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# The role of furyl substituents of pyrene on monomer and polymer properties

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#### ABSTRACT

This paper estimates the influence of substituents number on basic electrochemical, optical and electronic properties of monomers compared to their polymers. Results exhibit differences of these effects in monomers and polymers. The crosslinking effect has impact on basic properties of studied polymers. Polymers were created from their monomers by electropolymerization. Optical properties of a series of furyl derivatives of pyrene were investigated by UV–vis spectroscopy. Basic electrochemical properties of the studied compounds were investigated by cyclic voltammetry. ESR–UV–vis spectroelectrochemistry reveals differences in doping processes of obtained conjugated polymers. Good electrochemical stability of novel furyl-pyren  $\pi$ -conjugated polymers confirm the application potential of this group of materials for the development of organic semiconductors in particularly for possible applications in electrochromic devices, light emitting electrochemical cells and spintronic.

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#### 1. Introduction

Organic semiconductors have gained large interest through applications such as organic light emitting diodes (OLEDs) [1], solar cells [2] and organic field effect transistors (OFETs) [3,4]. The star-shaped and branched molecules are used as semiconducting materials in OFETs because of their easy processability and high solubility in organic solvents [5–7].

The pyrene ring is of special interest since it affords a possibility of substitution for wide variety of substituents, particularly for aryl groups such as thiophene and furane. The pyrene structure was precisely examined from the respective angleof various disciplines including biology, chemistry and physics. Moreover, due to the electroconductive properties of pyrene and its derivatives, both of them have been successfully applied to in many technologies including microenvironmental sensors [8], liquid crystals [9] and photoactive polypeptides [10]. Pyrene is a flat aromatic molecule and exhibits excellent fluorescent properties. It's pure

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http://dx.doi.org/10.1016/j.synthmet.2014.02.017 0379-6779/© 2014 Elsevier B.V. All rights reserved. blue emission permits a straightforward exploitation in organic light emitting diodes (OLEDs) [11].

Various aromatic and/or heteroaromatic cores have been utilized in the development of organic semiconductors. Furan has been less studied compared to other heteroaromatics such as thiophene and pyrrole [12]. This could partially be attributed to the chemical lability of furan and its derivatives. For example, furan serves as a diene in the [4+2] Diels–Alder reactions under milder conditions than those for thiophene and pyrrole [13]. On the other hand, the comparably lower aromaticity of furan relative to thiophene and pyrrole may give rise to different electronic properties in the resulting furan-based materials [14].

Organic structures containing furan units undergo both oxidation and reduction processes and play an important role in the search for new materials and their novel applications [15]. It has been recently reported that furan-incorporated  $\pi$ -conjugation molecules can exhibit a high charge mobility and efficient photoluminescence [16,17]. In addition, their potential application to field-effect transistors, photovoltaic devices, and organic electroluminescent devices has been investigated [18].

In this work, we performed a detailed optical and electrochemical properties study of a novel class of pyren derivatives (Scheme 1). We present cyclic voltammetry characteristics of molecular materials based on a pyrene core, which is connected to furan units.









Scheme 1. Furyl derivatives of pyrene.

Optical and electrochemical properties of monomers were compared to polymers. We report also fluorescence, UV–vis properties and electrochemical studies of obtained compounds. Finally, values of the ionization potential (IP), electron affinity (EA) and energy gap for both monomers and polymers are presented.

#### 2. Experimental

Electrosynthesis and studies on polymer films were performed in dichloromethane (POCH 99.8%) containing 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as a supporting electrolyte, using a CH Instruments Electrochemical Analyzer model 600. Polymer films were synthesized on a platinum wire at a scan rate of 100 mV/s. An Ag pseudo-reference electrode was used and its exact potential was calibrated vs. ferrocene. The platinum wire served as a counter electrode.

UV-vis spectral measurements recorded during monomer oxidation in a thin layer were carried out on a Hewlett Packard 8453 UV-Vis spectrophotometer. Measurements were carried out in a thin layer (50  $\mu m$ ) of monomer solution in an appropriate spectroelectrochemical cell. The thickness of the monomer solution in the optical length was provided by the Teflon gasket placed between the cell wall and the indium tin oxide (ITO) coated electrode, which serves as working electrode.

Appropriate vessels adapted for simultaneous spectroelectrochemical Electron Spin Resonance (ESR) and UV-vis-NIR measurements were used. The target polymer was synthesized



Scheme 2. Synthesis of furyl derivatives of pyrene.

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