Showcasing research from Masayoshi Higuchi’s laboratory, National Institute for Materials Science, Tsukuba, Japan.

Geometrically isomeric Pt(II)/Fe(II)-based heterometallo-supramolecular polymers with organometallic ligands for electrochromism and the electrochemical switching of Raman scattering

Heterometallo-supramolecular polymers with Pt(II) and Fe(II) ions introduced alternately were prepared by the 1 : 1 complexation of Fe(II) ions with cis- or trans-conformational organo-Pt(II) ligands.

As featured in:

See Masayoshi Higuchi et al., J. Mater. Chem. C, 2016, 4, 9428.
Geometrically isomeric Pt(II)/Fe(II)-based heterometallo-supramolecular polymers with organometallic ligands for electrochromism and the electrochemical switching of Raman scattering†

Chanchal Chakraborty,‡a Rakesh K. Pandey,‡a Utpal Rana,a Miki Kanao,a Satoshi Moriyama† and Masayoshi Higuchi*ab

Heterometallo-supramolecular polymers with Pt(ii) and Fe(ii) ions introduced alternately (cis-polyPtFe and trans-polyPtFe) in a precise way were prepared successfully by the 1:1 complexation of Fe(ii) ions with cis- or trans-conformational organo-Pt(i) ligands. The conformational difference between cis- and trans-greatly changed the morphology, crystallinity, ionic conductivity, electrochromic properties, and redox-triggered fluorescence of the polymers. The cis-polyPtFe exhibited better crystallinity and low ionic conductivity, whereas trans-polyPtFe showed an amorphous nature with high ionic conductivity. Both the polymers exhibited reversible electrochromism between purple and yellow colors due to the redox of Fe(ii)/(iii) upon applying a potential of 0 V or +3 V. The trans-polyPtFe showed better electrochromic stability and response times compared to cis-polyPtFe. In addition, the trans-polyPtFe also showed an improved response in redox-triggered Raman scattering switching compared to cis-polyPtFe over a long time range.

Introduction

Metallo-supramolecular polymers represent a new dimension that has been growing in interest over the last ten years in the area of polymer and materials science due to their utility in a wide range of applications, including sensors, memory devices, light emitting diodes, photovoltaic devices, nanolithographic templates, stimuli responsive materials in redox-tunable photonic crystals, controlled-drug release, electrochromic displays, and molecular motors.1–7 The main reason behind this considerable interest is the great versatility of their fabrication using a very simple self-assembling process between metal cations and organic ligands.8 Using such a methodology, many one (1D), two (2D), and three (3D) dimensional structures along with different metal ions have been produced and used as smart materials for various applications.9–11 The main benefits of these metallo-supramolecular polymers over their conventional covalent counterparts originate from the presence of metallic centers, providing a wide range of properties, such as optical, electrical, redox, photochemical, magnetic, or catalytic activities.12 Due to the large range of available organic ligands and metallic cations, metallo-supramolecular polymers offer the vast potential to develop smart materials with tunable properties. In this context, if two metal ions are introduced to a metallo-supramolecular polymer chain regularly, unique properties due to the neighboring metal–metal interactions are expected to appear in the polymer.13–15 The formation of heteronuclear metal complexes using different coordination environments of ditopic ligands has been widely investigated.16–23 Constable et al. used a one-pot synthesis at different temperatures to obtain two metal ion complex structures.16 Newkome et al. reported a Sierpinski hexagonal gasket-shaped supramolecule by connecting Fe, Ru, and tris-terpyridines.24 Licciardello et al. reported the electro-optical properties of trinuclear complexes with both Ru(n) and Os(n) ions.25 Again, Ag-Cu- and Ag-Zn-containing heterometallic coordination polymers were reported by Di Sun et al. to exhibit the interesting photoluminescence property of heterometallic aggregates.26–28 However, 1D heterometallo-supramolecular polymers where metal centers are incorporated alternatively are very rarely reported, except in our previous reports,13–15 while the reaction steps are not so precise to incorporate heterometals alternately.

Homometallo-supramolecular polymers were synthesized by the 1:1 complexation of metal ions and ditopic ligands (Scheme 1a), a

‡ Electronic Functional Macromolecules Group, National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan. E-mail: HIGUCHI.Masayoshi@nims.go.jp
§ International Center for Materials Nanoarchitectonics (MANA), NIMS, Tsukuba, Japan
† Electronic supplementary information (ESI) available: Characterizations of ligands and cis- and trans-polyPtFe by different 1H and DOSY NMR techniques, electrochromic device fabrication for electrochromic measurements, emission study and Raman spectroscopy. See DOI: 10.1039/c6tc02929a
but the alternate introduction of heterometallic centers precisely in a polymer chain is very challenging. Scheme 1b exhibits a preparation method of a heterometallo-supramolecular polymer using an asymmetrical ligand.\(^{14}\) The synthetic procedure is smart, but highly selective complexation between the two metal ion species and the two coordination sites of the asymmetrical ligand are required to obtain the desired polymer structure. In order to develop divergent syntheses of heterometallo-supramolecular polymers, in the present study we focused on organometallic bonds. When ditopic ligands include metal species by organometallic bonds formation, heterometallo-supramolecular polymers are considered to form by the 1:1 complexation of the organometallic ligand and another metal ion (Scheme 1c). The obtained polymers are also expected to show unique electronic/optical properties based on the metal-metal interactions through the organometallic bonds. Alongside this, the other advantage of organometallic ligands is that it is possible to prepare two geometrical isomeric organometallic ligands (cis- and trans-) and their corresponding heterometallo-polymer from one precursor organic ligand by just changing the metal salts used for preparing their corresponding heterometallo-polymers from one precursor.

