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AWARD ACCOUNTS
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Electrochromic Organic–Metallic Hybrid Polymers: Fundamentals and Device Applications

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Organic–metallic hybrid polymers are formed by the complexation of metal ions with organic ligands or polymers bearing coordination sites. Hybrid polymers consisting of bis(terpyridine)s and metal ions such as Fe(II) or Ru(II) have specific colors based on metal-to-ligand charge transfer (MLCT) absorption. The cyclic voltammograms of the polymers revealed a reversible redox wave that depends on the redox reaction of the metal ions. Interestingly, polymer films cast on indium tin oxide (ITO) electrodes have excellent electrochromic properties; the color of the film disappears when a potential higher than the redox potential of the metal ions is applied to the polymer film. Various colors such as purple, blue, red, and orange can be observed by changing the metal species and/or by modifying the organic ligands used to synthesize the polymers. In addition, multicolor electrochromic changes in a polymer film occur upon the introduction of two types of metal ions into the polymer. Electrochromic solid-state devices have been successfully fabricated by using these polymers.
KEY WORDS: Organic–Metallic Hybrid Polymers / Metallo-Supramolecular Polyelectrolytes / Electrochromic Properties / Electronic Papers / Smart Windows / Multicolor / Solid-state Devices /

Chromic material is a general term for material that reversibly changes color in response to external stimuli. Many chromic phenomena are known, and according to the different stimuli applied, they are named as thermochromic[1,2] (color change caused by exposure to heat), photochromic[3,4] (color change caused by exposure to light), solvatochromic[5,6] (color change caused by exposure to different solvent species), vapochromic[7,8] (color change caused by exposure to vapor) and electrochromic[9–11] (color change caused by electrochemical oxidation/reduction), etc. So far, many electrochromic materials have been discovered. Inorganic electrochromic materials such as molybdenum oxide,[12,13] Prussian blue,[14,15] and phthalocyanine metal complexes[16,17] are well known; viologen derivatives[18,19] and conductive polymers are examples of organic electrochromic materials. However, not many applications of electrochromic materials have been identified. This is because (a) inorganic materials offer limited color variation, and their use involves complicated processing, and (b) organic materials have poor stability. Shirakawa, McDiarmid, and Heeger won the Nobel Prize in Chemistry 2000 for their discovery of the conductive polymers,[20–24] that is, π-conjugate organic polymers such as polyacetylene, polyaniline, and polythiophene, which have high conductivity when charge is injected through doping.[25–27] Interestingly, these π-conjugate polymers also posses electrochromic properties.[28–40] The color of π-conjugate polymers is based on the polymer structure. The absorption spectra of π-conjugate polymers shift toward long wavelengths when the length of the π-conjugate chain is large. When such polymers are oxidized or reduced chemically or electrochemically, that is,

"doped," the gap (bandgap) between HOMO and LUMO potentials decreases and their color changes. By employing various synthetic organic reactions, π-conjugate polymers with different conjugated chain lengths can be synthesized. Therefore, such electrochromic materials can exhibit various colors. The electrochromic properties of conductive polymers have already been comprehensively studied over the last two decades, and applications have been proposed. However, most of these applications are not practical. This is primarily because conductive polymers have low stability. As mentioned earlier, electrochromic properties can be observed, when these polymers are injected with charges (or electrons), which causes changes in the electronic state and structure of the polymers. As a result, even if the original polymer is stable, the polymer structure after oxidization (reduction) is such that the material is often unstable against light, heat, or air, deteriorating while the electrochemical redox switching is operated repeatedly. In order to find practical applications, electrochromic materials have to be stable and reliable. In this respect, organic electrochromic materials have had a major disadvantage.

π-Conjugate polymers containing coordination sites, such as polyanilines and polypyridines, can trap metal ions in solution and can therefore be regarded as polymeric ligands. So far, we have reported several types of organic–metallic hybrid polymers, which were formed during the metal-ion assembly of polyaniline[41–43] and stepwise assembly of metal ions in dendritic[44–53] or cyclic[54–61] polyphenylazomethines. Organic–metallic hybrid polymers that are formed by the complexation of metal ions with π-conjugate organic ligands are promising electrochromic materials. In this review, I discuss the electro-

