Exploring Organometallic Bonding in Heterometallo-Supramolecular Polymers: A Path to NIR Electrochromism

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ABSTRACT
In our research endeavors, we have synthesized a series of metallo-supramolecular polymers with organometallic bonds, specifically PolyRuRu, PolyRuFe, and PolyRuZn. Notably, PolyRuZn exhibited absorption within the NIR region at around 1100 nm with high contrast ratio (ΔT > 60%), impressive color efficiency (η = 333 cm²/mC), within the NIR spectrum.

1 Introduction
Metallo-supramolecular polymers (MPSs), comprising metal ions and ditopic ligands, are anticipated to exhibit distinctive optical and electrochemical characteristics due to the interplay between these metals and ligands. Consequently, they have garnered significant attention for a broad range of applications, including but not limited to light-emitting devices, data storage, stimuli-responsive gels, and sensors.¹ Of particular note, these polymers excel in electrochromic (EC) properties, driven by the electrochemical redox reactions of the metal components. Recent research has placed a special emphasis on near-infrared (NIR) electrochromism, primarily for its potential in heat-shading smart windows that can contribute to energy conservation in vehicles, aircraft, and buildings. Various materials, such as metal complexes, small organic molecules, and covalent organic frameworks, have been explored for NIR-based electrochromism. However, challenges such as high crystallinity requirements and complex synthetic procedures have hindered their practical use in device fabrication, making MPSs a preferable alternative.

Despite their promise, achieving NIR electrochromism in MPSs is challenging, mainly because the bandgap associated with metal-to-ligand charge transfer (MLCT) absorption in MPSs typically exceeds 1.6 eV (770 nm), falling short of covering the NIR region. These materials did not display NIR electrochromism due to the large bandgap, prompting us to design a polymer that could induce intervalence charge transfer (IVCT) absorption with a smaller bandgap than the MLCT absorption.² In this work, we present a highly reversible NIR electrochromism in novel hetero-MPSs featuring organometallic moieties.

2 Experiment
Hetero-MPSs with Ru(II), Fe(II), and Zn(II) metal ions were successfully synthesized by complexation of L–Ru–L with metal salts (Figure 1). These were obtained as red, blue, and dark red solids, respectively, in quantitative yields (PolyRuRu: 98 %, PolyRuFe: 94 %, PolyRuZn: 96 %).

2.1 Synthesis of ligand L–Ru–L
To a 20 mL of CH₂Cl₂ solution of 4’-(4-Ethynylphenyl) -2,2’:6’,2’’-terpyridine (100 mg, 0.30 mmol) and Ru(dppe)Cl(OTf) (153.6 mg, 0.14 mmol) was added sodium hexafluorophosphate (126 mg, 0.75 mmol), and triethylamine (110 μL, 0.75 mmol). The mixture was stirred at room temperature under a nitrogen atmosphere for 24 h. After the filtration, the solvent was evaporated, and the residue was washed with Et₂O and purified by short column chromatography on alumina (elucent: CH₂Cl₂) to give a yellow solid (283 mg, 55.5 %). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) showed a peak corresponding to m/z: 1563 [M]+. C₉₈H₇₈Ne₆P₆Ru requires 1563

2.2 Synthesis of Polymer
An equimolar amount of L–Ru–L (23.0 mg, 14.7 μmol) and RuCl₂(DMSO)₄ (7.12 mg, 14.7 μmol) was stirred in argon-saturated ethylene glycol at 120 °C for 24 h. After the reaction solution cooled to room temperature, tetrahydrofuran (THF) was added until it became colorless. The precipitated polymers were collected by filtration, washed with THF three times, and then dried in vacuo overnight to obtain the corresponding PolyRuFe (yield: 25.0 mg, 98.2 %). Similar method was employed to synthesize PolyRuRu and PolyRuZn.

2.3 Preparation of EC film
The PolyRuRu, PolyRuFe, and PolyRuZn stock solutions were formulated through the dissolution of the polymers in methanol at a concentration of 2.5 mg/mL. To create uniform polymer films, we employed a spin-coating technique on ITO-coated PET sheets, following a rapid acceleration to 150 rpm within 10 seconds, maintaining that speed for 30 seconds; then,
accelerating to 200 rpm within 10 seconds, maintaining that speed for 200 seconds. Subsequently, the resulting polymer layers were air-dried at room temperature for 20 minutes.

