

Fabricating Electrochromic Thin Films Based on Metallo-Polymers Using Layer-by-Layer Self-Assembly: An Attractive Laboratory Experiment

Marco Schott,[†] Matthias Beck,[†] Franziska Winkler,[†] Henning Lorrmann,[‡] and Dirk G. Kurth^{*,†}

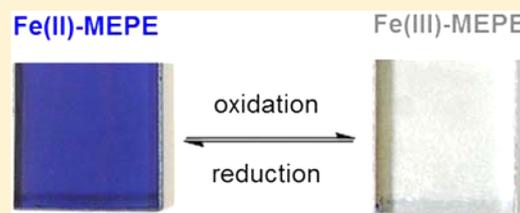
[†]Chemical Technology of Advanced Materials, Julius-Maximilians-University Würzburg, Röntgenring 11, D-97070 Würzburg, Germany

[‡]Fraunhofer Institute for Silicate Research ISC, Neunerplatz 2, D-97082 Würzburg, Germany

S Supporting Information

ABSTRACT: Metallo-supramolecular polyelectrolytes (MEPE) based on iron(II)-acetate and 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene are assembled by layer-by-layer deposition on transparent electrode surfaces. When a potential is applied, the color of the film can be switched from blue to transparent. Due to the strong absorption and the fast switching speed, the color change is readily observed with the eye. The device shows reversible switching and long-term stability. The experiment demonstrates the basic concept of electrochromic windows, an upcoming technology.

KEYWORDS: Graduate Education/Research, Continuing Education, Polymer Chemistry, Electrochemistry, Materials Science, Surface Science, UV-Vis Spectroscopy, Laboratory Instruction



Electrochromic materials change their color upon a redox stimulus. Integrating the electrochromic material into a window opens an avenue to control the transmittance of light. These so-called smart windows are potential candidates for various applications in buildings, automobiles, and airplanes for climate management, privacy, or a pleasant indoor atmosphere. Both inorganic and organic materials can exhibit electrochromic properties.¹ Tungsten oxide is a well known electrochromic material. It can be deposited through vacuum deposition methods as thin film on conducting substrates. Prussian blue² is another example of an inorganic material, whereas polyaniline³ or viologenes⁴ are examples of organic electrochromics. Both of these materials can be deposited from solution.

Recently, we discovered that metallo-supramolecular polyelectrolytes (MEPE) show remarkable electrochromic properties. MEPE are prepared by metal ion induced self-assembly of ditopic bis-terpyridines. If a rigid ligand, such as the ligand L₁ (Figure 1), is used, the resulting MEPE has a rigid-rod-like structure. The modular nature of metal ion induced self-assembly permits controlling the structure and the properties of MEPE by the judicious choice of the metal ions and the design of the ligands.

In aqueous solution, the binding constants of terpyridines are in general high, even for kinetically labile metal ions of the first transition row due to the chelate effect. Yet the binding constant is low enough to endow dynamic properties, and therefore, MEPE form equilibrium structures in solution. Their molar mass depends on concentration, stoichiometry and temperature, the design of the ligand, and the choice of the metal ion. With ligand L₁ and Fe(II), the length of the MEPE rods can exceed 500 nm.^{5,6}

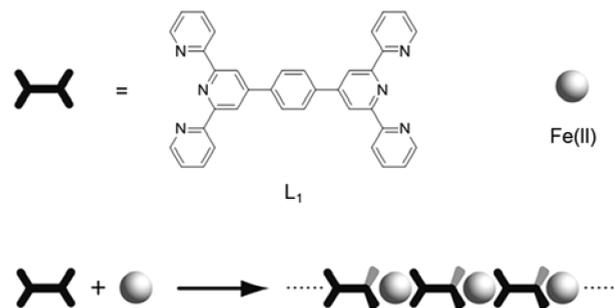


Figure 1. Structure of the ligand and the resulting Fe-MEPE.

Due to the polymeric nature, MEPE are readily deposited as thin films on various substrates by spin- and dip-coating or the layer-by-layer self-assembly (LbL) method.^{7–9} LbL deposition is based on sequential adsorption of oppositely charged polyelectrolytes onto a suitably modified substrate. The method provides, despite its simplicity, molecular level control over the structure and composition of the film. LbL assembly is a versatile, inexpensive, simple, and yet a powerful method to precisely customize the properties of thin films.