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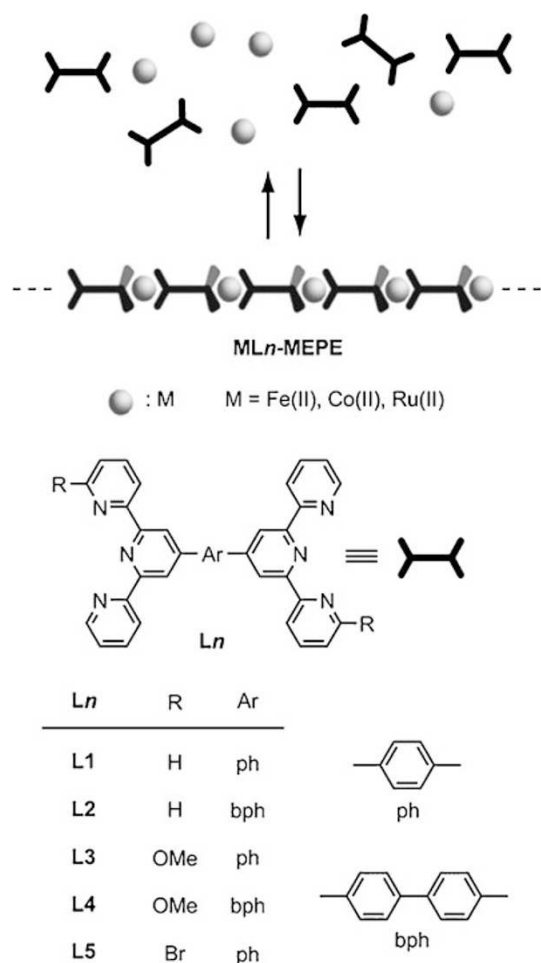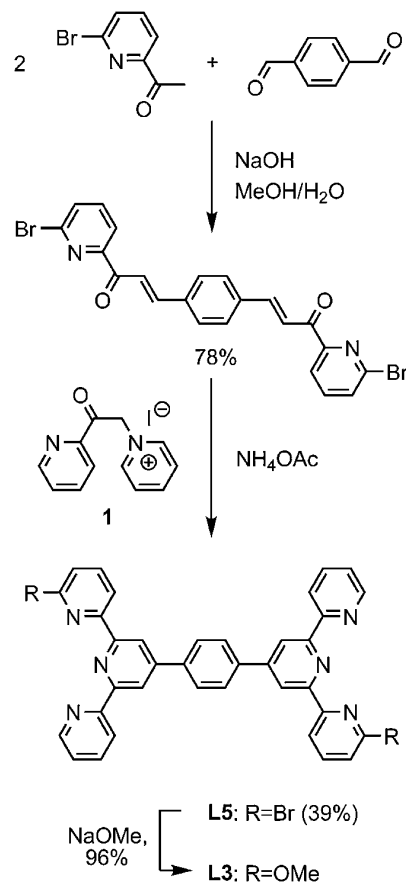
Figure 1. Organic–metallic hybrid polymers (**ML*n*-MEPE**) formed by complexation of bis(terpyridine)s (**L*n***) with metal ions such as Fe(II), Co(II), and Ru(II) ions.

Figure 2. Synthetic scheme of **L3** and **L5**.

chromic properties of organic–metallic hybrid polymers and the application of these polymers to several devices.[62–69]

SYNTHESIS OF ORGANIC–METALLIC HYBRID POLYMERS

Metallo-supramolecular polyelectrolytes (MEPEs) are regarded as organic–metallic hybrid polymers and are obtained *via* the complexation of metal ions with bis(terpyridine)s as the organic ligand (Figure 1).[70–74] The hybrid polymers have a polymer structure in which organic ligands and metal ions are connected alternatively by complexation. The typical procedure for the synthesis of MEPEs is as follows: equimolar amounts of 1,4-bis(2,2′:6′,2″-terpyridin-4-yl)benzene (**L1**) and Fe(OAc)$_2$ are refluxed in argon-saturated acetic acid (*ca.* 10 mL of solvent per 1 mg of **L1**) for 24 h. After the reaction is completed, the solution is cooled to room temperature and filtered to remove a small amount of insoluble residues. The filtrate is placed in a Petri dish, and the solvent is evaporated slowly until dry. The brittle film is collected and dried further *in vacuo* overnight to obtain **FeL1-MEPE** (yield > 90%).

The organic ligand **L1** is commercially available and was purchased from Aldrich. New ligands **L2**–**L5** are synthesized as follows (Figures 2 and 3): a bis(terpyridyl)benzene derivative with two bromo groups acting as the electron-withdrawing groups (**L5**) is prepared using the two-step Kröhnke procedure, which involves an aldol condensation of benzene-1,4-dicarboxaldehyde and 2-acetyl-6-bromopyridine, followed by a Michael addition of the resultant azachalcone with pyridinium iodide. Nucleophilic substitution of **L5** using NaOMe yields bis(terpyridyl)benzene containing two methoxy groups acting as the electron-releasing groups (**L3**). **L2** and **L4** are synthesized *via* a one-pot Suzuki type dimerization of the corresponding monoterpyridines. The hybrid polymers (**FeL*n*-MEPE** (*n* = 1–5)) are obtained by the complexation of **L1**–**L5** with iron(II) acetate in acetic acid.

Various MEPEs can be prepared by changing the organic ligand or metal species, but the synthesis conditions depend on the metal species used. By using ethylene glycol as the solvent and Ru(DMSO)$_4$Cl$_2$ as the Ru(II) precursor, a high yield (>95%) of high-purity **RuL*n*-MEPE**s can be obtained.

