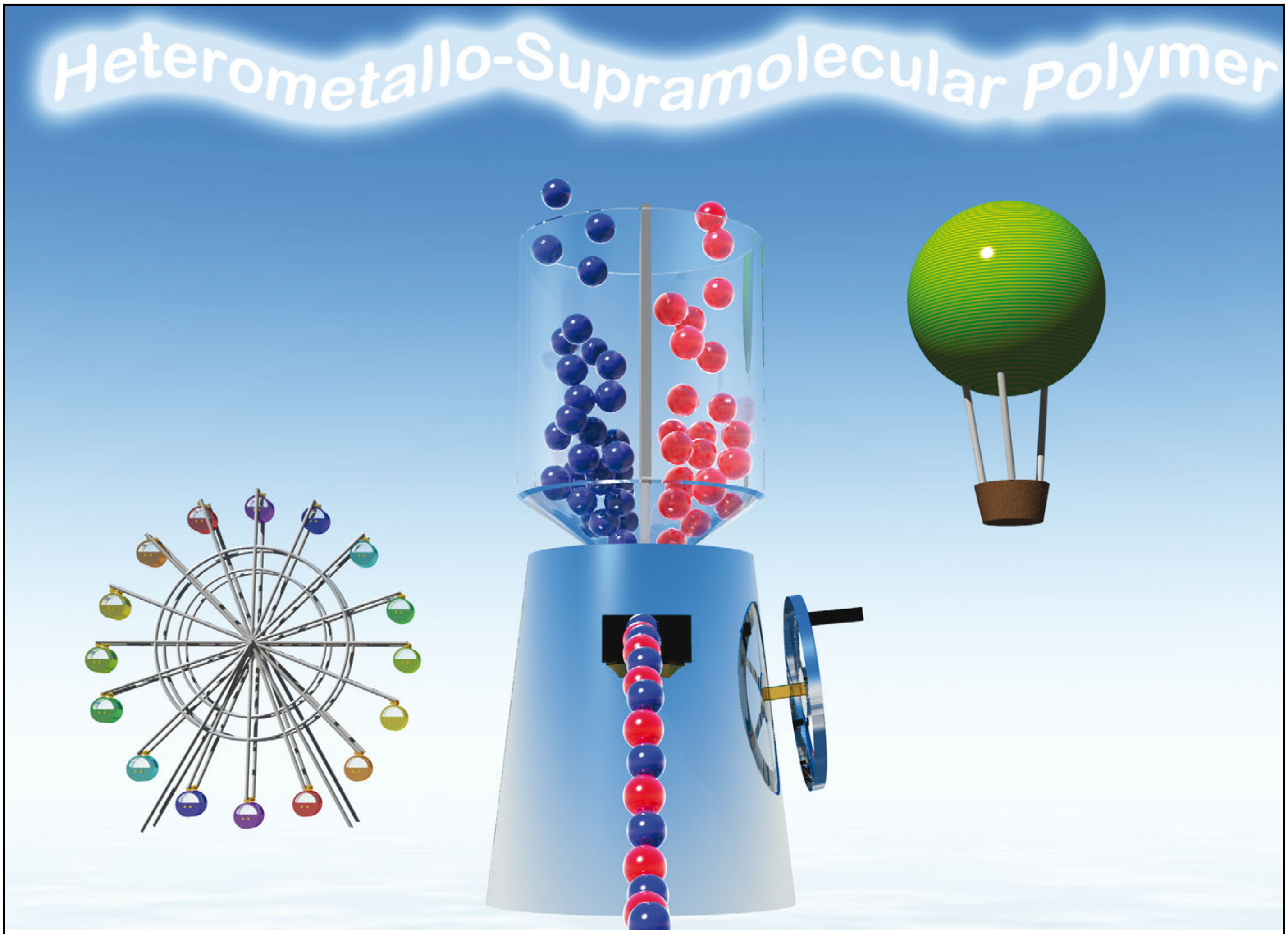

## Showcasing research from Takashi Sato and Masayoshi Higuchi at the National Institute for Materials Science, Tsukuba, Japan

**An alternately introduced heterometallo-supramolecular polymer: synthesis and solid-state emission switching by electrochemical redox**

A heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately was prepared by utilizing different coordination properties of the metal ions. Reversible "on-off" switching of the luminescence in the solid-state film was triggered by electrochemical redox.

