Terminal Group Engineering for Small-Molecule Donor Boosts the Performance of Nonfullerene Organic Solar Cells

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Nonfullerene acceptors propelled organic solar cell power conversion efficiencies (PCE) to above 15%. However, most of the reported nonfullerene systems with PCE >10% are composed of polymer donors and small-molecule acceptors, while only few small molecule (SM) donors have been reported. Herein, two new small molecule donors namely BDT-RO and BDT-RN with esterified rhodanine (ER) as terminal group are reported. The widely-used fused-ring acceptor IDIC is chosen to fabricate all-small-molecule solar cells with the new donors. A high PCE of over 9.0% is achieved with BDT-RO, while its isomer BDT-RN shows a PCE close to 8.4%. Comparison with the common small molecule donor DR3TBDTT using the same conditions yielded lower performance (7.6% with IDIC), indicating an 18% enhancement in PCE could be achieved through end group engineering. The efficiency differences are attributed to the different morphology and phase separation resulting from the crystallinity and aggregation ability of the donors. The results demonstrate that ER is a promising building block when designing SM donors for all-small-molecule systems.

Organic solar cells (OSCs) are attracting enormous attention due to their distinct advantages such as easy fabrication, flexibility, and solution-processability.^{1–3} Recently, nonfullerene acceptors (NFAs) have pushed the OSC efficiency to new records, stimulating further interest in the development of new NFAs and their characterization in combination with various donors, ranging from polymers to

small-molecule material systems. The unique tunable photophysical and electronic properties of NFAs and their relatively easy synthetic accessibility in scalable quantities, are undisputable benefits when compared with common fullerene derivatives.^{4–6} Among hundreds of NFAs, fused-ring organic semiconductors with NIR absorption such as ITIC and IDIC, specifically improved the power conversion efficiency (PCE) of OSCs.^{7–12} By combining ITIC-type acceptors with high performance wide-band gap polymer donors that exhibit complementary optical bandgaps (i.e. light absorption), a record PCE of up to 14% has recently been achieved in single-junction OSC devices.^{9,10}

As for organic small-molecule (SM) donor materials, most have shown lower device performance in NFA-based OSCs compared to their polymer counterparts up to now. While lagging behind, organic SM donor molecules nevertheless are regarded as highly promising materials in OSCs, because they possess several competitive advantages such as easy-purification, well-defined structure, and improved batch-to-batch consistency in photovoltaic behavior.^{13–15} Additionally, in fullerene systems, a PCE of >11.5% has already been reached with SM donors, which is in parity with the best result achieved with polymeric donors.^{16,17} Therefore, it is reasonable to believe that with rational molecular design and device optimization, SM donors can catch up in NFA-based OSCs.

When designing SM donor molecules, the A- π -D- π -A structure is the most frequently adopted strategy.^{18–19} In 2017, Yan et al. showed that the high-efficiency donor material DR3TBDTT (DR3) also works well with NFAs;²⁰ Cao's and Hou's groups suggested that combining a benzodithiophene (BDT) donor with thiophene-based linkers could be an effective route to design high efficiency SM donors for combination with NFAs, which was later experimentally confirmed.^{21–23} While various attempts are currently being carried out to further optimize the donor units (D) or thiophene linkers (π), electron-accepting terminal groups (A) have received less attention. So far, only few terminal groups were developed and employed in SM donor molecules, among which N-alkylated rhodanine is the most dominant.^{24–26} The alkyl group

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attached on the rhodanine ring plays a pivotal role, as it can not only improve the solubility or adjust the crystallinity, but also tune the aggregation of the SM donor. However, inconvenient and low-yield alkylation of rhodanine discouraged further attempts of modification of rhodanine-based terminal groups (TG).^{21,26}

In this contribution, we report a new type of TG, namely esterified rhodanine (ER). In our work, rhodanine-3-acetic acid was used to replace rhodanine as the core of the TG; furthermore, a more stable and more widely available alcohol displaced the alkyl bromide as the source of aliphatic chains; esterification was performed to obtain ER. In combination with a BDT core and terthiophene linkers, two ER-based A- π -D- π -A SM donors called BDT-RO and BDT-RN were synthesized, which exhibit good solubility in common organic solvents and strong absorption in films. When used in NFA-based OSCs, the high-crystallinity low-bandgap SM acceptor IDIC was chosen as acceptor. In turn, nonfullerene OSC devices of BDT-RO and IDIC achieve PCEs of up to *ca.* 9.0% (vs. *ca.* 8.4% for BDT-RN based devices). As a reference materials of identical π -conjugated backbone, the donor DR3²⁷ was synthesized, but showed a lower PCE of 7.6% under the same preparation conditions. Our systematic studies provide insight into the morphological and efficiency differences that prevail when comparing BDT-RO, BDT-RN, and DR3-based OSCs. Overall, this study shows that as a new terminal group, ER can also be conducive to efficient nonfullerene OSCs with SM donors – a strategy that paves the way to the development of a wider range of donor systems with tunable electronic and optical properties.

