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The Crucial Role of Fluorine in Fully Alkylated Ladder Type Carbazole Based Non-fullerene Organic Solar Cells

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Supporting Information Placeholder

ABSTRACT: Two fused ladder type non-fullerene acceptors, DTCCIC and DTCCIC-4F, based on an electron-donating alkylated dithienocyclopentacarbazole core flanked by electron-withdrawing non-fluorinated or fluorinated 1,1-dicyanomethylene-3-indanone (IC or IC-4F), are prepared and utilized in organic solar cells (OSCs). The two new molecules reveal planar structures and strong aggregation behavior, and fluorination is shown to red shift the optical band gap and down shift energy levels. OSCs based on DTCCIC-4F exhibit a power conversion efficiency of 12.6 %, much higher than that of DTCCIC-based devices (6.2 %). Microstructural studies reveal that while both acceptors are highly crystalline, bulk heterojunction blends based on the non-fluorinated DTCCIC result in overly coarse domains, while blends based on the fluorinated DTCCIC-4F exhibit a more optimal nanoscale morphology. These results highlight the importance of end group fluorination in controlling molecular aggregation and miscibility.

KEYWORDS: organic solar cells, non-fullerene acceptors, carbazole, fluorine effect, fully alkylated side chains

INTRODUCTION

The performance of solution processable organic solar cells (OSCs) based on non-fullerene acceptors (NFAs) has achieved impressive progress, with their power conversion efficiencies (PCEs) reaching beyond 16 % in this year for single junction devices.1-3 Compared to fullerene derivatives, NFAs possess several intrinsic advantages including increased flexibility of tuning chemical structures, broad absorbance across the solar spectrum, easily tunable energy levels, and relatively simple purification processes.4-6 NFAs based on a ladder type electron-donating backbone flanked with two strong electron-withdrawing endgroups have become dominate in high efficiency OSCs.7-13

Among many efficient molecular modulation strategies for photovoltaic applications, the introduction of fluorine atoms into NFA materials has been widely applied to adjust their optical absorption, energy levels and carrier mobility properties.14-32 The success of this strategy is associated with several factors. First, the small size of fluorine coupled with its high electronegativity, means the introduction of fluorine can effectively lower the energy levels without causing undesired steric hindrance. In addition, fluorination can promote intermolecular and
intramolecular interactions through noncovalent C–F...S and C–F...H bonds and hence enhance molecular crystallinity and facilitate charge transport. Moreover, comparing the 1,1-dicyanomethylene-3-indanone (IC) endgroup with its fluorinated derivative 2-((5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-dF), the stronger electron-withdrawing effect of the latter can enhance intramolecular charge transfer (ICT) in NFA materials resulted in a red-shift of the absorption spectra of NFAs to the near-IR region, thus enhancing device photocurrent. Several studies have demonstrated that OSCs based on ladder type NFAs with fluorinated endgroups show improved device performance than those based on non-fluorinated counterparts.

Chart 1. Chemical structures of indacenodithiophene, dithienocyclopentafluorene and dithienocyclopentacarbazole based nonfullerene acceptors with phenyl and alkyl side chains and their average (and best) reported PCE with the specified donor.

Based upon the strategy of introducing alkyl side chain as an effective method to modulate molecular packing and optoelectronics properties, in this work we focused on the development of new acceptors based on a fully alkylated dithienocyclopentacarbazole (DTCC) core end-capped with electron-withdrawing endgroups IC or IC-dF. Such acceptors can be thought of as analogues of the dithienocyclopentafluorene acceptor (FDICTF, Chart 1) in which the central fluorene unit is changed to a more electron rich carbazole unit. Electron rich cores have been shown to enhance the intramolecular charge transfer (ICT) effect and afford a desirable broadening of absorption. We further note that changing to a central carbazole unit also results in a reduction in overall alkyl chain density on the acceptor, since the carbazole only has a single octyl sidechain. The resulting acceptors, DTCCIC and DTCCIC-dF show red-shifted absorption spectra with respect to both their fluorine (FDICTF) and phenylalkyl analogues (HCN-C16 and HFCN-C16, Chart 1), with the
Figure 1. (a) Synthetic route to DTCCIC and DTCCIC-4F. (b) Simulated molecular geometries and LUMO and HOMO distribution of DTCCIC and DTCCIC-4F (alkyls are simplified to methyl) calculated by Gaussian 09 program at B3LYP/6-31G* level.

