Microwave-Assisted Quick Synthesis of Ru(II)-Based Metallosupramolecular Polymer for Improved Electrochromic Properties

Utpal Rana,[a †] Dines Chandra Santra,[a] Banchhanidhi Prusti,[a] Chanchal Chakraborty,[a ‡] Yuko Saito,[b] Kazuhiko Takeuchi,[b] Ritsuko Nagahata,[b] and Masayoshi Higuchi [a]**

[a] U. Rana, D. C. Santra, B. Prusti, C. Chakraborty, M. Higuchi
Electronic Functional Macromolecules Group, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan.
E-mail: HIGUCHI.Masayoshi@nims.go.jp

[b] Y. Saito, K. Takeuchi, R. Nagahata
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan.
Email: nagahata–ritsuko@aist.go.jp

[†] Present address: Panipat Naphtha Cracker, Indian Oil Corporation Limited (IOCL), Panipat, Haryana-132140, India.

[‡] Present address: Department of Chemistry, BITS Pilani, Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, Hyderabad-500078, India.

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Metallosupramolecular polymers (MSPs) have reversible electrochromic (EC) characteristics. Transition metal ions and ditopic organic ligands are complexed 1:1 to form MSPs, but the complexation conditions depend on the metal species ions. Herein, we report a microwave-assisted (MWA) quick synthesis of a Ru(II)-based MSP (**polyRu–MWA**) as a novel preparation method for MSPs. **PolyRu–MWA** was synthesized under microwave irritation for 60 min using 770 W and 2.45 GHz frequency, whereas a conventionally synthesized Ru(II)-based MSP (**polyRu–CS**) was obtained using oil-bath at 160 °C for 24 h. **PolyRu–MWA** was found to show much better EC properties than **polyRu–CS**. A film of **polyRu–MWA** prepared on an indium tin oxide glass exhibited higher optical contrast (transmittance change, ΔT: 81.39%) than **polyRu–CS** (67.73%). Coloration efficiency of **polyRu–MWA** (425.7 $cm^2 C^{-1}$) was also higher than that of **polyRu–CS** (318.3 $cm^2 C^{-1}$). Interestingly, the charge and discharge current ratio for bleaching and coloring in **polyRu–MWA** was approximately 1.7 times higher than that for **polyRu–CS**, probably because of the high molecular weight polymer formation in **polyRu–MWA**. A **polyRu–MWA** film also displayed a longer EC optical memory than **polyRu–CS**.

1. Introduction

The demand for carbo-neutralization in smart window applications has led to an increased research attention for electrochromic (EC) materials. [1-4] For EC applications, the material must possess a variety of qualities, including excellent redox stability, high contrast ratio and coloration efficiency, controllable switching, and good processability. Various EC materials such as Prussian blue, [5] viologens, [6] conducting polymers [7, 8] metal phthalocyanines, [9] and WO_3 [10, 11] have been previously investigated. However, these materials fail to match all of the aforementioned requirements. Instead, new EC materials must be developed, with superior properties to those of already known materials.

Metallosupramolecular polymers (MSPs) are a new class of EC material consisting of metal ions and organic ligands. [12-17] MSPs are generally synthesized by the 1:1 complexation of transition metal ions and ditopic organic ligands. The complexation conditions depend on the specific metal species, and temperatures greater than 150 °C are sometimes required to promote polymer formation. For example, Ru(II)-based MSPs are synthesized at high temperatures under reflux conditions for 24 h, which is a time-consuming and energy-intensive procedure. [15, 18-20] Thus, simple, rapid, economical, and environmentally friendly synthetic processes should be developed. To solve these problems, we introduce a microwave-assisted (MWA) complexation process, in which microwave radiation provides the driving force for the reaction. This is a branch of green chemistry because the chemical transformation is pollution-free, eco–friendly, time- and energy-saving, and simple to process and handle. [21-23] The major advantage of this method is that the solvent transforms electromagnetic radiation into heat, which accelerates the chemical reaction. By contrast, heating reactions with classic setups, such as oil baths and sand baths, are not only slow, but also create a heated surface in the reaction vessel where chemicals break down over time. To date, no studies have focused on the synthesis of MSPs using microwave radiation, which we found to be a quick and effective production process.

Herein, we report a facile and rapid synthesis of a Ru(II)-based MSP by a microwave method. The synthesized polymer was characterized by ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy and the EC properties were compared with those of a conventionally synthesized Ru(II)-based MSP.

2. Results and discussion

The Ru(II)-based MSP, **polyRu–MWA**, was synthesized under microwave irradiation for 60 min using 770 W and 2.45 GHz frequency (Figure 1), whereas a conventionally synthesized Ru(II)-based MSP, **polyRu–CS**, was obtained by heating 4',4''''-(1,4-Phenylene)bis(2,2'':6',2''-terpyridine) and dichlorotetrakis(dimethylsulfoxide) ruthenium(II) to 160 °C using an oil-bath for 24 h, in accordance with our previous report.[18] The molecular weights of the obtained polymers were calculated from the ^{1}H NMR spectra (Figure 2) by end group analysis. The peaks at 9.55, 9.07, 8.79, 8.10, 7.69, and 7.40 ppm are assigned to the protons in the positions a, b, c, d, f, and e, respectively.[14, 24, 25] The peak corresponding to the proton in the position b' was confirmed with the assistance of ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY spectra of the model complex (Figure S1 and S2). The proton assigned a' to the 4' position of the end terpyridine unit.

End group analysis, with respect to the a'–proton, was conducted to determine the molecular weight of the two polymers. For example, the average degree of polymerization of **polyRu-MWA** (calculated by the integration ratio of b and b'), was found to be 31, whereas the molecular weight of the repeat unit was determined to be 712.6 g The molecular weight of the polymer was estimated to be 2.2×10^4 Da. A similar approach was conducted for **polyRu–CS**, providing a molecular weight of 4.4×10^3 Da. Thus, a polymer with higher molecular weight can be produced using microwave synthesis. Moreover, it is significant to note that the conventional synthesis methodology results in the generation of by-products in the form of small metal complexes, even with a 24 h reaction time, resulting in lower yield of target polymer compared to that synthesized using the microwave heating conditions.

The UV–vis spectra of **polyRu–MWA** and **polyRu–CS** are comparable (Figure 3a), with both displaying a high-energy absorption peak at 310 nm, assigned to a ligand-centered (^{1}LC) π–π^* transition. Additionally, two lower energy bands are observed at 508 and 504 nm in the spectra of **polyRu–MWA** and **polyRu–CS**, respectively; these bands are assigned to a metal-to-ligand (dπ–π^*) charge transfer (MLCT) transition.[18, 20] The 4 nm red-shift of the low energy band can be attributed to the smaller MLCT energy gap in **polyRu–MWA**, which is a consequence of the high molecular weight long chain length. The metal complex behaves like an electron-withdrawing group, which typically stabilizes the π system, thus reducing the energy of the π* orbital on the ligand, and consequently red shifts the MLCT transition. [33] The sharper MLCT band observed for **polyRu–MWA**, along with the longer absorption maxima, indicates that relatively long polymeric chains are formed by the microwave assisted method compared with the conventional synthetic procedure. [26]

