Journal of Physics and Chemistry of Solids 86 (2015) 186–193

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Polyazomethine as a component of solar cells-theoretical and optical study

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ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form
3 July 2015
Accepted 6 July 2015
Available online 9 July 2015

keywords:
Organic solar cells
Azomethine
PCBM
TD-DFT
Luminescence
Electrical properties

ABSTRACT

A recently synthesized 25Th-cardo polyazomethine (PAZ) and its photocurrent generating junction with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have been examined as possible materials for construction of new-generation solar cells. Properties of a 25Th-cardo/PCBM system, where PAZ and PCBM act as donor and acceptor materials, respectively, have been studied theoretically by time-dependent density-functional theory (TD-DFT) and experimentally by means of optical absorption, photocurrent spectroscopy (PCS), and time-resolved luminescence (TRPL). Theoretical calculations show that highest occupied molecular orbital (HOMO) energy levels of PAZ and PCBM are almost equal (values of −6.01 and −5.98 eV were obtained with the B3LYP functional and the def2-TZVP orbital basis for PAZ and PCBM, respectively), what suggests a possibility of charge transfer in both directions for this system. The shape of the calculated absorption spectrum is in a qualitative agreement with the experiment. The PCS measurements of the new material show that the external quantum efficiency is the highest (about 0.3%) in the near UV range. The TRPL studies reveal a fast decay of a Langevin type (in picosecond range) of the PAZ-related photoluminescence, which accelerates in presence of PCBM, probably due to the charge transfer to PCBM. In addition, our measurements document a usually neglected process of the hole transfer from a donor to an acceptor. A leakage of holes from PAZ to PCBM is supported by a small energy difference of the HOMO energies, as predicted by theory.

1. Introduction

Optical techniques represent a fast and non-destructive way of investigations of new materials. They are particularly useful in the case of optoelectronic devices because of their potential application areas. In this study we report results of optical studies of absorption and recombination processes in new azomethine-type conductive materials, which can serve as building blocks for solar cells [1–3]. Among experimental techniques selected by us for this purpose the time-resolved photoluminescence (TRPL) spectroscopy plays an especially important role, as it allows to observe both recombination and charge transfer in the materials under study.

Experimental results are accompanied by theoretical calculations, which utilize time-dependent density functional theory (TD-DFT) to obtain excitation energies and oscillator strengths used afterward to generate simulated optical spectra, which help to explain the experimental results.

Solar-cell photovoltaic devices have been subjected to many studies but the vast majority of them have been devoted to crystalline inorganic semiconductors, like silicon, CdTe and many others. Nonetheless, in a pursuit for cheap materials for high-area solar cells, many researchers turned their attention to cells based on organic polymers [4,5]. A typical efficiency of organic cells is nowadays of order of a few percent (the record research-cell efficiency amounts to 11.1% [6]), what is already promising for some applications [7]. The important remaining problem affecting the majority of organic materials is their sensitivity to moisture and oxygen. Therefore, it is of utmost importance to develop new polymers with better stability properties against the factors mentioned above. To this end, we have selected to study the conjugated polymers possessing imine bonds (>C=N–), called polyazomethines (PAZs), which turned out to be very promising

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http://dx.doi.org/10.1016/j.jpcs.2015.07.002
0022-3697/

stable materials in this aspect. Up to now PAZs have been applied in such devices as organic LEDs or organic solar cells with some successes [1–3], however the materials with better optoelectronic and chemical stability properties are still welcome for more demanding applications. In particular, many researchers continue to look for materials with the electronic levels, which are better matched to the light coming from the Sun, what will have a direct impact on their efficiency. One of such promising candidates from the azomethine class is the 25Th-cardo compound [8,9], which will be studied in this paper.

The main geometry form for solar cells based on conducting conjugated polymers is bulk heterojunction (BHJ). The BHJ solar cells comprise of nanoscale interpenetrating networks of the donor material (in our case PAZ) and the acceptor material. Although the light can (under certain circumstances) directly excite an electron from a donor to an acceptor, most absorption is expected to occur inside donor molecules. Then, after the light creates there an exciton, the latter diffuses to the heterojunction, where it dissociates in a charge-transfer process, i.e. the hole stays at the donor and the electron is transferred to the acceptor material. Finally, the separated charges are transported by molecular networks to electrodes. Since all these processes take place inside molecules in a time scale of 10^{-13}–10^{-9} s [10,11], they are generally difficult to observe. Luckily, the TRPL technique is the one, which can be used to investigate the kinetics of these processes, therefore TRPL is a very important tool in the experimental part of our study.

The most popular acceptor in the BHJs is one of fullerene derivatives, [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) [4,12,13], therefore a mixture of the investigated polyazomethine with PCBM [8] has been utilized in our studies of the 25Th-cardo poliazomethine solar cell.