Here, we employ LbL to fabricate electrochromic coatings based on MEPE as active component. Due to the simplicity of MEPE assembly and LbL, the experiments are well suited for upper-level undergraduate students. In the experiments described, the students prepare MEPE from commercially available compounds in a simple one-step, one-pot reaction under inert gas. The reaction is readily verified by the blue color

of the MEPE containing solution. Then, the students prepare the multilayers by sequential deposition of MEPE and PSS. The deposition can be carried out by hand and requires only beakers. The multilayer growth can be detected by UV–vis spectroscopy. Finally, the electrochromic switching is carried out in solution either with a potentiostat, a regulated power supply, or even a battery. Students of natural sciences can thus gain experience in “state-of-the-art” research methods as well as upcoming technologies through this experiment. Our present work represents an alternative to the system published by P. T. Hammond “Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film”.³

EXPERIMENTAL SECTION

Synthesis of Fe-MEPE

1,4-Bis(2,2':6',2''-terpyridin-4'-yl)benzene (ligand L_1) can be synthesized according to literature.¹⁰ It is also commercially available. Fe-MEPE was synthesized with a metal ion to ligand L_1 molar ratio of 1:1.¹¹ A total of 104 mg (1.86 mmol) of iron powder were dissolved in 40 mL of refluxing acetic acid (100%) under inert gas to get dispersed iron acetate, $Fe(OAc)_2$. After the mixture cooled to room temperature, the $Fe(OAc)_2$ solution was added to a solution of L_1 (1.0 g, 1.85 mmol) dissolved in 150 mL of acetic acid (75%), and the mixture was stirred for 2 h while refluxing. The deep blue solution was dried under vacuum, and the obtained solid was solved in 200 mL of ultrapure water and dried again. 1.32 g (1.85 mmol) of a dark blue colored solid of Fe-MEPE was obtained (yield ~100%).

Preparing the Substrates

For the experiment, three types of substrates have been used, a microscope slide, an indium tin oxide (ITO)-coated PET (polyethylene terephthalate) foil, and a fluorine-doped tin oxide (FTO)-coated glass. While UV–vis spectroscopy was measured with the microscope glass slides, electrochemical measurements have been carried out with PET-ITO foil and FTO glass. The microscope slide was rinsed in ethanol, acetone, and ultrapure water to clean the surface. Pressurized air was deployed to dry the surface and free it from small particles. The PET-ITO foil and FTO glass were obtained by Sigma-Aldrich and used without further treatments.

Preparing the Multilayer-Film

The following solutions were used: 1×10^{-2} M solution of sodium polystyrenesulfonate in ultrapure water, 5×10^{-4} M solution of Fe-MEPE in ethanol, and 1×10^{-2} M solution of polyethylenimine (PEI) in ultrapure water. PEI solution is used to form the first layer on glass substrates to increase adhesion of the following layers to the substrate. PET-ITO foil and FTO glass substrates were used without PEI layer because the PEI layer affects the electrochemical measurements. The coating process was continued with a rinsing step in ultrapure water. Subsequently, the substrates were immersed in PSS solution for 5 min, rinsed, immersed in MEPE solution for 5 min, and rinsed again. This sequence of steps results in one bilayer and was repeated until the designated number of bilayers was reached.

HAZARDS

The students should wear nitril gloves and protective glasses during the experiments. The synthesis of Fe-MEPE should be carried out under the flue, whereas the coating process can be carried out on the bench of the laboratory. All materials are

nontoxic except the terpyridine ligand L_1 . The students should avoid contact with it. The acetic acid used for the Fe-MEPE synthesis is acidic and thus mildly corrosive. Lithium is very reactive and should be handled and stored in a water and oxygen free argon atmosphere at room temperature (glovebox). Lithium perchlorate ($LiClO_4$) can cause fire with combustible material. Thus, avoid exposition and contact with it. Propylene carbonate (PC) can cause skin and eye irritation; avoid contact with it. Be careful when handling glass microscope slides since they may have sharp edges. Do not look into the light source of the UV–vis spectrometer.

RESULTS

Characterization of Fe-MEPE/PSS Thin Films

Layer deposition is readily confirmed by inspection as shown in Figure 2. When the coating sequence is continued, an increase



Figure 2. Photographic image of $(Fe-MEPE/PSS)_n$ films after $n = 2, 4, 6, 8, 10$ dip-coating cycles on microscope slides.

of the color is observed. The Fe-MEPE/PSS films show high optical quality, low surface roughness, and good adhesion to the substrates.^{12,13}

UV–vis spectroscopy is a well-suited method to accurately quantify the deposition as shown in Figure 3. The measurement was performed every two bilayers.