The room-temperature luminescence properties of **polyRu–MWA** and **polyRu–CS** were measured by the excitation of the MLCT band. In MeOH solution, **polyRu–MWA** exhibited two emission bands at 588 and 675 nm, whereas **polyRu–CS** showed only one at 588 nm (Figure 3b). The peak at 588 nm can be assigned to the emission from the intra-ligand π–π* and n–π* transition, whereas the peak at 675 nm can be attributed to the ^{3}MLCT transition. Despite the emission from the ^{3}MLCT state being intense and well-resolved for **polyRu–MWA**, this emission was broadened for **polyRu–CS** because of the formation of an irregular structure using the conventional synthesis method. [18]

X–Ray powder diffraction (XRD) patterns of the **polyRu–MWA** and **polyRu–CS** are shown in Figure 4a. The polymer synthesized by the microwave irradiation method exhibited less intense diffraction peaks than the conventionally synthesized polymer. The less intense diffraction peaks of **polyRu–MWA** suggest a more amorphous nature. Interestingly, for **polyRu–MWA**, a strong reflection peak was observed in the low angle region with *d*-spacing of 1.46 nm ($2\theta = 6.02°$), which is consistent with the lateral stacking of polymer chains or lamella structure formation. [27, 28] In the high-angle region, only amorphous peaks were observed, which indicates long-range ordered structure were not formed by **polyRu–MWA** chains. [29]

Thermogravimetric analysis (TGA) of both polymers under N_2 at 10 °C min^{-1} scan rate is shown in Figure 4b. A higher thermal stability for **polyRu–MWA** was observed relative to **polyRu–CS** indicating that the former is a high-molecular-weight linear polymer. The weight losses at 600 °C for **polyRu–MWA** and **polyRu–CS** were 28% and 36%, respectively. [20]

The cyclic voltammograms (CVs) of the two polymers were measured in acetonitrile using a three-electrode system; the system employed a glassy carbon (GC) working electrode, Pt -flag counter electrode, and Ag/AgCl (KCl) reference electrode in a 0.1 M $LiClO_4$ electrolyte solution. The CV of **polyRu–CS** and **polyRu–MWA** (Figure 5a) displayed reversible oxidation peaks at 1.28 and 1.12 V with a 50 mV s^{-1} scan rate, respectively. For **polyRu–CS**, the oxidation peak of the Ru(II)/Ru(III) ions was shifted to a lower potential (from 1.28 to 1.26 V). The higher oxidation potential of **polyRu–MWA** can be explained by the metal–metal interactions in the high-molecular-weight polymer chains. [30, 31] Interestingly, the CV of **polyRu–CS** at a slower scan rate (10 mV s^{-1}) showed two oxidation peaks at 1.03 and 1.23 V, whereas **polyRu–MWA** retained only one oxidation peak at 1.25 V (Figure 5b). The appearance of the additional peak in the CV for **polyRu–CS** is a consequence of the low-molar-mass oligomer mixture in the system. The first peak corresponds to monocomplexes, low-molecular-weight oligomers, or terminates at the metal center of the polymer chain. The second peak indicates that the remaining metal sites are more difficult to oxidize because of their interactions with adjacent oxidized metal ions. [29, 32]

The electron transfer mechanism of both polymer films on ITO glass (1.5 × 1.5 cm^2) was investigated using scan-dependent CV studies. For a fair comparison, the thickness of both polymer EC films was carefully controlled by spin-coating under identical conditions. Figure 6 shows the relationship between the anodic peak current (i_{pa}) and the scan rate (ν) or the square root of scan rate ($\nu^{1/2}$) for both polymers. For **polyRu–MWA** (Figure 6b, c) and **polyRu–CS** (Figure 6e, f), a linear dependence was observed between i_{pa} and both ν and $\nu^{1/2}$, with the R^2 value close to 1.0. This indicates that a diffusion-controlled redox reaction takes place. The higher R^2 value obtained for **polyRu–CS** relative to that for **polyRu–MWA** from the i_{pa} *vs* ν plot (0.9682 and 0.9557, respectively) indicates that faster counter anion diffusion occurs in the small chains of the chaotic polymer structure in the **polyRu–CS** film compared to that of the homogeneous ordered **polyRu–MWA** film. [17, 33]

The *in situ* transmittance measurements of **polyRu–MWA** and **polyRu–CS** at two applied potentials (0 and 1.8 V) are shown in Figure 7 and S3, respectively. The polymer film was cathodically colored; the spectrum of the as-cast film showed absorbance in the visible region (~510 nm) owing to the MLCT transition which decreased with the applied potential. At 1.8 V of applied potential, the film was found to be colorless owing to the electrochemical oxidation of Ru(II) to Ru(III). A reversible color change occurred upon switching the potential from 0 V to 1.8 V vs Ag/Ag^+.

Double-potential-step chronoamperometry was performed to evaluate the response time of the EC films. The potential was stepped between 0 and 1.8 V, with a 5 s interval time, and the transmittance change (ΔT) at MLCT band was recorded. The transmittance changes for **polyRu-MWA** (at 510 nm) were recorded to be 81.4% and 22.6% at 5 and 2 s interval time, respectively. In comparison, for **polyRu-Cs** (at 505 nm), the transmittance changes were lower; 67.7% and 22.2% at 5 and 2 s interval time, respectively. The redox stability of EC devices must also be considered because the deterioration of redox activity reduces the EC contrast and, hence, the performance. Thus, the cycling stability of the devices was measured by non-stop cycling of the applied potential between 0 and 1.8 V for **polyRu–MWA** and **polyRu–CS**. As shown in Figure 8, after 200 cycles (100 cycles at intervals of 5 s and 2 s), the devices retained their original electroactivity, indicating adequate redox stability.

The switching speed of an EC material, that is, the time required for the coloring and bleaching process, is another important parameter to consider, especially in applications such as dynamic displays and switchable mirrors. The coloring time (t_c) and bleaching time (t_b) for the reappearance and disappearance of the MLCT absorption were calculated from Figure 8a and are characterized as the time needed for 95% change of ΔT. For **polyRu–MWA**, t_c and t_b were found to be 1.18 and 2.38 s, respectively, whereas for **polyRu–CS**, these values were 1.07 and 2.43 s, respectively (Table 1).

The coloration efficiency (η) at a given optical density is also an important characteristic for EC films and can calculated using Equation 1, where ΔOD is the optical density change, Q_d is the amount of injected/ejected electronic charges in the polymer, and T_c and T_b are the coloring and bleaching transmittance values, respectively.

$$\eta = \frac{\Delta OD}{Q_d} = log\frac{T_b}{T_c} / Q_d \qquad \textbf{(1)}$$

Using *in–situ* electrochemistry-transmittance measurements and Equation 1, η was calculated to be 318.6 $cm^2\ C^{-1}$ at 505 nm for **polyRu–CS** and 425.7 $cm^2\ C^{-1}$ at 510 nm for **polyRu–MWA**. The coloration efficiency of **polyRu–MWA** was ~1.3 times more than that of **polyRu–CS**. To the best of our knowledge, the coloration efficiency reported herein is the highest value reported to date for any MSP. The enhancement of the EC contrast and coloration efficiency of the **polyRu–MWA** film occurred because of the formation of a relatively smooth film owing to the homogeneous distribution of the microwave-synthesized long polymer chains. By contrast, short oligomeric chains were present in the EC film of **polyRu–CS**, leading to a higher number of nucleation centers and terminated oligomeric chains; the heterogeneous distribution of the oligomeric chains from the chain length distribution point results in the formation of a rougher film. All of these short-chain oligomers cannot be switched under the applied potential, resulting in the poor EC performance of **polyRu–CS**. [34, 35]

