Fabrication And Characterization Of Redox Active Viologen Based Electropolymerized Polymers In Ionic Liquids

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Abstract:

Polymers with redox properties are those with the ability of changing their electrochemical properties with the oxidation states due to the loss of electrons (oxidation) or the gain of electrons (reduction).The redox process is associated with changes in the properties of the polymeric materials. Thus, depending on their oxidation state (oxidized or reduced) polymers can present different electronic properties such as ionic and electrical conductivity, optical properties, mechanical or chemical properties.Due to the reversibility and easy external control of the redox process, these polymers are interesting for different applications and the designs of a number of electrochemical devices such as batteries, biosensors, electrochromic devices, and biofuel cells.

In this study, we have synthesized viologen based compounds with carbazole in the terminal position, which tends to form a polymeric backbone on electrode surface.The thickness, physical property, morphology and anionic composition of the polymers can be varied by using different mixtures of ionic liquids and organic solvents as the supporting electrolytes. In turn these changes enhance the conductivity of the polymer and also the depth of color change during electrochromism.

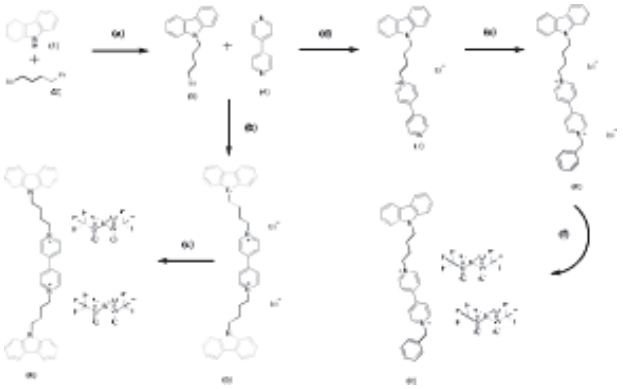
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1. Introduction

In general, viologen undergoes two successive electron transfer processes during the electrochemical reduction and thus exhibit three redox states; the dication, the radical cation and the neutral compound.[1] In these three redox states, it is known that the dication is the most stable; it is also a colorless species, unless optical charge transfer with the counter anion occurs.[2] On the other hand, the radical cation is intensely colored and the color is dependent upon the substituents on the nitrogen atoms.[3] In order to immobilizeviologen compound onto electrode surface, a polymerizablecarbazole group was introduced via an alkyl linkage.[4] Mono- and di-carbazole compounds were synthesized with high yield and purity.[5] To facilitate the polymerization process, various ionic liquids (BMP-TFSI, Bmim-PF_6, and etc.) and organic volatile solvents (ACN, PC, DMSO, DMF) were screened. For the mono- carbazole compounds, organic solvents were more preferable but the di-carbazole compounds were selectively soluble in ionic liquid/organic solvent mixtures. Polymer films were formed on ITO surface by using cyclic voltammetry, and a continuous growth of the polymers was observed with increasing the cycle number. The physical properties of the compounds were characterized with scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX). The electrochromic and molecular sensing properties of the polymers were also studied.

2. Experimental

2.1 Synthesis of carbazole functionalized viologen compounds:



Scheme 1: (a) NaH (60%), DMF, rt, 1 h; (b) Acetonitrile, 180 °C, 24 h; (c,f) LiTFSI, H_2O, rt, 24 h; (d) Acetonitrile, 120 °C, 24 h; (e) Benzyl bromide, DMF, 100 °C, 18 h

Viologen derivatives containing mono- and di-carbazole moieties (monomers **6**&**9**) were synthesized in three and four steps, respectively (Scheme 1). The carbazole N1 position reacted with 1,4-dibromobutane and 60% NaH in DMF to form intermediate **3**. Subsequently, resultant **3** reacted with 4,4-bipyridine in acetonitrile to form mono-substituted and di- substituted viologen, namely compounds **7** and **5,** at 120 °C and 180 °C, respectively. Their structures were confirmed by ^{1}H, ^{13}C NMR, and ESI-MS. Compound **7** further reacted with benzyl bromide in DMF at 100 °C to form compound **8** as an unsymmetrically di-substituted viologen. Metathesis was carried out by reacting compounds **5** and **8** with LiTFSI to form compound **6** as a yellow solid and compound **9** as an orange solid.

