Acceptor-Donor-Acceptor small molecules based on derivatives of 3,4-ethylenedioxythiophene for solution processed organic solar cells

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Acceptor-Donor-Acceptor small molecules based on derivatives of 3,4-ethylenedioxythiophene for solution processed organic solar cells

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Abstract

Three simple semiconducting acceptor-donor-acceptor (A-D-A) small molecules based on an electron-rich (3,4-ethylenedioxythiophene) EDOT central core have been synthesised (DIN-2TE, DRH-2TE, DECA-2TE) and characterised. Organic photovoltaic (OPV) devices incorporating these materials have been prepared and evaluated. The physical properties of the molecules were characterised by TGA, DSC, UV/vis spectroscopy and cyclic voltammetry. The HOMO-LUMO energy gaps of the molecules in the solid state were in the range 1.57 - 1.82 eV, and in solution 1.88 - 2.04 eV. Electrochemical HOMO-LUMO energy gaps determined by cyclic voltammetry were found to be in the range 1.97 - 2.31 eV. The addition of 1% diiodooctane (DIO) to photoactive blends of the A-D-A molecules and PC71BM more than doubled the power conversion efficiency (PCE) in the case of DRH-2TE:PC71BM devices to 1.36%.

Introduction

The use of organic materials as photoactive components in solar cells is of great interest1 due to their flexibility, ease of processing, large area applicability, tunability and the availability of raw materials,2-4 all of which are attributes that make them favourable compared to traditional silicon based devices. Recently, the use of small molecule, rather than polymeric, organic donors has gained attention due to their added advantages of well-defined molecular structure, low batch-to-batch variation5,6 and high open circuit voltages (Voc).7 This has led to some impressively high PCEs for the top performing small molecule OPV devices (9.95%),8 approaching the records of polymeric devices (11.5%).1,9 However,
many of these top performing materials have complex structures with multi-step syntheses which result in a high cost and low overall yield. As Roncali et al.\textsuperscript{10} recently remarked, ‘small is beautiful’ and truly small, simple organic donor molecules that have a simplistic and scalable synthesis\textsuperscript{5,11} should not be overlooked, even if their PCEs are lower than their more complex counterparts. Such materials are not only of interest as outright donors for OPV, but also as additives in ternary blend devices, which often exhibit enhanced PCE over their binary analogues.\textsuperscript{12,13}

In an effort to tune the properties of organic donor materials, several push-pull type structures have been explored where the conjugated backbone consists of alternating donor (D) and acceptor (A) units. This is most prevalent in D/A copolymers,\textsuperscript{14–16} but many small molecule architectures with D-A-D,\textsuperscript{17–20} A-D-A,\textsuperscript{21} D\textsubscript{1}-A-D\textsubscript{2}-A-D\textsubscript{1},\textsuperscript{22} A'(D'AD)\textsubscript{2},\textsuperscript{23} and D-A-D-π-D-A-D\textsuperscript{24} motifs (where π represents a conjugated linker) have also been investigated. Of these, the A-D-A architecture is particularly attractive due to the high device performances achieved\textsuperscript{8,25–27} and also because their synthesis is straightforward. In these molecules, alkyl cyanoacetate, rhodanine, indanedione and dicyanovinyl moieties\textsuperscript{27–34} are found to be efficient electron-acceptor groups, whilst typical donor components are; thiophene, benzodithiophene, dithienosilole, silafluorene, fluorene and carbazole.\textsuperscript{21} However, use of the strongly electron donating unit 3,4-ethylenedioxythiophene (EDOT) in A-D-A small molecule OPV devices has little precedent in the literature\textsuperscript{10,35} even though it has been commonly studied in other small molecule D/A architectures\textsuperscript{10,36,37} and polymeric devices.\textsuperscript{38–42} The ability of EDOT to induce planarity through non-covalent O---S interactions with neighbouring donor units increases the backbone rigidity and effective conjugation, which in turn narrows the HOMO-LUMO energy gap.\textsuperscript{43,44} This makes EDOT an attractive donor in the design of conjugated A-D-A small molecules for OPVs.

Herein, we report the first examples of A-D-A small molecules designed to utilise the planarising effect of EDOT in combination with acceptor units 1,3-indanedione, 3-ethylrhodanine and ethyl cyanoacetate.
The molecules were synthesised through a simple synthetic strategy utilising C-H activation to couple EDOT to 5-bromo-4-hexylthiophene-2-carbaldehyde to give 2TE, which then underwent subsequent Knoevenagel condensations with methylene containing acceptor units (Scheme 1). The resultant materials (DIN-2TE, DRH-2TE and DECA-2TE) showed good potential as electron donors, with LUMO energy levels suitable to work with that of PC71BM (-4.13 eV) for efficient exciton dissociation and charge transport. The device performances were optimised by varying the D/A weight ratio, applying various thermal annealing temperatures and changing the volume ratio of DIO additive.