Scheme 1. Synthetic route to esterified rhodanine and two SM donors. Structure of the SM acceptor IDIC used for device fabrication.

Scheme 1 depicts the synthetic pathway toward ER and SM donor analogues. In brief, two isomeric alcohols were used to esterify rhodanine-3-acetic acid and produce TG **1** and **2** in almost quantitative yield. Once obtained, TG **1** and **2** were subjected to Knoevenagel condensation with aldehyde **3** to yield the SM donors BDT-RO and BDT-RN, isolated as metallic purple dyes. It is worth noting that the condition used here to perform the Knoevenagel condensation was AcOH/NH₄OAc instead of the generally used CHCl₃/Et₃N. In our case, this

combination resulted in very high yields of up to 90% and high purity. The final products precipitate after cooling from the reaction mixture and thus can be obtained in high purity after simple recrystallization without using additional column chromatography. In comparison, DR3 was synthesized and purified by the regular procedure (CHCl₃/Et₃N environment, column chromatography, *etc.*) and was obtained in a yield of *ca.* 75%.

Figure 1a shows the normalized neat film UV-vis absorption spectra of the two isomeric SM derivatives BDT-RO and BDT-RN along with the SM acceptor IDIC; the normalized solution (3×10^{-5} M) UV-Vis absorption spectra and thin film absorption spectrum of DR3 are provided in **Figure S1**. BDT-RO, BDT-RN and DR3 have almost identical thin film absorption profiles, all of them exhibit a broad absorption from 400 to 700 nm. The absorption maximum is at *ca.* 580 nm, accompanied by a small shoulder around 640 nm. The absorption onset of BDT-RO and BDT-RN films is at 707 nm, corresponding to optical bandgaps (E_{opt}) of 1.75 eV. Importantly, the significant red-shift observed on going from solutions to thin solid films for both SM systems (*ca.* 85 nm judging from the λ_{onset}), and the occurrence of shoulders due at longer wavelengths, suggest that the SM donors are prone to form aggregates. The extended thin-film absorption of SM donors in the range from 450–650 nm makes them especially appealing as absorbers with the complementary SM acceptor IDIC, which has its main absorption band in the range of 600–800 nm. After blending with the SM acceptor IDIC (D:A = 1:0.8, w/w), as shown in **Figure 1b**, both two systems display a wider absorption spectrum from 400 to 800 nm. Moreover, the blend films show two equally strong absorption peaks, suggesting good compatibility of the two SM donors with IDIC, beneficial for achieving high photovoltaic performance.

Figure 1. (a) Normalized UV-Vis absorption spectra of the SM donor BDT-RO, BDT-RN, and the SM acceptor IDIC (model system) in film. (b) The absorption spectra of the blend films. (c) Cyclic voltammograms (positive scan) of BDT-RO and BDT-RN in 0.1 mol L⁻¹ Bu₄NPF₆ dichloromethane solutions. (d) The TGA plots of BDT-RO and BDT-RN.

Cyclic voltammetry with ferrocene as the internal standard was applied to estimate the highest occupied molecular orbital

(HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of SM donors, as shown in **Figure 1c**. Consistent with UV-Vis result, the SM donors also exhibit the same first oxidation potential of 0.75 V ($E_{\text{Fc}/\text{Fc}^+} = 0.50$ V). Calculated by $E_{\text{HOMO}} = [E_{\text{ox}} + (4.8 - E_{\text{Fc}/\text{Fc}^+})]$ eV, $E_{\text{LUMO}} = (E_{\text{HOMO}} - E_{\text{opt}})$ eV, the HOMO/LUMO energy levels of BDT-RO and BDT-RN are approximated to 5.05/3.30 eV, respectively. As can be seen in **Figure S2**, the HOMO offset between SM donors and IDIC (0.64 eV) and their LUMO offset (0.68 eV) are sufficient for charge separation. It is also noteworthy that BDT-RO and BDT-RN have very similar HOMO/LUMO energy levels compared to DR3 which coincides with their UV-Vis absorption spectra, this implies replacing alkylated with esterified rhodanine introduces only marginal changes on the energetics of the SM donor. In fact, this aids a clearer comparison between these two TGs and their effect on the OSC performance.

