An A-D-A Type Small-Molecule Electron Acceptor with End-Extended Conjugation for High Performance Organic Solar Cells

Huanran Feng,†,‡ Nailiang Qiu,†,‡ Xian Wang,‡ Yunchuang Wang,‡ Bin Kan,‡ Xiangjian Wan,† Mingtao Zhang,‡ Andong Xia,‡ Chenxi Li,‡ Feng Liu*,† Hongtao Zhang,‡,* and Yongsheng Chen*†

†State Key Laboratory of Elemento-Organic Chemistry, Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, College of Chemistry, Nankai University, Tianjin 300071, China
‡Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
§Department of Physics and Astronomy, Shanghai Jiaotong University, Shanghai 200240, China

ABSTRACT: A new non-fullerene small molecule with an acceptor-donor-acceptor (A-D-A) structure, FDNCTF, incorporating fluorenedicyclopentathiophene as core and naphthyl-fused indanone as end groups, was designed and synthesized. Compared with the previous molecule FDICTF with the phenyl-fused indanone as the end groups, the extended π-conjugation at the end group has only little impact on its molecular orbital energy levels, and thus, the open-circuit voltage (V_{oc}) of its solar cell devices has been kept high. However, its light absorption and mobility, together with the short-current density (J_{sc}) and the fill factor (FF), of its devices have been all improved simultaneously. Through morphology, transient absorption, and theoretical studies, it is believed that these favorable changes are caused by (1) the appropriately enhanced molecular interaction between donor/acceptor which makes the charge separation at the interface more efficient, and (2) enhanced light absorption and more ordered packing at solid state, all due to the extended end-group conjugation of this molecule. With these, the solar cells with FDNCTF as the acceptor and a wide band gap polymer PBDB-T as the donor demonstrated a high power conversion efficiency (PCE) of 11.2% with an enhanced V_{oc}, J_{sc}, and FF/FF, compared with that of the devices of FDICTF with the phenyl-fused indanone as the end groups. These results indicate that the unexplored conjugation size of the end group plays a critical role for the performance of their solar cell devices.

INTRODUCTION

Bulk heterojunction (BHJ) organic solar cells (OSCs) have attracted extensive attention due to their potentials in developing low cost, flexible, and semitransparent solar panels.1–5 Recently, benefiting from the rapid development of non-fullerene (NF) small-molecule acceptors due to their better absorption and tunable band structures, the overall performance of OSCs has improved significantly to 13%.6 On the basis of the equation of PCE = J_{sc} × V_{oc} × FF/P_{so}, it is best to improve open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (FF) simultaneously when further higher power conversion efficiency (PCE) is desired. Different with their inorganic counterparts, the charge separation of exciton in organic solar cells is mainly limited by its shorter effective diffusion length.7–9 Both theoretical and experimental results have indicated that the charge separation efficiency is expected to be potentially improved by appropriately increasing the donor (D)/acceptor (A) intermolecular interaction.10–14 On the other hand, V_{oc}, J_{sc}, and FF are often tangled together as both molecular properties (i.e., conjugation length, band structure, etc.) and film morphology (the domain size and interpenetrating network) in many cases may have an opposite impact on these factors. For example, while it is intrinsic to lower the lowest unoccupied molecular orbital (LUMO) level of the acceptor for higher J_{sc}, the corresponding V_{oc} could decrease accordingly.15,16 Also, while the increased conjugation size of molecules may improve optical absorption, over extended size of the backbone and high degree of coplanarity tend to make the molecules over aggregated, thus leading to poor morphology with a large phase separation often for poor FF.17 Therefore, a dedicated balance of molecule design is highly required to achieve not only high optical absorption and suitable energy level but also optimized film morphology.

