

Ligand Induced Low Operation Voltage Ru-based Metallo-supramolecular Polymer as Energy Saving Electrochromic Display Device

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ABSTRACT

Electron rich ligand induced low working voltage Ru²⁺ based metallosupramolecular polymer (MSP) has been reported for efficient and durable electrochromic (EC) display applications. The violet color polymer film exhibited switching at +0.6 V. The fabricated solid display device shows distinct color change with high optical contrast ratio, fast switching time, high coloration efficiency and long life stability within this voltage with enhance display memory effect.

1 INTRODUCTION

Electrochromism means a reversible change in color properties of a material through a redox process by applying external voltage [1]. EC materials have attracted much more attention in the last few decades for development of technological aspect such as adaptive camouflages [2], smart windows [3], antiglare mirrors [4] and displays [5] devices. EC materials are organic conducting polymers, electro-active organic small molecules, metal oxides, transition metal-organic complexes and metallo-supramolecular polymers (MSPs)[6]. Among them MSPs are one of encouraging materials for electrochromism which have intense MLCT band in the visible region. These MLCT energy band tuned by the redox state of the metal and ligand structure. One of the important ditopic ligands is bisterpyridine, have been used for MSPs formation. The bridging ligand can tune the MLCT properties in metal-organic. For this purpose, designing a new bridging ligand for preparation a new MSPs with some improved properties is one of the most challenging task in understanding the EC properties of the MSPs.

For the above proposal, we have we reported a new type of bridging ligand bis-(N-methylbenzimidazol-2-yl)-4,4'-bipyridine (**L_{Bimpy}**) as a ditopic tridentate ligand for MSPs formation with Ru²⁺ ions via 1:1 complexation. The ligand was synthesized by Suzuki homocoupling reaction from 4-bromo-2,6-bis(N-methylbenzimidazolyl)-pyridine. The synthesized polymer shows excellent properties

1. A uniform polymer films form.
2. Reversible EC color changes from violet to light greenish-yellow.

3. Low working voltage (0.6V)
4. High optical contrast ratio (~54%) and fast switching response
5. Long cycles stability.
6. Long time memory

Here we have report advance EC properties through the ligand structure modification.

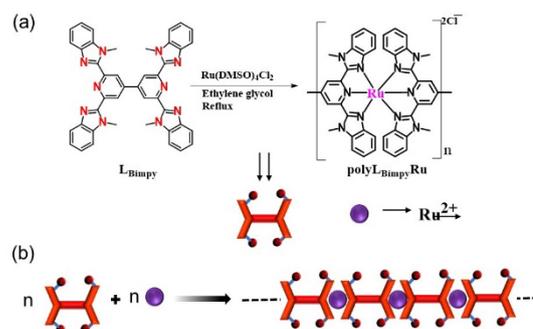
2 EXPERIMENT

Preparation of ITO-coated polymer film

Solution of polymer **polyL_{Bimpy}-Ru** in MeOH (3mg/mL) was spray coated on ITO coated glass substrate and dry for 24 hours at room temperature. For solid device fabrication another ITO-coated glass substrate was spray coated with NiHCF as a counter material. Finally, polymer coated ITO-glass was immediately covered with PMMA based electrolyte. After that it was kept and heated for 1 min at 95°C and 40% relative humidity in the thermostatic chamber to obtain a complete solid device.

3 RESULTS AND DISCUSSION

The ligand 2,2',6,6'-tetrakis (N-methylbenzimidazol-2-



Scheme 1 (a) Synthesis of polyBipRu via 1:1 complexation (b) Schematic presentation of polymer formation.

yl)-4,4'-bipyridine (**L_{Bimpy}**) was prepared by one step Suzuki homocoupling reaction from 4-Bromo-2,6-bis (N-methylbenzimidazol-2'-yl) -pyridine and final structure was characterized by different spectroscopic techniques. Ru (II) based MSP (**polyL_{Bimpy}-Ru**) by 1:1 complexation of **L_{Bimpy}** with Ru²⁺ ions as presented in **scheme 1**. The ligand has capability to bind with metal ions in a quasi-

octahedral geometry and can be formed high molecular weight polymer. The average number of monomeric units in polymer was about 1411. ^1H NMR, UV/vis, TGA and XPS analysis also suggest the formation of polymer.

