

Evidence of the improvement of photovoltaic efficiency by polar molecule orientation in a new semiconducting polymer

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Received 26 April 2007; received in revised form 21 June 2007; accepted 22 June 2007

Available online 2 August 2007

Abstract

Storage of an internal field in a polymeric semiconductor device should be of great interest for applications like photovoltaic solar cells to facilitate exciton dissociation and improve charge transport in the structure. Orientation of polar molecules, contained inside a polymer binder, induces a rectifying effect, behaving as a distributed homojunction within a single polymeric film. To investigate this concept, a new poly(*p*-phenylenevinylene) (PPV) derivative bearing push–pull like molecules was purposefully designed and synthesized. Effect of polar molecules' orientation on carrier injection and transport properties was studied. In the test systems, we demonstrate an increase of the external quantum efficiency upon orientation.

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Keywords: Organic solar cells; Polymer semiconductors; Molecular chain orientation; Carrier transport

1. Introduction

Photovoltaics is one of the most promising sustainable energy sources for the mid- and long-term future, and organic solar cells have the potential to realise a significant cost reduction for photovoltaic (PV) energy conversion if improvements of the power efficiency and the lifetime can be achieved. The very fast progress of plastic solar cells is very promising [1–4] even if there are still some crucial obstacles to overcome before large-scale production of this technology can be considered. Indeed, to date a small number of laboratories have reported stable cells [5–7] and even less have reported large-scale cells [8]. In addition to the incorporation of polymers with improved light harvesting and charge transport properties, breakdown may come

from the development of innovative concepts. A good illustration is the well-known interpenetrated network of an acceptor-type molecule with a donor-type conjugated polymer which has been shown to lead to the highest efficiencies in polymer-based photovoltaic solar cells [9]. In this case, the large improvement of the efficiency is due to the distribution of the exciton dissociating sites throughout the material volume. However, one of the main drawbacks remains the relatively low mobilities inherent to organic materials, which impose small thicknesses (usually less than 200 nm) to not limit charge collection. In this context, a promising alternative approach is based on the orientation of polar molecules [10]. The principle consists in building a rectifying junction, necessary to effectively dissociate photogenerated excitons and transport the resulting charge carriers, with the use of molecular rectification in an amorphous polymer incorporating oriented polar molecules. It has been previously demonstrated that in this way

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a built-in internal field is induced in the structure, which therefore behaves as a homojunction distributed throughout the entire thickness of the device [10,11]. Hence, all photogenerated excitons are likely to find a junction and split before recombination, thus, avoiding recombination channels (either radiative or non-radiative). The principle relies on the intrinsic polar nature of organic molecules, and therefore it cannot be readily applied to inorganic semiconductors which are built from spherical atoms, polarity being a crystal-cell property. First, experiments were performed on a copolymer of poly(methyl methacrylate) (PMMA) with Disperse Red 1 (DR1) (4-(*N*-(2-hydroxyethyl)-*N*-ethyl)-amino-4'-nitroazobenzene), as a polar molecule, covalently bound onto the polymer chains. Orientation of the polar molecules, also called push–pull molecules used in second-order nonlinear optics [12], was achieved by application of a static electric field through the polymer film, while heating near the glass transition temperature. Experimentally, it was demonstrated that the current–voltage characteristics of a device made of this copolymer film sandwiched between symmetric electrodes become strongly asymmetric [13] upon orientation of the DR1 molecules. It was also demonstrated by time-of-flight (TOF) experiments that the molecular induced orientation in a polymer device increases the charge mobility in the material and that the barrier height between the electrode material and the polymer decreases with growing polar order [10]. The influence of molecular orientation on carrier transport and trapping effects was confirmed by thermally stimulated currents (TSC) and current–voltage (I/V) characteristics [14]. Moreover, the potential of electroabsorption spectroscopy has been investigated to evaluate the internal field which is stored in the structure after polar molecule orientation [15]. At last, the photovoltaic efficiency improvement of cells based on a polymeric single layer bearing oriented polar chromophores was also clearly evidenced [11]. Although the materials used in this study were not optimised for device efficiency, but only designed to demonstrate rectification induced through orientation of diode-like molecules.