Scheme 1 Reagents and conditions: (i) Cs₂CO₃, pivalic acid, Pd(OAc)₂, PCy₃·HBF₄, DMF, 110°C 16 h; (ii) NEt₃, CHCl₃, reflux, 16 h; (iii) piperidine, CHCl₃, reflux, 16 h.
Results and discussion

Thermal Properties

The thermal behaviour of **DIN-2TE**, **DRH-2TE** and **DECA-2TE** was explored by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The melting points determined by DSC of **DECA-2TE**, **DRH-2TE** and **DIN-2TE** were 236°C, 249°C and 335°C, respectively (detailed plots in SI). TGA analysis (Figure 1) shows that the molecules have good thermal stability with 5% weight loss temperatures (Td) all above 350°C (Table 1).

**Table 1.** Electrochemical, thermal and optical characteristics of **DIN-2TE**, **DRH-2TE** and **DECA-2TE**.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optical measurements</th>
<th>Electrochemical measurements</th>
<th>Td (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution</td>
<td>Film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>E&lt;sub&gt;gap&lt;/sub&gt; (eV)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ε (L mol&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>DIN-2TE</td>
<td>570</td>
<td>1.88</td>
<td>7.3 × 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>DRH-2TE</td>
<td>545</td>
<td>1.93</td>
<td>5.2 × 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>DECA-2TE</td>
<td>510</td>
<td>2.08</td>
<td>4.0 × 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Solution and solid state optical HOMO-LUMO gaps were calculated from the onset of the longest wavelength absorption peak using E = hc/λ and converting to eV. <sup>b</sup>HOMO and LUMO levels were calculated in reference to the Fc/Fc<sup>+</sup> redox couple: E<sub>HOMO(LUMO)</sub> = (−4.80 − E<sub>onset ox(red)</sub>). <sup>c</sup>Electrochemical HOMO-LUMO gap = E<sub>HOMO</sub> - E<sub>LUMO</sub>.
Optical and electrochemical properties.

All three A-D-A molecules showed strong absorption from 400 – 600 nm, extending up to 700 nm for DIN-2TE, arising from electronic π-π* transitions resulting in narrow HOMO-LUMO energy gaps (Table 1). DIN-2TE, DRH-2TE and DECA-2TE showed a λ max of 570 nm, 545 nm and 510 nm, respectively. DECA-2TE showed the strongest absorption in the visible region with an extinction coefficient of 4.0 × 10^5 L mol^-1 cm^-1. Broader absorption peaks observed in the solid state spectra, compared to the solution state spectra (Figure 2b), led to a red-shifted absorbance which may be due to strong aggregation as well as rigid and planar backbones of the molecules in the solid state. This is in agreement with previous studies of molecules containing the same acceptor group. The optical HOMO-LUMO energy gaps, estimated from the lowest energy onset of the longest wavelength absorption band in both solution and thin film, are outlined in Table 1. The HOMO-LUMO energy gaps for all compounds narrowed in the solid state compared to solution. DIN-2TE showed the lowest energy gap (1.57 eV) in the solid state, followed by DRH-2TE (1.71 eV) and DECA-2TE (1.82 eV).

Cyclic voltammograms of DIN-2TE, DRH-2TE and DECA-2TE are shown in Figure 3. DIN-2TE showed two irreversible oxidation waves and one irreversible reduction wave with potentials at +0.69 V, +1.16 V and -
1.62 V, respectively. **DRH-2TE** showed two reversible oxidation processes at half-wave potentials of +0.33 V and +0.72 V, as well as an irreversible oxidation and reduction at +1.14 V and -1.64 V. Two reversible oxidation waves and one quasi-reversible reduction wave were found for **DECA-2TE** at half-wave potentials of +0.66 V, +1.15 V and -1.50 V respectively. We attribute the oxidation potentials to the electron-rich EDOT central donor and the reduction potentials to the electron deficient acceptor units. Therefore, an increasing order of acceptor electron withdrawing strength shows DECA (-1.50 V) > DIN (-1.62 V) > DRH (-1.64 V), resulting in LUMO energy levels of -3.30, -3.18 and -3.16 eV for **DECA-2TE**, **DIN-2TE** and **DRH-2TE** respectively (Table 1). The HOMO energy levels of **DECA-2TE** and **DIN-2TE** show little variation (-5.49 and -5.46 eV respectively), however a shallower HOMO energy level of **DRH-2TE** (-5.13 eV) results in a narrower HOMO-LUMO energy gap of (1.97 eV) compared to **DECA-2TE** and **DIN-2TE** (2.16 and 2.31 eV respectively).
Figure 2 Normalised absorption spectra of DIN-2TE, DRH-2TE, and DECA-2TE (a) in chloroform solution ($10^{-5}$ M) and (b) drop cast film on quartz glass.
Figure 3 Cyclic voltammograms of DIN-2TE, DRH-2TE, and DECA-2TE in dichloromethane solution (10^{-4} M) with Bu_{4}NPF_{6} as the supporting electrolyte (0.1 M). Recorded at a scan rate of 100 mV s^{-1} using platinum wire (counter), silver wire (reference) and glassy carbon (working) electrodes.

