig. S1†). The ionization potential (IP) of IDTA and IDTTA were -5.88 eV and -5.81 eV respectively, measured *via* photoelectron spectroscopy in air (PESA) (Fig. S2†). The IP values (Fig. 1c) of the IDTA and IDTTA acceptors indicate that when combined with typical high-performance OPV polymer donors, the formation of a type-II heterojunction should be expected. The extended core of IDTTA also results in a higher electron mobility [$1.8(\pm 0.15) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$] than IDTA [$7.6(\pm 0.64) \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$], as determined *via* space-charge limited current (SCLC) measurements on electron-only devices (Fig. S3†).

To demonstrate the potential of IDTA and IDTTA as NFAs in wide-bandgap OPVs, we blended them with the donor polymer PBDB-T¹⁹ (E_g^{opt} : 1.83 eV) and fabricated inverted BHJ OPVs cells consisting of glass/ITO/ZnO/PFN-Br²²/PBDB-T:IDTA or IDTTA/

Fig. 1 (a) Chemical structures of the donor (PBDB-T) and acceptors (IDTA and IDTTA) reported in this work, (b) absorption spectra of the donor and acceptors (CB: chlorobenzene), and (c) energy levels of PBDB-T, IDTA, and IDTTA; ionization potential (IP) values inferred from photoelectron spectroscopy in air (PESA) measurements while optical bandgaps estimated from the onset of UV-vis absorption spectra (films) (ESI, Fig. S1†).

Scheme 1 Synthetic routes to IDTA and IDTTA.

MoO₃/Ag. All layers were spun from CB solutions and yielded films with thicknesses in the range of 90–100 nm. Device optimization included: donor/acceptor (D/A) ratio, use of processing additives, and post-processing thermal annealing (see ESI and Tables S1–S4†). All devices were tested under AM1.5G solar illumination (100 mW cm⁻²). Table 1 summarizes the open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill-factor (FF), and PCE of optimized OPVs. Both acceptors exhibited optimal performance in a 1 : 1 D/A ratio and after thermal annealing at 80 °C for IDTA and at 110 °C for IDTTA. IDTA-based OPVs exhibited a PCE up to 7.4% (Fig. 2a) with a high V_{OC} = 0.996 V, J_{SC} = 12.4 mA cm⁻² and FF = 60%. On the other hand, IDTTA-based cells yielded markedly better performance with V_{OC} = 0.98 V, J_{SC} = 15.8 mA cm⁻², and FF = 70%, the combination of which resulted in a maximum PCE of 10.8% (Table 1). The latter PCE is the highest reported to date for wide-bandgap ($E_g^{opt} \geq 1.7$ eV) OPVs as evident in Fig. 2b and Table S5.† Fig. 2a also shows that the experimentally-determined J - V characteristics (symbols) are in excellent agreement with the theoretical curves calculated *via* drift-diffusion simulations (solid lines), the details of which will be discussed below.

The external quantum efficiency (EQE) spectra of optimized BHJ solar cells based on IDTA and IDTTA acceptors, are shown in Fig. 2c. In agreement with the absorption spectra of PBDB-T and IDTA (Fig. 1b), the IDTA-based devices show EQE in the range of 300–690 nm. On the other hand, the EQE spectra for the IDTTA-based cells extend up to 720 nm. The trends in J_{SC} depicted in Fig. 2a are also reflected across the EQE spectra, with the higher J_{SC} values obtained for IDTTA-based cells (≈ 15 mA cm⁻²) paralleling the higher EQE across the whole measured spectra range (300–720 nm), and nearing 80% at the maximum EQE (*ca.* 580 nm). Fig. 2c shows the internal quantum efficiency (IQE) spectra, accounting only for the

contribution of charge generation and charge extraction (see ESI and Fig. S4†). Noticeably, the IQE of optimized BHJ cells based on IDTTA remain >80% across most of the visible spectrum, reaching a maximum value of 87% at 520 nm. In comparison, the IQE of IDTA-based cells is slightly lower fluctuating between 70–80%.

