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Solar cells based on a fullerene–azothiophene dyad

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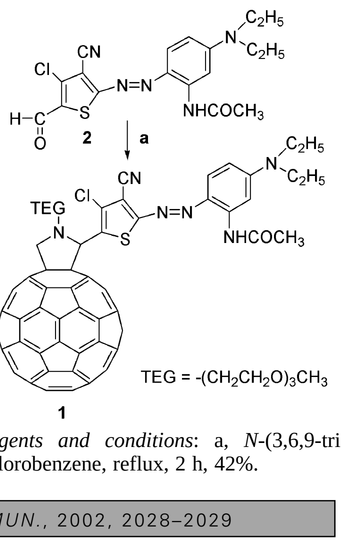
Received (in Cambridge, UK) 28th June 2002, Accepted 26th July 2002
First published as an Advance Article on the web 13th August 2002

A power conversion efficiency of 0.37%, under white light of 80 mW cm^{-2} intensity, was obtained when a fullerene–azothiophene dyad was used as the active layer of a photovoltaic cell.

The use of functionalized fullerenes as electron acceptor (A) in composite films with a π-conjugated polymer (the electron donor component, D) is anticipated to open the path toward the realization of high efficiency, all-organic solar cells.[1] As shown very recently, devices made of polymer/fullerene blends reached power conversion efficiencies (η) up to 3.3% under AM1.5 standard test conditions.[2] Although a 3.3% efficiency is still far from that of commercial silicon-based solar cells, the work demonstrated how a smart combination of synthesis, morphology control of the photoactive D/A layer and device processing is a key factor for efficiency enhancement. Parallel to the blend approach, the development of fullerene and conjugated polymer organic functionalization has enabled several groups to pursue alternative directions to enforce the spatial ordering of the D/A components in the solid state thus minimizing the detrimental fullerene–polymer phase segregation frequently present in the blends. Experiments to date have examined a number of so-called 'double-cable' structures[3,4] in which a functionalised fullerene is appended to a π-conjugated polymer. Solvent processable and electropolymerised double-cables have been prepared and, in a few cases, tested as active components in photovoltaic devices. η Values of *ca.* 0.1%, under 100 mW cm^{-2} white-light illumination, have been reported in the case of a methanofullerene covalently linked to a π-conjugated polymer.[4] Other promising approaches include the use of molecular dyads and triads made of a functionalised fullerene covalently linked to oligomeric, conjugated architectures that showed η values ranging from *ca.* 10^{-2}%[5,6] to the recently reported 0.2%[7] under 80 mW cm^{-2} white light illumination.

Here we describe the photovoltaic performance of cells incorporating the fullerene–azothiophene dyad **1** (Scheme 1) designed so that its absorption expands in the Vis spectral region for a better matching of the solar spectrum.



1

Scheme 1 *Reagents and conditions*: a, *N*-(3,6,9-trioxadecyl)glycine, [60]fullerene, chlorobenzene, reflux, 2 h, 42%.

Compound **1** was selected because our previous work on a similar azothiophene dyad, in which a methyl group was in place of the 3,6,9-trioxadecyl one, showed that the dyad could be selectively excited in the Vis region where the dye moiety has an absorption maximun at 567 nm.[8] Also, implementation of electrochemical and photophysical data revealed that, in solution, both intramolecular energy- and electron-transfer were thermodynamically feasible processes, the latter being an essential requisite for photovoltaic applications. The introduction of an oxyethylene chain was dictated by better solubility and film-forming characteristics. Dyad **1** was prepared in 42% isolated yield *via* the 1,3-dipolar cycloaddition of azomethine ylides to [60]fullerene[9] by treating *E*-azothiophene aldehyde **2** with *N*-(3,6,9-trioxadecyl)glycine and [60]fullerene in refuxing chlorobenzene. All spectroscopic and analytical data were consistent with the proposed molecular structure.†

Fig. 1 displays the absorption spectrum of a 80 nm film of dyad **1**, spin coated on indium–tin–oxide (ITO) from a chloroform solution, showing the characteristic dye absorption centered at about 570 nm.