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# An alternately introduced heterometallo-supramolecular polymer: synthesis and solid-state emission switching by electrochemical redox†

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**By utilizing different coordination properties of a lanthanide ion and a transition metal ion, a heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (polyEuFe) was precisely prepared *via* stepwise complexation of the metal ions to a new unsymmetrical ligand with both a dicarboxylate-substituted terpyridine and an unsubstituted terpyridine. The polymer showed unique, reversible "on–off" switching of the Eu(III) luminescence by electrochemical redox of the Fe ions in the solid-state.**

Lanthanide metal complexes have unique fluorescent properties including high emission quantum efficiency, a long-lived fluorescence lifetime, and a large Stokes shift.[1] Stimuli-responsive reversible "on–off" switching of the fluorescence is an attractive research target due to its potential applications such as sensors and displays.[2] The luminescence switching triggered by electrochemical redox has been already demonstrated in solution,[3] but there are no reports on the switching in the solid-state, as far as we know, despite the fact that it is essential to device application. One of the problems is difficulty in the film formation of the metal complexes on an electrode, because of their high crystallinity. So, introduction of amorphous polymeric structures into the complexes is considered to become a practical solution to obtain a uniform film.[4] Furthermore, if the fluorescent polymer complex has a redox-active site which quenches the fluorescence, a smart system of fluorescence switching driven by electrochemical redox will be constructed. We herein report alternately precise introduction of two metal ion species (Eu(III) and Fe(II)) into a metallo-supramolecular polymer structure and the reversible "on–off" switching of luminescence of Eu(III) triggered by redox of Fe(II) in a film state.

Metallo-supramolecular polymers were obtained *via* complexation of metal ions with organic ligands bearing two coordination sites.[5] We have already reported the electrochromic property of metallo-supramolecular polymers prepared from Fe(II) ions and bis(terpyridyl)benzene derivatives.[6] These polymers exhibited the metal-to-ligand charge transfer (MLCT) absorption at around 570 nm and the absorption disappeared upon the electrochemical oxidation of Fe(II) to Fe(III).[6,7] In addition, we recently succeeded in synthesizing a Eu(III)-based metallo-supramolecular polymer by complexation of Eu(III) ions with a bis(dicarboxylate-substituted terpyridyl)-benzene derivative which was prepared as a new ligand.[8] This Eu-based polymer showed red emission at 613 nm based on an f–f transition in the Eu ions. We chose Eu(III) and Fe(II) ions as the fluorescent and redox sites, respectively, in a new heterometallo-supramolecular polymer and intended to introduce them alternately into the polymer chain. An alternate alignment of two metal ion species in a metallo-supramolecular polymer is quite difficult when symmetrical ligands are used.[9] Newkome *et al.* reported an elegant higher-ordered macromolecular architecture using terpyridine derivatives and different metallic ions such as Fe and Ru,[9c,e] but heterometallo-supramolecular polymers incorporating lanthanide ions are not well known.

We synthesized an unsymmetrical bisterpyridine with both terpyridine and dicarboxylate-substituted terpyridine moieties (**L1**, Scheme 1) as a new ligand for alternate introduction of Eu(III) and Fe(II) ions into a metallo-supramolecular polymer structure. **L1** was prepared by Suzuki-coupling reaction of a dicarbonyl ester group-containing terpyridine[8] with an unsubstituted terpyridine[10] using a Pd catalyst, followed by hydrolysis. The structure of **L1** was confirmed by $^{1}$H-, $^{13}$C-NMR and HRMS spectroscopy (Fig. S1 and S2, ESI†).