Organic photovoltaic devices

OPV device performances of the A-D-A small molecules were investigated using the bulk-heterojunction architecture with indium tin oxide (ITO) and calcium as the electrodes and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) as a hole transport layer, with a device structure of glass/ITO/PEDOT:PSS/photoactive layer/Ca (40 nm)/Al (40 nm) (Figure 4). The photoactive layer was processed from a chloroform solution of each small molecule donor and [6,6]-phenyl C_{71} butyric acid methyl ester (PC_{71}BM) acceptor. However, unexpected limited solubility of DIN-2TE led to poor film formation, such that devices fabricated using this donor gave no electrical response. The greater solubility of DRH-2TE and DECA-2TE allowed for device fabrication and the study of varying donor/acceptor (D/A) weight ratios, annealing temperatures and the use of 1,8-diiodooctane (DIO) as an additive for DRH-2TE:PC_{71}BM and DECA-2TE:PC_{71}BM devices. The use of DIO in OPV devices often leads to an increased performance which has been attributed to the selective solubilising of the fullerene acceptor in the DIO. This improves intermixing between the donor and acceptor causing the formation of long, narrow donor rich and acceptor rich domains, which subsequently leads to an improved short circuit current (I_{sc}).^{46,47} Averaged optimised device performances are shown in Table 2.
**Figure 4** Structure of OPV devices fabricated. Ca/Al layer thickness 40 nm.

**DRH-2TE:**PC$_{71}$BM devices at an optimum D/A weight ratio (1:3) and annealing temperature (90°C) gave a power conversion efficiency (PCE) of 0.63%, with an open circuit voltage ($V_{oc}$) of 0.64 V, low fill factor (FF) (0.30) and $J_{sc}$ of 3.04 mA cm$^{-2}$. Optimised **DECA-2TE:**PC$_{71}$BM devices demonstrated a better PCE of 1.03% at a D/A weight ratio of 1:4 and annealing temperature of 60°C, attributable to a superior $V_{oc}$ (0.85 V) and FF (0.41), compared to **DRH-2TE:**PC$_{71}$BM devices. Diverse PCEs of A-D-A small molecules can be accredited to the differing $V_{oc}$ values which are related to the difference between the donor HOMO and acceptor LUMO energy levels.$^{45}$ Therefore, the deep HOMO level (-5.46 eV) of **DECA-2TE** resulted in a higher $V_{oc}$ (0.85 V) in comparison to the shallower HOMO level of **DRH-2TE** (-5.13 eV) and lower $V_{oc}$ (0.64 V). The LUMO level of the donor molecules also contributed to varied device performance, consistent with predictions made by Scharber *et al.*$^{48}$ Therefore, a donor with an improved $V_{oc}$ due to a deeper HOMO energy level, combined with a LUMO energy level close to that of PC$_{71}$BM (for efficient charge separation), will lead to higher $J_{sc}$ and enhanced PCE.

Accordingly, attempts to improve $J_{sc}$ by optimising device morphology were pursued through the use of DIO as an additive in the D/A blend at different volume ratios. As shown in Table 2, the efficiency of both **DRH-2TE:**PC$_{71}$BM and **DECA-2TE:**PC$_{71}$BM devices improved through the addition of 1% DIO. Other ratios of DIO were tested (see SI), but did not improve performance. PCEs of **DECA-2TE:**PC$_{71}$BM (1:4 weight
ratio) devices increased slightly from 1.03% to 1.05%, but DRH-2TE:PC71BM (1:3 weight ratio) PCEs more than doubled (0.63% to 1.36%). This can be attributed to a large improvement in $J_{sc}$ (3.04 vs 5.60 mA cm$^{-2}$). Figure 5 shows the $J$-$V$ curves of A-D-A small molecule:PC71BM devices with and without 1% DIO.

**Table 2.** Summary of the average optimised photovoltaic performance for DRH-2TE and DECA-2TE devices. AM 1.5G illumination.