The charge/discharge capacity of the polymer films when switching between 0 and 1.8 V were measured from the chronoamperometry curve and are shown in Figure 8a. Charge required when the EC material is bleached from 0 to 1.8 V and discharged when it is darkened from 1.8 to 0 V. The charge densities required for bleaching (charging) **polyRu–MWA** and **polyRu–CS** were 7.37 and 4.33 $mC\ cm^{-2}$, respectively, whereas, the charge densities required for coloring (discharge) were 6.77 and 4.29 $mC\ cm^{-2}$, respectively. Higher charge density value were observed during charge/discharge for **polyRu–MWA** for two reasons: first, the formation of an ordered structure by long polymer chains [36] and second, insolubility in the electrolyte.[37]. Open-circuit memory, the time during which the material retains its color state after the electric field is removed, is an important parameter in EC devices because it is directly related to its utilization and energy consumption. To test this property for the EC devices based on **polyRu–MWA** and **polyRu–CS**, a 1.8 V potential was applied for 10 s. After charging, the device was maintained under open-circuit conditions for 600 s. The percentage change in transmittance was monitored using the MLCT of the EC devices. The EC memory spectra of both polymers are shown in Figure 8b. T The change was *ca*. two times higher for the **polyRu–CS** film than that for the **polyRu–MWA** film. A significant level of EC memory was observed for **polyRu–MWA** because the electrons were trapped in the high-molecular-mass polymer film, preventing them from reverting to their equilibrium state. Faster mass transport to **polyRu–CS** can lead to a lower optical memory owing to the existence of more contacts among the oligomer chains in the chaotic structure of the polymer film. [38, 39]

3. Conclusion

We present a fast and facile microwave-assisted synthesis of high-molecular-weight Ru(II)-based MSP (**polyRu–MWA**) and characterize its photophysical and EC properties. For comparison, the same polymer (**polyRu–CS**) was synthesized using the oil-bath method. The molecular weights of **polyRu–MWA** and **polyRu–CS** were estimated through end group analysis by ^{1}H NMR spectroscopy, and the obtained values were 11×10^4 Da and 4.4×10^3 Da, respectively. Changes in molecular weight significantly affect solubility, photophysical properties, and EC properties. The **polyRu–MWA** film showed better reversible electrochemical processes and stable color changes with good coloration efficiency (425.7 cm^2 C^{-1} at 510 nm) and optical contrast (81.4% at 510 nm) than the **polyRu–CS** film (67.7% optical contrast with 318.6 cm^2 C^{-1} efficiency at 510 nm), when the EC device was switched between the neutral (red at 0 V) and oxidized states (transparent at 1.8 V). Furthermore, **polyRu–MWA** exhibited better optical memory and long-term stability. In particular, the high optical contrast, remarkable coloration efficiency, significantly fast switching, good open-circuit stability, and tremendous redox stability make **polyRu–MWA** a good candidate for commercial applications.

4. Experimental Section/Methods

Materials

Unless otherwise noted, all reagents were of reagent grade and were used without purification. 4′,4′′′′-(1,4-Phenylene)bis(2,2′:6′,2′′-terpyridine) (96%) was purchased from Sigma-Aldrich co. Ltd. Dichlorotetrakis(dimethyl sulfoxide) ruthenium(II) was purchased from Tokyo Chemical Industry Co., Ltd., and used as received. Dehydrated ethylene glycol and tetrahydrofuran (THF) were used as the reaction solvents. Methanol for the UV–vis and acetonitrile for the CV measurements were of spectroscopic grade. These solvents were purchased from Wako or Kanto Chemical Co. Inc., and used as received.

Instrumentation

Microwave irradiation was carried out using SMW-087 (μ Reactor®, Shikoku Instrumentation, Co. Ltd). The reaction temperature was measured using a fiber-optic thermometer (AMOTH FL-2000; Anritsu). UV−vis spectra were obtained using a Shimadzu UV-2550 UV-visible spectrophotometer. ^{1}H NMR spectra were recorded on a 300 MHz JEOL AL 300/BZ instrument (Tokyo, Japan). Mass spectra were measured using a Shimadzu/Kratos time-of flight mass spectrometer (Kyoto, Japan). High-resolution mass spectrometry was performed on a Shimadzu LCMS-ITTOF spectrometer. Wide angle XRD was measured by using a RINT ULTIMA III device with Cu K_α radiation (λ= 1.54 Å), a generator voltage of 40 kV, and a current of 40 mA. CV and amperometric experiments were performed by spin-coating the polymer solution onto an ITO electrode. The experiments were performed in an electrochemical analyzer (ALS/H CH instruments) using an anhydrous acetonitrile solution containing 0.1 M lithium perchlorate ($LiClO_4$) as the supporting electrolyte. A platinum flag was used as the counter electrode and Ag/AgCl was used as the reference electrode.

Synthesis of ***polyRu-MWA***

4’,4’’’’-(1,4-Phenylene)bis(2,2’:6’,2’’-terpyridine) (0.05 g, 0.09 mM) and dichlorotetrakis(dimethylsulfoxide)ruthenium(II) (0.04 g, 0.09 mM) were placed in a two-neck round-bottom flask. Dry ethylene glycol (50 mL) was added, and the reaction mixture was irradiated with microwave at 770 W and 2.45 GHz frequency along with constant stirring for 60 min. After completion of the reaction, the solvent was removed and concentrated to approximately 10 mL. The reaction mixture was then added to 200 mL THF. The polymer was precipitated in THF, collected by filtration, washed with THF, and dried in a vacuum oven overnight. Finally, **polyRu-MWA** was obtained as red powder (0.08 g, 80% yield).

Preparation of a polymer film on ITO

The **polyRu-MWA** and **polyRu-CS** films were prepared on ITO-coated glass using a spin-coating technique. First, the polymer was dissolved (5 mg mL^{-1}) in dry methanol. Then, 100 µL of the polymer solution was spin-coated on an ITO glass (1.5 × 1.5 cm^2) for 180 s at 100 rpm. The prepared films were dried for 30 min at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
^{1}H NMR spectra of **polyRu-MWA** and **polyRu-CS**, electrochromism of **polyRu-CS**, and ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY NMR spectra of the model complex.