In an effort to understand the differences in PCE and IQE spectra between the two acceptors, we studied the charge photogeneration and recombination by transient-photovoltage (TPV) and charge-extraction (CE) measurements (at open-circuit condition).^{23,24} The bimolecular recombination rate constants (k_{BMR}) were inferred from the charge carrier lifetime (τ), obtained from TPV measurements, and charge carrier densities (n), obtained from CE measurements, using $k_{BMR} = 1/(\lambda + 1)n\tau$,²⁵ where λ is the recombination order determined from these analyses (Fig. S5a†). Interestingly, for all carrier densities, the k_{BMR} for IDTTA-based cells is higher than that of IDTA-based cells (Fig. 3a), in agreement with the photocurrent *vs.* light-intensity dependence analyses shown in Fig. S5b–d.†

The higher recombination rate constant observed in IDTTA-based cells might be associated with the higher hole and electron mobilities in comparison to IDTA-based cells.²⁶ To investigate whether the carrier mobilities in optimized BHJs are different, we performed SCLC measurements using carefully engineered unipolar devices. The obtained electron mobilities for IDTA and IDTTA-based BHJs were 4.3×10^{-5} and 1.0×10^{-4} cm² V⁻¹ s⁻¹, respectively (Fig. 3b, S6 and Table S6†). Evidently, the electron mobility in PBDB-T:IDTTA blends appears to be approximately twice as high as that in PBDB-T:IDTA. The hole mobility in the PBDB-T:IDTTA blend is also two-times higher than that of IDTA-based devices (Fig. 3b). In addition to SCLC, the charge-carrier mobility of the blends was also determined using photo-induced charge-carrier extraction by linearly

Table 1 PV performance parameters of the wide-bandgap acceptors IDTA and IDTTA in inverted BHJ devices when blended with the donor polymer PBDB-T. The statistics of 20 cells based on IDTA and IDTTA. Cells based on IDTA were annealed at 80 °C, while IDTTA one at 110 °C

Acceptor	V_{OC} (V)	J_{SC} ($J_{SC,max}$) (mA cm ⁻²)	FF (%)	PCE _{avg} (PCE _{max}) (%)	Energy loss (eV)
IDTA	0.99 ± 0.01	12.2 ± 0.26 (12.4)	60 ± 1.8	7.1 ± 0.11 (7.4)	0.84
IDTTA	0.98 ± 0.01	14.9 ± 0.42 (15.8)	69 ± 1.4	10.2 ± 0.21 (10.8)	0.77

Fig. 2 (a) Current density–voltage (J – V) characteristics (black solid lines are simulated J – V using drift-diffusion modeling), (b) comparison of PCE versus optical bandgap between different OPVs in the literatures with E_{opt} between 1.7 to 2.0 eV with the OPV in this work (details can be found in Table S5†). We consider the optical bandgap from the lowest bandgap of either donor or acceptor component in the blend. (c) EQE and IQE spectra for optimized BHJ solar cells fabricated from PBDB-T and the acceptors IDTA and IDTTA; AM1.5G solar illumination (100 mW cm^{-2}).

increasing voltage (photo-CELIV).²⁷ Unlike SCLC, CELIV is more sensitive to the faster carrier component in the photoactive blend and thus could arguably provide more relevant information for OPV cells. Interestingly, the photo-CELIV data (Fig. S7†) appear to be in excellent agreement with the SCLC measurements, yielding mobility values for PBDB-T:IDTTA approximately two-times higher than that of PBDB-T:IDTA cells. The improved charge transport in IDTTA-based cells is responsible for its higher device performance compared to IDTA-based cells.

Next, the Langevin recombination constant of the IDTTA-based cells was calculated using $k_L = q(\mu_h + \mu_e)/\varepsilon$ ^{28,29} yielding values two-times higher than that of IDTA-based cells (Fig. 3b). In the Langevin model diffusion of charge carriers of opposite sign toward each other occurs in their mutual coulomb field.²⁹ However, in OPVs non-geminate recombination rate constants are often lower by several orders of magnitude as compared to those predicted by the classical Langevin recombination model.^{30,31} This difference can be accounted for by introducing a prefactor γ_{pre} which then yields the following expression for the bimolecular recombination rate (k_{BMR}):

Fig. 3 (a) Bimolecular recombination rate k_{BMR} , extracted from charge carrier lifetime (τ) and charge carrier density (n), as a function of n . (b) Hole, electron, and effective mobilities (μ_h , μ_e , μ_D) of IDTA and IDTTA-based blends (with PBDB-T) obtained from dark J – V analyses (upper panel); Langevin recombination and total bimolecular recombination rate of the PBDB-T:IDTA and PBDB-T:IDTTA devices (lower panel). (c) Temperature-dependent V_{OC} for PBDB-T:IDTA and PBDB-T:IDTTA devices. (d) Photothermal deflection spectroscopy (PDS) absorption spectra of IDTA, IDTTA, PBDB-T, PBDB-T:IDTA, PBDB-T:IDTTA films and exponential fits to the sub-bandgap region extract the Urbach energy, E_U .