ELECTROCHROMIC PROPERTIES

FeL1-MEPE synthesized using 1,4-bis(2,2′:6′,2″-terpyridin-4-yl)benzene as the organic ligand has a purple color
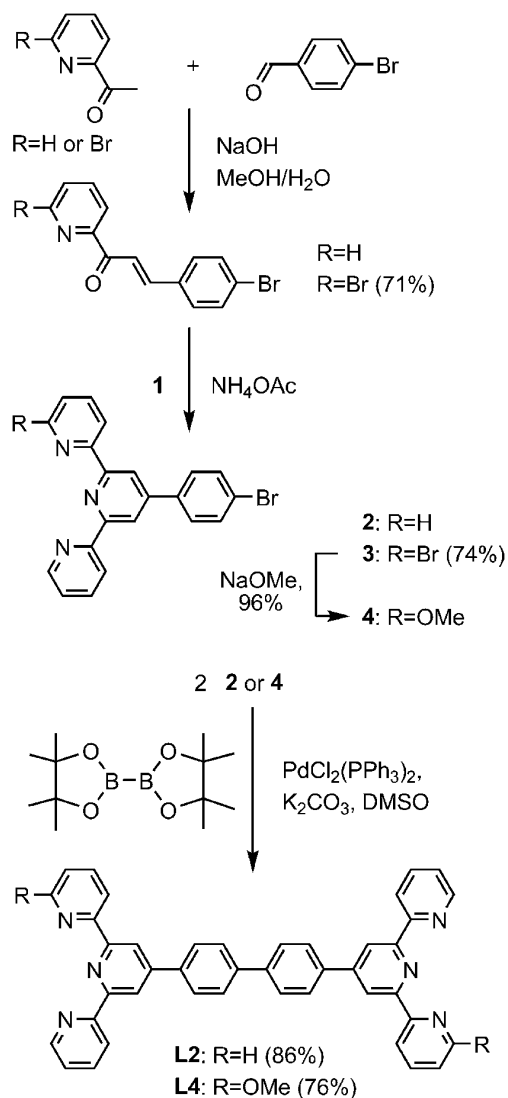
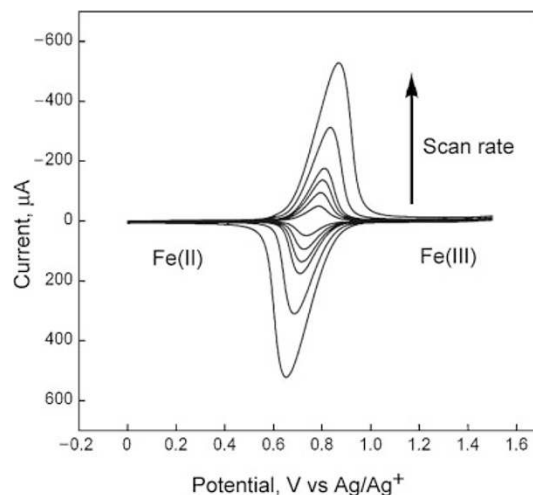**Figure 3.** Synthetic scheme of **L2** and **L4**.

Figure 4. Cyclic voltammograms of a **FeL1-MEPE** film cast on glassy carbon disk electrode at the sweep rate of 0.02, 0.05, 0.1, 0.15, 0.2, 0.4, and 0.8 V/s. The counter and reference electrodes are Pt and Ag/Ag$^+$. Solvent is 0.1 M tetra(n-butyl)ammonum perchlorate (TBAP)/acetonitrile.
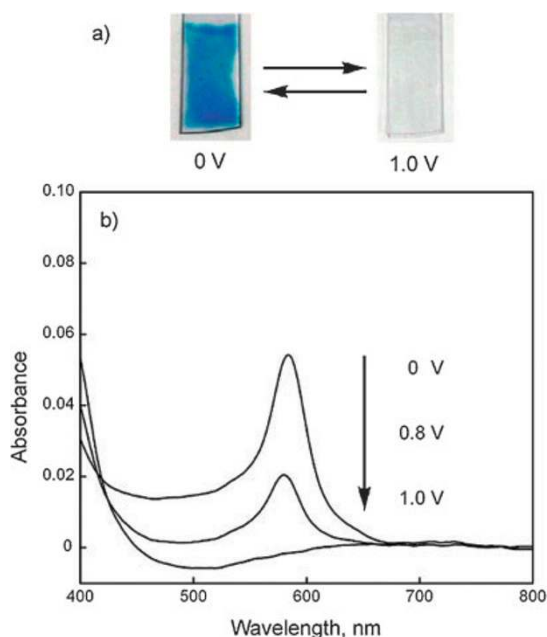

Figure 5. (a) Electrochromic behavior of **FeL1-MEPE**: a color of the polymer film changes from blue (left) to transparent/colorless (right) at 1.0 V vs. Ag/Ag$^+$. (b) Electrospectral measurements of **FeL1-MEPE** film: UV-vis spectra of the polymer film at 0, 0.8, and 1.0 V vs. Ag/Ag$^+$.

because of the metal-to-ligand charge transfer (MLCT) absorption from iron(II) ions to the terpyridyl units of the ligand. The wavelength of maximum absorbance (λ_{max}) of the MLCT absorption, as determined from UV-vis spectroscopic measurements, is 580 nm in methanol. **FeL1-MEPE** is highly soluble in polar solvents such as water and methanol, but it is not soluble in organic solvents such as chloroform and acetonitrile. Therefore, we successfully measured the electronic properties of the polymer film in an organic solvent.