In order to investigate the photophysical behaviour of **1**, time-resolved EPR (TR-EPR) spectra were recorded after photoexcitation at 140 K in both a frozen toluene solution and in a solid film obtained by evaporation of the solvent.[10] The EPR spectrum of **1** in frozen matrix (not shown) is that typical of a distribution of randomly oriented triplet state molecules (lifetime *ca.* 10 μs). It has been assigned to a triplet excitation localised on the dye moiety because the zero field splitting parameters $|D| = 645$ G and $|E| = 200$ G are much higher than those usually recorded for triplet states of fullerene derivatives.[11] On the other hand, the polarisation pattern (low field absorption/high field emission) is in line with that of fullerene derivatives, suggesting that the dye triplet state is populated from the fullerene triplet state by energy transfer. It is reasonable to assume that, in solution, photoexcitation populates the dye singlet excited state followed by energy transfer to the fullerene excited singlet state. Singlet–singlet energy

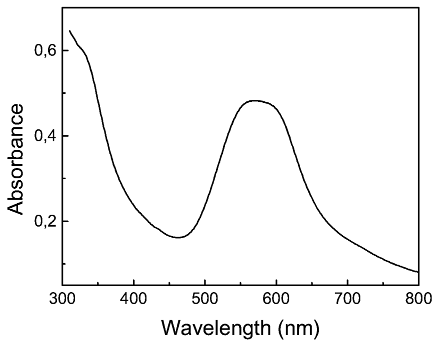


Fig. 1 Absorption spectrum of a 80 nm film of dyad **1** spin coated from chloroform.

DOI: 10.1039/b206275e

transfer was previously reported for a similar D/A system.[8] A fast intersystem crossing to the triplet excited state occurs in the fullerene and then energy is efficiently trasferred to the dye. Intramolecular charge separation, if any, should be followed by fast charge recombination, in a time shorter than the TR-EPR spectrometer response (about 0.1 μs). Interestingly, in the solid state dyad **1** gives a TR-EPR spectrum with a narrow (3 G) absorptive weak line overlapping a wide (14 G) emissive peak (see Fig. 2). The *g*-factor of the narrow line ($g = 2.0005 \pm 0.0005$) and its linewidth are typical of radical anions of fullerene derivatives.[12] The emissive line ($g = 2.0027 \pm 0.0005$) is tentatively assigned to the radical cation of the azothiophene moiety. From the lineshapes it can be inferred that the two radicals are sufficiently far apart to be non-interacting.

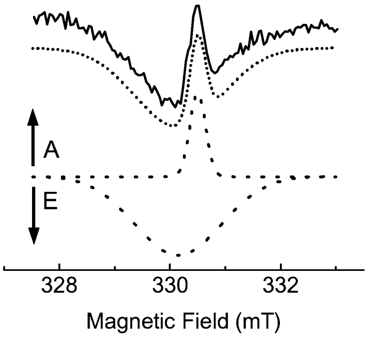


Fig. 2 Experimental (solid line) and calculated (upper dotted line) EPR spectra of **1** on film at $T = 140$ K and 0.2 μs after laser pulse. The calculated spectrum results from the sum of two different Gaussian lines (lower dotted traces) with opposite phase (A = absorption, E = emission). The signals decay is approximately 0.5 μs.

Therefore, in the solid state electron transfer (possibly intramolecular) is followed by charge hopping to neighbouring molecules, thus preventing recombination.

