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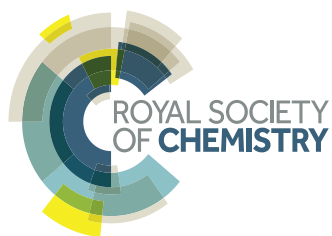


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# Stimuli-responsive metallo-supramolecular polymer films: design, synthesis and device fabrication

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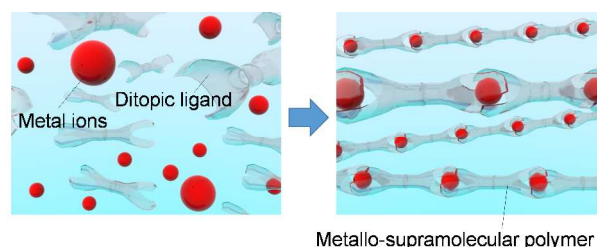
Metallo-supramolecular polymers, which were synthesized by the 1:1 complexation of metal ions with ditopic organic ligands, showed unique electro- and photo-chemical properties based on the metal-ligand or metal-metal interactions. Fe(II)-, Ru(II)- and Cu(II)-based metallo-supramolecular polymer films exhibited reversible electrochromic behaviour and the electrochromic display devices were successfully fabricated. The polymer with both Fe(II) and Ru(II) ions illustrated multi-colour electrochromic properties. Ionic conductivity of the Ni(II)-based polymer film was significantly enhanced with increasing humidity and real-time humidity sensing was realized by utilizing the polymer film. The Eu(III)-based polymer showed vapoluminescence. Reversible switching of emission was achieved in the polymer with Fe(II) and Eu(III) ions introduced alternately.

## 1. Introduction

Since Staudinger demonstrated the existence of “polymer” more than 90 years ago,<sup>1</sup> polymer science has greatly developed and the industrial products such as plastics and rubbers have made our daily life comfort and convenient. In general, organic polymers are synthesized *via* polymerization of the monomers, which is accompanied by covalent bonds formation. On the other hand, metallo-supramolecular polymers,<sup>2-4</sup> which are synthesized by the 1:1 complexation of metal ions and ditopic organic ligands (Scheme 1), are a new type of polymers in the point that the polymer backbone consists of coordination bonds. The most distinguished difference in the polymer structure between the conventional organic polymers and metallo-supramolecular polymers is that the chain length of metallo-supramolecular polymers is not fixed in solution unlike the conventional polymers, because the complexation is an equilibrium reaction. A major difference regarding the properties is that unique electronic and optical properties that are difficult to be realized using organic polymers are expectable in metallo-supramolecular polymers, by utilizing the intramolecular metal-ligand and/or metal-metal interactions through the polymer chain. It is also anticipated that electrochemical, photochemical or the other stimuli to the metallo-supramolecular polymers change the properties. For example, Rowan *et al.* reported multi-stimuli, multi-responsive metallo-supramolecular polymers.<sup>5</sup> I focus on the electro- and photo-chemical properties in the film state of metallo-supramolecular polymers from the viewpoint of device applications. Film preparation is essential to the solid-state device fabrication. Amorphous, uniform films of the metallo-supramolecular polymers were obtained by general film-preparation methods including spin-coating and spray-coating of the polymer solution.<sup>6-8</sup>

This feature article describes (1) design and synthesis of Fe(II)-, Ru(II)-, Cu(II)-, Ni(II)- and Eu(III)-based metallo-

supramolecular polymers and the bimetallic system (Fe(II)/Ru(II)- and Eu(III)/Fe(II)-based heterometallo-supramolecular polymers), (2) their unique electro- and photo-chemical properties including electrochromism, multi-colour electrochromism, ionic conductivity, humidity sensing, vapoluminescence and electrochemical switching of emission and (3) solid-state device fabrication using the polymer film.



Scheme 1. Metallo-supramolecular polymer formation *via* the 1:1 complexation of metal ions and ditopic organic ligands.

## 2. Electrochromism

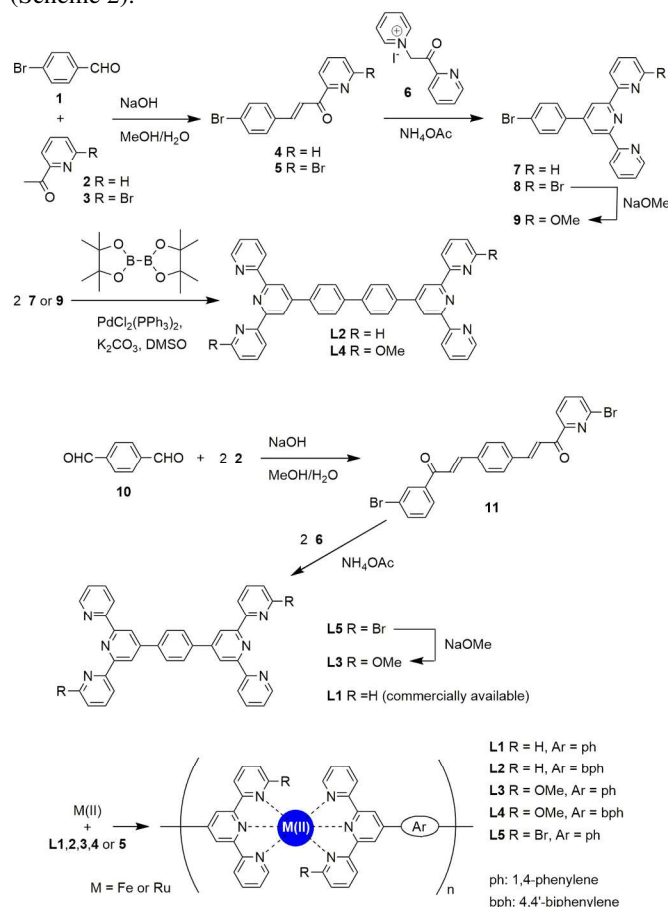
### 2.1 Chromism

Chromism is defined as colour change of materials by external stimuli. The colour change means absorption change in the visible region. Photo excitation of *d* electrons in metal complexes or  $\pi$ - $\pi^*$  transition in conjugated organic compounds are a main player in chromism due to the transition energy (1.65 – 3.26 eV) fitting the visible region (380 – 750 nm). The representative stimuli which cause chromism are heat, light, solvents, vapour and electrics. They are called thermochromism,<sup>9,10</sup> photochromism,<sup>11,12</sup> solvatochromism,<sup>13,14</sup> vapochromism<sup>15,16</sup> and electrochromism,<sup>6,17-27</sup> respectively. Electrochromism has received special attention for the display device application, because the electrically controlled colour

change is suitable to the device application. Actually, electrochromic “smart window” is now loaded in the newest airplane (Boring 787). Electrochromic (EC) materials have been widely studied for more than 40 years. Since the first report on an EC compound was done by Deb in 1969,<sup>17</sup> metal oxides,<sup>18,19</sup> transition metal complexes,<sup>20-23</sup> and organic molecules & conducting polymers<sup>24-27</sup> have been widely investigated. As a new (the fourth) generation of EC materials, we focus on electrochromism in metallo-supramolecular polymers.<sup>6,28</sup>

## 2.2 Fe(II)- and Ru(II)-based metallo-supramolecular polymers

Bis(terpyridine)s are often used as a ditopic ligand in the Fe(II)-, Co(II)-, Ru(II)- and Zn(II)-metallo-supramolecular polymers.<sup>3</sup> We tried to introduce an electron releasing or withdrawing group to the 6-position of the terpyridine moieties in bis(terpyridine)s for the purpose of controlling the metal-to-ligand charge transfer (MLCT) band electronically in the metallo-supramolecular polymers.<sup>6b,28a,29</sup> In addition, a 1,4-phenyl or 4,4'-biphenyl group was introduced as the rigid and linear spacer connecting two terpyridine units in the ligand in order to prevent macro-cyclization of the metallo-supramolecular polymer chain during the complexation (Scheme 2).