3 Results
The ligand L–Ru–L was soluble exclusively in chloroform and dichloromethane, while PolyRuRu and PolyRuFe exhibited solubility in methanol, DMSO, DMF, and ACN. These polymers, on the other hand, were insoluble in chloroform, dichloromethane, and hexane. PolyRuZn displayed solubility in DMSO and DMF but was insoluble in methanol, ACN, chloroform, dichloromethane, and hexane. Analysis of the $^1$H-NMR spectrum of PolyRuZn revealed a down-field shift in all terpyridine protons, along with an up-field shift in the ortho protons confirming the formation of MSPs. Notably, PolyRuZn did not exhibit any terminal group signals, and its molecular weight exceeded 30, as the limitations of $^1$H NMR spectroscopy detected only approximately 5%. The number average molecular weight ($M_n$) of PolyRuZn was calculated to be $6.6 \times 10^4$ through the integration of the terminal group signal. Additionally, the average molecular weight ($M_w$) of the polymers was determined using the SEC-RALLS-viscometry method (PolyRuRu: $11 \times 10^4$, PolyRuFe: $24 \times 10^4$, PolyRuZn: $29 \times 10^4$).

4 Discussion
The electrochemical properties of the polymers were studied. None of the three polymers initially displayed absorption in the near-infrared (NIR) region. When subjected to cyclic voltammograms (CVs) and differential pulse voltammograms in a 0.1 M TBAP/DMF solution, they exhibited a single reversible redox wave in the potential range of 0–0.5 V vs. Ag/Ag$^+$, corresponding to the Ru(II)/Ru(III) couple of the Ru-acetylide moiety. Moreover, PolyRuRu and PolyRuFe showed an additional reversible wave in the potential range of 0.5–1.0 V vs. Ag/Ag$^+$, attributed to Ru(II)/Ru(III) or Fe(II)/Fe(III) transitions in the transition metal–terpyridine complexes moiety, respectively.

4.1 NIR switching
The optical changes were monitored when applying a potential of +0.5 V vs. Ag/Ag$^+$ to PolyRuRu and PolyRuFe in a DMF solution, revealing that while PolyRuRu showed no NIR absorption, PolyRuFe exhibited a new broad absorption at approximately 1300 cm$^{-1}$ in the NIR region. This NIR absorption disappeared at +1.0 V vs. Ag/Ag$^+$. These findings indicated an intervalence charge transfer (IVCT) transition of Robin-Day Class II. To assess their electrochromic properties, the polymers were applied to a glassy carbon electrode using the solvent casting method, as the films’ electrochromic behavior is crucial for electrochromic materials (ECMs). Notably, PolyRuRu and PolyRuFe films did not demonstrate electrochromic or spectroelectrochemical properties due to their high solubility in electrolyte solutions. As a result, our focus shifted to investigating the electrochromic properties of PolyRuZn films. A thin film of PolyRuZn was prepared on an ITO glass by casting a methanol solution (c = 2.5 mg / mL, surface area: 8 x 20 mm). The absorption spectral changes of the polymer film upon application of two potentials between 0 and + 0.5 V vs. Ag/Ag$^+$ are shown in Figure 1. Interestingly, this film exhibited a high-absorbance band in the NIR region, with an increase in absorbance at 1147 nm and a decrease in absorbance at 516 nm, and the color changed from red to green. This film exhibited stronger absorbance in the NIR region and faster response than the solution state.

5 Conclusions
A novel approach involved synthesizing heterometallo-supramolecular polymers. Different transition metals induced reversible electrochromism in the near-infrared (NIR) region via intervalence charge transfer (IVCT) reactions. Notably, PolyRuZn films, produced through a solution process, exhibited impressive NIR electrochromic properties, including a high contrast ratio (>60%), excellent color efficiency ($\eta = 333$ cm$^2$/C), and rapid response (within 3 seconds) at 1147 nm. This method opens new avenues for electrochromic materials and organic-metallic hybrids, potentially enhancing the properties of other MSPs.

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