

The effect of the linking topology on the electrochemical and spectroelectrochemical properties of carbazolyl substituted perylene bisimides



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ABSTRACT

We report on electrochemical and spectroelectrochemical characteristics of two isomeric, carbazolyl substituted perylene bisimides and their polymers. Investigations were carried out in order to determine the effect of the linking topology on their properties.

Cyclic voltammetry (CV) measurements of the investigated monomers showed typical two-step reduction of the perylene diimide moiety. The electrochemical oxidation of the studied compounds gave the corresponding polymer, which was deposited on the electrode. The resulting films were also examined by cyclic voltammetry. Investigation indicated both: n-type and p-type doping of polymers. Analysis of redox process of the monomers and polymers was carried out using UV-Vis and EPR spectroscopy. Our studies point to differences in the kinetics of the reduction process, depending on the substitution of the carbazole moiety. Although both monomers easily undergo of electrochemical polymerization, an effect of the linking topology of carbazolyl substituted perylene bisimides on the polymerization process was evidently noticed. Monomer PE2 as well as PE3 led to stable polymers, but polymer based on PE3 displays the conjugation in a longer extend than that based on PE2, where carbazole is linked to perylene diimide at less favorable position 2.

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1. Introduction

In the age of rapidly developing technology, there is a necessity to search for compounds with better properties, meeting the increasingly sophisticated requirements. Nowadays, one of the rapidly growing sectors with major potential is organic electronics [1,2], which involves organic materials in such devices as light emitting diodes (OLEDs)[3], light-emitting electrochemical cells (LECs) [4], photovoltaic cells [5–7], organic thin film field effect transistors (OFETs) [8,9] and sensors [10]. The main advantage of organic semiconductors over conventional conductive materials is their flexibility and wide range of optical, optoelectronic and photo- and electroluminescent properties [11].

The previous investigation of organic, conjugated compounds which can be used as semiconductors in (opto)electronic systems are mainly related to the group of p-type semiconductors. Now, intense researches are focused on n-type semiconductors and ambipolar materials which are able to transport both kinds of charge carriers i.e. holes and an electrons. Despite of that fact, those types of compounds still lags behind p-type systems [12,13].

Among large number of conjugated materials, aryl imide derivatives appear to represent a promising group of organic compounds in the aspect of (opto)electronic applications mainly because of their good thermal and chemical stability. Additionally, due to their properties, the high value of electron affinity (strong electron withdrawing character), a low LUMO level and a good reversibility of the reduction process, aryl imide derivatives are the most important blocks for the preparation of n-doped materials [14–17].

There are known numerous perylene diimide derivatives with an excellent charge carrier transport properties, what makes them good candidates for the application in electronic and optoelectronic devices [18–28].

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On the other hand carbazole and its derivatives are widely used hole-transport (p-type semiconductor) materials, which also possess many other interesting properties. Carbazole-based compounds are known for their excellent photorefractive properties, intensive fluorescence and electroluminescence, high thermal and photochemical stability [29]. Carbazole derivatives are also able to form relatively stable radical cations. Because of that, compounds containing carbazole moieties are capable of electrochemical polymerization and formation of conductive layers during this process [30,31]. It is interesting to note that depending on the substitution of the carbazole ring, devices based on carbazole derivatives exhibit different properties. It was observed that, devices fabricated from 2,7-substituted carbazole derivatives demonstrate better results than those prepared using 3,6-substituted derivatives [32].

Taking into account all the facts described above we studied the possibility of obtaining ambipolar polymers from perylene diimide derivatives directly substituted in 1,7 positions with carbazole groups via the electrochemical method and estimated the effect of the substitution pattern on the electrochemical and spectroelectrochemical properties of the obtained layers. It is worth of noting that such derivatives of perylene diimide and carbazole have not been yet extensively studied. Ambipolar polymers based on imide derivatives described in literature, were mainly obtained by chemical polymerization. There are no reports on electrochemical polymerization of such compounds. This fact motivated us to take this topic.

