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Iron(II) and Copper(I) Coordination Polymers: Electrochromic Materials with and without Chiroptical Properties

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The electrochemical and optical properties of films prepared from two different Fe(II) coordination polymers (**TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ (**TPT** = terpyridine–phenyl–terpyridine) and **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ (**CTPCT** = chiral terpyridine–phenyl–chiral terpyridine)) and a coordination polymer based on Cu(I) metal centers (**PDP**[Cu^{I}**PDP**]$_n$(BF$_4$)$_n$) (**PDP** = phenanthroline–dodecane–phenanthroline) have been studied. The oxidation of a **PDP**[Cu^{I}**PDP**]$_n$(BF$_4$)$_n$ film coated on an indium–tin oxide (ITO) electrode by stepping the potential from 0.0 to +1.4 V vs Ag/AgCl led not only to the complete bleaching of the absorption in the visible region of the spectrum within 5 min but also to a redox-induced dissociation and dissolution of the polymer. The reverse reaction of binding and reassembling the polymer at the electrode surface, upon stepping the potential back to 0.0 V, occurred with a rate which was at least 1 order of a magnitude slower. In contrast, the bis(2,2′:6′,2′′-terpyridine)iron(II)-based redox polymers **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ and **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$, during similar spectroelectrochemical experiments, not only exhibited a dramatically enhanced switching rate but also displayed symmetric switching kinetics. The films did not show signs of deterioration over 150 switching cycles. Additionally, in an effort to assemble an electrochromic device with chiroptical properties, the electrochromism of films generated from the enantiomerically pure **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ polymer was studied through circular dichroism.

Introduction

There has been and continues to be a widespread interest in reversible and efficient molecular switches for optical and electronic applications. A major area of interest in this field is the development of electrochromic materials and devices. Electrochromism refers to the generation of different visible-region electronic absorption bands as a result of switching between two or more redox states. One of the main uses of electrochromic materials is in smart windows for cars and buildings and in antiglare rear-view mirrors. Potential applications in information storage can also be envisioned.[1] Electrochromic applications require materials with a high ratio between the absorbance change and the transferred charge/unit area (coloration efficiency) as well as high reversibility. The fact that many redox-active transition metal coordination complexes exhibit intense coloration due to metal-to-ligand charge transfer (MLCT), intervalence CT, intraligand excitation, or related visible region electronic transitions renders them attractive candidates as electrochromic materials.[2] Although Prussian Blue, [Fe(Fe(CN)$_6$]$^-$, is probably the most widely used coordination compound for this purpose,[3] there has also been considerable interest in polypyridine- and phthalocyanine-containing transition metal complexes. While it is possible to fabricate solution-phase electrochromic devices with mononuclear transition metal compounds, solid-state devices generally require polymeric systems. A well-known approach to prepare polymeric systems takes advantage of the fact that vinyl-substituted polypyridine−metal complexes can be readily and controllably electropolymerized upon ligand reduction.[4] These electropolymerized films exhibit high stability to redox cycling and excellent counterion transport ability, the latter being a necessity for fast switching kinetics. Meyer and co-

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(1) (a) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147. (b) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, Germany, 1995. (c) Green, M. *Chem. Ind.* **1996**, *17*, 641.

(2) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum Press: New York, London, 1994.

(3) Koyuma, T.; Hayashi, R.; Masuda, E.; Kurose, A.; Hanabusa, K.; Shirai, H.; Hayakawa, T.; Hojo, N. *Polym. Commun.* **1988**, *29*, 38.

(4) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc.* **1993**, *89*, 333.