Thermogravimetric analysis (TGA, **Figure 1d**) shows that either SM donor exhibits good thermal stability and decomposes (5% loss) only above 385 °C. Differential scanning calorimetry (DSC) results indicate that BDT-RO and BDT-RN exhibit a melting temperature (T_m) upon heating at 186 °C and 180 °C, respectively (**Figure S3**), while the cooling scans indicate the propensity of crystallization for both SM donors.

Figure 2. (a) J - V curve of a BDT-RO:IDIC, BDT-RN:IDIC, and DR3:IDIC cell under AM1.5G illumination with an irradiation of 100 mW cm^{-2} (one Sun). (b) EQE spectra of BDT-RO and BDT-RN based organic solar cells. (c) J_{sc} vs. light intensity and (d) V_{oc} vs. light intensity plots for BDT-RO and BDT-RN BHJ devices.

Nonfullerene acceptor solution-processed thin-film BHJ solar cells with BDT-RO and BDT-RN were fabricated with the conventional device structure ITO/PEDOT:PSS/SM:IDIC/DPO/Ag (device area: 0.1 cm^2) and tested under simulated AM1.5G illumination (100 mW cm^{-2}). Phenyl(2-naphthyl)diphenylphosphine oxide (DPO) was utilized as an interfacial layer;^{28,29} detailed experimental and optimization protocols are provided in the SI, along with the corresponding results (**Table S1**). **Table 1** summarizes the figures of merit of optimized BHJ devices made from blends of

the SM donors and IDIC; further device statistics are given in the SI (see **Tables S1**). As shown in **Table 1** and **Figure 2a**, the optimized BDT-RO based BHJ device exhibits a high fill factor (FF), short-circuit current (J_{sc}), and open-circuit voltage (V_{oc}) of 66.56 %, 15.37 mA cm^{-2} , and 0.88 V, respectively, resulting in a maximum solar cell PCE of 9.01 %. For the BDT-RN donor, the corresponding optimized device showed a high V_{oc} , FF and J_{sc} of 0.87 V, 64.88 %, and 14.85 mA cm^{-2} , which leads to an average PCE of >8 % (max. 8.36 %). Parallel control devices made of DR3 and IDIC reported in the same table showed a device performance of 7.3 % (avg.), along with slightly lower FF (61.19 %) and J_{sc} (14.39 mA cm^{-2}). While many nonfullerene All-SM devices suffer from low FF and J_{sc} , these device results suggest that the rhodanine-esterified SM donors, BDT-RO and BDT-RN, are promising candidates for further tests with the nonfullerene acceptor IDIC.

Table 1. PV performance of the SM donors BDT-RO, BDT-RN, and DR3 in conventional BHJ devices under optimized conditions when combined with the nonfullerene SM acceptor IDIC.

SM:IDIC ^a	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	Avg. PCE [%]	Max. PCE [%]
BDT-RO ^b	0.88	15.37	66.56	8.85	9.01
BDT-RN ^b	0.87	14.85	64.88	8.03	8.36
DR3 ^c	0.86	14.39	61.19	7.30	7.61

^a Average values across more than 10 devices, additional device statistics are provided in the SI (**Tables S1**). ^b D:A = 1:0.8 (wt/wt). ^c D:A = 1:1 (wt/wt).

In line with higher J_{sc} values (>14 mA cm^{-2}) achieved with optimized BHJ solar cells made of BDT-RO and BDT-RN, the external quantum efficiency (EQE) spectra of optimized BDT-RO and BDT-RN-based devices confirm the trend observed from the J - V curves as shown in **Figure 2b**. In **Figure 2b**, the EQE spectra of BDT-RO and BDT-RN photoactive layers extend to longer wavelengths (ca. 730 nm), in agreement with the UV-absorption of the SM acceptor IDIC. While both BDT-RO and BDT-RN-based BHJ solar cells exhibit EQE values >50% in the range of 460-730 nm, the higher EQE between 480 nm and 640 nm from optimized devices made with BDT-RO results in a current difference compared to BDT-RN, in line with the different J_{sc} observed from the J - V curves and **Table 1**.

