Preparation and Electrochromic Properties of Co(II)–Bis-2,2':6',2"-terpyridine Metallo-supramolecular Polymer

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ABSTRACT

A metallo-supramolecular polymer CoL was prepared by coordination of Co(II) ions to ligand L: 1,4-bis(2,2’:6’,2"-terpyridine-4-yl)benzene. Electrochemical and electrochromic properties of the polymer film were analyzed in acetonitrile with 0.1 M tetra-n-butylammonium perchlorate as an electrolyte. The polymer film exhibited excellent electrochromic property with absolutely reversible color change between orange and pale yellow by the redox reaction of Co ions. Its optical contrast was 13% at 524 nm with bleaching time of 2.8s and darkening time of 24s. The coloration efficiency of the polymer film was 20.7 cm²/C. After 300 switching cycles, the optical contrast only decline 2%. The long-term redox switching study confirmed the high stability of the polymer to the test environment.

INTRODUCTION

Being applied in a large of areas, such as anti-glare mirrors and glasses, indicators and labels, smart windows, electronic papers, and information storages, electrochromic materials (ECMs) have received widespread interests as molecular switches for optical and electronic applications [1]. Recently, metallo-supramolecular polymers, as a novel emerging ECM, has attracted special attentions for it has strong optical contrast, high coloration ability, fast response time and low switching potential, combining advantages of both inorganic and organic ECMs, which is formed by complexation of transition metal ions with an organic molecule that bears two coordination sites [2,3]. The electrochromic response is readily tuned by the choice of the metal ions as well as by the design of the ligands [4]. At present, many reports have focused on the preparation and properties of metallo-supramolecular polymers. For example, Dongfang Qiu [5] et al. found a polymer prepared by coordination of Fe(II) and Ru(III) ions to terpyridine, the polymer film of donor-acceptor (D-A) structure has good electrical properties. He et. al. [6] prepared a kind of electrochromic...
device, taking the metallosupramolecular coordination polyelectrolyte as the electrochromic layer and carbon nanotube–polyaniline as the ion storage layer, the result showed that the optical contrast of the device was about 20% at 580nm and the response time is less than 0.5s. These researches showed great potential of metallo-supramolecular polymers in developing new kinds of practical electrochromic materials. However, the electrochromic properties of bis-terpyridine-based metallo-supramolecular polymers have not been fully researched. This report described comprehensive research of the Co(II)–bis-2,2’:6’,2″-terpyridine metallo-supramolecular polymer containing cyclic voltammogram, UV-Vis spectra at different voltage, square-wave potential test and the stability test. The results show that this kind of material is a promising electrochromic material for application.

EXPERIMENTAL

Materials and Measurement

2-acetylpyridine, terephthalaldehyde, cobalt(II)acetate tetrahydrate and tetra-n-butylammonium perchlorate were purchased from J&K Scientific Ltd. Methanol, acetic acid, acetonitrile, ammonium acetate, potassium hydroxide were provided by Beijing Chemical Plant. All reagents were analytical reagent grade and used without purification. Water used in the experiments was de-ionized H₂O. Indium tin oxide conductive glass (ITO) was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.

The UV-Vis spectra were obtained with a Perkinelmer Lambda 750 UV-Visible spectrometer. Cyclic voltammetry (CV) and amperometric experiments were carried out in a nitrogen-saturated acetonitrile solution containing 0.1M tetra-n-butylammonium perchlorate as supporting electrolyte by using a Zahner IM6 electrochemical workstation. A platinum wire was used as a counter electrode and a saturated calomel electrode as the reference electrode. The films for CV analysis and in situ CV-UV/Vis experiments were prepared by casting the methanol solution of the polymer (1mg polymer/2mL methanol) on an ITO coated glass slide with an area of ca. 0.8×2cm² which was used as the working electrode.

Synthesis of 1,4-bis(2,2’:6’,2″-terpyridine-4-yl)Benzene [7]

2-Acetyl-pyridine (6.75mL, 0.06mol) and terephthalaldehyde (2.03g, 0.015mol) were mixed together using a mortar and pestle, after 5 min, the sodium hydroxide(2.41g,0.06mol) was added, after grinding 30min, a yellow power 1,4-bis[1,5-dioxo-1,5-bis(2-pyridyl)pentan-3-yl]benzene was formed. Then the suspension of yellow powder and ammonium acetate (70.0g) in ethanol (300mL) was heated to reflux for 15h. Then, the reaction mixture was cooled, and the solid product collected by filtration, washed well with ethanol, isolated by recrystallization with CH₂Cl₂, and dried in vacuum to give 1,4-bis(2,2’:6’,2″-terpyridin-4’y)benzene (L) as a yellow solid (3.85g, 47.3%).
Preparation of Co(II)-bis-terpyridine Metallo-supramolecular Polymer

