

Conjugated Polymeric Donor – Fullerene Type Acceptor Systems For Photoelectrochemical Energy Conversion

A. Gusenbauer¹, A. Cravino¹, G. Possamai², M. Maggini², H. Neugebauer^{*1}, N. S. Sariciftci¹

¹Linz Institute for Organic Solar Cells (LIOS),
Physical Chemistry, Johannes Kepler University Linz, 4040 Linz, Austria

²Department of Chemistry and ITM-CNR,
University of Padova, 35131 Padova, Italy

Abstract. The usage of fullerenes as electron mediator in photoelectrochemical cells with a conjugated polymer as electron donor and a dissolved redox couple as acceptor is described. To prevent solubility problems, the fullerenes are covalently linked to the conjugated polymer polybithiophene (“double cable”). Copolymers with different amount of fullerenes are studied in respect to light absorption and photovoltaic device properties. Compared with polybithiophene, the introduction of fullerenes in the devices enhances the photovoltaic response significantly.

INTRODUCTION

Photoelectrochemical solar cells with inorganic semiconductors, e.g. TiO₂, have been investigated since many years [1]. In the last decade, the versatility of organic compounds, in respect to enhanced light absorption and spectral sensitivity, was utilized for the construction of both inorganic/organic devices (e.g. dye sensitized inorganic semiconductor solar cells [2]) and polymeric organic semiconductor solar cells [3]. In the devices, the basic process is a charge transfer from the excited light absorber to a redox couple in an electrolyte solution. It has been shown, that the introduction of compounds with LUMO levels intermediate between the LUMO level of the absorber and the level of the redox system, e.g. fullerenes, acts as an electron mediator and may enhance the efficiency of the device [4]. In this paper, the usage of fullerenes covalently linked to a polymeric donor backbone (“double cable”) is described. The energy of the LUMO level of the fullerene is inbetween the valence band edge of polybithiophene, which is used as the polymeric donor, and the energy level of a redox system (I₃⁻/I⁻) in the electrolyte solution. The covalent linkage prevents possible dissolution of the fullerene in the electrolyte solution, which may occur under illumination, leading to rapid deterioration of the device properties. To increase the absorption in the visible part of the spectrum, copolymers with different amounts of the fullerene part are used. Compared with polybithiophene, the introduction of fullerenes in the devices enhances the photovoltaic response significantly.

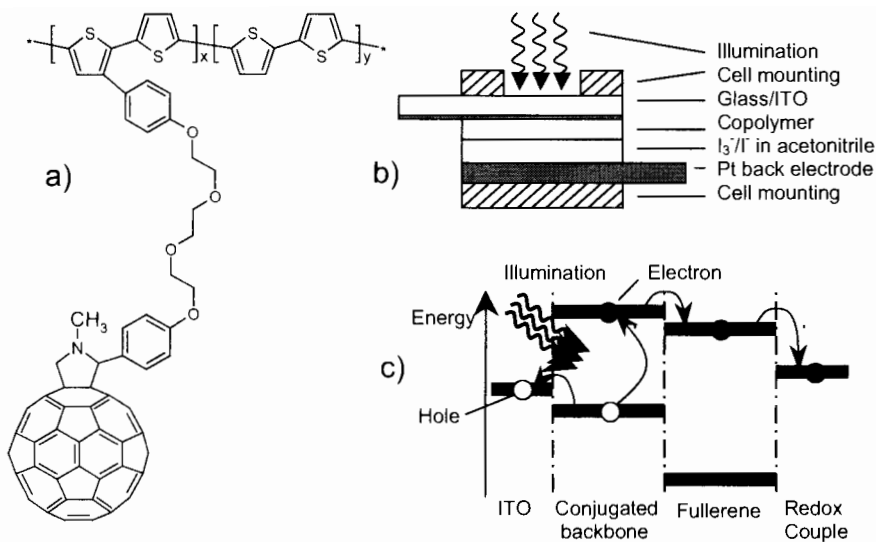


FIGURE 1. a) Structure of the copolymer of ITB-C60 and bithiophene; b) Scheme of the photoelectrochemical cell; c) Sketch of the energetics of the electron transfer.

EXPERIMENTAL

The synthesis the monomer ITB-C60 (x-component of the copolymer structure shown in Fig. 1a) has been described in a previous paper [5]. For the formation of the copolymers, the monomers ITB-C60 and bithiophene in different concentrations were dissolved in electrolyte solution (0.1 M $(C_4H_9)_4NPF_6$ in acetonitrile/toluene (30:70, v:v)), electro-copolymerized on ITO/glass substrate at 1.25 V vs. Ag/AgCl quasireference electrode and reduced to the neutral form in 0.1 M $(C_4H_9)_4NPF_6$ in acetonitrile. UV-vis spectra were recorded with an HP 8453 spectrometer. The photoelectrochemical properties were studied in a cell shown in Fig. 1b with illumination from a solar simulator (80 mW/cm^2).

RESULTS AND DISCUSSION

Figure 2 shows absorption spectra of films of polybithiophene, poly-ITB-C60, and copolymers obtained from solutions with mass concentration ratios bithiophene:ITB-C60 of 3:1, 2:1 and 1:1. As can be seen, the absorption of pure poly-ITB-C60 in the visible part of the spectrum is low. By increasing the bithiophene content in the copolymers, the relative absorption around 500 nm, which is important for solar cell applications by better matching the solar emission spectrum, increases.