To investigate the non-geminate recombination kinetics in optimized BHJ active layers with BDT-RO and BDT-RN and the nonfullerene SM acceptor IDIC, we examined the variations of J_{sc} under various light intensities; in these experiments, a white-light LED (200 mW cm^{-2} ; spectral mismatch accounted for; cf. experimental details in the SI) was used to reproduce the J_{sc} values normally obtained under standard AM 1.5G solar illumination (100 mW cm^{-2}). Previous studies have shown how bimolecular recombination losses in BHJ solar cells can be estimated by fitting the J_{sc} vs. light intensity data plotted in log scales, making use of the power law equation $J \propto I^\alpha$, where α is the power factor. In short, a value of α equal to unity reflects weak/no bimolecular recombination (here, carriers are extracted before they recombine).^{30,31} From fitting the data of J_{sc} vs. light intensity as illustrated in **Figure 2c**, we obtain α

values of 0.991 and 0.992 for BDT-RO and BDT-RN devices, respectively, indicative of negligible bimolecular recombination losses at short circuit conditions. The low bimolecular recombination losses direct us to analyse another loss mechanism: trap-assisted recombination. To detect the trap-assisted loss, we turned to an examination of the variations of V_{oc} with light intensity – data plotted in a natural log scale in **Figure 2d**; data fitted to $V_{oc} \propto nkT/q \ln(I)$, where k , T , and q are the Boltzmann constant, temperature in Kelvin, and the elementary charge, respectively.

The parameter n (usually in the range of 1 to 2) reflects the presence/absence of carrier traps across the active layer or at interfaces to the electrodes. Any deviations from $n = 1$ (trap-free condition) point to the existence of recombination events and, more specifically, to the existence of trap-assisted recombination.^{31,32} The fitted data shown in **Figure 2d** indicates a slope value of 1.14, which suggests that trap-induced losses are reduced across the BDT-RO:IDIC active layer. On the other hand, the V_{oc} vs. light intensity data for BDT-RN-based devices obeys a slope of $n=1.67$ kT/q , pointing to a significant extent of trap-assisted recombination close to V_{oc} . Overall, both BDT-RO and BDT-RN based devices show low bimolecular recombination losses at J_{sc} , however, the distinct difference of n suggests low trap-induced losses in the BDT-RO device and significant trap-assisted recombination occurs in the BDT-RN device, in line with the device PCE (**Table 1**).

The observed recombination channels in the active layer can be correlated with the extent of structural order and BHJ morphology. Grazing incidence wide angle X-ray scattering (GIWAXS) data shown in **Figure 3a-b**, **Figure S9-10**, and **Table S2-4** are employed to examine the optimized BHJ thin films made with BDT-RO and BDT-RN (cf. experimental details in section 12 of SI).³³ As shown in **Figure S9-10**, the IDIC pure films show intermolecular ordering, exhibiting an obvious lamellar peak (100) at in-plane (IP) direction and a strong π - π stacking peak (010) in the out-of-plane (OOP) direction, located at $1.84 \text{ \AA}^{-1}$ and at $\approx 0.404 \text{ \AA}^{-1}$ (with d-spacing of $15.6 \text{ \AA}$), respectively, indicating a typical face-on orientation. Both, BDT-RO and BDT-RN exhibit (100) diffraction peaks at $\sim 0.30 \text{ \AA}^{-1}$ corresponding to a coherence length of $\sim 20 \text{ \AA}$, which is attributed to the extended side chains and the addition of the thiophene moiety. In addition, the BDT-RO and BDT-RN show higher order of lamellar packing, having (200) and (300) diffraction peaks distinct in the OOP direction, while the (010) diffraction peak of BDT-RN and BDT-RO are located only in the IP direction, indicating that these materials are preferentially edge-on oriented. Turning to BDT-RO:IDIC and BDT-RN:IDIC blends illustrated in **Figure 3a-b**, we observe the pronounced peaks pertaining to BDT-RO and BDT-RN remain at ~ 0.3 , ~ 0.6 and $0.85 \text{ \AA}^{-1}$ in the OOP direction, while the characteristic peak at $0.4 \text{ \AA}^{-1}$ initially in the IP for IDIC re-organized to the OOP position, suggesting that the crystallinity pattern in the active layer is governed by SM donor, which reduces the crystallinity of the IDIC acceptor. We previously reported that high-resolution TEM imaging coupled with electron energy loss spectroscopy (EELS) analyses can provide a clear morphology picture of the active layers and donor-acceptor distribution for

