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End Group Tuning in Acceptor-Donor-Acceptor Nonfullerene Small molecules for High Fill Factor Organic Solar Cells

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High fill factors have only recently become commonplace in nonfullerene-based organic solar cells, with the balance of charge carrier mobilities often cited as the contributing factor. Here we report an end-group modification to a commonly used nonfullerene acceptor (O-IDTBR), in which the rhodanine end groups were replaced with dicyano moieties, resulting in the acceptor O-IDTBCN. This new acceptor afforded significant improvement in the fill factor (73%) and photocurrent (19.8 mA cm^{-2}) in organic solar cells with the low bandgap polymer PTB7-Th. A narrowing of the bandgap, as a result of greater push-pull hybridization, allowed

complementary absorption to the donor and thus improved photon harvesting. Additionally, the measurement of charge carrier mobilities and lifetimes in both systems revealed that the PTB7-Th:O-IDTBCN blend possessed more balanced charge carrier mobilities, and longer lifetimes. Morphology studies revealed a slightly greater degree of molecular mixing of the O-IDTBCN when blended with PTB7-Th, despite the greater and more balanced charge carrier mobilities in this blend.

1. Introduction

The use of nonfullerene acceptors (NFAs) has afforded significant improvements in the field of organic photovoltaics over the last few years, with organic solar cells now regularly able to achieve power conversion efficiencies (PCEs) from 12% to over 15%.^[1-3] The key advantages that NFAs possess over the traditional fullerene acceptors are strong light absorption in the visible region of the solar spectrum and high lying lowest unoccupied molecular orbitals (LUMOs), which contribute to the generation of larger photocurrents and device photovoltages respectively.^[4,5] As such, nonfullerene organic solar cells have been able to achieve higher open circuit voltages (V_{OC}) and short circuit photocurrents (J_{SC}) than the analogous fullerene devices for some time; thus enabling them to surpass the PCEs that can be achieved with fullerene acceptors. One parameter that initially proved more difficult to enhance, relative to fullerene-based devices, was the fill factor (FF); this has been shown to be dependent on both the blend morphology of the active layer and the charge transport properties of the donor polymer and acceptor, since it closely related to the recombination present in a blend.^[6,7] Recently, there have been a number of NFA-based solar cells able to achieve a FF of over 70%.^[1,3,8] In most cases this improved FF is attributed to an interpenetrating morphology of donor and acceptor domains with percolation pathways for efficient charge collection or balanced electron and hole mobilities, which have been shown to reduce non-geminate recombination in blends.^[9-11]

PTB7-Th is a thoroughly studied low bandgap donor polymer, originally designed to be used in combination with fullerene acceptors.^[12] PTB7-Th exhibits excellent photon harvesting properties due to its narrow bandgap, and its relatively amorphous nature allows it to be used in combination with strongly aggregating acceptors.^[13] Despite being tailored for use with fullerenes, there have been a number of reports showing that PTB7-Th also works well in combination with medium and narrow bandgap nonfullerene acceptors.^[14,15] One noticeable feature of these PTB7-Th:NFA blends is that very few are able to simultaneously achieve both a high J_{SC} and FF.^[16-19] As such, only a handful of PTB7-Th:NFA blends can achieve a PCE of over 10%, none of which are able to rival the 14% PCEs achieved with the medium bandgap polymers PBDB-T and PBDB-TF.^[1,3,20] Of those examples that were able to achieve a FF of 70% or greater with PTB7-Th, the authors attributed this to improved electron mobility of the acceptor, and consequently, more balanced charge carrier mobilities in the blend.^[13,16,19]

O-IDTBR has been widely studied in NFA-based solar cells since it was first reported in 2015.^[21] It has been shown to work well in bulk heterojunction solar cells with a number of medium and narrow bandgap donor polymers, achieving high photocurrents and voltages.^[22,23] Additionally, its branched chain analogue, EH-IDTBR, has recently been reported to achieve > 12% when combined with PTB7-Th, as a result of excellent charge separation and low geminate recombination. However, this blend was only able to achieve a maximum FF of 0.63.^[24] In fact, this is a common feature throughout the reported IDTBR-based devices, where relatively modest fill factors that are obtained, in the range of 0.60-0.66. In many cases this is the limiting factor in producing exceptionally high efficiency IDTBR-based devices.

In acceptor-donor-acceptor (A-D-A) nonfullerenes, the π - π stacking interactions between the acceptor end-groups of neighbouring molecules has been shown to be critical to their charge transport properties.^[25] Extending the conjugation of the end groups of A-D-A acceptors has

been shown to successfully improve their performance in devices, by improving the charge transport properties.^[26,27] Fluorination of the end groups, or the addition of alkyl groups, have also led to improved device performance, through the modulation the energy levels and improving the absorption coefficient of acceptors.^[1,3] The use of dicyanovinyl end-groups has been previously reported, acting to reduce the bandgap of the material in comparison to its rhodanine terminated analogue; however, no improvement in charge transport properties was observed due to the dominant twisted nature of these NFAs.^[28] Thus, end group engineering can be considered to be an effective method in improving the optoelectronic and charge transport properties of nonfullerene acceptors. Here we report O-IDTBCN, an analogue of O-IDTBR, which through end group engineering, is able to produce an improved PCE when blended with PTB7-Th. This is a result of extended photon absorption and more balanced charge carrier mobilities, consequently both a high J_{sc} and FF were achieved simultaneously.