Co(II)-bis-terpyridine metallo-supramolecular (CoL) was prepared by complexing of the ligand L with Co(II) ions. L (6.2mg, 1.15×10^{-5} mol) and cobalt(II) acetate tetrahydrate (2.9mg, 1.15×10^{-5} mol) were added in acetic acid (60mL). The mixture was heated to reflux for 24h under nitrogen atmosphere. The solution was cooled to room temperature and filtered to remove the insoluble residues. The filtrate was slowly evaporated to remove the solvent, and the product was further dried in vacuum to give the polymer CoL.

RESULTS AND DISCUSSION

Cyclic Voltammogram

Figure 1 showed the cyclic voltammogram (CV) of the CoL film with a scan rate of 20mV/s. It is found that the redox activity of the film is completely reversible and the CV of the film has a redox pair at 0.39V and 0.15V. Interesting, the polymer film casting on the ITO slide exhibited excellent electrochromic properties in 0.1M tetra-n-butylammonium perchlorate/acetonitrile electrolyte. The original orange color became pale yellow color gradually during the voltage increasing from 0V to 0.5V as the inset picture shown.

UV-Vis Spectra at Different Voltage

The reversibility of the CoL film coated on ITO slide was investigated by using in situ UV-Vis spectral measurement at different applied voltage (Figure 2). The spectrum of the original film (0V) showed characteristic absorption peak at 524nm based on the d-d transition absorption of the Co(II) ions. It revealed that the polymer was anodically coloured: the transition absorption decreased with increasing oxidative potential (Figure 2). The spectra decreased gradually with the increase of the voltage and the transition absorption nearly disappeared completely at the voltage of 1.0V.

Figure 1. Cyclic voltammogram and color change (the inset picture) of CoL film coated on ITO slide with a scan rate of 20 mV/s.

Figure 2. Absorbance changes of CoL film coated on an ITO electrode at different potentials.
Square-wave Potential Test

The optical contrast and the optical switching rate of the polymer film were investigated by stepping the potential between -1.0V and 1.0V using chronoamperometric methods with an interval time of 45s (Figure 3). The optical contrast of the polymer film is 13%, which is consistent with the color change of the cyclic voltammogram (CV) of the polymer film. The response time was defined as the time needed for 90% change of ΔT. The bleaching time (R_{Tb}) and the coloring time (R_{Tc}) were calculated to be 2.8s and 24s, respectively.

The coloration efficiency (η) was an index to measure the power needed by an electrochromic material. The amount of optical density change (ΔOD) induced as a function of the injected/ejected electronic charge (Q_d) was measured and was given by the equation 1:

$$\eta = \Delta OD = \frac{T_b}{Q_d}$$

(Eq.1)

where η was the coloration efficiency at a given ΔOD, and T_b and T_c were the bleached and coloured transmittance values, respectively.

Figure 4 showed the charge/discharge amount in the polymer film when switching between -1.0V and 1.0V. The charge required for color switching was calculated by integration. The η value was estimated to be 20.7 cm²/C.

Stability

The stability of the bleached or colored states toward multiple redox steps represents one of the most important parameters for the practical utilization of ECMs. Figure 5 showed the transmittance change of the polymer film at 524nm when continuously stepping the voltage between -1.0V and 1.0V for a long-term redox switching. During 1~300 switching cycles, we observed a 10% loss of the colored transmittance (T_c) of the coloured transmittance, and a 4% loss of the bleached transmittance (T_b) in every 300 redox cycles, the optical contrast (ΔT) only decrease 2%. The result shows that the polymer has excellent circulation stability, and the test environment has little influence on it.
CONCLUSIONS

A metallo-supramolecular polymer CoL was prepared by coordination of Co(II) ions to ligand L, 1,4-bis(2,2′:6′,2′″-terpyridine-4-yl)benzene. The comprehensive research of the CoL polymer film showed the polymer film excellent electrochromic property with absolutely reversible color change between orange and pale yellow by the redox reaction of Co ions. The optical contrast was 13%@524nm with bleaching time of 2.8s. The coloration efficiency of the polymer film was 20.7 cm²/C. It has a high cycle stability with only 2% decline of optical contrast after 300 switching cycles. It is proved that CoL is a kind of promising electrochromic material for real application.

REFERENCES