In the past few years, to maximize PCE, much work has been focused on the design of various small molecules containing different electron-deficient groups, such as perylene diimide (PDI), naphthalene diimide (NDI), diketopyrrolopyrrole (DPP), tetraazabenzo[15IACS Publications © 2017 American Chemical Society

DOI: 10.1021/acs.chemmater.7b02811
7908

Received: July 6, 2017
Revised: August 29, 2017
Published: August 29, 2017
2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (INCN) as NF acceptors. Interestingly, it should be noted that, currently, the most successful NF molecules all have the same acceptor-donor-acceptor (A-D-A) molecular architecture which has been proved to be very successful for many donor molecules in the last 10 years. Some of these high performance A-D-A type NF molecules include ITIC (3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]-dithiophene), INCIC (3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-6,6,12,12-tetrakis(4-hexylphenyl)-indacenobis(dithieno[3,2-b:2′,3′-d′]-thiophene), and IDTBR (5Z,5′Z)-5,5′-{[5,5,11,11-tetrakis(n-octyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]-dithiophene==2,8-diyl][bis[2,1,3-benzothiadiazole-7,4-diy-Z(methyl-lidene)]]-bis[3-ethyl-2-thioxo-1,3-thiazolidin-4-one]}), and PCEs over 13% based on these A-D-A small-molecule acceptors. The reasons behind the much success of the A-D-A architecture might be very complicated and are yet to be fully understood. However, some arguments we have are (1) the spatial distribution of the electron density of frontier molecular orbitals (HOMO and LUMO) of this type of molecules might favor the important charge separation at the interface of the donor and acceptor; (2) the easily tuned absorptions and energy levels of these A-D-A molecules; and (3) the optimal (not too high not too low) aggregation of the molecules due to their structure at solid state. It should be noted that most of these successful NF acceptors comprise aromatic fused rings with extended conjugation as the donor core and an electron-deficient conjugation unit as the end groups, which would prompt intermolecular π−π overlaps and enhance intermolecular charge transport. The large central π-conjugated unit would result in better absorption; thus, higher Jsc could be achieved. However, compared with many studies on the central core unit for these A-D-A small-molecule acceptors, no larger conjugation end unit (almost all are based on INCN end unit) has been studied to understand the influence of extended end groups on the properties of these molecules. This is contrary to the intensive studies carried out for the small-molecule donors, where tuning the end groups would improve the material performance significantly. On the other hand, extending the π-conjugated length of the end groups may provide a new solution for the trade-off of Voc and Jsc by achieving a red-shifted absorption while minimizing the adverse impact on the LUMO level and thus the Voc, which has been used much for the design of many small-molecule A-D-A type donors. In addition, the introduction of a large π-conjugated moiety onto the end of small molecules would benefit the intermolecular end-to-end π−π interaction and molecular packing, leading to enhanced charge separation and transport and thus improving FF. With these, we believe that not only it is urgent and important to design some new NF small-molecule acceptors with extended end conjugation units and study the impact of the end groups overall but also such design might provide molecules with better performance.

Very recently, we reported an A-D-A type small-molecule acceptor 2,9-bis(2-methylene(3-(1,1-dicyanomethylene)-indanone)-7,12-dihydro-4,4,7,7,12,12-hexaoctyl-4H-cyclopenta[2′,1′:5′,6′:4′,5′:5′,6′]diindenol[1,2-b:1′,2′-b′]-dithiophene (named as FDICTF, Figure 1a) and a PCE of 10.06% with a
Scheme 1. Synthetic Scheme of FDNCTF