Fig. 4 Topography AFM images of (a) as-cast and (b) thermally annealed (TA) at 80 °C PBDB-T:IDTA BHJ layers, and (c) as-cast, (d) thermally annealed (TA) at 110 °C PBDB-T:IDTTA BHJ layers (the Z-value denoting the maximum height). (e–h) Topography AFM images with colour bar corresponding to the height in (a–d). (i–l) Phase AFM images corresponding to the topography AFM images in (a–d). (m) Surface height histograms of PBDB-T:IDTA extracted from the AFM images in (a) and (b) (the Z-value denoting the maximum phase). (n) Surface height histograms of PBDB-T:IDTTA extracted from the AFM images in (c) and (d).

$$k_{\text{BMR}} = \gamma_{\text{pre}} k_{\text{L}} = \gamma_{\text{pre}} q(\mu_{\text{h}} + \mu_{\text{e}})/\varepsilon \quad (1)$$

The values of γ_{pre} were determined using the analytical model proposed by Wetzelaer *et al.*³² (see Fig. 3b and Table S6†). The latter is based on the derivation of an analytical expression employing the concept of charge neutralization, a process that is competing with charge recombination. While charge recombination is the process of annihilation of two carriers of opposite sign, the oppositely charged carriers coexist in the case of charge neutralization. If charge recombination is sufficiently slow (meaning charge neutralization is effective), then the total amount of charge in the layer can exceed the net space charge, giving rise to an enhancement of the current.³² For both IDTA and IDTTA-based cells, it is evident that the double-carrier current exceeds the hole current (hence $\mu_{\text{D}} > \mu_{\text{h}}$, Fig. 3b), implying a similar reduction prefactor γ_{pre} in both cells. By using the hole, electron, and double-carrier mobility in eqn

(S1),† γ_{pre} can be calculated. Table S6† summarizes the extracted γ_{pre} values of the BHJ layers. For the PBDB-T:IDTA blend, we calculate a γ_{pre} value of 0.020 while for the PBDB-T:IDTTA blend, γ_{pre} is slightly lower, 0.016. While, the extracted recombination rate constants deviate from the predicted Langevin rates (Table S6†), they are in general agreement with the rate constants obtained from TPV and CE analyses in Fig. 3a.

To evaluate whether the parameters determined from our recombination analyses can accurately reproduce the experimentally-measured J - V characteristics, we performed drift-diffusion simulations using the device simulator Setfos 4.4 (FLUXim AG), assuming a device structure similar to that used in our experiments. The simulation assumes bimolecular recombination is the main recombination loss pathway and the charge generation efficiency is electric-field independent.⁷ Here, the refractive index n and extinction coefficient k of the photoactive layer as determined by ellipsometry, the charge mobility

Fig. 5 (a) 2-D GIWAXS images of the neat IDTA, neat IDTTA, blend PBDB-T:IDTA (as-cast and thermally annealed (TA) at 80 °C), and blend PBDB-T:IDTTA (as-cast and thermally annealed (TA) at 110 °C) films. (b) In-plane and out-of-plane line cut profiles.

obtained from SCLC measurements and the bimolecular recombination rate obtained from our analyses (Fig. 3b) were used as input parameters. Further details of the simulations and relevant procedures can be found elsewhere.^{7,26} As evident from Fig. 2a the bimolecular rate constant and the charge carrier mobility obtained from our analyses (dark J - V of unipolar and double-carrier devices) yields excellent agreement between the experimental and simulated OPV device performance (simulation input and output parameters are given in Tables S7 and S8†). This good match suggests that geminate recombination losses in IDTA and IDTTA-based cells are negligible and that the main recombination pathway is bimolecular recombination.

Although the IDTTA-based devices have a slightly lower V_{OC} , from Table 1 we conclude that the energy loss for this cell (0.77 eV) is lower than that of IDTA-based device (0.84 V). Extrapolating the temperature-dependent V_{OC} predicts the maximum interfacial band offset V_{OC} , approximated by the energy difference of acceptor's lowest unoccupied molecular orbital (LUMO) and donor's highest occupied molecular orbital (HOMO) $[(E_{A,LUMO} - E_{D,HOMO} - \Delta)/q]$.³³ Interestingly, a maximum V_{OC} of 1.25 V at $T = 0$ K is predicted for IDTTA-based cells while for IDTA-based cells the maximum V_{OC} is lower, 1.08 V (Fig. 3c). Additionally, the dependence of V_{OC} on temperature (T) deviates