Scheme 2. Synthesis of **L2-4**, the structure of **L1**, and formation of Fe(II)- and Ru(II)-based metallo-supramolecular polymers by the 1:1 complexation of the metal ions and bis(terpyridine)s (**L1-5**).<sup>6a-c</sup>

1,4-Bis(2,2':6',2''-terpyridine-4'-yl)benzene (**L1**) is commercially available (Ardrich). 4,4'-Bis(2,2':6',2''-terpyridine-4'-yl)biphenyl (**L2**) was synthesized *via* Suzuki-

type cross-coupling of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**7**). In order to introduce a bromo group to the 6-position of the terminal pyridine ring in **7**, two-step Kröhnke procedure was used: an aldol condensation of 4-bromobenzaldehyde (**1**) and 2-acetyl-6-bromopyridine (**2**), followed by a Michael addition of the resultant azachalcone (**5**) with pyridinium iodide (**6**). Interestingly, nucleophilic substitution of the obtained 2-bromo-4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**8**) by NaOMe yielded 2-methoxy-4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**9**) preferentially, though **8** has two bromo groups. 4,4'-Bis(6-methoxy-2,2':6',2''-terpyridine-4'-yl)biphenyl (**L4**) was obtained *via* Suzuki-type cross-coupling of **9**. Similarly to the synthesis of **8**, 1,4-bis(6-bromo-2,2':6',2''-terpyridine-4'-yl)benzene (**L5**) was prepared by two-step Kröhnke procedure: an aldol condensation of benzene-1,4-dicarboxaldehyde (**10**) and **2**, followed by a Michael addition of the resultant azachalcone (**11**) with **6**. 6,6''-Disubstituted bis(terpyridine)s were also synthesized,<sup>28a</sup> but they showed very low complexation ability to Fe(II) ions, probably because the complexation was prevented by the steric hindrance of the two substituents. On the other hand, the non-substituted bis(terpyridine)s (**L1** and **L2**) and the mono-substituted bis(terpyridine)s (**L3-5**) were complexed with the transition metals to form the corresponding metallo-supramolecular polymers. Fe(II)- and Ru(II)-based metallo-supramolecular polymers (**polyFeL1-5** and **polyRuL1-5**) were synthesized by the 1:1 complexation of Fe(II) or Ru(II) ions with **L1-5**.<sup>6a-c</sup>

In UV-vis spectra of **polyFeL1-5** and **polyRuL1-5**, the MLCT absorption of the Fe(II) and Ru(II) complex moieties appeared around 580 and 520 nm, respectively.<sup>6a-c,n</sup> The maximum wavelength ( $\lambda_{\max}$ ) and absorption coefficient ( $\epsilon$ ) were summarized in Table 1. As to the Fe(II) polymers, the absorption was blue-shifted by the introduction of a biphenyl group to the ligand as the spacer. The introduction of methoxy groups to the ligand as an electron releasing group caused the large decrease of  $\epsilon$  without changing the  $\lambda_{\max}$ . The introduction of bromo groups as an electron withdrawing group resulted in the large decrease of  $\epsilon$  and the red-shift of  $\lambda_{\max}$ . In **polyRuL1-5**, similarly to the Fe(II) polymers, the introduction of a biphenyl group to the ligand as the spacer led to the blue-shift of absorption. The introduction of methoxy groups to the ligand caused the large decrease of  $\epsilon$  and the red shift of  $\lambda_{\max}$  by 20 nm. The introduction of bromo groups resulted in the large decrease of  $\epsilon$  and the blue-shift of  $\lambda_{\max}$ . It is considered that the different substituent effects to  $\lambda_{\max}$  and  $\epsilon$  between **polyFeL1-5** and **polyRuL1-5** depend on subtle difference in the complex structure of the metal species. As the whole tendency, the MLCT absorption in **polyRuL1-5** appeared shorter wavelength and have higher  $\epsilon$  than that in **polyFeL1-5**, probably due to the stronger  $\pi$ -backbonding of **L1-5** to Ru(II) than Fe(II)<sup>30</sup> and a stronger dynamic chelate effect of **L1-5** to Ru(II) than Fe(II).<sup>31</sup>

In cyclic voltammograms (CVs) of **polyFeL1-5** and **polyRuL1-5**, a redox wave was observed according to the redox of Fe(II)/(III) and Ru(II)/(III).<sup>6a-c</sup> The results clearly show the shift to less oxidative potential by the introduction of electron releasing groups (methoxy groups) and the shift to more oxidative potential by the introduction of electron withdrawing groups (bromo groups), because the strong electron donation of the methoxy groups stabilized the oxidized Fe(III) state and the electron deficiency of the bromo groups unstabilized the state. The same trend was observed in **polyRuL1-5**.

Table 1. Absorption spectroscopy and electrochemistry of **polyFeL1-5** and **polyRuL1-5**.<sup>6c</sup>

	Maximum wavelength ( $\lambda_{\max}$ ), nm <sup>a</sup>	Absorption coefficient ( $\epsilon$ ), $\times 10^4$ <sup>a</sup>	Redox potential ( $E_{1/2}$ ), V vs. Ag/AgCl <sup>b</sup>
<b>PolyFeL1</b>	585 <sup>6m</sup>	3.03 <sup>6m</sup>	0.77
<b>PolyFeL2</b>	579	2.57	0.78
<b>PolyFeL3</b>	585	1.43	0.70
<b>PolyFeL4</b>	578	1.67	0.70
<b>PolyFeL5</b>	612	0.77	0.93
<b>PolyRuL1</b> (in methanol)	513	4.10	0.95
	508 <sup>6m</sup>	4.00 <sup>6m</sup>	
<b>PolyRuL2</b>	502	3.55	0.95
<b>PolyRuL3</b>	536	2.54	0.84
<b>PolyRuL4</b>	524	2.25	0.85
<b>PolyRuL5</b>	507	3.25	1.16

<sup>a</sup>For the UV-vis. spectral measurements of **polyFeL1-5** and **polyRuL1-5**, methanol and methanol/water (4:1) were used, respectively. <sup>b</sup>The CV measurement was done under the following conditions: working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: 0.10 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile; scan rate: 100 mV/s.