high $V_{oc}$ of 0.94 V for its OSC devices.\textsuperscript{33} While we thought the $V_{oc}$ was high, it seems that there is large potential for the improvement of the $J_{sc}$ and FF. From the discussion above, we thought that extending the end-group conjugation might be able to manage the trade-off of $J_{sc}$ and $V_{oc}$ and achieve the goal of improving the $J_{sc}$ while maintaining its high $V_{oc}$. This is based on the assumption that, different from the approaches of introducing a strong electronegative group on the end,\textsuperscript{24,31} the extended end conjugation length/size might not only minimize the impact on the LUMO and thus $V_{oc}$ but also enhance the light absorption and molecular packing and thus make the $J_{sc}$ and FF improved simultaneously due to both the appropriately increased D/A interfacial interaction for better exciton separation and the more ordered packing.\textsuperscript{34} On the basis of these thoughts, we extended the benzene unit of the previously widely used end group INCN and replaced the benzene unit with a naphthalene unit and synthesized a new active end-group moiety, NINCN (2-3-oxo-2,3-dihydro-1H-cyclopenta[\textit{b}]naphthalen-1-ylidene)malononitrile. Using NINCN as the end group, a new small-molecule FDNCTF, (2,9-bis(2-methylene(3(1,1-dicyanomethylene)benz[f]indanone))7,12-dihydro-4,4,7,7,12,12-hexaoctyl-4H-cyclopenta[\textit{2}′,\textit{1}′:\textit{5},\textit{6}:\textit{3}′,\textit{4}′:\textit{5},\textit{6}′]dindeno[1,2-\textit{b}:1′,2′-\textit{b}′]dithiophene (Figure 1a), was synthesized. Indeed, the LUMO energy level was little changed compared with the previous molecule FDICTF when INCN was at the end. Importantly, as designed, at solid state, a much red-shifted optical absorption than that of the previous INIC molecules FDICTF was achieved. This is due to the better molecular ordering than that of FDICTF at solid state arising from the stronger intermolecular interactions between the end groups. In the OSC devices with the same donor material (PBDB-T), due to the appropriately increased D/A interfacial interaction, the charge separation efficiency improved significantly as evidenced by the transient absorption (TA) spectra and other analysis. Thus, the OSCs based on PBDB-T:FDNCTF demonstrated a significantly improved PCE of 11.2% with maintained $V_{oc}$ and improved $J_{sc}$ and FF, compared with the corresponding OSCs with FDICTF as the acceptor. These results indicate using extended conjugation end groups might provide another important strategy to design higher performance NF acceptors.

■ RESULTS AND DISCUSSION

Synthesis and Thermal Properties. The synthetic route of FDNCTF is shown in Scheme 1, and the detailed procedures of it are provided in the Supporting Information (SI). The central unit and its dialdehyde compound FDTCCHO have been prepared as before.\textsuperscript{36} The Compound 2 (NINCN) was obtained by Knoevenagel condensation of Compound 1 with malononitrile.\textsuperscript{37} The targeted compound FDNCTF was prepared by the Knoevenagel condensation of NINCN and the dialdehyde compound FDTCCHO\textsuperscript{35} in a 62% yield. The solubility of FDNCTF is quite good in common organic solvents, e.g., chloroform, chlorobenzene, and ortho-dichlorobenzene. Thermogravimetric analysis (TGA, Figure S3a) indicates its high thermally stability with the decomposition temperature ($T_d$) of 383 °C with 5% weight loss.