from linearity for both blends at lower T . Specifically, V_{OC} follows a nonlinear relation with T and tends to saturate for low T in the case of OPVs with large energetic disorder.³⁴ Fig. 3d shows that the energetic disorder obtained from photothermal deflection spectroscopy (PDS) measurements³⁵ for both blend systems is quite similar (Urbach energies of 36–37 meV). In addition, we observe that V_{OC} starts to decrease at different temperatures for both BHJ systems (200 K for IDTTA and 240 K for IDTA, see Fig. 3c). The reason for the different temperature (*i.e.* the point at which the V_{OC} starts to saturate or decrease) is likely due to reduced charge separation owing to a decrease in electron-hole distance in charge transfer (CT states) at low temperature as discussed by Gao *et al.*³⁴ From this data we infer that the charge separation in IDTA-based cells is more difficult. Finally, the limited V_{OC} can also be partly attributed to reduced mobility at low temperatures when carrier mobility becomes limited by localized states.³⁶

Having identified the differences in carrier recombination and transport within the two different active layers (*i.e.* IDTA and IDTTA-based BHJs), we studied the surface morphology of the BHJ *via* atomic force microscopy (AFM). Fig. 4a–k presents the AFM topography and phase images for the PBDB-T:IDTA and PBDB-T:IDTTA BHJ layers [as-cast and thermally annealed (TA)]. The surface of BHJs with PBDB-T:IDTA contains smaller

Fig. 6 Normalized PCE degradation over time for IDTA and IDTTA-based BHJ solar cells (a) shelf storage lifetime (dark, in air, un-encapsulated) (b) after long-term annealing at 80 °C. Determination of thermal properties (glass transition T_g) from plasmonic nano-spectroscopy measurements of (c) as-cast PBDB-T:IDTA film, (d) 8 h annealed PBDB-T:IDTA film, (e) as-cast PBDB-T:IDTTA film, and (f) 8 hours annealed PBDB-T:IDTTA film. (g) Absorption spectra of PBDB-T:IDTA film during annealing at 80 °C in Argon. (h) Absorption spectra of PBDB-T:IDTTA film during annealing 80 °C in Argon.

features, while PBDB-T:IDTTA blends show significantly larger aggregates. Evidently, TA reduces the aggregation in both BHJ systems. In the case of IDTTA-based BHJs, we observe a more pronounced decrease of the surface root-mean-square (rms) roughness from 4.4 nm (for as-cast) to 1.9 nm (after annealing at 110 °C). In contrast, for IDTA-based layers, the rms reduces from 2 to 1.4 nm, before and after annealing at 80 °C, respectively. Fig. 4m and n presents the surface height histograms extracted from the AFM images. For both BHJs, the height distribution undergoes clear shifts toward lower heights after TA indicative of surface smoothening. The phase images (Fig. 4i–l) show a good correlation with the topography images.

Grazing incident wide-angle X-ray scattering (GIWAXS) measurements were used to study the structural order of the various layers (Fig. 5). As seen in 2-D diffraction patterns (Fig. 5a), the IDTA shows weak crystallinity, with an in-plane (100) peak at $0.43 \text{ \AA}^{-1}$ and broad π - π stacking in the out-of-plane direction at $1.37 \text{ \AA}^{-1}$. Interestingly, the IDTTA film shows strong structural order, with the (100) diffraction at $0.34 \text{ \AA}^{-1}$ in-plane (q_{xy}) and strong π - π stacking at 0.56 and $1.69 \text{ \AA}^{-1}$ out-of-plane (q_z), indicating that IDTTA is more crystalline than IDTA in line with its higher electron mobility (Fig. S3†). The scattering peaks of BHJ films (PBDB-T:IDTA and PBDB-T:IDTTA) are also shown in Fig. 5. For the as-cast PBDB-

T:IDTA film, the (100) peak located at $0.30 \text{ \AA}^{-1}$ is strong and mainly composed of PBDB-T lamellar packing features (see Fig. S8† for GIWAXS image of neat PBDB-T). The π - π stacking is broader in out-of-plane direction, and located at $1.71 \text{ \AA}^{-1}$ and is composed of features from both materials. After annealing at 80 °C, PBDB-T:IDTA exhibited slightly pronounced scattering signals at $0.29 \text{ \AA}^{-1}$ in in-plane (q_{xy}) and $1.71 \text{ \AA}^{-1}$ out-of-plane (q_z), suggesting that annealing improves lamellar packing as well as π - π stacking in the PBDB-T:IDTA BHJ system. The improved packing in PBDB-T:IDTA blend after TA, certainly contributes to the higher cell performance leading to higher FF and J_{SC} (Table S1†).