Recently, Fe(II)-based metallo-supramolecular polymers with bis(terpyridine) as ditopic ligands were extensively investigated as fourth generation electrochromic materials due to its redox-triggered color change from purple (Fe(II)) in the reduced state to colorless (Fe(III)) in the oxidized state.\(^{1,7,9,14,15,29–32}\) The electrochromic behaviors of metallo-supramolecular polymers have been widely investigated, but the correlation between the polymer structures, especially the structural characteristic, and the electrochromic activities has not been elucidated yet.

It has been reported that platinum acetylide-based organometallic oligomers and polymers are \(\pi\)-conjugated materials with enhanced photophysical properties\(^{33–36}\) and that one can tune the geometry of the Pt-complex by the proper choice of precursor Pt salt used in the complexation. It is anticipated that, if we could effectively synthesize alternatively introduced Fe(II)- and Pt(II)-containing metallo-supramolecular polymers by using a Pt(II)-based organometallic ligand, it must have an effect on the properties of the particular metal center due to the presence of hetero-metallic interaction. Thus, trans- and cis-conformational organo-Pt(II) ligands (trans-PtL and cis-PtL) were prepared by the 1:2 organometallic bond formation of Pt(II) and a terpyridyl- and ethynyl-containing compound. Heterometallo-supramolecular polymers with Pt(II) and Fe(II) ions to be introduced alternately (trans-polyPtFe and cis-polyPtFe) were precisely prepared via the 1:1 complexation of Fe(II) ions with the organo-Pt(II) ligands (Scheme 2). To the best of our knowledge, this is the first report to prepare heterometallo-supramolecular polymers using organometallic ligands. We then studied the redox-triggered optical properties, e.g., electrochromism and solid-state emission, and their effects due to the heterometallo interaction in the bimetallic Pt(II)/Fe(II) supramolecular polymers. We also investigated the geometric aspects of the trans- and cis-bimetallic polymers on their material properties, such as the electrochromism and ionic conductivity. These studies can provide a correlation between the structural aspects and the electro-optical properties, specifically the electrochromism, of metallo-supramolecular polymers in detail that has not been studied before.

### Experimental

#### Materials and methods

Unless otherwise noted, all the reagents were reagent grade and were used without purification. Dehydrated ethanol, dichloromethane, and methanol were used as the reaction solvents. Spectroscopic grade methanol was used for the spectral analysis. These solvents were purchased from either Aldrich or Wako or Kanto Chemical Co. Inc. and were used as received. Deionized \(\text{H}_2\text{O}\) was used in the experiments where required. 4-Ethynyl benzaldehyde, 2-acetylpyridine, sodium hydroxide, ammonia solution, cis-dichlorobis(triphenylphosphine)platinum(II), trans-dichlorobis(triphenylphosphine)platinum(II), trimethylamine, copper(i) iodide, and iron(II)tetrafluoroborate were purchased from either Sigma-Aldrich co. Ltd or Tokyo Chemical Industry Co. Ltd and used as received.

#### Instrumentation

\(^1\)H-NMR spectra were recorded at 300 MHz on a JEOL AL 300/BZ instrument using DMSO-\(d_6\) and CDCl\(_3\) as the solvent. Chemical shifts are given herein relative to TMS. DOSY NMR spectra were

---

**Scheme 1** Different synthesis routes of (a) homometallo- and (b–d) heterometallo-supramolecular polymers.
recorded on a JNM-ECA400 spectrometer (JEOL Resonance). MALDI mass spectra (MALDI-TOF) were measured by using the AXIMA-CFR, Shimadzu/Kratos, TOF mass spectrometer. UV-vis spectra were recorded using a Shimadzu UV-2550 UV-visible spectrophotometer. The fluorescence was measured by a Shimadzu RF-5300PC spectrofluorophotometer. The molecular weights of the polymers were determined by SEC-viscometry-RALLS (size exclusion chromatography-viscometry-right angle light scattering) on a Viscotek 270 Dual Detector instrument using polyethylene oxide PEO-22K as the standard in methanol solvent (flow rate: 1 mL min$^{-1}$). Flash column chromatographic separations were performed on silica gel 60 N (neutral, 40–100 μM), Kanto Chemical Co. Inc. Wide angle XRD was done by using a RINT ULTIMA III device with Cu Kα radiation (λ = 1.54 Å), a generator voltage of 40 kV, and a current of 40 mA. Polymer powder was placed on a glass holder and scanned in a range of 2θ = 2–60° at a scan rate of 1 s per step with a step width of 0.01° at room temperature. Cyclic voltammetry (CV) and amperometric experiments were carried out by drop casting the polymer solutions onto a glassy carbon working electrode and then slowly evaporating the solution. The experiments were executed in nitrogen–saturated anhydrous acetonitrile solution containing 0.1 M of lithium perchlorate (LiClO$_4$) as the supporting electrolyte by using an electrochemical analyzer, ALS/H CH instruments. A platinum wire was used as counter the electrode, and Ag/AgCl as the reference electrode. The scan rate for CV analysis was 10 mV s$^{-1}$. For the ionic conductivity measurements, polymer powder was pressed into the form of a pellet using a press. The thicknesses of all the polymer pellets were within 0.2 to 0.4 mm. The pellet was then inserted in between the two electrodes of a sample holder. The sample holder used in the conductivity experiments was composed of two electrodes with an attached micrometer on the upper electrode and another fixed electrode with a guard ring on the electrode, which reduces the effect of stray field lines existing at the edge of the sample. The guard ring ensures that the electric field lines remain parallel all over the sample. Besides this, the ac impedance results were also normalized using the empty cell measurements by carrying out the experiment in an air-gap created with the help of the attached micrometer. This procedure eradicates the errors due to connection and equipment, etc., thus making the measurement more trustworthy. A Solartron 1260 impedance gain/phase analyzer coupled with a Solartron 1296 dielectric interface was used for the ac impedance measurements with high sensitivity. A frequency range of 50 Hz to 10 MHz was used to determine the resistance of the film under humid conditions. For comparison with various studies, polyFe was prepared according to the literature.}$^{37}$ Raman spectroscopy of the compounds was done with a 532 nm laser as the excitation source using a Raman 11 instrument (Nanophoton Corporation, Japan). An equimolar

