Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Efficient truxenone-based acceptors for organic photovoltaics

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Two electron-deficient truxenone derivatives are designed and synthesised for organic photovoltaic applications. The promise of this class of compounds as acceptor materials is illustrated by the fabrication of efficient bilayer solar cells with a subphthalocyanine (SubPc) donor, clearly outperforming reference cells with a soluble fullerene derivative as the acceptor.

Faced with the continued improvement of organic photovoltaic (OPV) devices, most materials research has been focused on the development of new polymeric donors.¹ These donor materials are routinely tested with phenyl-C61-butyric acid methyl ester (PCBM) or closely related fullerene derivatives and solar cell efficiencies are fast approaching 10%.² A common theme of this research is the judicious adjustment of donor properties to obtain an advantageous interaction, both energetically and morphologically, with the fullerene acceptor.^{3–5} Less effort, on the other hand, has been put into the development of new acceptor materials to complement existing or newly developed donor materials, to increase the understanding of the donor-acceptor interactions and to address some of the disadvantages associated with fullerene acceptors such as poor optical absorption and limited solubility especially in non-halogenated solvents.^{6–10} In order to investigate some of these aspects, there is the possibility to explore novel electron acceptors with curved isotropic electron-accepting motifs. By controlling the molecular curvature and the solubilising substituents, we aim to control the charge transport properties as well as the tendency for these small molecules to crystallise.

Here, we present two new truxenone-based acceptor materials that are highly soluble in many common organic solvents and highly absorptive in most of the ultraviolet-visible region of the spectrum, complementary to the absorption spectra of the majority of low bandgap donor polymers. Our synthetic design allows for easy control of the frontier energy levels and the promise of this new class of acceptors is illustrated with the fabrication of bilayer solar cells with efficiencies around 1% using subphthalocyanine (SubPc) as the donor constituent.

The synthetic route employed for the preparation of the two truxenone-based acceptors is shown in Scheme 1. Starting from 4,9,14-tribromotruxenone,¹¹ the two thienyl-substituted truxenones **1a-b** were easily obtained in moderate yields through a Suzuki-coupling with 5-hexyl and 3-hexylthiophene-2-boronic acid pinacol ester, respectively. A subsequent Knoevenagel-

condensation with malononitrile afforded the dicyanomethylene-derivatives **2a** and **2b** in moderate yields. Acceptors **2a-b** are highly soluble in both halogenated and non-halogenated solvents such as tetrahydrofuran, toluene and xylene. Thermogravimetric analysis indicated good thermal stability of both compounds (Table 1), while no clear thermal transitions were observed by differential scanning calorimetry.

Scheme 1 Synthesis of truxenone-based acceptor compounds **2a-b**. Fig. 1 Minimum-energy conformation of **2b** (with a methyl group instead of a hexyl group) calculated with Gaussian at the B3LYP/6-31G* level visualising the HOMO (left) and LUMO (right)

A computational study of the minimum-energy conformations, as illustrated for compound **2a** in Figure 1, shows that the introduction of the dicyanomethylene moieties forces the truxene core to adapt a bowl-shaped conformation; this finding is in agreement with crystal structures of related compounds.^{12, 13} For **2a**, the thienyl group is predicted to be twisted 26° relative to the adjacent phenyl group, whereas the corresponding dihedral angle is 41° for **2b** due to the repositioning of the hexyl group. This highlights the fact that the alkylated thienyl moiety can be used effectively to control the degree of conjugation as well as the tendency to crystallise through control of the torsional twist. For both acceptor molecules, the highest occupied molecular orbital

Table 1 Thermal, optical, electrochemical and computational properties of truxenone derivatives **2a-b**.

Compound	T_d (°C) ^a	$\lambda_{\max}$ (nm)		HOMO (eV)		LUMO (eV)		E_g (eV)	
		soln ^b	film ^c	exp ^d	calc ^e	exp ^d	calc ^e	opt ^f	CV ^d
2a	338	298, 423	315, 451, 557, 602	-5.94	-6.12	-4.07	-4.05	1.87	1.87
2b	340	287, 415	290, 423	-6.17	-6.29	-4.08	-4.16	2.04	2.09
PCBM				-5.89		-3.75			2.14

^a 5% weight loss by thermogravimetric analysis. ^b Dichloromethane solution. ^c Spin-cast from chloroform solution (10 mg/ml). ^d Cyclic voltammetry in dichloromethane solution with tetrabutylammonium hexafluorophosphate electrolyte. ^e Calculated with Gaussian at the B3LYP/6-31G* level. ^f Determined from the onset of absorption in the solid state.