Fluorinated materials exhibiting a narrower band gap and strong molar extinction coefficient than the non-fluorinated version. Notably, we find that OSC devices based on PFDBD-T:DTCCIC-4F achieve an impressive PCE of up to 12.6% while OSC devices based on PFDBD-T:DTCCIC only obtained a moderate PCE of 6.2%. The unexpected short circuit current ($J_{sc}$) and fill factor (FF) losses of PFDBD-T:DTCCIC based devices are ascribed to excessive self-aggregation of DTCCIC and the formation of large phase-separated domains in the active layer, as observed from thermal analysis and microstructure measurements (vide infra). Flurination of the
endgroups results in a fine tuning of acceptor crystallinity and improved miscibility with the polymer donor PFDBDB-T, resulting in a better performance in OSCs.

RESULTS AND DISCUSSION

The synthetic route to DTCCIC and DTCCIC-4F is shown in Figure 1a. More detailed procedures are provided in Scheme S1, Supporting Information. The ladder type fused core DTCC was synthesized according to the literature method. Formylation of the core was achieved by the Vilsmeier-Haack reaction using POCl₃ (phosphorus oxychloride) and DMF (dimethylformamide) in good yield. Subsequent Knoevenagel condensation between DTCCCHO and the electron-withdrawing units IC or IC-4F afforded the target alkylated carbazole acceptors DTCCIC and DTCCIC-4F in high yields. The chemical structure of DTCCIC and DTCCIC-4F were fully characterized by MALDI-TOF MS, ¹H and ¹³C NMR and elemental analysis. Both molecules exhibited good solubility in common organic solvents, such as dichloromethane, chloroform and chlorobenzene at room temperature.

Thermal stability was investigated using thermogravimetric analysis (TGA, Figure S1) under nitrogen atmosphere. The results indicated that DTCCIC and DTCCIC-4F have good thermal stability with a weight loss lower than 5% up to 317 °C and 345 °C, which meets the requirement of device fabrication. From differential scanning calorimetry (DSC, Figure S2), DTCCIC exhibits an initial broad endotherm at 120 °C on first heating, followed by two sharp endothermic peaks at 225 °C and melting at 272 °C. These latter two transitions were also observed on the second heating/cooling cycle, and on cooling two exothermic peaks were observed. Examination by polarized optical microscopy (POM) suggested that the first endotherm was associated with a crystal-to-crystal phase transition, whilst the second was a melt to an isotropic phase. Fluorination has a significant effect on the thermal behavior with DTCCIC-4F only displaying a distinct thermal transition on the first cycle, with an endothermic peak at 192 °C and no further peaks apparent up to 300 °C. No peaks were observed on cooling, or on subsequent cycles. Examination by POM shows the transition at 192 °C appears to be a crystal-to-crystal transition and that no isotropic phase was observed up to the limit at 280 °C, suggesting the melt is at higher temperature.

Theoretical calculations were conducted using density functional theory (DFT) with the B3LYP/6-31G(d,p) basis set to compare the molecular geometry of DTCCIC and DTCCIC-4F. The two molecules of DTCCIC and DTCCIC-4F exhibit a similar planar molecular structure, and their frontier molecular orbitals electron distributions are accordant with different electronic property in each building block (Figure 1b). Additionally, the calculations show that DTCCIC-4F has a downshifted highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, originating from the electron-withdrawing property of the fluorine atoms.

