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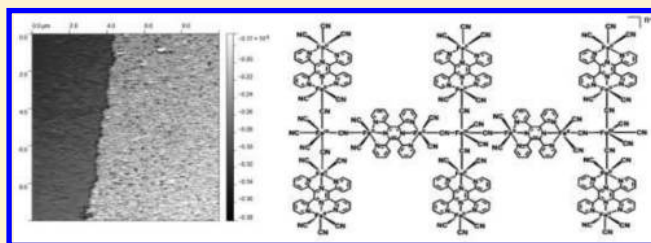
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ABSTRACT: The electrochromic behavior of iron complexes derived from tetra-2-pyridyl-1,4-pyrazine (TPPZ) and a hexacyanoferrate species in polyelectrolytic multilayer adsorbed films is described for the first time. This complex macromolecule was deposited onto indium–tin oxide (ITO) substrates via self-assembly, and the morphology of the modified electrodes was studied using atomic force microscopy (AFM), which indicated that the hybrid film containing the polyelectrolyte multilayer and the iron complex was highly homogeneous and was approximately 50 nm thick. The modified electrodes exhibited excellent electrochromic behavior with both intense and persistent coloration as well as a chromatic contrast of approximately 70%. In addition, this system achieved high electrochromic efficiency (over 70 cm² C^{−1} at 630 nm) and a response time that could be measured in milliseconds. The electrode was cycled more than 10³ times, indicating excellent stability.



INTRODUCTION

Mixed valence systems, particularly oligomers based on transition metals, such as Prussian blue (PB), have been widely investigated in the literature because their interesting optical properties are suitable for electrochromic device (ECD) development.^{1–4} However, few studies of the electrochromic properties of metallo-supramolecular polymers with organic ligands have been reported in the literature.^{5–7} Polymer materials based on terpyridines, bipyridines, porphyrins, and tetra-2-pyridyl-1,4-pyrazine (TPPZ) metal complexes are very attractive^{8–12} because these ligands are both chemically and thermally stable and have high binding constants that produce macromolecular assemblies with distinct electrochemical properties.

The properties of solid-state supramolecular architectures can be adjusted by introducing different metal ions and ligands as well as controlling the hydrogen bonding and electrostatic interactions of the coordination compounds.^{13,14} Moreover, the properties of these materials can be controlled at the molecular level using layered nanostructure films constructed using noncovalent interactions,^{7,15,16} which allow for the development of inorganic nanostructures that can be tailored by selecting suitable constituents. Organized films can be efficiently self-assembled through the spontaneous deposition of the assembled molecules onto the substrate surface and molecules in the adjacent layers.¹⁷ The primary driving force for self-assembly is the reduction of the overall chemical potential. Self-assembly is one of the few practical strategies available to

create ensembles of nanostructures based on a bottom-up approach to nanotechnology. Many mechanisms exist for the self-assembly of molecules and nanoclusters, including the use of electrostatic and surface forces,^{18–20} electrophoretic deposition,²¹ chemical interactions,²² hydrophobic and hydrophilic interactions,²³ and biomolecule-mediated techniques.^{24–26}

Our group has previously chemically modified an electrode through the electropolymerization of iron complexes derived from TPPZ and a hexacyanoferrate species to form the very stable supramolecular complex poly[Fe(TPPZ)FeCN], which probably has a structure similar to PB.²⁷ This inorganic polymer possesses a special structure that combines a mixed valence system with an organic ligand that has both a strong π character and high electronic conduction. It was found that, for supramolecular films of poly[Fe(TPPZ)FeCN], anion transport is faster in a solution containing K⁺ rather than Li⁺.²⁸

In this work, we report a unique strategy to immobilize the supramolecular complex poly[Fe(TPPZ)FeCN] onto a transparent conducting substrate [indium–tin oxide (ITO)] via both the layer-by-layer (LbL) self-assembly method and the spontaneous formation of the assembled molecules on the electrode surface. This composite film showed remarkable electrochromic properties compared to the analogous com-

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pound PB and achieved high electrochromic efficiency, with response times measured in milliseconds and long-term cycling stability even in solutions containing Na^+ ions, which is opposite the results for PB electrodes.