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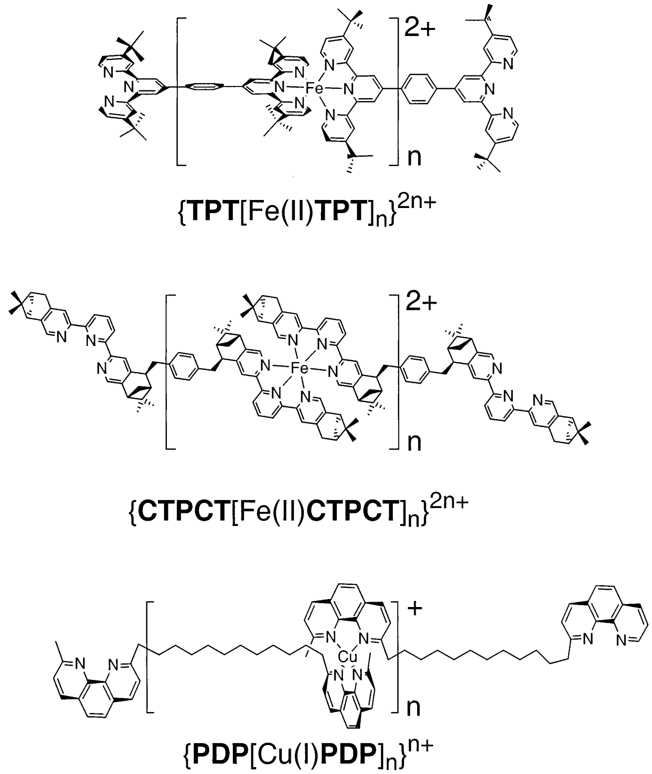
workers combined this electropolymerization technique with the photolability of the [Ru(4-methyl-4′-vinyl-2,2′-bipyridine)$_2$(py)$_2$]$^{2+}$ complex (py = pyridine) and successfully prepared spatially segregated, bicomponent electrochromic film assemblies.[5] In a related approach, Elliott and co-workers emplyed Ru complexes of acrylate-substituted bipyridines and chemically polymerized thin films of the same. The resulting films could be cycled through 4 color changes.[6] Another approach for the development of electrochromic devices is to synthesize coordination polymers from tailored bridging ligands and transition metal ions and study the spectroelectrochemical response of films prepared from these materials. Kimura and co-worker showed that an indium−tin oxide ITO electrode with a cast film of an Fe(II) coordination polymer prepared from a rigid linear bridging ligand composed of two 2,2′:6′,2″-terpyridine moieties and a phenyl spacer unit exhibited a reversible color change from blue to transparent upon oxidation.[7]

An especially attractive, yet seldomly exploited, feature of octahedral transition metal complexes is the possibility of helical chirality at the metal center, resulting in unique chiroptical properties.[8] (For additional information on this subject, the interested reader can consult refs 8a,b.). It has been shown that one can predetermine the chirality at metal centers through the use of chiral ligands, which can be prepared by the separation of the respective enantiomers through diastereomers or by their preparation from optically pure precursors.[9] Von Zelewsky and co-workers employed the latter strategy in pioneering the ability to control the helical chirality around metal centers through the use of chiral terpene building blocks.[10] The unique spectroelectrochemical properties of coordination polymers and the possibility of efficiently controlling the chirality of the metal centers renders chiral coordination polymers unique candidates for the preparation of stereoscopic displays.[11]


$\{\mathbf{TPT}[\mathrm{Fe(II)}\mathbf{TPT}]_n\}^{2n+}$

$\{\mathbf{CTPCT}[\mathrm{Fe(II)}\mathbf{CTPCT}]_n\}^{2n+}$

$\{\mathbf{PDP}[\mathrm{Cu(I)}\mathbf{PDP}]_n\}^{n+}$

Figure 1. Structures of the of the coordination polymers employed in this study.

The work presented herein describes the electrochemical and optical properties of films prepared from two different Fe(II) coordination polymers, $\mathbf{TPT}[\mathrm{Fe^{II}}\mathbf{TPT}]_n(\mathrm{PF_6})_{2n}$ (**TPT** = terpyridine−phenyl−terpyridine) and $\mathbf{CTPCT}[\mathrm{Fe^{II}}\mathbf{CTPCT}]_n(\mathrm{PF_6})_{2n}$ (**CTPCT** = chiral terpyridine−phenyl−chiral terpyridine) and a coordination polymer based on Cu(I) metal centers, $\mathbf{PDP}[\mathrm{Cu^{I}}\mathbf{PDP}]_n(\mathrm{BF_4})_n$ (**PDP** = phenanthroline−dodecane−phenanthroline) (Figure 1). The intent of this work was to understand the relation between the optical properties and the structure of the polymers, as determined by the identity of the bridging ligand and of the metal center. Additionally, in an effort to assemble an electrochromic device with chirooptical properties, the electrochromism of films generated from an enantiomerically pure Fe(II)-based coordination polymer was studied through circular dichroism.