DTCCIC in chloroform solution exhibits strong absorption in the 500 nm to 750 nm region with a maximum extinction coefficient of 2.02 × 10⁵ mol L⁻¹ cm⁻¹ at 673 nm (Figure S3 and Table 1). As shown in Figure 2b, the film of DTCCIC shows strong absorption in the wavelength region from 500 nm to 800 nm, and the

![Figure 2](https://example.com/figure2)

**Figure 2.** (a) Chemical structure of polymer donor PFDBDB-T. (b) Normalized UV-vis absorption spectra of PFDBDB-T, DTCCIC and DTCCIC-4F in neat film. (c) Energy levels of PFDBDB-T, DTCCIC and DTCCIC-4F.

### Table 1. Optical and electrochemical properties of DTCCIC and DTCCIC-4F

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>λₘₐₓₜₐₜₜ (nm)</th>
<th>T_d (°C)</th>
<th>solution</th>
<th>film</th>
<th>E_g (eV)</th>
<th>ε (mol L⁻¹ cm⁻¹)</th>
<th>E_{ox}/E_{red} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTCCIC</td>
<td>317</td>
<td>673</td>
<td>658, 712</td>
<td>1.62</td>
<td>2.02 × 10⁵</td>
<td>1.34/−0.80</td>
<td>−5.72</td>
<td>−3.58</td>
<td></td>
</tr>
<tr>
<td>DTCCIC-4F</td>
<td>345</td>
<td>685</td>
<td>695, 753</td>
<td>1.53</td>
<td>2.29 × 10⁵</td>
<td>1.46/−0.76</td>
<td>−5.84</td>
<td>−3.62</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Optical and electrochemical properties of DTCCIC and DTCCIC-4F.
absorption onset of 765 nm corresponds to an optical bandgap of 1.62 eV. Compared to the HCN-16 acceptor with phenyl sidechains (Chart 1), the maximum absorption peak of DTCCIC in thin film is slightly redshifted by 3 nm to 712 nm with a strong shoulder peak at 658 nm. Fluorination results in a red-shifting of the optical absorption, with the solution and film absorption of DTCCIC-4F at 685 nm and 753 nm respectively. This is consistent with a more intensive intramolecular charge transfer (ICT) effect induced by fluorinated IC-4F endgroups. Moreover, DTCCIC-4F exhibits a higher maximum extinction coefficient (2.29 × 10^5 mol L⁻¹ cm⁻¹) and narrower optical bandgap (1.53 eV) than DTCCIC.

Cyclic voltammetry measurements were employed to investigate the electrochemical properties of DTCCIC and DTCCIC-4F (Figure 2c and Figure S4). The HOMO and LUMO energy levels were calculated from the onset

![Graphs](image_url)

**Figure 3.** (a) J–V characteristic curves, (b) EQE spectra, (c) J_ph versus V_eff characteristics and (d) J_ph versus light intensity of the optimized DTCCIC and DTCCIC-4F based OSC devices.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Annealing</th>
<th>V_OC (V)</th>
<th>J_SC (mA cm⁻²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFDB-T:DTCCIC</td>
<td>RT</td>
<td>1.01 (1.0 ± 0.01)</td>
<td>12.6 (12.3 ± 0.3)</td>
<td>0.48 (0.47 ± 0.01)</td>
<td>6.2 (5.8 ± 0.4)</td>
</tr>
<tr>
<td>PFDB-T:DTCCIC</td>
<td>100 °C</td>
<td>1.01 (1.0 ± 0.01)</td>
<td>12.0 (11.7 ± 0.2)</td>
<td>0.44 (0.43 ± 0.01)</td>
<td>5.3 (5.0 ± 0.3)</td>
</tr>
<tr>
<td>PFDB-T:DTCCIC-4F</td>
<td>RT</td>
<td>0.84 (0.82 ± 0.02)</td>
<td>21.9 (21.7 ± 0.2)</td>
<td>0.63 (0.62 ± 0.01)</td>
<td>11.6 (11.0 ± 0.6)</td>
</tr>
<tr>
<td>PFDB-T:DTCCIC-4F</td>
<td>100 °C</td>
<td>0.85 (0.84 ± 0.01)</td>
<td>22.1 (21.9 ± 0.3)</td>
<td>0.67 (0.66 ± 0.01)</td>
<td>12.6 (12.1 ± 0.5)</td>
</tr>
</tbody>
</table>
oxidation and reduction potentials and calibrated by ferrocene/ferrocenium (Fc/Fc\(^{-}\), \(-4.8\) eV below vacuum). The HOMO energy levels of DTCCIC and DTCCIC-4F are estimated to be \(-5.72\) eV and \(-5.84\) eV and the LUMO energy levels are \(-3.58\) eV and \(-3.62\) eV, respectively. The slightly downshifted energy levels of DTCCIC-4F are related to the electron-withdrawing property of fluorine, which is also in agreement with theoretical DFT calculation.