Complexation behavior of **L1** with $Eu(NO_3)_3$ and $Fe(BF_4)_2$ was investigated in detail by UV-vis spectroscopic measurements (Fig. 1). The spectrum of a methanol solution of **L1** (20 μM), which was deprotonated with two equivalents of tridodecylamine, changed with addition of $Eu(NO_3)_3$ up to a molar ratio of $[Eu(NO_3)_3]/[\mathbf{L1}] = 0.5$ (Fig. 1a): the **L1** absorbance

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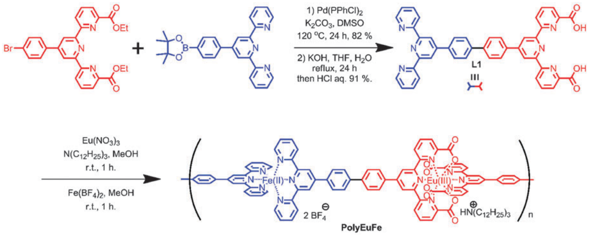
† Electronic supplementary information (ESI) available: Experimental procedures, synthesis of the polymer, UV-vis and photoluminescence spectra. See DOI: 10.1039/c3cc41176a



**Scheme 1** Synthesis of an unsymmetrical ligand (**L1**) and the heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (**polyEuFe**).

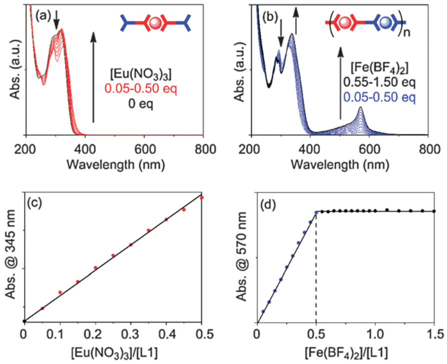


**Fig. 1** (a) UV-vis spectral change of a methanol solution of **L1** in the presence of 2 equivalents of tridodecylamine during the titration of 0–0.5 equiv. of $Eu(NO_3)_3$ at room temperature. (b) UV-vis spectral change of the solution during the addition of 0–1.5 equiv. of $Fe(BF_4)_2$. (c) The normalized absorption at 345 nm as a function of the molar ratio of $Eu(NO_3)_3$/**L1** in Fig. 1a. (d) The normalized absorption at 570 nm as a function of the molar ration of $Fe(BF_4)_2$/**L1** in Fig. 1b.

at around 345 nm increased and the one at 303 nm decreased (Fig. 1a). The absorbance at 345 nm and the molar ratio of added Eu(III) ions to **L1** showed a linear relationship (Fig. 1c). Then $Fe(BF_4)_2$ was added to the solution (**Eu(L1)$_2$**) up to a molar ratio of $[Fe(BF_4)_2]/[\mathbf{L1}] = 1.5$ (Fig. 1b). A new absorption at 570 nm based on the MLCT band appeared during the titration.[11] The MLCT absorption was clearly saturated at the ratio of $[Fe(BF_4)_2]/[\mathbf{L1}] = 0.5$ (Fig. 1d). These spectral changes suggest the formation of a heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (**polyEuFe**), according to a stepwise complexation behavior shown in Fig. S3a of ESI.† The spectrum didn't change upon the further addition of $Eu(NO_3)_3$, indicating that **polyEuFe** was stable in solution (Fig. S4, ESI†).

The proposed stepwise complexation behavior was also supported by the following additional experiments (Fig. S3a, ESI†). When $Eu(NO_3)_3$ was added to the **L1** solution at a molar ratio of $[Eu(NO_3)_3]/[\mathbf{L1}]$ greater than 0.5, the spectral change continued up to the ratio of $[Eu(NO_3)_3]/[\mathbf{L1}] = 0.66$ (Fig. S5, ESI†), which means that Eu(III) was also complexed with the unsubstituted terpyridine moiety (tpy) of **L1** with a molar ratio of Eu(III) ions : tpy = 1 : 3 after finishing 1 : 2 complexation of Eu(III) ions and a dicarboxylate-substituted terpyridine moiety ($tpy\text{-}COO^-$) of **L1**, because Eu(III) ions can form a 1 : 3 ratio complex with tpy as shown in Fig. S3b of ESI,†[12] though the binding constant is lower than that with $tpy\text{-}COO^-$.[13]