Experimental Section

The synthetic procedures to prepare the coordination polymers have been described elsewhere.[12] Solvents and supporting electrolytes used for electrochemical studies were as previously described.[12] Chemicals used for synthesis were obtained from Aldrich Chemical Co. or Sigma Chemical Co. and were used without further purification. Films of the Fe(II) polymers on a glassy carbon electrode (5 mm diameter) were spin-coated from 100 μL of an acetone solution (1 mg/mL) at a rotation speed of 500 rpm. Substrates for the spectroelectrochemical experiments were prepared by casting the same solution on an ITO slide (75 × 9 × 1.2 mm, 100 Ω/square, Delta Technologies Ltd., Stillwater, MN) and slowly evaporating the solvent. The average film thickness estimated from the absorbance, the density of the materials, and the molar absorptivity in solution, for these coated ITO electrodes, ranged from 100 to 500 nm. The ITO substrates were cleaned prior to use by immersing in HNO_3 for 15 min, rinsing with water, sonicating in water for 5 min, and subsequently rinsing with acetone.

Electrochemical experiments were carried out with a BAS CV-27 potentiostat in a one-compartment cell or directly in a quartz

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(5) Leasure, R. M.; Ou, W.; Moss, J. A.; Linton, R. W.; Meyer, T. J. *Chem. Mater.* **1996**, *8*, 264.

(6) (a) Elliott, C. M.; Redepenning, J. G. *J. Electroanal. Chem.* **1986**, *197*, 219−232. (b) Pichot, F.; Beck, J. H.; Elliott, C. M. *J. Phys. Chem. A* **1999**, *103*, 6263−6267.

(7) Kimura, M.; Horai, T.; Muto, T.; Hanabusa, K.; Shirai, H. *Chem. Lett.* **1999**, 1129.

(8) (a) Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121−151. (b) Von Zelewsky, A. *Stereochemistry of Coordination Compounds*; John Wiley & Son Ltd.: New York, 1996.

(9) (a) Gladiali, S.; Pinna, L.; Delogu, G.; de Stefano, M.; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, *1*, 635. (b) Von Zelewsky, A.; Mamula, O. *J. Chem. Soc., Dalton Trans.* **2000**, 219. (c) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 302.

(10) (a) Hayoz, P.; Von Zelewsky, A.; Stoeckli-Evans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111. (b) Muerner, H.; Belser, P.; von Zelewsky, A. *J. Am. Chem. Soc.* **1996**, *118*, 7989.

(11) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506.

(12) (a) Bernhard, S.; Takada, K.; Díaz, D. J.; Abruña, H. D.; Mürner, H. *J. Am. Chem. Soc.* **2001**, *123*, 3098. (b) Bernhard, S.; Takada, K.; Jenkins, D. Abruña, H. D. *Inorg. Chem.* **2001**; *Inorg. Chem.* **2002**, *41*, 765.

