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Coordinative Supramolecular Assembly of Electrochromic Films Based on Metal Ion Complexes of Polyiminofluorene with Terpyridine Substituent Groups

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The formation and characteristic properties of organized films that are based on metal ion complexes of poly(4-(2,2′:6,2″-terpyridyl)phenyliminofluorene) (**P1**) with thickness control in the nanometer range are reported. The films were obtained upon multiple sequential assembly of divalent metal ions (Zn, Co, Ni) and the terpyridine(tpy)-substituted polymer **P1** on solid supports via coordinative interactions between metal ions and tpy ligands. The influence of deposition parameters is described, and the optical, electrochemical, and electrochromic properties of the polymer films are compared. Under optimized conditions, 12 dipping cycles and a time period of < 5 min are sufficient to obtain a homogeneous film of 100 nm in thickness. Films containing Zn(II) and Ni(II) ions are yellow in the neutral state and change color to red and finally blue if anodically oxidized up to 560 mV vs FOC. Films containing Co(II) ions are purple in the neutral state and change to blue in the oxidized state. All color changes are highly reversible, even under ambient conditions. For films prepared upon 12 dipping cycles, the switching from the neutral to the fully oxidized state proceeds within 300 and 700 ms, and the contrast at 800 nm is up to 18%. The films might be useful as active layers in electrochromic devices.

1. Introduction

Design and arrangement of polymers in defined supramolecular structures represents an important current research topic. Of special interest is the design of functional assemblies, in which the functional properties are a consequence of the tailored structure of the molecules and the assembly. Important access to novel functional materials results from the combination of tailor-made polymers with transition metal ions.[1,2] Especially the combination of polymer chains with metal-terpyridine (tpy) complexes[3−8] leads to new materials with interesting liquid-crystalline, optical, electrical, and sensory properties.[5−8] Although the great majority of tpy-based polymers contains the metal−ligand complex in the main chain,[4,6] only a few studies were concerned with polymers containing the tpy group in the side chain,[3,5,7,8] and only in very few cases were polymer chain and substituent groups polyconjugated.[7] However, π-conjugation in main chain and side groups is advantageous to induce interesting electroactive and chemosensory properties in the materials.[7a,7b]

The polymer used in our study is poly(4-(2,2′:6,2″-terpyridyl)phenyliminofluorene) (**P1**), a polyconjugated polyiminofluorene[9] with terpyridylphenyl substituent groups. Its chemical structure is shown in Scheme 1. **P1** was previously tailored for metal ion coordination and sequential assembly of electroactive thin films: the tpy substituent groups enable the coordination of di- and trivalent metal ions and formation of bis-tpy complexes with D_{2d} symmetry,[10] the complex formation of the polytopic ligand proceeds under formation of a coordination polymer network, which is only slightly soluble and therefore can be easily deposited on a substrate surface, and the easily oxidizable nitrogen atoms in the polymer backbone induce donor properties and

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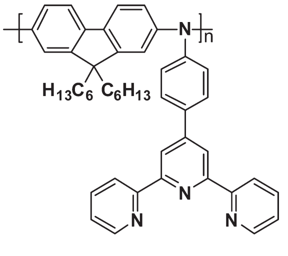
Scheme 1. Molecular Structure of P1



P1

electrochromic behavior. In a previous study, the synthesis of the polymer, its complex formation with a variety of metal ions, its luminescent and ionochromic behavior, and its use as a chemosensor were described,[11] and the multiple sequential assembly of **P1** and zinc hexafluorophosphate resulting in fast-switching electrochromic films was reported in a recent communication.[12]

The purpose of the present paper is to present a comprehensive study on formation and properties of coordination polymer films of **P1** with a variety of metal ions such as zinc(II), nickel(II), and cobalt(II). The influence of the deposition conditions such as variation of dipping time, concentration of dipping solutions, and solvents used for dipping and washing of the substrates on film thickness and morphology are described, and the optical, electrochemical, and electrochromic properties of the various polymer films are compared.

Studies were carried out using UV/vis spectroscopy, cyclic voltammetry, spectroelectro-chemical characterization, scanning electron and scanning force microscopy, and XPS characterization.