Three peaks can be detected in the spectra. The strong peak at around 590 nm is assigned to a metal-to-ligand charge transfer (MLCT) transition, which is responsible for the blue color. The metal centered d–d transition occurs at 386 nm, and a π – π^* transition is detected at 329 nm. To prove the linear growth of the layers, the absorbance at 329, 386, and 590 nm is plotted versus the number of bilayers n and a linear regression is carried out (Figure 3). R^2 , the regression coefficient, is a simple parameter to quantify the quality of data. A value of 1 indicates that all data points fit exactly to a straight line. From the data in Figure 3, R^2 was determined to be 0.99 (590 nm), 0.99 (386 nm), and 0.98 (329 nm), which confirms the linear growth of the film.

In-situ Electrochemical and Spectroelectrochemical Characterization of Fe-MEPE/PSS Thin Films

The electrochemical properties of LbL assembled Fe-MEPE were investigated by cyclic voltammetry. The Fe-MEPE/PSS-coated PET-ITO foil or FTO glass as the working electrode (WE) were measured versus Li/Li^+ as the reference electrode (RE) in 1 M $LiClO_4$ in PC against a Li counter electrode (CE). The electrochemical cell for the measurements is shown in Figure 4.

The cyclic voltammogram is obtained by measuring the current at the working electrode during a potential scan from 3.40 to 4.50 V against a Li/Li^+ reference electrode. Figure 5 shows the cyclic voltammogram of Fe-MEPE recorded from thin films on PET-ITO foil at room temperature. As the

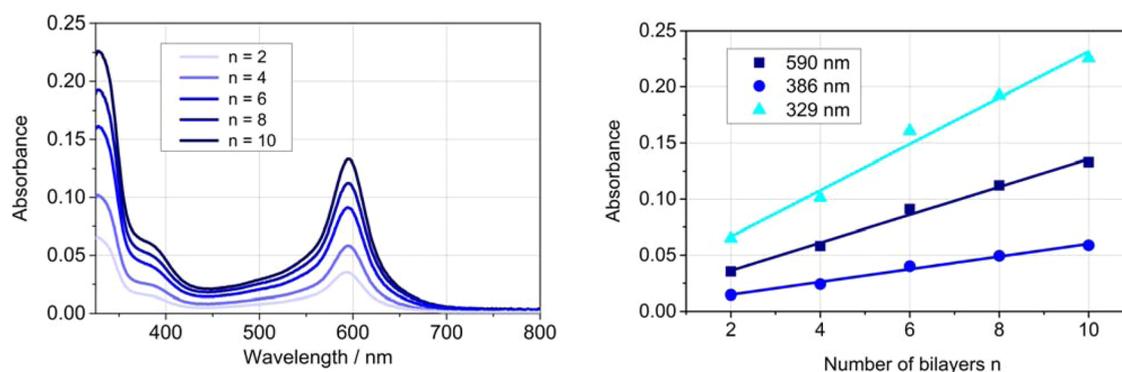


Figure 3. UV-vis spectra of (Fe-MEPE/PSS)_n films (left) and linear regression of absorbance versus the number of bilayers *n* (right).

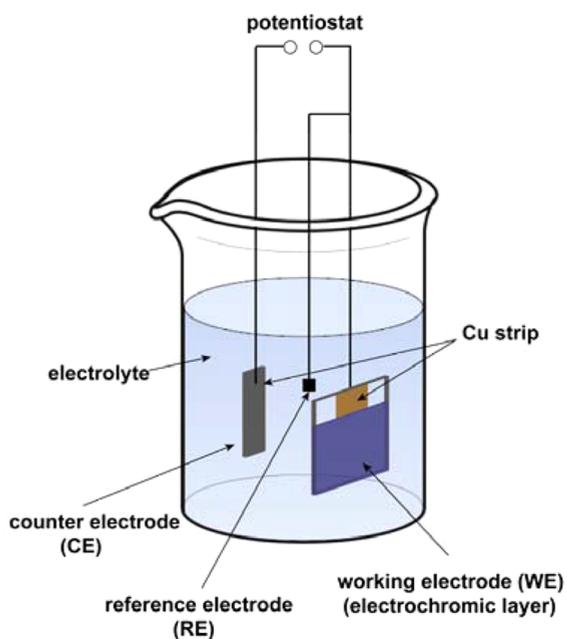


Figure 4. Three-electrode electrochemical cell.