For the as-cast PBDB-T:IDTTA layer, the (100) peak is split into two peaks located at 0.30 and $0.34 \text{ \AA}^{-1}$, respectively. The relatively weaker (100) peak is attributed to PBDB-T whilst the stronger (100) peak to IDTTA, in line with the diffraction data for the neat layers. The π - π stacking in the blend layer of PBDB-T:IDTTA is broader in out-of-plane direction located at $1.59 \text{ \AA}^{-1}$ and consists of both materials' features, since the π - π stacking of PBDB-T and IDTTA is located at 1.72 and $1.55 \text{ \AA}^{-1}$, respectively. Moreover, the diffraction peak at $0.56 \text{ \AA}^{-1}$ in the out-of-plane direction is attributed to IDTTA, possibly suggesting a phase separation of IDTTA in the BHJ layer. Interestingly, we notice that TA at 110 °C reduces IDTTA crystallization, as the

Fig. 7 (a) Chemical structures of the active layer in back cells, (b) tandem OPV device structure, (c) PCE of tandem OPV devices predicted from optical-electrical modeling, (d) J - V curves of the optimized front-cell (PBDB-T:IDTTA), back-cell (PTB7-Th:IEICO-4F), and tandem cells.

intensity of both the in-plane ($q_{xy} = 0.35 \text{ \AA}^{-1}$) and out-of-plane ($q_z = 0.57 \text{ \AA}^{-1}$) weakens. On the other hand, the (010) peak of PBDB-T at $1.72 \text{ \AA}^{-1}$ increases after the TA. We thus conclude that TA increase the crystallization of PBDB-T but also improves the material mixing within the PBDB-T:IDTTA blend, resulting in higher FF and J_{SC} , but slightly reduced V_{OC} (see Table S3†).

Next, we studied the ambient stability and shelf lifetimes of the IDTA and IDTTA-based BHJ cells (Fig. 6a). For the stability test, as-prepared cells (*i.e.* un-encapsulated) were stored in air and under dark conditions and characterized *via* intermittent J - V measurements under simulated solar illumination. After 300 h exposure to air, the PBDB-T:IDTTA cells still retained nearly 90% of the initial PCE, whereas the PBDB-T:IDTA device retained only 68%. Even more impressive, after 700 h exposure to air, the PBDB-T:IDTTA cells retained 78% of their initial PCE, clearly demonstrating the long-term stability of this BHJ system. Moreover, the thermal stability was investigated by keeping the samples at 80°C for 250 h (Fig. 6b) inside a dry-nitrogen

glovebox ($<10 \text{ ppm O}_2$). PBDB-T:IDTTA appears quite robust with a gradual reduction in PCE by approximately 40% of its initial value. This is not the case for the PBDB-T:IDTA cells, which underwent a rapid decrease in performance, before a second more gradual drop occurred leading to a 73% PCE reduction.

In order to rationalize the improved thermal stability of PBDB-T:IDTTA cells, when compared to IDTA, we employed the plasmonic nanospectroscopy technique performed under inert atmosphere (Fig. 6c-f).^{37,38} Due to the non-equilibrium morphology of BHJ blends, the glass transition temperature (T_g) of the BHJ is critical and determines the thermal stability of the OPV cell.³⁹ Our measurements yield a $T_g = 116^\circ\text{C}$ for the as-cast PBDB-T:IDTA layer (Fig. 6c). Interestingly, the T_g of the layer reduces to 98°C following thermal annealing at 80°C for 8 h (Fig. 6d). On the other hand, as-cast PBDB-T:IDTTA BHJs exhibit a significantly higher T_g of 160°C (Fig. 6e), which decreases to 129°C after annealing at 80°C for 8 h (Fig. 6f). The results are

Table 2 Photovoltaic performance parameters of sub-cells and tandem OPVs [from experiment (Exp) and simulation (Sim)]. Device statistics from 15 devices

	Thickness (nm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (PCE_{max}) (%)
Front-cell	110	0.98 ± 0.01	14.9 ± 0.49	68 ± 1.3	10.0 ± 0.26 (10.4)
Back-cell	80	0.71 ± 0.01	21.0 ± 0.33	66 ± 3.0	9.8 ± 0.31 (10.3)
Tandem (Exp)	110/80	1.65 ± 0.007	13.1 ± 0.29	68 ± 1.5	14.7 ± 0.14 (15.0)
Tandem (Sim)	120/80	1.68	13.1	68	15.0

consistent with the inferior thermal stability of PBDB-T:IDTA blend as compared to PBDB-T:IDTTA.