2. Experimental Section

Materials. The preparation of **P1** was described previously.[11] Zinc acetate ($Zn(OAc)_2 \cdot 2H_2O$), cobalt acetate ($Co(OAc)_2 \cdot 4H_2O$), and nickel acetate ($Ni(OAc)_2 \cdot 4H_2O$) were obtained from Merck, and potassium hexafluorophosphate was purchased from Aldrich. Both salts were used without further purification. Tetrahydrofuran (THF) was distilled over sodium hydride under nitrogen. *N*,*N*-Dimethylformamide (DMF) was distilled over calcium hydride. Toluene, n-hexane, methanol, and acetonitrile (HPLC grade) and tetrabutylammonium hexafluorophosphate were obtained from Acros and Aldrich and used without further purification.

Substrates. Quartz substrates ($30 \times 12 \times 1$ mm^3) were cleaned in a fresh piranha solution (7:3 mixture of 98% H_2SO_4/30% H_2O_2) (***Caution!*** *The mixture is strongly oxidizing and may detonate upon contact with organic material*), washed with Milli-Q water, and successively subjected to ultrasonication in alkaline isopropanol and 0.1 M aqueous HCl at 60 °C for 1 h each. Then, after careful washing with Milli-Q water, the substrates were silanized with 3-aminopropylmethyldiethoxysilane (Fluka) in toluene and finally coated with three polyelectrolyte layers in the sequence PSS (polystyrene sulfonate), PEI (polyethyleneimine), PSS as previously described.[13]

ITO-coated glass substrates were cleaned upon ultrasonication in ethanol and water at 60 °C for 30 min each. Then two polyelectrolyte layers were deposited in the sequence PEI−PSS in the same way as reported for the quartz substrates.

Dipping Solutions. If not especially indicated, the dipping solutions of the metal hexafluorophosphates were prepared by mixing identical volumes of a 0.02 M solution of potassium hexafluorophosphate in THF/DMF (9:1 v/v) with a 0.01 M solution of the corresponding metal acetate in THF/DMF (9:1 v/v). The dipping solution of the ligand was a 5×10^{-4} monomolar solution of **P1** in pure THF.

Methods. *Film Preparation.* If not especially mentioned, the pretreated substrates were dipped into (a) the THF/DMF solution of the metal hexafluorophosphate, (b) pure THF/DMF (9:1 v/v), (c) pure THF, (d) the THF solution of **P1**, (e) pure THF, (f) THF/DMF (9:1 v/v), and again the sequence (a−f) was applied. Immersion times were 10 min each for steps (a) and (d) and 30 s for steps (b), (c), (e), and (f).

Instrumentation. UV−visible absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. All spectra were corrected by subtracting the signal of the precoated quartz substrate. Electrochemical experiments were performed on a Heka potentiostat/galvanostat (model PG 390, Heka Electronic, Lambrecht, Germany). Data acquisition and potentiostat control were accomplished using the Potpulse software, version 8.4 (Heka). All experiments were carried out in a conventional three-electrode glass electrochemical cell at room temperature employing the polymer film on an ITO-coated glass substrate; reference counter electrodes were platinum. The experiments were carried out in acetonitrile (saturated with N_2) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte salt. SEM images were obtained using a Zeiss Supra 40 VP scanning electron microscope. SFM images were obtained using a scanning force microscope from FRT GmbH, Bergisch Gladbach, Germany. EDX spectra were monitored using an INCA DryCool instrument coupled to an SEM (Zeiss Neon 40). The accelerating voltage was 20 kV, the area was 2500 μm^2, the time for the measurement was 250 s. Film thickness was measured with a Dektak 3 apparatus from Vecco. The film was partially scratched from the surface, and a height profile of the surface was scanned. The error in the measurements was ±2.5 nm.

3. Results and Discussion

3.1. Synthesis and Metal Ion Coordination of the Polymer. The preparation of **P1**[11] is based on a polycondensation of 2,7-dibromo-9,9′-di-*n*-hexylfluorene[14] and 4′-(p-aminophenyl)-2,2′:6,2″-terpyridine[6b,11] using the $Pd_2(dba)_3$/X-Phos system as catalyst and sodium *t*-butoxide as the base. The polymer is obtained as a lime green powder, which is readily soluble in common organic solvents such as toluene, chloroform, dichloromethane, or tetrahydrofurane (THF). Solutions exhibit a yellowish color and a bluish or greenish fluorescence depending on the nature of the solvent. A MALDI-TOF study of the molecular weight distribution indicated two maximum peaks corresponding to the pentamer and hexamer; the maximum degree of polymerization was 14.[11]

