Diketopyrrolopyrrole (DPP) functionalized tetrathienothiophene (TTA) small molecules for organic thin film transistors and photovoltaic cells†

Nanjia Zhou,‡a Sureshraju Vegiraju,‡b Xinge Yu, C Eric F. Manley, C Melanie R. Butler, C Matthew J.Leonardi, C Peijun Guo, a Wei Zhao, d Yan Hu, d Kumaresan Prabakaran, d Robert P. H. Chang, ‡a Mark A. Ratner, C Lin X. Chen, C Antonio Facchetti, ‡c,cd Ming-Chou Chen* b and Tobin J. Marks*ac

Two novel π-conjugated small molecules based on the electron-deficient diketopyrrolopyrrole (DPP) and the electron-rich fused tetrathienoacene (TTA) frameworks are synthesized and characterized. As verified in the bandgap compression of these chromophores by electrochemistry and density functional theory (DFT) computation, these DPP-TAA derivatives exhibit substantial conjugation and ideal MO energetics for light absorption. The large fused TTA core and strong intermolecular S–S interactions enforce excellent molecular planarity, favoring a close-packed thin film morphologies for efficient charge transport, as indicated by grazing incidence wide angle X-ray scattering (GIWAXS), atomic force microscopy (AFM), and transmission electron microscopy (TEM) analysis. Top-gate/bottom-contact thin film transistors based on these systems exhibit hole mobilities approaching 0.1 cm² V⁻¹ s⁻¹. Organic photovoltaic cells based on DPPP-TTA:PC71BM blends achieve power conversion efficiencies (PCE) > 4% by systematic morphology tuning and judicious solvent additive selection.

For the design of small molecule OSC semiconductors, a donor–acceptor (D–A) strategy is commonly employed to specifically tune the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for broader solar light absorption, for ohmic contact at electrode interfaces, and to maximize built-in OSC potentials. Among various conjugated building blocks, the electron-deficient diketopyrrolopyrrole (DPP) moiety has received extensive attention due to its tunable solubility and relatively high electron affinity for adjusting orbital energetics.6–15 By installing proper alkyl side chains at the DPP nitrogen atoms, the processability of the resulting DPP derivatives can be enhanced, rendering them compatible with roll-to-roll solution processing.16 The most noteworthy examples of DPP-based polymers have high hole mobilities, up to 12–13.9 cm² V⁻¹ s⁻¹ in OTFTs,17,18 (structures shown in Scheme 1A), and DPP based polymers combined with fused thiophenes such as thienothiophene (TT) and dithienothiophene (DTT) as donor units have p-type charge-carrier mobilities as high as 10.5 cm² V⁻¹ s⁻¹19 and power conversion efficiencies up to 6.05–9.4% in OSCs20,21 (structure shown in Scheme 1B and C).

Despite the success of the aforementioned DPP-based polymers, the development and understanding of DPP-based small molecules has lagged far behind. Unlike polymer syntheses and properties, which are typically susceptible to batch-to-batch variations, small molecule syntheses generally provide excellent reproducibility,
purity, and yields, leading to far more uniform materials properties.\textsuperscript{3,22–25} For these reasons, solution-processable small molecules offer great potential for applications in technologically relevant organic electronic devices. Furthermore, small molecules can achieve precisely controlled molecular packing and ordered nanophase morphologies, via either self-assembly or controlled solution coating techniques.\textsuperscript{26,27} Thus, the design and implementation of small molecules also opens up new possibilities for understanding fundamental organic semiconductor structure–property relationships and further optimizing device parameters. Nevertheless, to date only relatively low p-type mobilities and PCEs have been achieved using DPP-based small molecules.\textsuperscript{10} For example, our team first reported NDT(TDPP)\textsubscript{2} (Scheme 1) exhibiting OPV PCEs of up to 4%,\textsuperscript{28} followed by alkyne functionalized (TDPP)\textsubscript{2}-EBT exhibiting a mobility of 0.17 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} and a PCE of 1.7%.\textsuperscript{29} More recently, Huang et al.\textsuperscript{30} and Lin et al.\textsuperscript{14} combined DPP with the widely implemented benzodithiophene (BDT) moiety and demonstrated OSC PCEs of 4.5%. While these results are promising, more detailed investigations will be necessary to better understand and further enhance the TFT and OPV device performance of DPP-based small molecules.