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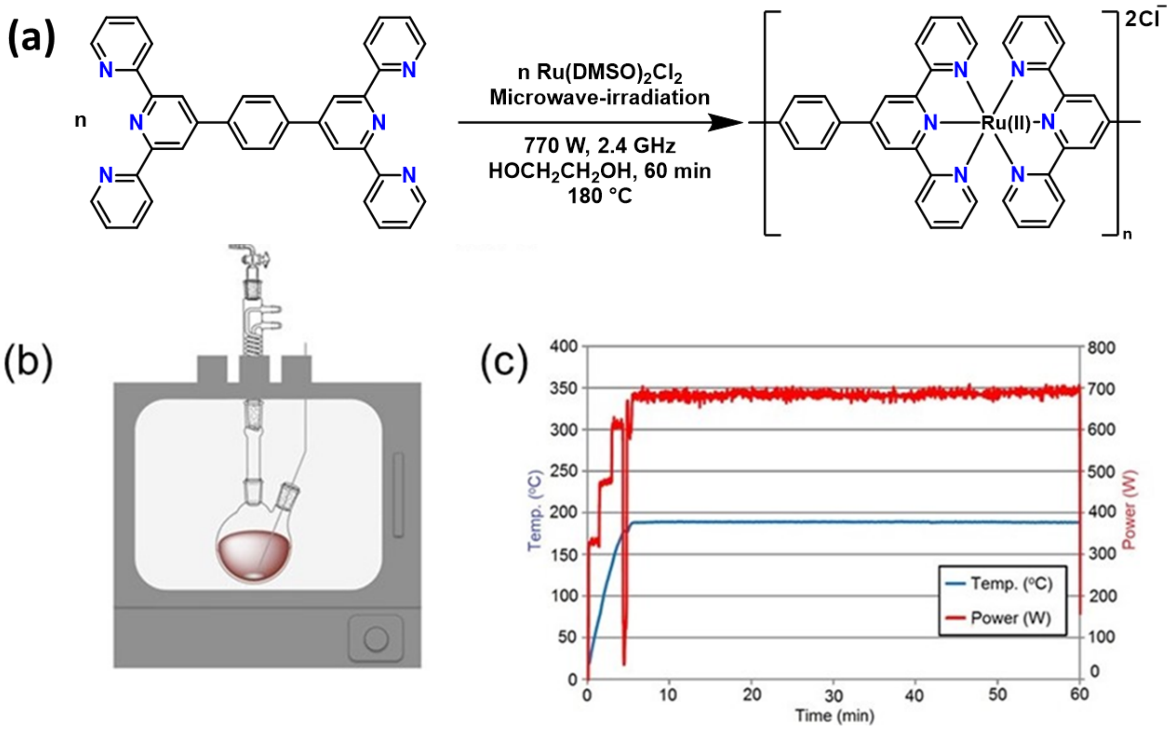


Figure 1. (a) Microwave synthesis of **polyRu**, (b) an illustration of the microwave synthesis, and (c) the power and temperature profiles.

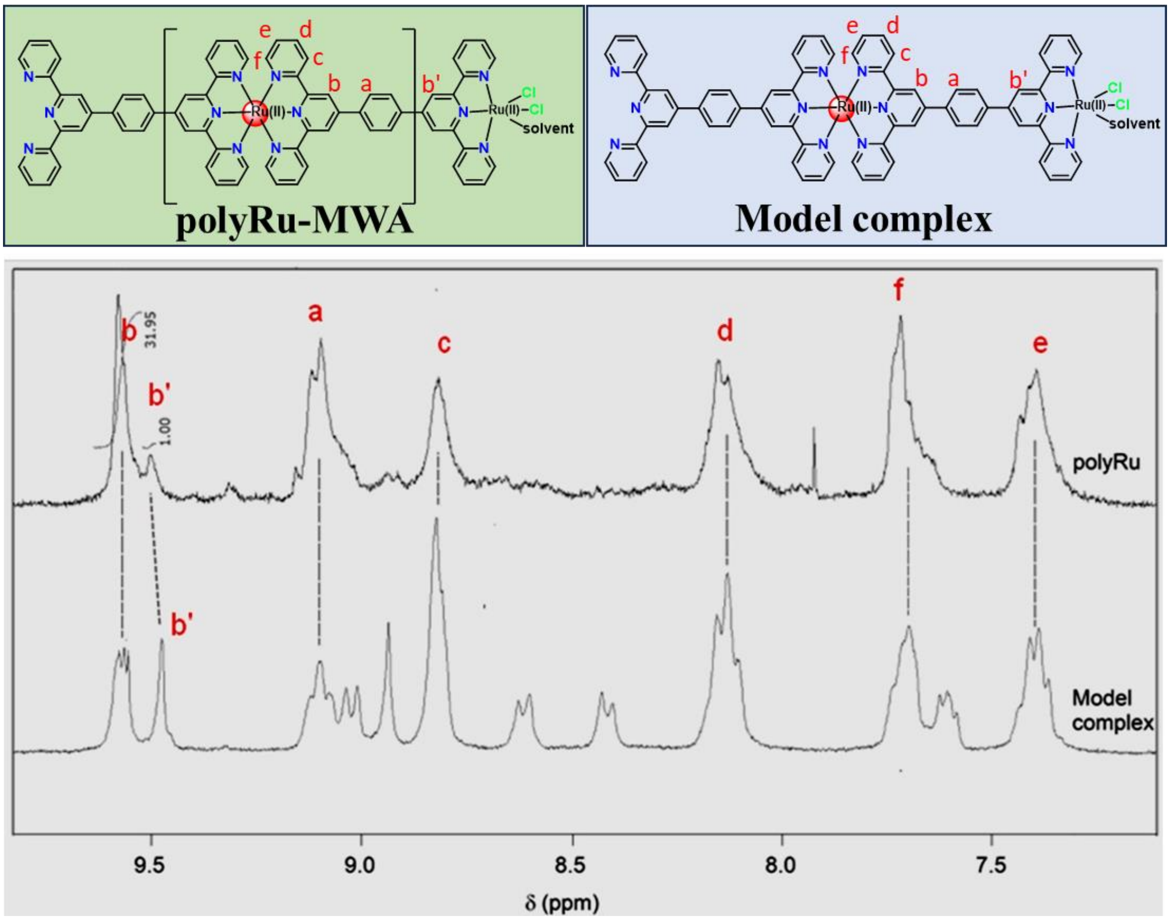


Figure 2. ^{1}H-NMR spectra of **polyRu-MWA** and model complex (solvent: CD_3OD at room temperature).

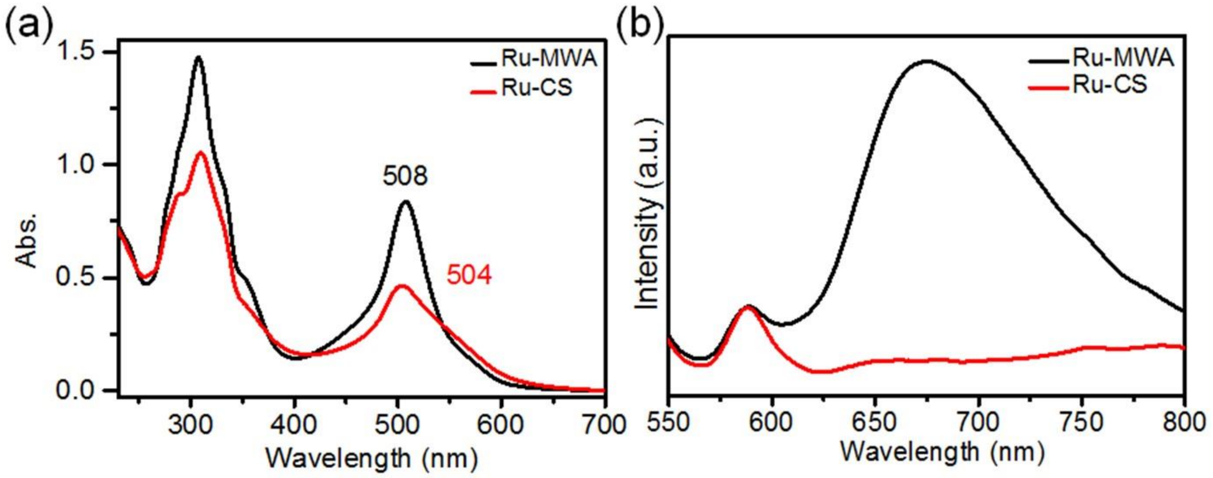


Figure 3. (a) UV–vis and (b) emission spectra of **polyRu-MWA** and **polyRu-CS** in MeOH (concentration: 2.5 × 10^{-5} M).