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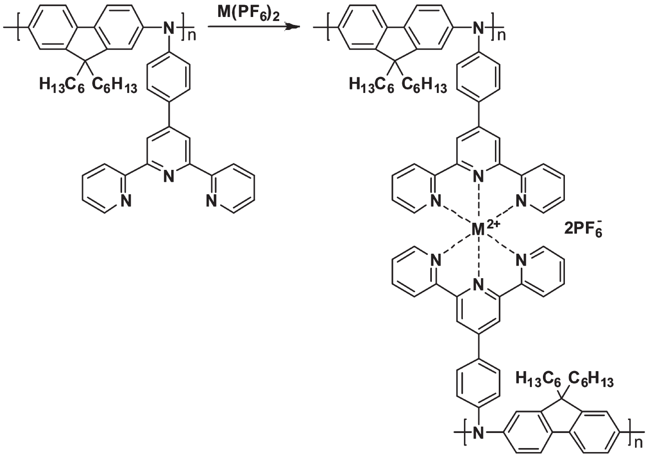
Addition of divalent transition metal salts to the solution of the polymer leads to complex formation of the metal ions with the tpy units. From a titration study, the formation of bis-complexes was evident as indicated in Scheme 2.[11] Upon zinc acetate addition, UV spectra indicate that the maximum absorption of the polymer at 407 nm decreases in intensity, and new bands at 450 and 340 nm appear involving three isosbestic points. Fluorescence studies show that metal ion complexation is accompanied by a strong decrease in the polymer luminescence.[11]

3.2. Sequential Assembly of Films. For the film preparation we used pretreated quartz supports (for pretreatment see Experimental Section) and indium−tin−oxide (ITO) coated glass substrates. **P1** was dissolved in THF, the metal salt was dissolved in THF/DMF mixture (9:1, v/v). Originally we used zinc(II), cobalt(II), or nickel(II) acetate as metal salts. However, after it turned out that PF_6^- anions favor precipitation of the polymer−metal complex, we added potassium hexafluorophosphate to the dipping solutions of the metal salts. The sequence of the deposition steps a−f is shown in Scheme 3.

The usual method of film preparation was as follows: first the pretreated substrate was dipped into the solution of the metal salts and the metal hexafluorophosphate is adsorbed at the substrate surface (step a). After being washed twice in THF/DMF mixtures of volume ratio 9:1 (steps b and c), the substrate was dipped into the polymer solution in THF (step d). Subsequently nonadsorbed material was removed upon dipping into pure THF (step e) and finally into THF/DMF (9:1) (step f). Dipping times in step a and d were 10 min, and in the residual steps 30 s. Upon successive repetition of the dipping sequence (a−f), the films of the coordination polymer were built up (Table 1, sample 4).

Scheme 2. Metal Ion Coordination of P1 Involving Cross-Linking of Polymer Chains



3.3. Optical Properties of Films and EDX Characterization. Depending on the kind of metal salt used, the resulting films had different colors, the depth of the color increasing with the number of dipping cycles applied. Films containing zinc(II) were yellow. Films with cobalt(II) were purple, and the nickel(II)-based films were pale yellow. The different colors of the films reflect the ionochromism of **P1** observed in solution[11] and can be taken as a proof for the presence of metal−tpy complexes in the film. Further proofs arise from the fact that the absorption maxima in the film are similar to those of the metal complexes in solution,[11] from the lack of any fluorescence of the films, and from EDX spectra of self-assembled films of the **P1**−zinc complex. Elemental analysis of the films by EDX confirmed the presence of zinc and fluorine (see the Supporting Information) from signals at 1.0, 8.63, and 9.58 keV (for zinc) and 0.68 keV (fluorine). The fluorine signals can be ascribed to the presence of hexafluorophosphate ions in the film. Although the noncomplexed polymer only provides a carbon peak at 0.28 keV, the self-assembled film shows the carbon peak and three zinc signals, which can be taken as a proof for the formation of the coordination polymer. The additional strong signals in the EDX spectrum from silicon, indium and tin are background signals originating from the indium−tin oxide coated glass substrate (see also the EDX spectrum of the blank substrate). The presence of potassium is not safe because the typical peaks at 3.31, 3.59, 3.61, and 0.26 keV overlap with peaks of other elements (carbon, indium, tin).