Motivated by the potential of introducing fused thiophene units into electronic polymers, here we investigate fused thiophene systems for the design of high performance small molecule materials. From our previous results, fused thiophene motifs enhance structural planarity and strong intermolecular S⋅⋅⋅S interactions.\textsuperscript{31–33} These properties promote extensive intramolecular π-conjugation and close intermolecular π–π stacking, thereby enhancing charge transport.\textsuperscript{34,35} Indeed, dithienothiophene-(DTT)\textsuperscript{36–39} and tetrathienoacene(TTA)\textsuperscript{35} derivatives achieve field-effect mobilities as high as 10.2 and 0.30 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} for p- and n-channel OTFTs, respectively. However, on combining fused thiophenes with DPP units, DPP-end-capped DTT (DTT2DPP) and DTTDPP derivatives yield only modest OTFT mobilities of ~0.02 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} and OSC PCEs approaching ~2.2%.\textsuperscript{41} To enhance device performance based on this design principle, we now integrate an additionally conjugated fused thiophene, TTA (Scheme 2), with DPPs as acceptor moieties. Such acene-based chromophores are expected to have more expansive planarity for π–π stacking and enhanced charge transport characteristics which are crucial for OTFT and OSC performance.

In this contribution we report two new semiconductors based on a β-alkyl substituted TTA core\textsuperscript{42} end-capped with two DPP moieties: N-alkylated DPPs and O-alkylated DPPs\textsuperscript{43} (referred to as DPP herein). Note that DPP\textsuperscript{0} derivatives are known to have smaller energy gaps and lower-lying HOMO energies than the DPP analogues.\textsuperscript{43} These characteristics are beneficial for both OTFT and OSC devices. However to date no DPP\textsuperscript{0}-based small molecules have been explored for applications in organic electronics and are thus investigated here for comparison. Solution-processed OTFT and OSC devices are fabricated here based with these two molecules, and exhibit PCEs of up to 4% and hole mobilities approaching 0.1 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, rendering these the highest performing fused thiophene OSC chromophores and some of the highest mobility fused thiophene semiconductors reported to date.

Results and discussion

1. Synthesis

A generalizable synthetic approach to molecules 1 and 2 is presented in Schemes 2 and 3. DPP functionalized TTAs (1) and
(2) are synthesized via Stille coupling, as shown in Scheme 2. Alkylated tetrathienothiophene (TTAR; 3), prepared according to literature procedures, is first doubly-deprotonated with n-BuLi, and then di-alkylstannylated to generate distannyl tetrathienothiophene (4), which can be recrystallized from ether and obtained in 67% yield. The mono-brominated N-alkyl and the O-alkyl DPP-based aryl bromides 5, and 6 are prepared in ~50% yields according to previously published procedures (Scheme 3). These units are then coupled with 4 to give the DPP end-capped DDPP-TTAR (1) and DDPP′-TTAR (2) in ~66% and 62% yield, respectively. The new molecules were then purified by chromatography and recrystallization from CHCl₃ to give materials suitable for use in OTFT and OSC devices. To the best of our knowledge this newly synthesized DDPP′ acceptor moiety is employed for the first time in small molecules for organic electronics objectives. All new compounds are characterized by conventional chemical and physical methodologies. Full experimental details can be found in the ESL.

2. Thermal, optical, and electrochemical properties of DDPP-TTARs (1 and 2)

For the new molecular semiconductors 1 and 2, differential scanning calorimetry (DSC) data reveal sharp endotherms at 222 °C and 128 °C, respectively, while thermogravimetric analysis (TGA) plots demonstrate negligible weight loss (~5%) until ca. 375 °C and 294 °C, respectively, as summarized in Table 1. Thus, under the same conditions, a higher melting point as well as greater thermal stability is observed for 1 versus isomer 2.