Electrochemical reduction/oxidation (redox) of **FeL1-MEPE** is based on the redox reaction between iron (II) and (III). The electrochemical properties are investigated by cyclic voltammetry using a Glassy Carbon electrode, covered with a thin film of **FeL1-MEPE**, as working electrode. **FeL1-MEPE** shows a large current response when oxidized in acetonitrile solution as shown in Figure 4. The redox activity is completely reversible ($\Delta E = 75$ mV at 0.1 V/s scan rate). The half-wave potential ($E_{1/2}$) of the redox reaction is 0.77 V vs. Ag/Ag$^+$.

Interestingly, the polymer film cast on an indium tin oxide (ITO) electrode using methanol exhibits electrochromic properties in acetonitrile: the blue-colored polymer film becomes almost colorless when a voltage of 1.0 V is applied to the electrode (Figure 5a). The film regains its original blue color when a reduction voltage of 0 V is applied to it. The oxidized film remains colorless for several hours (memory effect), however, under ambient conditions it gradually turns back to blue, which means that it must be reduced to Fe(II). The

thickness of the spin-coated film is 30–100 nm estimated by CV, absorption spectra, and AFM.

UV-vis spectra of the oxidized polymer film can be monitored by means of *in situ* electrospectral measurements; the UV-vis spectra of the polymer film cast on an ITO electrode are measured while applying the voltage to the electrode in a quartz cuvette (1 mm-path length) with three necks. The disappearance of MLCT absorption during electrochemical oxidation is investigated by using this technique, and it is confirmed that MLCT absorption disappears at an oxidative potential of 1.0 V (Figure 5b). This provides strong evidence that color change in the polymer film occurs according to the electrochemical redox reaction of the iron ions. MLCT absorption occurs in the presence of Fe(II) ions but disappears in the case of **FeL1-MEPE** containing Fe(III) ions.

In addition to stability, it is extremely important for electrochromic materials to be colorless when used for the fabrication of electronic papers or smart windows. However, there exist only a few organic electrochromic compounds that can exhibit colorlessness. Organic materials such as conductive polymers generally change colors. Therefore, organic–metallic hybrid polymers, which can exhibit color-lessness, might be suitable for the fabrication of devices such as those listed above. In addition, color changes based on MLCT absorption are not accompanied by structural changes in the polymers; this has a good influence on the stability of the polymer.

TUNING THE COLOR

Color variation in organic electrochromic materials is certainly abundant; however, controlling and fine tuning the color changes are not easy because each organic material has its own individual color. The colors of organic–metallic hybrid polymers depend on the potential gap between the LUMO of the organic ligand and the HOMO of the metal ions; MLCT absorption shifts toward short wavelengths when the potential gap increases and toward long wavelengths when the gap decreases. Therefore, the colors of hybrid polymers can be easily adjusted by changing the metal species and/or by modifying the organic ligands used for their synthesis. In order to use electrochromic materials in display devices, it is necessary that they exhibit RGB colors. Therefore, we attempt to control the colors of hybrid polymers.

The potential-gap corresponding to MLCT absorption is controlled by incorporating an electron-withdrawing or elec-tron-releasing group in the organic ligand. Interestingly, **FeL3-MEPE** and **FeL4-MEPE** bearing electron-releasing methoxy groups are blue powders while **FeL5-MEPE** bearing electron-withdrawing bromo groups is green. This clearly shows that the electronic properties of the substituents in the organic ligands influence the potential gap corresponding to MLCT absorption in the polymer. In fact, the λ_{max} of the MLCT absorption in **FeL5-MEPE** (612 nm) is longer than that of the MLCT absorption in **FeL1-MEPE** (586 nm) (Figure 6). This indicates that the potential gap corresponding to MLCT absorption
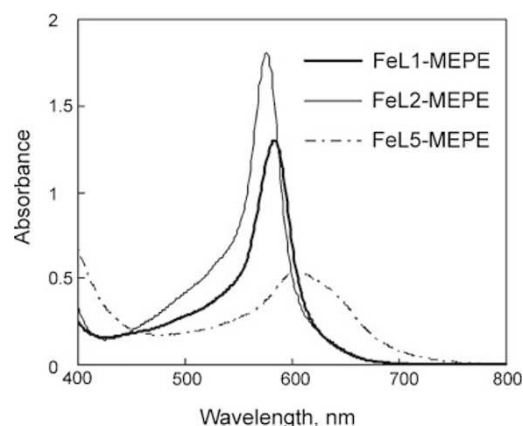