Inverted OSC devices were utilized to investigate the performance of DTCCIC and DTCCIC-4F as non-fullerene acceptors using an ITO/ZnO nanoparticle/active layer/MoO\(_3\)/Ag structure. The previously reported PFDBB-T\(^{4+}\) was utilized as the donor polymer due to its well matched energy levels and non-overlapping absorption spectra (Figure 2). Devices were optimized using various blend ratios and annealing treatments (see supporting information). The current density–voltage (\(J–V\)) curves of the optimal devices based on DTCCIC and DTCCIC-4F are shown as Figure 3a, and their corresponding photovoltaic parameters are summarized in Table 2. PFDBB-T:DTCCIC-based devices showed 6.2 % PCE with a high \(V_{OC}\) of 1.01V, benefitting from the high-lying LUMO energy level of DTCCIC. Encouragingly, compared with PFDBB-T:DTCCIC-based devices, PFDBB-T:DTCCIC-4F-based devices achieved a much higher \(J_{SC}\) of 21.9 mA cm\(^{-2}\), better fill factor of 0.63, and improved PCE of 11.6 %, due to their broader and stronger complementary absorption, albeit with a lower \(V_{OC}\) of 0.84 V. After thermal annealing of the active layer, PFDBB-T:DTCCIC-4F based devices exhibited better performance than the unannealed devices while the performance of PFDBB-T:DTCCIC based devices slightly decreased. The morphology of neat DTCCIC and DTCCIC-4F films and their blends with PFDBB-T were further studied to explain these phenomenon. Interestingly, in both cases annealing affected only the fill factor, with the \(V_{OC}\) and \(J_{SC}\) both remaining unchanged.

External quantum efficiency (EQE) measurements were performed to determine the spectral origin of the photocurrent and verify the \(J_{SC}\) values for optimal DTCCIC

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**Figure 4.** 2D GIWAXS patterns for PFDBB-T:DTCCIC (a, b) and PFDBB-T:DTCCIC-4F (c, d) blend films. Results for as-cast (a, c) and annealed (b, d) films are shown.
and DTCCIC-4F based devices. As shown in Figure 3b, the
DTCCIC-4F based devices reach a maximum EQE value of
8.4 % and retain an average of over 60 % across the range
of 460 nm to 780 nm, a higher photo-to-current response
than that of DTCCIC based devices across the whole visible
range, indicating a more efficient photoelectron
conversion process. Additionally, DTCCIC-4F based
devices displayed a redshifted photocurrent response edge
compared to the DTCCIC based device, in accordance with
the trend of their corresponding films absorption profiles.
The broader and increased EQE values of the DTCCIC-4F
based device is in good agreement with the observed
higher $J_{SC}$ and demonstrates the beneficial effect of
fluorination of DTCCIC on the photo-harvesting ability of
these devices. The $J_{SC}$ values calculated from the EQE
curves are (1.92 and 20.89) mA cm$^{-2}$ for the DTCCIC and
DTCCIC-4F based devices, respectively, which are close to
those from the $J$–$V$ measurements.