3. Results and Discussion

3.1 Voltammetric study and characterization of poly(Cz-V^{2+}-Cz) and poly(Cz-V^{2+}-Bn) compounds:

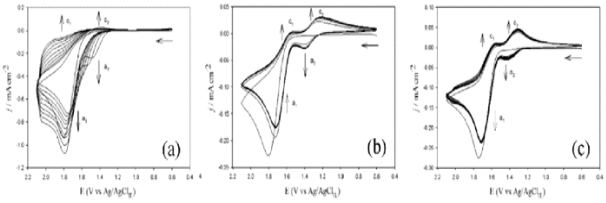


Figure 1. Cyclic voltammograms of 1 mM compound 6 and 9 recorded on ITO electrode in (a,b) BMP-TFSI/ACN (1:1) vol % respectively, and (c) 1 mM compound 9 in 0.1 M $NaClO_4$/ACN; potential was scanned for 10 cycles, at a scan rate of 50 mV s^{-1} at rt.

The voltammetricbehavior of compounds **6** (Cz-V^{2+}-Cz) and **9** (Cz-V^{2+}-Bn) were studied initially in individual IL or organic solvent but the solubility of compound 6 is too low, hence a mixed electrolyteof IL BMP-TFSI/ACN in which compound 6 is soluble was used and both compounds were electropolymerized onto ITO electrodes using cyclic voltammetry. The corresponding cyclic voltammograms (CVs) are shown in Fig. 1 (a,b). The horizontal and the vertical arrows indicate the initial directions of potential scan and the directions of current change, respectively. Two redox couples, c_1/a_1 and c_2/a_2, were observed for both compounds. The c_2 wave initially appeared in the first reversed half cycle, and the a_2 wave initially appeared in the second cycle. For compound **9**, the c_1 wave and c_2/a_2 couple gradually increased, and then approached a ceiling. The a_1 wave, however, gradually decreased. These observations indicate that the c_1/a_1 and c_2/a_2 redox couples respectively belong to the redox reactions of the monomer and the oligomer/polymer. For compound **6**, the c_1 wave and c_2/a_2 couple continuously increased. The a_1 wave gradually decreased for the initial 5 to 6 cycles and then increased continuously with the potential scan. The current of the redox couples changed with the cycle number of potential scan in a different manner for compounds **6** and **9**, which resulted from the higher solubility of compound **9** oligomers/polymers in ILs. Hence the electrolyte for compound **9**electropolymerization was changed to acetonitrile containing 0.1 M $NaClO_4$, and the corresponding CVs are shown in Fig. 1. (c). Two continuously growing redox couples c_1/a_1 and c_2/a_2 were observed.

3.2 Electrochromic properties of poly(Cz-V^{2+}-Cz) and poly(Cz-V^{2+}-Bn):

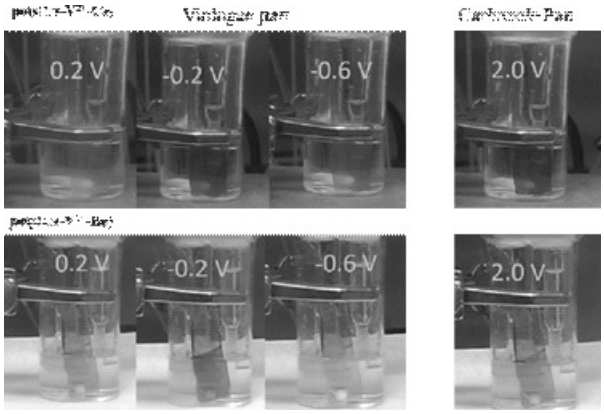


Figure 2.Electrochromicbehavior of poly(Cz-V^{2+}-Cz) and poly(Cz-V^{2+}-Bn) studied in deaerated BMP-TFSI/ACN (1:1) vol % at (0.2 V to -0.6 V) for viologen part and (2.0 V) for carbazole part. Electrodes were prepared in BMP-TFSI/ACN (1:1) vol % with 1 mM compound 6 using CPC at 1.8 V for 2400 s and 0.1 M $NaClO_4$/ACN with 2 mM compound 9 using CPC at 1.8 V for 4800 s, respectively.

poly(Cz-V^{2+}-Cz) and poly(Cz-V^{2+}-Bn) prepared in this study showed an electrochromicbehavior. Solid polymer films were prepared on ITO from BMP-TFSI/ACN (1:1) vol % containing 1 mM compound 6 via constant-potential coulometry (CPC) at 1.8 V for 2400 s and from 0.1 M $NaClO_4$/ACN containing 2 mM compound 9 via CPC at 1.8 V for 4800 s, respectively. To study the electrochromicbehavior of these polymer-coated ITO electrodes, cyclic voltammetry was performed in BMP-TFSI/ACN (1:1) vol %. The corresponding color changes of the electrodes during the potential cycling is shown in Fig. 2 The color changed in the potential range of 0.2 V ~ -0.6 V, which corresponds to the formation of a radical cation and then a neutral species involving the viologen group. On the other hand, the color change between 1.6 V and 2.0 V corresponds to the oxidation of the carbazole group in the polymer. The behavior of the color change significantly depends on the substitution in the viologen moiety, and a more apparent color change is observed for compound 6 in contrast to compound 9. Because the poly(Cz-V^{2+}-Cz or -Bn) films simultaneously possess the electronically and ionically conductive structures, it should be possible to develop an electrochromic device based on a single component of the poly(Cz- V^{2+}-Cz or -Bn). However, more experiments will be needed to achieve this purpose.