![Scheme 2](image-url)
amount of 4',4''',4''''-(1,4-phenylene)bis(2,2',6',2''-terpyridine) (Sigma-Aldrich) and Fe(BF₄)₃ was refluxed in methanol for 6 h. The reaction mixture was dried on a petri dish, washed several times with water and chloroform, and again dried in vacuum overnight to yield the corresponding polyFe (> 95%).

**Synthesis of 4'-((4-ethynylphenyl)-2',2'-6',2''-terpyridine (L))**

2-Acetylpyridine (3.63 g, 30 mmol) and 4-ethylbenzaldehyde (1.95 g, 15 mmol) and NaOH (1.2 g, 30 mmol) were taken in a round bottom flask. Subsequently, a solution of ethanol (200 mL) and concentrated aqueous NH₃ solution (100 mL) was added to the mixture. The suspension was stirred at room temperature for 3 days. Soon after, it became a clear solution and after 3 days it formed a yellow precipitation. The formed precipitate was isolated by vacuum filtration and washed with water and ethanol. After performing flash column chromatography using chloroform in silica gel and then following recrystallization from ethanol, L was obtained as white needles (3.5 g, 70%).

1H NMR (300 MHz, DMSO-d₆): 8.77 (d, J = 4.8 Hz, 2H, H₆,α), 8.72 (s, 2H, H₃,β), 8.69 (d, J = 9.0 Hz, 2H, H₃,γ), 8.04 (t, 2H, H₄,γ), 7.98 (d, J = 9.0, 2H, H₆,β), 7.70 (d, J = 9.0, 2H, H₆,γ), 7.54 (m, 2H, H₃,γ), 4.38 (s, 1H). MALDI-TOF: [M⁺] found 334.13, [(M + H)⁺] found 334.92, [(M + Na)⁺] found 356.79 and [(M + K)⁺] found 372.74.

**Synthesis of ligand cis-PtL**

4'-((4-Ethynylphenyl)-2',2'-6',2''-terpyridine (L) (100 mg, 0.33 mmol) was added with cis-dichlorobis(triphenylphosphine)platinum(II) (118.5 mg, 0.15 mmol) under an argon environment in the presence of dry triethylamine (10 mL) and anhydrous dichloromethane (20 mL). Copper(i) iodide (6 mg, 0.075 mmol) was added under inert conditions. The mixture was refluxed for 3 days. Soon after, it became a clear solution and after 3 days it formed a yellow precipitation. The formed precipitate was isolated by vacuum filtration and washed with water and ethanol. After performing flash column chromatography using chloroform in silica gel and then following recrystallization from ethanol, L was obtained as white needles (3.5 g, 70%).

1H NMR (300 MHz, DMSO-d₆): 8.77 (d, J = 4.8 Hz, 2H, H₆,α), 8.72 (s, 2H, H₃,β), 8.69 (d, J = 9.0 Hz, 2H, H₃,γ), 8.04 (t, 2H, H₄,γ), 7.98 (d, J = 9.0, 2H, H₆,β), 7.70 (d, J = 9.0, 2H, H₆,γ), 7.54 (m, 2H, H₃,γ), 4.38 (s, 1H). MALDI-TOF: [M⁺] found 334.13, [(M + H)⁺] found 334.92, [(M + Na)⁺] found 356.79 and [(M + K)⁺] found 372.74.

**Synthesis of ligand trans-PtL**

4'-((4-Ethynylphenyl)-2',2'-6',2''-terpyridine (L) (100 mg, 0.33 mmol) was added with trans-dichlorobis(triphenylphosphine)platinum(II) (118.5 mg, 0.15 mmol) under an argon environment in the presence of dry triethylamine (10 mL) and anhydrous dichloromethane (20 mL). Copper(i) iodide (6 mg, 0.075 mmol) was added under inert conditions. The mixture was refluxed for 3 days. Soon after, it became a clear solution and after 3 days it formed a yellow precipitation. The formed precipitate was isolated by vacuum filtration and washed with water and dichloromethane. The yellow precipitation was filtered and successively washed with several times with water and dichloromethane, respectively. The product was dried in vacuum at 50 °C, affording a greenish yellow solid (186 mg, 90%).