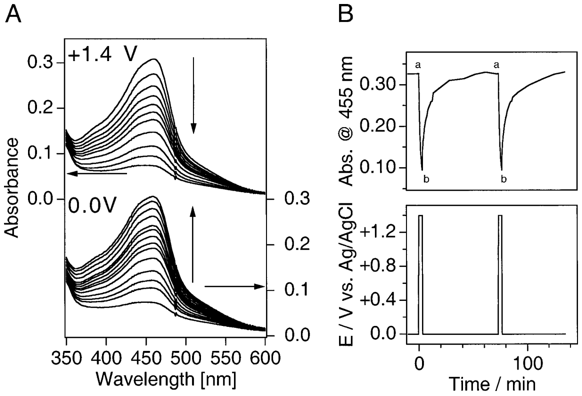

Figure 2. (A) Spectral changes for a **PDP**[Cu^{I}**PDP**]$_n$(BF$_4$)$_n$ film cast onto an ITO electrode upon stepping the potential (vs Ag/AgCl) from 0.0 to +1.4 V in 0.1 M LiClO$_4$ in 1:1 ethanol−water (top) and back to 0.0 V (bottom). (B) Potential steps (bottom) and resulting absorbance (top) changes at the same electrode through multiple cycles (a, 0.00 V → +1.40 V; b, +1.40 V → 0.00 V). Time intervals between successive spectra were the following: (i) for oxidation (bleaching), 15 s.; (ii) for reduction (coloration), first four scans obtained at 1 min intervals and then every 5 min.

cuvette. A large area platinum mesh was used as a counter electrode, and all potentials are referenced to a saturated Ag/AgCl electrode without regard for the liquid junction. UV−vis absorption spectra were recorded using a Hewlett-Packard 8453 diode-array spectrometer. An Aviv 62DS circular dichroism (CD) spectrometer was used to acquire CD spectra.

Results and Discussion

PDP[Cu^{I}PDP]$_n$(BF$_4$)$_n$. The electrochemistry of this polymer is characterized by a Cu(I)/Cu(II) redox process at a formal potential value of + 1.1 V vs Ag/AgCl. Figure 2A depicts the spectral changes of a film of **PDP**[Cu^{I}**PDP**]$_n$(BF$_4$)$_n$ on an ITO electrode at applied potentials of 0.0 or +1.4 V vs Ag/AgCl in 0.1 M LiClO$_4$ in 1:1 ethanol−water. The disappearance of the absorption peak at 455 nm, which is attributed to a metal-to-ligand charge transfer (MLCT) transition in the complex, upon stepping the potential from 0.0 to +1.4 V indicates the complete oxidation of the Cu(I) centers to Cu(II). The kinetics of these spectral changes are shown in Figure 2B and offer clear evidence that the process is reversible. However, as can be ascertained from the figure, whereas oxidation at +1.4 V results in a rapid decrease in the absorbance, reaching a minimum in about 5 min, stepping the potential back to 0.0 V results in a much slower recovery (75 min) of the absorbance at 455 nm. Given the lability of Cu(II) 1,2-diimine complexes (phenanthroline in the present case), the Cu(I)/Cu(II) oxidation process leads to the redox-induced dissociation and subsequent dissolution of the polymer coated onto the electrode. As a consequence of this dissociation and dissolution process, the kinetics of the reverse process, binding and reassembling of the polymer at the electrode surface, takes place at a much slower rate.[12b] In fact we have previously carried out an extensive study of these redox-induced transformations.[12b] To prevent this fragmentation, it was necessary to employ redox polymers assembled from a kinetically more stable moiety, thus the use of bis(2,2′:6′,2″-terpyridine)iron(II) coordination complexes.

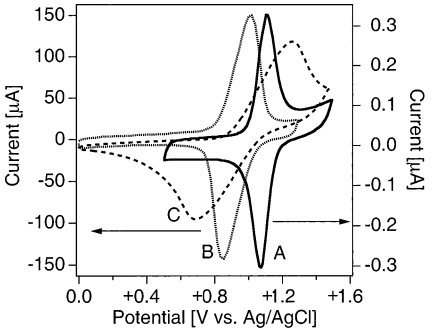

Figure 3. Cyclic voltammogram of **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ (A) in acetonitrile solution (0.1 mM, 0.1 M tetrabutylammonium hexafluorophosphate) and as films (B) spin-coated onto glassy carbon or (C) cast onto ITO at a sweep rate of 100 mV/s in 0.1 M LiClO$_4$ in 1:1 ethanol−water.