2. Results & Discussion

O-IDTBCN is an A-D-A nonfullerene acceptor, consisting of an indacenodithiophene (IDT) donor core, flanked on either side by electron-deficient benzothiadiazole (BT) and dicyanovinyl (DCV) moieties. This acceptor can be considered as analogous to the previously reported O-IDTBR, however, the final Knoevenagel condensation reaction with malononitrile introduced DCV moieties to the periphery of the molecule, rather than 3-ethylrhodanine. The synthesis of this acceptor is discussed in the experimental methods below and shown in **Scheme S1**.^[21] The structures of these acceptors are summarized in **Figure 1a**. The DCV end group is more electron-deficient in nature than rhodanine, leading to a lowering of both O-IDTBCN's HOMO and LUMO energy levels, relative to O-IDTBR, as measured by photoelectron spectroscopy in air (PESA), the HOMO and LUMO values are shown in **Figure 1b**. The greater electron-withdrawing nature of the DCV group also afforded greater push-pull hybridization in O-IDTBCN, and hence a narrower bandgap (1.52 eV). This is

accompanied by a red shift in the absorption spectrum of O-IDTBCN in **Figure 1c**, where the wavelength at which the absorption is maximal (λ_{max}) is 763 nm, compared to 731 nm in O-IDTBR, for thin films annealed at 130 °C. Both O-IDTBR and O-IDTBCN exhibit a bathochromic shift upon annealing; in both cases the red-shift is approximately 40 nm, see **Figure S1**. This indicates a narrowing of the optical bandgap, and thus greater conjugation, which is a consequence of more ordered π -stacking upon thermal annealing. The replacement of the rhodanine end groups with the DCV moieties, in O-IDTBCN, does not impact the strength of absorption in the NFAs, as both acceptors possess comparable extinction coefficients, see Figure S1. Overall, greater photocurrents were expected in O-IDTBCN devices, relative to the analogous O-IDTBR devices, as a result of the more complementary absorption of O-IDTBCN with PTB7-Th. A drawback, however, is the deeper lying LUMO level of O-IDTBCN, which limits the V_{OC} in such devices.

The greater degree of push-pull hybridization in O-IDTBCN was verified by calculating the dipole moments of the half-molecule models, using density functional theory (DFT) calculations, using ω B97XD/6-31G*, where the dipole moment of the O-IDTBR half molecule is 7.7 D and the O-IDTBCN half molecule is 11.6 D. This is summarized in **Figure S2** and **Table S1**. The HOMO and LUMO distributions of O-IDTBR and O-IDTBCN were also estimated by DFT calculations, using ω B97XD/6-31G*. This revealed that the LUMO is distributed over the entirety of the DCV end group in the case of O-IDTBCN, however the LUMO is distributed unevenly on the rhodanine moieties of O-IDTBR, see **Figure S3**.

Inverted bulk heterojunction solar cells (ITO/ZnO/PTB7-Th:NFA/MoO₃/Ag) were fabricated by blending PTB7-Th with either O-IDTBR or O-IDTBCN. The J-V characteristics and EQE spectra of these devices are summarized in **Figure 2** and **Table 1**. As expected, the V_{OC} of the O-IDTBCN based devices was substantially lower (~0.3 V) than that achieved in O-IDTBR devices; a result of the much deeper LUMO of the DCV-terminated acceptor. Despite this, PTB7-Th:O-IDTBCN devices were able to achieve greater PCEs (11.1 %) due to the

attainment of greater J_{SC} (19.8 mA cm^{-2}), and more importantly, vastly improved fill factors (0.73). By considering the EQE spectra in Figure 2b, it is clear that the O-IDTBCN blend is able to harvest a greater fraction of the incident photon flux, afforded by the narrower bandgap of the acceptor, which can in part explain the improvement in J_{SC} seen in the PTB7-Th:O-IDTBCN devices. It is pertinent to note that a thermal annealing step in the fabrication of both the O-IDTBR and O-IDTBCN devices allowed improved photon harvesting in comparison to the as-cast blends. As discussed above, both acceptors exhibit a red-shift upon annealing, the effect of which can be seen in the UV-vis spectra of as-cast and annealed PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends, see **Figure S4**. Conventional architecture (ITO/PEDOT:PSS/PTB7-Th:NFA/DPO/Ag) devices were also fabricated and were able to achieve relatively similar J-V characteristics, see **Table S2**, which suggests that is unlikely that beneficial vertical phase separation in the PTB7-Th:O-IDTBCN blend is responsible for the difference in FF between the O-IDTBR and O-IDTBCN devices.