Although films of the zinc complex show absorption maxima at 450, 385, 335, and 292 nm (Figure 1a), the cobalt-containing films exhibit maxima at 500, 361, and 295 nm (Figure 1b), and the nickel-based films at 450, 381, 330, and 280 nm (Figure 1c). The insets of Figure 1a−c show a linear increase of the optical absorption with the number of dipping cycles, a clear indication that the same

Scheme 3. Supramolecular Sequential Assembly of Coordination Polymer Films Containing Metal(II) Salts and P1 (small counterions are omitted for clarity)

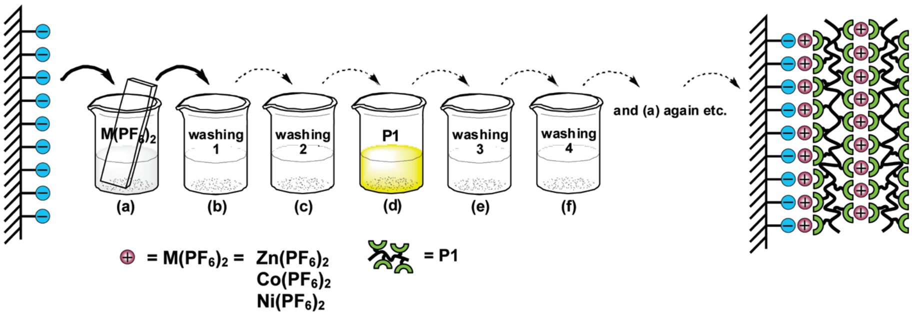


Table 1. Influence of Dipping Conditions on Film Preparation (support: pretreated quartz slide, 12 dipping cycles applied)

	(a)[a]		(b)	(c)	(d)		(e)	(f)	t (s)	abs. at 375 nm (a.u.)	film[b] thickness (nm)
sample	$Zn(PF_6)_2$ [M]	solvent	solvent for washing 1	solvent for washing 2	P1 [monoM]	solvent	solvent for washing 3	solvent for washing 4			
1	0.005	THF:DMF (9:1)		THF	0.0005	THF	THF	THF:DMF (9:1)	5	0.045	4.5
2	0.005	THF:DMF (9:1)		THF	0.0005	THF	THF	THF:DMF (9:1)	30	0.056	8.7
3	0.005	THF:DMF (9:1)		THF	0.0005	THF	THF	THF:DMF (9:1)	60	0.064	15.0
4	0.005	THF:DMF (9:1)		THF	0.0005	THF	THF	THF:DMF (9:1)	600	0.690	46.7
5	0.005	THF:DMF (9:1)		THF	0.0010	THF	THF	THF:DMF (9:1)	60	0.087	17.3
6	0.005	THF:DMF (9:1)		THF	0.0025	THF	THF	THF:DMF (9:1)	60	0.098	19.9
7	0.050	THF:DMF (9:1)		THF	0.0010	THF	THF	THF:DMF (9:1)	60	0.120	21.8
8	0.050	THF:DMF:MeOH:n-hexane (1:0.01:0.5:1)	THF:MeOH:n-hexane (1.5:0.5:2)		0.0050	THF:n-hexane (1:1)	THF:MeOH:n-hexane (1.5:0.5:2)		5	0.900	109.7
9	0.050	THF:DMF:MeOH:n-hexane (1:0.01:0.5:1)	THF:n-hexane (1:1)		0.0050	THF:n-hexane (1:1)	THF:n-hexane (1:1)		5	1.450	598,0
10	0.005	H_2O	H_2O	drying	0.0005	toluene	toluene	drying	600	0.096	7.6
11	0.005	toluene:DMF (9:1)	toluene: DMF (9:1)	toluene	0.0005	toluene	toluene		600	0.367	55.7
12	0.005	toluene:DMF: MeOH: n-hexane (1:0.1:0.9:1)	toluene:MeOH:n-hexane (1:0.9:1)		0.0005	toluene: n-hexane (1:1)	toluene:n-hexane (1:1)		600	0.656	228

[a] The notations a−f refer to the dipping and cleaning steps shown in Scheme 3. [b] Thickness data are average values of three measurements per sample.

