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Indan-1,3-dione electron-acceptor small molecules for solution-processable solar cells: a structure–property correlation†

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A structure-device performance correlation in bulk heterojunction solar cells for new indandione-derived small molecule electron acceptors, FEHIDT and F8IDT, is presented. Devices based on the former exhibit higher power conversion efficiency (2.4%) and higher open circuit voltage, a finding consistent with reduced intermolecular interactions.

There is intense interest in the development of new organic semiconductors for use in organic photovoltaic (OPV) applications. Solution processed bulk heterojunction (BHJ) devices feature a photoactive layer consisting of a bi-continuous interpenetrating network of an electron donor and an electron acceptor.[1] In this paper, we describe a new small molecule electron acceptor and show a clear correlation between molecular structure and device performance.

The most studied BHJ system is a blend of poly(3-hexylthiophene) (P3HT) and a solubilised fullerene such as [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM). While considerable progress has been made in the development of new electron donor small molecules and polymers,[2,3] this is not true for electron acceptors. Indeed, the handful of reports on high performing electron acceptors have focused mainly on the chemistry of these materials. Detailed analyses of the effect of non-fullerene electron acceptors on device open circuit voltages have not previously been reported and an understanding of the behaviour of non-spherical molecules has not been developed. To a large degree, the field of BHJ OPVs remains a two component problem where changes to one of the variables have not been extensively studied.

The interest in new electron acceptors arises from some of the shortcomings associated with the use of fullerenes. Fullerene-derived electron acceptors have disadvantages arising from weak absorption of sunlight, high cost of production, and LUMO energy levels that generally fall within a limited range with respect to the HOMO energy level of the electron donors, resulting in low open-circuit voltages (V_{OC}) for devices fabricated from these materials.[4] The search for high-performance, readily accessible, non-fullerene, small molecule electron acceptors that can be fabricated into BHJ devices using inexpensive solution processing has, until very recently, met with limited success.[5] Small molecules based upon the bifluorenylidene,[6a] benzothiadiazole–malonitrile,[6b] naphthalene-fused diimide,[6c] quinacridone,[6d] fluoranthene-fused imide,[6e] decacyclene-fused trisimide[6f] and diketopyrrolopyrrole[6g] templates have been used with P3HT to make solution-processed BHJ devices with power conversion efficiencies (PCEs) up to 2%.[6] The highest reported PCE (2.54%) for a solution-processed, P3HT/non-fullerene BHJ solar cell used a benzothiadiazole-imide-derived small molecule.[4] In this communication we report the design, synthesis and performance of a new family of electron acceptors based upon the 2,3-dihydro-1*H*-indene-1,3-dione template, and demonstrate that one of these soluble new materials, when blended with P3HT in BHJ solar cells, can deliver PCE's >2%.

2,3-Dihydro-1*H*-indene-1,3-dione (ID) was identified as a potentially suitable electron-deficient template from a report of the use of this building block in a high performance, merocyanine dye small molecule electron donor.[7] Our design strategy used thiophene and fluorene as well-established ''privileged structural templates'' for organic semiconductors, the fluorene building block also providing a means of facilitating solubility *via* attachment of alkyl substituents. We speculated that structures such as FxIDT (X = 8 or EH) (Scheme 1), containing two 1*H*-indene-1,3-dione units linked *via* a conjugated pathway, might exhibit sufficiently low LUMO energies to enable their use as electron acceptors with P3HT. Quantum chemical calculations using density functional theory were used to screen a series of molecules and calculations on FxIDT indicated that the LUMO energy levels of these compounds were similar to that reported for PCBM. Notably, the calculations also showed the LUMO electron density was delocalised over the entire π-system (see ESI†).

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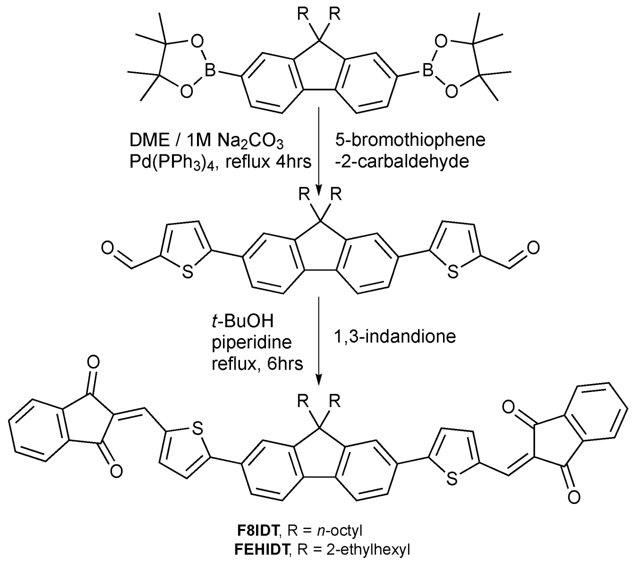

Scheme 1 Synthetic routes to F8IDT and FEHIDT.