EXPERIMENTAL SECTION

TPPZ (Aldrich), $\text{K}_3\text{Fe}(\text{CN})_6$ (Aldrich), $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (Aldrich), acetonitrile (Aldrich), poly(allylamine hydrochloride) (PAH; $M_w = 10\,000$; Aldrich), poly(vinylsulfonic acid) (PVS; $M_w = 242\,000$; Merck), and Carbopol 940 ($M_w = 4\,000\,000$; Goodrich) were used as received without further purification. All solutions were prepared using ultrapure water (Elga System UHQ; resistivity = $18\text{ M}\Omega\text{ cm}^{-1}$). The isolated dinuclear iron(II) complex $[\text{Fe}_2(\text{TPPZ})(\text{H}_2\text{O})_6](\text{SO}_4)_2$ was prepared according to a previously published procedure.²⁷ The LbL films were assembled onto ITO (Delta Technologies; sheet resistance < $20\ \Omega/\text{sq}$) electrodes via the LbL self-assembly method.

The topography of the poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ films was analyzed using Agilent 5500 AFM/SPM atomic force microscopy (AFM) in intermittent contact (tapping) mode. The supramolecular film formed on the ITO was analyzed using an ultraviolet/visible (UV/vis) spectrophotometer (Cary 50, Varian). Cyclic voltammetry (CV) experiments were performed using an Autolab PGSTAT30 (EcoChemie) potentiostat/galvanostat. The electrochromic and electrochemical analyses were obtained simultaneously using a solid-state light source (WPI, Inc.). Plastic optical fiber cables, 1 mm in diameter, were used to transport the light from the electrochemical cell to a photodiode amplifier (PDA 1; WPI, Inc.), connected to the potentiostat to obtain *in situ* current/transmittance profiles as a function of the potential. Prior to these experiments, the electrolytic solution was sparged with pure nitrogen to achieve thoroughly anaerobic conditions, and the gas stream was maintained over the solution during the measurements.

Using the LbL strategy,¹⁷ two complementary polymers, PAH and PVS, were previously deposited directly onto ITO glass, by dipping the substrate alternately into the respective aqueous polymer solutions (0.5 g L^{-1}) at pH 7 for 15 min. After each layer deposition, the substrate was carefully washed with water and dried under a N_2 flow to form a PAH/PVS/PAH/ITO mattress. This system was then placed upside down on the surface of an aqueous poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ solution (3 mmol L^{-1}) that had been recently created through the self-assembly of $[\text{Fe}_2(\text{TPPZ})(\text{H}_2\text{O})_6]^{4+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ (1:3, v/v), as shown in Figure 1A. The polymer structure is shown in Figure 1B, and the schematic image of the electrode assembly is shown in Figure 1C. The optimized time for chemical adsorption was 24 h; after that, the electrode was removed, washed with water, and dried at room temperature. A bluish, insoluble, and homogeneous film then formed over the ITO glass surface.

RESULTS AND DISCUSSION

The supramolecular complex poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ forms a coordination polymer network in aqueous solution, but it is only slightly soluble and, therefore, can be easily deposited onto ITO-coated glass substrates via an alternate layer deposition process with PAH and PVS, as described in the Experimental Section. Figure 2 illustrates an AFM image of the modified electrode. The hybrid film is approximately 50 nm thick and has a homogeneous smooth surface; seven points on the sample were analyzed, and all exhibited the same morphology.

The LbL film-coated electrodes exhibited the redox response of the poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ ion when the outermost surface of the LbL film was the cationic polymer PAH, but virtually no response was observed for the LbL film-coated electrodes with a PVS outer surface because of the electrostatic repulsion between poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ and the negatively charged PVS layer. The structure of the present poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]/\text{PAH}/\text{PVS}/\text{PAH}$ films on an ITO electrode is highly interpenetrating based on the interaction between the