In this paper, we present the first results obtained with a functionalised soluble poly(*p*-phenylene vinylene) (PPV) grafted with push–pull-like molecules specifically developed to investigate the molecular orientation concept for photovoltaic applications.

2. Experimental details

A functionalized soluble PPV derivative bearing push–pull like molecules (NLO-PPV) has been synthesized. The chemical structure of the soluble NLO-PPV copolymer and the synthesis method are presented in Fig. 1. The active polar molecule is the 4-(*N*-butyl-*N*-2-hydroxyethyl)-1-nitro-benzene group (**1**) on the copolymer (**8**). It is a typical push–pull molecule with a donor/transmitter/acceptor structure and it possesses a large ground state

dipole moment μ which is necessary for efficient DC-field orientation. Moreover, this grafted dye polar molecule presents no photoinduced molecular movements avoiding that way disorientation following illumination with the solar light. It was not the case of the DR1 previously used in a model system. Compound (**1**) is attached onto a soluble PPV copolymer containing 50% of [2-methoxy-5-(3',7'-dimethyloxy)-*p*-phenylene vinylene] MDMO-PPV units. This copolymer is used as an isotropic polymer binder as MDMO-PPV is one of the best conjugated polymer system leading to high solar efficiency so far. The resulting copolymer (NLO-PPV) (**8**) contains 50%-molar chromophore concentration.

2.1. Synthesis of 4-(*N*-butyl-*N*-2-hydroxyethyl)-1-nitrobenzene (**1**)

In a round bottom flask, 1-fluoro-4-nitrobenzene (18.6 g, 0.13 mol, 1 eq), 2-(butylamino) ethanol (19.8 g, 0.17 mol, 1.3 eq) and potassium carbonate (21 g, 0.15 mol, 1.2 eq) were stirred and heated in dry DMSO (100 mL) overnight (16 h) at 65 °C. The mixture was then poured onto 500 mL water and extracted with methylene chloride (3 × 150 mL). The organic solution was dried with sodium sulphate, and concentrated to give a yellow solid.

The crude product was purified by chromatography on silica gel column, eluting by a gradually more polar mixture: CH₂Cl₂/AcOEt 95/5 (to separate a less polar impurity), 90/10 and finally 85/15.

The yellow solid was crystallised in isopropyl alcohol. Yield: 16.6 g, melting point (capillary): 73 °C.

2.2. Synthesis of compound (**2**)

In a three-necked 250 mL flask, 4-(*N*-butyl-*N*-2-hydroxyethyl)-1-nitro-benzene (**1**) (3.57 g, 0.015 mol, 1 eq), *p*-hydroxyanisole (2.79 g, 0.0225 mol, 1.5 eq) and triphenyl phosphine (4.72 g, 0.018 mol, 1.2 eq) are dissolved in 120 mL diethylether. The mixture is stirred for 1 h under Ar atmosphere until complete dissolution. The temperature is decreased down to 0 °C by means of an ice batch. Diisopropyl azocarboxylate (DIAD) (3.73 mL, 0.018 mol, 1.2 eq) is then added dropwise with a syringe. The mixture is stirred overnight at room temperature. The reaction is monitored by means of a TLC in CH₂Cl₂.

When the reaction is completed, water is added and an extraction is made (× 3) with CH₂Cl₂. The organic layers are collected and are dried with MgSO₄. MgSO₄ is filtered off; the solvent is then evaporated and dried under vacuum. Purification by means of a chromatography column using CH₂Cl₂ as eluent is necessary. Compound (**2**) is obtained as a yellow solid with a purity of 95% and a yield of 95%.

¹H NMR(300 MHz, ppm, CDCl₃): σ = 8.2 (2H, H1); 6.8 (4H, H3); 6.6 (2H, H2); 4.1 (2H, H5); 3.8(2H, H6); 3.7 (3H, H4); 3.5 (2H, H7); 1.6 (2H, H8); 1.4 (2H, H9); 0.9 (3H, H10).

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