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Unusual properties of electropolymerized 2,7- and 3,6- carbazole derivatives

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ABSTRACT

Differently linked carbazole derivatives possessing pyrene and selenophene moieties were electrochemically investigated. Cyclic voltammetric as well as differential pulse voltammetric studies demonstrated that they display comparatively low oxidation potentials. One-step cyclic voltammetric process was used for the preparation of their highly dimensional, stable and electroactive polymers. The electrodeposited polymers displayed unusual properties upon electrochemical doping that may help tailoring the dimensional features of these polymers. The electrodeposited polymers were investigated by electrochemical and optical tools and correlation between different parameters such as oxidation characteristics or absorption behavior and the effective conjugation length was established. Spectroelectrochemical investigations showed the polaronic and bipoloronic features of the electropolymers. Multielectrochromic properties of electrodeposited polymers on successive doping suggested their application as electroactive layers in electrochromic devices.

1. Introduction

The era of flexible and highly stable electronic devices demands π-conjugated organic polymers with the certain sets of properties including mechanical strength and with the possibilities of tailoring of the properties by structural modification. Thus, it is necessary to develop novel materials with the required sets of properties for specific applications. A large number of applications of conjugated polymers depend mainly on their electrochromic properties, which rely on the reproducible switching of characteristics of conjugated polymers [1–6]. The properties of conducting polymers strongly depend on their structural characteristics, which imply the modification of their monomer structures to tune the properties of the polymers (electronic, optical, charge-transporting etc.) according to the intended applications. The physical and chemical properties of the conjugated polymers can be controlled efficiently by some basic factors such as bond length alternation, variation of aromaticity and substitution [7]. For this purpose, functionalization of the electroactive monomer structures prior to electropolymerization and combination of the conducting polymers with other materials are widely used [8,9].

Conjugated polymeric systems based on selenophene or carbazole are among the most promising materials for the development of new generation, highly efficient OLED devices [10–12]. Carbazole and selenophene-based monomer units, especially in combination with electron-poor aromatic units, lead to novel polymeric electron donor structures [13–17] that possess a number of properties useful for the improvement of the photovoltaic characteristics [11], such as energy level alignment with that of electron acceptors [18], low energy gap which favors light harvesting and increase the short-circuit current of the device [13], high charge mobility [19] and good solubility in organic solvents and good film-forming properties [20]. Polycarbazoles are known not only as efficient short wavelength emitters but also as strong electro-donating (p-type) chromophores [21–26]. The advantage of carbazole moiety is that it can be easily functionalized at its C-2, C-3, C-6, C-7 or N-positions [27–29]. Furthermore, poly (3,6-carbazole)s demonstrate interesting electrochromic properties because of the conjugation breaks that are present due to the possession of 3,6-linkages. The ability of poly (3,6-carbazole) derivatives to form multi-oxidation states results in the exhibition of many colors on the ITO/glass surface upon applied positive potentials [30,31]. Since 2,7-substituted carbazoles have been theoretically found to have