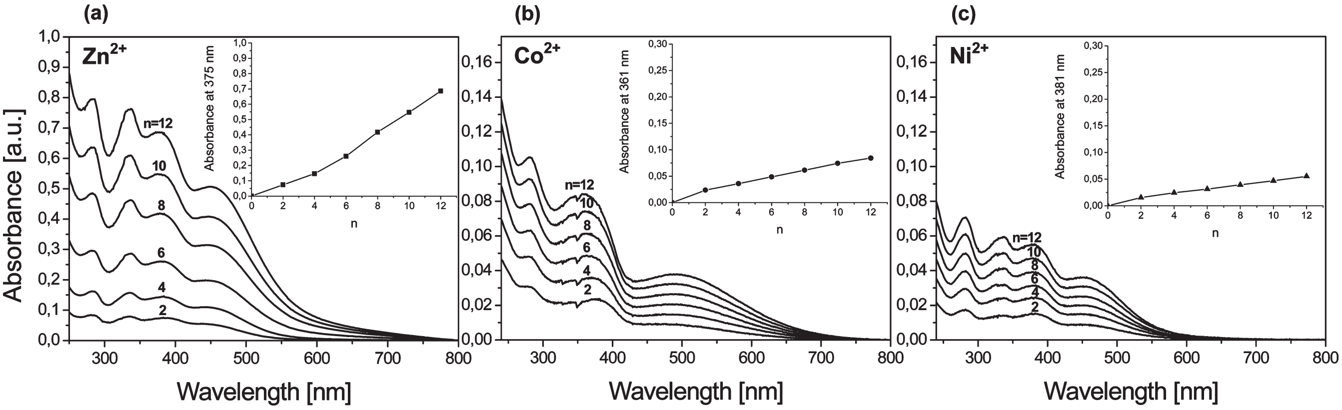


Figure 1. UV/vis absorption spectra of coordination polymer films of **P1** and (a) zinc(II), (b) cobalt(II), and (c) nickel(II) monitored after *n* different numbers of dipping cycles. The insets show plots of the absorbance at (a) 375, (b) 361, and (c) 381 nm vs *n*.

Table 2. Characteristic Data of Electrochromic Coordination Polymer Films[a]

	dipping cycles *n*	film thickness *d* (nm)	switching time Δt (s)	contrast Δ%*T*
P1−Zn	12	46.7	0.450	18
	24	109.2	2.200	54
P1−Co	12	12.8	0.325	8.5
P1−Ni	12	11.6	0.500	5

[a] Preparation conditions: see sample 4 in Table 1

amount of polymer complex is adsorbed in each dipping cycle. However, striking differences exist for the optical densities of the films with different metal ions. If same conditions of film deposition were applied, the zinc-based films always had a much deeper color than the other ones. The reason is a different thickness of the films, as was demonstrated using profilometric studies. After 12 dipping cycles, zinc-based films had a thickness of 47 nm, whereas cobalt- and nickel-based films were only 13 and 12 nm in thickness, respectively (see Table 2). The different thickness can be ascribed to different solubility of the metal ion-tpy complexes in the solvent (or solvent mixture) used in the dipping solutions during film preparation. The nature of the counterion of the metal salt also plays a role. Hexafluorophosphate, for example, was found to favor precipitation of the complex rather than the acetate counterion did. A careful variation of the preparation conditions may therefore help to optimize the film morphology and to increase the film thickness.

3.4. Optimization of Film Preparation. The different growth behavior of the various coordination polymer films prompted us to study the growth conditions of the films in greater detail. Additional stimulus came from the idea to change the dipping conditions in order to obtain films of good quality at much shorter dipping times. For this purpose, the most important parameters were varied: dipping time, concentration of dipping solutions, composition of solvent mixtures used for the dipping solutions and for the cleaning of the substrates. The experiments were carried out with films of the zinc complex of **P1** as a standard system. Twelve dipping cycles were applied. As a measure for the amount of coordination polymer deposited, the absorbance at 375 nm was evaluated, and