Further electronic characterization of the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends were carried out in order to elucidate the significant improvement in the FF of the O-IDTBCN devices. Firstly, the charge carrier mobilities were investigated using space-charge limited current (SCLC) measurements on both the O-IDTBR and O-IDTBCN blends. Electron-only (ITO/ZnO/PTB7-Th:NFA/Ca/Al) and hole-only (ITO/MoO₃/PTB7-Th:NFA/MoO₃/Ag) devices were fabricated, and using a modified SCLC model,^[29] it was possible to extract the electron and hole mobilities of both blends, the results of which are summarized in **Table 2**, and the J-V characteristic curves for the electron-only and hole-only devices are shown in **Figure S5**. The SCLC measurements revealed that the PTB7-Th:O-IDTBCN devices possess much more balanced charge carrier mobilities, with hole-only (μ_h) and electron-only (μ_e) mobilities of 2.6×10^{-4} and $2.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, resulting in a μ_h/μ_e ratio of 1.1. On the other hand, although the PTB7-Th:O-IDTBR blend possessed a similar μ_h ($1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) the μ_e was approximately an order of magnitude lower ($4.8 \times 10^{-5} \text{ cm}^2$

$\text{V}^{-1} \text{ s}^{-1}$), resulting in a $\mu_{\text{h}}/\mu_{\text{e}}$ ratio of 2.9. The more balanced charge carrier mobilities in the PTB7-Th:O-IDTBCN blend is in good agreement with the greater FF, an observation that has previously been reported.^[16,19,30] The electron mobilities of the neat acceptors were also measured by SCLC, revealing that both O-IDTBR and O-IDTBCN possess similar electron mobilities ($\sim 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), see **Figure S6**. Thus, the electron mobility of the neat O-IDTBCN thin-film is comparable to that of the PTB7-Th:O-IDTBCN blend, however the electron mobility of neat O-IDTBR is not preserved when blended with PTB7-Th. This suggests that the differing morphologies adopted in the blends of these NFAs with PTB7-Th is most likely responsible for the differences in electron mobilities.

Moreover, transient photovoltage (TPV) measurements were also carried out to investigate the lifetime of charge carriers (τ) in the blends, the results of which are summarized in **Figure 3**. From the TPV measurements it was found that the charge carrier lifetime at 1 sun is $4.3 \mu\text{s}$ in PTB7-Th:O-IDTBCN devices, which is significantly longer than the $0.8 \mu\text{s}$ charge carrier lifetime measured for the PTB7-Th:O-IDTBR devices. This suggests a reduction in non-geminate recombination in the O-IDTBCN, which can be attributed to the more balanced charge carrier mobilities as observed by SCLC. In combination with the mobility data from SCLC measurements, the mobility-lifetime ($\mu\tau$) product was calculated. In line with the high FF achieved, O-IDTBCN based devices, possessed a greater $\mu\tau$ of $1.03 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1}$, compared to $7.52 \times 10^{-11} \text{ cm}^2 \text{ V}^{-1}$ in O-IDTBR solar cells, see Table 2.

Charge carrier recombination dynamics were also investigated, by exploring the J_{SC} and V_{OC} dynamics as a function of light intensity. By first considering the J_{SC} evolution with light intensity, for both the O-IDTBR and O-IDTBCN devices, the slopes of the plots (**Figure S7a**) are 0.95 and 0.97 respectively. This suggests no severe bimolecular recombination in either of the two systems. Consequently, despite the increased electron mobility in the PTB7-Th:O-IDTBCN blend, an increase in bimolecular recombination is not observed. Moreover, the variation in V_{OC} with light intensity is indicative of a stark difference in the presence of traps

in the PTB7-Th:O-IDTBR and O-IDTBCN blends, see **Figure S7b**. The slope of 1.2 kT/q of the PTB7-Th:O-IDTBCN blend is consistent with reduced trap assisted recombination in the system, whereas the slope of 1.7 kT/q obtained from the PTB7-Th:O-IDTBR blend suggests that this system is approaching trap-limited behaviour. Furthermore, this reduced trap-assisted recombination in the PTB7-Th:O-IDTBCN blend is likely to contribute towards the improved FF seen in these devices, in comparison to the O-IDTBR devices.

