

# Electrochromic Display Devices with Metallo-Supramolecular Polymers

Masayoshi Higuchi\*

\*National Institute for Materials Science (NIMS), Tsukuba, Japan

## Abstract

*Metallo-supramolecular polymers (MSPs) show reversible electrochromic (EC) properties by electrochemical redox of metal ions included in the polymers. This presentation introduces recent three research achievements on EC devices (ECDs) using MSPs: (1) fabrication of highly durable ECDs with cycle stability more than 100,000 times, (2) a new electro-polymerization method of a thin MSP layer on an ITO-coated glass or PET-film, and (3) rewritable multicolor EC paper using MSPs.*

## Author Keywords

Electrochromic; metallo-supramolecular polymer; display device; smart window; metal-to-ligand charge transfer; rewritable paper

## 1. Introduction

Metallo-supramolecular polymers (MSPs) are synthesized by simple complexation of metal salts and ditopic organic ligands. The obtained MSPs have strong color based on the metal-to-ligand charge transfer (MLCT) absorption of the metal complex moieties. We found that the color of an MSP disappeared by the electrochemical oxidation of the metal ions included in the MSP. For example, Fe(II)-based MSP (polyFeL1) shows reversible electrochromic (EC) changes by the electrochemical redox between Fe(II) and Fe(III) states (Figure 1).<sup>1</sup> MSPs are soluble in polar solvents such as methanol and a thin layer of an MSP can be prepared on an ITO surface by a spray-coating method.

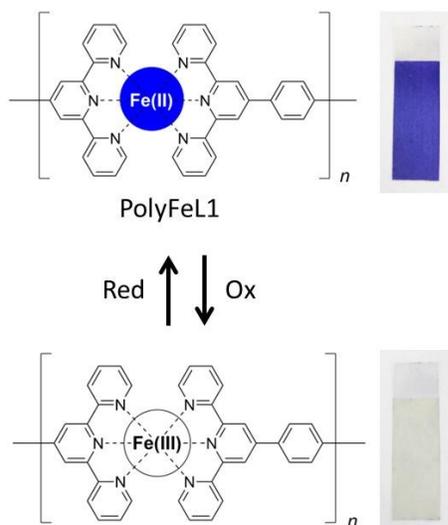


Figure 1. EC changes of polyFeL1.

EC devices with an MSP layer were fabricated by the combination with an electrolyte layer and a counter material layer.<sup>2</sup> EC display devices have received attention as smart window or electronic paper applications, because of the nonvolatile properties. However, high durability or flexibility are required for the commercial uses. This presentation introduces recent research achievement on the cycle stability for the repeated color changes in an ECD, electro-

polymerization of an MSP layer on an ITO substrate, and a rewritable paper application, using MSPs.

## 2. Results and Discussion

**(1) Highly durable ECDs with cycle stability more than 100,000 times:** The EC changes of MSPs themselves are very stable and we already conformed the high stability for the repeated EC changes more than 10,000 cycles. This is because the EC changes are caused by the stable redox reactions of the metal ions included in the polymers. However, the cycle stability was not so high in the devices. Therefore, we investigated the device components to reveal the reason why the device performance became worse during the repeated color changes. The device structure is shown in Figure 2. The ECD is composed of an MSP layer, an electrolyte layer, a counter material layer, and two ITO glass. The ECD with a polyFeL1 layer as an EC layer changes the color between purple and colorless at 3 V, when a counter material layer is not included, but the introduction of the counter material layer decreases the driving voltage, because the voltage is decided by the potential difference between polyFeL1 and the counter material. We found Ni derivative of Prussian Blue (NiHCF) is the best counter material of polyFeL1 in the device and the driving voltage was decreased to 1.5 V. The low driving voltage greatly contributed the improvement of the cycle stability. In addition, we tuned the amount polyFeL1 and NiHCF, so that the amount of charge became same. As the result, high cycle stability more than 100,000 times has been achieved in the ECD.<sup>3</sup>

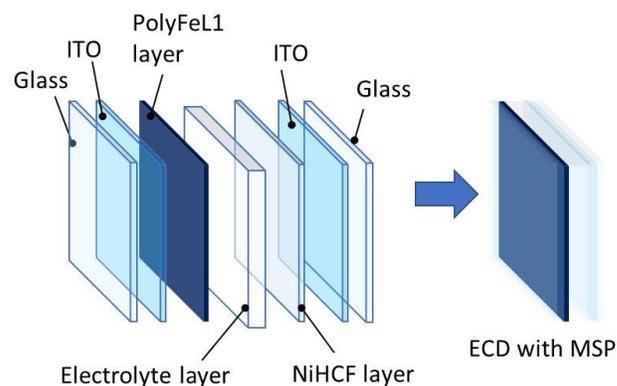
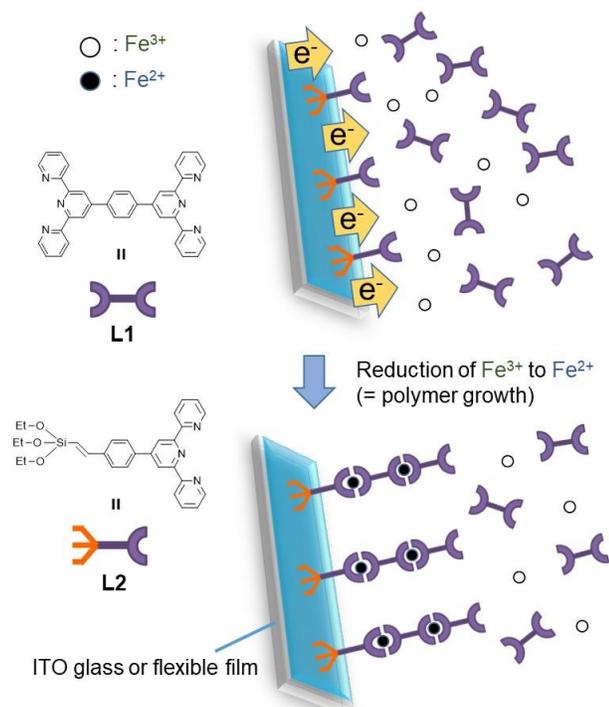


