Electrosynthesis of Electrochromic Polycarbazole Films from 3,6-Di(carbazol-9-yl)-*N*-phenylcarbazole Derivatives

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Abstract

Two compounds with tri-carbazole (**3Cz**) structure were synthesized, namely 3,6-di(carbazol-9-yl)-*N*-(4-nitrophenyl)carbazole [**NO_2-3Cz**] and 3,6-di(carbazol-9-yl)-*N*-(4-aminophenyl)carbazole [**NH_2-3Cz**]. These **3Cz**-derivatives can be electropolymerized into polymer films on the electrode surface in an electrolyte solution via the carbazole-carbazole and NH_2-carbazole coupling reactions. These electro-generated polymer films exhibited reversible electrochemical oxidation processes, with a significant electrochromic behavior. The color of **P(NO_2-3Cz)** film changed from pale yellow neutral state to yellow-green as a radical cation and then to blue when fully oxidized. Upon oxidation, the color of **P(NH_2-3Cz)** film changed from colorless to pale green and finally to blue.

Introduction

Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, electroluminescent, electrochromic, and photorefractive materials [1]. The electrochemical oxidation of carbazole and *N*-substituted derivatives was first studied by Ambrose and Nelson [2,3]. For the *N*-phenylcarbazoles with both the 3 and 6 carbazole ring positions unprotected, these compounds underwent an initial one-electron oxidation to generate a very reactive cation radical; two of these then coupled at the 3 positions to yield a *N,N*'-diphenyl-3,3'-bicarbazyl. This carbazole oxidative dimerization reaction has been employed efficiently to fabricate electroactive polymeric films for potential applications in electronic and optoelectronic devices. Compared with the chemical routes, electrochemical polymerization has several advantages in the syntheses of conducting polymer films, such as one-step polymer film formation with good mechanical properties on the electrode. This is not only enlarges the scope of candidate polymers, but also omits the procedure of the film casting.

In this work, two *N*-phenyl-3,6-bis(*N*-carbazolyl)-carbazole derivatives, i.e., **NO_2-3Cz** and **NH_2-3Cz**, were prepared and the **P(NO_2-3Cz)** and **P(NH_2-3Cz)** films were prepared directly on the electrode surface via electrochemical oxidative coupling of carbazole-carbazole and amine-carbazole. The electrochromic properties of the resulting polycarbazole films were evaluated by the spectroelectrochemical and electrochromic switching studies.

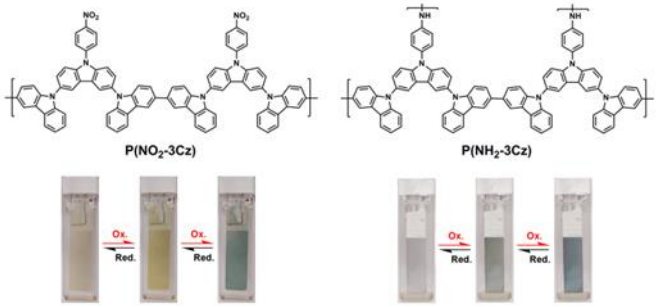

Fig.1: Structures and electrochromism of the electrodeposited polycarbazole films.

References

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