DFT Calculation. While the density functional theory (DFT) at the B3LYP/6-31G(d,p) level is probably over-simplified, as it is widely adopted in literatures and consumes less computing power, it was used to investigate the possible influence of the extended end groups on the geometry properties of A-D-A small molecules. If we recall the major steps of the photovoltaic process, including the generation of an exciton by photon absorption, exciton migration/diffusion to the donor:acceptor interface, the charge separation of the exciton at the interface, and the free charge transportation to the electrodes, clearly, the interfacial interaction between the donor and the acceptor plays a critical role for the efficient charge separation of the exciton generated by light absorption. Thus, such interaction, mainly depending on the LUMO orbitals of the donor and acceptor after photo-caused excitation and generation of an exciton (the donor’s electron is excited to its LUMO from its HOMO), proper interaction between such two LUMO orbitals could favor an efficient charge separation to generate free charges of electron and hole. Also, such interaction should be not too weak or too strong. Generally, the factors affecting the molecular orbital interaction include the orbitals’ symmetry, energy difference, overlap, and spatial distance. For our case, with the new end group having a larger and planar conjugation system and considering the general over bulky and rigid core structure of these NF molecules, it is expected that such an expanded end-group structure would enhance the frontier orbital interaction between the donor:acceptor at the interface; thus, a more favorable charge separation process would be achieved to improve the overall photovoltaic performance. With these, we have analyzed the calculated HOMO electron density and LUMO spatial distribution of FDNCTF and FDICTF to understand the effect of the larger end group on the HOMO and LUMO. While the quantitative results may not be accurate, the calculated HOMO electron density and LUMO spatial distribution of FDNCTF and FDICTF in Figure 2a indicate that the new molecule FDNCTF has more LUMO spatial distribution extended to the end. The isosurface of charge density difference of LUMO/HOMO between FDNCTF and
Absorption Spectra and Electrochemical Properties.
As shown in Figure 1d, in chloroform solution, FDNCTF exhibits strong and broad absorption in the region of 550–760 nm with a maximum extinction coefficient of 3.2 $\times$ 10$^5$ M$^{-1}$ cm$^{-1}$ at 697 nm, which is higher than that of FDICTF (2.7 $\times$ 10$^5$ M$^{-1}$ cm$^{-1}$ at 665 nm). In thin film (Figure 1e), both FDNCTF and FDICTF exhibit red shifts and broader absorption than their corresponding solution spectra with the maximum absorption peak at 714 nm for FDNCTF and 689 nm for FDICTF. The red-shifted absorption of FDNCTF is consistent with the increased effective $\pi$-conjugation.43 The improved light absorption of FDNCTF should contribute more current than FDICTF. The electronic energy levels of FDNCTF were measured by electrochemical cyclic voltammetry (CV) in dichloromethane (Figure S4). The experimental LUMO energy level of FDNCTF was estimated from the CV to be $-3.73$ eV, 0.02 eV lower than that of FDICTF. The HOMO energy level ($-5.43$ eV) of FDNCTF is slightly upshifted compared with that ($-5.41$ eV) of FDICTF, consistent with the theoretical calculated HOMO/LUMO results of FDICTF ($-5.56/-3.30$ eV) and FDNCTF ($-5.52/-3.32$ eV). As expected, FDNCTF as an acceptor exhibits only a slightly lower LUMO energy level, thus minimizing the impact on $V_{oc}$ of the corresponding OSC devices. The above absorption and energy level data are summarized in Table 1.

Photovoltaic Properties. With better absorption and likely better charge separation, it is expected that FDNCTF should have a better photovoltaic performance when the same donor polymer material PBDB-T (Figure 1b) is used. Thus, the OPV devices of this new electron acceptor were fabricated and evaluated with a conventional device configuration of ITO/PEDOT:PSS/PBDB-T:FDICTF/PDINO/Al, where PDINO is an efficient cathode interlayer developed by Li et al.44 The detailed device optimization processes are described in the Tables S2–S5, including different donor/acceptor weight ratios, different processing solvents, and solvent additives. The FDNCTF optimized performance was obtained by utilizing chlorobenzene as the processing solvent with donor/acceptor weight ratio 1:0.8 and the active-layer thickness of $\sim 120$ nm.

The optimized current density–voltage ($J$–$V$) curve of the device based on PBDB-T:FDICTF is shown in Figure 3a, and the corresponding photovoltaic parameters are listed in Table 2. Meanwhile, the optimized $J$–$V$ and photovoltaic parameters of the PBDB-T:FDICTF device are also provided for comparison.35 As shown in Table 2, the optimized OSC devices based on PBDB-T:FDNCTF exhibited a high PCE of 11.2% with a $V_{oc}$ of 0.93 V, a $J_{sc}$ of 16.5 mA cm$^{-2}$, and an FF of 72.7%. Compared with the FDNCTF-based device, the FDNCTF-based device exhibited almost the same $V_{oc}$ but enhanced $J_{sc}$ consistent with the little changed LUMO level and red-shifted and stronger absorption of FDNCTF. Note the FF was improved significantly too. Meanwhile, the FDNCTF-
based device exhibited decreased energy loss ($E_{\text{loss}} = E_{\text{g, opt}} - eV_{\text{oc}}$) of 0.67 eV comparing with that (0.69 eV) of the FDICTF-based device. The external quantum efficiency (EQE) curve of FDNCTF-based device (Figure 3b) shows stronger and wider photoresponse than that of the FDICTF-based device, which could be attributed to the stronger and red-shifted absorption of FDNCTF.