![Figure 5. R-SoXS scattering profiles of as-cast and
annealed films of PFDBB-T:DTCCIC and PFDBB-
T:DTCCIC-4F. An energy of 283.9 eV was used for
the PFDBB-T:DTCCIC blend while an energy of 283.6 eV was
used for the PFDBB-T:DTCCIC-4F. In both cases the
photon energy chosen was found to maximize scattering
contrast. Note that $q^2$ scaling is used to magnify the
differences in scatter. Profiles represent spatial material
fluctuations within the film. Unscaled data is provided in
the supporting information.](image)

The exciton dissociation and charge recombination
behavior was investigated in the optimized devices for
each blend, using a combination of photocurrent ($J_{ph}$)
versus the effective applied voltage ($V_{eff}$) and light-
intensity measurements of $J_{SC}$.

The devices exhibited significantly different behaviour in their trends of $J_{ph}$ versus $V_{eff}$ (Figure 3c), with $J_{ph}$ for DTCCIC devices not saturating ($J_{sat}$) until $V_{eff}$ exceeds 2.5 V, whereas DTCCIC-4F saturated
at much lower values. The ratio of $J_{ph}/J_{sat}$ allows the charge
dissociation and collection probabilities of the blends to be
estimated, with the DTCCIC-4F being much higher than
the DTCCIC based device under both short circuit condition (97.8 % for DTCCIC-4F vs 89.4 % for DTCCIC)
and maximal power output conditions (90.8 % for
DTCCIC-4F vs 59.9 % for DTCCIC). The dependence of the
$J_{SC}$ on the light-intensity is shown in Figure 3d for both
blends. A steeper slope (0.913) is found for the DTCCIC-
4F based device compared to the DTCCIC based device
(0.878), suggesting lower bimolecular recombination in
the DTCCIC-4F device, in agreement with its higher
extraction probability.

The electron and hole mobilities of PFDBB-T:DTCCIC
and PFDBB-T:DTCCIC-4F blends were measured using the
space-charge-limited current (SCLC) method. Device
structures comprising ITO/ZnO nanoparticle/active
layer/Ca/Al were utilized for electrons and ITO/PEDOT:PSS/active layer/MoO$_3$/Ag for holes,. As
shown in Figure S5 and Table S2, the electron and hole
mobilities for PFDBB-T:DTCCIC blends were measured to be (2.15 x 10$^{-6}$ and 4.0 x 10$^{-5}$) cm$^{-2}$ V$^{-1}$ s$^{-1}$, respectively. On the contrary, PFDBB-T:DTCCIC-4F blend films exhibited
electron and hole mobilities of (4.27 x 10$^{-6}$ and 0.26 x 10$^{-5}$)
cm$^{-2}$ V$^{-1}$ s$^{-1}$, which are higher than those of PFDBB-
T:DTCCIC blend films. This improved charge transport
also helps to explain the higher observed current for
DTCCIC-4F based devices.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was applied to investigate the microstructural
differences between neat DTCCIC and DTCCIC-4F and
their blends. Figure 5 shows the GIWAXS results of as-
cast and annealed neat films. Both DTCCIC and DTCCIC-
4F exhibit complex scattering patterns consistent with
highly crystalline materials. Neat DTCCIC films exhibit
a higher degree of mosaicity (spreading of crystal plane
orientations) with neat DTCCIC-4F films being more
strongly oriented. In both cases, annealing of neat films
leads to an improvement in the degree of crystallinity. The
2D GIWAXS patterns of the blends are shown in Figure 4.
Scattering from the acceptor phases in both blends is
characterized by powder-like diffraction rings indicating a
significantly higher degree of mosaicity. The scattering
features from the acceptor molecules are also less sharp,
inducing reduced crystallinity in the blend, although
these molecules still exhibit a higher degree of crystallinity
in the bulk heterojunction blend compared to other
acceptors such as ITIC and ITIC-C8. Scattering from the
polymer can also be discerned, characterized by a broad
lamellar stacking peak at $\sim$ 3 nm$^{-1}$ and broad $\pi$-$\pi$ stacking
peak at $\sim$ 17 nm$^{-1}$. The effect of annealing on the GIWAXS
patterns is slight, with the PFDBB-T:DTCCIC blend
showing some sharpening of the diffraction features (see
1D line profiles in the Supporting Information), while the
GIWAXS patterns of the PFDBB-T:DTCCIC-4F not
showing any obvious change.