1H NMR (300 MHz, CDCl₃): 8.71–8.59 (m, 12H), 7.86–7.77 (m, 24H), 7.53–7.40 (m, 22H). MALDI-TOF: [M⁺] found 334.13, [(M + H)⁺] found 334.92, [(M + Na)⁺] found 356.79 and [(M + K)⁺] found 372.74.

**Synthesis of cis-polyPtFe**

To a 20 mL methanol solution of cis-PtL (50 mg, 0.034 mmol), a methanolic solution (10 mL) of Fe(BF₄)₃ (11.48 mg, 0.034 mmol) was added under inert conditions. The mixture was refluxed for 6 h with continuous stirring. The reaction mixture was dried on a petri dish, washed several times with water and chloroform, and again dried in vacuum overnight to give the corresponding cis-polyPtFe as a violet solid (46 mg, 88%).

1H NMR (300 MHz, DMSO-d₆): 9.58 (br, s), 9.06 (br, s), 9.06 (br, m), 8.26 (br, m), 8.04 (br, m), 7.92–7.55 (br, m), 7.23 (br, m). Mw = 2.27 × 10⁴ Da.

**Synthesis of trans-polyPtFe**

The trans-polyPtFe was synthesized by the same procedure applied for the synthesis of cis-polyPtFe by using trans-PtL ligand in place of cis-PtL. The reaction mixture was dried on a petri dish, washed several times with water and chloroform, and again dried in vacuum overnight to yield the corresponding trans-polyPtFe as a violet solid (51 mg, 88%).

1H NMR (300 MHz, DMSO-d₆): 9.55 (br, s), 9.04 (br, s), 8.62 (br, m), 8.22 (br, m), 8.01–7.59 (br, m), 7.20 (br, m). Mw = 2.22 × 10⁴ Da.

**Preparation of the semi-gel electrolyte**

The semi-gel electrolyte was prepared by mixing 0.9 g LiClO₄ and 2.1 g poly(methylmethacrylate) (PMMA) in 6 mL propylene carbonate. The mixture was added to 5 mL of acetonitrile to make a semi-gel material. The mixture was stirred at room temperature to make a well-blended semi-gel electrolyte.

**Preparation of the electrochromic (EC) devices and the measurements**

The semi-gel electrolyte consisting of poly(methylmethacrylate) (PMMA), propylene carbonate, and lithium perchlorate in acetonitrile was put on a polymer-coated ITO. The ITO was kept for 15 min at room temperature. Finally, another ITO was put over it and it was kept at 60 °C for another 1 h for thermal curing. These devices were used for the electrochromism studies. The EC devices were oxidized or reduced by applying a voltage between the two ITO electrodes in between a potential window of +3 to 0 V by chronoamperometric studies with a 5 s interval time using an electrochemical analyzer, ALS/H CH instruments, attached to a UV-vis and fluorescence spectrophotometer.

**Result and discussions**

A terpyridyl- and ethynyl-containing asymmetric ligand (L) was prepared by the reaction between 2-acetylpyridine and 4-ethylbenzaldehyde in the presence of NaOH and ammonia (Scheme 2).
The ligand L was characterized by MALDI-TOF and 1H NMR spectroscopy, as shown in Fig. S1 in the ESI.† L (2 equiv.) was treated with cis- or trans- dichlorobis(triphenylphosphine)-platinum(II) in dichloromethane solution and catalyzed by CuI in the presence of NEt₃ to prepare the corresponding cis- or trans-PtL ligands with a good yield. Both the ligands (cis- and trans-PtL) were sparingly soluble in common solvents and could be readily purified by washing with water and dichloromethane to remove the small impurities. The ligands were characterized by 1H NMR and MALDI-TOF mass spectroscopy (ESI,† Fig. S2 and S3). A comparison of the 1H NMR spectra of L and cis- and trans-PtL in Fig. S6a and b (ESI†) reveals that the characteristic singlet 1H signal of the ethynyl proton of L at 4.38 ppm completely disappeared after complexation with Pt(n). This desorption of the ethynyl proton along with no change in the terpyridine proton position of cis- and trans-PtL clearly confirmed the attachment of Pt(n) with the ethynyl binding site of L to prepare cis- and trans-PtL.

The complexation behavior of cis- and trans-PtL with Fe(n) was investigated in detail by UV-vis spectroscopic measurement. The spectrum of a methanol solution of cis-PtL (6 µM) exhibited a metal-to-ligand charge transfer (MLCT) band for the complexation of Pt(n) ions with the ethynyl moiety of L at 383 nm (Fig. 1a). A methanol solution of Fe(BF₄)₂ was successively added to the cis-PtL solution up to a molar ratio of [Fe(BF₄)₂]/[cis-PtL] of 2. A new absorption at 574 nm based on the MLCT band of Fe(II) complexed with the terpyridine moieties of cis-PtL appeared during the titration. The MLCT absorption was increased linearly and was clearly saturated at a ratio of [Fe(BF₄)₂]/[cis-PtL] of 1 (Fig. 1a and b). The spectrum of a methanol solution of trans-PtL (6 µM) also demonstrated a MLCT band for the complexation of Pt(n) ions with the ethynyl moiety of L at 398 nm (Fig. 1c).