Molecules 1 and 2 both show visible light absorption over a broad range, making them excellent candidates for OSCs. The optical absorption spectrum of 2 in o-C₆H₄Cl₂ (Fig. 1) is significantly red-shifted versus that of 1 (E_{opt, gap} = 1.69 eV), indicating greater π-electron delocalization and a compressed optical band gap (E_{opt, gap} = 1.66 eV; Table 1), in good agreement with the band gap values obtained from electrochemical measurements (vide infra). The stability of these two compounds with respect to photooxidation was also investigated by monitoring the decay of the optical absorption maxima in aerated o-C₆H₄Cl₂ solutions exposed to a white fluorescent lamp light at room temperature. No decomposition is observed after several days of continuous illumination.

Differential pulse voltammograms (DPVs; see Fig. S1, ESI†) of 1 and 2 were next recorded in o-C₆H₄Cl₂ at 25 °C, and data are summarized in Table 1. The DPV of 1 exhibits an oxidation peak at +0.92 V and a reduction peak at −1.02 V, whereas those of 2 are located at lower potentials (E_{ox} = +0.86 V and E_{red} = −0.91 V). The estimated HOMO (−5.12 eV) and LUMO (−3.17 eV) of 1 thus lie below than those of 2 (−5.06 eV and −3.28 eV, Fig. 2b, Table 1), corresponding to a smaller band gap for the latter.

HOMO energies (EHOMO) were estimated using the conventional equation, E_{HOMO} = −(4.20 + E_{ox}); assuming ferrocene/ferrocenium oxidation at −4.8 eV. The low-lying HOMO energies for the

Table 1  Thermal, optical, and electrochemical properties of semiconductors 1 and 2

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>DSC T_m (°C)</th>
<th>TGA (°C; 5%)</th>
<th>UV-Vis λ_{max} (nm)</th>
<th>E_{red} (V)</th>
<th>LUMO (eV)</th>
<th>E_{ox} (V)</th>
<th>HOMO (eV)</th>
<th>ΔE_{gap} (eV)</th>
<th>UV</th>
<th>DPV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>222</td>
<td>375</td>
<td>615</td>
<td>−1.02</td>
<td>−3.17</td>
<td>0.92</td>
<td>−5.12</td>
<td>1.69</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>128</td>
<td>294</td>
<td>643</td>
<td>−0.91</td>
<td>−3.28</td>
<td>0.86</td>
<td>−5.06</td>
<td>1.66</td>
<td>1.77</td>
<td></td>
</tr>
</tbody>
</table>

* In o-C₆H₄Cl₂.  b By DPV in o-C₆H₄Cl₂ at 25 °C. All potentials referenced to an Fe+/Fe internal standard (at +0.6 V). E_{red} = reductive potential; E_{ox} = oxidative potential.  c Using HOMO = −(4.2 + E_{ox}); LUMO = −(4.2 + E_{red}).  d Energy gap estimated from optical absorption.
two DDPP-TTARs suggest that the two molecules should have good air stability versus pentacene and other previously reported fused thiophenes employing DTTs or TTAs.\textsuperscript{28,30} Furthermore, the HOMO energies of the present TTA compounds have ideal alignment favoring hole injection from contacting Au electrodes in p-type TFTs.

Electronic structure calculations were performed at the B3LYP/6-31G** level of density functional theory (DFT; Fig. 2b). Both molecules have similar ground state geometries characterized by relatively coplanar backbones, with the HOMO level electron density clearly localized on the DPP donor and the TTA moieties. The computed HOMO energies are $-4.79 \text{ eV}$ and $-4.90 \text{ eV}$ for 1 and 2, respectively, and the excited state (LUMO) energies for 1 and 2 are $-2.80 \text{ eV}$ and $-2.99 \text{ eV}$, respectively, yielding optical gaps of 1.99 and 1.91 eV for 1 and 2, respectively. That 2 has lower computed HOMO/LUMO energies as well as a compressed band gap versus 1, agrees well with the experimental optical absorption and DPV data.\textsuperscript{43} Time-dependent DFT (TDDFT) computations show that the principal optical transitions of 1 and 2 exhibit similar oscillator strengths, (2.67 and 2.64, respectively), in good agreement with the experimental extinction coefficients for 1 and 2 (82 900 and 125 000 $\text{M}^{-1} \text{cm}^{-1}$, respectively).

