Materials Chemistry and Physics 147 (2014) 476–482

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Optoelectronic properties of a perylene substituted (cholesteryl) benzoateethynylene co-polymer

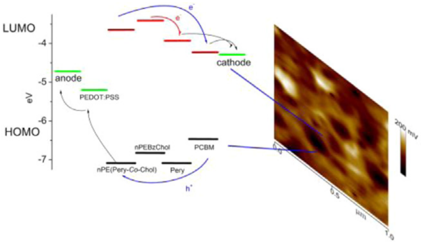
Stefania Zappia [a,b], Arxel de León [b], Marina Alloisio [a], Eduardo Arias [b], Giovanna Dellepiane [a], Giovanni Petrillo [a], Ivana Moggio [b,*], Sergio Thea [a], Carlos Gallardo-Vega [b], Marlene Rodríguez [b]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genoa, Italy*
[b] *Centro de Investigación en Química Aplicada, Boulevard Enrique Reyna 140, 25294 Saltillo, Coahuila, Mexico*

HIGHLIGHTS

- Synthesis of a benzoateethynylene backbone co-polymer with perylene substituent.
- Optical and electrochemical properties consistent with photoinduced energy transfer.
- Enhancement of photovoltaic efficiency when PCBM is added to the co-polymer.
- EFM studies of active layers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form
9 January 2014
Accepted 10 May 2014
Available online 6 June 2014

Keywords:
Polymers
Luminescence
Optical properties
Atomic force microscopy (AFM)

ABSTRACT

A perylene cholesteryl-benzoateethynylene co-polymer was synthesized by Sonogashira reaction and characterized by NMR, UV–Vis, static and dynamic fluorescence spectroscopy and cyclic voltammetry. The optical and electrochemical properties in solution are consistent with photoinduced energy transfer from the electron donor conjugated backbone to the electron acceptor perylene substituent. Photovoltaic properties are indeed found, even if the performance of the solar cells is quite low due to the formation of aggregates. The incorporation of (6,6)-phenyl C61–butyric acid methyl ester (PCBM), however, increases by an order of magnitude the efficiency of the prototype (from 10^{-4} to 10^{-3}%) due to both better phase mixing and improved electrical continuity as supported by Atomic Force Microscopy (AFM) and Electrical Force Microscopy (EFM) studies.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) based on conjugated p-type polymers and n-type fullerene derivatives have been intensively investigated in recent years for generation of affordable, clean and renewable energy [1]. Advantages of the BHJ PSCs include low-cost fabrication of large-area devices, lightweight, mechanical flexibility and easy tunability of chemical properties of the polymer materials. The bulk heterojunction of regioregular poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C61–butyric acid methyl ester (PCBM) represents one of the most successful systems [2]. However, further improvement of its performance is intrinsically hindered by the narrow absorption spectrum (300–650 nm) and the high-lying HOMO energy level (−4.9 eV) of P3HT. On the other hand, a major drawback of bulk heterojunction devices in general is its dependence on morphological aspects. In fact, if the distance between the acceptor and donor materials is higher than

---

* Corresponding author. Tel.: +52 8444389830; fax: +52 8444389839.
E-mail address: ivana.moggio@ciqa.edu.mx (I. Moggio).

http://dx.doi.org/10.1016/j.matchemphys.2014.05.017
0254-0584/

the exciton diffusion length (typically 10–20 nm), the separated charges recombine [3].

An alternative strategy is thus to combine covalently in the same structure a donor and an acceptor group. In this context, the easier synthetic way is to co-polymerize an electron acceptor (A) with an electron donor (D) monomer. Different structures can be obtained depending on the location of A and D groups, which could be either part of the main chain or side substituents of it. The main-chain donor and side-chain acceptor co-polymers were derived from the extended concept of two-dimensional conjugated polymers proposed by Li. et al. [4] Compared with the well-developed main-chain donor–main-chain acceptor co-polymers, this type of polymer is expected to have several interesting features, such as isotropic charge transport and inside carrier transfer (from backbone to side chain). Since the first successful demonstration of this concept by Huang [5], this family of co-polymers has attracted great interests [6]. Zhang et al. pioneered the use of the concept of main-chain donor with pendant acceptors in photovoltaic materials and reported alternating co-polymers of fluorene and triphenylamine with mono-cyano, di-cyano or aldehyde pendant acceptors [7]. Compared to linear donor–acceptor polymers, however, this family of polymers usually exhibits low fill factor (FF) values due to the poor packing of their polymer chains.