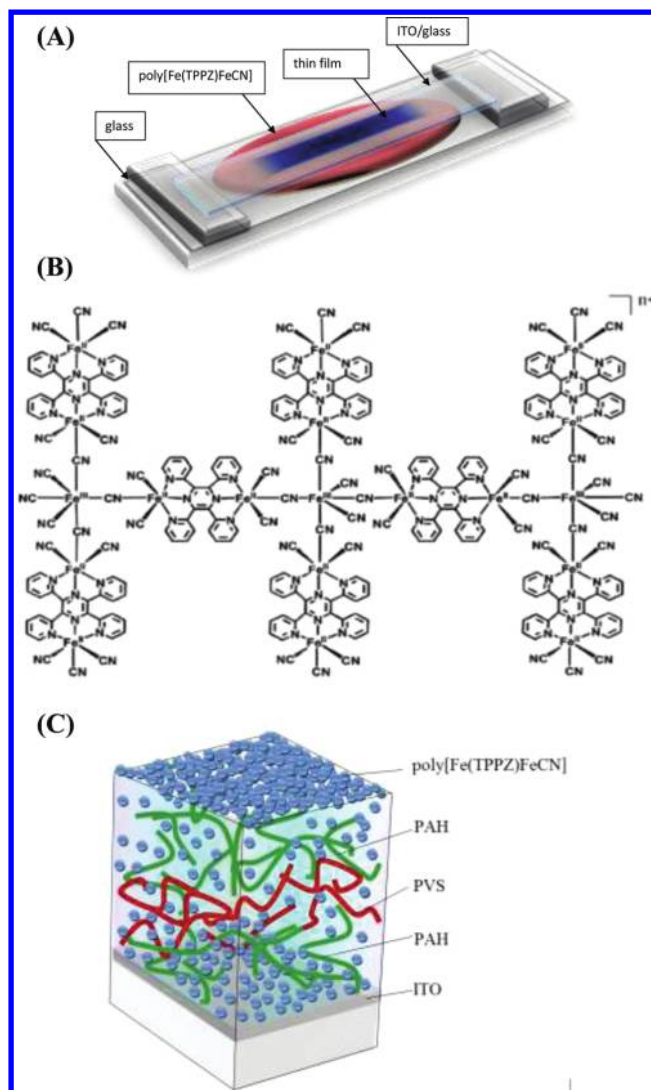


Figure 1. (A) *In situ* redox functionalization of PAH/PVS/PAH/ITO by the self-assembly of $[\text{Fe}_2(\text{TPPZ})(\text{H}_2\text{O})_6]^{4+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ species onto the modified electrode surface by sequential covalent processes. (B) Polymeric supramolecular structure of a poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ film. (C) Idealized structure of poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]/\text{PAH}/\text{PVS}/\text{PAH}$ films on an ITO electrode.

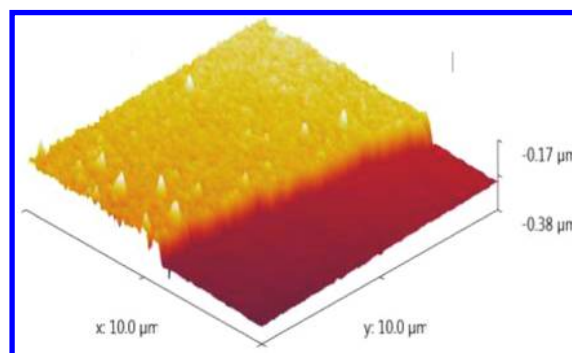


Figure 2. Topographic image of a poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]/\text{PAH}/\text{PVS}/\text{PAH}/\text{ITO}$ -modified electrode.

polyelectrolyte polymer chains and the iron complex (see Figure 1C). Here, the LbL self-assembly method has been successfully applied to the assembly of poly $[\text{Fe}(\text{TPPZ})\text{FeCN}]$ onto an ITO electrode surface via electrostatic attraction, but

lack of electrical connectivity was observed in the function of the growth of the multilayers, leading to an irreversible electrochemical behavior and higher response times (data not shown). However, this technique was better than that films grown using standard electropolymerization methods,^{27,28} where the poly[Fe(TPPZ)FeCN] supramolecular film presented lower electrochromic stability and lower chromatic contrast.

ITO electrodes modified with poly[Fe(TPPZ)FeCN]/PAH/PVS/PAH films exhibited a pair of reversible redox peaks at approximately +0.23 V versus Ag/AgCl, as seen in Figure 3,

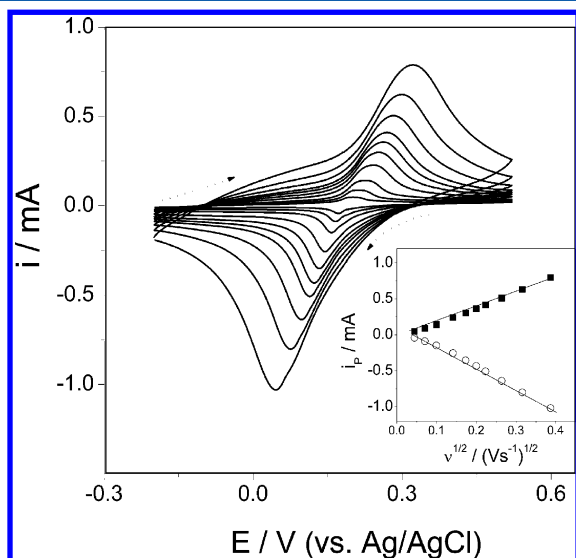


Figure 3. Cyclic voltammograms of a poly[Fe(TPPZ)FeCN]/PAH/PVS/PAH/ITO electrode at various scan rates in a 0.1 mol L⁻¹ KCl electrolytic solution. The scan rates lie in the range from 2 to 150 mV s⁻¹.