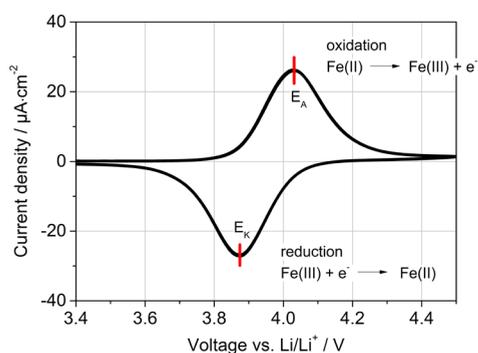


Figure 5. Cyclic voltammogram of (Fe-MEPE/PSS)_n films on PET-ITO foil (*n* = 20), fabricated by LbL-assembly. Scan rate: 10 mV·s⁻¹.

waveform shows, the forward scan produces a current peak for Fe-MEPE oxidized through the range of the potential scanned. The current will increase as the potential reaches the oxidation potential at 3.90 V with an anodic peak potential E_A at 4.02 V. The reduction process begins at 4.10 V with a cathodic peak potential E_K at 3.87 V.

The long-term stability of the electrochromic materials under switching conditions is one of the most important parameters

for the application of ECDs (electrochromic devices). Figure 6 illustrates the cycle stability of the Fe-MEPE/PSS films on FTO

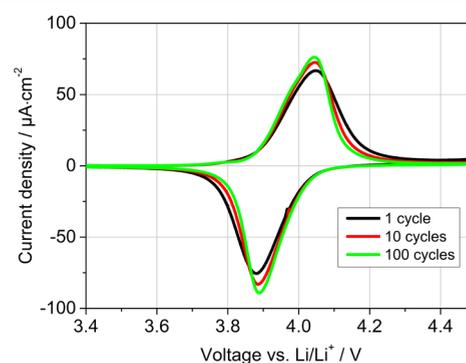


Figure 6. Cyclic voltammogram of (Fe-MEPE/PSS)_n films on FTO glass (*n* = 20) after 1, 10 and 100 redox cycles. Scan rate: 10 mV·s⁻¹.

glass. After 100 cycles, the redox peaks are essentially identical to those after 1 and 10 cycles. A degradation of the layers would change the curves shape noticeably. Small, sharp redox-peaks suggest a nearly ideal Nernstian behavior and fast electron transfer. And indeed, a rapid change of the color can be observed upon switching.

To examine the redox process and the color change, the UV-vis spectra of Fe-MEPE/PSS-coated FTO glass slides are recorded at different potentials. We observed that the MLCT absorbance of Fe-MEPE decreases upon increasing the potential to 1.5 V and finally is lost completely. Figure 7 shows the UV-vis spectra and the photographs of the colored film (reduced form) on the top and the bleached film (oxidized form) on the bottom.

The in-situ spectroelectrochemical experiment can be performed by a regulated power supply as a two-electrode experiment, with a Pt mesh as counter electrode and 1 M KCl in water as electrolyte. Switching voltage of Fe-MEPE is around 1.5 V, depending on experiments conditions such as the distance between the electrodes, temperature, and deployed electrode material.

SUMMARY

Here, we describe a simple protocol for the construction of an electrochromic device based on MEPE. With the use of LbL-assembly, homogeneous and defect-free Fe-MEPE/PSS thin films are readily prepared. With the application of a potential of approximately 1.5 V, the color change from blue to transparent in case of Fe-MEPE is observed by visual inspection. The

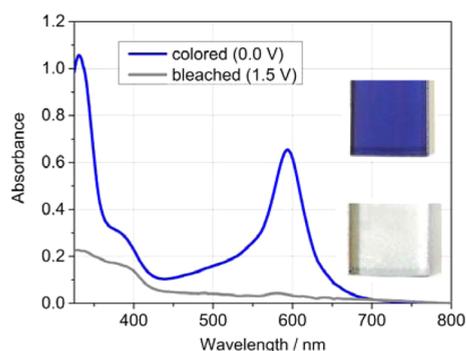


Figure 7. UV-vis spectra of the colored (reduced) and bleached (oxidized) form of $(\text{Fe-MEPE/PSS})_n$ films on FTO glass ($n = 20$).

experiments are suitable for an upper-level undergraduate laboratory. This experiment is part of a student lab-course. All data and results were obtained by upper undergraduates. The resonance we gained according to this experiment was positive without exception.