Figure 6. UV-vis spectra of **FeL1-**, **FeL2-**, and **FeL5-MEPE** in MeOH (7×10^{-5} M).
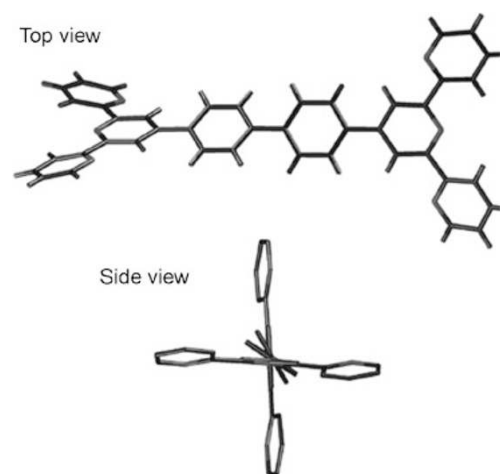

Figure 7. X-Ray crystal structure of **L2**.

decreases because of the incorporation of the electron-with-drawing bromo groups into the organic ligand.

In addition, the absorption coefficient (ε) of the MLCT absorption increases when a biphenyl spacer is used instead of phenyl spacer. For example, the ε of **FeL1-MEPE** is 18500, while that of **FeL2-MEPE** is 25700 (Figure 6). Distance isolation of the iron ions is achieved by using a biphenyl unit as the spacer in **FeL2-MEPE**, resulting in an increase in the ε value. Furthermore, the decrease in the conjugation between the metal ions results in an increase in the ε value; such decrease in conjugation is confirmed in **FeL2-MEPE** by means of single-crystal X-ray analysis. The result of the X-ray analysis of **L2** indicated that this ligand assumes a straight rigid conformation along the central axis of the ring (Figure 7).[75] The side view reveals that the two terpyridine planes are almost perpendicular, with a calculated dihedral angle of 83.243 (2)°.

The color of the polymer can be controlled not only by modifying the organic ligand but also by changing the metal species used in the synthesis. In particular, the color of the polymer changes considerably in the latter case: the color of
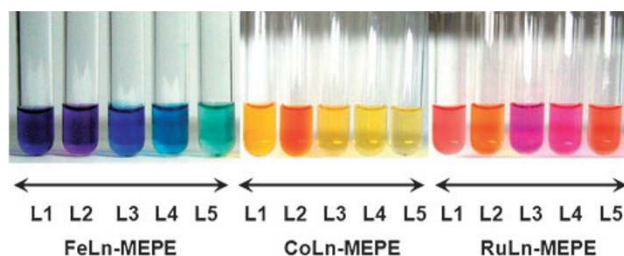
Figure 8. Color of **FeL*n*-**, **CoL*n*-**, **RuL*n*-MEPE**s.

FeL*n*-MEPEs is purple, blue, or green, that of **CoL*n*-MEPE**s is yellow or orange and that of **RuL*n*-MEPE**s is reddish (Figure 8). In addition, it is also possible to introduce more than two metal species into the polymer. A polymer containing both iron and cobalt ions has a red color; this phenomenon is described later.

REPETITION STABILITY

The main feature of electrochromic hybrid polymers is that the change from the colored form to the bleached form is controlled by the electrochemical redox reactions of the metal ions in the polymers, because the color of the polymers depends on MLCT absorption from metal ions to organic ligands.

In general, the electrochromic properties of organic electrochromic materials deteriorate fairly rapidly because the color change in such materials is a result of structural changes based on the electrochemical redox mechanism discussed above. Therefore, the long-term stability of these materials is low. Repetition stability can be significantly improved by using organic–metallic hybrid polymers because the structures of the organic ligands do not change during the redox reactions of the metal ions. The results on the experiment on the electrochromic cycling behavior of an **FeL1-MEPE** film cast on ITO glass revealed that the response time does not change even when the experiment is repeated 4000 times and that **FeL1-MEPE** is highly durable toward repetitive electrochromic changes. Thus, the major drawback associated with the earlier electrochromic organic materials has been overcome.

ELECTRONIC PAPER

Rapid development of telecommunication system such as the Internet and cellular phones has resulted in daily lives becoming more comfortable. On the other hand, the amount of carbon dioxide released from electronic devices such as computers and displays is constantly increasing. Given this scenario, it is difficult to disregard problems pertaining to energy consumption and global warming. However, at present, displays such as liquid-crystal displays,[76–80] plasma displays,[81–85] and organic electroluminescent (EL) displays[86–95] require electricity to continue to display. In addition, the increasing popularity of personal computers was expected to result in people using less paper. However, people continue to

print documents and pictures from computers, perhaps because many people are still more comfortable reading text printed on paper than reading text off a computer screen.