(HOMO, Figure 1 left) is predominantly located on the electron-rich periphery, while the lowest unoccupied molecular orbital (LUMO, Figure 1 right) is distributed over the electron-poor core of the system.

Optical absorption spectroscopy supports the increased torsional twist predicted for **2b** relative to **2a** as illustrated in Figure 2. While compound **2a** shows an absorption maximum at 451 nm in the solid state with additional low-energy peaks at 557 and 602 nm, compound **2b** is significantly blue-shifted with a $\lambda_{\max}$ at 423 nm. We moreover find that **2a** displays a significantly larger red-shift than **2b** upon transition from solution to the solid state as evident from the data in Table 1. The optical band gap is 1.87 eV for **2a** and 2.04 eV for **2b**, which again is in agreement with the reduced conjugation caused by the twisted thiophene.

Fig. 2 Normalised UV-vis absorption spectra of **2a** and **2b** in dichloromethane solution and as spin-cast films from chloroform.

In order to assess the frontier energy levels of compounds **2a-b**, electrochemical characterisation was carried out by means of cyclic voltammetry (CV). The HOMO and LUMO energy levels were estimated from the onsets of oxidation and reduction, respectively (Table 1). The HOMO levels were found to be -5.94 eV for **2a** and -6.17 eV for **2b**, which is in good agreement with the predicted values from the computational study. The electron-rich 5-hexyl-2-thienyl substituent in compound **2a** is less twisted than the 3-hexyl-2-thienyl substituent (**2b**) and will therefore provide a higher degree of π -conjugation and thus a higher-lying HOMO level. The LUMO levels, on the other hand, are found to be almost identical for the two compounds; -4.07 eV for **2a** and -4.08 eV for **2b**. These results corroborate nicely the assumption from the computational study that the HOMO level is mainly governed by the peripheral substituents, while the LUMO level is largely controlled by the electron-poor dicyanomethylene-functionalised truxenone core, which is identical for the two

compounds. For comparison under identical conditions, we also tested PCBM by CV and found a HOMO level of -5.89 eV and a LUMO level of -3.75 eV indicating that the two truxenone-based acceptors presented herein have slightly larger electron affinities than PCBM.

Acceptor compounds **2a** and **2b** were tested in inverted bilayer solar cells fabricated with a vacuum-deposited donor material in conjunction with our solution-processed truxenone-based acceptor materials. Devices with inverted architectures were prepared as this allowed for solution-deposition of the truxenone acceptors prior to vacuum-deposition of the donor materials. The bilayer device configuration was chosen over a bulk-heterojunction device architecture in order to eliminate any potential morphology-related issues that could obscure evaluation of the OPV properties of this new class of acceptor compounds. As donor material in the bilayer devices, we investigated both a wide band gap donor, SubPc with HOMO/LUMO levels of -5.5/-3.4 eV and a narrower band gap material, zinc phthalocyanine (ZnPc) with HOMO/LUMO levels of -5.2/-3.5 eV.^{14, 15}

Prior to device preparation, the topography of the truxenone thin films was characterised by atomic force microscopy (Fig. S10). Compound **2a** forms ordered features (root mean square (rms) roughness = 5.3 nm) in agreement with the large red-shift in absorption upon transition from solution to the solid state indicative of aggregation and/or crystallisation. In contrast, films of **2b** are featureless and smooth (rms roughness = 0.6 nm), suggesting an amorphous film.

Photovoltaic parameters of the best devices are listed in Table 2 and corresponding current-voltage characteristics are shown in Fig. S11 and S12. Bilayer devices comprising SubPc and **2a** or **2b** achieve short-circuit current densities (J_{SC}) around 2 mA/cm², which is comparable to the J_{SC} obtained for reference cells with PCBM. Bilayer devices with ZnPc and **2a** or **2b** have a J_{SC} of 2.4 mA/cm² and 1.9 mA/cm², respectively, whereas the PCBM-based device displays a higher J_{SC} of 3.0 mA/cm². Complementary and red-shifted absorption (Fig. 3) of ZnPc explain the higher J_{SC} -values obtained for the ZnPc cells in comparison to the SubPc cells. External quantum efficiency (EQE) spectra of the devices as shown in Fig. 3 indicate that both donor (SubPc and ZnPc) and acceptor (**2a** and **2b**) compounds contribute to the photocurrent. This confirms that the energy level alignment at the heterojunction permits an efficient separation of the bound geminate pairs generated both on the truxenone acceptor and SubPc or ZnPc layers. J_{SC} -values extracted from the EQE spectra by integration (Table 2) correlate well with the values obtained from the J - V measurements. The open-circuit voltage (V_{OC}) of the SubPc devices with **2a** (947 mV) and **2b** (923 mV) is approximately 100 mV lower than the value obtained

