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A novel polythiophene with pendant fullerenes: toward donor/acceptor double-cable polymers

Antonio Cravino,[a] Gerald Zerza,[a] Michele Maggini,[b] Stefania Bucella,[b] Mattias Svensson,[c] Mats R. Andersson,[c] Helmut Neugebauer*[a] and N. Serdar Sariciftci[a]

[a] *Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, Linz, A-4040 Austria. E-mail: helmut.neugebauer@jk.uni-linz.ac.at*
[b] *Organic Chemistry Department, University of Padova, Via Marzolo 1, I-35131 Padova, Italy*
[c] *Department of Polymer Technology, Chalmers University of Technology, SE-412 96, Goteborg, Sweden*

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The synthesis of a novel bithiophene with a pendant fullerene substituent and its electrochemical polymerisation are reported; light induced ESR measurements on the electrodeposited films reveal a photoinduced electron transfer from the donor cable (polythiophene) to the pendant acceptor cable (fullerene moieties).

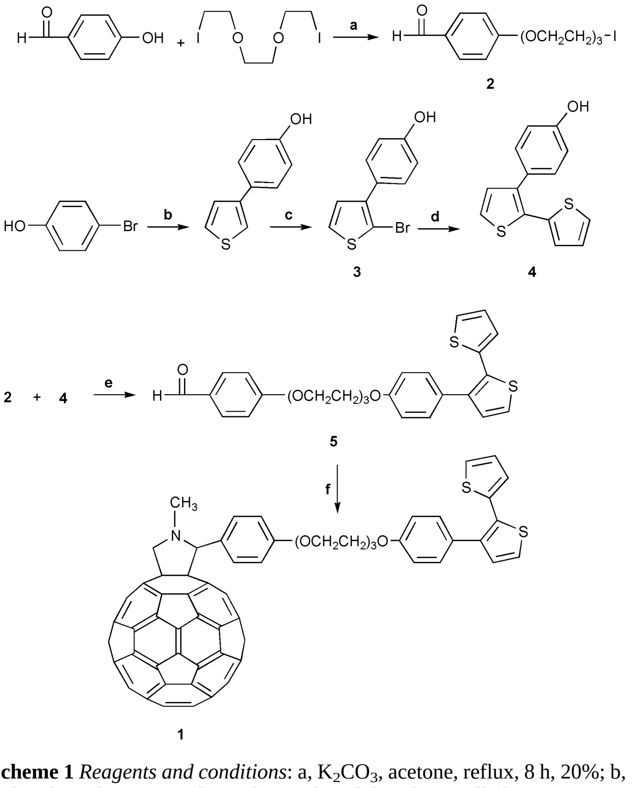
The ultrafast photoinduced electron transfer from non-degenerate ground state conjugated polymers to fullerenes,[1] in association with the existing technologies for processing polymers, makes these materials potentially suitable for low-cost photovoltaic applications as large-area, flexible solar cells.[2] Within this frame, the most promising devices so far obtained are the so-called bulk heterojunction solar cells.[3–5] The active layer of such devices is a blend of conjugated polymer and fullerene: after photoinduced charge separation, the polymer matrix ensures the transport of positive carriers, while electrons travel through contacting fullerene domains. Because of the limited miscibility of the two components, clusters of fullerenes can form within the active film, so that the transport of electrons is hindered by the 'void' between such separated domains.[4] A convenient solution to overcome phase segregation and reach a homogeneous distribution of the electron transporting sites within the bulk heterojunction should be the preparation of so-called double-cable molecular systems with fullerene substituents grafted to a conjugated polymer chain. Polythiophene/C_{60} mixtures have been already employed for the preparation of prototype bulk heterojunction solar cells,[5] suggesting the investigation of double-cables consisting of a polythiophene backbone with covalently linked fullerene units. Zotti and coworkers and Ferraris *et al.* showed that such fullerene substituted polythiophenes mostly retain the favourable ground state properties of the individual polymer and fullerene moieties.[6] However, the occurrence of photoinduced electron transfer in this type of polymers has, as yet, not been observed.