A **polyFeL1** film prepared on an indium tin oxide (ITO) glass by casting the methanol solution showed electrochromic change from blue to colourless by applying a positive potential more than 1.0 V vs. Ag/AgCl (Fig. 1).<sup>6a-c</sup> On the contrary, the colourless film changed to the original blue colour by applying a negative potential less than 0.0 V vs. Ag/AgCl. These electrochromic changes were reversible.

The electrochromic change in a **polyFeL1** film was monitored by *in situ* UV-vis. spectral measurement while applying a voltage: UV-vis. spectra of a thin film of **polyFeL1**, which was prepared on an ITO glass by casting the methanol solution and inserted into a quartz cuvette (path length: 10 mm) bearing necks to introduce counter and reference electrodes and argon gas, were measured while applying a voltage (working electrode: ITO; counter electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: 0.10 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile). The MLCT absorption around 586 nm disappeared at an oxidative potential more than 1.0 V vs. Ag/AgCl. On the other hand, the MLCT absorption reappeared by applying 0.0 V vs. Ag/AgCl. From the comparison with the redox potential of Fe ions (0.77 V vs. Ag/AgCl) in **polyFeL1**, it was concluded that the disappearance/reappearance of the MLCT absorption was caused by the electrochemical redox between Fe(II) and Fe(III) states. **PolyFeL2-5** and **polyRuL1-5** also showed electrochromic behaviour by changing the applied potential between 0 and a positive potential more than 1.0 V vs. Ag/AgCl.

The electrochromic change is explained by the energy diagram (Fig. 2): the MLCT in the visible region occurs from HOMO (the highest occupied molecular orbital) of Fe(II) (or Ru(II)) to LUMO (the lowest unoccupied molecular orbital) of the ligand in the complex moieties of the polymers. When the Fe(II) (or Ru(II)) ions are oxidized to Fe(III) (or Ru(III)), a *d*-electron is removed from the metal ion and the charge transfer to the ligand does not happen any more due to the increase of bandgap by the lowering of the HOMO potential of the metal ions.

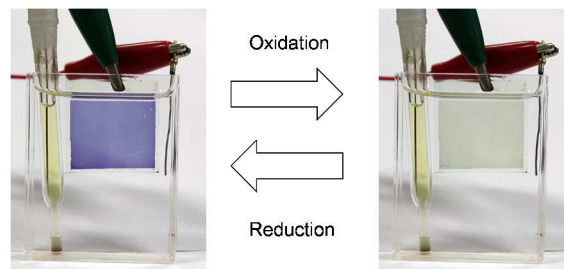


Figure 1. Electrochromic behaviour of a **polyFeL1** film on an ITO electrode (counter electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: 0.10 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile).

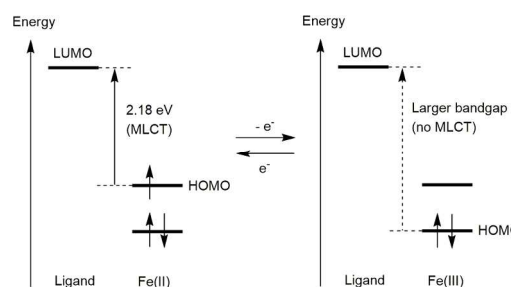


Figure 2. A possible mechanism for the electrochromic change in a **polyFeL1** film.

The colour of metallo-supramolecular polymers is decided by the bandgap of MLCT, which is controllable by selecting the metal ion species, because their HOMO potentials are different. **PolyFeL1-5** were bluish coloured polymers and **polyRuL1-5** were reddish. In addition, the modification of bis(terpyridine)s also altered the colour of metallo-supramolecular polymers to some extent, though it was not drastic, due to the different LUMO potentials of the ligands. These results indicate that various colours can be realized by the proper combinations of metal ions and ditopic ligands in the metallo-supramolecular polymer synthesis.

An electrochromic solid-state device with a **polyFeL1** film was successfully fabricated by combining with a gel electrolyte (Fig. 3a).<sup>6g,6h,6o</sup> A **polyFeL1** film was prepared on an ITO glass by spin-coating the methanol solution (2.0 mg/mL). A gel electrolyte, which was made by mixing poly(methylmethacrylate) (PMMA) (7.0 g), propylene carbonate (PC) (20 mL) and LiClO<sub>4</sub> (3.0 g), was coated on another ITO glass. The **polyFeL1** film on an ITO glass and the gel electrolyte layer on an ITO glass were stuck through an insulating film in which an arbitrary image was cut off. When a voltage more than 2.5 V was applied between two ITO electrodes of the fabricated device, the colourless image appeared immediately on the blue screen (Fig. 4), because Fe(II) ions in the **polyFeL1** film was oxidized to Fe(III) electrochemically (Fig. 3b). It was found that the device has a memory property: the colourless image was maintained even after turning off the power. The bleaching/colouring speed and the memory time greatly depended on the applied voltage and the thickness of the gel electrolyte layer, respectively. When the opposite voltage was applied, the colourless image disappeared by changing the colourless part to blue. The behaviour means that Fe(III) ions were reduced to Fe(II) electrochemically. The insulating film was important to exhibit an image, because the film prevents the ion transfer between the gel electrolyte layer and the **polyFeL1** film in the device. When the colour of **polyFeL1** in the device changes from blue to colourless,



electron transfer happens from the **polyFeL1** film to the ITO electrode. At the same time, anion transfer occurs from the gel electrolyte layer to the **polyFeL1** film to neutralize the change in the positive charge of the metal ions (from Fe(II) to Fe(III)). Therefore, the **polyFeL1** part covered with the insulating film did not show any colour changes even when a voltage was applied to the device, because the anion transfer did not occur.

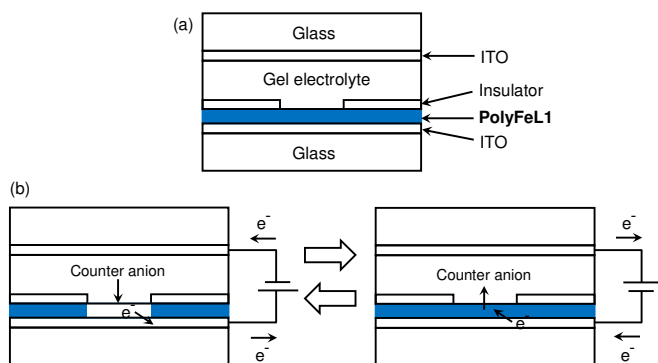


Figure 3. (a) A solid-state device structure with a **polyFeL1** film as the EC layer. (b) A mechanism of the EC behaviour.<sup>6g,6h,6o</sup>

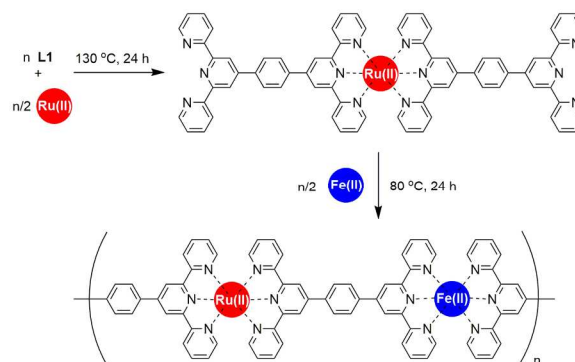


Figure 4. An electrochromic device with a **polyFeL1** film.