"Electronic papers"[96–101] was recently introduced as a new display device; this device has attracted considerable attention as the use of this device is expected to solve many problems pertaining to energy, environment, and resources. Electronic papers resemble ordinary paper; they have good flexibility, are thin and lightweight, and display characters and images electronically. These displays reflect light in a manner identical to ordinary paper; hence, they do not require power to display text and images, that is, the text/images do not disappear even if the power is turned off. Because these displays require neither a power supply nor a battery, they are portable and rewritable. Therefore, in an era in which every industry and utility is driven by the keywords "energy conservation" and "power saving," electronic paper can be prove to be a significant display device. It is expected that in the future, electronic papers will substitute normal printed papers such as newspapers and posters.

ELECTROCHROMIC METHOD FOR ELECTRONIC PAPER

Various methods have been proposed for developing the display mechanism of electronic paper including the micro-capsule method. However, most of these methods are for the fabrication of monochromatic (black and white) displays; electronic papers with color display are yet to be realized. Electrochromic display[102–105] (a display method involving the use of electrochromic material, which changes color through the electrochemical oxidation-reduction process) is known to be suitable for fabricating electronic papers with color displays, but research on such displays is limited in comparison to research on other methods. This is because (a) the material has many drawbacks such as low durability, slow response, difficulty associated with use in the fabrication of solid-state devices, and (b) the efficiency of the method is extremely dependent on the superiority or inferiority of the material. In other words, if electrochromic material suitable for use in electronic paper is developed, it is possible this method could be a breakthrough in the area of color electronic paper.

MULTICOLOR ELECTROCHROMIC DISPLAYS

Since organic–metallic hybrid polymers are formed through a self-assembly process, it is possible to not only select the various combinations of organic ligands and metal species but also to introduce several different types of organic ligands or metal species into a single polymer. For instance, an organic–metallic hybrid polymer containing both iron(II) and cobalt(II) ions (**Co/FeL1-MEPE**) changes color from red to blue to transparent/colorless at potentials of 0, 0.6, and 1.0 V, respectively (Figure 9). Such multicolor electrochromic change is a result of the difference in the redox potentials of iron and cobalt ions (0.77 and 0.10 V *vs.* Ag/Ag$^+$, respectively). The
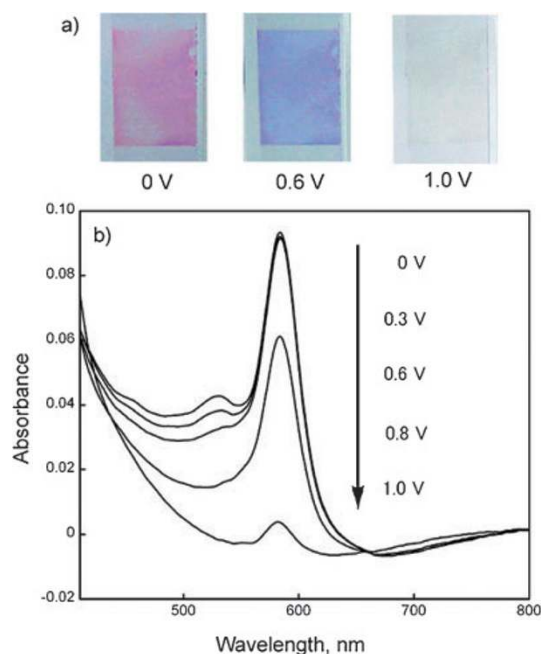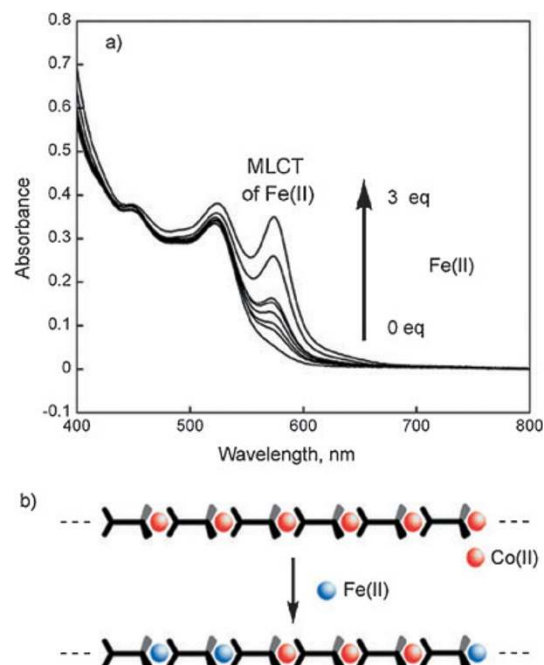
Figure 9. (a) Photographs of a spin-coated **Co/FeL1-MEPE** film on a quartz-ITO substrate in a UV-cuvette at 0 (red-purple), 0.6 (blue) and 1.0 V (transparent). (b) UV-vis. spectra of **Co/FeL1-MEPE** during electrochemical oxidation from 0 to 1.0 V vs. Ag/Ag+.