To further understand the reasons behind the improved FF of the FDNCTF-based devices, the exciton dissociation, charge collection, and charge recombination were investigated by

Table 2. Optimized Photovoltaic Parameters of the Devices Based on PBDB-T:FDICTF and PBDB-T:FDNCTF under the Illumination of AM 1.5G (100 mW cm$^{-2}$)

<table>
<thead>
<tr>
<th>acceptor</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE$_{\text{max}}$ (%)</th>
<th>PCE$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDICTF$^a$</td>
<td>0.94 ± 0.01</td>
<td>15.8 ± 0.2</td>
<td>66.0 ± 1.0</td>
<td>10.0</td>
<td>9.7 ± 0.2</td>
</tr>
<tr>
<td>FDNCTF</td>
<td>0.93 ± 0.01</td>
<td>16.3 ± 0.2</td>
<td>72.5 ± 0.8</td>
<td>11.2</td>
<td>10.9 ± 0.4</td>
</tr>
</tbody>
</table>

$^a$Refer to ref 35. $^b$The average PCE value was calculated from 50 devices.
measuring the photocurrent density ($J_{ph}$) versus effective voltage ($V_{eff}$) and the dependence of the $J_{sc}$ on light intensity.\textsuperscript{45}

As can be seen from Figure 3c, $J_{ph}$ values for both devices are saturated ($J_{sat}$) at $\sim 2$ V, suggesting that charge recombination in both devices is minimized at higher voltage due to the high internal electric field. The $J_{ph}/J_{sat}$ ratio is up to 93\% for the FDNCTF-based devices under short-circuit conditions, compared with 91\% for the FDICTF-based devices. Furthermore, these ratios are 80\% and 74\% for FDNCTF- and FDICTF-based devices, respectively, at the maximal power output conditions. These results indicate that the FDNCTF-based device possesses more efficient exciton dissociation and charge collection relative to those of the FDICTF-based devices, reflecting our initial design. The light-intensity ($P$) dependence of $J_{sc}$ was also measured to study the charge recombination kinetics.\textsuperscript{46} As shown in Figure 3d, the power-law exponents of the equation $J_{sc} \propto P^\alpha$ for the FDNCTF- and FDICTF-based devices are 0.99 and 0.96, respectively, indicating less bimolecular recombination occurred in the FDNCTF-based device, supporting its improved FF and $J_{sc}$.\textsuperscript{45,46} In addition, the enhanced fluorescence quenching efficiency (96\%) of FDNCTF over that of FDICTF (94\%) obtained by the photoluminescence (PL) spectra (Figure S7) indicated a higher exciton dissociation in the PBDB-T:FDNCTF blend. With all of these together, thus a better photovoltaic performance would be expected of FDNCTF-based OSCs than that of FDICTF.

**Morphology Characterization.** To understand why the end-group modulation causes an obvious difference in the photovoltaic performance, the molecular ordering in acceptor thin films was studied using two-dimensional grazing-incidence X-ray diffraction (2D-GIXD). As shown in Figure 4a,c, FDICTF shows a quite low intensity diffraction peak at around 0.38 Å$^{-1}$ and a strong diffraction halo at around 1.3 Å$^{-1}$; thus, it is highly amorphous in neat film.\textsuperscript{35} When a larger size of end groups is introduced, the packing of FDNCTF makes a fundamental change. A quite strong (100) lamellar diffraction peak is seen at 0.32 Å$^{-1}$ with an interlamellar distance of 19.5 Å in the in-plane direction; a sharp $\pi-\pi$ stacking (010) diffraction peak is seen at 1.82 Å$^{-1}$ in the out-of-plane direction with a $d$-spacing of 3.4 Å (Figure 4c). Thus, the minor structural change if proper could lead to a completely new molecular ordering, turning an amorphous solid into a highly ordered thin film. The NINCN end group is surely successful in inducing structure order, which can be extended to other material systems. Highly ordered thin film leads to a rough surface. As shown in Figure 4d,e, a larger surface roughness root-mean-square (RMS) of FDNCTF (0.90 nm) is seen over that of FDICTF (0.33 nm). In properties, the electron mobility of FDNCTF (2.83 $\times$ 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) is an order of magnitude larger than that of FDICTF (3.79 $\times$ 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) in a single carrier space-charge-limited current (SCLC) measurement, correlating well with structure details in thin film.