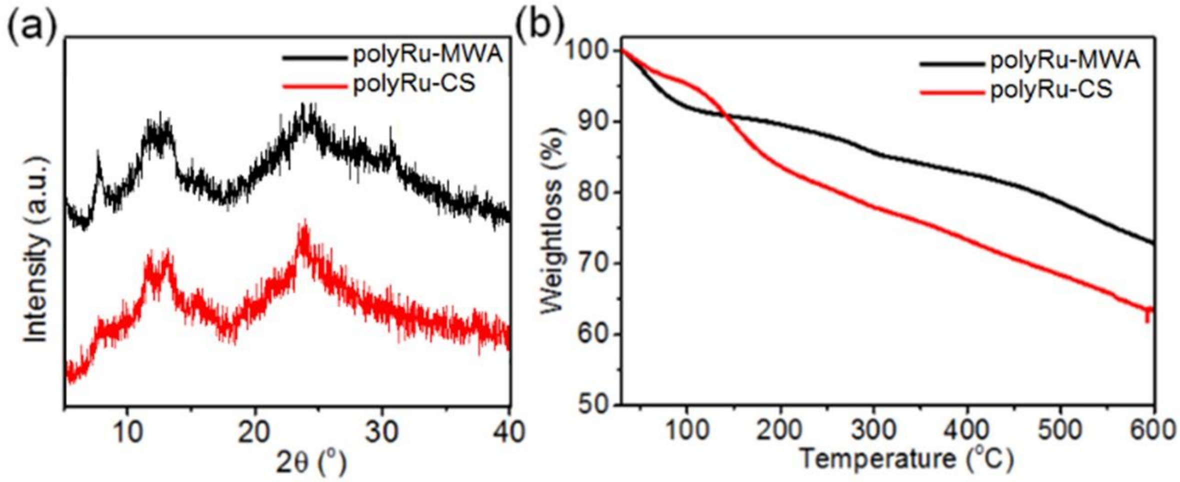


Figure 4. (a) Powder XRD analysis and (b) TGA data (heating rate: 10 °C /min) of **polyRu-MWA** and **polyRu-CS**.

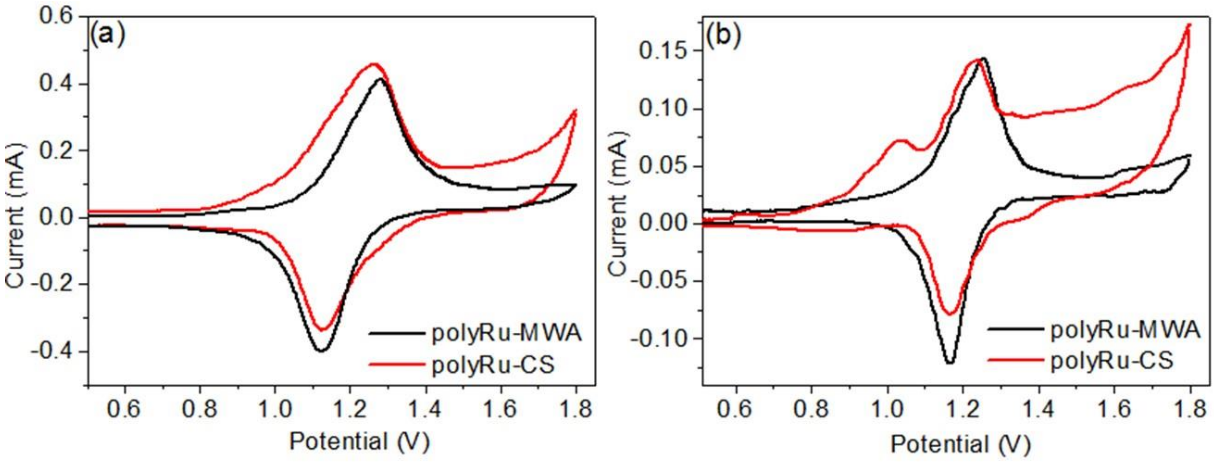


Figure 5. Cyclic voltammograms of **polyRu-MWA** and **polyRu-CS** (scan rate: (a) 50 mV s^{-1} and (b) 10 mV s^{-1}) in 0.1 M $LiClO_4$/ACN electrolyte solution.

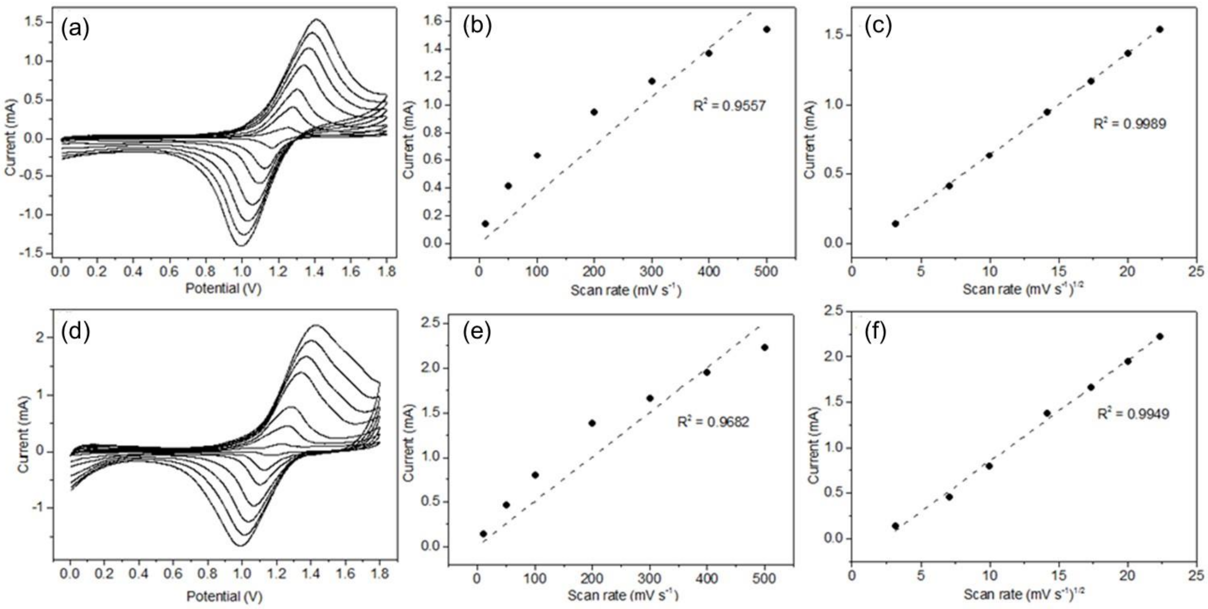


Figure 6. (a) CVs of a **polyRu-MWA** film with different scan rates (10–500 mV/s), (b) a graph of the peak current *vs.* the scan rate, and (c) a graph of the peak current *vs.* the square root of the scan rate. (d) CVs of a **polyRu-CS** film with different scan rates (10–500 mV/s), (e) a graph of the peak current *vs.* the scan rate, and (f) a graph of the peak current *vs.* the square root of the scan rate. The electrolyte solution is 0.1 M $LiClO_4$/ACN.