Time-resolved photoluminescence (TRPL) measurements were also carried out on the neat materials, PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends, in order to investigate the charge transfer of these systems. The samples were excited at 635 nm. The decays of the TRPL intensity, at 780 nm, are displayed **Figure 4**, **Figure S8** and **Table S3**. It should be noted that due to the similar emission profiles of PTB7-Th and the NFAs it is not possible to definitively assign the decay to either PTB7-Th or acceptor PL. However, the NFAs are usually more emissive than the donor polymers, thus the TRPL intensity is likely to be dominated by the O-IDTBR and O-IDTBCN in their respective blends with PTB7-Th. In comparison with the neat materials, both PTB7-Th:O-IDTBR and O-IDTBCN blend systems exhibit shorter exciton lifetimes, indicating that excitons are quenched at the interface of the blends as a result of charge transfer. The PL decay in both systems is seemingly monoexponential, indicating we are only probing the exciton decay. The exciton lifetimes of the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends are 370 ps and 158 ps respectively, suggesting more efficient exciton separation in the O-IDTBCN blend, relative to PTB7-Th:O-IDTBR. A possible reason for this is a greater degree of mixing or increased interfacial area in the case of the PTB7-Th:O-IDTBCN blend. Steady state photoluminescence (PL) measurements of the neat materials, and their respective blends, were also carried out in order to compare the PL quenching efficiency (PLQE) in the blends. Due to the similar absorbance spectra of the polymer and acceptors, the selected excitation wavelength (700 nm) would excite both the donor and acceptors in the blends. However, as can be seen in **Figure S9a**, a

distinction can be made between the spectral signature of the PTB7-Th and the acceptors' PL spectra. As such, the PL spectra of the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends can be ascribed to PL of the acceptors, since the spectral signature of the blends is consistent with that of the neat acceptors. From **Figure S9b**, it is clear that the PL quenching observed in the PTB7-Th:O-IDTBCN blend is extremely efficient, with a PLQE of 98%. The PTB7-Th:O-IDTBR blend exhibits less efficient quenching, with a PLQE of 84%. The greater PLQE observed in the PTB7-Th:O-IDTBCN blend is indicative of a greater degree of mixing between the donor and acceptor, relative to PTB7-Th:O-IDTBR.

Furthermore, basic morphological characterization of the two blends was also carried out, in order to identify any notable differences in blend morphology which may contribute to the improved charge separation and collection, and therefore the improved FF, seen in PTB7-Th:O-IDTBCN devices. As noted above, the similar performance of conventional and inverted architecture devices suggests that vertical phase separation does not play a role in these systems. Atomic force microscopy (AFM) indicated that the PTB7-Th:O-IDTBCN blend displays a lower root-mean-square surface roughness of 0.91 nm, in comparison to that of 2.44 nm in the PTB7-Th:O-IDTBR blend, see **Figure S10 and Table S4**. Reduced surface roughness has previously been correlated to greater mixing of the donor and acceptor, hence the lower surface roughness suggests that the O-IDTBCN blend exhibits more mixing than the analogous O-IDTBR blend.³¹ Differential scanning calorimetry (DSC) measurements on the neat acceptors and their respective blends with PTB7-Th were carried out to further investigate the mixing, shown in **Figures S11 and S12**. It is clear that in both O-IDTBR and O-IDTBCN blends, the acceptor melting temperature remains unchanged when compared to the neat acceptors. Upon cooling, the crystallisation temperature (T_c) of O-IDTBCN is supercooled, suggesting the transition is hindered by the presence of PTB7-Th, an observation not seen in the O-IDTBR blend. Additionally, the melt of O-IDTBR was broadened in the blend, indicating a wide distribution of crystallite sizes, whilst the melt of O-IDTBCN

remains sharp in the PTB7-Th blend. It was seen that the measured and calculated enthalpy of fusion (ΔH_f) values for O-IDTBR are in reasonable agreement, while the reduction in ΔH_f of O-IDTBCN is significantly larger than expected, see **Table S5**. A possible interpretation of the above thermal analysis is that the crystallisation of O-IDTBCN in the blend is more hindered compared to that of O-IDTBR, as suggested from the significant reduction of ΔH_f in the O-IDTBCN blend and the supercooled O-IDTBCN crystallisation upon cooling. Whether this is due to the formation of amorphous O-IDTBCN aggregates or to O-IDTBCN molecules molecularly dispersed in the polymer matrix cannot be determined from DSC. However, taking into account the above observation from AFM, it is reasonable to suggest that molecular mixing is the more likely cause for the larger than expected reduction in ΔH_f in the O-IDTBCN blend. It should be noted that the phase behaviour observed for drop-cast samples from DSC cannot be assumed to be the same as spin-cast device active layers, but the technique is used as a comparative tool here. Dark-field transmission electron microscopy (DF-TEM) measurements of the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends were also carried out in order to further investigate the morphology adopted by both active layers, see **Figure S13**. This verified that a greater degree of mixing is present in the PTB7-Th:O-IDTBCN blend, as shown by the smaller domains and fine texture. Despite this fine mixing of the PTB7-Th:O-IDTBCN blend, the electron mobility is significantly higher than that of the O-IDTBR blend. This would suggest that the presence of an improved percolation network for charge extraction is present in the PTB7-Th:O-IDTBCN blend, which can be seen in the DF-TEM image of the PTB7-Th:O-IDTBCN blend.

