

Electrodeposition and Properties of Donor-Acceptor Double-Cable Polythiophene with High Content of Pendant Fulleropyrrolidine Moieties



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ABSTRACT

In this work we report electrochemical copolymerization of thiophene (Th) with thiophene-substituted fulleropyrrolidine (C₆₀-ThFP) on Pt electrode from dichloromethane solution. A structure of the resultant donor-acceptor copolymer with high fullerene content, corresponding to one C₆₀-ThFP per two thiophene units was determined by XPS and FTIR spectroscopy. The ratio of the two monomers in the polymer film was independently determined by electrochemical quartz crystal microbalance. Electroactivity of C₆₀-ThFP and copolymer film in p- and n-doping ranges was studied by cyclic voltammetry. Geometry of a representative fragment of the synthesized copolymer was simulated by means of DFT calculations.

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1. Introduction

Conducting polymers containing thiophene rings and their composites are attractive materials for electronic applications [1–4] owing to high electric conductivity, environmental stability, low potential of oxidation, easiness in modifying the thiophene ring and commercial availability [5–7]. On the other hand, interesting electric properties of fullerenes and their derivatives including capacity of accepting up to six electrons per single fullerene cage [8] allow their successful application in so called bulk heterojunction solar cells [9–18]. The fullerene derivatives incorporated into the conducting polymer phase are responsible for effective dissociation of photogenerated electron-hole pairs (excitons). However, integration of C₆₀ units to the π -conjugated polymer remains still a challenge (see [19] and references therein). One of the most popular methods is blending of soluble conducting polymer with fullerene derivatives. One of the problems in this approach is limited miscibility of the components and phase separation which may hinder the photogenerated electron transport leading to decrease of overall efficiency of the photovoltaic cell. Therefore, a promising method is preparation of so-called *double-cable* polymer in which one, hole transporting

cable is formed by the conjugated backbone of conducting polymer, while electron transporting cable is established by fullerene units attached to the polymer chain [20]. There are two main strategies of preparation of double cable polymers in the form of thin films on the electrodes, by spin coating of soluble fulleropyrrolidine-substituted polymers prepared via chemical synthesis [21–23] or electropolymerization of the monomers with covalently linked fullerene [24–29]. The latter method provides good electrical contact between the electrode and the polymer film, proximity of electron donor and acceptor units and allows controlling easily the thickness of deposited layer by the charge passed during polymerization. However, as it has been pointed out by Cravino and Sariciftci [20], the double-cable polymers for photovoltaic applications must meet the requirement of no charge transfer between the donor and acceptor in the ground state. This may be achieved by selection of a suitable linker between fullerene and conducting backbone.

Herein, we report the formation of conducting double cable polymer with high content of pendant fullerene moieties along the polymer chain by a simple electrochemical copolymerization of low-cost starting materials, thiophene and thiophene-substituted fulleropyrrolidine. The thiophene/fullerene ratio in the resultant film has been determined by XPS as well as from electrochemical quartz crystal microbalance measurements. The synthesized double cable copolymer has been characterized by FTIR, UV-vis

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and electrochemical methods. Geometry of a representative fragment of the synthesized copolymer was simulated by means of DFT calculations.

2. Experimental

2.1. Reagents

Thiophene (Th), 3-thiophenecarboxaldehyde, N-methylglycine, tetrabutylammonium hexafluorophosphate (TBAPF₆), acetonitrile, toluene, n-hexane, dichloromethane (DCM) and silica gel 70-230 mesh were bought from Sigma-Aldrich. Fullerene C₆₀, 99.9%, was obtained from MER Corp. Solvents were analytical grade reagents and were used as received except toluene that was dried by ordinary methods and distilled under argon atmosphere.

2.2. Instruments

All electrochemical experiments were carried out using potentiostat AUTOLAB PGSTAT 30 (Ecochemie, Netherlands) in conventional, one compartment cell with Pt or Au disc electrodes (geometric surface area 0.03 cm²), Pt wire counter electrode and double junction Ag/Ag⁺ (0.01 M AgNO₃, in CH₃CN) reference electrode. All potentials in this work are referred to the formal potential of ferrocene/ferrocenium (Fc/Fc⁺) couple as internal standard, added to the solutions after measurements. The formal potential of Fc/Fc⁺ redox couple was 0.15 ± 0.01 V vs. Ag/Ag⁺ electrode. Copolymer for XPS, FTIR and UV-vis reflectance measurements was deposited on Pt sheets.

Gravimetric measurements were performed by means of quartz crystal microbalance (QCM) unit (Type M106, UELKO, Poland) combined with AUTOLAB. The working electrode was a gold thin film deposited on 10 MHz AT-cut quartz crystal (International Crystal Manufacturing Co. Ltd., Oklahoma City), with piezoelectrically and electrochemically active areas of 0.21 cm² and 0.23 cm², respectively. All measurements were performed in deaerated solutions at room temperature (23 ± 2 °C).