### 2.3 Fe(II)/Ru(II)-based heterometallo-supramolecular polymers

Since Fe(II) and Ru(II) have a similar octahedral coordination structure with six coordination sites, it is anticipated that the complexation of the two metal ion species and a bis(terpyridine) derivative at the molar ratio of 0.5:0.5:1 results in the formation of Fe(II)/Ru(II)-based heterometallo-supramolecular polymers bearing the both ion species. Though the basic concept of heterometallo-supramolecular polymers was reported in 2007,<sup>6a</sup> a series of Fe(II)/Ru(II)-based heterometallo-supramolecular polymers (**polyFe<sub>0.75</sub>Ru<sub>0.25</sub>L1**, **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** and **polyFe<sub>0.25</sub>Ru<sub>0.75</sub>L1**) were recently synthesized by changing the molar ratio of Fe(II) and Ru(II) to 0.75:0.25, 0.5:0.5 and 0.25:0.75.<sup>6n</sup> The synthetic procedure of **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** was shown in Scheme 3. The obtained polymers (**polyFe<sub>0.75</sub>Ru<sub>0.25</sub>L1**, **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** and **polyFe<sub>0.25</sub>Ru<sub>0.75</sub>L1**) showed different colours (bluish purple, purple, reddish purple, respectively) based on the different absorbance ratio of two MLCT absorptions, which originated from the Fe(II) complex (blue) and Ru(II) complex (red) moieties. In CVs of **polyFeL1** and **polyRuL1**, the redox waves ( $E_{1/2}$ ) of Fe(II)/(III) and Ru(II)/(III) appeared at 755 and 933 mV, respectively (working electrode: ITO glass (active area:  $1 \times 1 \text{ cm}^2$ ); reference electrode: Ag/Ag<sup>+</sup>; counter electrode: Pt wire; electrolyte: 0.1 M LiClO<sub>4</sub>, scan rate: 20 mV/s; polymer film preparation on the ITO glass: spray coating). In CVs of the Fe(II)/Ru(II)-based heterometallo-supramolecular polymers, two redox waves were observed ( $E_{1/2}$ s of the two redox waves

in **polyFe<sub>0.75</sub>Ru<sub>0.25</sub>L1**: 759 and 913 mV; **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1**: 764 and 919 mV; **polyFe<sub>0.25</sub>Ru<sub>0.75</sub>L1**: 769 and 927 mV) (Fig. 5). The redox potential of Fe(II)/(III) was positive-shifted with increasing the ratio of Ru ions in the polymers. At the same time, the redox potential of Ru(II)/(III) was negative-shifted with increasing the ratio of Fe ions in the polymers. These shifts clearly suggest the intramolecular metal-metal interaction between the adjacent Fe and Ru through the  $\pi$ -conjugated ligand.



Scheme 3. Stepwise synthesis of an Fe(II)/Ru(II)-based heterometallo-supramolecular polymer.<sup>6n</sup>

These shifts also indicate that successive Fe-Fe and Ru-Ru sequences exist in **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1**, because the redox potentials of Fe ions between **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** and **polyFe<sub>0.25</sub>Ru<sub>0.75</sub>L1** (or the redox potentials of Ru ions between **polyFe<sub>0.75</sub>Ru<sub>0.25</sub>L1** and **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1**) are different. If the alternate introduction of Fe(II) and Ru(II) ions is perfectly achieved in **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1**, the two potentials should be almost same, because the adjacent ions of each Fe ion are Ru ions (or the adjacent ions of each Ru ion are Fe ions) in the both polymers. It is considered that the irregular sequences of Fe(II) and Ru(II) ions in **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** were caused by the formation of Ru(II) dimer, trimer and the other oligomers during the first complexation of **L1** and 0.5 equivalent of Ru(II) ions.

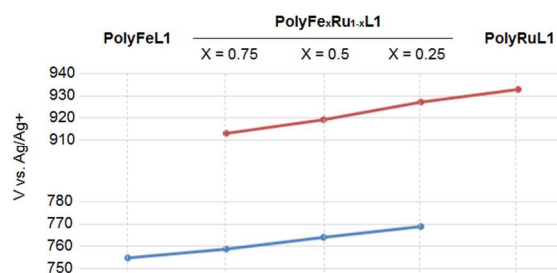


Figure 5. The shift of redox potentials in Fe(II)/Ru(II)-based heterometallo-supramolecular polymers.<sup>6n</sup>

The Fe(II)/Ru(II)-based metallo-supramolecular polymer films showed multi-colour electrochromic properties (from purple, orange to colourless) by increasing an applied potential from 0 to 1.1 V vs Ag/Ag<sup>+</sup>, because the Fe and Ru ions in the polymers have different redox potentials. In the UV-vis. spectrum of a **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** film, two MLCT absorptions based on the Fe(II) and Ru(II) complex moieties were observed at 585 and 508 nm, respectively. *In situ* UV-vis. spectral measurement revealed the absorbance change while applying a

voltage (electrolyte: 0.1 M LiClO<sub>4</sub>/acetonitrile). When applying a positive potential to the polymer film, only the MLCT absorption attributed to the Fe(II) complex moieties at 585 nm slightly decreased at 0.7 V vs Ag/Ag<sup>+</sup>. At 0.8 V vs Ag/Ag<sup>+</sup>, the absorption decreased greatly and that of Ru(II) at 508 nm also began to decrease. At 0.9 V vs Ag/Ag<sup>+</sup>, the absorption of Fe(II) almost disappeared, but that of Ru(II) still remained. Finally, the absorption of Ru(II) totally disappeared at 1.1 V vs Ag/Ag<sup>+</sup>. Based on the different oxidation potentials of Fe(II) and Ru(II) ions in the polymer, the two MLCT absorptions disappeared stepwise by the electrochemical oxidation of Fe(II) to Fe(III) and the subsequent oxidation of Ru(II) to Ru(III).

To evaluate the response time and durability of the polymer film for the EC change, the transmittance change at 508 nm in a **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** film was monitored between 0 and 1.1 V vs Ag/Ag<sup>+</sup> while changing the interval time. The polymer film showed the transmittance difference ( $\Delta T$ ) of 69.8, 68.3 and 67.2% between the coloured and bleached states by the potential application with the interval of 10, 5 and 2.5 sec, respectively. The colour change was so quick: the bleaching and colouring times (the time needed for 95% change of  $\Delta T$ ) were calculated to be 1.5 and 0.4 sec, respectively. High durability (reversibility) in the electrochromic changes was confirmed by applying 0 and 0.9 V repeatedly (only 0.7 and 1.8% charge loss in 5,000 and 10,000 cycles, respectively).