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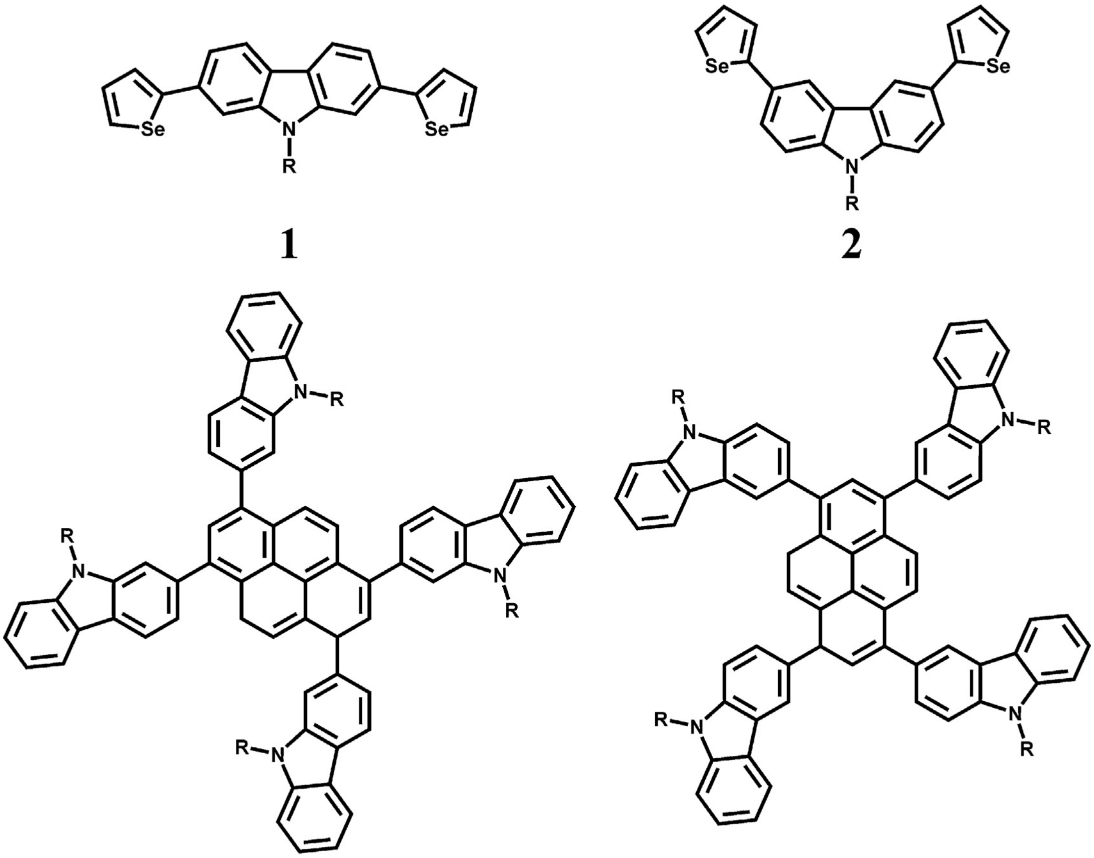

1 2 3 4

R: C_2H_5, C_9H_{19}

Fig. 1. Structures of investigated compounds.

smaller band gaps than the 3,6-substituted carbazoles, the small energy gaps of these monomers are expected to contribute to a lowering of the band gaps in the resulting polymers [22–25]. Due to the simplicity of the synthesis, there are many reports regarding poly (3,6-carbazole)s [32]. Oligo- and poly(2,7-carbazole) derivatives have been successfully used in polymer light emitting diodes (PLEDs) and organic field-effect transistors (OFETs) [31]. Carbazole moiety is fully aromatic and possess good chemical and environmental stability. Taking all these considerations into account we expect, that development of new carbazole-based low-band gap copolymers will lead to interesting properties useful for photovoltaic applications. However, one possible problem that still concerns 2,7-carbazole-based copolymers is their electrochemical instability due to the build-up of charge at the free para-(3- and 6-) positions [33]. Big progress has been made recently in the field of electrochemically deposited polyselenophene derivatives for electrochromic devices [34,35], and chemically synthesized regioregular poly(3-hexylselenophene) for solar cells [36–38]. In addition, there are also some applications of the copolymers in organic light emitting diodes [39], OFETs [40] and near IR emitter [39,41] applications. The new aspect of the investigation into selenophene derivatives is use of selenophene moieties as a donor groups in donor-acceptor copolymers. Lee and co-workers [42] presented the synthesis, optical and photovoltaic characteristics of alkylselenophene-substituted quinoxaline based donor-acceptor low band-gap polymers. It was observed that the length of the C-C bond between selenophene rings is shorter than that between thiophene rings (ref). Therefore oligoselenophenes with enhanced conjugation in the polymer backbone show red shift in the absorption spectra as compared to oligothiophenes [42–46]. In the present study, a comparison of differently linked carbazole derivatives is presented. In selenophene derivatives 2,7- and 3,6-substituted carbazole moieties are inside the molecules while in pyrene-based derivatives they serve as the side arms.

Fig. 1.

2. Experimental

2.1. Materials

All solvents for the synthesis were dried and then distilled before use. Other commercially available substances and reagents were used as received. The solutions of 1.0 mM concentration of all monomers were used for all cyclic voltammetry measurements. Electrochemical studies were conducted in 0.1 M solutions of Bu_4NBF_4, 99% (Sigma Aldrich) in dichloromethane (DCM) solvent, (CHROMASOLV®, 99.9% from Sigma Aldrich) at room temperature. UV-Vis spectroelectrochemical measurements were performed on Indium Tin Oxide (ITO) quartz glass working electrode coated with polymers. Polymeric layers were synthesized on an ITO electrode under conditions similar to those of cyclic voltammetry measurements.