ESI-MS spectra were acquired in positive ion mode using a 4000 Q-TRAP Applied Biosystems mass spectrometer. ¹H NMR spectra were recorded in CDCl₃ with a Varian Unity Plus 200 MHz spectrometer. XPS measurements were carried out using a VG ESCALAB 210 electron spectrometer calibrated using the binding energy of C1s 285.0 eV as the internal standard. The FTIR spectra were registered using a spectrometer Nicolet iS50 (Thermo Scientific).

UV-Vis spectra of the monomers were carried out with spectrophotometer Lambda 12 (Perkin-Elmer), whereas the polymer films deposited on the Pt electrodes were studied in reflection mode by means of spectrophotometer UV-3600 (Shimadzu).

2.3. Synthesis of thiophene – functionalized C₆₀ fullerene

Preparation of 1-methyl-2-thiophen-2-yl-3,4-fulleropyrrolidine (C₆₀-ThFP) was accomplished using the modified Prato synthesis [30] (yield: 23%) (Fig. 1). The mass spectrum (ESI-MS) showed a [M + H]⁺ peak at 860.1; IR (KBr disk) ν_{max}(cm⁻¹) 2944.3,

2775.6, 1639.2, 1459.4, 1424.2, 1330.2, 1239.0, 1180.7, 1121.4, 771.9, 726.5, 632.5, 507.8, 574.6, 557.3, 526.0; δ¹H NMR (200 MHz; CDCl₃; TMS) 2.84 (3H, s), 4.20–4.24 (1H, d), 4.94–4.99 (1H, d), 5.08 (1H, s), 7.36–7.40 (1H, m), 7.48–7.51 (1H, m), 7.61–7.63 (1H, m) ppm; UV-Vis 262 nm, 328 nm, 437 nm.

2.4. Theoretical calculations

The computational calculations were performed by using Gaussian09 [31] software package. The geometry of the copolymer chain fragment was initially optimized using HyperChem 6.03 software on the semi-empirical PM3 level. The optimized geometry was further improved by the hybrid density functional B3LYP method [32,33] and the 6-31G(d) basis set [34,35] to a stationary point on the Born-Oppenheimer potential energy surface. This method is extensively used to elucidate the electronic structures of fullerenes and their solar cell oriented derivatives [36,37]. The frontier HOMO and LUMO were calculated on a fully optimized structure.

3. Results and discussion

3.1. Electrochemical and UV-vis properties of C₆₀-ThFP

Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) obtained for electrochemical reduction of C₆₀-ThFP at Pt electrode in DCM solution are presented in Fig. 2a and Fig. 2b, respectively. Three well resolved reduction peaks at about -1.09 V, -1.48 V and -2.05 V vs. Fc/Fc⁺ and corresponding reoxidation waves visible in CV are the result of sequential one-electron reversible processes, typical of C₆₀ derivatives. This indicates that the fullerene moiety attached to thiophene preserves electrochemical properties characteristic of the extended π-electron system for unsubstituted fulleropyrrolidine [8,38].

A comparison of UV-vis spectra of thiophene, C₆₀ and C₆₀-ThFP in dichloromethane is presented in Fig. 3. The spectrum of C₆₀ (curve 1) with characteristic intense absorption bands at 258 and 328 nm typical of the π → π* transition in aromatic systems, matches very well the spectra reported in the literature [39,40]. The band at 328 nm has several small but distinguishable shoulders extending into the visible range, indicative of vibrational structure. One of them is visible at 405 nm. In the spectrum of thiophene (curve 2) one can observe one strong absorption peak at 234 nm corresponding to π → π* transition (5.1 eV), [41]. After attachment of thiophene to fulleropyrrolidine to form C₆₀-ThFP, the absorption peak of Th overlaps with an intense band of C₆₀ at 262 nm (curve 3) and therefore, it is visible as a shoulder on the short wavelength side of this band (in the range 240–250 nm). The second band corresponding to electronic transition in fullerene is visible in the spectrum of C₆₀-ThFP as a broad shoulder in the region between 310 and 330 nm. This broadening is a consequence of the functionalization of fullerene and chemical modification of the molecular structure of the C₆₀ cage [42,43]. A small peak at 437 nm distinguished in the spectrum of C₆₀-ThFP is ascribed in the literature to absorption of mono- adduct of fullerenes and exhibits the common feature of [6,6]-closed structure [44,45].

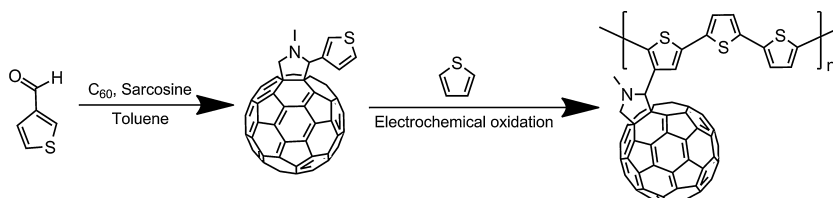


Fig. 1. A scheme of synthesis of thiophene-functionalized C₆₀ fullerene film on platinum electrode.

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