Colouration efficiency ( $\eta$ ) is a useful index to evaluate the energy consumption during the EC change. The amount of optical density change ( $\Delta OD$ ) induced as a function of the injected/ejected electronic charge ( $Q_d$ ) was measured and is given by eq. 1.

$$\eta = \Delta OD / Q_d = \log(T_b/T_c) / Q_d \quad (\text{eq. 1})$$

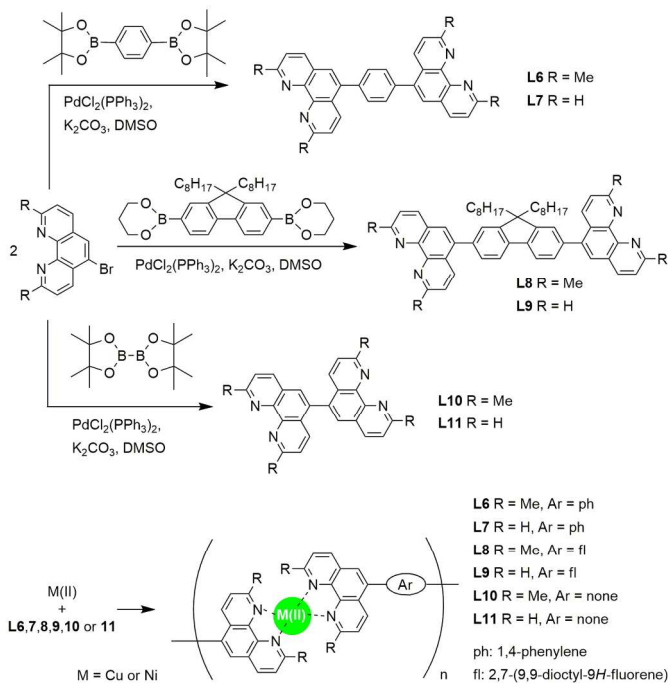
where  $\eta$  (cm<sup>2</sup>/C) is the colouration efficiency at a given  $\Delta OD$  and  $T_b$  and  $T_c$  are transmittance in the bleached and coloured states, respectively. The  $Q_d$  was calculated from the current change as a function of time while applying a potential. The  $\eta$ s of a **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** film were calculated to be 188.2 and 242.1 cm<sup>2</sup>/C for the switching between 0 and 0.9 V and 0 and 1.1 V, respectively.

When the CVs of a **polyFe<sub>0.5</sub>Ru<sub>0.5</sub>L1** film were measured at various scan rates from 10 to 500 mV/s, the peak currents of the Fe and Ru ions were linearly enhanced upon an increase of the scan rate. This result suggests that the redox reactions are kinetically controlled, probably because the diffusion of the counter anions in the electrolyte solution to compensate the positive charge's change of metal ions during the redox is faster than the electron transfer in the polymer film. It also indicates low conductivity of the polymer film.

## 2.4 Cu(II)-based metallo-supramolecular polymers

In order to introduce metal ions with a tetrahedral or square planar coordination structure such as Ni(II), Cu(II) and Pt(II) to the metallo-supramolecular polymer chain, new ditopic ligand with two bidentate coordination sites are necessary to be synthesized. 1,10-Phenanthroline is the good candidate because of the high binding affinity to the metal ions,<sup>32</sup> but the previous reports on bis(1,10-phenanthroline)s are limited to 2,2'-linked ones.<sup>33</sup> It is considered that 5,5'-linked bis(phenanthroline)s are more suitable to obtain linear metallo-supramolecular polymers than the 2,2'-linked ones due to the lower steric hindrance.<sup>34</sup> So, we synthesized novel 5,5'-linked bis(1,10-phenanthroline)s (**L6-11**).<sup>6k,6l</sup> A Cu(II)-based metallo-supramolecular polymer

(**polyCuL9**) was prepared by the 1:1 complexation of **L9** and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Scheme 4).<sup>6k</sup>



Scheme 4. Synthesis of bis(phenanthroline)s (**L6-11**) and formation of Cu(II)- and Ni(II)-based metallo-supramolecular polymers by the 1:1 complexation of metal ions and bis(phenanthroline)s.<sup>6k,6l</sup>

The colours of Fe(II)- and Ru(II)-based metallo-supramolecular polymers are blue and red, respectively. In order to achieve RGB colours using only metallo-supramolecular polymers, a green-coloured electrochromic polymer is desired. When the green colour of **polyCuL9** was investigated by visible reflection spectroscopy, the reflection peak appeared at 524 nm, which is in the range of green colour (480-560 nm). In addition, the green colour was confirmed in CIE 1931 chromaticity diagram ( $x = 0.236$ ,  $y = 0.675$ ).

A reversible redox wave of Cu(II)/(I) was observed at around -0.8 V vs. Ag/Ag<sup>+</sup> in the cyclic voltammogram of a **polyCuL9** film (working electrode: glassy carbon; counter electrode: Pt wire; electrolyte: 0.1 M TBAP/acetonitrile; scan rate: 100 mV/s). However, the **polyCuL9** film was gradually dissolved to the electrolyte solution during the measurement. So, we investigated the electrochromic property of **polyCuL9** in the solution state. When -1.2 V vs. Ag/Ag<sup>+</sup> was applied to the solution, the green colour of **polyCuL9** disappeared. The colourless state changed to green again by applying 1.2 V vs. Ag/Ag<sup>+</sup> to the solution. The green colour is based on the MLCT absorption between Cu(II) and the ligand.<sup>35</sup> It is considered that the absorption disappeared by the reduction of Cu(II) to Cu(I).

## 3. Ionic conductivity

### 3.1 Ni(II)-based metallo-supramolecular polymers

Ionically conductive materials such as Nafion<sup>36</sup> have received much attention for energy-related applications including fuel cells and secondary batteries. It is considered that formation of hydrophilic ion channels in the hydrophobic rigid backbone is important to achieve both highly ionic conductivity and durability of the material. Metallo-supramolecular polymers,

which are synthesized by the 1:1 complexation of metal ions and ditopic ligands, have both the hydrophilic metal complex and the hydrophobic ligand moieties. Therefore, it is expected that the polymers are a good candidate of ionic conductive materials. However, there are no reports on the ionic conductivity of these polymers in the film state, as far as I know, probably because of the low ionic conduction. We revealed that ionic conductivity in Ni(II)-based metallo-supramolecular polymer films much increased at high humidity.<sup>7b</sup>

Ni(II)-based metallo-supramolecular polymers (**polyNiL8-11**) were synthesized by the 1:1 complexation of Ni(II) ions with the ligand (**L8-11**) (Scheme 7).<sup>7b</sup> Similarly, **polyNiL6** was also obtained.<sup>6l</sup>

