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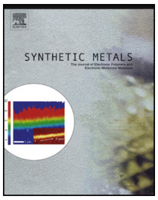

Investigation of optical and electrical properties of new aromatic polyazomethine with thiophene and *cardo* moieties toward application in organic solar cells

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ABSTRACT

New polyazomethine (25Th-cardo) based on thiophene and cardo moieties was synthesized, characterized and tested as active layer in solar cells. The structure of polymer was characterized by means of FTIR and ^{1}H NMR spectroscopy. The temperatures of 5% weight loss of the polyazomethine range from 435 to 455 °C in nitrogen, depending on the heating rate applied. 25Th-cardo has electrochemical energy band gap of approximately ~1.85 eV, and HOMO energy level at −5.21 eV. Optical absorption properties of pure 25Th-cardo and of its mixtures with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) were investigated on different substrates: glass or glass/PEDOT:PSS. Electrical properties of the two kinds of devices: ITO/25Th-cardo:PCBM/Al and ITO/PEDOT:PSS/25Th-cardo:PCBM/Al were tested by impedance spectroscopy. The investigated polymer solar cells contained different amounts of PCBM. Bulk heterojunction solar cells with the architecture ITO/PEDOT:PSS/25Th-cardo:PCBM/Al gave a power conversion efficiency 3.5 times higher for the mixture of 25Th-cardo to PCBM 1:2 (w/w) than for 1:1 (w/w) under 100 mW/cm^2 AM1.5G sunlight illumination in air. The external quantum efficiency value of 25Th-cardo:PCBM solar cell was the highest (about 0.3%) in the near UV range from 3.1 to 3.7 eV.

1. Introduction

Polyazomethines, polymers possessing imine bonds (—HC=N—) are mainly investigated as optical, biological and liquid crystal materials [1,2]. A few groups of scientists created new architecture of polyazomethines in order to obtain soluble polymers with high molecular weight [1–6]. The other groups try to apply polyazomethines in such devices as OLEDs [1–4,6–9] or organic solar cells [10–15]. However, it is still a lot of work to do to improve polyazomethine properties to the level of practical application in the mentioned devices. Especially, electrical properties including photovoltaic (PV) study of polyazomethines are scarce [10–21] and including our PV experiments [10,11,14–17] or other scientists work. Conjugated poly(azomethine)s in undoped form are mainly isolators (10^{-11}–10^{-9} S/cm), while after doping with I_2 or H_2SO_4 their conductivity increase even to 10^{-6} S/cm [2].

Hindson et al. [12] investigated photovoltaic properties of polyazomethines with triphenylamine moieties (TPA), obtained from three different dialdehydes such as 2,5-thiophenedicarboxaldehyde, terephthalaldehyde or 1,3-isophthalaldehyde and 4,4′-diaminotriphenylamine. Bulk heterojunction (BHJ) devices with the architecture ITO/PEDOT:PSS/TPA:PCBM/Al based on polyazomethine with TPA moieties, blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) in the weight ratio 1:3 gave power conversion efficiency (PCE) in the range of 0.02–0.12% [12]. Sharma et al. [13] studied the photovoltaic properties of poly(phenyl azomethine furane) (PPAF) device with the architecture Ag/PPAF/ITO and obtained a value of PCE about 0.019% [13]. In our previous works [11,14,15] different polyazomethines were tested as polymers for photovoltaic applications. BHJ devices based on polyazomethine, prepared from 2,7-diaminofluorene and three different dialdehydes blended with PCBM (1:1), gave value of PCE in the range of 0.12–0.31% [14]. The value of PCE equal to 0.31% reached in our previous work [14] for polyazomethine was the highest value of power conversion efficiency obtained for this group of polymers at the present time, to the best of our knowledge. On the other hand, investigated by us liquid crystalline poly(siloxane-azomethine)s (PAZ-Si) with vinylene units [11] or polyazomethine with TPA and octafluorobiphenyl moieties [15] gave values of PCE in the range of 0.01–0.04% [11,15]. Our previous [11,15] PCE results

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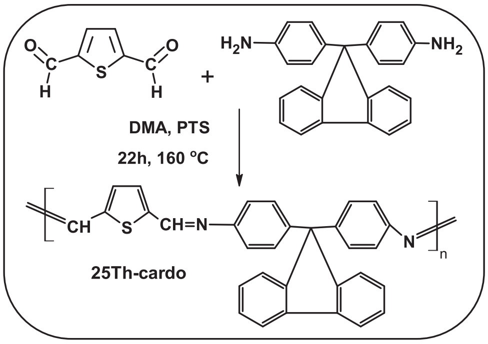

Fig. 1. Synthetic route and chemical structure of 25Th-cardo.

are similar to the results obtained for polyazomethines by Hindson [12] and Sharma [13] groups.

In order to investigate the usefulness of aromatic polyazomethines with thiophene rings in photovoltaic applications we report the synthesis and investigation of the thermal, optical, electrical, electrochemical and photovoltaic properties of polyazomethine based on thiophene and *cardo* moieties. The molecular structure of 25Th-cardo is shown in Fig. 1. The authors [12] suggested that the main reason of low photovoltaic performance is low conjugation in polymer chain and problems with solubility. We agree with these suggestions, and for this reason we introduced *cardo* moieties in the polyazomethine structure investigated in this work, to improve solubility and consequently processability of the polymer.