2. Technical details

The polyazomethine 25Th-cardo was synthesized in a one-step high temperature condensation using 2,5-thiophenedicarboxaldehyde and 4-[9-(4-aminophenyl)-9H-fluoren-9-yl] aniline [8]. The molar mass of monomer was M_m=464 g and polymer molecule M_p about 4400 g. The polycondensation reaction was carried out for 22 h at 160 °C. Since the obtained polymer was soluble in chloroform and smooth layers of a good quality were obtained after solvent evaporation, standard procedures [8] could be used for the preparation of solar cells, i.e. the PAZ/PCBM blend was obtained by a 20-h mixing of PAZ and PCBM solutions in chloroform and by drying of the obtained mixture. The devices had an area of a few square millimeters.

For optical measurements the material was dissolved in chloroform. Then the samples were prepared by evaporating a drop of PAZ or of the PAZ/PCBM mixture onto the glass or copper foil. The UV–vis absorption spectroscopy measurements of the thin film of PAZ were performed at a room temperature using the Cary 5000 spectrophotometer in the range 200–1200 nm.

Photoluminescence (PL) spectroscopy measurements were performed in the range of 300–900 nm using the Hamamatsu C7557 CCD detector. The components were dissolved in chloroform or chlorobenzene in this case.

TRPL measurements were performed using frequency-tripled (to wavelength of 300 nm) output pulses (t_p=130 fs) from a mode-locked Ti:sapphire laser. The spectral and temporal distribution of the PL was analyzed by the spectrometer (1 meV resolution) and the Hamamatsu streak camera. An additional temperature stabilization of the synchroscan circuit enabled measurements with a 2.5 ps resolution. The maximum measurement period was limited to 12 ns by the laser frequency (f=80 MHz).

Photocurrent spectroscopy (PCS) measurements were performed in the range from 290 to 1000 nm (1.24–4.2 eV) using the light of the Xe lamp passing through the monochromator. The current was measured in a short circuit mode with a Keithley pikoammeter, so the I_{SC} spectra (short-circuit photocurrent vs. wavelength) were registered.

3. Theoretical calculations

3.1. Optimization of molecular geometry

The 25Th-cardo azomethine monomer, $C_{32}H_{20}N_2S$, is built from a thiophene ring and an aminophenyl-9H-fluoren-aniline complex connected by imine bonds. Because of a complicated structural formula allowing for angle rotations along single-bond axes, already the monomer possesses several energetically close conformations, which should be taken into account in any quantitative study.

As can be expected, the situation becomes more complicated with each added mer. In the present study of the excitation spectrum of PAZ we utilized the optimized geometries from Ref. [14], where first three energetically lowest conformations (denoted as conformations c1, c2, and c3 in the following) have been selected and optimized on the DFT level for the monomer and then connected to form dimers and trimers without further reoptimization. One of the trimer conformations is depicted in Fig. 1B, where also the electrostatic potential (ESP) of this molecule on the electron density isosurface is presented. For the PAZ trimer a pattern of electronegative and electropositive regions in the molecule can be seen, what signifies that it can bind to both Lewis donors and acceptors. The ESP figure for the PCBM molecule shows that the fullerene cage should be quite inert as far as interactions with polar species are considered. On the other hand,

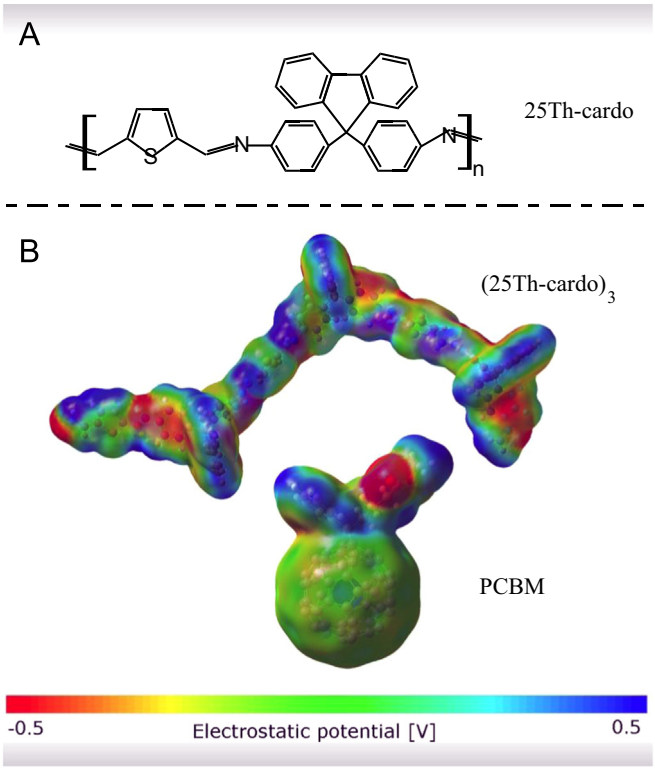

Fig. 1. (A) Chemical formula of the 25Th-cardo azomethine. (B) A map of the electrostatic potentials (ESP) on the electron density isosurface, overimposed on chemical structures of a trimer of the 25Th-cardo azomethine (the upper figure) and PCBM (the lower figure) The figures in color are available on-line.