Fig. 6g shows the absorption spectra of the two BHJs measured during TA. In the case of PBDB-T:IDTA, the absorption peaks shift to higher wavelength upon annealing at 80 °C (Fig. S9†). We attribute this to a diffusion-limited crystallization into a polymorph for temperatures below T_g in line with previous observations reported for other NFA-based BHJs.³⁸ The process seems to evolve with time as evident from the evolution of the absorption spectra shown in Fig. 6g. In contrast, the PBDB-T:IDTTA film shows no significant changes in the absorption spectra during annealing (Fig. 6h), a direct result of the system's higher thermal stability, further highlighting its potential for OPV applications.

Finally, we exploited the possibility of using the PBDB-T:IDTTA BHJ as the front-cell in a tandem OPV device and combined it with the near-infrared (NIR) absorbing PTB7-Th:IEICO-4F BHJ as the back-cell (Fig. 7a and S10a†). The EQE curves of the single-junction PBDB-T:IDTTA and PTB7-Th:IEICO-4F cells are presented in Fig. S10b† showing a broad and relatively high EQE response in the range 300–1000 nm. The sub-cells were then integrated to form the two-terminal inverted tandem OPV device shown in Fig. 7b. Further details on the cell fabrication can be found in the Experimental section. Device optimization was aided by optical and electrical modeling which enabled us to predict the optimal combination of the active layer thicknesses for both sub-cells.^{40,41} The modeling approach is based on the optical parameters and the performance of different single-junction cells, assuming no losses at the recombination contact. Fig. S11† provides the optical constants and the measured $J-V$ curves for different cells based on PBDB-T:IDTTA and PTB7-Th:IEICO-4F BHJs with different thicknesses.⁴¹

Fig. 7c displays the evolution of the calculated PCE as a function of the sub-cells' thicknesses. The predicted V_{OC} , J_{SC} , and FF are shown in Fig. S12.† Our calculations predict that front and back-cells with thicknesses of 120 and 80 nm, respectively, should yield cells with the highest attainable PCE. Fig. 7d presents the $J-V$ curves of an optimally designed tandem OPV for which maximum and average PCE values of up to 15% and 14.7%, respectively, in excellent agreement with our modelling results (Table 2). Specifically, tandem cells incorporating a front PBDB-T:IDTTA cell with a thickness of 110 nm and a back-cell of PTB7-Th:IEICO-4F with a thickness of 85 nm, yield the highest PCE of 15%, $V_{OC} = 1.65$ V, $J_{SC} = 13.6$ mA cm⁻², and a FF = 67%, which is among the best performance reported to date for tandem OPVs.⁴² Importantly, the experimental results are consistent with the theoretically-predicted PCE values, further validating its predictive power and usefulness for the design of advanced OPVs.

Conclusion

We have synthesized two novel wide-bandgap NFAs namely IDTA and IDTTA and investigated their potential in OPVs. Both molecules feature absorption characteristics suitable for application as front sub-cell in tandem OPVs, with the IDTTA

exhibiting higher electron mobility (1.8×10^{-4} cm² V⁻¹ s⁻¹) than IDTA (7.6×10^{-5} cm² V⁻¹ s⁻¹). When blended with PBDB-T, IDTA and IDTTA-based OPVs yielded PCE values of 7.4% and 10.8%, respectively. The latter value represents the highest PCE reported to date for BHJ OPVs with optical bandgap of ≥ 1.70 eV (Fig. 2b). Analysis of the cells' operating characteristics revealed that the main recombination pathway in IDTA and IDTTA-based devices is *via* bimolecular recombination, with the higher PCE of IDTTA-based cells attributed primarily to improved charge transport. These conclusions were corroborated by extensive device simulations. Importantly, un-encapsulated IDTTA-based cells were found to exhibit remarkably enhanced shelf lifetime and improved thermal stability as compared to IDTA-based cells. Finally, with the aid of optical-electrical modelling, we were able to develop two-terminal tandem OPVs where PBDB-T:IDTTA and PTB7-Th:IEICO-4F were used as the front and back sub-cells, respectively. Best performing tandem OPV cells yielded a maximum PCE of 15%, $V_{OC} = 1.65$ V, $J_{SC} = 13.6$ mA cm⁻², and a FF = 67%. This is an impressive accomplishment since the achieved PCE is >40% higher than that of the single-junction OPV. The work demonstrates the tremendous potential of the two new NFAs as wide-bandgap materials for application in tandem and/or (semi)transparent OPVs.