![Fig. 1](image_url) (a) UV-vis spectral change of a methanol solution of cis-PtL during titration with Fe(BF₄)₂ at room temperature. (b) The absorption change at 574 nm as a function of the [Fe(BF₄)₂]/[cis-PtL] ratio. (c) UV-vis spectral change of a methanol solution of trans-PtL during titration with Fe(BF₄)₂ at room temperature. (d) The absorption change at 574 nm as a function of the [Fe(BF₄)₂]/[trans-PtL] ratio.

The red-shift of the MLCT transition in trans-PtL, compared to cis-PtL, is due to the enhancement of the MLCT energy gap in cis-PtL rather than in trans-PtL. As the π-orbitals of cis-PtL are not aligned to extend the conjugation. The successive addition of a methanol solution of Fe(BF₄)₂ to trans-PtL solution up to a molar ratio of [Fe(BF₄)₂]/[trans-PtL] of 2 also revealed the generation of a new absorption peak at 574 nm based on the MLCT band of Fe(n) complexed with the terpyridine moieties. Here also, the MLCT absorption was linearly increased and saturated at the ratio of [Fe(BF₄)₂]/[trans-PtL] of 1 (Fig. 1c and d). These spectral changes suggest the formation of a heterometallo-supramolecular polymer with Pt(n) and Fe(n) ions introduced alternately to prepare 1D linear cis- and trans-polypPtFe, according to a stepwise complexation behavior with complexation between cis- or trans-PtL and Fe(n) with a 1:1 molar ratio, as shown in Schemes 1 and 2. Furthermore, the MLCT absorption of Fe(n) did not change upon the further addition of Fe(n), indicating that the polymers were stable in solution.

The cis- and trans-polypPtFe were obtained by refluxing the corresponding Pt(n)-containing ligand with Fe(BF₄)₂ in methanol as a violet solid in a satisfactorily high yield (> 80%), as shown in Scheme 2. The polymers were soluble in alcohols, such as methanol, ethanol, and ethylene glycol, and polar solvents, such as DMSO and DMF, but sparingly soluble in the common organic solvents, such as n-hexane, chloroform, dichloromethane, and tetrahydrofuran. The molecular weights of the polymers were determined by SEC-Viscometry/RALLS method using PEO as the standard (for cis-polypPtFe: Mw = 2.27 × 10⁴ Da; and for trans-polypPtFe: Mw = 2.22 × 10⁴ Da), which strongly indicated that both cis- and trans-polypPtFe form a polymer structure with moderate polydispersity. The 1H NMR spectrum of the polymers is shown in ESI† Fig. S4 and S5. The comparison of the 1H NMR spectra of L and the cis- and trans-PtL ligands and the corresponding cis- and trans-polypPtFe in the ESI† Fig. S6a and b also revealed a broadening of the proton signals along with some downfield shifting of the terpyridyl protons after polymerization of the cis- or trans-PtL ligands by Fe(BF₄)₂. To gain a clearer idea about the formation of cis- and trans-metallo-supramolecular polymers, we performed two dimensional Diffusion-Ordered NMR Spectroscopy (DOSY) analysis. Generally, 1H DOSY NMR can distinguish between cis- and trans-polymers as their diffusion is different, and hence their diffusion coefficients are also different. The 1H DOSY NMR study of the cis- and trans-polypPtFe (ESI† Fig. S7 and S8) revealed average diffusion coefficients of about 9.14 × 10⁻¹¹ m² s⁻¹ and 1.7 × 10⁻¹⁰ m² s⁻¹, respectively, for the two polymers. The diffusion coefficient in the trans-polymer is quite a bit higher due to the better mobility in the trans-polymer chains than in the cis-configuration. The diffusion coefficient of cis-polypPtFe is one order lower due to its aggregated structure (which was further confirmed by the XRD study also), such that the diffusion is slower.

The UV-vis spectra of both cis- and trans-polypPtFe exhibited strong absorptions based on the MLCT (Fig. 2a). After polymerization with Fe(n) metal ions, the MLCT band for complexation of the Pt(n) ions with the ethynyl moiety of the two organo-metallic ligands were further red-shifted to 407 nm (Fig. 2a).
Fig. 2 (a) UV-vis spectra of polyFe and the cis- and trans-polyPtFe polymers in methanol solution and (b) cyclic voltammograms for polyFe and the cis- and trans-polyPtFe films coated on a glassy carbon electrode in nitrogen–saturated acetonitrile (electrolyte: 0.1 M LiClO4, counter electrode: Pt wire; reference electrode: Ag/Ag+; scan rate: 10 mV s⁻¹). (c) Powder XRD of cis- and trans-polyPtFe.