which can be related to the Fe^{III}/Fe^{II} redox process containing a TPPZ ligand, and it is equivalent to the first redox couple in the PB system.²⁹ These redox peaks are broader than those observed for PB films, probably because of the existence of non-equivalent electrochemical sites, as reported by Bard et al.³⁰ The electroactive film undergoes a diffusion-controlled process (see the inset of Figure 3) that is linearly dependent upon the peak current and the square root of the scan rate.³¹

The electrochromic behavior of the poly[Fe(TPPZ)FeCN]-modified electrode was verified *in situ* using UV/vis spectroscopy by placing the electrode in an electrochemical cell containing a 0.1 mol L⁻¹ KCl solution and obtaining a spectrum after applying a potential for 30 s. The results (Figure 4A) indicate that increasing the applied potential increases the absorbance signal, especially in the red region; this result is consistent with the development of a blue color by the modified electrode and contrasts with the result obtained with the transparent reduced state. Figure 4B illustrates the various measured monochromatic responses of the cyclic voltammogram. It can be seen from the figure that maximum contrast is achieved using red radiation, in agreement with the UV/vis spectrum; additionally, it is clear that the quasi-reversible behavior and large hysteresis of the potential are a function of the scan rate and are caused by ion diffusion effects in the electrolyte.

PB electrodes lack electroactivity in electrolytes containing Na⁺, NH₄⁺, or larger cations.^{15,29,32,33} To further characterize

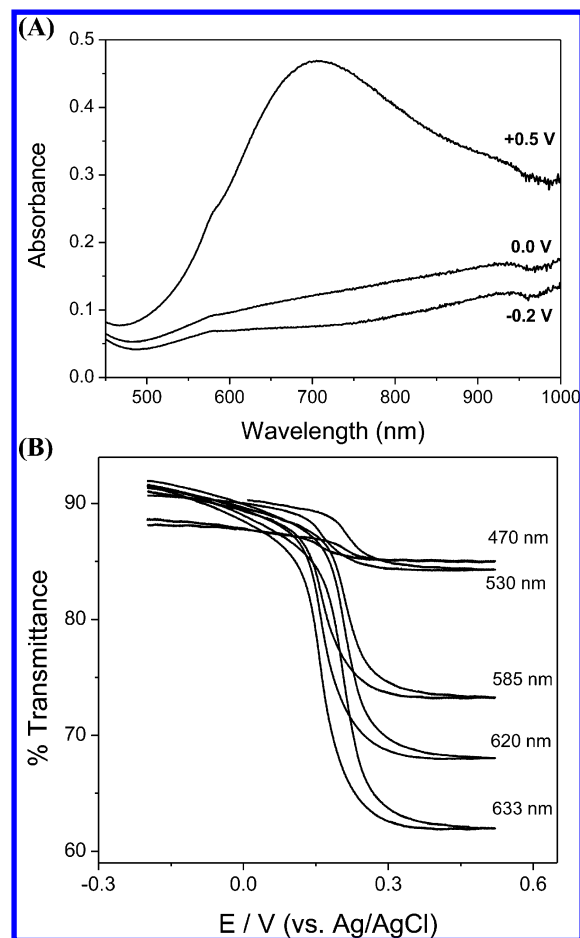


Figure 4. (A) *In situ* UV/vis spectral response of a poly[Fe(TPPZ)-FeCN]-modified electrode to various applied potentials. Electrolyte = 0.1 mol L⁻¹ KCl. (B) Optical contrast presented by the modified electrode when exposed to various wavelengths of monochromatic radiation during the electrochemical experiment. Electrolyte = 0.1 mol⁻¹ KCl, and scan rate = 10 mV⁻¹.

