

New Cross-Linked Multielectrochromic Polymeric Films through the Electro-coupling Reactions of Arylamino Groups

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Introduction

With the objective of obtaining a system displaying good charge transport ability, enhanced optoelectronic properties, and facile electropolymerization, we designed a novel electropolymerizable monomer **5** (Scheme 1) featuring an aromatic diamide segment as an interior core bridged by *p*-phenylene units to terminal electroactive triphenylamine (TPA) groups. In addition to the polymer formed through TPA dimerization of monomer **5**, we expected that the presence of a second oxidizable group, the carbazole (CBZ) moiety, would allow efficient cross-linkage during the electropolymerization because of the recognized capability of CBZ to form electrogenerated dimers. CBZ dimers and polymers usually exhibit high electrical conductivity and good optical quality, giving them great potential for use in optoelectronic applications.

Results and Discussion

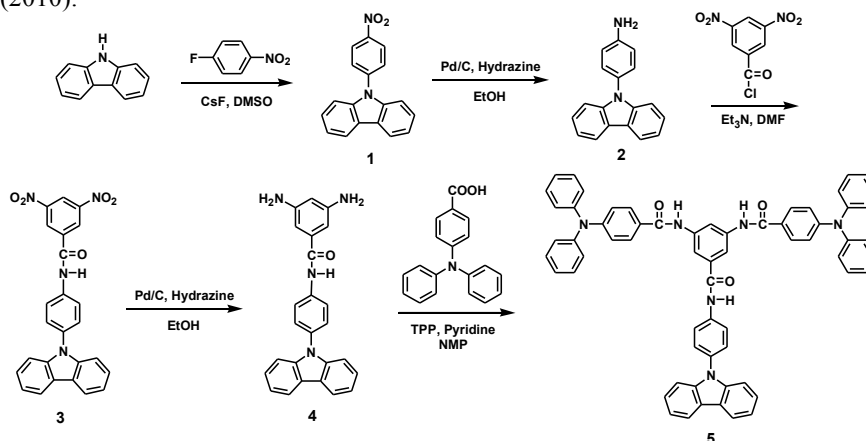
Figure 1a presents CV of monomer **5** in 0.1 M Bu₄NClO₄/ACN solution. For the first positive potential scan, we observe two oxidation processes: a clear shoulder at ca. 1.14 V and a peak at 1.24 V. In the second scan, a new oxidation peak appeared at 1.05 V that was the complementary anodic process of the cathodic peak at a lower potential. The oxidation of monomer **5** at lower potential (ca. 1.2 V) provides two separated TPA radical cations that subsequently dimerize to generate TPB moieties, giving rise to a linear polymer (Figure 1b). At higher potentials (>1.35 V), oxidation of the carbazole moiety and concomitant dimerization at either the C3 or C6 positions then produces a cross-linked structure. Scheme 2 illustrates a possible structure for the polymer prepared from monomer **5** that agrees with the observed CV responses and that the continuous film growth led to films exhibiting superior conductivity. For poly-**5**, during the scan from 0 to 0.9 V (Figure 3a), the absorption band at about 342 nm decreased, and new absorption bands were observed at 484 nm (Figure 3b). At higher potentials (0.9–1.2 V) (Figure 3a), a strong absorption band at around 720 nm was observed, whereas the absorption peak at 484 nm decreased gradually in intensity (Figure 3b). The film showed a multicolored electrochromism from colorless neutral state to orange, green, and then blue oxidized states.

Conclusions

Herein, we synthesized and characterized a novel electropolymerizable monomer composed of two electropolymerizable sites (TPA and CBZ). The electropolymerization process was dependent upon the structural features of the TPA-encapping groups. The resulting polymer could be cross-linked further at higher oxidation potentials through electro-dimerization occurring at the C3 and C6 positions of the CBZ group. The polymer film obtained exhibited reversible electrochemical oxidation, accompanied by strong color changes with high coloration efficiency and contrast ratio, which could be switched through potential modulation. These characteristics suggest that these electro-deposited polymers have great potential for the use in optoelectronics applications.

References

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Scheme 1. Synthetic route to monomer **5**

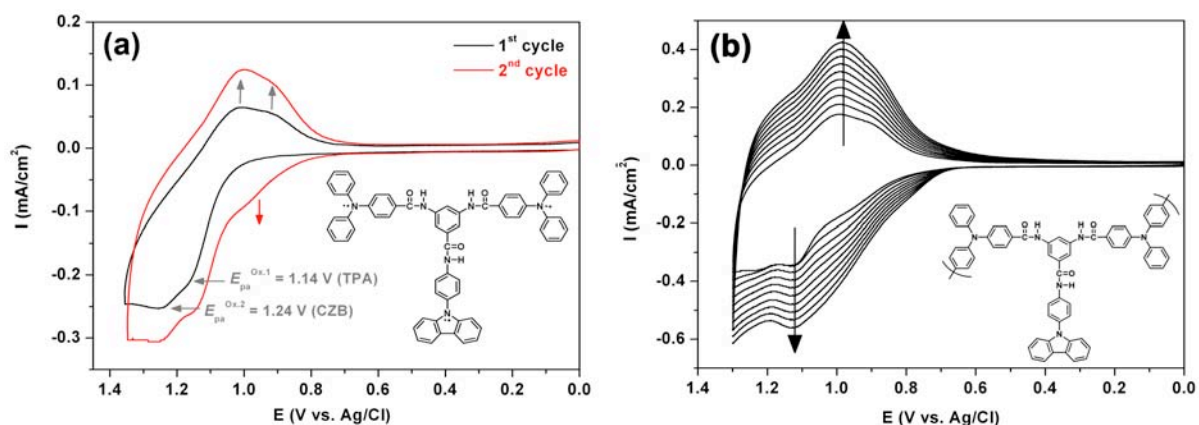


Figure 1. (a) Cyclic voltammograms of and (b) repeated potential scanning of monomer 5 with a scan rate of 50 mV/s in 0.1 M Bu₄NClO₄/ACN solution.