3. Film morphology and charge transport properties

Grazing incidence X-ray diffraction (GIXRD) and AFM were employed to characterize the film morphologies of the two TTAR materials, and were performed on thin films prepared by spin-coating chloroform (CF) solutions of 1 and 2 onto Si/SiO$_2$ substrates (Fig. 3). Furthermore, to identify the effects of post-annealing on molecular ordering, which can provide guidelines for OTFT fabrication, GIXRD and AFM data were also collected on films processed at various post-annealing temperatures. The pristine films fabricated at room temperature show relatively modest crystallinity for both 1 and 2 (Fig. 3a and b).

The first-order diffraction peaks (100) are located at $2\theta = 4.2^\circ$ and $4.5^\circ$, corresponding to $d$-spacings of 21.0 and 19.6 Å, for 1 and 2, respectively. However, film crystallinity for both molecules is dramatically enhanced upon thermal annealing. For 1, the GIXRD patterns exhibit increasing intensities of the (100) diffraction peaks with increasing annealing temperatures, showing second-order reflections for films annealed above 110 $\text{°C}$ (at $2\theta = 9.3^\circ$). Enhanced crystallinity on annealing can also be inferred from the AFM images (Fig. 3c). Interestingly for 2, the crystallinity gradually increases with increasing temperature up to $\sim 110 ^\circ \text{C}$, but then falls for temperatures above 150 $\text{°C}$. This result agrees well with the AFM topographical images, with the film annealed at 150 $\text{°C}$ exhibiting significantly smaller grains than those annealed at 110 $\text{°C}$.

To investigate the charge transport properties of 1 and 2, bottom-gate top-contact (BGTC) OTFTs were first fabricated using heavily n-doped Si as the gate, 300 nm SiO$_2$ as the dielectric, and spin-coated organic semiconductor layers. The films were examined at room temperature after annealing at 70, 110, or 150 $\text{°C}$. Finally, gold (Au) source/drain (s/d) electrodes with a channel width/length of 1000/50 $\mu\text{m}$ were evaporated on top of the organic layer, and the completed TFTs were characterized in ambient air (Fig. 4). All devices show p-type transistor behavior and no ambipolar characteristics, with the relevant FET metrics summarized in Table 2. The TFT films based on the unannealed 1 yield an average hole mobility of $3.8 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. With thermal annealing at various temperatures, the $\mu_h$ of 1 is found to significantly increase to $7.7 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 70 $\text{°C}$, and further reach $1.2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for annealing at 110 $\text{°C}$. However, annealing 1 films at higher temperatures decreases the hole mobility, with $4.5 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ measured for 150 $\text{°C}$ annealing. In contrast, the TFT performance of semiconductor 2 decreases upon post-deposition thermal annealing, which is likely the result of grain boundary formation. These transport results are consistent with the AFM images shown in Fig. 3d, where higher annealing temperatures result in small “island” formation,
thus compromising the connectivity required for efficient charge transport.

Next, the top-gate/bottom-contact (TGBC) TFT architectures were adopted to further enhance the OTFT performance. Thus, Si/SiO2 wafers with patterned Au s/d electrodes were utilized as substrates, and both 1 and 2 solutions were spin-coated on these and post-annealed at various temperatures. Subsequently, a Cytop layer with a unit capacitance of 4.9 nF cm⁻² was spun-cast as the top gate dielectric layer. Finally, Au contacts were evaporated onto the dielectric as the gate electrodes. Here, optimum results are achieved by measuring 1 and 2 in vacuum and after annealing at 110 °C. TFTs based on semiconductor 1 yield a hole mobility of \(0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), whereas those based on 2 yield a \(\mu_h\) value up to \(2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). Clearly Cytop improves device characteristics, likely via reduction of the interfacial traps arising from the suboptimal film morphology, particularly for semiconductor 2. Despite having favorable energetics, the fact that semiconductor 2 exhibits overall lower TFT performance can be explained by a combination of relatively poor intermolecular packing and macroscopically suboptimal morphology (Fig. 3).