the electrochemical responses of poly[Fe(TPPZ)FeCN] and demonstrate its advantages over PB, cyclic voltammograms were obtained using a NaCl electrolyte, as shown in Figure 5A. It can be seen that the redox peaks were broadened and shifted to cathodic potentials; however, the electroactive response remained, and no drastic changes were observed in the dynamic transmittance (Figure 5B) as expected. This is the great difference of this supramolecular film when compared to PB, because when the TPPZ ligand space is used, it promotes an increase of the cavity inside the crystalline structure and facilitates the insertion and withdrawal of the sodium ions, because the radius of the sodium ions is about twice as big as the other ions depicted in the literature.^{27,28,33} Moreover, we have previously shown that, for the poly[Fe(TPPZ)FeCN] film, anion transport is greater in a K⁺-containing solution than in Li⁺ solution.²⁸ Therefore, the ionic compensation dynamics depends upon the chemical nature of the cation, specifically, on the mass/charge relationship. This behavior is different when compared to PB films, where the contribution of anions to the charge neutralization process is negligible. The oxidation process decreases the transmittance signal, which reaches a chromatic contrast ($\Delta\%T$) of approximately 30 and 25% in KCl and NaCl solutions, respectively. The plot of the differential equation $|d\%T/dE|$ inserted in Figure 5C demonstrates that the

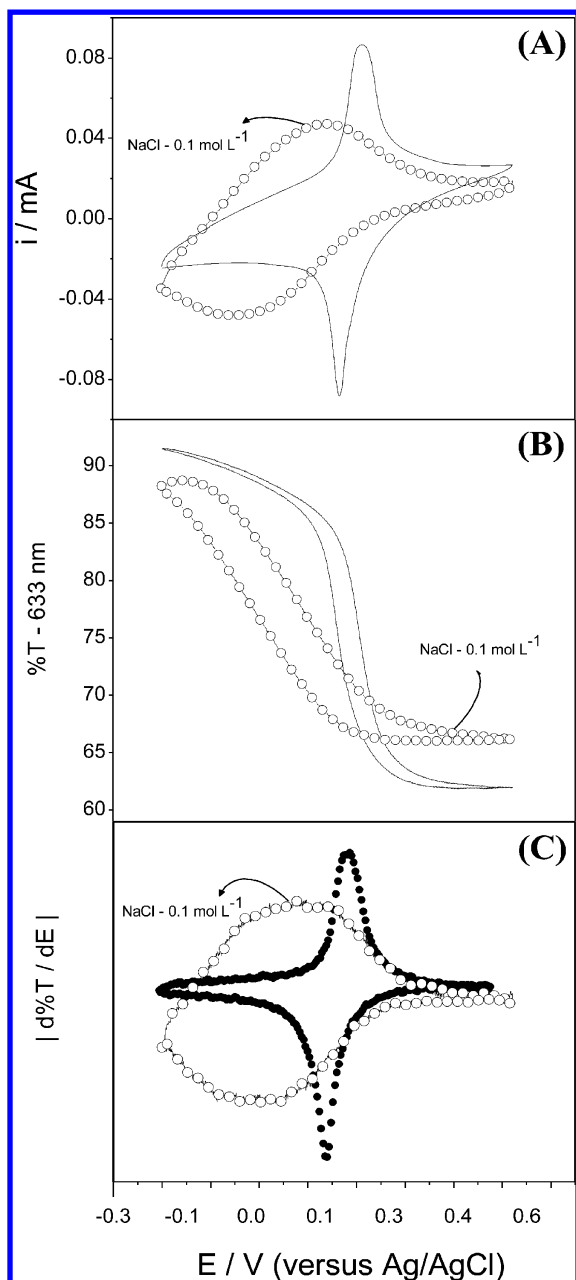


Figure 5. (A) Cyclic voltammograms, (B) %T at 633 nm, and (C) $|d\%T/dE|$ potentiodynamic profiles of a poly[Fe(TPPZ)FeCN]/PAH/PVS/PAH/ITO electrode. The electrolytic solution in panel A was 0.1 mol L⁻¹ KCl, and the electrolytic solution in panel B was 0.1 mol L⁻¹ NaCl. The scan rate was 10 mV s⁻¹.