The preliminary photovoltaic properties of the synthesized aromatic polyazomethine with thiophene and *cardo* moieties were tested by fabrication of the organic photovoltaic devices with the following configurations of ITO/PEDOT:PSS/polyazomethine:PCBM (1:1, and 1:2 w/w)/Al and investigated in dark and under AM1.5G illumination (100 mW/cm^2). For the constructed devices impedance spectroscopy in dark and under illumination were analyzed.

2. Experimental

2.1. Materials and synthetic procedure

2,5-thiophenedicarboxaldehyde, 4-[9-(4-aminophenyl)-9H-fluoren-9-yl]aniline, *N,N*-dimethylacetamide (DMA), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) were purchased from Sigma-Aldrich and used as received. Methanol, acetone, and chloroform were purchased from POCH and used as received. ITO was purchased from Ossila company. Surface resistance of ITO was about 20 ohm/square.

2.1.1. Polymer 25Th-cardo synthesis

Polymer was made using a one-step high temperature condensation technique with anhydrous $CaSO_4$ as a water trap. An one-neck flask with a magnetic stir bar was charged with dialdehyde (1 mmol), diamine (1 mmol), *p*-toluenesulfonic acid (PTS) and 10 mL DMA.

The reaction mixture was allowed to stir for 22 h at 160 °C in an oil bath. The polymer solution was precipitated in methanol and the polymer was collected by filtration. The solid was washed with hot methanol and hot acetone. The final polymer was dried overnight at 80 °C.

2.2. Characterization

The obtained polymer was characterized by several techniques. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC 400 MHz spectrometer using chloroform ($CDCl_3$) as solvent and TMS as the internal standard. FTIR spectra were recorded on a 560 MAGNA-IR NICOLET spectrometer using KBr pellets. Molar masses and dispersities of polymer were obtained by means of size exclusion chromatography (SEC) on a Shimadzu Prominence UFLC instrument at 40 °C on a Shodex 300 mm × 8 mm OHpac column using tetrahydrofurane (THF) as a solvent. Polystyrene was used as calibration standard.

UV-vis spectra were recorded for thin films on the glass substrate by Jasco V670 spectrophotometer. The solutions were spread on the glass with the spin-coating method. The glass substrates were purified using organic solvents like chloroform and acetone. Appropriate settings related to speed (10,000 rpm) and time (25 s) of rotation were applied to spin-coating equipment. All parameters (transmission, reflectivity, and film thickness) which are necessary to calculate the absorption coefficient (α) were measured using JASCO V670 spectrophotometer and its original software. Calculation of layer thickness (d) was made in UV/Vis range from reflectance measurements ($d \sim 150$ nm). The scattering phenomenon was taken into consideration.

Electrochemical measurements were carried out using Eco Chemie Autolab PGSTAT128n potentiostat, using glassy carbon electrode (diam. 3 mm), platinum coil and silver wire as working, auxiliary and reference electrodes, respectively. Potentials were referenced with respect to ferrocene (Fc), which was used as the internal standard. Cyclic and differential pulse voltammetry experiments were conducted in a standard one-compartment cell, in dry acetonitryle, under argon. 0.2 M Bu_4NPF_6 (Aldrich, 99%) was used as the supporting electrolyte.

Thermogravimetric analyses (TGA) were performed on a Perkin Elmer apparatus at heating rate of 10 and 20 °C/min under nitrogen.

The polymer:PCBM mixture and devices were measured with impedance spectroscopy by Solartron precision LCR meter Model SI1260, in the frequency range of 1 Hz to 1 MHz with 20 mV test signal. In order to study photogeneration of charge carriers in BHJ devices, measurements in dark and under illumination (halogen lamp, 100 mW/cm^2) were performed.

2.3. Fabrication and characterization of photovoltaic cells

Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate, with the structure ITO/PEDOT:PSS/25Th-cardo:PCBM/Al in air atmosphere. The ITO-coated glass substrate was first cleaned with deionised water, and ultrasonicated in isopropanol for about 20 min. PEDOT:PSS was spin cast (10,000 turns per minute, 25 s) from aqueous solution, to form a film on the ITO substrate. A mixture of 25Th-cardo:PCBM in chloroform solution with weight ratio 1:1 and 1:2 was then spin cast on top of the PEDOT:PSS layer. Then, an aluminum electrode was deposited by thermal evaporation in vacuum of about 5×10^{-4} Torr. Current density–voltage (J–U) characteristics of the devices were measured using a Solartron Model 1287A Potentiostat/Galvanostat. For solar cell performance a xenon lamp with an irradiation intensity of 100 mW/cm^2 was used. The area of one photovoltaic pixel was about 4.5 mm^2.

The UV–vis absorption spectra of the solar cells were measured at room temperature, using UV–vis spectrophotometer (Cary 5000) in the 250–1000 nm range. In photo-electric measurements a xenon lamp and 0.5-meter monochromator were used. The irradiation intensity depended on the wavelength, being from 0.1 mW/cm^2 at 250 nm to 100 mW/cm^2 at 1000 nm. The photo-excited current was measured with a Keithley logarithmic