Electrochromic Performance

In three electrode system EC properties of **polyL_{Bimpy}-Ru** was investigated. During cyclic voltammetry (CV) study of polymer film exhibits reversible redox in nature between 0 to 1 V. Polymer film shows strong oxidation peak at $\sim 0.57\text{V}$ vs. Ag/Ag^+ responsible for $\text{Ru}^{2+} \rightarrow \text{Ru}^{3+}$ transition and another strong reduction peak at $\sim 0.45\text{V}$ vs. Ag/Ag^+ assign for $\text{Ru}^{3+} \rightarrow \text{Ru}^{2+}$ transformation of metal center. Another low intense redox peak was observed at $\sim 0.29\text{--}0.33\text{V}$ vs. Ag/Ag^+ because of the involvement of ligand for partial redox reaction of metal center.

Device study of polyL_{Bimpy}-Ru (ECDs)

For practical use, we have fabricated the solid state display devices. The lab made-up device structure and details configuration to the different layers are presented in Figure 4a. The ECD showed intense violet to light greenish-yellow color at $+0.6\text{V}$ and it revert to its original color at 0V (Figure 1a) and transmittance changes for the coloring and bleaching states were shown in Figure 1

The complete switching time between fully bleaching (t_b) and coloration (t_c) because of MLCT band generation and disappearance at $\lambda_{\text{max}} = 578\text{nm}$ were calculated by 95% change of transmittance change (ΔT) in terms of time. were calculated to be 1.67 and 0.33s for **polyL_{Bimpy}-Ru**. The CE of polymer film calculated to be $571\text{cm}^2/\text{C}$

Stability test of ECDs

The durability of the device was measured by repeatedly cyclic switching of the applied very low voltage between 0 and 0.6V with interval time 3 s with UV/vis transmittance analysis. After 20,000 cyclic switching, the device shows 88% retention of its EC activity. The long durability arises because of the low working voltage and there is no possibility of ITO electrode degradation through oxidation or reduction. This is the first report achieving a very low working voltage with long term stable ECD of ruthenium ions based EC polymer.

The ECD exhibited 80% retention of its full oxidized state till 1 hour and 70% retention of bleached state until 4h. Previously reported most of the MSPs based ECD have the tendency to very fast self-coloration of metal center at open circuit condition. Our polymer **polyL_{Bimpy}-Ru** exhibited long time optical memory and does not come back to colored state because of the four electron rich moieties in each monomer unit, the oxidized state Ru^{3+} of polymer (colorless state) is stabilized and protect to reduction of metal center. The stabilized high oxidation state of metal center will able to have a long time optical memory. So our **polyL_{Bimpy}-Ru** based ECD first displayed lengthiest memory time in the class of MSP based ECD [8].

4 CONCLUSIONS

Our electrons rich ligand based polymer shows

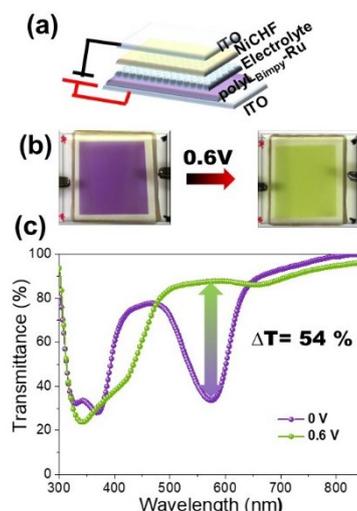


Figure 1 (a) Fabricated ECD structure. (b) Color change of polymer ECD. (c) Transmittance spectral change upon applying 0 to 0.6V voltages.

significant low potential value EC properties in solution state as well as solid device state. The fabricated device exhibited high optical contrast, fast switching, high CE and long cycle stability. Stabilized the high oxidation state of metal center by the ligand to enhance the optical memory time of **polyL_{Bimpy}-Ru** based ECD at open circuit condition. So far our polymer based ECD is the first report to exhibit low working voltage and longest optical memory which could be used as highly durable energy saving display application in near future.

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