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Electrochemical synthesis and electrochromic properties of new conjugated polycarbazoles from di(carbazol-9-yl)-substituted triphenylamine and *N*-phenylcarbazole derivatives

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ABSTRACT

Two carbazole end-capped monomers containing triphenylamine or *N*-phenylcarbazole as an interior core, namely 4,4′-di(carbazol-9-yl)-4″-methoxytriphenylamine (TPA-2Cz) and 3,6-di(carbazol-9-yl)-*N*-(4-methoxyphenyl)carbazole (PhCz-2Cz), were prepared by a well-known chemistry from readily available reagents. The electrochemistry and electropolymerization of these two monomers were investigated and compared with those of structurally similar analogs with *tert*-butyl groups attaching on the active sites of the end-capped carbazole units. The polymeric films were built onto ITO/glass surface by repetitive cyclic voltammetry (CV) scanning of the monomer solutions containing an electrolyte. The electro-generated polycarbazole films exhibited high redox-activity and strong color changes upon electro-oxidation, which can be switched by potential modulation. The remarkable electrochromic behavior of the film was clearly interpreted on the basis of spectroelectrochemical studies, and the electrochromic stability was evaluated by the electrochromic switching studies.

1. Introduction

Electrochromic materials have been studied for different technological applications, such as anti-glare mirrors, smart windows, and electrochromic displays [1,2]. Examples of commercially available electrochromic technology include the Boeing 787 Dreamliner dimmable windows manufactured by Gentex [3,4]. Conjugated polymers stand for a family of important electrochromic materials that have received increasing attention due to their several advantages over inorganic compounds; for instance, high coloration efficiency, fast response speed, multiple colors with the same material, good processability, and fine-tunability of the band gap [5–10]. The conjugated polymers can be synthesized by either chemical or electrochemical polymerization. Compared with the chemical routes, electrochemical polymerization can obtain conjugated polymer films on conductive substrates directly. This not only enlarges the scope of candidate polymers, but also avoids the procedure of the film coating.

Carbazole and triarylamine derivatives are well-known for their electroactive and photoactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters [11–13]. In recent years, carbazole derivatives have been widely used as effective host materials in phosphorescent light-emitting diodes because of their sufficiently high triplet energy and good hole-transporting ability [14–19]. Carbazole can be substituted or polymerized either at the 3- and 6- positions or 2- and 7- positions and a wide variety of alkyl and aryl chains can be added on the nitrogen atom without altering the planar conformation of the resulting polymers. Using different synthetic strategies and substitution patterns, the physic-chemical properties of poly(3,6-carbazole)s and poly(2,7-carbazole)s can be fine-tuned, leading to high performance materials for a number of electronic applications [20–22]. As reported by Ambrose and co-workers in their pioneering work [23,24] devoted to anodic oxidation of carbazole and various *N*-substituted carbazoles, ring–ring coupling is the predominant decay pathway, the carbazole radical cation yielding 3,3′-bicarbazyls. The resulting 3,3′-bicarbazyls display two successive, reversible, one-electron redox steps to yield quinoid, green-colored radical cation and blue dications, respectively. Although these bicarbazyls possess a lower first oxidation potential than the corresponding monomers and are therefore, potentially, more suitable for electrochemical polymerization, dimers were cleanly obtained in quantitative yields, due to the high stability of the oxidized states (bicarbazylium cations). Polymerization may occur anodically by using di-carbazoles, *N*-linked by suitable spacers, to produce materials with redox properties characteristic of bicarbazyls.

In the past decade, many condensation-type high-performance polymers (typically, aromatic polyamides and polyimides) carrying the triarylamine unit have been reported as potential electrochromic materials [25–30]. On the other hand, redox-active and electrochromic

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