For this reason, more investigations are needed to further understand their structure–property relationship and improve their performances. In general, the most important roles to design D–A co-polymers for photovoltaic applications are: 1) a proper combination of D–A units to achieve low band gap and deep HOMO energy level; 2) high planarity of the D–A units and the whole backbone to enhance absorption and hole mobility; 3) the proper incorporation of side chains to offer good solubility without causing steric hindrance. On these bases, in this work we report the synthesis and physicochemical characterization of a benzoateethynylene co-polymer with perylenic side group in one monomeric unit. The other unit presents a cholesteryl side chain that has been previously reported to give interesting optical and structural properties, together with high solubility [8]. Phenyleneethynylenes are known as strong fluorescent materials and have been successfully applied in light emitting diodes and sensors [9]. Their application in solar cells is still limited with reported efficiency in the order of 10^{-4}%, due substantially to the high energy absorptions, rather far from the maximum sun emission [10]. For this reason, perylene is used in this macromolecule not only as acceptor group [11] but also to increase the optical overlap with the terrestrial solar radiation. It is important to notice that perylene imides are promising acceptor materials also because of their high photostability and chemical facility to be functionalized and their use in solar devices has been recently reviewed [12]. In particular, photoinduced electron transfer has been proven in donor–acceptor systems based on perylene and conjugated molecules such as oligo(phenylene vinylene)s [13] or thiophenes [14]. However, to the best of our knowledge, no reports have been published on phenyleneethynylene polymers with lateral perylene bisimides groups. Moreover, in this paper we demonstrate that the efficiency can be increased by an order of magnitude, reaching 10^{-3}%,when PCBM is added in the active layer, thanks to a better phase mixing and improved electrical continuity.

2. Experimental section

2.1. Synthesis

Experimental procedure for the synthesis of poly[(*N*-((pentyl)-2,5-benzoate)-*N*′-(1-hexylheptyl) perylene-3,4,9,10-tetracarboxyl bisimide))-*Co*-((cholesteryl)-2,5-(benzoate) ethynylene], hereafter named nPE(Pery-*Co*-Chol), chemical and physicochemical characterization of the co-polymer and its intermediaries are given in the supporting information.

2.2. Reagents and materials

All the reactants were purchased from Sigma–Aldrich and Alfa Aesar and used as received. Spectroscopic grade toluene was from Sigma–Aldrich. Acetonitrile from Sigma–Aldrich was passed through a plug of silica gel and distilled from NaH. Triethylammine (Et_3N) was distilled from KOH. Electrochemical grade tetrabutylammonium hexafluorophosphate was purchased from Fluka. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios P) was from Clevios while PCBM and Woods metal were from Sigma–Aldrich. Quartz and Indium Tin Oxide (ITO, 8–12 $\Omega\ cm^{-2}$) substrates were supplied by Spi.Inc.

2.3. Equipment and techniques

^1H and ^{13}C NMR spectra were recorded on Varian Mercury at 300 MHz (^1H) and 75 MHz (^{13}C) at room temperature in $CDCl_3$ and using tetramethylsilane (TMS) as internal standard. UV–Vis spectra were recorded on a Shimadzu 2401PC or an Agilent 8453 spectrophotometer. Fluorescence spectra were obtained on a Perkin Elmer LS50B spectrofluorimeter by exciting at 10 nm below the absorption maximum. The quantum yield (ϕ) in solution was obtained according to literature method [15]. Quinine sulfate in 0.1 M H_2SO_4 water solution ($\phi = 0.54$ at $\lambda_{exc} = 310$ nm) was used as standard. Temperature was kept at $25.0 \pm 0.3\ ^\circ C$ with a water circulating bath. Four different solutions with absorbance between 0.03 and 0.09 were analyzed and the value of ϕ was averaged. The error in the reported values is the standard deviation between the four determinations. Fluorescence lifetime (τ) was obtained on a Tempro Single Photon Counting equipment with 370 nm or 560 nm nanoLED lasers. Ludox was used for pump measurements. Voltagrams were obtained by cyclic voltammetry (CV in a Basi cell) with a potentiostat/galvanostat ACM Gill AC. The reference electrode was an Accumet calomel electrode and the electrolyte was a 0.1 M CH_3CN solution of Bu_4NPF_6. The experiments were carried out in a nitrogen atmosphere at a scanning rate of 50 mV s^{-1}. The working electrode was a film of the material deposited on ITO (from Sigma–Aldrich; 15–25 $\Omega\ cm^{-2}$) prepared by drop casting.

2.4. Thin films and solar cells

The active layers of the solar cells were prepared by dip coating with a TL0.01 MTI corporation, making 4 immersions (speed of 16 cm min^{-1} and time of immersion of 20 min) in order to get a thickness of 100 nm. From one dipping to the other, the layers were kept at room temperature for 15 min. After the fourth immersion, the films were annealed at 150 °C in an Imperial V laboratory oven (that was previously set at the temperature) for 30 min. As term of comparison for morphological studies, films were also prepared by spin coating at 2000 rpm with a WS-400B-6NPP-LITE spin processor from Laurell Technologies. Thicknesses were measured by a Dektak 6M Stylus profilometer at a scanning rate of 50 μm s^{-1} and an applied force of 2 mg. AFM morphological characterization was performed on a Nanoscope III DimensionTM 3100 from Digital Instruments with a Pt-coated Si tip (20 nm nominal radius) in tapping and Electrical Force Microscopy (EFM) at a scanning rate (256 lines) of 0.2 Hz. For EFM studies, a voltage of 12 V was applied to the tip and the separation distance was 100 nm. The surface roughness (R_q), given by the root mean square average (RMS) of height deviation, is taken from the data plane. Grain size analysis was made in the software available in the microscope.