■ ASSOCIATED CONTENT

📄 Supporting Information

A listing of materials, equipment, precautions and laboratory supplies. Detailed description of the synthesis of Fe-MEPE, LbL-assembly and electrochemical/in-situ spectroelectrochemical measurements of Fe-MEPE/PSS thin films. A brief background on electrochemistry and LbL deposition as well as some questions. This material is available via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dirk.kurth@matsyn.uni-wuerzburg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported primarily by the Federal Ministry of Education and Research under VDI Grant No. 13N11283.

■ REFERENCES

- (1) Baetens, R.; Jelle, B. P.; Gustavsen, A. Properties, Requirements and Possibilities of Smart Windows for Dynamic Daylight and Solar Energy Control in Buildings: A State-of-the-Art Review. *Sol. Energy Mater. Sol. Cells* **2010**, *2*, 87–105.
- (2) Neff, V. D. Electrochemical Oxidation and Reduction of Thin Films of Prussian Blue. *J. Electrochem. Soc.* **1978**, *6*, 886–887.
- (3) Schmidt, D. J.; Pridgen, E. M.; Hammond, P. T.; Love, J. C. Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film. *J. Chem. Educ.* **2010**, *2*, 208–211.
- (4) Kim, S.-h.; Shim, N.; Lee, H.; Moon, B. Synthesis of a Perylene-3,4,9,10-tetracarboxylic diimide-Viologen Dyad (PDI-2V) and Its Electrochromism in a Layer-by-Layer Self-Assembled Multilayer Film with PEDOT:PSS. *J. Mater. Chem.* **2012**, *27*, 13558–13563.
- (5) Sievers, T. K.; Vergin, A.; Möhwald, H.; Kurth, D. G. Thin Films of Cross-Linked Metallo-Supramolecular Coordination Polyelectrolytes. *Langmuir* **2007**, *24*, 12179–12184.
- (6) Schwarz, G.; Sievers, T. K.; Bodenthin, Y.; Hasslauer, I.; Geue, T.; Koetz, J.; Kurth, D. G. The Structure of Metallo-Supramolecular Polyelectrolytes in Solution and on Surfaces. *J. Mater. Chem.* **2010**, *20*, 4142–4148.

(7) Decher, G.; Hong, J. D.; Schmitt, J. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: III. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces. *Thin Solid Films* **1992**, *210–211*, 831–835.

(8) Decher, G. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science* **1997**, *5330*, 1232–1237.

(9) Han, F. S.; Higuchi, M.; Kurth, D. G. Metallo-supramolecular Polyelectrolytes Self-Assembled from Various Pyridine Ring-Substituted Bisterpyridines and Metal Ions: Photophysical, Electrochemical, and Electrochromic Properties. *J. Am. Chem. Soc.* **2008**, *6*, 2073–2081.

(10) Winter, A.; van den Berg, A.; Hooogenboom, R.; Kickelbick, G.; Schubert, U. A Green and Straightforward Synthesis of 4'-Substituted Terpyridines. *Synthesis* **2006**, *17*, 2873–2878.

(11) Bodenthin, Y.; Schwarz, G.; Tomkowicz, Z.; Geue, T.; Haase, W.; Pietsch, U.; Kurth, D. G. Liquid Crystalline Phase Transition Induces Spin Crossover in a Polyelectrolyte Amphiphile Complex. *J. Am. Chem. Soc.* **2009**, *8*, 2934–2941.

(12) Schütte, M.; Kurth, D. G.; Linford, M. R.; Cölfen, H.; Möhwald, H. Metallo-supramolecular Thin Polyelectrolyte Films. *Angew. Chem., Int. Ed.* **1998**, *20*, 2891–2893.

(13) Schott, M.; Szczerba, W.; Kurth, D. G. Detailed Study of Layer-by-Layer Self-Assembled and Dip-Coated Electrochromic Thin Films Based on Metallo-Supramolecular Polymers. *Langmuir* **2014**, *30* (35), 10721–10727.