Photovoltaic cells were prepared, at ambient conditions, by spin coating the active layer of dyad **1** from chloroform onto ITO substrates covered with a film of poly(ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) and depositing an aluminum top electrode in vacuum. The junctions were illuminated with white light of 80 mW cm^{-2} intensity through the ITO contact. The electrical characterisation was performed under a pressure of about 5×10^{-3} mbar. As expected, the cell performance was dependent on the active layer thickness: A progressive increasing of both η and the short-circuit current (j_{sc}) was observed by reducing the film thickness from 100 to about 60 nm. However, no meaningful improvement was obtained with a further reduction of the thickness to 40–50 nm, possibly because of the low amount of absorbed photons. The current/voltage characteristics of cells made from dyad **1** are shown in Fig. 3 whereas the related photovoltaic parameters are listed in Table 1.

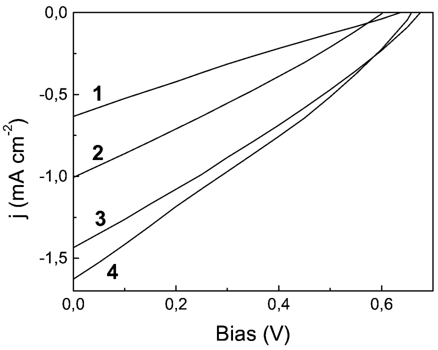


Fig. 3 Current–voltage curves (fourth quadrant only) of cells made from dyad **1**. Active layer thickness: 105 nm (1); 85 nm (2); 60 nm (3); 45 nm (4). White light irradiation power: 80 mW cm^{-2}.

Table 1 Cells photovoltaic parameters under 80 mW cm^{-2} white light irradiation at room temperature

Thickness/nm	j_{SC}/A cm^{-2}	V_{OC}/V	FF	η (%)
105	6.3×10^{-4}	0.64	0.23	0.12
85	1.0×10^{-3}	0.60	0.28	0.21
60	1.4×10^{-3}	0.67	0.28	0.33
45	1.6×10^{-3}	0.66	0.28	0.37

For the thinnest cells, a power conversion efficiency of 0.37% was obtained, being, to our knowledge, the highest reported for a fullerene-based, single component organic solar cell. The difference in the open-circuit voltage (V_{oc}) could be due to shunt effects. A fill factor (FF) of 0.28 was calculated for all the investigated cells, except for that with the thickest layer (Table 1). Generally, the FF reported so far for fullerene-based double-cable or D/A dyads solar cells are rather poor and this aspect should be investigated. A series resistance higher than that relative to cells made from fullerene/polymer blends could be acconted among possible reasons of the observed low FF, although other factors, related to the diode and/or the material transport properties, cannot be ruled out.

We have made photovoltaic cells from a fullerene–azothiophene dyad that showed a relatively high η value if compared to those recorded to date for fullerene-based, single component solar cells. The strong absorption of the dyad in the visible spectral region coupled to the optimization of the active layer thickness contributed to enhance the overall device performance. Although the molecular system is not yet optimized in terms of photoinduced electron transfer reaction, we believe that the use of new donor-linked fullerenes that absorb in the Vis range will be important for a better harvestigng of the solar light and as models for the study of charge mobility and transport.

We are grateful to Dr T. Gessner (BASF-AG, Ludwigshafen, Germany) for calling our attention to derivative **2** and providing a sample. We thank CNR (Progetto Finalizzato Materiali Speciali II and Agenzia 2000) and MIUR (contract No. MM03198284) for financial support.

Notes and references

† *Selected data* for **1**: ^{1}H NMR (250 MHz, CDCl$_3$, TMS): δ 8.27 (br s, 1H), 7.65 (br s, 1H), 6.52 (d, 1H), 5.80 (s, 1H), 5.22 (d, 1H), 4.40 (d, 1H), 4.19–3.56 (m, 16H), 3.56 (s, 3H), 2.34 (s, 3H), 1.29 (t, 6H); λ_{max}(CH$_2$Cl$_2$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 254 (97554), 316 (34802), 430 (6740), 567 (49822); *m*/*z* (HR-MS) $C_{86}H_{35}ClN_6O_4S$ (1282.2129), found 1282.2159.

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