Here, we report preliminary results on a novel electrosynthesised polythiophene with pendant fullerene substituents, obtained from bithiophene-fulleropyrrolidine dyad **1** (Scheme 1). Compound **1** combines solubility and the superior electropolymerisability of bithiophenes[7] and gives a double-cable polymer that is heavily loaded with fullerene electron conducting moieties.

The synthetic strategy toward bithiophene-fulleropyrrolidine **1** is outlined in Scheme 1. The route to **1** starts with commercially available 4-hydroxybenzaldehyde and 1-iodo-2-[2-(2-iodoethoxy)ethoxy]ethane. Reaction between 4-hydroxybenzaldehyde and the bis-iodo derivative in the presence of K_2CO_3 in acetone at reflux temperature afforded the product of monosubstitution **2** in 20% isolated yield. Palladium-catalysed coupling[8] of 4-bromophenol with 3-thiophene-boronic acid[9] followed by NBS-bromination gave the highly reactive derivative **3** that was coupled directly with 2-thiophene-boronic acid[9] to afford **4**. Reaction of **2** with the potassium salt of bis-thiophene phenol **4** gave functionalised bithiophene **5** in 50% yield. Condensation of **5** with sarcosine in the presence of C_{60}[10] provided **1** in 49% isolated yield. All spectroscopic and analytical data were consistent with the proposed molecular structures.†

The cyclic voltammogram (CV) of **1** shows one anodic peak at *ca.* 1.3 V, which corresponds to the generation of radical cations that *via* subsequent coupling and re-aromatisation steps afford the substituted polythiophene chain[7,11] (Fig. 1). Potential sweeping between 0 and +1.6 V leads to the rapid growth of a new redox wave centered at *ca.* 0.9 V and related to the formed double-cable poly-**1**. Similar results have been obtained in different conditions, *e.g.* by using different electrodes, solvents and substrates. Insoluble and yellow-brownish films, whose UV–VIS absorption spectra show a band ranging from *ca.* 600 nm to the glass cut-off at 300 nm, have been obtained. No photoluminescence could be observed.

The CV of poly-**1** films in monomer-free electrolyte medium (Fig. 2) shows, in positive direction, a stable redox system with



Scheme 1 *Reagents and conditions*: a, K_2CO_3, acetone, reflux, 8 h, 20%; b, 3-thiophene-boronic acid, tetrakis(triphenylphosphine)palladium(0), DME, $NaHCO_3$ (1 M), 12 h, 76%; c, NBS, DMF, 12 h, 87% (crude); d, 2-thiophene-boronic acid, tetrakis(triphenylphosphine)palladium(0), DME, $NaHCO_3$ (1 M), 12 h, 48%; e, K_2CO_3, acetone, reflux, 8 h, 50%; f, *N*-methylglycine, C_{60}, chlorobenzene, reflux, 2 h, 49%.

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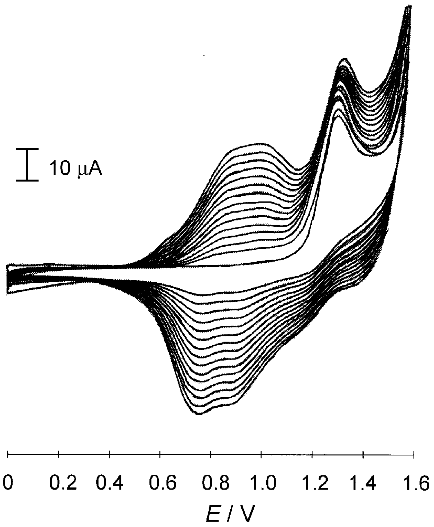

Fig. 1 Anodic CV of **1** (0.1 M Bu_4NPF_6 in CH_2Cl_2). Working electrode: Pt foil; quasi-reference electrode: Ag/AgCl wire. Scan rate: 100 mV s^{-1}.