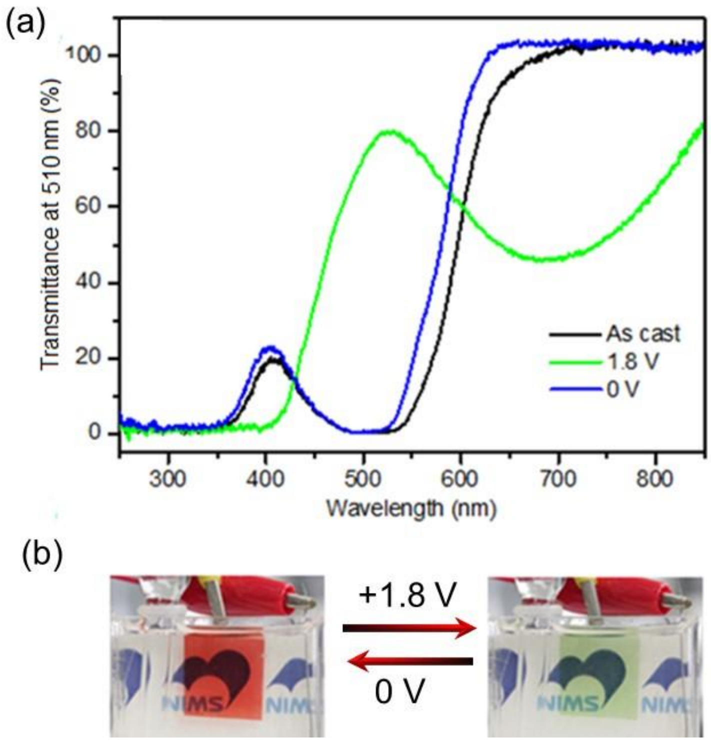


Figure 7. (a) *In-situ* UV–vis spectra of a **polyRu-MWA** film in 0.1 M $LiClO_4$/ACN at 0 and 1.8 V. (b) The color changes of a **polyRu-MWA** film (2.5 × 2.5 cm) at 0 and 1.8 V.

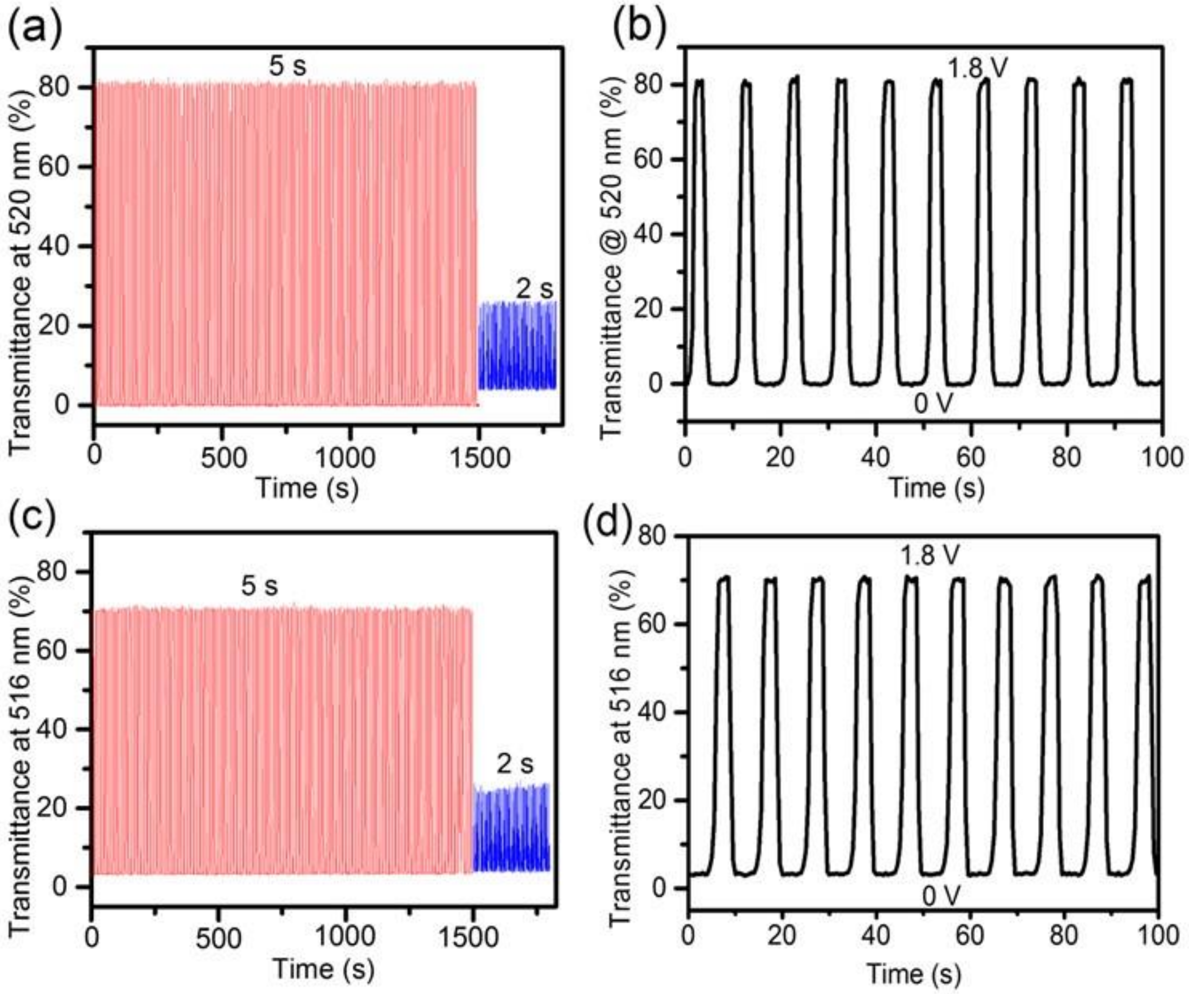


Figure 8. (a) Transmittance change (ΔT %) at 510 nm of a **polyRu-MWA** film switched between 0 and 1.8 V with 10, 5, and 2 s interval times. (b) The magnified view of the ΔT% for interval time of 5 s. (c) ΔT% at 505 nm of a **polyRu-CS** film switched between 0 and 1.8 V with 10, 5, and 2 s interval times. (d) The magnified view of the ΔT% for interval time of 5 s. All measurements were performed in 0.1 M $LiClO_{4}$/ACN electrolyte solution.

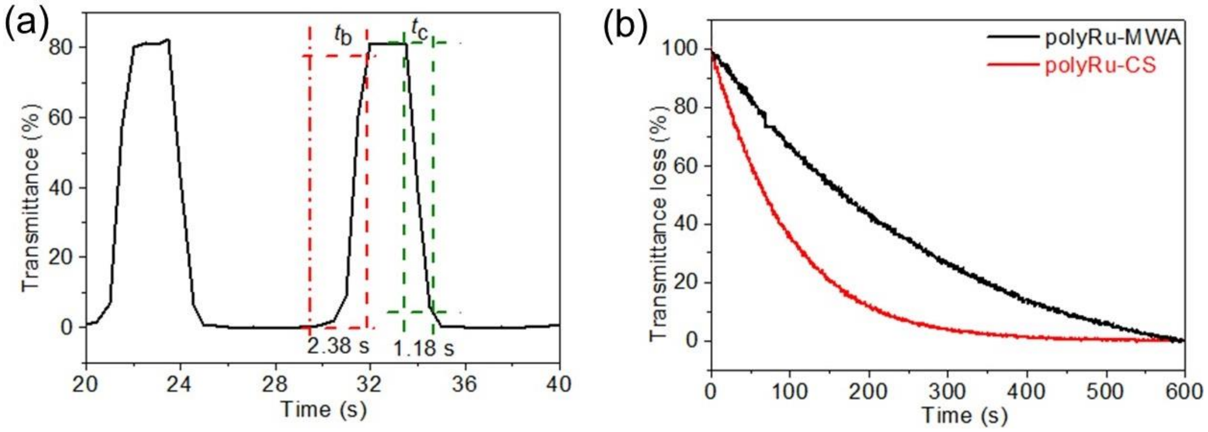


Figure 9. (a) Chronoamperometry plots of **polyRu-MWA**. (b) Open circuit memory of **polyRu-MWA** and **polyRu-CS** electrochromic devices monitored at 510 and 505 nm, respectively (the initial applied potential: 1.8 V).