Figure 2. The structure of an ECD with an polyFeL1 Layer.

**(2) An electro-polymerization method of a thin MSP layer on an ITO-coated glass or PET-film:** As mentioned in Introduction, a thin layer of an MSP on an ITO substrate can be prepared by spray-coating the methanol solution. However, it is not so easy to prepare a thin MSP layer on a non-flat surface such as an ITO-coated PET-film with this method. In order to achieve a uniform layer formation of MSPs on a flexible ITO film, we investigated an electro-polymerization method of an MSP, by utilizing the different complexation ability to terpyridine moieties between Fe(II) and Fe(III) states in solution. That is, an Fe(II) ion has high binding affinity to a terpyridine moiety in solution to form

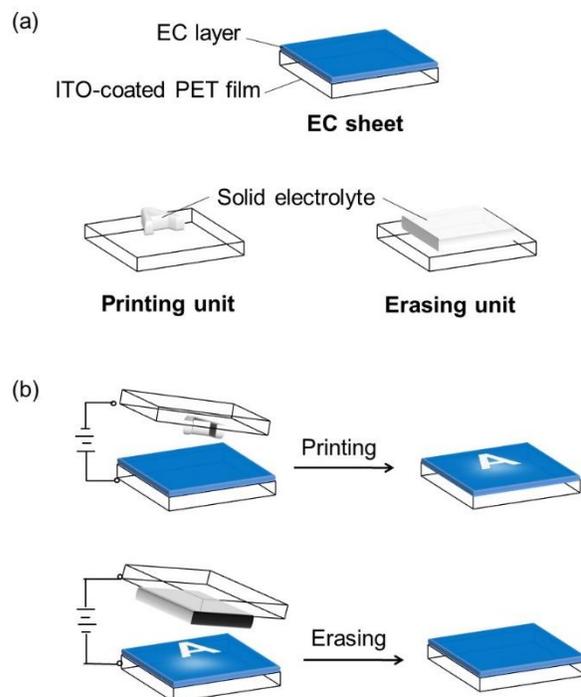
the complex, but an Fe(III) ion does not form the complex with the terpyridine moiety. Therefore, we tried to make a thin MSP layer on an ITO surface by electrochemical reduction of Fe(III) to Fe(II) in a solution including bis(terpyridine) (L1, Figure 3) and Fe(III) ions. However, we could not obtain the polymer layer on the ITO surface, probably because of the weak interaction between the ITO surface and the generated MSP. So, we introduced a terpyridine compound with an anchor unit (L2, Figure 3) before the electro-polymerization. As the result, we could obtain a thin layer of polyFeL1 on the ITO surface successfully (Figure 3). This method was also applicable on a bended ITO PET-film. The obtained MSP layers showed reversible EC properties. These results indicate that an Fe(III) ion form a complex with bis(terpyridine) in the solid state without re-dissolved.<sup>4</sup>



**Figure 3.** The structure of an ECD with a polyFeL1 Layer.

**(3) Rewritable multicolor EC paper using MSPs:** Easy preparation of a thin MSP layer on ITO substrates (glass or PET film) by the spray coating or electro-polymerization methods expanded the display application of the EC materials. In addition, the colors of MSPs are abundant, because the bandgap of the MLCT absorption depends on the potential difference between the d orbital of the metal and  $\pi^*$  orbital of the organic ligand in the MSPs. It is considered that the colorful feature of MSPs is suitable to the electronic paper applications. So, we developed a multicolor rewritable EC paper system. In this writing (printing) and erasing system, solid electrolyte on an ITO glass was used as the printing unit and the erasing unit to an EC sheet (a thin EC layer on a flexible ITO-coated PET-film) (Figure 4a). As shown in Figure 4b, the printing was done by stacking the printing unit and an EC sheet and applying an oxidation potential to the EC paper. The erasing process was performed by stacking the erasing unit and the printed EC paper and applying the reduction potential to the EC paper. The

printed state of the EC sheet is shown in Figure 5. When a mixture of Fe(II)-based MSP and Ru(II)-based MSP was used as the EC layer, the EC sheet was multi-color printed. As Fe(II)-based MSP and Ru(II)-based MSP have different colors and different redox potentials, three different colors could be printed on the EC sheet by changing the applied potential or the applying time.



**Figure 4.** (a) The three units (an EC sheet, a printing unit, and erasing unit) and (b) the printing and erasing process.



**Figure 5.** A flexible EC sheet in the printed state.

### 3. Conclusion

In this presentation three EC technologies using MSPs (highly durable ECDs, an EC later formation by electro-polymerization, and rewritable EC paper) were introduced. These research results will be useful for EC smart windows or digital signages etc.

### 4. Acknowledgements

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