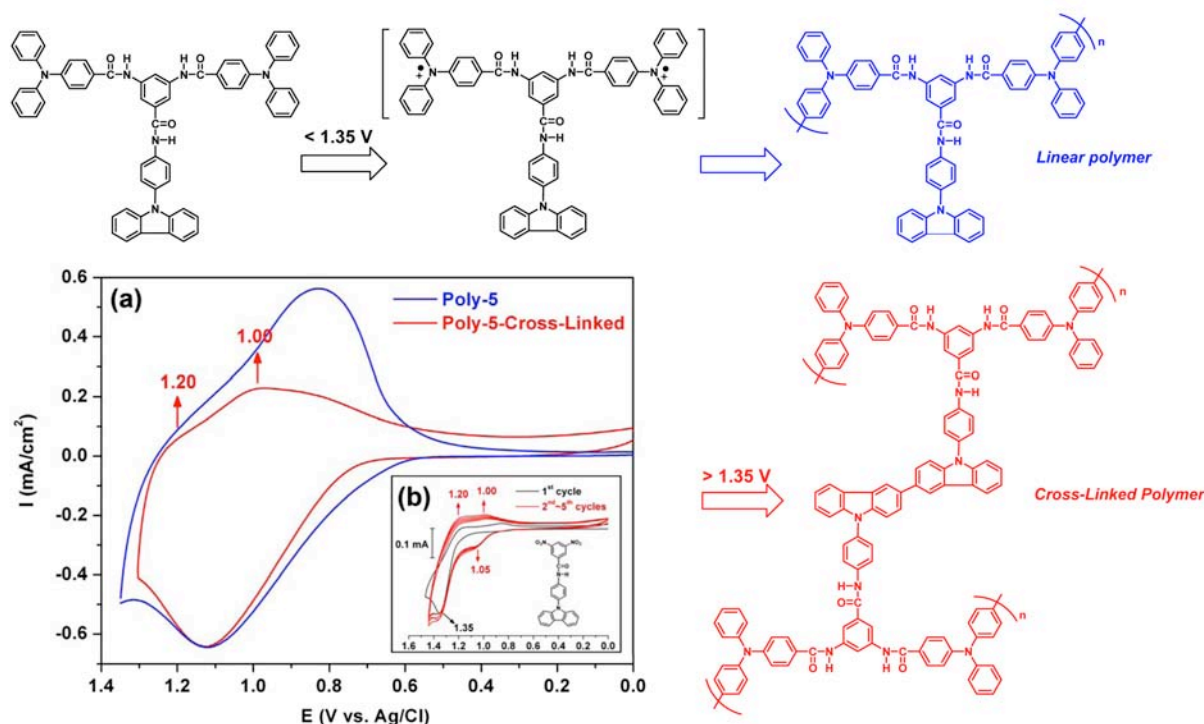


Figure 2. Cyclic voltammograms of (a) Poly-5 and Poly-5-Crosslinked and (b) dinitro compound 3 in 0.1 M Bu₄NClO₄/ACN solution at scan rate 50 mV/s.

Scheme 2. Proposed structure of the electrogenerated Poly-5-Crosslinked film

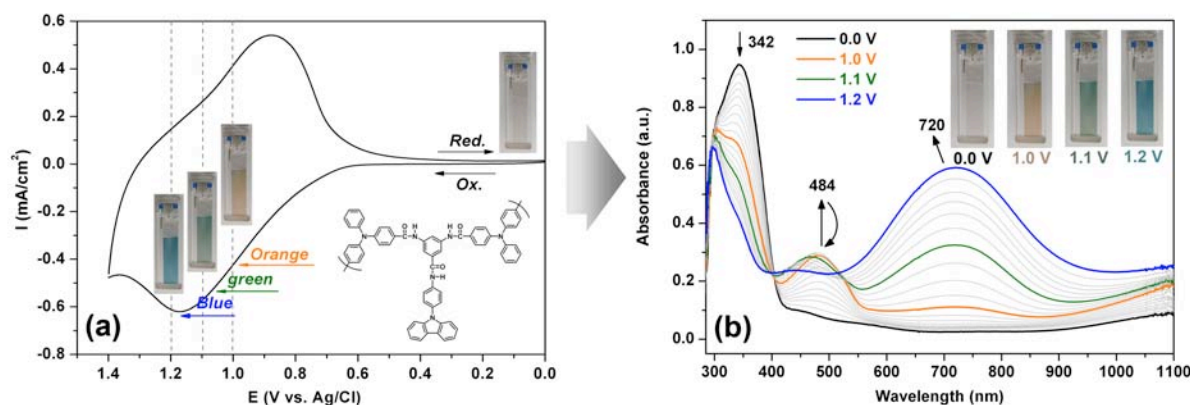


Figure 3. Spectroelectrochemical measurements and color changes of Poly-5 film on an ITO-coated glass in 0.1 M Bu₄NClO₄/CH₃CN at various applied potentials (v.s. Ag/AgCl).