



Electrosynthesis of redox-active and electrochromic polymer films from triphenylamine-cored star-shaped molecules end-capped with arylamine groups

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ABSTRACT

Four starburst molecules with a triphenylamine (TPA) core through the amide group linked to the terminal triphenylamine or (*N*-phenyl)carbazole (NPC) unit, coded as **T-3(NHCO-TPA)**, **T-3(NHCO-NPC)**, **T-3(CONH-TPA)**, and **T-3(CONH-NPC)**, were synthesized and their electrochemistry and electropolymerization were investigated. The oxidation potential and the stability of the oxidized forms of the starbursts are affected by the orientation of amide linkage and the structure of terminal triarylamine unit. Robust polymeric films could be built onto ITO/glass surface by repetitive cyclic voltammetry (CV) of the **T-3(NHCO-TPA)** solution containing an electrolyte. The electrodeposited films exhibited reversible electrochemical processes and strong color changes upon electro-oxidation, which can be switched by potential modulation. The electrochromic behavior of the film was clearly interpreted on the basis of spectroelectrochemical studies. **T-3(CONH-TPA)** did not undergo electropolymerization effectively. **T-3(CONH-NPC)** also could electrochemically polymerize to polymer films upon repeated CV scans. However, their electrochromic switching stability is less than that of the polymer film from **T-3(NHCO-TPA)**.

1. Introduction

Electrochromism suggested by Platt in 1961 refers to the reversibly changing color of an electroactive species resulted from the redox reaction by applying an external voltage [1–3]. In recent decades, electrochromic materials attract much attention because of their possibility in energy saving applications. Potential products such as anti-glared rear view mirrors [4], smart windows [5], and displays [6] are based on electrochromic technologies. Recent high-profile commercialization of electrochromics includes the Boeing 787 Dreamliner windows [7]. Organic π -conjugated polymers [8–10] and triarylamine-based condensation polymers [11] have been studied extensively for electrochromic applications. Since the electrochromic properties of organic polymers can be easily tunable by tailoring their molecular structures [12–18], these materials have become popular in recent years.

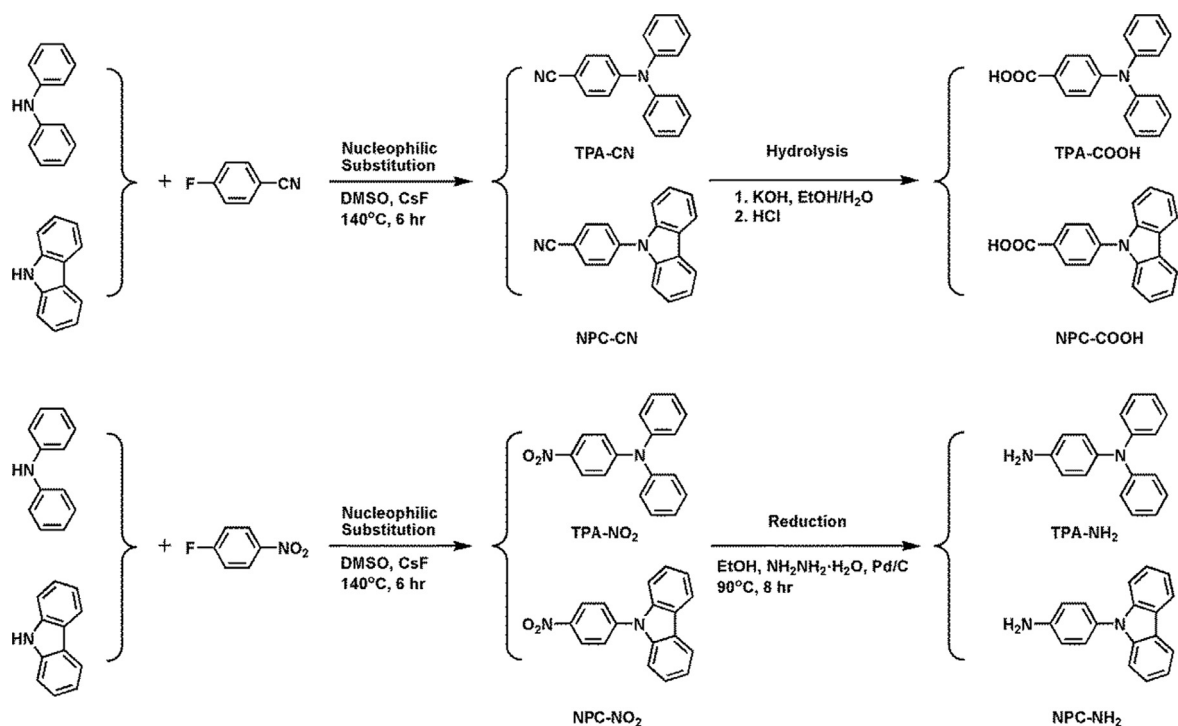
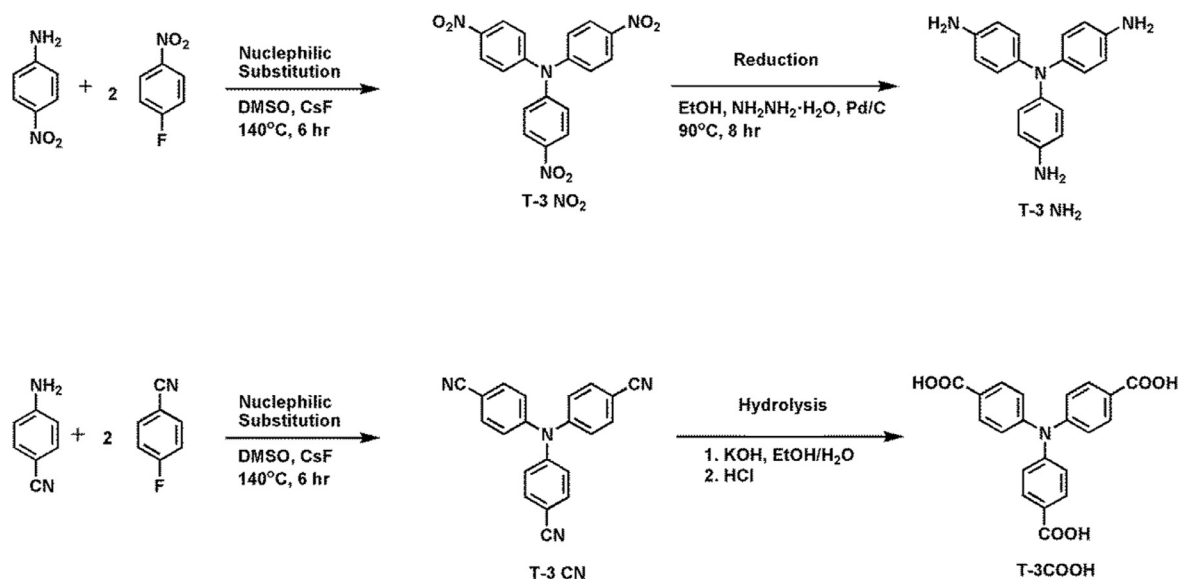
Carbazole and triarylamine derivatives and polymers are well-known for their electro- and photoactive properties that may find optoelectronic applications in electrophotography, light-emitting diodes, field-effect transistors, solar cells, memory devices, and electrochromic devices [19–23]. During the past decade, many triarylamine-based high-performance polymers such as aromatic polyamides and