Figure 10. (a) UV-vis spectral change during the titration of Fe(OAc)$_2$ (0 eq. to 3 eq.) to **CoL1-MEPE** solution (1.2×10^{-4} M in methanol). (b) Incorporation of Fe(II) ions into **CoL1-MEPE**.

absorptions processes in which the iron(II) and cobalt(II) ions participate disappear at potentials higher than these redox potentials. The initial red color observed is caused by a combination of two absorptions in which both the iron(II) and cobalt(II) ions participate. The color of the polymer changes to blue at a potential of 0.6 V. At this potential, cobalt(II) ions are electrochemically oxidized to cobalt(III) ions, and the absorption in which the cobalt(II) ions participate disappears. Finally, the polymer becomes colorless at a potential of 1.0 V because the MLCT absorption involving iron(II) also disappears as a result of the oxidation of iron(II) to iron(III). Such multicolor electrochromic polymers will assist in the simplification of devices such as multicolor electronic paper and in the reduction of the thickness of such devices.

Metal ion exchange in the hybrid polymer was confirmed by the reaction of **CoL1-MEPE** with Fe(II) ions. As can be seen in Figure 10a, addition of Fe(OAc)$_2$ to **CoL1-MEPE** gives rise to the characteristic MLCT absorption at 580 nm demonstrating the incorporation of Fe(II) ions into the **CoL1-MEPE** backbone (Figure 10b).

FABRICATION OF SOLID-STATE DEVICES

Thus far, the electrochromic properties of polymer film have been demonstrated only in solution; however, solid-state devices that use electrochromic films can find practical applications in electronic devices and displays. Therefore, a solid-state electrochromic device was developed using a mixture of polymethylmethacrylate, propylene carbonate, and LiClO$_4$ as the polymer gel electrolyte (Figure 11). The details
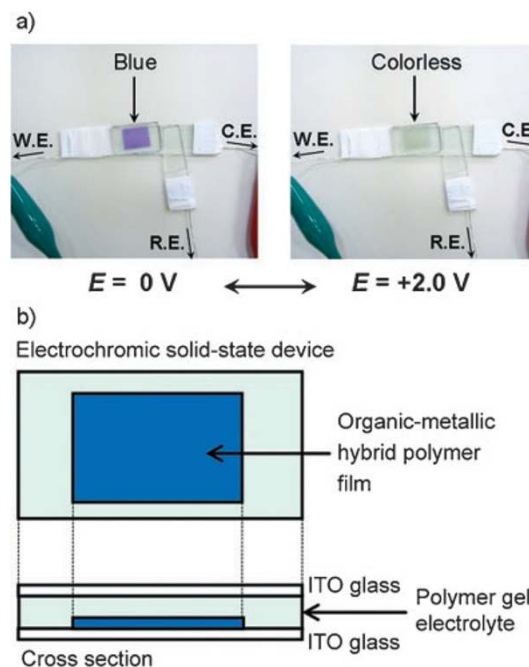
Figure 11. (a) Color change of **FeL1-MEPE** film in electrochromic solid-state device and (b) the device structure.

of fabrication are as follows: 20 μL of a methanol solution (1.0 mg MEPEs/0.5 mL MeOH) is cast or spin-coated (500 rpm for 60 s) on ITO electrodes (20 Ω). A mixture of polymethylmethacrylate (7.0 g), propylene carbonate (20 mL), and LiClO$_4$ (3.0 g) was used as the polymer gel electrolyte. The film changes from colorless to blue faster (within one second) than
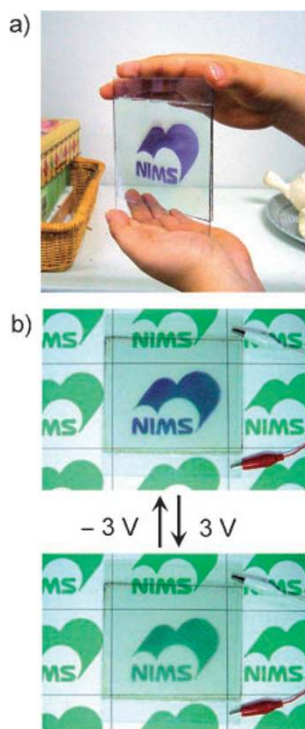
Figure 12. (a) A 5-inch electrochromic display using **FeL1-MEPE** and (b) the electrochromic change (Green "NIMS" logos are printed on the paper of the groundwork).

Figure 13. Several electrochromic displays including a 10-inch one.

vice versa (a few seconds), probably because Fe(II) is more stable than Fe(III) in the polymer. We also succeeded to fabricate 5-inch displays using the electrochromic materials (Figure 12).

