

# Electrochromic Composites of Metallo-supramolecular Polymers and a Layered Inorganic–organic Covalently Bonded Hybrid

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## ABSTRACT

*Metallo-supramolecular polymer (MSP), composed of metal ions and multi-topic organic ligands, is known as a good electrochromic (EC) material. To improve EC properties, we prepared composites of MSPs and a layered inorganic-imidazoline covalently bonded hybrid (LIlm) by simply mixing them and examined effects of LIlm on the EC properties.*

## 1 Introduction

Electrochromic (EC) materials have received considerable attention as an important material of e-papers, smart windows, antiglare rearview mirrors in cars etc. [1-13]. Many types of EC materials have been reported and are often categorized as follows. Metal oxides such as tungsten oxide are the first generation of EC materials; transition metal complexes, such as Prussian blue, are the second generation of EC materials; and organic molecules and  $\pi$ -conjugated polymers are the third generation of EC materials [1-3]. Recently, metallo-supramolecular polymers (MSPs, Scheme 1), composed of metal ions with multi-topic organic ligands, such as bis-terpyridine, were reported as the fourth generation of EC materials [4–7].

MSPs demonstrate absorption in the visible region because of the metal-to-ligand charge transfer (MLCT) ( $d \rightarrow \pi^*$ ) from the metal ion center to the organic ligand. The appearance/disappearance of MLCT absorption is switched by the electrochemical redox of the metal ion in MSPs because the enhanced  $d$ - $d$  splitting width is too large to allow the MLCT in the visible region for oxidized MSPs. The colors and redox potentials of MSPs are tunable by changing metal ions (such as Fe(II), Ru(II), and Os(II)) or the substituents and spacer of organic ligands [4–7]. The high molar extinction coefficient of MLCT absorption in the complex moieties

and abovementioned tunability on the bandgap of MLCT have enabled fine EC properties with high optical contrast and abundant color variation. However, the durability and optical memory properties remain as issues of MSPs, thereby limiting practical applications [8].

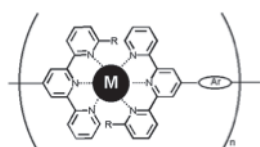
The formation of composites with inorganic materials is often applied to enhance the physical properties of organic polymer materials [8–13]. They have investigated combining MSP and/or  $\pi$ -conjugated polymers with clay minerals, e.g., saponite (layered) [9] and halloysite (tubular) [10, 11], and organically modified phyllosilicate [12, 13] and achieved improvements of EC properties, e. g., sub-second EC switching times and ultra-high coloration efficiencies. However, the optical contrast ( $\Delta T$ ) decreased when MSP has been combined with clay minerals.

In this study in order to improve EC properties of MSPs we focused on preparing composites of MSPs and LIlm. An imidazoline group is covalently immobilized between inorganic layers in LIlm. The prepared composites exhibited EC. Further the combining with LIlm has achieved improvement on the EC properties, e.g., elongated optical memory and enhanced coloration efficiencies.

## 2 Experiment

Fe(II)-based (polyFe) and Ru(II)-based MSPs (polyRu) and LIlm were synthesized as per previously reported method [6, 7, 14]. PolyFe and polyRu were separately dissolved in methanol (MeOH) to obtain each stock solutions. Stock dispersions of LIlm were prepared by dispersing LIlm in MeOH. The stock solution of polyFe and/or polyRu was mixed with the stock dispersion of LIlm. The mixtures were stirred sufficiently and then drop-casted on quartz glass and spin-coated on ITO-coated glass to obtain polyFe/LIlm and/or polyRu/LIlm composite films.

The prepared polyFe and polyRu/LIlm composites were characterized by scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX), X-ray



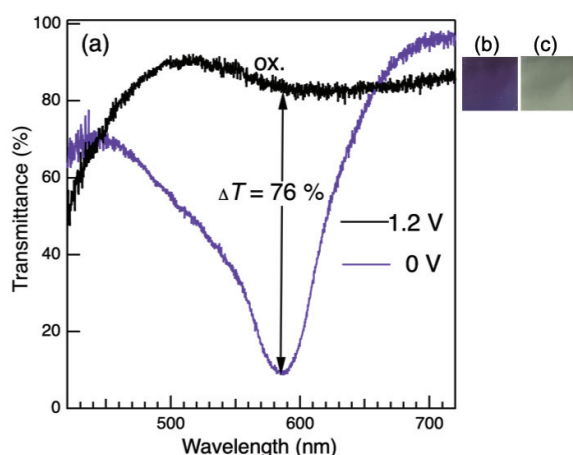
Scheme 1 MSP

diffraction (XRD), and ultraviolet-visible (UV-vis) spectroscopy. Cyclic voltammogram (CV) was performed to examine the redox properties of the prepared polyFe and polyRu/LIIm composites. A conventional three-electrode system was set with polyFe and/or polyRu/LIIm composite spin-coated films on an ITO-coated glass as working electrodes, spring-type Pt wire as a counter electrode, and a Ag/Ag<sup>+</sup> electrode as a reference electrode in an electrolyte solution. *In situ* electrochemistry-UV/vis measurement was performed with using polyFe and/or polyRu/LIIm composite spin-coated films in the three-electrode system.

### 3 Results and Discussion

UV-vis spectroscopy demonstrated a characteristic strong absorption at around 600 nm and/or 500 nm attributed to metal-to-ligand charge transfer (MLCT) from Fe(II) and/or Ru(II) ion to the organic ligand for polyFe and/or polyRu/LIIm composites. PolyFe and/or polyRu/LIIm composites exhibited a pair of redox waves, assigned to the redox between Fe(II) and Fe(III) and/or between Ru(II) and Ru(III), in CVs.

Figure 1 (a) shows transmittance spectra for polyFe/LIIm composite before and after oxidation upon applying voltage in the three-electrode system. The MLCT absorption disappeared upon the applying voltage (Figure 1 (a)). Simultaneously blue-purple polyFe/LIIm composite films (Figure 1 (b)) turned to transparent (Figure 1 (c)) with large optical contrast more than 70 %. We will report EC properties of elongated optical memory, improved coloration efficiencies, and faster switching times for the composite films.



**Fig. 1 (a) Transmittance spectra and (b and c) photographs for Fe(II)-based MSP/LIIm composite film (a and b) before and (a and c) after oxidation upon applying 1.2 V vs. Ag/Ag<sup>+</sup>**

### 4 Conclusions

We prepared EC composites consisting of MSPs and a layered inorganic-organic covalently bonded hybrid (LIIm). The combining with LIIm improved the EC properties, the large optical contrast ( $\Delta T$ ), elongated optical memory and so on. We hope that a small piece of these knowledge revealed in this study will contribute to application to e-paper and smart windows using MSPs.

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