Thin films of **polyNiL8-10** were prepared on a conductivity measuring electrode (CME). The film thickness was determined using ellipsometry to be 24.2, 21.5 and 16.0 nm, respectively. It was found that the electronic conductivity itself of the **polyNiL8-10** films is very low: only a negligible current was detected by applying a voltage of up to 6 V to the films under vacuum-dried conditions. However, interestingly, the ionic conductivity of the polymer films greatly enhanced with increasing the humidity. The Nyquist plots were obtained from the ac impedance measurement of the polymer films under the precise control of temperature and humidity using a chamber. The ionic conductivity of **polyNiL8-10**, which was calculated from the diameter of the semicircle at the high frequency region of the Nyquist plots, reached  $1.44 \times 10^{-6}$ ,  $3.2 \times 10^{-5}$  and  $0.75 \times 10^{-3}$  S/cm, respectively, at room temperature and 98%RH (relative humidity). The logarithm of the ionic conductivity ( $\log\sigma$ ) as a function of %RH showed almost linear relationship with an average slope of 0.046. The slope around  $0.07 \pm 0.03$  has been reported for ionically conductive organic polymers.<sup>37</sup>

Surprisingly, the order of hydrophobicity in the ligand moiety (**L8** (with alkyl chains and methyl groups) > **L9** (with alkyl chains) > **L10** (with methyl groups)) of **polyNiL8-10** was completely in agreement with the order of low ionic conductivity. This result indicates that the hydrophobicity of the ligand moiety prevents the ionic conduction in the polymer film. The activation energy for the ionic conduction in **polyNiL10** was investigated by the measurement of dc current at different temperatures and 98%RH (the applied voltage: 1.0 V) and determined from the Arrhenius plot to be 0.43 eV. The low activation energy indicates that the ionic conduction in the polymer film includes proton conduction based on the Grotthuss mechanism at high humidity,<sup>38</sup> probably due to the ion channel formation through the polymer chains.

### 3.2 Ionic conductivity: influence of the counter anions

Very recently we reported synthesis of Ni(II)-based metallo-supramolecular polymers with different counter anions, the ionic conductivity of the polymer film, and the real-time humidity sensing properties.<sup>7c</sup>

Ni(II)-based metallo-supramolecular polymers with different counter anions (chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), acetate (CH<sub>3</sub>COO<sup>-</sup>) and acetylacetate (CH<sub>3</sub>C(=O)CH=C(O<sup>-</sup>)CH<sub>3</sub>)) (**polyNiL10-Cl**, **-NO<sub>3</sub>**, **-ac** and **-acac**, respectively) were synthesized by the 1:1 complexation of the Ni(II) salts and **L10**.<sup>7c</sup> The polymer films were prepared on CME with 10 μm of an electrodes gap by drop-casting the polymer solution (solvent: acetonitrile/ethanol (1:1)). The prepared film thicknesses were 30.0, 36.1, 68.8 and 67.1 nm, respectively, which were determined by ellipsometry. The Nyquist plots of the polymer films were obtained by the ac impedance

measurement at 25 °C and 98%RH. The ionic conductivity of **polyNiL10-Cl**, **-NO<sub>3</sub>**, **-ac** and **-acac** was calculated from the diameter of the semicircle at the high frequency region of the Nyquist plots to be  $5.0 \times 10^{-2}$ ,  $2.4 \times 10^{-3}$ ,  $1.0 \times 10^{-5}$  and  $0.6 \times 10^{-3}$  S/cm, respectively. The results indicate the influence of the counter anion to the ionic conductivity of the polymer films. Interestingly, the polymer with "harder" anions showed higher ionic conductivity: the order of the hardness in the anions (chloride > nitrate > acetate > acetylacetate)<sup>39</sup> was in good agreement with the order of the ionic conductivity of the polymers (**polyNiL10-Cl** > **polyNiL10-NO<sub>3</sub>**, > **polyNiL10-ac** > **polyNiL10-acac**).

The ionic conductivity of the polymer films greatly depends on the humidity and increased by about four orders of magnitude while increasing the humidity from 30 to 98%RH. The plots of the logarithm of the ionic conductivity ( $\log\sigma$ ) as a function of relative humidity (%RH) for the polymer films showed almost linear relationship with similar slopes (0.05-0.06). This result suggests that the ion conduction mechanism is same among the polymers though the counter anion is different. Therefore, it is considered that water molecules play an important role in the ionic conduction in the polymer film.

*I-V* properties of **polyNiL10-Cl**, **-NO<sub>3</sub>**, **-ac** and **-acac** were measured at 98%RH and different temperature (20-80 °C). Their activation energies for the ionic conductivity were determined using the Arrhenius plots (logarithm of current as a function of 1/T) to be 0.21, 0.31, 0.32 and 0.80 eV, respectively. It is known that an activation energy less than 0.4 eV suggests the Grotthuss-type mechanism, in which protons pass along the hydrogen bonds.<sup>38</sup> These results indicate that the high ionic conductivity in **polyNiL10-Cl**, **-NO<sub>3</sub>**, **-ac** films at high humidity is achieved by efficient proton transfer through the ion channels formed by water molecules, which were assembled along the polymer chains with the help of the positive charge of Ni(II) ions and/or the negative charge of the counter anions. The activation energy more than 0.4 eV in the **polyNiL10-acac** film, on the other hand, indicates the proton transfer by the aid of a moving vehicle (additional ions or molecules),<sup>40</sup> probably because the bulky anions prevent the proton channel formation through the polymer chains.

Capacitive, thermal, and resistive methods *et al.* have been used for humidity sensing so far.<sup>41</sup> It was revealed that Ni(II)-based metallo-supramolecular polymer films serve as a humidity sensor owing to the highly humidity-responsive ionic conductivity. A **polyNiL10-Cl** film, which showed the highest ionic conductivity among **polyNiL10-Cl**, **-NO<sub>3</sub>**, **-ac** and **-acac**, was prepared on an interdigitated electrode composed of 65 pairs of Pt wires printed on quartz substrate with 10 μm gap between the paired Pt electrodes. The current of the film was measured with changing humidity (bias voltage: 1.0 V). Interestingly, with increasing the humidity from 25 to 90%RH, the conductance (1/R) of the film enhanced simultaneously. In the humidity higher than 95%RH the conductance was almost constant. The real-time humidity sensing property of the film was also confirmed by the following experiment, too. When the humidity was changed stepwise from 30%RH to 50, 70, 90, 98, 90, 70, 50 and 30%RH (duration: 30 min), a stepwise change of the conductance was observed corresponding to the humidity change.