polyimides have been developed for potential electrochromic applications [24–28]. On the other hand, it has been demonstrated that unsubstituted triphenylamine (TPA) undergoes dimerization (coupling) to tetraphenylbenzidine (TPB) after the formation of an unstable monocation radical [29–31]. *N*-Phenylcarbazoles (NPCs) with both the 3 and 6 carbazole ring positions unprotected 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 [32,33]. In general, the TPA and NPC dimerization reactions do not extend into a polymerization effectively because of the relatively higher stability of TPB and *N,N'*-diphenyl-3,3'-bicarbazyl radical-cations [34,35]. Their electrochemical inertness and their relatively lower first oxidation potentials are attributed to resonance delocalization of the radical-cations between two nitrogen centers. The introduction of a nonconjugated spacer or a blocking group between the amino units prevents the radical-cations from delocalization and renders the electropolymerization feasible. In recent years, the TPA and carbazole electrochemically oxidative dimerization reactions have been employed extensively to fabricate electroactive polymer films with potential applications in electronic and optoelectronic devices [36–44].

Electrochromic devices have been extensively prepared using

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solution processable electroactive polymers [45–47]. This is in part because accurate assessment of optical and electrochemical polymer properties rely on solution based techniques. Electrochromic devices also could be assembled using electrochromic polymers electro-deposited on ITO glass electrodes [48–54]. Electrochemical polymerization provides the unique advantage to combine both synthesis and direct fabrication of electroactive polymer films on the electrode surface. This procedure significantly shortens the experimental time and avoids the solubility issues often encountered with conventional chemical methods, thus enlarging the scope of candidate polymers for electrochromic applications. Additionally, thin films obtained by the electrochemical method generally have good adherence and electrical contact to the electrode surface. In this article, we report the synthesis and electrochemical characterization of functional starburst monomers

featuring a TPA unit as an interior core bridged by amide linkage (–CONH– or –NHCO–) to terminal electroactive TPA or NPC groups. Effects of the orientation of the amide linkage and the peripheral triarylamine structure on the electrochemical and electropolymerization properties were studied. The electrochromic properties of the electro-generated films were evaluated by the spectroelectrochemical studies.

2. Results and discussion

2.1. Synthesis of monomers and model compounds

Tris(4-carboxyphenyl)amine (T-3COOH) and tris(4-aminophenyl)amine (T-3NH₂), as the core reagents, were synthesized according to

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