Experimental section

Materials

PBDB-T ($M_w = 75.6$ kDa, PDI = 3.63), PTB7-Th (poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene)-2-carboxylate-2,6-diyl)], $M_w = 247.2$ kDa, PDI = 2.06), IEICO-4F (2,2'-((2Z,2'Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile), and PFN-Br (poly[9,9-bis(6'-bromohexyl)fluorene-*alt*-co-1,4-phenylene]) were purchased from Solarmer Materials Inc (Beijing). ZnO nanoparticle (NP) dispersion in isopropanol was purchased from Avantama AG.

Single solar cell fabrication

Indium tin oxide (ITO) coated glass substrates (Kintec Company, 10 Ω sq.⁻¹) were cleaned by sequential ultrasonication in dilute Extran 300 detergent solution, deionized water, acetone and isopropanol for 20 min each. These substrates were then cleaned by UV-ozone treatment for 30 min. The ZnO precursor solution was prepared by dissolving 0.2 g of zinc acetate dihydrate in 60 μ l of ethanolamine and 2 ml of 2-methoxyethanol. Then, the ZnO precursor solution was spin-cast onto the UV-treated substrates, dried on a heating plate at 200 °C for 15 minutes. The samples were then transferred into a dry nitrogen glovebox (<10 ppm O₂). Subsequently, a thin layer of PFN-Br (PFN-Br was dissolved in methanol with concentration 0.5 mg ml⁻¹) was spin-coated with speed of 2000 rpm on ZnO for improving the interfacial properties. PBDB-T:IDTA or PBDB-T:IDTTA (ratio 1 : 1, 20 mg ml⁻¹ in

chlorobenzene) were then spun at different speeds. The samples were then annealed (80 °C for IDTA- and 110 °C for IDTTA-based blends) on the hot plate for 10 minutes. For PTB7-Th:IEICO-4F based device, the active layer was spin-coated at 1400 rpm for 60 s from CB solution (weight ratio 1 : 1.5, 20 mg ml⁻¹, 4% by volume chloronaphthalene (CN)). Finally, the samples were placed in a thermal evaporator and 100 nm of silver were then thermally evaporated under 5×10^{-6} mbar.

Tandem solar cell fabrication

The tandem devices were fabricated with an architecture of ITO/ZnO/PFN-Br/PBDB-T:IDTTA/MoO₃/Ag/ZnO NP/PTB7-Th:IEICO-4F/MoO₃/Ag. The PBDB-T:IDTTA active layers were fabricated *via* the same process as the single cells with different thicknesses. Subsequently, the MoO₃ layer (*ca.* 16 nm) was thermally evaporated on top of the active layer of the front sub-cell, followed by evaporation of 1 nm of silver. The ZnO nanoparticles layer in isopropanol (thickness *ca.* 15 nm) then spin-coated and annealed at 100 °C for 10 min in glove box. Then, the PTB7-Th:IEICO-4F active layers were fabricated *via* the same process as the single cells with different thicknesses. A MoO₃ layer (7 nm) and an Ag layer (100 nm) were then deposited on the active layer by vacuum evaporation under 5×10^{-6} mbar. The effective areas of cells were ~ 0.1 cm² defined by shadow masks.

Device characterization

J-*V* measurements of solar cells were performed in a N₂ filled glovebox using a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5G, with a KG-5 silicon reference cell certified by Newport. The carrier mobilities (hole, electron, and double-carrier mobilities) of PBDB-T:IDTA and PBDB-T:IDTTA BHJ devices were determined by fitting the dark currents of hole/electron-only/double-carrier diodes (device structures are shown in Fig. S6a†) to the space-charge-limited current (SCLC) model. EQE was characterized using a specially designed EQE system (PV measurement Inc.). Measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST. The IQE spectra were calculated from EQE spectra using the relation: $\text{IQE} = \text{EQE}/(1 - \text{Reflectance} - \text{Parasitic Absorption})$. The reflectance spectra were collected with the integrating sphere using the same EQE system while the parasitic absorption spectra were obtained from transfer matrix modelling. Temperature dependent *V*_{OC} measurements of the optimized devices were taken from high to low temperature values with 5 K intervals using Lakeshore CRX-4K cryogenic probe station where the samples are illuminated with white light (Thorlabs, MCWHL5). The light intensity is set to be the same during the measurements. All light-intensity dependence measurements on *J*-*V* curves, photo-CELIV, transient photovoltage (TPV), and charge extraction (CE) analyses were performed using the all-in-one measurement system PAIOS 3.2 (FLUXiM AG). PAIOS exploits a first function generator to control the light source (a

calibrated white LED with a rise/fall time of 100 ns) and a second function generator to control the applied voltage bias.