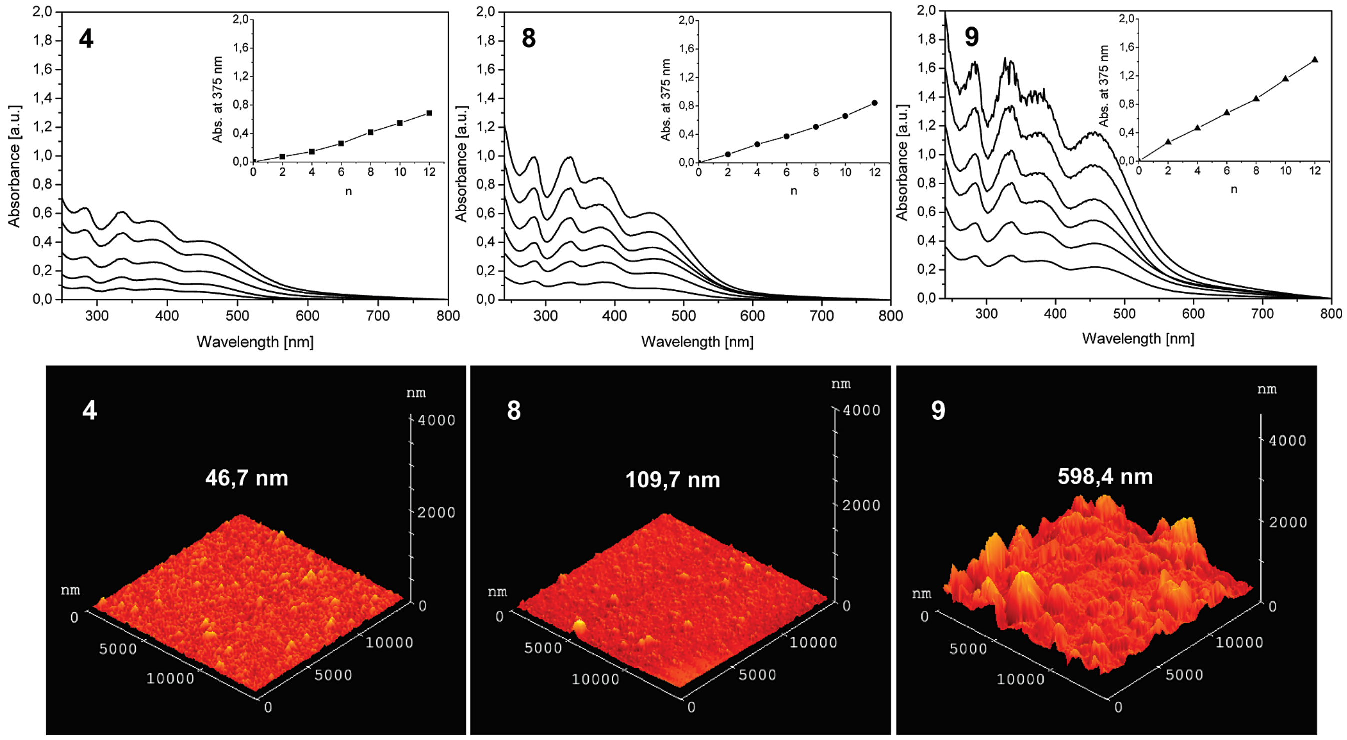


Figure 2. Optical spectra (upper row) and AFM pictures (lower row) of films of **P1**-zinc complex prepared under different conditions. Sample numbers refer to Table 1. Optical spectra were monitored after different numbers *n* of dipping cycles, the insets showing plots of the absorbance at 375 nm vs *n*. AFM pictures were measured from samples subjected to 12 dipping cycles. The film thickness is also indicated (in nm).

the film thickness was measured. Some of the films were also studied using AFM and SEM.

Data of samples 1−4 listed in Table 1 indicate that the absorbance decreased strongly, if the dipping time was shortened and all other conditions were kept constant. If the dipping times were 10 min, the absorbance was 0.690. Applying dipping times of 1 min, the absorbance was 0.064, and for 5 s it was only 0.045. Simultaneously, the film thickness decreased from 46.7 nm (10 min) to 4.5 nm (5 s). Increasing the concentration of zinc salt and polymer in the dipping solutions had only a minor effect, if the dipping time was 1 min (samples 5 to 7). We also varied the rinse times of the substrate. Usually, the substrates were immersed in the pure solvents for 30 s in order to remove surplus nonadsorbed metal salt or polymer chains from the coated substrate. For a sample prepared in the same way as sample 4 (Table 1), we increased the immersion times in THF:DMF (9:1) and pure THF to 10 min. After 12 dipping (and rinse) cycles, the final absorption was only 2% lower and the thickness value was 5% percent lower (data not shown in Table 1). This indicates that there was no need to use prolonged rinse times. Of greater importance was the composition of the solvent mixture. For sample 8, small amounts of methanol and/or n-hexane were added to the dipping and cleaning solutions. n-Hexane is a nonsolvent for metal salt, polymer and polymer−metal complex, and therefore its presence strongly favored the deposition of the complex at the substrate surface. After 12 cycles at dipping times of only 5 s an absorbance of 0.900 was reached, and the film thickness was 109.7 nm. An AFM study indicated that the surface roughness was about the same as for sample 4 with a dipping time of 10 min (Figure 2, left and middle). If methanol was left away in the cleaning solutions, the effect of the nonsolvent hexane was even stronger, and large amounts of the polymer−metal complex precipitated at the substrate surface (sample 9). The absorbance was 1.45, the thickness about 600 nm. However, as indicated by the AFM picture (Figure 2, right), the surface structure was very rough.