The solid-state packing of molecules in BHJ blends was characterized by 2D-GIXD (Figure 5a,e), transmission electron microscopy (TEM, Figure 5f), and resonant soft X-ray scattering (RSoXS, Figure S10). As shown in Figure 5a,b, the GIXD diffraction of PBDB-T:FDICTF blends without DIO was dominated by the polymer diffraction signals with a (100) peak at 0.29 Å$^{-1}$ and a $\pi-\pi$ stacking (010) peak at 1.69 Å$^{-1}$, and there is no clear peak from the acceptor FDICTF. However, PBDB-T:FDICTF blends processed without DIO showed some differences by comparing Figure 5a,b with Figure...
(1) there is clearly a new peak at 0.32 Å−1 from the new acceptor FDNCTF, close to the original polymer (100) peak; and (2) the original (010) peak at 1.69 Å−1 has been broadened due to the new acceptor FDNCTF. Thus, the introduced extended end groups could significantly improve the morphology of BHJ blends, with results corresponding well with the device characteristics, owing to the better crystallinity nature of FDNCTF that breaking away from the intimate mixtures with polymer donor.

When a tiny amount of solvent additive was used, the low boiling nature of additive molecules could effectively plasticize the blended thin films, making the glass transition much lower than that of conventional mixtures, and the quicker kinetics of small molecules in self-assembling made pronounced molecular crystals in both cases, which directed better morphologies and thus device performances. As seen from PBDB-T:FDNCTF blends processed with DIO (Figure 5a,c), FDNCTF showed obvious crystallization peaks, which, by fitting, gave a CCL of 20.0 nm (polymer showed a CCL of 22.5 nm.) from in-plane diffraction profiles. While PBDB-T:FDICTF processed with DIO exhibited a rather similar diffraction pattern as shown in Figure 5a,e with that (Figure 5a,c) of PBDB-T:FDNCTF with DIO, quantitatively it gave a CCL of 16.2 nm for FDICTF (polymer showed a CCL of 24.5 nm.). The original fitting results are provided in Figure S9 with the fitting details and data accuracy. Thus, better crystallization of FDNCTF was observed in its BHJ blends, which should help to improve device performances as shown in previous discussions. However, the global morphology is more complicated than just the crystalline network; the phase separation and material aggregation also played an important role. As seen from TEM characterizations (Figure 5f), PBDB-T:FDNCTF blends processed with additive showed a fibril network structure as well as dark area material agglomerations, but the PBDB-T:FDICTF thin film was smoother under the same electron microscopy resolution and, though a larger in-plane (100) polymer CCL was seen, the fibril network structure was less obvious (Figure 5h). These features were due to the better mixing of PBDB-T and FDICTF, where, as in PBDB-T:FDNCTF blends, the FDNCTF better crystallization led to stronger FDNCTF aggregated domains that defines a multilength scaled morphology (fibril network in small length scale and material aggregation in large length scale). Such a structure was quite well resolved with further help of RSoXS where a length scale of phase separation at around 160 nm was seen for PBDB-T:FDNCTF and the scattering intensity was much stronger.
comparing to PBDB-T:FDICTF blends (Figure S10). These morphological features correspond well with their SCLC mobility characterizations, which show the higher hole and electron mobilities of $1.77 \times 10^{-4}$ and $1.00 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ of PBDB-T:FDNCTF than those of PBDB-T:FDICTF ($3.37 \times 10^{-5}$ and $2.40 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) measured by the SCLC method (Figure S5) and are consistent with the microstructure analysis and accounted for the improved FF in devices.