### Table 2: TFT performance metrics (hole/electron mobilities, \(I_{on}/I_{off}\) ratios, and threshold voltages, \(V_t\)) for small molecule films in bottom-gate/top-contact (BGTC) devices upon post-deposition annealing at the indicated temperatures. Average values for five devices are shown.

<table>
<thead>
<tr>
<th>Semi-conductor</th>
<th>Annealing temperature (°C)</th>
<th>(\mu_h) (cm² V⁻¹ s⁻¹)</th>
<th>(I_{on}/I_{off})</th>
<th>(V_t) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RT</td>
<td>(3.8 \times 10^{-4})</td>
<td>(10^3)</td>
<td>-9.5</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(7.7 \times 10^{-4})</td>
<td>(10^4)</td>
<td>-18</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>(1.2 \times 10^{-2})</td>
<td>(10^5)</td>
<td>-4.9</td>
</tr>
<tr>
<td></td>
<td>110 (BCTG)</td>
<td>(9.1 \times 10^{-2})</td>
<td>(10^6)</td>
<td>-26.4</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>(4.5 \times 10^{-3})</td>
<td>(10^4)</td>
<td>-8.7</td>
</tr>
<tr>
<td>2</td>
<td>RT</td>
<td>(1.4 \times 10^{-3})</td>
<td>(10^5)</td>
<td>-11.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(6.4 \times 10^{-4})</td>
<td>(10^6)</td>
<td>-9.7</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>(1.7 \times 10^{-4})</td>
<td>(10^5)</td>
<td>-6.4</td>
</tr>
<tr>
<td></td>
<td>110 (BCTG)</td>
<td>(1.8 \times 10^{-2})</td>
<td>(10^6)</td>
<td>-15.6</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>(5.3 \times 10^{-5})</td>
<td>(10^2)</td>
<td>-10.3</td>
</tr>
</tbody>
</table>

\(a\) Bottom contact, top gate device geometry.
4. Bulk-heterojunction film properties and OSC fabrication

It is well-known that the nanophase morphology of bulk-heterojunction OSC donor–acceptor blends can be strongly affected by the processing conditions.22,45,46 Straightforward out-of-plane GIXRD can provide insightful information regarding molecular crystallinity and packing, thus directly yielding guidelines for the fabrication conditions to be used for OSCs. Specifically, here we investigate the effects of 1,8-diiodooctane (DIO) as a solvent additive, which can play a significant role in modifying the crystallinity of small molecule blends and D–A phase separation.32,47 To identify the effects of DIO on the molecular packing of the new semiconductors, GIXRD measurements were first performed on neat films of 1 and 2, spin-cast from chloroform (CF) solutions with varying amounts of DIO as the processing additive. The GIXRD measurements (Fig. 5) indicate that DIO addition introduces a higher degree of ordering for both 1 and 2, identified by the higher intensities of the Bragg reflections.

Because of the promising 1 and 2 HOMO and LUMO energetics and favorable OTFT charge transport properties, OSCs were next fabricated using PC71BM as the acceptor with an inverted cell architecture: ITO/ZnO/active layer/MoO3/Ag (Fig. 6, with data in Table 3). Furthermore, based on the GIXRD results, DIO was used to optimize the BHJ blend film morphology for OSC performance. For blends based on 1, a modest PCE of 0.59% is obtained for films processed without DIO. This result agrees well with the poor morphology identified by TEM and PL measurements (see details below and Fig. S3, ESI†). With increasing amounts of DIO loading, the PCE gradually increases to 4.02% at 1.0 vol% DIO, mainly due to a significant increase in Jsc. This behavior can also be readily understood by the enhanced crystallinity of 1, benefiting from the appropriate domain size for exciton separation and efficient charge transport (see more below). However, higher DIO loadings result in decreased PCE metrics (Table S1, ESI†), suggesting that ideal small molecule crystallinity is obtained using ~1.0 vol% DIO as the processing additive. Interestingly, 2 films without DIO show even poorer OSC performance than to 1 (Fig. S2, Table 3 and Table S1, ESI†). Similar to the trends observed for 1, the addition of DIO up to 0.5–1.0 vol% gradually increases the PCE from 0.36% to 0.48%, which is mainly attributed to higher FFs. However, a slightly lower Jsc is also observed. The device parameters achieved using these and several other fabrication variants are summarized in Table S1 (ESI†). Noticeably, all OPVs based on 2 show lower Voc than blends based on 1, consistent with their HOMO energies (Fig. 2).