transparent state fully recovers after reduction, indicating that the reaction is highly reversible in agreement with the electrochemical processes and color modulation. The electrochromic efficiency for the electrode was 78 cm² C⁻¹ (at 633 nm, using KCl as the electrolyte), which is comparable to results obtained with other nanostructure-based inorganic electrodes, such as Ni(OH)₂,¹⁵ WO₃,¹ Co(OH)₂,³⁴ K₂Cu[Fe(CN)₆],¹⁵ KFe[Fe(CN)₆], and TiO₂-modified electrodes.¹

The durability and response time of the poly[Fe(TPPZ)-FeCN]-modified electrodes were also analyzed. Herein, both coloration and bleaching times are defined as the time needed to reach a $2/3$ change in the total transmittance. Figure 6 illustrates the absorbance profile at 633 nm as a function of

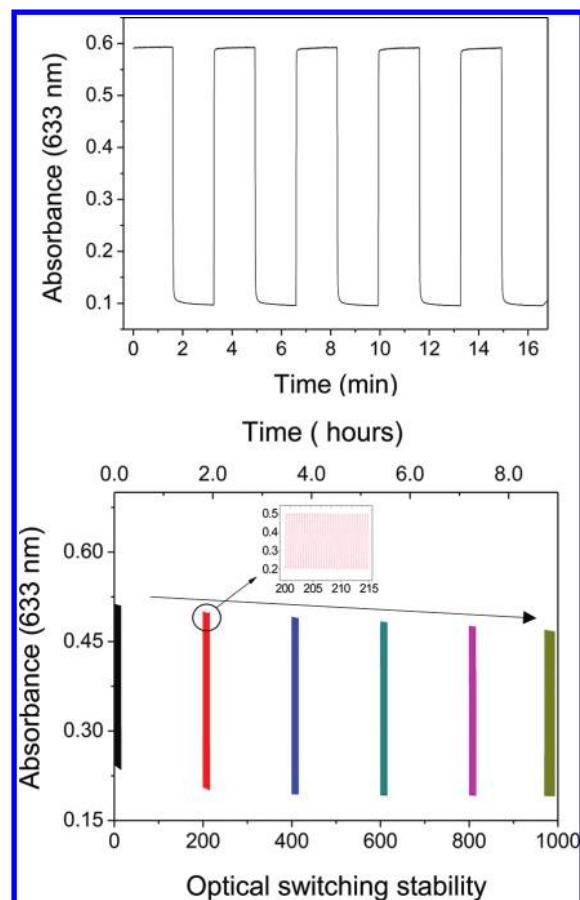


Figure 6. Absorbance profile as a function of time recorded by switching the potential between -0.2 and 0.5 V for a poly[Fe(TPPZ)-FeCN]/PAH/PVS/PAH/ITO electrode. Electrolyte solution = 0.1 mol L⁻¹ KCl.

time when the electrode is subjected to cycles of repeated oxidation ($+0.5$ V) and reduction (-0.2 V). The bleaching and coloration time for the electrode was calculated to be 620 ms, which is comparable to other nanostructured electrodes; it is well-known that these electrodes possess a huge superficial electroactive area, which indicates that fast and efficient mass transport is achieved by the poly[Fe(TPPZ)FeCN]-modified electrode. When the electrode was submitted to continuous cycles of coloration and bleaching, it exhibited reasonable stability with no significant changes in the chromatic contrast as a function of time. After 1000 cycles, 90% of its electroactivity was retained, indicating that this ECD has both good environmental and redox activity. The high stability of this device was ascribed to the formation of well-ordered monolayers (via the LbL technique), which appears to allow for better diffusion of the counterions into the film and improve the reversibility and stability of the system.

It is important to compare the stability obtained here to that obtained by other researchers. Hammond and co-workers^{35,36} have demonstrated that the absorbance of PB nanoparticle films continuously decreases when LbL-modified electrodes are subjected to long-term cycling. Apparently, this loss in the chromatic contrast can be attributed to gradual destabilization of the electrostatic assembly upon cycling once the oxidized nanoparticles form Fe^{III}[Fe^{III}(CN)₆], which diminishes the excess negative charge and leads to the loss of the nanoparticles to the bulk solution. However, the presented film assembly

maintains its integrity over several hours, and this can be attributed to the stability conferred to the modified electrode by the unique polymeric structure of poly[Fe(TPPZ)FeCN] and its strong interaction with the PAH cationic layer.