3. Conclusions

In summary, a new A-D-A type nonfullerene acceptor, O-IDTBCN, was synthesized and the inclusion of the strongly electron-withdrawing DCV end-group afforded deeper lying HOMO and LUMO levels and a slight narrowing of the optical bandgap. When organic solar cells

were fabricated using PTB7-Th as the donor and O-IDTBCN as the acceptor, a significant improvement in FF and J_{SC} were observed (73% and 19.8 mA cm^{-2} respectively), in comparison to O-IDTBR reference devices. However, the deep lying LUMO of O-IDTBCN reduced the V_{OC} somewhat (0.72 V) in devices. Despite this, the new DCV-terminated acceptor was able to achieve a greater overall PCE than O-IDTBR, 11.1% in comparison to 9.9%. SCLC measurements revealed that the PTB7-Th:O-IDTBCN blend possessed more balanced charge carrier mobilities ($\mu_h/\mu_e = 1.1$) than the O-IDTBR blend, an observation that has previously been suggested as the reason for high FF in organic solar cells. This is despite the two acceptors having virtually identical electron mobilities in neat films. Moreover, TPV analysis revealed that the charge carrier lifetimes in the O-IDTBCN blend were substantially longer than those in PTB7-Th:O-IDTBR, $4.3 \mu\text{s}$ and $0.8 \mu\text{s}$ respectively. Thus, greater average charge carrier mobilities and lifetimes in the PTB7-Th:O-IDTBCN blend suggest improved charge separation and collection, as shown by the $\mu\tau$ product, resulting in the greater FF in these devices. AFM, DSC and DF-TEM measurements indicate a greater degree of mixing is present in the PTB7-Th:O-IDTBCN blend. This was corroborated by investigating the exciton lifetimes in the two blends using TRPL; this revealed a significantly shorter exciton lifetime in the O-IDTBCN blend as expected for a more mixed system. Also, a greater PLQE of the PTB7-Th:O-IDTBCN blend, from steady state PL, further suggests the presence of a more mixed system. Thus, we suggest that the greater mixing affords more efficient exciton separation and charge generation in the PTB7-Th:O-IDTBCN blend; despite the greater degree of mixing, the electron mobility of the neat O-IDTBCN is preserved in the blend with PTB7-Th, which is likely due to the presence of improved percolation pathways in this blend, relative to PTB7-Th:O-IDTBR. To conclude, the replacement of the rhodanine end-groups for DCV has been successfully employed to improve the electron mobility in blends with PTB7-Th, leading to more balanced charge transport, and thus a substantially higher FF in

organic solar cells. This may prove to be a good strategy to improve the FF in nonfullerene-based devices.

4. Experimental Section

Materials: O-IDTBR was synthesised according to literature procedures,^[21] PTB7-Th was acquired from 1-material and all reactions were carried out under an inert argon atmosphere using conventional Schlenk techniques. All other chemicals and solvents were purchased from Sigma Aldrich and Acros Organics and used as received.

Synthesis of O-IDTBCN: To a solution of 7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-4-carbaldehyde) (0.55 g, 0.53 mmol) and malononitrile (0.11 g, 1.67 mmol) in anhydrous toluene (30 mL) was added basic aluminum oxide (2 g), with stirring under N₂. This mixture was heated at 75 °C for 2.5 h, then cooled to room temperature and filtered to remove the solid. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica, with dichloromethane as the eluent, to give product as dark purple solid (0.31 g, 52%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.85 (s, 2H, =CH), 8.82 (d, *J* = 8.0 Hz, 2H, Ar-H), 8.39 (s, 2H, Ar-H), 8.13 (d, *J* = 8.0 Hz, 2H, A-H), 7.58 (s, 2H, Ar-H), 2.24-2.01 (m, 8H, CH₂), 1.28 – 1.10 (m, 40H, CH₂), 1.05-0.86 (m, 8H, CH₂), 0.81 (t, *J* = 6.9 Hz, 12H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 157.61, 154.63, 152.15, 151.05, 148.25, 141.03, 136.68, 134.06, 130.81, 125.53, 123.23, 121.03, 114.42, 114.36, 113.56, 81.10, 54.50, 53.64, 39.10, 31.78, 29.90, 29.26, 29.15, 24.24, 22.58, 13.79.

Density Functional Theory Calculations: DFT calculations were carried out using Gaussian 16.A01. The charge transfer excitation data, calculated at tuned ωB97XD/6-31G* level in chlorobenzene polarisable continuum model (PCM) for IDTBR and IDTBCN, and their model half molecules, was used to estimate the half-molecule dipole moments. Calculations used the approach of Le Baher.^[32] Note that using the full NFA molecule suggests very small

charge transfer distance, due to the symmetrical charge transfer to both end groups in opposite directions.

