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COMMUNICATION

A donor-acceptor-acceptor molecule for vacuum-processed organic solar cells with a power conversion efficiency of 6.4%[†]

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A D–A–A-type molecular donor (DTDCTP) featuring electronaccepting pyrimidine and dicyanovinylene blocks has been synthesized for vacuum-deposited planar-mixed heterojunction solar cells with C_{70} as the acceptor, giving a power conversion efficiency as high as 6.4%.

Organic photovoltaics (OPVs) have attracted considerable research interest due to their low energy consumption in fabrication, mechanical flexibility, and low-cost manufacturing.1 Among various OPVs device architectures, polymer bulk heterojunction (BHJ) solar cells utilizing a self-assembly phase-separated blend of polymeric donors (D) and fullerene acceptors (A) as an active layer have been proven to be the most successful design with state-of-the-art power conversion efficiencies (PCEs) of 6-8%.² The BHJ active layers can provide large exciton dissociation interfaces while maintaining bicontinuous interpenetrating networks for carrier transport. In contrast, small-molecule OPVs3 featuring low-molecular-weight compounds as donors showed relatively lower efficiencies due to the comparable sizes of donors and acceptors, rendering spontaneous formation of nanoscale phase-separated domains difficult. Without the preferred film morphology, there will be too many isolated traps inside the D/A blending layer, which is unfavorable for efficient charge transport because of discontinuous pathways. In this regard, many research endeavors have adopted several approaches to controlling the favorable D/A nanomorphology in small-molecule OPVs similar to those performed in polymer solar cells. For instance, with thermal annealing,⁴ solvent annealing,⁵ or self-assembly formed columnar structure,⁶ the PCEs have reached respectable values of over 5%.

Along another line, the molecular design strategies employed to improve performance of OPVs include (i) reducing the

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bandgaps of materials, which is beneficial for robust spectral coverage, and (ii) lowering the highest occupied molecular orbital (HOMO) of donors to increase the open circuit voltage $(V_{\rm oc})$ of the cell. To meet these requirements, small molecules with acceptor-donor-acceptor (A-D-A)^{4c,7} architectures have been successfully applied as donors and exhibited exceptional performance. On the other hand, the donor-acceptor $(D-A)^8$ molecules incorporating arylamines as the donor moieties also show promise due to their intrinsically effective photoinduced intramolecular charge transfer (ICT) characteristics and the flexibility in structural modification. Notably, the merocyanine dves based devices^{8c,d} have demonstrated PCEs surpassing 6%.8d Very recently, we developed a donor molecule (DTDCTB, Scheme 1) with a donor-acceptor-acceptor (D-A-A) configuration,⁹ in which an electron-donating ditolylaminothienyl moiety is connected to an electron-withdrawing dicvanovinylene moiety through another electron-accepting 2,1,3-benzothiadiazole (BT) block. The elaborate combination of two acceptors enables the resulting molecules to not only effectively narrow the optical bandgaps but also possess lower HOMO levels as compared to those of their parent analogs.¹⁰ Accordingly, such D-A-A architectures show potential capabilities of concurrently enhancing the short circuit current density (J_{sc}) and V_{oc} as employed in OPVs. Vacuum-processed devices based on DTDCTB exhibited distinguished light-harvesting abilities with solar responses extending to the near-IR region and achieved PCEs of up to 5.81%. However, the moderate $V_{\rm oc}$ value (~0.79 V) attained in **DTDCTB**-based devices leaves room for improvement. In this communication, we report a



Scheme 1 Synthetic route to DTDCTP and the structure of DTDCTB.

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[†] Electronic supplementary information (ESI) available: Synthesis, characterization, absorption spectra of **DTDCTP**, copies of ¹H and ¹³C NMR spectra, procedures for device fabrication and photovoltaic characterization, device optimization, mobility diagrams, and a total absorption spectrum. CCDC 848943 (**DTDCTP**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2cc16390j

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new D–A–A-type molecule, **DTDCTP** (Scheme 1), where the pyrimidine acceptor is employed to replace the BT block. We envisaged that the HOMO of **DTDCTP** would be lower than that of **DTDCTB** and thus an augmented V_{oc} can be anticipated, although an inevitable loss of photocurrent is foreseeable. Likewise, **DTDCTP** was designed to adopt a nearly coplanar conformation to ensure a compact stacking in the solid state, thus realizing high extinction coefficients throughout the spectral coverage.