Upon the formation of the polymer by cis- and trans-PtL with Fe(II) through terpyridyl chelation, apart from the occurrence of a new intense absorption at ca. 574 nm from the MLCT for terpyridine–Fe(II) complexation, the absorption bands due to the Pt(n)-metal-perturbed π → π* (C=C) and/or MLCT transitions were red-shifted ca. 24 nm for the cis-PtL and 9 nm for the trans-PtL organometallic ligands. The terpyridyl chelating to Fe(n) lowers the π* orbital energy in the C=Ctpy and reduces the energy gap between the HOMO (d) and LUMO (π), thus inducing an obvious red-shift of the Pt–metal-perturbed π → π* (C=C) and/or MLCT absorption. The red-shift was quite a bit lesser in trans-polyPtFe as the MLCT energy gap was already reduced in the trans-PtL ligand compared to its cis-counterpart. Again, the MLCT absorption due to Fe(n) complexation with terpyridine in the polypFe polymers is meagerly blue-shifted compared to that of the bisterpyridine ligand containing the Fe(II) metallo-supramolecular polymer polyFe (MLCT band at 583 nm). This small but significant blue-shift indicates the lowest unoccupied molecular orbital (LUMO) potential of the Pt(n)-containing ligand in the heterometallo polymer was increased rather than in the normal 4ʹ,4ʺʹʹ-(1,4-phenylene)bis(2,2ʹ,6ʹ,2ʺ-terpyridine) ligand in polyFe due to the incorporation of Pt(n) in the ligand structure. The cyclic voltammogram of polyFe in Fig. 2b exhibits a reversible redox wave of the Fe(n)/Fe(n⁺) couple (E₁/₂ = 0.77 V). The redox potential of the reversible Fe(n)/Fe(n⁺) couple in both trans- and cis-polyPtFe showed similar values of E₁/₂ (0.73 V and 0.74 V for trans- and cis-polyPtFe, respectively) with a smaller negative shift of the E₁/₂ of the Fe(n)/Fe(n⁺) couple than that of polyFe. This negative shift of the E₁/₂ of the Fe(n)/Fe(n⁺) couple clearly supports the intramolecular metal–metal interactions between the neighboring Pt and Fe ions. Again, the ΔE of the Fe(n)/Fe(n⁺) couple in polyFe (0.13 V) is slightly higher than the ΔE of the Fe(n)/Fe(n⁺) couple in the cis- and trans-polyPtFe (0.09 V and 0.08 V for trans- and cis-polyPtFe, respectively) indicating the good electronic communication in the film of Fe/Pt-containing polymers.

The comparison of the powder XRD study of cis- and trans-polyPtFe revealed very sharp peaks from the cis-polyPtFe compared to from the trans-polyPtFe (Fig. 2c). From this study, we can assume that cis-polyPtFe possessed a better crystallinity, whereas trans-polyPtFe was amorphous in nature. In the cis-polymer structure, we can assume a polarization occurred as the individual Pt-complex centers have some dipole moment due to its angular shape (Fig. S9, ESI†); whereas the trans-polymer is linear in shape and the individual Pt-complex centers do not possess any dipole moment as it is cancelled out due to their linear shape. As the polarization and dipole moment are higher in individual Pt centers in the cis-polymer, we can assume there is a better crystallinity in the cis-polymer.⁴⁰,⁴¹

The morphological characteristics of the two polymers were studied by a SEM image study (Fig. 3a–d). The SEM images revealed an agglomerated polymer network in cis-polyPtFe (Fig. 3a and b) whereas, in trans-polyPtFe, the polymer network was very well defined to produce high-aspect-ratio fibers (Fig. 3c and d). In the trans-polymer, self-assembly between the polymer chains is reasonably easier due to its linear structure, which gives more structural preference rather than in the cis-polymer to produce a well-defined polymer network.

Electrochromic materials (ECMs) have received increasing interest for their use in optoelectronic applications, such as smart windows and electronic papers. Recently, it has been revealed that metallo-supramolecular polymers synthesized by the 1:1 complexation of transition metals, such as Fe(II)/Ru(II) and Fe(II)/Cu(I) ions with some ditopic ligands, are an excellent ECM with both high durability and ample color variation. These polymers display a specific color based on MLCT absorption and can show electrochromic behavior based on the disappearance/reappearance of MLCT absorption, which is triggered by the electrochemical redox reaction of the metal ions. A solid-state device (2 × 1 cm, Fig. 4a) was fabricated using a cis- or trans-polyPtFe film on ITO and a semi-gel electrolyte layer including a lithium perchlorate salt was sandwiched between
the ITO-containing polymer film and another ITO (ESI† Fig. S10). Both devices showed reversible electrochromic behavior (from purple to blue to yellow) when the applied voltage was changed from 0 to +3 V (Fig. 4b and d). This electrochromic color change could be clearly monitored by UV-vis spectroscopy (Fig. 4c and e).

For the device with cis-polyPFe, the UV-vis spectrum showed two absorptions around 467 and 580 nm based on the MLCT absorptions of the Pt(II)–ethynyl and Fe(II)–terpyridyl complex moieties, respectively (Fig. 4c). Generally the λmax of the polymer in the solid state is bathochromically shifted when compared to the solution spectra, due to the major conformational order, resulting in a different energy levels distribution. So, the MLCT peak for the Pt(II)–ethynyl complex at 407 nm in methanol solution in Fig. 2a is red-shifted to 467 nm in the solid film in EC devices in Fig. 4c and e. Again, the MLCT transitions are typically extremely sensitive to the solvent polarity because they give rise to a strong change in the molecular dipole moment in the excited state. Using a polar solvent, like methanol, can enhance the energy gap between the HOMO (d) and LUMO (π*), thus inducing the obvious blue-shift to 407 nm in methanol solution in Fig. 2a from 467 nm in the solid film in EC devices in Fig. 4c and e.