Device Fabrication: Inverted architecture bulk heterojunction solar cells (glass/ITO/ZnO/PTB7-Th:NFA/MoO₃/Ag) were fabricated as follows. Glass substrates, prepatterned with ITO (15 Ω sheet resistance per square), were cleaned by sonication in acetone, detergent, deionized water, and isopropanol before ozone plasma treatment for 10 min. A layer of ZnO, ≈ 30 nm (from Zn(OAc)₂ in monoethanolamine (60 μ L) and 2-methoxyethanol (2 mL)), was deposited by spin-coating onto the ITO substrate at 4000 r.p.m. for 40 s, followed by annealing at 150 $^{\circ}$ C for 20 min. Active layer solutions (PTB7-Th:NFA, weight ratio 1:2.5) were prepared from CB with a total concentration of 24 mg mL⁻¹. The solutions were heated to 60 $^{\circ}$ C overnight, and the active layer was deposited by spin-coating at 2500 r.p.m. for 1 min. The active layers were then annealed at 130 $^{\circ}$ C for 12 min, under an inert atmosphere. A MoO₃ anode interlayer (10 nm) and Ag anode (100 nm) were then deposited by thermal evaporation through a shadow mask, giving an active area of 0.045 cm² per device. Conventional architecture bulk heterojunction solar cells (glass/ITO/PEDOT:PSS/PTB7-Th:NFA/DPO/Ag) were prepared using the same substrate cleaning protocol, before a thin layer (~ 30 nm) of PEDOT:PSS was spin-cast onto the ozone-treated substrates, dried on a heating plate at 140 $^{\circ}$ C for 10 minutes. The active layers were deposited using the same protocol as described for the inverted devices, above. A (2-(1,10-phenanthroline-3-yl)naphthalene-6-yl)diphenylphosphine oxide (DPO) interlayer was spin-coated (0.5 mg/mL in methanol) in the glovebox on top of the active layers at a speed of 2000 rpm for 20 s.^[33] Next, the samples were placed in a thermal evaporator for evaporation of a 100-nm layer of silver electrode through a shadow mask, giving an active layer of 0.045 cm² per device. The *J-V* characteristics were measured under AM1.5G (100 mW cm⁻²) irradiation using an Oriel Instruments Xenon lamp calibrated to a Si reference cell to correct for spectral mismatch, and a Keithley 2400 source meter. EQE was measured by comparing the

photocurrent from a calibrated photodiode to the photocurrent of the sample cell at the same monochromatic light intensity within the same spectral range. The monochromatic light was achieved using a CVI DIGIKROM 240 grating spectrometer in combination with a xenon arc light source.

SCLC Measurements: The mobilities of the blends (electrons and holes) and neat acceptors (electrons only) were determined by fitting the dark current hole/electron-only diodes to the modified space-charge-limited current (SCLC) model.^[29] Hole-only diode configuration (Glass/ITO/MoO₃/BHJ/MoO₃/Ag), $V_{bi} = 0$ V (flat band pattern formed by MoO₃-MoO₃). First, MoO₃ (10 nm) was thermally evaporated onto the ITO-coated glass. After deposition of the active layer, using the same deposition conditions as discussed for organic solar cells above, MoO₃ (7 nm) and Ag (100 nm) were deposited via thermal evaporation in a vacuum chamber through a shadow mask defining an active area of 0.1 cm². Electron-only diode configuration (Glass/ITO/ZnO/BHJ/Ca/Al), $V_{bi} = 1.5$ V. A 30 nm layer of ZnO was deposited according to the procedure for inverted architecture solar cells above. The active layers were then deposited on top of the ZnO/ITO-coated substrates. Ca (7 nm) and Al (100 nm) was deposited as the top electrode. The electric-field dependent SCLC mobility was estimated using the following equation:

$$J(V) = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp \left(0.89 \beta \sqrt{\frac{V - V_{bi}}{L}} \right) \frac{(V - V_{bi})^2}{L^3}$$

TPV Measurements: In transient photovoltage (TPV) measurements, a 405 nm laser-diode was settled for keeping the solar cells in approximately V_{OC} condition. Driving the laser intensity with a waveform generator Agilent 33500B and measuring the light intensity with a highly linear photodiode allowed to reproducibly adjust the light intensity with an error below 0.5% over a range of 0.2 to 1 suns. A small perturbation was induced with a second 405 nm laser diode driven by a function generator from Agilent. The intensity of the short (50 ns)

laser pulse was adjusted to keep the voltage perturbation below 10 mV, typically at 5 mV. After the pulse, the voltage decays back to its steady state value in a single exponential decay. The characteristic decay time was determined from a linear fit to a logarithmic plot of the voltage transient and returned the small perturbation charge carrier lifetime.

TRPL Measurements: The DeltaFlex TCSPC system (Horiba Scientific) was used to measure the time-resolved PL of thin film samples. Samples were excited by a NanoLED at 635 nm. Photons were detected with a PPD detector. Thin films were prepared by spin-coated onto glass substrates. For the blends, the same conditions as used for the OPV devices were employed. Neat PTB7-Th films were obtained from solution of 10 mg mL⁻¹ and 20 mg mL⁻¹ solutions were used to prepare films of the neat acceptors. The spectra were corrected accounting thickness variation.