The synthetic pathway of **DTDCTP** is shown in Scheme 1. Palladium-catalyzed Negishi coupling reaction of 2-[N,N-di-(p-tolyl)amino]thiophene with 5-bromo-2-iodopyrimidine afforded 1, which was then converted to the corresponding carbaldehyde 2 by lithiation with n-butyllithium and subsequently quenching with ethyl formate. Finally, the aldehyde 2 was condensed with malononitrile to yield the target compound **DTDCTP** *via* the Knöevenagel reaction in the presence of basic aluminium oxide.

The molecular structure of **DTDCTP** was analyzed by X-ray crystallography. As shown in Fig. 1(a), **DTDCTP** displays a nearly coplanar conformation between thiophene and pyrimidine with a dihedral angle of 5.8° due to the lack of *ortho–ortho* steric interactions. This coplanarity facilitates the electronic coupling between the electron-donating and electron-withdrawing blocks, thus enhancing the ICT efficiency to increase the spectral response range. The highly polar character and coplanar conformation of the heteroaryl components lead **DTDCTP** crystals to pack in an antiparallel manner along both molecular axis directions. The cofacial arrangement of two pyrimidine rings of neighboring **DTDCTP** molecules with a shortest distance of around 3.3 Å indicates significant π - π interactions, which may facilitate charge carrier transport.

The absorption band of **DTDCTP** in CH₂Cl₂ exhibits a maximum at 556 nm ($\varepsilon = 53\,900 \text{ M}^{-1} \text{ cm}^{-1}$), which broadens in the vacuum-deposited thin film, possibly due to π - π stacking in the solid state (Fig. S1 in ESI†). The extinction coefficient (k) spectrum of the **DTDCTP** thin film (60 nm) measured by spectroscopic ellipsometry is depicted in Fig. 1(b). The film

shows high k across the 470–630 nm wavelength range with $k_{\text{max}} \approx 1$ at 550 nm. The observed k_{max} value is among the highest values reported for organic solar-absorbing thin films,¹¹ implying the existence of compact-packing absorption dipoles in the **DTDCTP** thin film that may substantially increase the absorption efficiency.

Vacuum-processed planar-mixed heterojunction (PMHJ) devices¹² composed of a donor-acceptor blend sandwiched between a pure donor and acceptor layer as active layers were adopted in photovoltaic characterization. After fine-tuning the thicknesses of active layers (Fig. S2-S5 and Tables S2 and S3, ESI[†]), the optimized device structures were configured as follows: (i) device DTDCTP:C₆₀: ITO/MoO₃ (20 nm)/DTDCTP (7 nm)/**DTDCTP**:C₆₀ (1 : 1, by volume, 40 nm)/C₆₀ (20 nm)/2,9dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (10 nm)/Ag, and (ii) device DTDCTP:C₇₀: ITO/MoO₃ (20 nm)/DTDCTP (7 nm)/**DTDCTP**:C₇₀ (1:1, by volume, 40 nm)/C₇₀ (6 nm)/BCP (10 nm)/Ag. The MoO₃ thin film acts as the hole-transporting layer and the BCP thin film serves as the electron-transporting layer with exciton blocking characteristics. Fig. 2 shows the current density-voltage (J-V) characteristics of DTDCTP:fullerene solar cells. The **DTDCTP**: C_{60} device gave a V_{oc} of 0.95 V, a $J_{\rm sc}$ of 8.3 mA cm⁻², and a fill factor (FF) of 0.54, leading to a PCE of 4.3% under AM 1.5G, 1 sun (100 mW cm⁻²) simulated solar illumination. Moreover, the DTDCTP:C₇₀ device delivered a markedly high spectra-mismatch-corrected PCE of 6.4% with a $V_{\rm oc}$ of 0.95 V, $J_{\rm sc}$ of 12.1 mA cm⁻², and FF of 0.56. The high $V_{\rm oc}$ values for the devices are stemmed from the low-lying HOMO level (-5.46 eV) of DTDCTP acquired by using ultraviolet photoelectron spectroscopy, which is deeper than that of **DTDCTB** (-5.30 eV). It is noteworthy that this difference in HOMO levels significantly contributes to the increase in $V_{\rm oc}$ for **DTDCTP**-based devices. Apparently, an enhanced Voc can be successfully achieved through molecular structure modification, and the electronwithdrawing nature of pyrimidine effectively limits the HOMOlifting effect that is usually encountered in thiophene-embedded π -conjugated systems. The larger J_{sc} obtained in the DTDCTP:C₇₀ device can be ascribed to higher and broader extinction



Fig. 1 (a) The X-ray analyzed molecular structure and crystal packing of **DTDCTP**. (b) Extinction coefficient (k) spectra of **DTDCTP**, C₆₀, and C₇₀ thin films.