Furthermore, we fabricated electrochromic 10-inch solid-state devices equipped with two polymer films, which can exhibit two different displays by reversing the direction of current (Figure 13). Therefore, the device equipped two **Ru/FeL1-MEPE** films (**Ru/FeL1-MEPE** is a copolymer of **RuL1-MEPE** and **FeL1-MEPE** bearing 1,4-bis(2,2′:6′,2″-terpyridin-4-yl)benzene as the organic ligand) has five kinds of displays that can be activated changing the applied potentials between −2.5 and 2.5 V (Figure 14); this is because
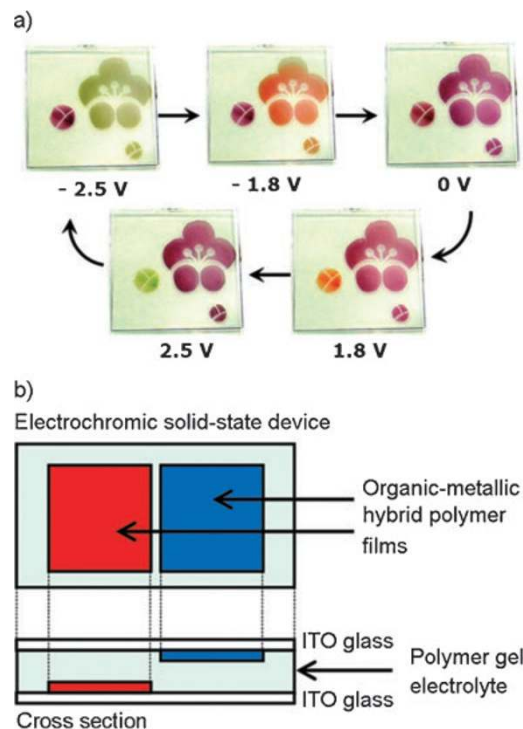
Figure 14. (a) Multi-color electrochromic change of **Ru/FeL1-MEPE** film in the solid-state device and (b) the device structure.

Ru/FeL1-MEPE films exhibit different colors such as red, orange, and pale green at 0, 1.8, and 2.5 V, respectively.

Because the electrochromic properties of hybrid materials are a result of the MLCT interaction between the organic ligands and metal ions, a polymeric structure is not always necessary for obtaining these properties. However, polymeric structures have several advantages; for example, materials with polymeric structures can be readily deposited as films for use in solid-state devices.

In the case of conventional organic polymers, the degree of polymerization is controlled solely by the polymerization conditions because polymer chains are formed with strong covalent bonds. The length of the polymer chain, once formed, does not change subsequently. However, hybrid polymers are in a state of equilibrium in solution because these polymers are formed with coordination bonds. The degree of polymerization is reversible, depending on the concentration of the polymer in the solution; when the concentration is low, a portion of the metal ions complexed with the organic ligands dissociates, thus reducing the length of the polymer chain. Moreover, the degree of polymerization changes depending on the solvent in which the polymer is dissolved. Each hybrid polymer has a binding constant that characterizes the complexation between the metal ions and the organic ligands, and this binding constant varies according to the solvent that is used.

Generally, organic polymers with high molecular masses have a lower solubility due to strong stacking of the polymer chains. Low solubility decreases processability of the polymers, and this often prevents their practical application.

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However, in the case of the organic–metallic hybrid polymers, even when the polymer has a high molecular mass (that is, it has a large binding constant), it remains highly soluble in the solvent, although the molecular mass can decrease under diluted conditions. Polymers with such properties are suitable for the fabrication of films. Even if the polymer in the solution has a low molecular mass before casting, the polymer regains a high molecular when the solution becomes concentrated as the solvent is removed.

CONCLUSION

Ever since Staudinger demonstrated the existence of polymers about 90 years ago,[106] polymer chemistry has developed significantly; polymers consisting covalent bonds have become indispensable materials in our lives in the form of plastics, synthetic rubbers, etc., and our daily lives have become much more comfortable than earlier. On the other hand, the development of self-assembled polymers formed with noncovalent bonds has been attracting a fair amount of attention in recent times because these polymers are expected to have unique electronic, photonic, magnetic, and catalytic properties, which are entirely different from those of conventional organic polymers. These properties are attributed to the strong interaction between metal ions and organic ligands in organic–metallic hybrid polymers that are formed by the self assembly of a metal ions with organic ligands, polymers, or dendrimers. Organic–metallic hybrid polymers that are formed by the complexation of bis(terpyridine)s and metal ions develop color through absorption based on charge transfer from metal ions to the organic ligands (MLCT). We discovered the phenomenon of color disappearance in such polymers upon the application of certain electric potential (electrochromic phenomenon); this phenomenon was observed when such polymers were cast onto ITO glass and underwent electrochemical oxidation/reduction. This transition between color development and color disappearance occurs at a threshold voltage corresponding to the oxidation–reduction potential of the metal in the polymer. Therefore, we fabricated electrochromic solid-state display devices by spin-coating ITO glass with the polymer and covering it with a layer of gel electrolyte and another sheet of ITO glass. By applying an electric potential (3 V) using two dry batteries, we could observe the alternate development and disappearance of color.

Materials that exhibit electrochromic properties have a wide range of applications such as in the fabrication of electronic papers, which are being touted as next-generation displays, and smart windows. A wide range of hybrid polymers can be developed by using various combinations of organic ligands and metal ions, and the study and development of such hybrid polymers will soon constitute an important part of polymer chemistry.

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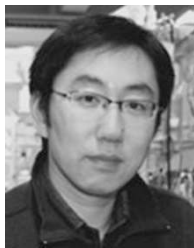
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