PL Measurements: The FluoroMax-4, HORIBA spectrofluorometer was used to record the PL spectra of thin films of the neat materials and their respective blends, upon excitation at 700 nm. Thin films were prepared by spin-coated onto glass substrates. For the blends, the same conditions as used for the OPV devices were employed. Neat PTB7-Th films were obtained from solution of 10 mg mL⁻¹ and 20 mg mL⁻¹ solutions were used to prepare films of the neat acceptors. The spectra were corrected accounting thickness variation.

DSC Measurements: DSC measurements were carried out with a TA Instruments DSC Q20 at a rate of 5 °C per min under nitrogen (50 mL min⁻¹). Chlorobenzene solutions (24 mg mL⁻¹) of neat and blend materials were stirred overnight at 50 °C. Samples were prepared by drop-casting the solutions onto glass slides and allowing the films to dry under ambient conditions overnight. The films were then scraped off and transferred into standard Tzero Aluminium pans and sealed.

AFM Measurements: AFM scans were carried out using the NEXT II (Roman 2) from NT-MDT on samples in actual device configuration. The scans were carried out on 5 × 5 μm² surface areas, using tapping mode.

DF-TEM Measurements: DF-TEM measurements were carried out using a FEI Tecnai Bio-twin Transmission Electron Microscope (TEM) operated at 120 kV and a Titan 80–300 kV (ST) equipped with GIF TridiemER energy filtered detector and 2 CDD cameras, operating at 300 kV in Dark field mode. Samples for TEM were prepared by spincoating the active layer blends, using the optimized device processing conditions, on top of a water-soluble sacrificial layer and then emerged in water. Floating layers were placed on copper grids (300 Mesh) with lacey carbon film and were dried overnight under vacuum to remove any water residue.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. a) The chemical structures, b) the HOMO and LUMO energy levels, as measured by PESA, and c) the thin-film UV-vis absorption spectra of PTB7-Th, O-IDTBR and O-IDTBCN.

Figure 2. a) The J-V characteristics and b) the EQE spectra of inverted PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN bulk heterojunction solar cells.

Table 1. The J-V characteristics of inverted PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN bulk heterojunction solar cells.

Active Layer Blend (1:2.5)	V_{oc} [V] ^{a)}	J_{sc} [mA cm ⁻²] ^{a)}	FF [%] ^{a)}	Average PCE [%] ^{a)} / Maximum PCE [%]
PTB7-Th:O-IDTBR	1.02	15.5	60	9.5 / 9.9
PTB7-Th:O-IDTBCN	0.72	19.8	73	10.5 / 11.1

a) J-V parameters are averaged over six devices.

Table 2. The SCLC charge carrier mobilities for the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN devices and $\mu\tau$ from SCLC and TPV measurements respectively.

Active Layer Blend (1:2.5)	μ_h [cm ² V ⁻¹ s ⁻¹]	μ_e [cm ² V ⁻¹ s ⁻¹]	μ_h/μ_e	$\mu\tau$ [cm ² V ⁻¹]
PTB7-Th:O-IDTBR	1.4×10^{-4}	4.8×10^{-5}	2.9	7.52×10^{-11}
PTB7-Th:O-IDTBCN	2.6×10^{-4}	2.2×10^{-4}	1.1	1.03×10^{-9}

Figure 3. a) Charge carrier lifetime (τ) as a function of V_{OC} and b) representative normalized photovoltage (at 0.4 suns) as a function of time for PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN devices.

Figure 4. Normalized TRPL intensity decay at 780 nm over time for the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN blends, from which the exciton lifetimes were estimated. (Samples were excited at 635 nm).

O-IDTBCN is a new non-fullerene acceptor making use of dicyanovinyl end groups to improve the electron mobility in blends with PTB7-Th, relative to its predecessor, O-IDTBR. Blends with O-IDTBCN possess more balanced charge carrier mobilities, resulting in longer charge carrier lifetimes which ultimately manifests in the attainment of fill factors of over 70% in devices.

Keywords: non-fullerene, IDTBR, fill-factor, organic photovoltaics

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End Group Tuning in Acceptor-Donor-Acceptor Nonfullerene Small molecules for High Fill Factor Organic Solar Cells

Supporting Information

End Group Tuning in Acceptor-Donor-Acceptor Nonfullerene Small molecules for High Fill Factor Organic Solar Cells

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Scheme S1. Synthesis of O-IDTBCN.

Figure S1. The as-cast and annealed thin film UV-vis spectra of a) O-IDTBR and b) O-IDTBCN, c) the extinction coefficients of the as-cast neat acceptor films. Thin films were cast by spincoating from 5 mg mL⁻¹ solutions and annealing was carried out for 10 min at 130 °C.