Interestingly, the absorption around 580 nm for the MLCT absorption of the Fe(II)–terpyridyl complex disappeared when the device was exposed at +3 V, because of the electrochemical oxidation of Fe(II) to Fe(III). This phenomenon was also reflected in the solid-state color change of the devices from purple to yellow in Fig. 4b. The yellow color is dominant due to only the MLCT of the Pt(II)–ethynyl complex. The spectral change was reversible; the original spectrum could be re-obtained by applying the opposite voltage (0 V) to the device (Fig. 4b). As Fe(III) centers were reduced to Fe(II) at 0 V, the prominent purple color of the MLCT absorption of the Fe(II)–terpyridyl complex reappeared. We observed the same phenomenon with the device made of trans-polyPFe (Fig. 4d and e). It also showed same reversible electrochromic behavior by the electrochemical redox of Fe ions, whereby the MLCT absorption at 580 nm of the Fe(II)–terpyridyl complex disappeared to give a color change from purple to yellow, upon the oxidation of Fe(II) to Fe(III) by exposing the film at +3 V and then reappeared upon the reduction of Fe(III) to Fe(II) at 0 V.

In order to confirm the device durability in these EC changes, a long-term redox-switching repeatability study was done by applying two voltages (+3 and 0 V) alternately (interval time: 5 s for each step) to both the devices for up to 200 s, and the MLCT absorption at 580 nm was monitored as a function of time. Fig. 5a and b show the switching behavior of the MLCT absorptions from 0 to 200 s for cis- and trans-polyPFe, respectively. Both the polymer devices revealed good switching stability with the applied potential; however, the device with the cis-polyPFe polymer film showed some decrement of the absorbance difference of the Fe–terpyridine MLCT between the reduced and oxidized states with time (Fig. 5a). We calculated the response times for the disappearance (bleaching time τb) and reappearance (coloring time τc) of the MLCT absorption at 580 nm, and for the cis-polyPFe polymer device the values were 4.23 and 2.17 s, respectively (Fig. 5c); whereas, the response times for the disappearance (τb) and reappearance (τc) of the MLCT absorption at 580 nm.
Fig. 7 The Nyquist plots for cis- and trans-polyPtFe at 25 °C and 98% RH.
film rather than the trans-polyPtFe, which has a higher amorphous content. Owing to its higher crystalline nature in film, the cis-polyPtFe showed poor electrochemical performance, as electrochemical reactions are harder in a rigid structure with higher crystallinity. In the cis-polymer, the interchange and diffusion of the counter anion is difficult than in the trans-polymer due to its more crystalline nature. As a result, the cis-polymer showed a weaker and slow response rather than its trans-counterpart.

Conclusions

cis- and trans-conformational heterometallo-supramolecular polymers with Pt(n) and Fe(n) ions introduced alternately (cis- and trans-polyPtFe) were synthesized by the 1:1 complexation of Fe(n) ions with organo-Pt(n) ligands. Both polymers exhibited similar molecular weights, but their crystallinity and the ionic conductivity of their solid films were different due to their different spatial arrangements. An electronic interaction between the two hetero-metal ions through the π-conjugated spacer unit of the ligand was observed in the cyclic voltammetry measurements. Both the polymers exhibited reversible electrochromism between purple and yellow based on the electrochemical redox of Fe(n) to Fe(n). The trans-polyPtFe showed better electrochromic stability and response times compared to the cis-polyPtFe owing to its better ionic conductivity and higher crystalline nature of the film. The bimetallic polymers also revealed reversible Raman scattering switching by triggering the redox of the Fe(n) ions in the solid thin film. The trans-polyPtFe also showed improved response in redox-triggered Raman scattering switching compared to the cis-polyPtFe over the long-time range. The studies have tremendous impact for understanding the correlation between the structural characteristic and ionic conductivity and the electrochromic behavior of metallo-supramolecular polymers with different geometries. As we successfully prepared two precise heterometallo-supramolecular polymers with Pt(n) and Fe(n) ions introduced alternately via stepwise complexation, these polymers can also be used as a precursor to fabricate patterning of FePt nanoparticles.

Acknowledgements

The authors thank the CREST Project, Japan Science and Technology Agency (JST) for financial support. Authors also acknowledge Dr Miharu Eguchi for her help regarding photophysical discussion.