Photothermal deflection spectroscopy PDS

Measurements were performed using a home-built PDS setup. The light from a 250 W quartz tungsten-halogen lamp (Newport 66996-250Q-R1) was dispersed in a monochromator (LOT MSH-300) and used as pump, providing excitation across the UV-to-near-infrared spectral region. The pump light was modulated by a chopper operating at a constant frequency of a few hertz and focused on the sample, which was immersed in a chemically inert liquid (perfluorohexane (C6F14); Sigma-Aldrich) during the measurement. A small fraction of the monochromatic pump light was split off as intensity reference and measured by lock-in detection (Stanford Research Systems SR830 lock-in amplifier) using a pyroelectric detector (Newport DET-L-PYC5-R-P). Thin-film samples for PDS were prepared on cleaned quartz substrates by spin coating from the solution. A stabilized continuous-wave laser (Thorlabs HR S015 HeNe, 633 nm) was used as a probe beam source focused closely on the sample surface. The deviation of the probe beam was detected by a Si quadrant detector (Thorlabs PDP90A) using lock-in detection (Stanford Research Systems SR830). The entire setup was controlled by a home-built LabVIEW-based data acquisition and device control code. The Urbach energy (*E*_u) was extracted from $a = a_0 \exp(E/E_u)$, where *a* is the absorption coefficient, *a*₀ is a pre-exponential factor, and *E* is the photon energy.

Numerical device simulator

1D numerical drift-diffusion device simulator (Setfos 4.4 from FLUXiM AG) was used to predict the single-junction OPV device *J*-*V* curves. The optical constants (refractive index and extinction coefficient) for the active layers were collected by variable angle spectroscopic ellipsometry (VASE) with an M-2000 ellipsometer (J.A. Woolam Co., Inc). The active layers were cast on clean silicon substrates coated with SiO₂ (100 nm). The VASE measurements were performed with incident angles being varied from 50 to 80° in steps of 5° relative to the samples. The software Complete Ease (J.A. Woolam Co., Inc) was used to process all collected data, and the optical constants were inferred from the B-splines model.

GIWAXS characterization

GIWAXS characterization of active layer was performed at beamline 7.3.3, Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). X-ray energy was 10 keV and operated in top off mode. The scattering intensity was recorded on a 2D image plate (Pilatus 2M). The GIWAXS experiment was done in a closed chamber purged with Helium gas to suppress air scattering. The chamber was sealed using Kapton films, which give rise to blank cell scattering features.

Plasmonic nanospectroscopy

Measurements were done using nanoplasmonic sensor chips comprising 170 × 20 nm (diameter × height) Au nanodisk

arrays, coated by 10 nm Si_3N_4 thin film. Materials were deposited on the sensor by spin-coating from a 20 mg ml^{-1} chlorobenzene solution. The experiments were carried out under constant flow of 100 ml min^{-1} of Ar with heating rate of 5 $^\circ\text{C min}^{-1}$ in an insulated quartz tube gas flow reactor system with optical access, as described in detail elsewhere.³⁷

Modeling of multi-junction device J - V curves

In all tandem OPV device simulations, input characteristics obtained from optical transfer matrix modeling (sub-cell J_{sc} values) are combined with the analysis of the J - V curves for single-junction devices measured for different thicknesses. The optical constants (refractive index and extinction coefficient) of all the layers in the device were collected by variable angle spectroscopic ellipsometry (VASE) with an M-2000 ellipsometer (J.A. Woolam Co., Inc). The expected photocurrent produced by the tandem device was obtained from optical modeling using transfer matrix formalism: the photocurrent of each sub-cell was calculated knowing the IQE and the measured single-cell photocurrent (for a set active-layer thickness); the measured J - V were compensated with the calculated photocurrent in sub-cells to extrapolate the J - V of the sub-cells. The J - V curves of the tandem OPV devices were then inferred using Kirchhoff's laws assuming no losses at the recombination contact, and the figures of merit are subsequently represented in 3D maps depicting performance as a function of sub-cell thicknesses and optical gap of the front- and back-cells.

Conflicts of interest

There are no conflicts to declare.

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