TPT[Fe^{II}TPT]$_n$(PF$_6$)$_2$*n*. Figure 3 depicts the electrochemical properties of **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ in 0.1 M LiClO$_4$ in 1:1 ethanol−water as a cast film on a glassy carbon electrode (Figure 3B) and as a spin-coated film on an ITO electrode (Figure 3C), as well as in acetonitrile solution (Figure 3A), the latter for comparison. Due to the more efficient stabilization of the Fe(III) state in aqueous solvents, the potential of the peak assigned to the Fe(II)/Fe(III) process shifts by 200 mV when compared to acetonitrile. The solution as well as the spin-coated film voltammograms exhibit wave shapes typical for surface confined redox processes. Whereas such behavior was expected for the film experiments, the shape of the solution voltammogram indicates adsorption of the polymer onto the electrode surface as well. The large peak to peak separation in the case of the ITO electrode is attributed to the high resistance of the electrode material, as compared to the others. It should be noted that although there is an apparent shift in the formal potential for the film on ITO, we believe that this is due to to the fact that the scan was reversed at ca. +1.5 V, a value at which there was incomplete redox conversion and thus the resulting apparent shift in $E^{\circ\prime}$.

Absorbance changes of the coated ITO electrode were monitored during multiple double potential step experiments. Figure 4A shows the spectral changes of a **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ film (ca. 100 nm thick) using 0.1 M LiClO$_4$ in 1:1 ethanol−water as electrolyte in the region of the MLCT transition upon stepping the potential from 0.0 to +1.8 V and back to 0.0 V. First, it should be mentioned that this transition is red-shifted by over 30 nm in the polymer when compared to the [Fe(tpy)$_2$]$^{2+}$ ion in solution. This shift can be ascribed to the more extended π-system of the bridging ligand, which is also the reason for the significantly higher absorptivity ($\epsilon = 33200$ mol^{-1} cm^{-1}) when compared to [Fe(tpy)$_2$]$^{2+}$ ($\epsilon = 11500$ mol^{-1} cm^{-1}).[13] The decrease in absorption is complete upon oxidation of the Fe(II) centers to Fe(III) leading to the decoloration of the initially blue film leaving the modified ITO electrode essentially colorless. Subsequently stepping the potential back from +1.8 to 0.0 V reduces the Fe(III) centers of the polymer to Fe(II) and therefore gives rise to the reemergence of the MLCT

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(13) Ottaway, J. M. In *Indicators*; Bishop, E., Ed.; Pergamon Press: Oxford, New York, Toronto, 1972; p 647.

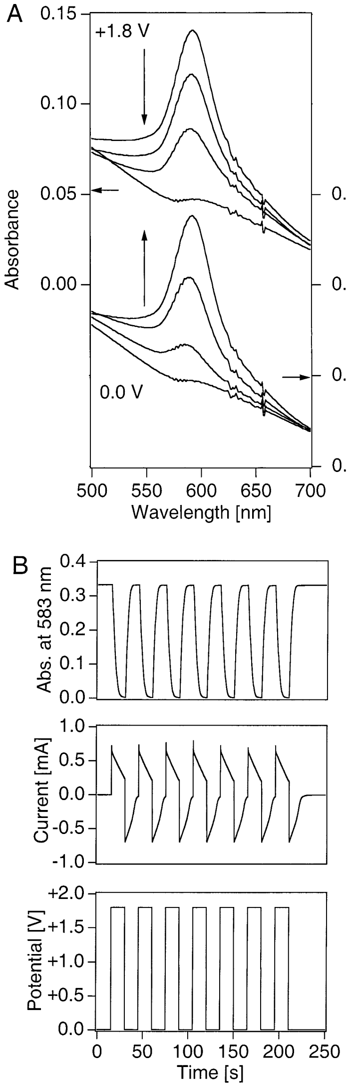

Figure 4. (A) Spectral changes for a **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ film cast onto an ITO electrode upon stepping the potential (vs Ag/AgCl) from 0.0 to +1.8 V (top) and back to 0.0 V (bottom) in 0.1 M LiClO$_4$ in 1:1 ethanol−water. (B) Potential steps (bottom) and simultaneous current (middle) and absorbance (top) changes using a similar electrode (film thickness: ca. 100 nm) over multiple cycles. Time intervals between successive spectra were the following: (i) for oxidation (bleaching), 3 s; (ii) for reduction (coloration), 3 s.