Upon addition of only $Fe(BF_4)_2$ to an **L1** solution, the MLCT absorption increased until the ratio of $[Fe(BF_4)_2]/[\mathbf{L1}] = 1.5$ (Fig. S6, ESI†). Fe(II) is first complexed with $tpy\text{-}COO^-$, probably because the binding constant of Fe(II) with $tpy\text{-}COO^-$ is higher than that with tpy due to the counter anion exchange from $BF_4^-$ to carboxylate groups. However, the bulky dicarboxylate substituents in $tpy\text{-}COO^-$ prevent the second complexation of **FeL1** with another $tpy\text{-}COO^-$. Therefore, this complexation behavior indicates that the molar ratio of Fe(II) ions and $tpy\text{-}COO^-$ in the complex is not 1 : 2 but 1 : 1 (Fig. S3c, ESI†). In fact, UV-vis titration of **L1** with the addition of $Fe(BF_4)_2$ and the second addition of $Eu(NO_3)_3$ showed no spectral change, indicating that **polyEuFe** was not obtained (Fig. S7, ESI†). Therefore, the order to add metallic ions is important for the synthesis of **polyEuFe**.

**PolyEuFe** was obtained in a one-pot synthesis by complexation of **L1** with the addition of 0.5 equiv. of $Eu(NO_3)_3$ and the further addition of 0.5 equiv. of $Fe(BF_4)_2$ in the presence of tridodecylamine (Scheme 1) as a violet solid in a 36% yield. It was soluble in alcohols such as methanol and ethylene glycol or polar solvents such as DMSO and DMF, but insoluble in the common organic solvents such as *n*-hexane, chloroform, dichloromethane, and tetrahydrofuran. Molecular weight of **polyEuFe** was determined by the SEC-Viscometry/RALLS method using poly(ethylene glycol) as standard ($M_w = 1.7 \times 10^4$, $M_w/M_n = 1.3$) (Fig. S8, ESI†),[8,11] which strongly indicated that **polyEuFe** forms a polymer structure. Polydispersity of metallo-supramolecular polymers is generally large.[14] Analyzing the structure of **polyEuFe** by NMR spectroscopy was difficult because of paramagnetic Eu(III) ions, but it was fully identified by the emission spectrum and cyclic voltammogram. The emission spectrum in ethylene glycol dilute solution exhibited characteristic peaks corresponding to the $^5D_0 \rightarrow {}^7F_{1-4}$ transitions of Eu(III) ions between the 550 and 720 nm range, which is close to the wavelength of the MLCT band of the Fe(II)–tpy complex (Fig. S9, ESI†). The intensity of emission peaks was very low (absolute quantum yield ($\Phi$): 0.07) compared with that of **polyEu** (Fig. S10, ESI†) because of the energy transfer from Eu(III) to the Fe(II)-tpy moiety. The intensity was also lower than that of the mixture of **polyEu** and metallo-supramolecular polymer including Fe(II) ions (**polyFe**)[7] ($\Phi = 0.12$) (Table S1, ESI†), which indicated that the alternate complexation of Eu(III) and Fe(II) ions promoted the effective quenching.

Cyclic voltammogram of **polyEuFe** exhibited a reversible redox wave of the Fe(II)/Fe(III) couple ($E_{1/2} = 0.8$ V) (Fig. 2a). The redox potential is similar to that of **polyFe** (0.78 V),[7] which supports the observation that Fe(II) ions form complexes with the tpy moiety of **L1** in the polymer. A film of **polyEuFe** can be prepared by many methods such as solvent-casting, spin-coating, dip and spray-coating. Among them, a thin film of **polyEuFe** was prepared on an ITO glass substrate by a solvent-casting method from an ethylene glycol solution (1 mg $mL^{-1}$) and dried *in vacuo*. The UV-vis spectra of the **polyEuFe** film in an electrolyte solution of $n\text{-}Bu_4NClO_4$ (0.10 M) showed a reversible electrochromic behavior by the electrochemical redox of Fe ions (Fig. 2b): the MLCT absorption at 570 nm of the Fe(II)–tpy complex disappeared upon the oxidation of Fe(II) to Fe(III)