Figure S2. Dipole moments of the half-molecule models of O-IDTBR and O-IDTBCN, as estimated from DFT calculations using wB97XD/6-31G*.

Table S1. Summary of the energy (E), the distance between the charge transfer excitation barycentres (dCT) and the amount of charge transferred (qCT).

	E [eV]	dCT [Å]	qCT [e]
half-IDTBR	2.32	3.75	0.569
IDTBR	2.10	0.22	0.561
half-IDTBCN	2.33	4.58	0.591
IDTBCN	2.08	0.06	0.581

using wB97XD/6-31G*.

Figure S4. Normalized as cast and thermally annealed (130 °C, 12 min) thin-film UV-vis absorption spectra for a) the PTB7-Th:O-IDTBR blend and b) the PTB7-Th:O-IDTBCN blend.**Table S2.** The J-V characteristics of inverted PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN bulk heterojunction solar cells.

Active Layer Blend (1:2.5)	Device Architecture	V_{oc} [V] ^{a)}	J_{sc} [mA cm ⁻²] ^{a)}	FF [%] ^{a)}	Average PCE [%] ^{a)} / Maximum PCE [%]
PTB7-Th:O-IDTBR	Conventional	1.03	15.1	59	9.2 / 9.4
PTB7-Th:O-IDTBR	Inverted	1.02	15.5	60	9.5 / 9.9

PTB7-Th:O-IDTBCN	Conventional	0.73	19.9	69	10.0 / 10.3
PTB7-Th:O-IDTBCN	Inverted	0.72	19.8	73	10.5 / 11.1

a) J-V parameters are averaged over six devices.

Figure S5. J-V characteristic curves for hole-only and electron only PTB7-Th:O-IDTBR devices, a) and b) respectively, and PTB7-Th:O-IDTBCN devices, c) and d) respectively.

Figure S6. J-V characteristic curves for electron only O-IDTBR O-IDTBCN devices.

Figure S7. a) J_{sc} dynamics of PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN devices with light intensity, b) V_{oc} dynamics of PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN devices with light intensity.

Figure S8. Normalized TRPL intensity decay at 780 nm over time for PTB7-Th, O-IDTBR and O-IDTBCN, from which the exciton lifetimes were estimated. (Samples were excited at 635 nm).

Table S3. Summary of the exciton lifetimes (τ_{ex}) of the neat materials and blends as measured from TRPL

Material	τ_{ex} [ps]
PTB7-Th	455
O-IDTBR	736
O-IDTBCN	250
PTB7-Th:O-IDTBR	370
PTB7-Th:O-IDTBCN	158

Table S4. Summary of the RMS roughness of PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN active layer blends from AFM measurements.

Active Layer Blend (1:2.5)	RMS [nm]
PTB7-Th:O-IDTBR	2.44
PTB7-Th:O-IDTBCN	0.91

Figure S11. DSC thermograms of the first heating cycles of the neat materials and the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN (1:2.5) active blends, offset for clarity.

Figure S12. DSC thermograms of a) the second heating cycles, b) the first cooling cycles and c) the second cooling cycles of the neat materials and the PTB7-Th:O-IDTBR and PTB7-Th:O-IDTBCN (1:2.5) active layer blends, offset for clarity.

Table S5. Summary of the DSC data on the neat acceptors and their respective blends with PTB7-Th, detailing the onset temperatures of thermal transitions and the enthalpy changes (ΔH) associated with each transition, H1 denotes first heating cycle, H2 denotes second heating cycle, C1 denotes first cooling cycle and C2 denotes second cooling cycle.

Cycle	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	$\Delta H_{\text{neat}}/\Delta H_{\text{blend}}$	$\Delta H_{\text{neat calc}}$
		O-IDTBCN		PTB7-Th:O-IDTBCN		
H1 (a)	214.7	53	214.3	17	3.1	38
H1 (b)	208.9	~ 2	197.9	8		
H2 (a)	201.5	33	201.1	16	2.1	24
H2 (b)	214.6	1				
C1	143.5	-23	103.6	-8		
C2 (a)	133.5	-14	97.5	-5		
C2 (b)	79.8	-2	78.9	-2		
		O-IDTBR		PTB7-Th:O-IDTBR		
H1 (a)	228.3	41	224.5	32	1.3	29
H1 (b)	128.9	-12	109.6	-14		
H2 (a)	228.2	41	223.7	32	1.3	29
H2 (b)	115	-6				
C1 (a)	146.7	-14	160	-28		
C1 (b)	102.9	-3				
C2 (a)	149.2	-17	159.4	-28		
C2 (b)	102.6	-2

Figure S13. DF-TEM images of a) the PTB7-Th:O-IDTBR blend and b) the PTB7-Th:O-IDTBCN blend.

Figure S15. ^{13}C NMR spectrum for O-IDTBCN, measured in CD_2Cl_2 .