The practical application of the electrochromic film poly[Fe(TPPZ)FeCN]/PAH/PVS/PAH/ITO electrodes consisted of making an ECD, as shown in Figure 7A. These devices were

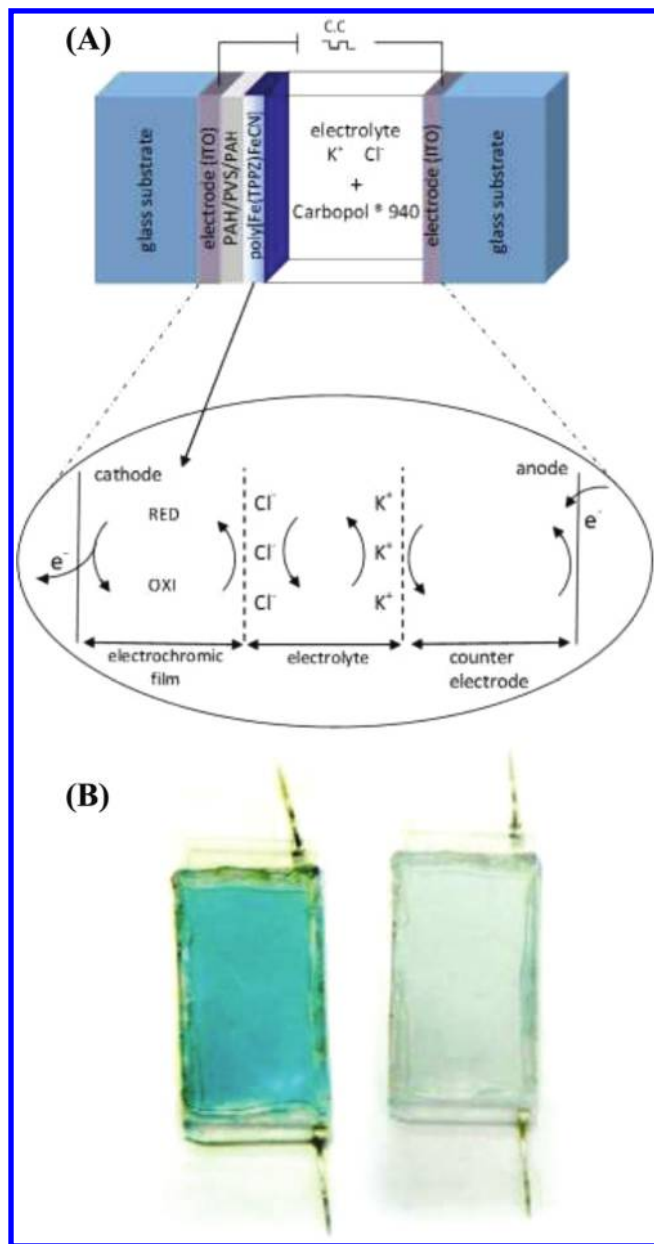


Figure 7. (A) Schematic representation of the ECD. (B) Appearance of the analyzed ECD at applied potentials of 0 and +1.6 V.

assembled by sandwiching the poly[Fe(TPPZ)FeCN]/PAH/PVS/PAH/ITO-coated working electrode with a transparent ITO counter electrode. To avoid short circuits between the electrodes, a layer of gelled electrolyte consisting of a 1.0 mol L⁻¹ KCl solution and 5% Carbopol 940 polymer was used, both dissolved in water. Then, an approximately 1 mm thick layer of a thermo-sealing plastic (ethylene–vinyl acetate) was applied to the edges of the working electrode to seal the device,

preventing contact with the external environment and evaporation of the gel.

The electrochromic properties of the ECD were measured by applying a +1.6 V potential and a 100 mA current to the terminals, and the color modulation was measured using an IC 555-type electronic circuit (Figure 7B), which functions as a monostable oscillator and allows for the potential application of the ECD in displays or smart windows. This ECD exhibited high chemical stability, and a consistent and stable color variation was maintained for more than 30 days.

CONCLUSION

We have studied the electrochromic properties of the poly[Fe(TPPZ)FeCN] coordination polymer and incorporated it as a functional component in polyelectrolyte multilayer thin films using electrostatic LbL self-assembly. In this case, good color efficiency, reversibility, and electrochromic stability was found for working potentials between −0.2 and +0.5 V. These versatile, multicolor electrochromophores provide interesting opportunities as ECDs as a result of their performance being conveniently modulated via the electronic nature of the polypyridyl ligand, because the structure of the ligands may affect the charge density in the polymer backbone as well as the morphology of the films, thereby changing the diffusion of ions and the response times.⁸

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