In Fig. 3 current/voltage curves of devices made from polybithiophene, poly-ITB-C60 and different copolymers under solar simulator illumination are compared, and the values for the open circuit voltage (V_{oc}), short circuit current (j_{sc}), fill factor and

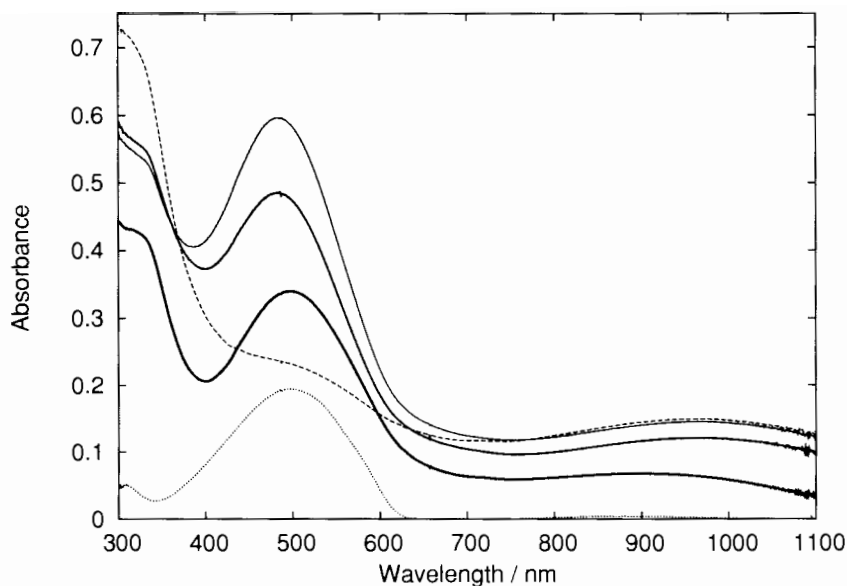


FIGURE 2. Absorption spectra of films of polybithiophene (dotted curve), poly-ITB-C60 (dashed curve), and copolymers obtained from solutions with mass concentration ratios bithiophene:ITB-C60 of 3:1 (thin solid curve), 2:1 (medium solid curve) and 1:1 (thick solid curve).

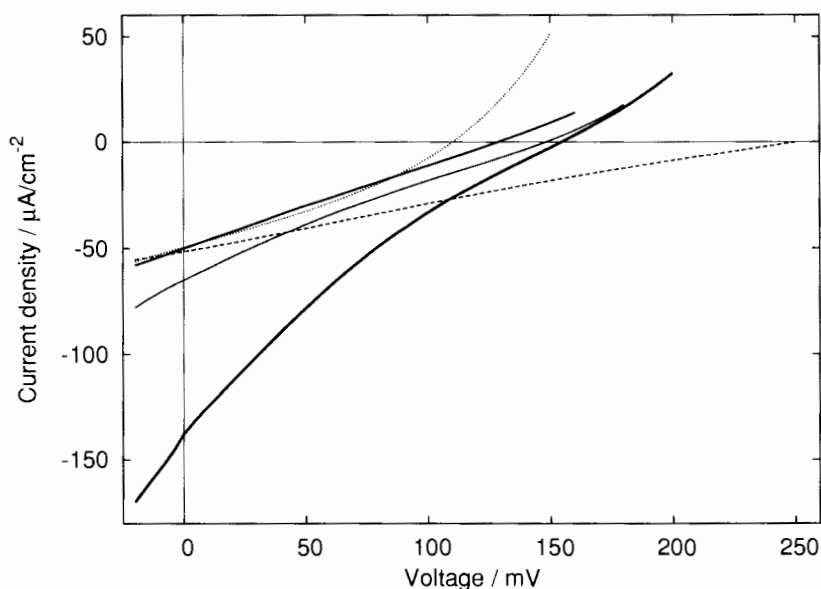


FIGURE 3. I/V characteristics under illumination of photoelectrochemical cells made with polybithiophene (dotted curve), poly-ITB-C60 (dashed curve), and copolymers obtained from solutions with mass concentration ratios bithiophene:ITB-C60 of 3:1 (thin solid curve), 2:1 (medium solid curve) and 1:1 (thick solid curve).

TABLE 1. Photovoltaic I/V characteristics

Sample (ratio)	V_{oc}/mV	$j_{sc}/\mu Acm^{-2}$	Fill factor	Efficiency %
Poly-Bithiophene	110	-49.5	0.32	0.0022
PBiTh/ITB-C60 (3 : 1)	148	-64.9	0.22	0.0026
PBiTh/ITB-C60 (2 : 1)	129	-49.1	0.25	0.0020
PBiTh/ITB-C60 (1 : 1)	155	-137.8	0.19	0.0051
Poly-ITB-C60	250	-51.1	0.23	0.0037

efficiency are compared in Table 1. Devices with pure polybithiophene show the best diode behaviour (dotted curve in Fig. 3), however with low values for V_{oc} and j_{sc} . With devices containing poly-ITB-C60 the fill factor decreases, probably related to poor morphology of the fullerene containing films. However, both the open circuit voltage and the short circuit current are generally higher. The highest open circuit voltage is reached with pure poly-ITB-C60 (dashed curve in Fig. 3). Fill factor and short circuit current are not improved compared with pure polybithiophene, which gives only a moderate improvement of the efficiency. The highest improvement is found in devices using copolymers obtained from solutions with mass concentration ratio bithiophene:ITB-C60 of 1:1 (thick solid line in Fig. 3). Especially the short circuit current is significantly improved. Even with the lowest fill factor obtained in the series measured (due to the “wrong” curvature of the I/V curve), the overall efficiency is more than doubled compared with pure polybithiophene.

The results show, that the incorporation of fullerene containing units into photoelectrochemical devices using conjugated polymers as absorbers and electron donors improve the photovoltaic properties significantly. However, the overall efficiencies in all devices are found to be only moderate. Improvements can be expected by influencing the morphology and by the usage of other redox couples with more negative redox potentials, which should give higher values of the open circuit voltage and therefore also higher efficiencies.

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