The FxIDT compounds (Scheme 1) were efficiently prepared by Suzuki coupling of the appropriate fluorene bis-boronic ester with 5-bromothiophene-2-aldehyde followed by a Knoevenagel condensation reaction with 2,3-dihydro-1*H*-indene-1,3-dione. F8IDT and FEHIDT were obtained as red crystalline materials in yields of 74 and 53%, respectively. Significantly, this synthetic route has provided ready access to multi-gram quantities (>20 g) of these materials by scale-up of the procedure in batch mode. F8IDT and FEHIDT are structural isomers, both having the same molecular formula. In common with similar compounds that use chiral ethylhexyl solubilising groups, FEHIDT must exist as three stereoisomers (RR, RS and SS in a ratio 1 : 2 : 1). However, the isomeric mixture was used in all experiments.

F8IDT and FEHIDT were fully characterized by MS, ^{1}H and ^{13}C NMR spectroscopy and elemental analyses. The X-ray crystal structure of F8IDT shows classical 2-D brickwork packing while the RS isomer of FEHIDT (see ESI†) shows a 2-D sandwich-brickwork motif. The degree of non-planarity along the indane dione–thiophene–fluorene axis is greater for FEHIDT than for F8IDT. However, in both molecules the adjacent indandione–thiophene structural units show parallel alignment, suggesting favourable prospects for charge transport along the π-stack direction. Thermogravimetric analysis indicated that both F8IDT and FEHIDT are stable up to 350 °C. Differential scanning calorimetry (see ESI†) with heating and cooling cycles shows that F8IDT has a sharp melting point at 208 °C. By contrast, FEHIDT shows a broad melting point over the range 225–250 °C, consistent with the fact that this material is obtained as a mixture of stereoisomers, and a crystallisation transition around 174 °C.

Previous work in our group has shown that intermolecular interactions in thin films can have an effect on the energy levels of materials.[8] As such, the HOMO and LUMO energy levels were estimated using a combination of photoelectron spectroscopy in air (PESA) and UV-visible spectroscopy on thin films (see ESI†). The HOMO energy level was estimated as −5.85 eV for F8IDT and −5.95 eV for FEHIDT. When annealed at 120 °C, the onset of the UV/Vis absorbance of FEHIDT was at slightly lower energy than for F8IDT, 2.00 *vs.* 2.10 eV. These values were used to calculate a LUMO energy level of −3.95 eV for FEHIDT and −3.75 eV for F8IDT. These estimates indicated that both compounds were suitable electron acceptors for BHJ solar cells in combination with the electron donor P3HT.

Thin films of blends of P3HT with FxIDT (in a ratio of 1.2 : 1 w/w) show quenching of the photoluminescence (see ESI†). AFM analyses of the top surface are consistent with a film microstructure that is dominated by P3HT (see ESI†). Thin film X-ray diffraction analyses showed no reflections for as-deposited films of pristine FxIDT. Upon annealing at 120 °C films of F8IDT did not change but a reflection peak was observed for FEHIDT. For all P3HT:FxIDT blends only P3HT peaks were observed, a result that is consistent with P3HT dominating the blend microstructure. On annealing, the blend with F8IDT showed an increase in the intensity of the reflection while the blend with FEHIDT shows no change (see ESI†).

BHJ solar cells based on P3HT:FxIDT blends were prepared using a range of solvents, ratios, deposition conditions, annealing temperatures and device structures. Data for some of these combinations are shown in Table 1 and Fig. 1 (see ESI†). Briefly, it was observed that devices made using *o*-dichlorobenzene outperformed those made using chlorobenzene (due particularly to an increase in the fill factor); a donor : acceptor ratio of 1.2 : 1 was optimum; a calcium/aluminium electrode gave significantly better results than aluminium alone; thermal annealing (120 °C for 10 min) of the as-deposited devices showed an improvement in the PCE for all P3HT:FxIDT devices and devices made with FEHIDT showed a significantly higher

Table 1 Photovoltaic cell parameters for P3HT:FxIDT blends[a]

Donor	Acceptor	Solvent[b]	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Best PCE (%)	Average PCE (± std dev)[c] (%)
P3HT	F8IDT	*o*-DCB	0.72	−4.82	0.48	1.67	1.52 (± 0.08)
P3HT	F8IDT	CB	0.68	−3.55	0.35	0.85	0.73 (± 0.09)
P3HT	FEHIDT	*o*-DCB	0.95	−3.82	0.67	2.43	2.12 (± 0.18)
P3HT	FEHIDT	CB	0.96	−3.72	0.50	1.77	1.57 (± 0.14)
P3HT	PCBM	CB	0.59	−9.02	0.59	3.16	2.95 (± 0.15)

[a] Device structure was ITO/PEDOT:PSS/P3HT:acceptor/Ca/Al. [b] CB = chlorobenzene, *o*-DCB = *o*-dichlorobenzene. [c] A total of 18 devices were made for each combination. The active layer of the devices was annealed at 120 °C for 10 minutes.