with PCBM; this observation is in agreement with the lower lying LUMO levels of the truxenones reported in Table 1. Owing to a fill factor (FF) of 52%, the **2a**/SubPc device reaches a power conversion efficiency (PCE) of 1.0%, outperforming the PCBM reference device, which has a FF of 34% and a PCE of 0.8%. The **2b**/SubPc device performs similarly to the PCBM reference device with a FF of 36% and a PCE of 0.7%.

Table 2 Photovoltaic properties of bilayer solar cells with SubPc^a

Acceptor	Donor	V_{oc} (mV)	J_{sc} (mA/cm ²)	J_{sc} (EQE) (mA/cm ²)	FF (%)	PCE (%)
2a	SubPc	947	1.9	1.8	52	1.0
2b	SubPc	923	2.0	1.7	36	0.7
PCBM		1060	2.1	1.6	34	0.8
2a	ZnPc	448	2.4	1.8	50	0.6
2b	ZnPc	276	1.4	1.2	28	0.1
PCBM		612	3.0	2.9	61	1.1

^a Device architecture and thicknesses: ITO/ZnO (10 nm) /**2a** (65-70 nm) or **2b** (50 nm) or PCBM (10 nm)/SubPc (30 nm) or ZnPc (50 nm)/MoO₃ (5 nm)/Ag (120 nm).

Fig. 3. External quantum efficiency (EQE) of **2a** or **2b**/SubPc (top panel) and **2a** or **2b**/ZnPc (bottom panel) devices and absorption spectra of the various compounds.

In contrast to the truxenone/SubPc devices, the truxenone/ZnPc bilayer devices display significantly reduced V_{oc} -values in comparison to the PCBM reference device. Although the truxenone-based devices have elevated leakage currents (Fig. S12), it cannot explain entirely the reduced V_{oc} . Altered growth of the donor molecules on the different acceptor layers might also influence the energy levels of ZnPc and, consequently, reduce the V_{oc} .¹⁵ Truxenone derivative **2a** affords a V_{oc} of 448 mV, which in conjunction with a FF of 50%, results in a moderate PCE of 0.6%, while a much lower V_{oc} of 276 mV and a lower FF of 28% is responsible for a low PCE-value of

0.1% for **2b**. Both truxenone-based acceptors in this case show inferior performance to the PCBM reference device, which has a PCE of 1.1% due to a higher V_{oc} of 612 mV and a FF of 60%. It is notable that, with both donor materials, devices with **2a** have higher FFs than devices with **2b**. This suggests that **2a**, with the nearly coplanar 5-hexyl-2-thienyl substituents, is likely to have a higher charge carrier mobility than **2b**, which has the more twisted 3-hexyl-2-thienyl substitution pattern.

In conclusion, we have developed two new truxenone-based acceptor materials (**2a** and **2b**) and shown how chemical modification of the central truxenone core can be used to adjust the LUMO level, while chemical modification of the peripheral substituents can be used to adjust the HOMO level without further affecting the LUMO level. Additionally, the peripheral substituent can very effectively be used to control the degree of torsional twist and hence the degree of intermolecular aggregation.

The two new acceptors were proven to work satisfactorily in bilayer photovoltaic devices with two common donor materials, SubPc and ZnPc. In both cases, acceptor **2a** performs significantly better than **2b** and with a SubPc donor material compound **2a** even outperforms the PCBM acceptor, giving a 25% higher power conversion efficiency. This initial screening clearly suggests that this novel class of acceptors has potential in photovoltaic applications. However, both thin film deposition and growth of the donor materials could be further optimized to reach higher performance. Further device characterisation could also yield insight into the efficiency of the photogeneration process and eventual loss mechanisms limiting the performance of ZnPc/truxenone devices.

This work was in part carried out with financial support from SUPERGEN, EC FP7 Project X10D and EC FP7 Project ONE-P with support from BASF.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra, TGA and DSC traces, cyclic voltammograms, AFM micrographs, J-V curves and photoluminescence spectra. See DOI: 10.1039/b000000x/

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