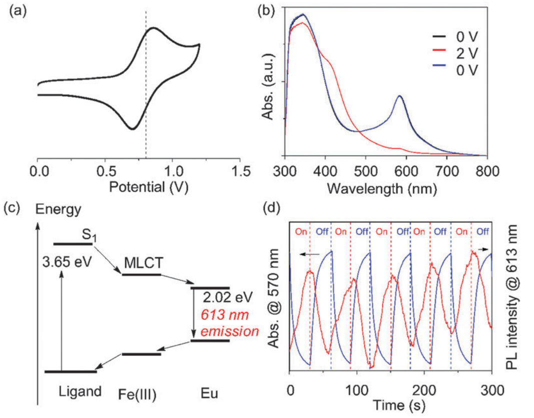


**Fig. 2** (a) A cyclic voltammogram of a **polyEuFe** film coated on a glassy carbon electrode as a working electrode at room temperature (an electrolyte solution: $n$-$Bu_4NClO_4$ (0.10 M) in argon-saturated acetonitrile; a counter electrode: a platinum wire; a reference electrode: Ag/AgCl; scan rate: 100 mV $s^{-1}$). (b) The UV-vis absorption spectra of a **polyEuFe** film on an ITO electrode at potential of 0.0 and 2.0 V (*vs.* Ag/AgCl) in an argon-saturated acetonitrile solution of $n$-$Bu_4NClO_4$ (0.10 M). (c) The estimated energy diagrams of **polyEuFe** at the oxidized state of Fe ions. (d) Photoluminescence intensity at 613 nm (ex: 340 nm) (red data) and the absorption of the MLCT band at 570 nm (blue data) of a **polyEuFe** film (switching period: 30 s).

at 2.0 V and reappeared upon the reduction of Fe(III) to Fe(II). This behavior is similar to that in **polyFe** and strongly supports the formation of the 1 : 2 complex of Fe(II) ions and tpy in **polyEuFe**.[6,7,15]

A **polyEuFe** film showed very weak photoluminescence (PL), but remarkable enhancement of the red luminescence at 613 nm was observed upon the electrochemical oxidation of Fe(II) ions to Fe(III) at 2.0 V (Fig. S11, ESI†). The red luminescence was reversibly quenched by the reduction of Fe(III) to Fe(II). The excitation spectrum of **polyEuFe** ($\lambda_{em}$ = 613 nm, Fig. S9, ESI†) indicated that **L1** acts as a photosensitizer. Therefore, the Eu emission is efficiently quenched by the energy transfer from Eu(III) to Fe(II) ions (Fig. S12, ESI†).[16] In contrast, when Fe(II) ions in **polyEuFe** were oxidized to Fe(III), the Eu emission appeared, because the energy transfer from Eu(III) to Fe(III) ions didn't occur due to the lowering of the HOMO level of Fe ions (Fig. 2c), which was confirmed by the blue-shift of the MLCT absorption band. The repeated spectral changes of the **polyEuFe**-coated ITO glass were recorded as a function of the applied potential. The luminescence intensity at 613 nm increased gradually upon incrementally increasing the potential and the absorbance of the MLCT band at 570 nm decreased at the same time. The luminescence switching was reversible at least 10 times (Fig. 2d). Therefore, **polyEuFe** works as an "on–off" luminescence switch. Exchange of counter anions from $BF_4^-$ to $ClO_4^-$ during redox reaction was indicated by the change in the solubility of **polyEuFe** after redox reaction, but the electrochromic and emission properties were not changed during the redox switching. This means that the counter anions and electrolyte do not affect the photophysical properties.

In summary, based on the different coordination properties of a lanthanide metal ion and a transition metal ion, a heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (**polyEuFe**) was precisely prepared *via* stepwise complexation of the metal ions to a new unsymmetrical ligand with both a dicarboxylate-substituted terpyridine and an unsubstituted terpyridine. **PolyEuFe** showed reversible "on–off" switching of the Eu(III) luminescence by the electrochemical redox of the Fe(II) ions in the solid-state. This strategy utilizing different coordination properties among metal species in the synthesis of heterometallo-supramolecular polymers will open the door toward designing new soft materials and exploiting smart functions to lead to applications.

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