Table 1. EC properties of a **polyRu-MWA** and **polyRu-CS** film when switched between 0 and 1.8 V with an interval of 5 s.

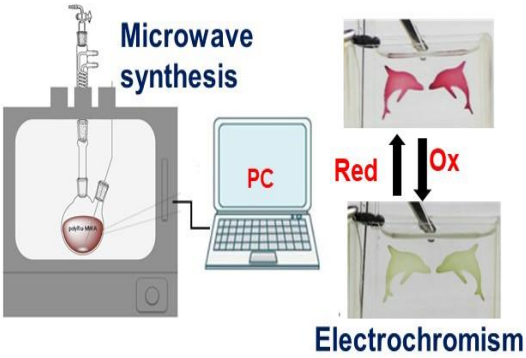
	Bleaching time (t_b, s)	Darkening time (t_d, s)	Transmittance Change (ΔT, %)	Charge/discharge amount (Q, mC cm^{-2})	Coloration efficiency (η, cm^2 C^{-1})
PolyRu-MWA	2.38	1.18	81.39	7.37/6.77	425.7
PolyRu-CS	2.43	1.07	67.73	4.33/4.29	318.6

A Ru(II)-based metallosupramolecular polymer was successfully synthesized by the 1:1 complexation of bis(terpyridyl)benzene and Ru(II) in ethylene glycol at 180 º C under microwave-irradiation (2.4 GHz, 770 W) for 60 min. An exceptional quality polymer with a high molecular weight (2.2×10^4 Da) was obtained in this reaction. The polymer film exhibited improved electrochromic properties with large optical contrast (81.4%) and high coloration efficiency (η) (425.7 cm^2/C) compared to the polymer synthesized using conventional methods.

Utpal Rana, Dines Chandra Santra, Banchhanidhi Prusti, Chanchal Chakraborty, Yuko Saito, Kazuhiko Takeuchi, Ritsuko Nagahata*, and Masayoshi Higuchi*

Microwave-Assisted Quick Synthesis of Ru(II)-Based Metallosupramolecular Polymer for Improved Electrochromic Properties

TOC



Supporting Information

Microwave-Assisted Quick Synthesis of Ru(II)-Based Metallosupramolecular Polymer for Improved Electrochromic Properties

Utpal Rana,[a] *Dines Chandra Santra* [a]*, Banchhanidhi Prusti,*[a] *Chanchal Chakraborty,*[a] *Yuko Saito,*[b] *Kazuhiko Takeuchi,*[b] *Ritsuko Nagahata,**[b] *and Masayoshi Higuchi**[a]

[a]*Electronic Functional Macromolecules Group, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[b]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan.*

Contents

1. ^{1}H-^{1}H COSY NMR spectrum of the model complex

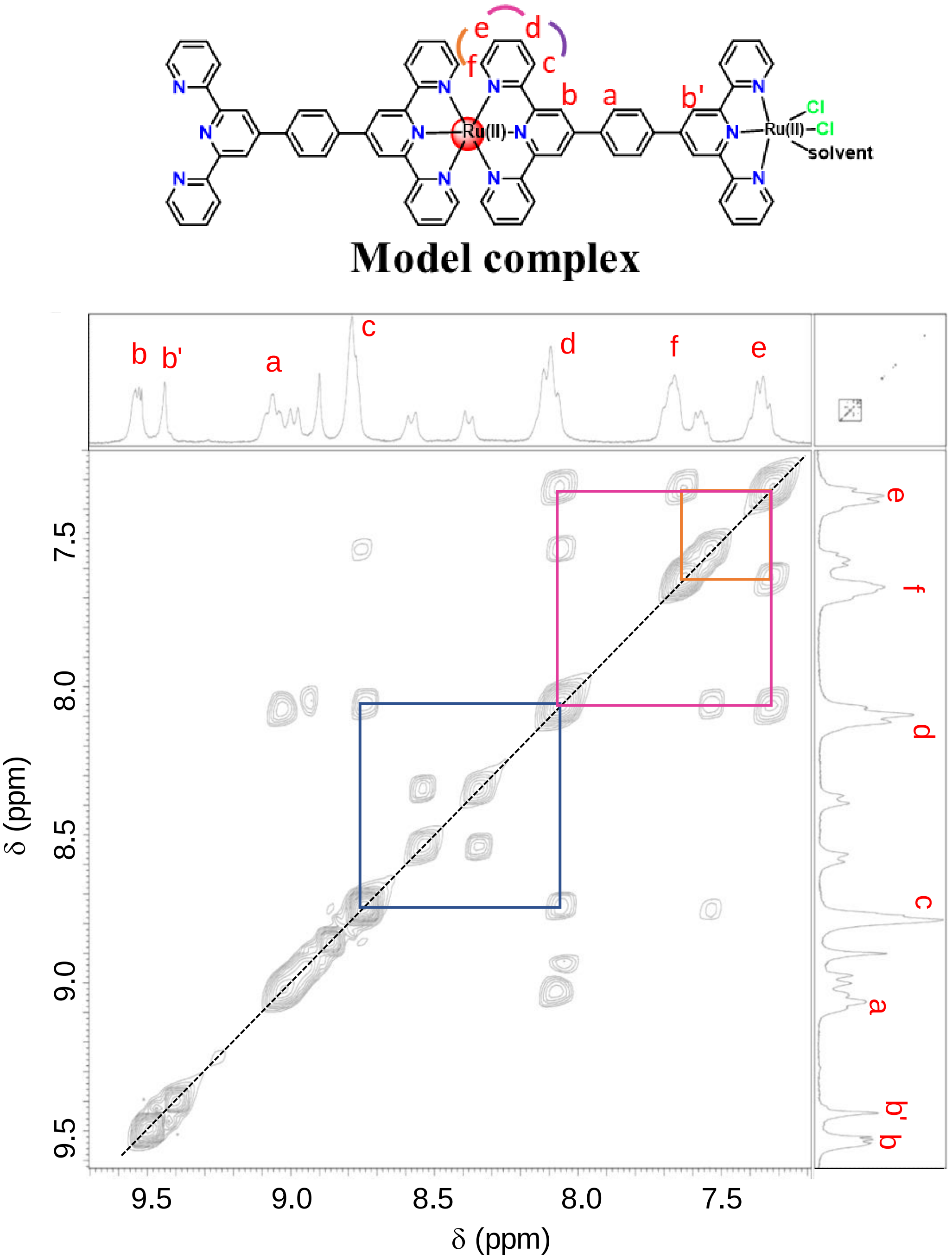


Figure S1. ^{1}H-^{1}H COSY NMR spectrum of the model complex in CD_3OD at room temperature.