<table>
<thead>
<tr>
<th>Photoactive blend (weight ratio)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRH-2TE: PC71BM (1:3) $^a$</td>
<td>3.04</td>
<td>0.64</td>
<td>0.30</td>
<td>0.63</td>
</tr>
<tr>
<td>DRH-2TE: PC71BM (1:3) $^a c$</td>
<td>5.60</td>
<td>0.68</td>
<td>0.35</td>
<td>1.36</td>
</tr>
<tr>
<td>DECA-2TE: PC71BM (1:4) $^b$</td>
<td>2.96</td>
<td>0.85</td>
<td>0.41</td>
<td>1.03</td>
</tr>
<tr>
<td>DECA-2TE: PC71BM (1:4) $^b c$</td>
<td>2.99</td>
<td>0.90</td>
<td>0.39</td>
<td>1.05</td>
</tr>
</tbody>
</table>

$^a$60°C and $^b$90°C annealing temperatures for 20 mins, $^c$1% diiodooctane.

**Figure 5.** Current–voltage curves of optimised (a) DRH-2TE:PC71BM and (b) DECA-2TE:PC71BM bulk-heterojunction devices without and with 1% DIO additive under AM 1.5 G illumination.

**Morphological Study**

Atomic force microscopy (AFM) was used to investigate the morphology of the enhanced device performance for optimised DRH-2TE:PC71BM (1:3) (90°C) and DECA-2TE:PC71BM (1:4) (60°C) devices, with and without 1% DIO as shown in Figures 6 and 7, respectively.
Devices containing **DRH-2TE**:PC$_{71}$BM (1:3) showed a smoother surface morphology (RMS roughness 18.3 nm) with 1% DIO compared to those without (RMS roughness = 44.9 nm) (Figure 6), indicating reduced D/A domain sizes giving rise to a more uniform film and improved device performance.$^{49}$ Accordingly, the smaller domains of interpenetrating D/A aggregates in the **DRH-2TE**:PC$_{71}$BM devices with 1% DIO (compared to the larger aggregates in devices without DIO, Figure 6) resulted in enhanced charge separation, leading to an improved $J_{sc}$ (3.04 vs 5.60 mA cm$^{-2}$) and PCE (0.63 vs 1.36%).

**Figure 6:** Tapping mode AFM height images of the best performing **DRH-2TE**:PC$_{71}$BM device without DIO (left) and with 1% DIO (right). 1:3 D/A weight ratio, annealed at 90°C.

**Figure 7:** Tapping mode AFM height images of the best performing **DECA-2TE**:PC$_{71}$BM device without DIO (left) and with 1% DIO (right). 1:4 D/A weight ratio, annealed at 60°C.
In contrast, the surface morphologies of DECA-2TE with and without 1% DIO look similar (Figure 7), suggesting that the DIO did not have any significant effect on the micromorphology, and thus gave no significant improvement in $J_{SC}$ or PCE. Figure 7 shows that narrow fibre-like domains which are favourable for charge transport are already present without the addition of DIO, demonstrating that DECA-2TE/PC$_{71}$BM blends have the ability to aggregate into optimal domain sizes without the need of an additive or co-solvent. This effect has been reported previously$^{50}$ and attributed to strong aggregation of the donor, resulting in no morphological change through DIO addition. Given that DIO has been shown to cause decreased photostability in the active layer of OPV devices,$^{51}$ there is an advantage in using donor materials such as DECA-2TE, which do not require use of a co-solvent to form a suitable morphology.

**Summary**

Three simple, low HOMO-LUMO energy gap semiconducting A-D-A small molecule donors (DIN-2TE, DRH-2TE and DECA-2TE) have been synthesised and fully characterised. DIN-2TE demonstrated the lowest optical HOMO-LUMO energy gap in both solution and solid state (1.88 and 1.57 eV, respectively). A shallower HOMO (-5.13 eV) of DRH-2TE contributed to a narrower electrochemical HOMO-LUMO energy gap (1.97 eV) compared to DIN-2TE (2.31 eV) and DECA-2TE (2.16 eV). Working OPV devices were realised for DRH-2TE:PC$_{71}$BM and DECA-2TE:PC$_{71}$BM, with PCEs for DRH-2TE-based devices more than doubling with the addition of 1% DIO (0.63 vs 1.36%). Devices containing DECA-2TE showed very little improvement with the addition of 1% DIO, which can be attributed to the optimal film morphology achieved without the addition of DIO. These results demonstrate that the choice of acceptor unit in A-D-A type molecules has an impact on more than just the optical and electrochemical properties of the resultant material. As such, careful consideration of aggregation, solubility and the use of additives should be employed when designing such materials and their device structures.
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Investigation into the use of EDOT as a central donor unit in A-D-A small molecules for OPV application
Lower HOMO-LUMO gap

Increased PCE

High $V_{oc}$