nonfullerene-based solar cells, superior to the general TEM images obtained in bright field.³² Therefore, high-resolution TEM imaging with EELS was employed to unravel the active layer morphologies. The EELS analyses shown in **Figure 3c-f** indicates that donor and acceptor molecules form networks on different scales. The energy loss spectra pertaining to BDT-RO, BDT-RN, and to IDIC (range: 2-8 eV) are shown in **Figure S8**, allowing to distinguish between the SM donor and nonfullerene acceptor across the BHJ active layers. In the dark-field scanning TEM mode (STEM), our EELS analyses (**Figures 3d**; also see neat materials in **Figures S8**), provide a clear map of the phase-separated networks present across the BDT-RO All-SM BHJ active layer; Red: SM donor-rich domains, Green: SM acceptor-rich domains (scale bars: 500 nm). Here, SM donor-rich domains of $< 80 \text{ nm}$ can be observed in the blend films of BDT-RO and IDIC. Interestingly, optimized BDT-RN BHJ active layers shown in **Figure 3f** exhibit significantly finer scale domains of SM donor- and SM acceptor-rich phases. In brief, **Figures 3d** and **3f** display distinct donor-acceptor networks of different length scales (more phase-separated D-A network for BDT-RO and more intimately mixed D-A networks for BDT-RN) across all optimized SVA BHJ active layers, which concurrently yield high BHJ solar cells PCEs ($> 8 \%$, **Table 1**).

Figure 3. GIWAXS analyses for optimized (a) BDT-RO and (b) BDT-RN BHJ active layers, where the intensity scales are all identical. Morphology analyses for (c,d) BDT-RO and (e,f) BDT-RN BHJs in optimized conditions: (c,e) Dark-field STEM images of the BHJ active layers. (d,f) Corresponding EELS maps D-A distribution patterns between SM donor-rich (red) and nonfullerene acceptor-rich domains (green). Scale bars: 500 nm; Note: ca. 50 nm thick films were used for these analyses to improve spectral resolution and reduce domain overlap when projected through the film thickness.

Favorable morphologies can be conducive to high device FFs (here >64% in optimized BHJs with BDT-RO and BDT-RN) and J_{sc} values, due to optimized charge transport properties in BHJ solar cells. The FF difference between BDT-RO and BDT-RN molecules can originate from limitations of the charge transport, which can be probed by space-charge-limited current (SCLC) mobility measurements (cf. details in SI, **Table S5** and **Figure S11**).^{34,35} **Figures 4a-b** show the dark current density-voltage characteristics at room temperature of the BHJ active layers in hole-only diodes (ITO/PEDOT:PSS/active layer/MoO₃/Ag) and electron-only diodes (ITO/ZnO/DPO/active layer/DPO/Ag); detailed carrier mobility data and statistics are provided in the SI, section 13. The zero-field hole mobilities of BDT-RO-based BHJs is $3.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, approximately a factor of two higher than observed for BDT-RN BHJs ($1.87 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The electron mobilities in BDT-RO and BDT-RN-based BHJs in optimized SVA-treated conditions are $6.45 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. $5.44 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Overall, the mobilities of optimized BHJ thin films that use BDT-RO and BDT-RN as donors fall within the same range (differing only by a factor of two). These results are consistent with the figures of merit summarized in **Table 1** for optimized BHJ solar cells made with BDT-RO and BDT-RN.

Figure 4. (a) Hole mobilities and (b) Electron mobilities of BDT-RO:IDIC and BDT-RN:IDIC blend films.

In summary, we showed esterification of rhodanine represents a facile and efficient strategy in the design of terminal groups for SM donors. Compared with the common DR3 donor, the introduction of ER introduced no change to the energy levels of BDT-RO and BDT-RN, but simultaneously improved their hole- and electron-mobilities in blend films with the SM acceptor IDIC. NFA BHJ solar cells made with BDT-RO and BDT-RN as donor achieve PCEs as high as ca. 9% and 8%, respectively. The carrier recombination analyses through light-intensity-dependent device characteristics indicate BDT-RN based devices exhibit low bimolecular recombination losses, but pronounced trap-induced recombination, while BDT-RO devices benefit from both low bimolecular and trap-assisted recombination losses. The degree of crystallinity and orientation observed by GIWAXS indicates similar structural order of BDT-RO and BDT-RN when blended with IDIC, however, different length scales of the D-A network of BDT-RO and BDT-RN are observed as evidenced by EELS analyses in STEM mode. These results are further supported by SCLC-estimated charge carrier transport measurements, showing concurrently high hole and electron mobilities in both systems.

Conflicts of interest

There are no conflicts to declare.

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