Resonant soft X-ray scattering (R-SoXS) was performed
to probe the nanoscale to mesoscale morphology, see
Figure 5. The scattering profile of the PFDBB-T:DTCCIC
blend is characterized by a scattering feature at $\sim$ 1.5 $\times$ 10$^{-3}$
Å$^{-1}$ and $\sim$ 2 $\times$ 10$^{-2}$ Å$^{-1}$. The scattering feature at $\sim$ 1.5 $\times$ 10$^{-3}$ Å$^{-1}$
would correspond to a spatial fluctuation at $\sim$ 400 nm
which is much larger than the optimum domain spacing
for an efficient bulk heterojunction solar cell. In contrast
the PFDBB-T:DTCCIC-4F blend only shows scattering at
higher q values corresponding to a finer morphology. In particular the prominent scattering feature at ≈1.5 × 10^3 Å⁻¹ observed in the PFDBB-T:DTCCIC blend is missing for the PFDBB-T:DTCCIC-4F blend, with a broad scattering profile instead seen extending between ≈3 × 10^3 Å⁻¹ to ≈2 × 10^3 Å⁻¹ corresponding to spatial fluctuations ranging from ≈30 nm to ≈200 nm. This large difference in the characteristic spatial fluctuations for PFDBB-T:DTCCIC and PFDBB-T:DTCCIC-4F can help explain the large difference in solar cell efficiency between the two blends, with the morphology of the PFDBB-T:DTCCIC blend being too coarse for efficient photovoltaic operation. For both blends annealing leads to an increase in scattering intensity and a slight shift in the scattering profiles to the left, corresponding to a coarsening of the blends and increase in domain purity. For the case of the PFDBB-T:DTCCIC blend this coarsening leads to a worsening of device performance since the domains are likely already too large. For the case of the PFDBB-T:DTCCIC-4F blend this slight coarsening and increase in domain purity seems to benefit solar cell performance.

The morphologies of the PFDBB-T:DTCCIC and PFDBB-T:DTCCIC-4F blend layers were also studied by tapping-mode atomic force microscopy (AFM). As observed from the AFM images (Figure S8), the neat DTCCIC and DTCCIC-4F films shows large crystallites consistent with the GIWAXS results that found these materials to be highly crystalline. The surface morphologies of the blends also show features consistent with acceptor aggregates, with the PFDBB-T:DTCCIC blend showing larger feature sizes than the PFDBB-T:DTCCIC-4F blend consistent with the R-SoXS results, indicating that the spatial fluctuations observed likely correspond to domain features.

CONCLUSIONS

In conclusion, we designed and synthesized two new ladder type non-fullerene acceptors DTCCIC and DTCCIC-4F based on alkylated dithienyclopentacarbazole core capped with non-fluorinated or fluorinated electron-withdrawing units (IC or IC-4F), and investigated the aklylation and fluorination effects on the morphological, optical, electronic and photovoltaic device properties. By replacing phenyl side chains, fully alkylated DTCCIC and DTCCIC-4F exhibit strong molecular aggregation and stronger redshifted absorption. Compared to non-fluorinated DTCCIC, fluorinated DTCCIC-4F exhibits further redshifted absorption spectra with a smaller optical bandgap of 1.53 eV and downshifted energy levels. PFDBB-T:DTCCIC-4F blend shows better nanoscale morphology and increased domain purity relative to PFDBB-T:DTCCIC blend. OSC devices based on PFDBB-T:DTCCIC-4F blends exhibit PCEs of 12.6 %, significantly higher than those of PFDBB-T:DTCCIC based devices (6.2 %) and among the highest efficiencies for dithienyclopentacarbazole based non-fullerene acceptors. These results further highlight that end group fluorination is an important approach to enhance overall photovoltaic performance compared to the analogous non-fluorinated material.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures including synthesis, device fabrication and additional characterization data, such as NMR, TGA, DSC, UV–vis absorption, CV data, SCLC, AFM, GIWAXS, R-SoXS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES


Non-fluorinated
PCE: 6.2 %

Fluorinated
PCE: 12.6 %