**Charge Separation Dynamics.** To understand the mechanism for higher performance (meaning higher $J_{sc}$ and FF) of this end-extended new acceptor, a series of studies were carried out for the decay dynamics of the exciton in the devices. As it is well-known that, different from fullerene acceptors, for NF electron acceptors, the current contribution due to the exciton dissociation or charge transfer; see the inset in Figure 6d) was observed in PBDB-T:FDICTF blended films with weakening Coulombic attraction at interfaces. A new bleach band peaking at 580 nm in the spectral profile of the CS state relative to CT/EX occurs, which matches the GS character of the donor, suggesting efficient separation of hole-electron pairs. The relative red shift of the bleach band peak (722 nm) of CS to that (715 nm) of CT in Figure 6d is attributed to the Stark effect induced exciton band shift, further verifying the generation of free carriers (holes). At the same pumplength, the HT process is also seen in PBDB-T:FDICTF blend film (Figure 6c) as the formation of the CS state with clear GSB character of PBDB-T (maxima at 630 and 580 nm). As the fitting results show in Table S1, the hole transfer from FDNCTF to PBDB-T is much faster with a time constant of 4.8 ps than that from FDICTF with a time constant of 9.5 ps, implying a more efficient hole transfer in PBDB-T:FDICTF than that in PBDB-T:FDICTF. Comparing panels (e) and (f) in Figure 6, there is higher concentration of the CS state for PBDB-T:FDNCTF at 1 ns. In addition, the yield of CS (hole) in PBDB-T:FDNCTF blend is estimated to be about ~54%, much higher than that (~43%) of PBDB-T:FDICTF, confirming the fact that better power conversion efficiency was obtained in PBDB-T:FDNCTF blend. With these results, it is clear that both the current generation channels are favored for the new molecule. These dynamic studies strongly support our initial thought that the extended conjugation would improve the charge separation and thus yield a better FF and overall performance under the same situation.

**CONCLUSION**

In conclusion, a new small-molecule acceptor FDNCTF with an A-D-A structure and incorporating NINCN as the new extended end group was designed and synthesized. FDNCTF exhibited red-shifted optical absorption, little changed LUMO energy level, higher charge carrier mobility, and more ordered molecular packing. Non-fullerene OSCs using FDNCTF as the acceptor and a wide band gap polymer PBDB-T as the donor demonstrated a high PCE of 11.2% with a $V_{oc}$ of 0.93 V, a $J_{sc}$ of 16.5 mA cm$^{-2}$, and an FF of 72.7%, which is much higher than the PCE of 10.06% for the corresponding FDICTF-based device. The higher $J_{sc}$ and nearly maintained $V_{oc}$ are benefited from the better complementary absorption and suitable LUMO energy level. The significantly improved FF should be ascribed to the higher charge separation efficiency and efficient hole transfer from FDNCTF to PBDB-T, confirmed by the transient absorption study. These should be due to the appropriately enhanced intermolecular interaction between the donor and the acceptor because of the extended conjugation of the end groups. These results indicate that employing larger conjugation end groups to the small-molecule acceptors is an effective way to enhance both the absorption and the molecular interaction of the NF acceptor while keeping the LUMO level. This should offer a good strategy to manage the difficult balance and trade-off of $J_{sc}$ and $V_{oc}$ in many cases and achieve...
higher $J_c$ and FF while keeping the $V_{oc}$ relatively unchanged, simultaneously. A similar strategy might be applied for the donor design.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b02811.

Experimental details, characterization data for the new compounds, thermogravimetric analysis, differential scanning calorimetry, cyclic voltammogram, internal quantum efficiency, photoluminescence spectra, $J-V$ characteristics of SCLC, NMR spectra, mass spectra, and other device data (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: fengliu82@jstu.edu.cn (F.L.).
*E-mail: htzhang@nankai.edu.cn (H.Z.).
*E-mail: yscchen99@nankai.edu.cn (Y.C.).

**ORCID**
Xian Wang: 0000-0003-3520-7397
Andong Xia: 0000-0002-2325-3110
Yongsheng Chen: 0000-0003-1448-8177

**Author Contributions**
H.F. and N.Q. contributed equally to this work.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
The authors gratefully acknowledge the financial support from the Ministry of Science and Technology of China (MoST) (2014CB643502 and 2016YFA0200200), NSFC (91433101, 51422304, 51373078, and 91633301).

**REFERENCES**