Fig. 2 J-V characteristics of DTDCTP:C₆₀ PMHJ (square) and DTDCTP:C₇₀ PMHJ (circle) solar cells. Inset: external quantum efficiency spectrum of DTDCTP:C₆₀ PMHJ (square) solar cells, external (circle) and internal (solid line) quantum efficiency spectra of DTDCTP:C₇₀ PMHJ solar cells.





Fig. 3 Tapping-mode atomic force microscopy images of the **DTDCTP**: C_{70} mixed layer shown in a 500 nm × 500 nm surface area. (a) The topography and (b) the corresponding phase image.

coefficients of C70 as compared to those of C60 shown in Fig. 1(b). Therefore, the better light-harvesting capabilities of C₇₀ significantly contribute to the higher external quantum efficiencies (EQE) of the DTDCTP:C70 device in comparison to those of the **DTDCTP**: C_{60} counterpart (inset of Fig. 2). Note that the integrated values of EQE spectra with the standard AM 1.5G solar spectrum always agree with the J_{sc} values with deviation less than 5% in this study. The FF values were comparable for DTDCTP:C₆₀ and DTDCTP:C₇₀ devices, suggesting similar blending layer morphologies and charge carrier percolated networks in both devices. In addition, the nanoscale morphology of the **DTDCTP**:C₇₀ mixed thin film was probed by tapping-mode atomic force microscopy (AFM). Surface topography and phase images of the thin film show a smooth morphology with root-mean-square roughness of ~ 0.86 nm (Fig. 3). Interestingly, the phase image clearly shows the appearance of phase-separated domains with sizes of tens of nanometres. This result indicates that a preferred morphology was formed in the blending layer and thus provided sufficient D/A interfaces for exciton dissociation and effective pathways for charge carrier transport. The results together with balanced electron and hole mobilities in the **DTDCTP**: C_{70} mixed layer ($\sim 3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 700 (V cm⁻¹)^{1/2}, for details see Fig. S6 and Table S4, ESI[†]) contribute to high FF values of up to 0.56 offered in DTDCTP:C₇₀ PMHJ cells.

The total absorption and EQE spectra of the **DTDCTP**: C_{70} device were extracted to give the corresponding internal quantum efficiency (IQE) spectrum according to the formula: IQE $(\lambda) = EQE (\lambda)/absorption (\lambda)$ (for details see Fig. S7, ESI[†]). As shown in the inset of Fig. 2, the IQE of the DTDCTP:C₇₀ device exhibits a high plateau of over 80% throughout the entire visible spectrum (380-700 nm). Considering the light absorption and scattering loss by other layers (the ITO, metal, and glass substrate), such high IQE values indicate that most of the photons absorbed by the active composite layers lead to separated carriers, and all photogenerated carriers are efficiently collected at the electrodes. To gain more insight into the collection efficiency of free carriers, transfer matrix simulation of optical field and exciton formation distribution was performed.¹³ Under the assumption that 95% of photons are absorbed by a 40 nm DTDCTP:C70 mixed layer and successfully dissociated into free charge carriers that are all collected at the electrodes, the simulated EQE spectrum matches well with the experimental data. This result reveals that only $\sim 5\%$ of free charges recombine during the course of transport towards electrodes. The remarkably high collection efficiency is mainly due to faultless interpenetrating networks of the very thin (40 nm) mixed layer.

In conclusion, a tailor-made molecule **DTDCTP** with a D–A–A molecular architecture has been synthesized and developed as the donor material in small-molecule OPVs. The adoption of the pyrimidine acceptor in **DTDCTP** has successfully improved the $V_{\rm oc}$ as compared to our recent work,⁹ and an enhanced PCE of 6.4% has been realized through striking a balance between photovoltage and photocurrent. This efficiency is among the highest ever obtained for organic vacuum-deposited single cells. Further engineering of molecular structures is currently in progress and will be reported in due course.

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