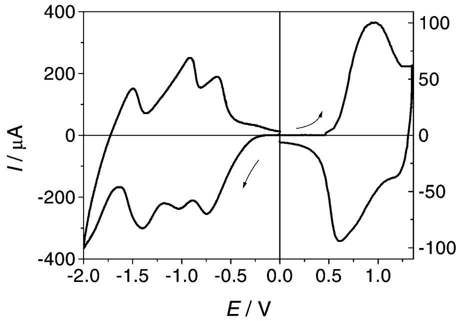

Fig. 2 Anodic (right) and cathodic (left) CV of poly-**1** (0.1 M Bu_4NPF_6 in MeCN). Conditions as in Fig. 1.

anodic and cathodic peak potentials at 0.96 and 0.61 V, respectively, corresponding to the oxidation/re-reduction ('p-doping/dedoping') of the polythiophene chain. Scanning to negative potentials up to −2.0 V shows several waves related to the multiple reduction processes of the fullerene moiety (Fig. 2).[12] The electrochemical behaviour suggests that both the polythiophene chain and the pendant fullerene moieties of the double-cable retain their individual electrochemical properties.

The photogeneration of separated charged states in poly-**1** has been observed by means of light-induced electron spin resonance (LESR) measurements. The LESR spectrum, obtained by subtracting the light-off signal from the light-on signal, is shown in Fig. 3. The spectrum reveals the photoinduced generation of two species with spin = 1/2. The signal at g = 2.0022 corresponds to delocalised radical cations (widely accepted to be polarons) on the conjugated backbone while the signal at g = 2.0004 is typical of low g-factor fullerene radical anions.[13] These results prove the occurrence of a photoinduced electron transfer from the conjugated backbone to the pendant fullerene moieties of poly-**1**, which is an essential prerequisite for photovoltaic applications. In addition, also sub-gap electronic and IR-active vibration (IRAV) bands are observed in the photoinduced UV–VIS and IR spectra of poly-**1** (not shown here). These spectral features are related to the photoinduced generation of long-living charged states.[14]

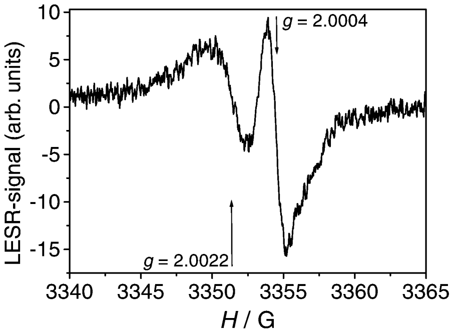

Fig. 3 LESR (light-on minus light-off) spectrum of poly-**1** on ITO coated foil. T = 77 K; excitation at λ = 488 nm (20 mW cm^{-2}).

In conclusion, we have shown the synthesis of a novel bithiophene-fulleropyrrolidine dyad suitable as a monomer for electrochemical polymerisation. The resulting double-cable polymer retains the peculiar characteristics of polythiophene/fullerene blends, including the ability to generate a charge-separated state after photoinduced electron transfer. Since no phase separation is expected in this type of material, donor–acceptor double-cables represent attractive candidates for photovoltaic applications.

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Notes and references

† *Selected data* for **1**: ^1H NMR (400 MHz, $CDCl_3$–CS_2 1:2) δ 7.63 (br s, 2H), 7.16 (m, 3H), 7.09 (dd, 1H), 6.95 (d, 1H), 6.87 (m, 4H), 6.77 (m, 2H), 4.92 (d, 1H), 4.83 (s, 1H), 4.21 (d, 1H), 4.06 (m, 4H), 3.80 (m, 4H), 3.68 (s, 4H), 2.75 (s, 3H); $\lambda_{max}(CH_2Cl_2)$/nm (ε/dm^3 mol^{-1} cm^{-1}) 230 (112530), 256 (125060), 431 (3963); *m/z* (MALDI) 1242 (M^+).

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