transition. Figure 4B depicts the changes in the absorbance at 583 nm and the simultaneous current response upon repeatedly stepping the potential between 0.0 and +1.8 V. It is evident that the changes in absorbance observed upon reduction and oxidation are reversible and have similar time scales. These observations suggest that no fragmentation of the polymer takes place and that the redox processes are entirely surface confined, as opposed to the behavior of the above-discussed copper polymer. The films showed no sign of deterioration during multiple redox steps, and the cyclic voltammogram remained unchanged after over 150 cycles. The current−time profile did not exhibit Cottrell behavior, and this is likely related to the fact that the ITO electrode has a large resistance, as mentioned earlier. It should also be mentiond that, as is evident in the central panel of Figure 4B, during the "bleaching" step at +1.80 V, there is still significant curret flow just prior to stepping the potential back to 0.0 V where "coloration" takes place. We believe that this residual current is largely due to water oxidation. Consistent with this is the fact that during the "coloration" step at 0.0 V the residual current was essentially negligible.

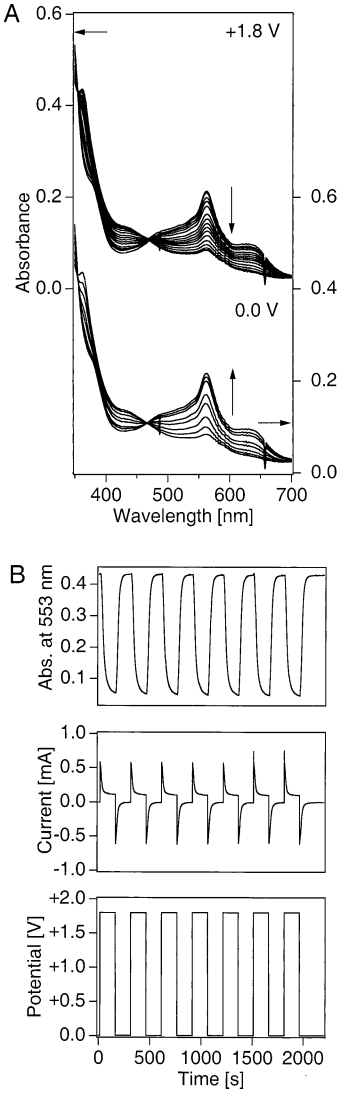

Figure 5. (A) Spectral changes for a **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ film cast onto an ITO electrode upon stepping the potential (vs Ag/AgCl) from 0.0 to +1.8 V (top) and back to 0.0 V (bottom) in 0.1 M LiClO$_4$ in 1:1 ethanol−water. (B) Potential steps (bottom) and simultaneous current (middle) and absorbance (top) changes at a similar electrode (thickness: 530 nm) over multiple cycles. Time intervals between successive spectra were the following: (i) for oxidation (bleaching), 8 s; (ii) for reduction (coloration), 15 s.

CTPCT[Fe^{II}CTPCT]$_n$(PF$_6$)$_{2n}$. Initial studies performed with the chiral **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ polymer were aimed at comparing its spectroelectrochemical properties to those of the above-discussed **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ polymer. To obtain a film with similar MLCT absorbance (0.3−0.4) (due to the difference in molar absorptivity) it became necessary to cast the **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ films to a thickness of about 500 nm.[14] Figure 5A presents results for an experiment analogous to that in Figure 4A where it is evident that **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ exhibits an MLCT transition similar to that of [Fe(tpy)$_2$](PF$_6$)$_2$. Bleaching of

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(14) Braude, E. A. *J. Chem. Soc.* **1950**, 379.