To investigate the efficiency of photoinduced charge transfer in the OSC active layer, photoluminescence (PL) measurements were first performed on neat 1 and 2 films, as well as their small molecule:PC71BM blends prepared using several different solvents (Fig. S3, ESI†). Interestingly, the neat films exhibit a

---

**Fig. 5** GIXRD patterns of 1 and 2 films prepared in CF with different vol% of DIO as the processing solvents. (a) Semiconductor 1; (b) semiconductor 2.

**Fig. 6** Inverted OSC device performance: (a) illuminated J–V characteristics of 1:PC71BM (1:1) with varying DIO vol%. (b) External quantum efficiency (EQE) spectra of best-performing OSCs.
strong PL signal for 1, but no detectable PL for 2. This indicates that 2 undergoes radiationless energy transfer processes responsible for energy loss after photon absorption. In principle, PL quenching can be used to qualitatively diagnose the active layer morphology of the films made with fullerene derivatives, with a higher PL quenching efficiency suggesting more intimate D–A mixing and smaller domain sizes. Indeed, the blend films based on 1:PC71BM processed without DIO exhibit more intense PL intensity signals versus the neat 1 films, indicating a suboptimal morphology where domain sizes may be larger than the typical exciton diffusion lengths of 5–20 nm. However, with 0.5 vol% and 1.0 vol% DIO as the processing additive, the PL quenching efficiencies are significantly increased, suggesting an improved morphology for exciton dissociation.

Grazing incidence wide angle X-ray scattering (GIWAXS) spectra were next acquired to examine the microstructural details of the OSC active layers. The neat films of both 1 and 2 exhibit similar GIWAXS patterns, with a single lamellar Bragg feature (Fig. 7a and d). The paucity of reflections indicates similar d-spacings and domain sizes for 1 and 2 films. However, upon the addition of PC71BM, the ordering of the small molecules in these blends diverges substantially for 1 and 2, resulting in drastically different film morphologies. In the case of 1-based films, the lamellar reflection is retained upon PC 71BM addition (Fig. 7b and g), and when the blend film is processed with 1 vol% DIO it develops significantly more crystallinity, exhibiting both $n=2$ and $n=3$ order reflections for the lamellar stacking (Fig. 7c and g). In contrast, semiconductor 2 appears to lose all order upon blending with PC71BM (Fig. 7e and h). When processed with DIO, a single lamellar Bragg peak does appear, but not the $n=2$ and $n=3$ order reflections (Fig. 7f and h). Additionally, the DIO-processed blend films of 2 exhibit a reduced intensity for the PC71BM reflection, likely attributable to extensive interpenetration of 2 and PC71BM, suggestive of creating blend films with a predominantly mixed phase.

Transmission electron microscopy (TEM) images and AFM surface tomography images for blend films with PC 71BM are
shown in Fig. 8. Without DIO, 1:PC_{71}BM films evidence relatively large-scale phase separation on the order of 20–50 nm, which likely indicates a limited interface between 1 and PC_{71}BM. However, when 0.5 vol% DIO is added, the blend film morphology changes, revealing semicrystalline nanofibrillar structures that are well-blended with PC_{71}BM. Further addition of DIO up to 1 vol% induces higher crystallinity in the 1-based films, which is consistent with the enhanced zero-field mobility, $m^{eq}$ (Fig. 9 and Table S2, ESI†). This result also agrees well with the GIWAXS measurements, where the bulk-heterojunction mixture of small molecule 2:PC_{71}BM shows predominantly miscible, amorphous characteristics.