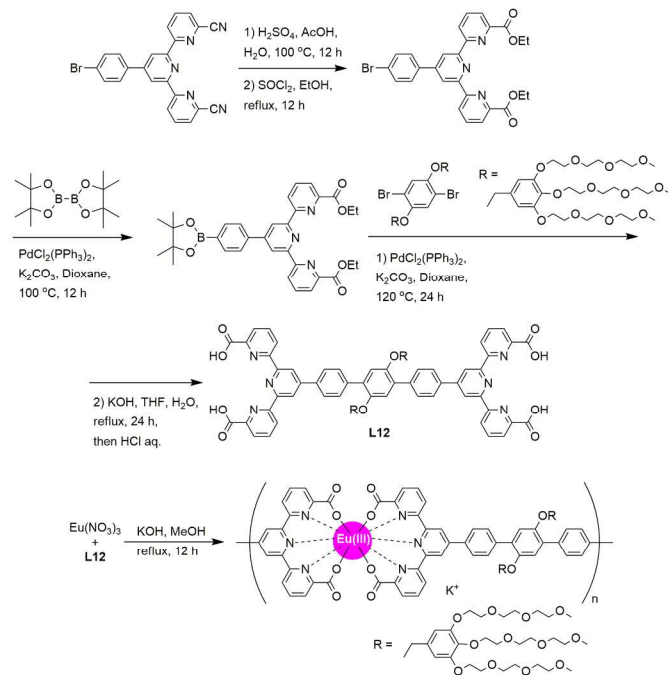
### 4. Vapoluminescence

Introduction of Fe(II), Ru(II) and Cu(II) ions to metallo-supramolecular polymer chains brings redox activity. On the



other hand, emission properties are expected in the lanthanide ion-based metallo-supramolecular polymers. The ON-OFF switching of emission by stimuli will be suitable for the applications such as sensors and displays. The luminescent change by vapour is called vapoluminescence. Some Pt or Au complexes have been reported as vapoluminescent compounds,<sup>42</sup> but the change is slow and often irreversible because the structural change of the complexes in the crystal state is required. We found that a Eu(III)-based metallo-supramolecular polymer shows quick and reversible vapoluminescence for acidic/basic vapour.<sup>8c</sup>

In general lanthanide ions have high coordination affinity to oxygen. So, we synthesized **L12**, in which two carboxylate groups were substituted to the 6,6'-positions of terpyridine moieties.<sup>8c</sup> Ethyl ester groups were introduced to terpyridine by the conversion from cyano groups. A spacer with tetra(ethylene glycol) chains was necessary to improve the solubility of the ligand. In addition, the dehydration of the ester to carboxylic acid was done last in order to prevent the decrease of the solubility during the synthesis. A Eu(III)-based metallo-supramolecular polymer (**polyEuL12**) was synthesized as a yellow solid in a 93% yield by the 1:1 complexation of Eu(NO<sub>3</sub>)<sub>3</sub> and **L12** in the presence of KOH as a base (Scheme 5).



Scheme 5. Synthesis of **L12** and **polyEu**.<sup>8c</sup>

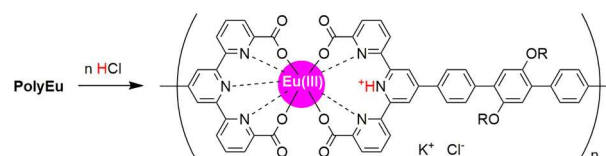
**PolyEuL12** is soluble in methanol and the free-standing polymer film was prepared by a solvent-casting method. The film showed bright-red emission under a UV lamp ( $\lambda_{\text{ex}} = 365$  nm) (Fig. 6). In order to investigate the photophysical properties, a thin film of **polyEuL12** was prepared by spin-coating the methanol solution (20  $\mu\text{M}$ ). In the emission spectrum of the **polyEuL12** film, sharp peaks based on the  $^5\text{D}_0 \rightarrow ^7\text{F}_{1-4}$  in Eu(III) ions appeared upon the excitation at 365 nm. Especially, the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is hypersensitive. The excitation wavelength (365 nm) is overlapped with a broad absorption (200 – 400 nm) in the spectrum of **L12**. Therefore, it is considered that the red emission of Eu(III) ions is caused by

the energy transfer from the ligands to Eu(III) ions in the polymer. A broad emission peak around 450 nm is observed in the emission spectrum of **L12**, but the emission peak of the ligand totally disappeared in the emission spectrum of the **polyEuL12** film. It suggests the efficient energy transfer from the ligands to Eu(III) ions in the polymer. The PL quantum yield ( $\Phi_{\text{FL}}$ ) of **polyEuL12** was 0.24 even in the film.



Figure 6. Red emission in a **polyEuL12** film.

Interestingly, a free-standing film of **polyEuL12** showed vapoluminescence: the ON/OFF switching of the photoluminescence occurred by exposure to basic/acidic vapour. The red emission was quenched by the exposure of HCl vapour for five seconds. The quenched film showed red emission again by the exposure of Et<sub>3</sub>N vapour for five seconds. The photoluminescence (PL) spectra of a **polyEuL12** film (thickness: 290  $\mu\text{m}$ ) supported that the emission change is caused by appearance/disappearance of the luminescence based on the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition the Eu(III) ions. The switching in the film state was reversible at least up to eight times. In addition, the switching durability of **polyEuL12** in the methanol solution was more than 40 times (600 equiv. of HCl aq. and Et<sub>3</sub>N were added as the acid and base for each switching). The high reversibility in both the solid and solution states indicate that the vapoluminescence in **polyEuL12** is not caused by the association/dissociation of the metal complex moieties. In order to investigate the stability of the emission/quenched states, the PL intensity of **polyEuL12** films kept in a polyethylene bag at room temperature was monitored after they had been exposed by acidic/basic vapour. A **polyEuL12** film exposed by Et<sub>3</sub>N vapour showed the red emission at least for 100 hours, while a **polyEuL12** film in which the emission had been quenched in the presence of HCl vapour began to show the emission in 48 hours. These results suggest that gradual evaporation of HCl from the polymer film resulted in the reappearance of the red emission. Therefore, it is considered that the partial protonation of the ligand moiety in **polyEuL12** causes the quenching of the emission. A possible structure of the protonated **polyEuL12** is shown in Scheme 6. The UV-vis spectral measurement revealed that a broad absorption around 500 nm appears in **polyEuL12** by the exposure of HCl vapour, probably because the intramolecular charge transfer (CT) absorption in the ligand moiety occurs by the partial protonation. The quenching mechanism is not still clear, but it is considered that the energy transfer to Eu(III) ions is prevented by the energy transfer to the CT band.



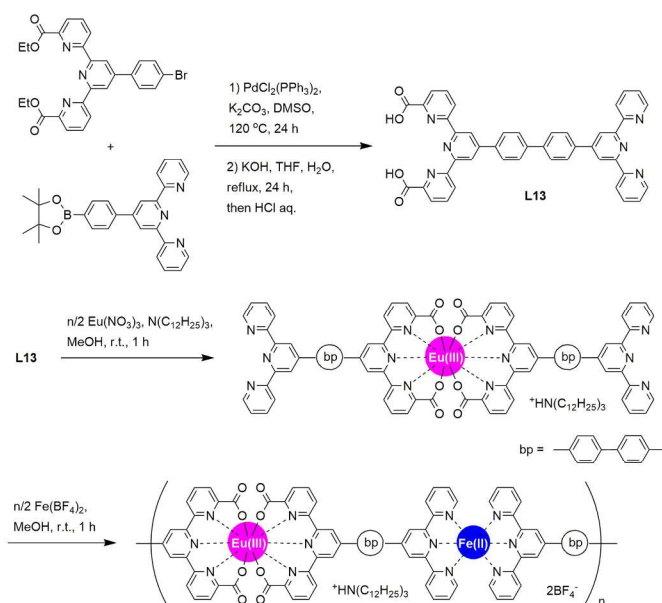


Scheme 6. A possible structure of the protonated **polyEuL12**.