In a second set of experiments, THF was replaced by water and toluene as solvents for dipping and cleaning solutions. Sample 10 was first dipped into an aqueous solution of the metal salt, cleaned with water and subsequently dried before it was dipped into a solution of the polymer in toluene. After subsequent cleaning with pure toluene, the substrate was dried and dipped into the aqueous metal salt solution again. The dipping times were always 10 min. The result was surprising. Only small amounts of the polymer−metal complex were deposited, the absorbance was only 0.096, the film thickness 7.6 nm, but a scanning electron micrograph indicated a very smooth film morphology (Figure 3, left). To get thicker films, water was replaced by toluene/DMF (9:1 v/v) (sample 11). No drying was needed anymore between the dipping steps. A thicker film was obtained (absorbance, 0.367; thickness, 55.7 nm), but the surface structure was rather inhomogeneous (Figure 3, middle). A further increase in film thickness was obtained, if methanol and n-hexane were added to the toluene/DMF solvent mixture for the metal salt, and toluene was replaced by a toluene/n-hexane (1:1, v/v) solvent mixture for the polymer. For sample 12, the absorbance was 0.656 and the film thickness was 228 nm, but the

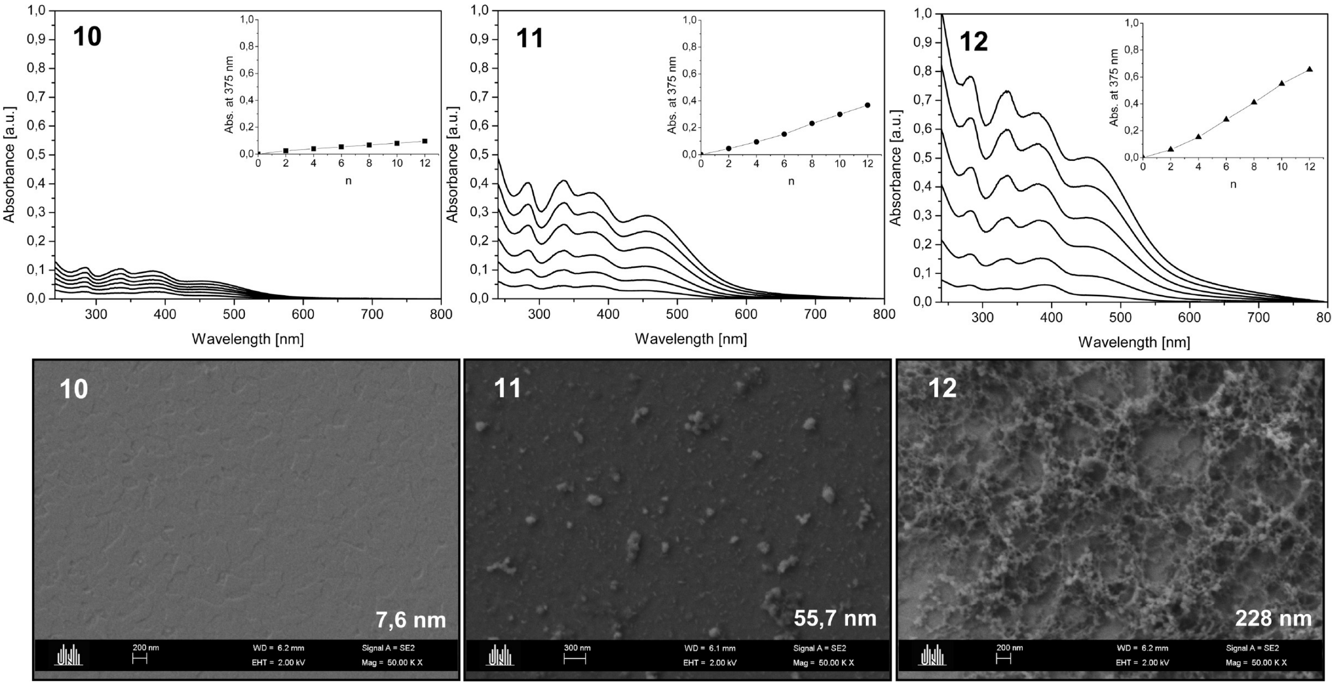


Figure 3. Optical spectra (upper row) and SEM pictures (lower row) of films of **P1**−zinc complex prepared under different conditions. Sample numbers refer to Table 1. Optical spectra were monitored after different numbers *n* of dipping cycles, the insets showing plots of the absorbance at 375 nm vs *n*. SEM pictures were measured from samples subjected to 12 dipping cycles. The film thickness is also indicated (in nm).

surface structure was very inhomogeneous (Figure 3, right). Instead of a homogeneous film, an unorganized precipitate of the polymer−metal complex was obtained at the substrate surface. Obviously n-hexane, which acts as a nonsolvent of the complex, favors precipitation rather than a controlled adsorption at the substrate surface. Our study shows that the choice of the solvents used for dipping and cleaning is crucial for the film thickness and morphology. Thin or thick films with either smooth or rough surface were obtained. The best results were obtained for sample 8. This sample represents a film of about 100 nm in thickness with a smooth surface, which was obtained after 12 dipping cycles with individual dipping and cleaning times of only 5 s, the total preparation time being less than 5 min.