2. Experimental details

2.1. Materials

The synthesis and basic properties of the investigated compounds were described in the earlier published paper [33]. Their chemical structures are shown in Fig. 1. All the measurements were carried out in supporting electrolyte which was 0,1 M solution of tetrabutylammonium hexafluorophosphate (Sigma Aldrich 98%) in dichloromethane (Sigma Aldrich $\geq 99.9\%$). Electrodeposition and electrochemical characterization of the studied monomers was performed in 1 mM solution of a corresponding compound in the supporting electrolyte. Spectroelectrochemical investigations were made in 10^{-5} M solution of each monomer. The studies of

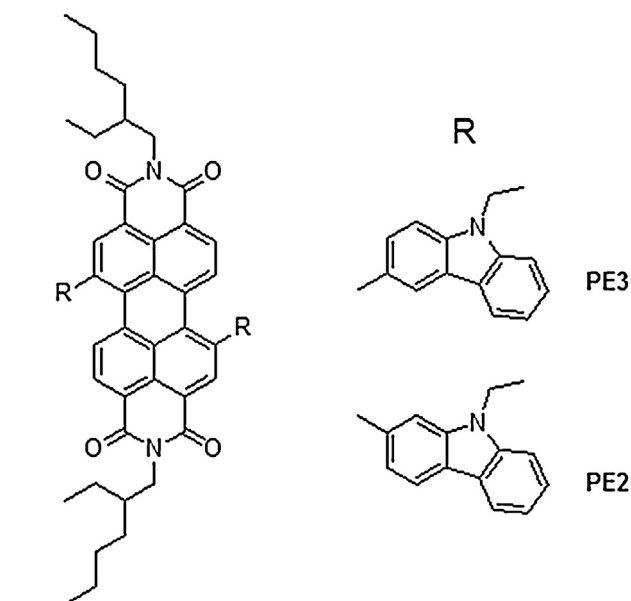


Fig. 1. Chemical structures of investigated monomers.

electrodeposited films were carried out in monomer-free solutions of the supporting electrolyte.

2.2. Instrumental characterization

Electrochemical measurements were performed on Ecochemie AUTOLAB potentiostat-galvanostat model PGSTAT20. The obtained data were analyzed using the GPES program. Cyclic voltammetry (CV) was used for the electrochemical characterization. The typical three-electrode cell was applied. The platinum wire was used as working electrode, the platinum spiral was employed as an auxiliary electrode and the silver wire was used as a pseudo reference electrode which was calibrated versus ferrocene/ferrocinium redox couple. The solutions were purged with argon.

Spectral measurements were carried out using UV-Vis Hewlett Packard spectrophotometer 8453 and JEOL JES-FA 200, X-band CW-EPR spectrometer operating at 100 kHz field modulation. Spectroelectrochemical investigations were made by connected spectrometers described above with OMNI potentiostat.

UV-Vis measurements during reduction processes were carried out in a 2 mm quartz cell equipped with a platinum mesh as a working electrode, a platinum spiral as a auxiliary electrode and a silver wire as a pseudo reference electrode. UV-Vis measurements of oxidation processes which lead to the formation of the films on the surface of working electrode were performed with employed indium-tin-oxide (ITO) coated quartz electrode as working electrode. Investigations of redox process of polymer films by UV-Vis measurements were carried out with a ITO working electrode coated with films, which were obtained by electropolymerization.

EPR measurements were carried out in a cylindrical cell equipped with set of electrode like in the case of electrochemical measurements. The spectra of the radical anions of investigated monomers were recorded during potentiostatic reduction. Investigations of polymer films by EPR measurements were carried out with the working electrode coated with films, which were obtained by electropolymerization.

3. Results and discussion.

In this work the electrochemical and spectroelectrochemical characterization of the monomers and of their polymers obtained by electrochemical deposition on the surface of working electrodes was performed. The chemical structures of the investigated compounds give the opportunity to obtain ambipolar polymers capable of both n and p doping. The main purpose of this work was estimation of the influence of the linking topology of the carbazole units to the perylene core on the electrochemical and spectroelectrochemical properties of the compounds and of the electrochemically obtained polymers.

3.1. Electrochemical characterization

The basic electrochemical properties of the monomers were described in the former paper [33]. In this report we focus on the process of electropolymerization and on investigation of the obtained films.

Both the investigated monomers undergo processes of electrochemical oxidation as well as reduction. The voltammograms of the monomers show that oxidation process starts at 0.71 V for PE2 and at 0.62 V for PE3. The potential of 0.71 corresponds to the value of ionization energy (IE) of 5.51 eV for PE2. The IE value of PE3 was found to be a little lower (5.42 eV). This observation indicates more extended conjugation in PE2 molecule than in PE3. Analysis of the shape of the monomer voltammograms revealed the wider peaks for PE3 monomer. In terms of the shape of cyclic voltammetry curves, the reduction processes for both compounds are very

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