## 5. Electrochemical ON/OFF switching of luminescence

An Fe(II) ion has an octahedral coordination structure with six coordination sites. On the other hand, the coordination number of a Eu(III) ion is 8-10 and Eu(III) ions especially have high affinity to oxygen. The totally different coordination structures gave a chance to introduce them alternately through the polymer chain by an unsymmetrical ligand.<sup>7d</sup>

An unsymmetrical ligand with a terpyridine and a dicarboxylic acid-substituted terpyridine moieties (**L13**) was synthesized by a Suzuki-coupling reaction of ethylcarboxylate-substituted terpyridine with an unsubstituted terpyridine using Pd catalyst, followed by the hydrolysis. A metallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (**polyEuFeL13**) was one-pot synthesized by the complexation of **L13** with 0.5 equivalent of Eu(NO<sub>3</sub>)<sub>3</sub> and the further addition of Fe(BF<sub>4</sub>)<sub>2</sub> in the presence of tridodecylamine (Scheme 7).

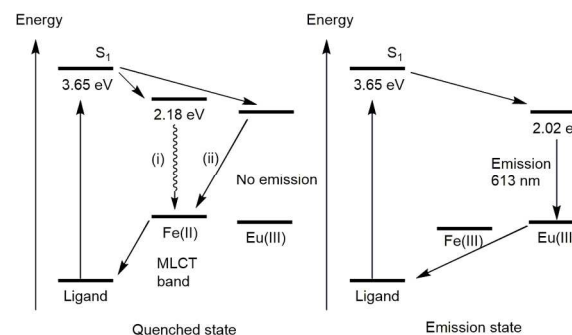
Scheme 7. Synthesis of **L13** and **polyEuFeL13**.<sup>7d</sup>

The emission spectrum of **polyEuFeL13** dissolved in ethylene glycol showed specific peaks around 550 - 720 nm attributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1,4</sub> of Eu(III) ion. However, the emission was weak (the absolute quantum yield (Φ) = 0.07) compare to that of polyEu (Φ = 0.27), probably due to the efficient energy transfer to the MLCT band (wavelength: 450 - 650 nm) from the Fe(II) ion to the ligand.

A reversible redox wave based on the redox of Fe(II)/(III) in a **polyEuFeL13** film was observed at 0.8 V vs. Ag/AgCl (*E*<sub>1/2</sub>) in the cyclic voltammogram (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile; scan rate: 100 mV/s). The redox potential is close to that of **polyFeL2** (0.78 V).<sup>6c</sup> It indicates that they have the same coordination structure, which are formed by the complexation of Fe(II) and two (non-substituted) terpyridine units. A **polyEuFeL13** film, which was prepared by solvent-casting the ethylene glycol solution on an

ITO glass, showed reversible electrochromic behaviour by applying 2.0 V vs. Ag/AgCl for the bleaching and 0 V vs. Ag/AgCl for colouring. The result suggests that the colour change is triggered by the electrochemical redox between the Fe(II) and Fe(III) states.

As abovementioned, a **polyEuFeL13** film exhibited very weak photoluminescence (PL), but it was found that the emission at 613 nm greatly enhanced at 2.0 V vs. Ag/AgCl. On the contrary the red emission was re-quenched at 0 V vs. Ag/AgCl. The ON/OFF switching of emission by the electrochemical redox could be repeated at least for 10 times. The emission change clearly corresponds to the electrochromic change: the quenching and emitting occurs simultaneously with the colouring and bleaching, respectively. The excitation spectrum of the emission was overlapped with the absorption spectrum of **L13**. It indicates that the ligand acts as the photosensitizer. The switching mechanism is not still clear, but there will be two possibilities for the quenching (Fig. 7): (i) the energy transfer from the excited state of the ligand to the MLCT band of the Fe(II) moiety and the subsequent quenching in the MLCT band and (ii) the energy transfer from the excited state of the ligand to Eu(III) and the quenching by the energy transfer to Fe(II). When Fe(II) is oxidized to Fe(III) electrochemically, the unfavourable energy transfer for the emission of Eu(III) does not occur due to disappearance of the MLCT absorption and/or lowering of the HOMO potential of Fe ions.

Figure 7. An estimated energy diagrams of the emission switching in a **polyEuFeL13** film during the electrochemical redox between Fe(II) and Fe(III).

## 6. Conclusions

In this feature article I introduced our recent research on design, synthesis, electrochemical/photochemical properties and device fabrication of Fe(II)-, Ru(II)-, Cu(II)-, Ni(II)- and Eu(III)-based metallo-supramolecular polymers and Fe(II)/Ru(II)- and Eu(III)/Fe(II)-based heterometallo-supramolecular polymers. The redox active polymers such as Fe(II)-, Ru(II)- and Cu(II)-based polymers showed electrochromic properties by the electrochemical control of the MLCT absorption. Electrochromic display devices were successfully fabricated by the combination of a gel electrolyte. The Fe(II)/Ru(II)-based polymer exhibited multi-colour electrochromism by changing the applied potential. It was revealed that high ionic conduction appeared in the nano-space inside the Ni(II)-based polymer films at high humidity. A device with the polymer film served as a real-time humidity sensor. The Eu(III)-based polymer showed a red emission even in the film state. It was found that the appearance/disappearance of the emission was reversibly

controlled by basic/acidic vapour. The ON/OFF switching of emission was achieved in the Eu(III)/Fe(II)-based polymer.

In the formation of metallo-supramolecular polymers, the number of combination of metal ions and ditopic ligands is almost infinite, as long as new ligands are created. Not only the metal-ligand and metal-metal interaction in the polymers give unique properties, but also nano-space formed by the polymer chains leads to novel functions. Actually, we are also investigating the bio-applications of the polymers by utilizing the interaction with DNA *et al.*<sup>43</sup> As described in this paper, metallo-supramolecular polymer chemistry will be further developed in the future by the fusion of wide research fields including organic synthesis, metal-coordination chemistry, physical chemistry, polymer science and device fabrication/processing *et al.*

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### Notes and references

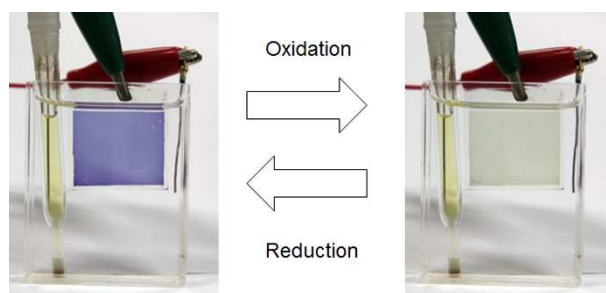
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Based on the metal-ligand or metal-metal interactions, metallo-supramolecular polymer films showed stimuli-responsively electro- and photo-chemical properties such as electrochromism.