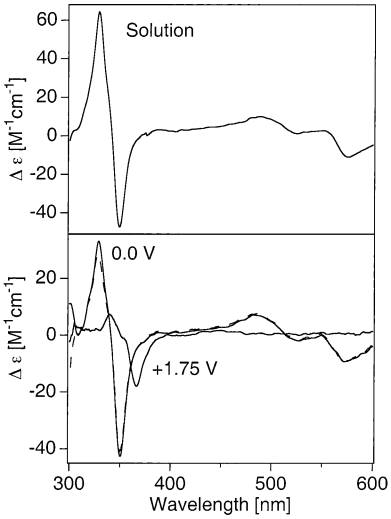

Figure 6. Top panel: CD spectrum of a 10 μM solution of **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ in acetonitrile. Bottom panel: CD spectrum of a film of **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ cast onto a ITO electrode at 0.0 V (—), at +1.75 V (—), and after stepping the potential back to 0.0 V (---) (electrolyte: 0.1 M LiClO$_4$ in 1:1 ethanol−water).

this transition was induced by stepping the potential from 0.0 to +1.8 V. Subsequent reduction of the Fe(III) centers to Fe(II) by stepping the potential back to 0.0 V lead to the reappearance of this transition, and the film recovered its magenta color. Kinetic measurements of this electrochromic process are presented in Figure 5B. The switching was highly reversible over 150 cycles, but it is also apparent that the switching time for **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ is over 1 order of magnitude slower than that of **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$. Murray and co-workers have previously shown that charge transport in polymer-coated electrodes can be treated similar to diffusion with an apparent diffusion coefficient D_{app}.[15] We believe that the increase in switching times for the **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ film compared to the **TPT**[Fe^{II}**TPT**]$_n$(PF$_6$)$_{2n}$ device is largely due to the 5-fold increase in thickness. In fact, if one were to assume similar D_{app} values for both polymer films, the rate difference would be expected to be even higher (ca. 25-fold).

Chiroptical Devices. Another objective of the preparation of **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$, was to study the optical anisotropy properties of films prepared from this material. An especially valuable means of gaining an understanding of the chiroptic properties of such materials is through the measurement of their circular dichroism. Figure 6 depicts the solution CD spectrum (top panel) and the results of the chiro-electrochromic response of a **CTPCT**[Fe^{II}**CTPCT**]$_n$(PF$_6$)$_{2n}$ film cast onto an ITO electrode (bottom panel). It is apparent that the peak positions for the film do not shift significantly when compared to those in solution. Also, clear changes can be observed upon stepping the potential from 0.0 to +1.75 V resulting in the oxidation of the Fe(II) centers to Fe(III). The CD signals, initially present in the visible region of the spectrum, disappear completely during this process, as was the case for the electronic absorption. Nonetheless, it is worth mentioning that shifts were also observed in the UV region of the spectrum, a fact that can be related to a change in π-bonding between the ligand and the iron center. However, the magnitude of the changes in the CD spectrum is not sufficient for use in stereoscopic displays. It needs to be pointed out that the chirality of the polymers arises only from the chiral nature of the ligand periphery and thus the small magnitude of the effect is not surprising. On the other hand, the CD effect that would be anticipated from intrinsically chiral complexes (e.g. Δ-[Ru(bpy)$_3$]$^{2+}$) would be considerably larger. As in the previous cases, stepping the potential back to 0.0 V (from +1.75 V) lead to the complete reversal of the above-described changes.

Conclusions

We have studied the electrochromic properties of films prepared from three different coordination polymers. Whereas a bis-chelating 1,10-phenanthroline-based Cu(I) polymer exhibited dissociation upon oxidation, the bis(2,2′:6,2″-terpyridine)iron(II)-based polymers were extremely stable for over 150 redox cycles. Kinetic measurements indicated that switching speeds were mostly influenced by film thickness and were independent of the electronic coupling between the ligand moieties. Circular dichroism studies of an enantiomericaly pure polymer revealed the complete disappearance of the CD signal in the visible region and significant shifts in the UV part of the spectrum upon oxidation of the Fe(II) centers. The reverse processes could be observed upon rereduction. To improve the switching kinetics by employing thinner films, we are currently exploring polymers with a higher molar absorptivity of the MLCT transition. We are also investigating the possibility of enhancing the magnitude of the chiroptical electrochromic response by replacing the bis(2,2′:6,2″-terpyridine)iron(II) moieties with intrinsically chiral tris(1,2-diimine) complexes.

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(15) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (b) Daum, P.; Lenhard, J. R.; Rolison, D. R.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649. (c) Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389.