To investigate the charge transport characteristics more closely related to the photodiode, space charge limited current (SCLC) measurements were performed on the neat semiconductor films, as well as on the blend films processed with various DIO loadings (Fig. 9 and Table S2, ESI†). In the hole-only diodes, the current density ($J$) as a function of applied electric field ($E$) in the space charge limited regime is given by eqn (1), where by fitting the $J$–$E$ curve it is possible to extract the zero-field mobility, $\mu_{0}$.

$$J = \frac{9}{8} \varepsilon_{0} E^{2} \mu_{0} \exp \left( \frac{\gamma}{\sqrt{E}} \right) \quad (1)$$

Single diode hole-only and electron-only devices were fabricated using MoO_{3}/Au contacts. For neat 1 and 2 films, the SCLC mobilities are as high as $2.5 \times 10^{-3}$ cm$^{2}$ V$^{-1}$ s$^{-1}$ and $4.9 \times 10^{-3}$ cm$^{2}$ V$^{-1}$ s$^{-1}$, respectively. These SCLC mobilities are comparable to those achieved in optimized OTFTs, corroborating the excellent, nearly omnidirectional charge transport characteristics of both materials. For the blend films with PC_{71}BM added, the SCLC mobilities for 1 and 2 fall to $1.6 \times 10^{-4}$ cm$^{2}$ V$^{-1}$ s$^{-1}$ and $2.3 \times 10^{-3}$ cm$^{2}$ V$^{-1}$ s$^{-1}$, respectively. Note that the addition of DIO to the processing solvent introduces opposite trends in SCLC mobilities for the BHJ films of 1 and 2. Specifically, DIO greatly increases the SCLC mobility for 1:PC_{71}BM blend films up to $\mu_{0} = 1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with 1.0 vol% DIO, which is only slightly less than that observed for the neat film of 1. This indicates that the greater crystallinity induced by DIO can promote vertical percolative pathways for blend films of 1. This result is in excellent agreement with the increased OPV FFs for blend films of 1 processed with DIO. However, we also note that further FF enhancements may be precluded by limited carrier lifetimes, as a result of the currently suboptimal morphology. Interestingly, DIO negatively influences the SCLC mobilities for 2:PC_{71}BM blend films, with $\mu_{0}$ as low as $5.0 \pm 0.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured upon using 1.0 vol% DIO. Such a steep reduction in mobility is consistent with the reduced $J_{sc}$ metrics and poor blend film morphologies observed by the GIWAXS and TEM measurements discussed above.
Conclusions

In this study two novel DPP-based small molecules employing a central electron-rich fused tetrathienoacene (TTA) core, DDPPTTAR and DDPP’-TTAR, were designed, synthesized, and characterized. The expansive TTA cores provide excellent molecular coplanarity and close π-stacking, thus enhancing intermolecular interactions and affording favorable macroscopic morphologies for charge transport. Benefiting from the electron-deficiency of the DPP cores, both materials have small optical band gaps and suitable HOMO energies for hole injection in OTFTs. These properties yield sizable OTFT mobilities in the range 0.02–0.09 cm$^2$ V$^{-1}$ s$^{-1}$.

Furthermore, XRD and GIWAXS measurements indicate that the spin-coated thin film morphologies of both molecules are strongly susceptible to the use of DIO as a solvent additive. Specifically, small quantities of DIO of up to 1 vol% significantly enhance the crystallinity of DDPP-TTAR films. When incorporated into inverted OSC active layers, good PCEs of 4.0% are achieved, which are among the highest yet reported for fused thiophene based small molecules. These results indicate the TTA cores are promising donor moieties for organic electronic materials development.\textsuperscript{49,50} However, the DDPP’-TTAR isomer, despite good OTFT mobility, is found to predominantly form phase separation morphologies, hence poor PCEs. This study of structure–property relationships in TTA-based small molecules identifies the importance of fine-tuning the molecular stacking and thin film morphologies by selecting compatible D–A moieties and processing solvents – a key ingredient for achieving high performance OTFTs and OSCs.

Acknowledgements

This research was supported as part of the ANSER Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award Number DE-SC0001059, by AFOSR (FA9550-08-1-0331), and by Polycera Corp. We thank the NSF-MRSEC program, through the Northwestern University Materials Research Science and Engineering Center, for characterization facilities (DMR-1121262), and the Institute for Sustainability and Energy at Northwestern (ISEN), for partial equipment funding. Financial assistance for this research was also provided by the National Science Council, Taiwan, Republic of China (Grant Numbers NSC102-2113-M-008-004 and NSC102-2923-M-008-004-MY2).

References