2. ^{1}H-^{1}H NOESY NMR spectrum of the model complex

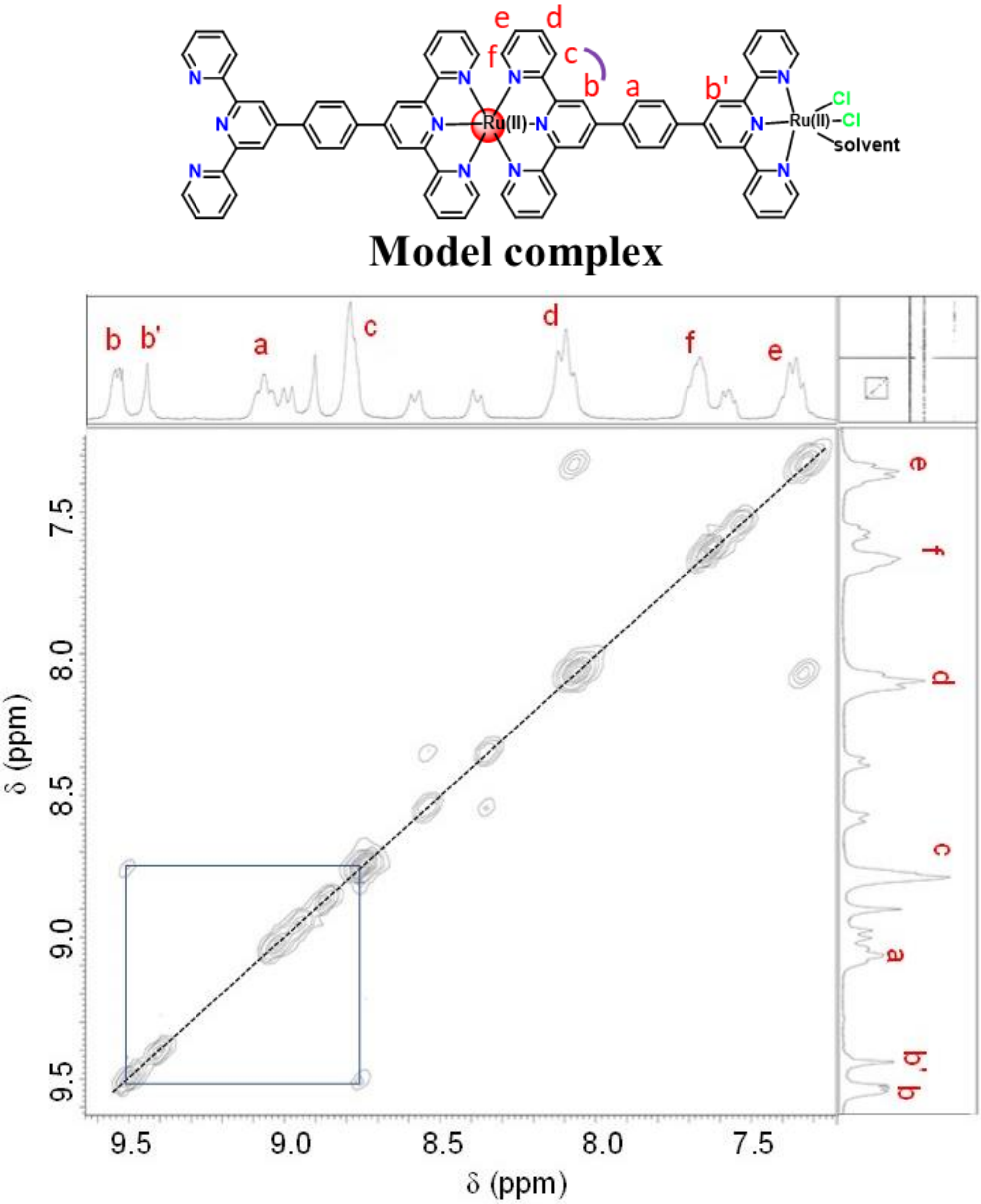


Figure S2. ^{1}H-^{1}H NOESY NMR spectrum of the model complex in CD_3OD at room temperature.

3. Electrochromism of polyRu-CS

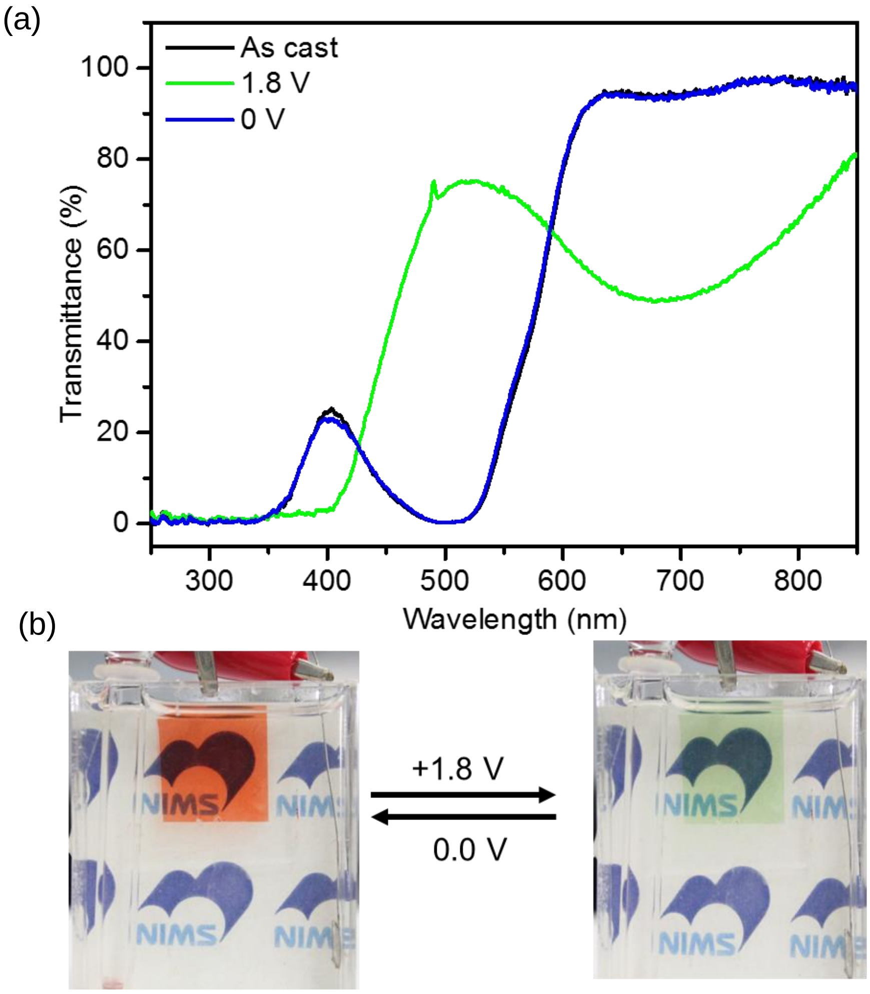


Figure S3. (a) *In situ* UV–vis spectra of a **polyRu-CS** film in 0.1 M $LiClO_4$/ACN at switching potentials of 0 and 1.8 V. (b) Corresponding color switching of a **polyRu-CS** film operated at 0 and 1.8 V (2.5 × 2.5 cm).