Notes and references

1 G. R. Whittell, M. D. Hager, U. S. Schubert and I. Manners, Nat. Mater., 2011, 10, 176.
2 J.-C. Eloi, L. Chabanne, G. R. Whittell and I. Manners, Mater. Today, 2008, 11, 28.
3 M. Higuchi, J. Mater. Chem. C, 2014, 2, 9331.
4 A. Bandyopadhyay, S. Sahu and M. Higuchi, J. Am. Chem. Soc., 2011, 133, 1168.
5 T. Sato and M. Higuchi, Chem. Commun., 2012, 48, 4947.
6 R. I. Wojtechki, M. A. Meador and S. J. Rowan, Nat. Mater., 2011, 10, 14.
7 F. S. Han, M. Higuchi and D. G. Kurth, Adv. Mater., 2007, 19, 3928.
8 D. G. Kurth and M. Higuchi, Soft Matter, 2006, 2, 915.
9 C.-W. Hu, T. Sato, J. Zhang, S. Moriyama and M. Higuchi, ACS Appl. Mater. Interfaces, 2014, 6, 9118.
10 S. B. Clendenning, S. Fournier-Bidoz, A. Pietrangelo, G. Yang, S. Han, P. M. Brodersen, C. M. Yip, Z.-H. Lu, G. A. Ozin and I. Manners, J. Mater. Chem., 2004, 14, 1686.
11 C. Chakraborty, R. K. Pandey, M. D. Hossain, Z. Futera, S. Moriyama and M. Higuchi, ACS Appl. Mater. Interfaces, 2015, 7, 19034.
12 J. Lombard, D. A. Jose, C. E. Castillo, R. Pansu, J. Chauvin, A. Deronzier and M.-N. Collomb, J. Mater. Chem. C, 2014, 2, 9824.
13 M. D. Hossain, J. Zhang, R. K. Pandey, T. Sato and M. Higuchi, Eur. J. Inorg. Chem., 2014, 3763.
14 T. Sato and M. Higuchi, Chem. Commun., 2013, 49, 5256.
15 C.-W. Hu, T. Sato, J. Zhang, S. Moriyama and M. Higuchi, J. Mater. Chem. C, 2013, 1, 3408.
16 E. C. Constable, A. J. Edwards, P. R. Raithby and J. K. Walker, Angew. Chem., Int. Ed. Engl., 1993, 32, 1465.
17 E. C. Constable and A. W. C. Thompson, J. Chem. Soc., Dalton Trans., 1995, 1615.
18 C. D. Buchecker, B. Colasson, M. Fujita, A. Horii, N. Geum, S. Sakamoto, K. Yamaguchi and J. P. Sauvage, J. Am. Chem. Soc., 2003, 125, 5717.
19 D. Imbert, M. Cantuel, J. C. G. Bunzli, G. Bernardinelli and C. Piguet, J. Am. Chem. Soc., 2003, 125, 15698.
20 C. Piguet, G. Hopfgartner, B. Boquet, O. Schaad and A. F. Williams, J. Am. Chem. Soc., 1994, 116, 9092.
21 R. J. Abergel and K. N. Raymond, Inorg. Chem., 2006, 45, 3622.
22 A. R. Stefańkiewicz, J. Harrowfield, A. Madalan, K. Rissanen, A. N. Sobolev and J. M. L. Lehn, Dalton Trans., 2011, 40, 12320.
23 H. Fenton, I. S. Tidmarsh and M. D. Ward, Dalton Trans., 2010, 39, 3805.
24 G. R. Newkome, P. S. Wang, C. N. Moorefield, T. J. Cho, P. P. Mohapatra, S. N. Li, S. H. Hwang, O. Lukoyanova, L. Echegoyen, J. A. Palagallo, V. Iancu and S. W. Hla, Science, 2006, 312, 1782.
25 F. Puntoriero, S. Serroni, A. Licciardello, M. Venturi, A. Juris, V. Ricevuto and S. Campagna, J. Chem. Soc., Dalton Trans., 2001, 1035.
26 D. Sun, L. Zhang, H. Lu, S. Feng and D. Sun, Dalton Trans., 2013, 42, 3528.
27 D. Sun, L. Zhang, Z. Yan and D. Sun, Chem. – Asian J., 2012, 7, 1558.
28 D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang and L.-S. Zheng, Chem. Commun., 2011, 47, 746.
29 M. Higuchi, Y. Akasaka, T. Ikeda, A. Hayashi and D. G. Kurth, J. Inorg. Organomet. Polym. Mater., 2009, 19, 74.
30 M. Higuchi, Polym. J., 2009, 41, 511.
31 F. Han, M. Higuchi and D. G. Kurth, J. Am. Chem. Soc., 2008, 130, 2073.
32 A. Bandyopadhyay and M. Higuchi, Eur. Polym. J., 2013, 49, 1688.
33 V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong and K.-K. Cheung, Organometallics, 2001, 20, 4476.
34 M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, Inorg. Chem., 2000, 39, 447.
35 W.-Y. Wong, J. Inorg. Organomet. Polym. Mater., 2005, 15, 197.
36 Y. Liu, S. Jiang, K. Glusac, D. H. Powell, D. F. Anderson and K. S. Schanze, J. Am. Chem. Soc., 2002, 124, 12412.
37 M. Higuchi and D. G. Kurth, Chem. Rec., 2007, 7, 203.
38 A. Wild, A. Teichler, C.-L. Ho, X.-Z. Wang, H. Zhan, F. Schlüter, A. Winter, M. D. Hager, W.-Y. Wong and U. S. Schubert, J. Mater. Chem. C, 2013, 1, 1812.
39 H.-B. Xu, J. Ni, K.-J. Chen, L.-Y. Zhang and Z.-N. Chen, Organometallics, 2008, 27, 5665.
40 V. Bharti, H. S. Xu, G. Shanthi and Q. M. Zhang, J. Appl. Phys., 2000, 87, 452.
41 A. Dey and G. R. Desiraju, Chem. Commun., 2005, 2486.
42 R. J. Mortimer, Annu. Rev. Mater. Res., 2011, 41, 241.
43 S. Shankar, M. Lahav and M. E. van der Boom, J. Am. Chem. Soc., 2015, 137, 4050–4053.
44 E. Glimsdal, M. Carlsson, B. Eliasson, B. Minaev and M. Lindgren, J. Phys. Chem. A, 2007, 111, 244.
45 S.-H. Lee, H. M. Cheong, N.-G. Park, C. E. Tracy, A. Mascarenhas, D. K. Benson and S. K. Deb, Solid State Ionics, 2001, 140, 135.