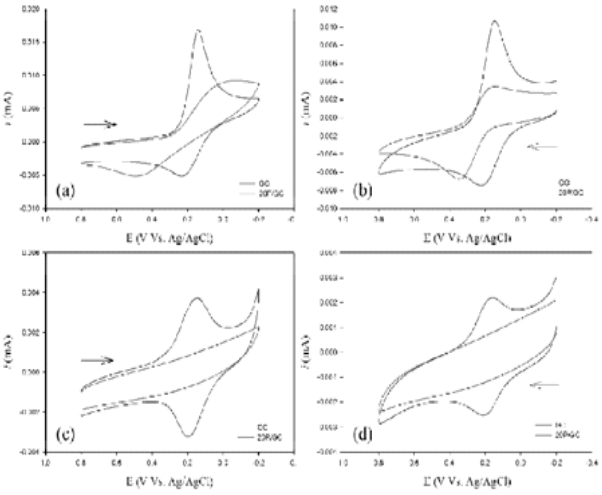


Figure 3. CVs recorded at GC and poly(Cz-V^{2+}-Cz)-coated GC electrodes, respectively, in 0.05 M KCl containing (a) 1 mM $K_3[Fe(CN)_6]$, and (b) 1 mM $K_4[Fe(CN)_6]$. (c) and (d) show the CVs recorded at the same electrodes that have been used for (a) and (b), rinsed with DI water, and then immersed in neat 0.05 M KCl. The poly(Cz-V^{2+}-Cz)- coated GC electrode was prepared via the cyclic voltammetricelectropolymerization (20 cycles) from BMP-TFSI/PC (1:1) vol % containing 1 mM compound 6.

The voltammetricbehavior of the well-known reversible redoxspecies, ferricyanide and ferrocyanide, was respectively studied at bare GC and poly(Cz-V^{2+}-Cz)-coated GC (Figs. 3a and b). The reductive current of ferricyanide recorded at the poly(Cz-V^{2+}-Cz)-coated GC electrodesshowed an enhanced behavior, compared to that observed at the bare GC electrode. The potential was scanned at the poly(Cz-V^{2+}-Cz)-coated GC electrode for 20 cycles in 0.05 M KCl containing 1 mM $K_3[Fe(CN)_6]$, and then the electrode was cleaned with DI water, and immersed in a neat 0.05 M KCl solution for another cyclic voltammetric study. The corresponding CV is shown in Fig. 3c which shows a redox wave corresponding to $Fe(CN)_6^{3"}/Fe(CN)_6^{4"}$ when compared to bare GC electrode. A similar behavior was observed for the electrodes used for the cyclic voltammetric study in 0.05 M KCl

containing 1 mM $K_4[Fe(CN)_6]$ (Fig. 3d). The behaviors shown in Figs. 3c and d indicate that the anionic species ($Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$) can be adsorbed as the counter anions of the viologen groups on the polymer-modified electrodes. For the bare GC electrodes, no such behavior was observed because the ferricyanide/ferrocyanide anions were unable to be adsorbed on the electrode surface. This behavior may help in concentrating metal ions onto the electrode surface, and the adsorbed redox couples can be used as redox mediators in various reactions. To understand this phenomenon, further experiments will be performed.

4. Conclusions

In summary, mono- and di-carbazole-functionalized viologen compounds were synthesized with high yield and purity. They can be polymerized via convenient electropolymerization technique with increasing film stability. The physicochemical properties of the electropolymerizedviologen can be easily altered by changing the supporting electrolytes in the solutions where the polymers are formed. These materials showed interesting electrochromic properties as the viologen group presenting in the polymer shows promising color change corresponding to the conversion from divalent cations, radical cation, to neutral species. The redox of the carbazole moieties in the polymer also producecolor change. In addition, the substituted functional groups of carbazole and/or viologen may alter the electrochromic properties. This tailoring approach can be helpful to form electrochromic materials via single step electropolymerization to form a stable film in-tack to the electrode surface. We have also explore the electrochemical sensing property of these polymers.

5. Acknowledgement

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5. References

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