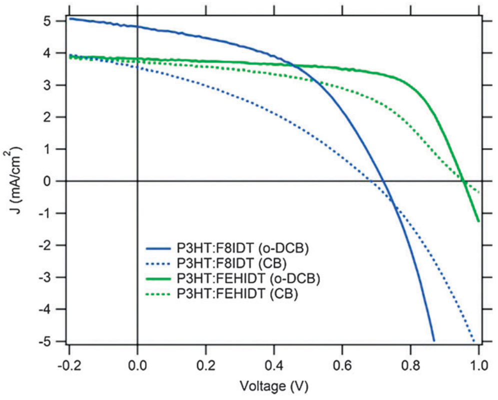

Fig. 1 Current–voltage curves for optimised devices based on P3HT:FxIDT blends under simulated sunlight (AM1.5, 1000 W m^{-2}).

V_{OC} and PCE than devices made with F8IDT. In fact, the PCE of 2.4% observed for a P3HT:FEHIDT device is amongst the highest reported PCEs for a BHJ OPV with a non-fullerene derivative.

IPCE spectra for the devices (see ESI†) are consistent with FxIDT having largely coincident absorption with P3HT. However, they do show some contribution from FxIDT, particularly FEHIDT. This is a promising result with regards to the potential for these materials to be used in combination with low bandgap donors such that charge generation could be achieved across a wider range of wavelengths.

In an attempt to measure the electron mobility of the FxIDT compounds, pristine films and blends with P3HT were analysed using the photo-CELIV technique (see ESI†). No charge mobility was observed for either of the pristine FxIDT materials. However, the charge mobility of the blends with P3HT was only slightly reduced from that seen for pristine P3HT. This suggests that the charge mobility in P3HT is not overly disrupted by the presence of the FxIDT, a conclusion that is also consistent with the thin film X-ray diffraction data.

The isomeric compounds F8IDT and FEHIDT show, in general, very similar properties. However, devices based on blends of them with P3HT show significant differences, see Table 1. The optimised PCE for a device based on FEHIDT (2.4%) is around 30% higher than that obtained for F8IDT. The key reason for this is the very large difference in the measured open circuit voltage of devices. Recently, a number of groups have shown that an analysis of the dark *J–V* curves can provide insight into factors other than just the HOMO–LUMO gaps that play a role in determining the V_{OC}.[9] The generalised Shockley equation for solar cells includes a parameter, J_{S0}, that can be directly related to the strength of the intermolecular interactions in the active layer of organic solar cells. Specifically, a smaller J_{S0} is found for devices where there is less electronic coupling between molecules. This leads to reduced recombination in devices and increases the V_{OC}. Kippelen *et al.*[10a] and Thompson *et al.*[10b] demonstrated this type of analysis for bi-layer devices while You *et al.* have performed similar analyses on BHJ devices.[11] In particular, it has been shown that side chains on electron donors can have a significant influence on the V_{OC}.[11] Ito *et al.* have also used an analysis of the J_{S0} values to demonstrate that substituents on fullerenes have a similar effect.[12] Dark current analyses of *J–V* curves from devices based on P3HT:FxIDT blends reveal J_{S0} values for F8IDT that are 3–4 orders of magnitude higher than for FEHIDT (see ESI†). Furthermore, the use of these J_{S0} values and the measured energy levels for the materials gave calculated V_{OC} values that are a close match to the measured values. In combination, these data are consistent with a conclusion that the degree of electronic coupling (and therefore the rate of recombination) in P3HT:FEHIDT devices is significantly lower than in the F8IDT blends. The presence of branched alkyl chains and the use of an isomeric mixture are both possible explanations for the reduced electronic coupling in FEHIDT. Further study of these factors remains as future work.

In summary, the FxIDT molecules described here represent an important new class of electron acceptors for BHJ solar cells. In particular, our findings confirm, for the first time, that electronic coupling and not just the absolute energy levels is an extremely important parameter in the design of non-fullerene electron acceptors for BHJ solar cells. These results, along with the observation that the FxIDT molecules have relatively deep LUMO energies and extremely low electron mobilities, challenge rigid rules that state that high performing electron acceptors must have low-lying LUMOs and high mobilities.[6d,g] The basic chemical design implication of our findings is that, as articulated by Anthony *et al.*,[13] the design of new electron accepting materials should not focus solely on good π-stacking. Rather, the degree of electronic coupling between molecules must be considered. This work further enhances the prospects for the design of other, non-spherical electron acceptors that will help realise significant improvements in BHJ solar cell device performance.

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