3.5. Electrochemical Properties. The electrochemical properties of the coordination polymer films were studied using cyclic voltammetry (CV). For this purpose, films were built up on ITO-coated glass substrates. In Figure 4, oxidative and reductive cycles of films containing the zinc, cobalt, and nickel complex are shown. The oxidative cycles of the zinc complex (upper row, left) and the nickel complex (upper row, right) are similar. Two closely connected and partially overlapping oxidation/ reduction waves occur, the midpotentials being 310 and 560 mV for the zinc complex, and 410 and 560 mV for the nickel complex. The oxidation steps are highly reversible. For the cobalt-based film only a single, broad oxidative wave at 310 mV is found, whereas subsequent reduction shows two waves at 300 and 150 mV (Figure 4, upper row, middle). We assume that the broad oxidative wave contains two oxidation steps with potentials being close to each other. Again the oxidative cycle is highly reversible. Reductive cycles of the films (Figure 4, lower row) show peaks at −2.5 and −3.3 V (vs FOC). The CV diagrams indicate that the reduction is only partially reversible.

The similarity of the oxidative and reductive cycles suggests that in the three films the same electron transfer reactions of the polymer take place. As recently discussed,[12] the first oxidative wave can be ascribed to oxidation of nitrogen in the polymer backbone resulting in formation of a cation radical, which may partially delocalize. The second peak we ascribe to oxidation of nitrogen atoms in the backbone adjacent to the already oxidized ones. The radicals recombine and a dication is formed, which is separated by the fluorene unit exhibiting a quinoid structure. The reductive processes at −2.5 and −3.3 V can be ascribed to reduction of the tpy unit.

3.6. Electrochromic Behavior. Oxidation and reduction of the coordination polymer films are accompanied by remarkable color changes depending on the kind of metal ions complexed by the polymer. To analyze the color changes in detail, we carried out a spectroelectrochemical study. Absorption spectra in Figure 5 were monitored while different potentials were applied to the films. Photographs of the films at different potentials are also shown as insets. The zinc-containing film changes color from yellow to orange-red at 310 mV where the first oxidation takes place. The color change involves a decrease in the bands at 375 and 450 nm, formation of a shoulder at 537 nm, and the occurrence of an isosbestic point at 482 nm. At 560 mV, the color of the film is changed into blue. The red-blue transition is accompanied with an isosbestic point at 544 nm and the appearance of a very broad absorption at about 900 nm with a long wavelength tail extending to the infrared. In

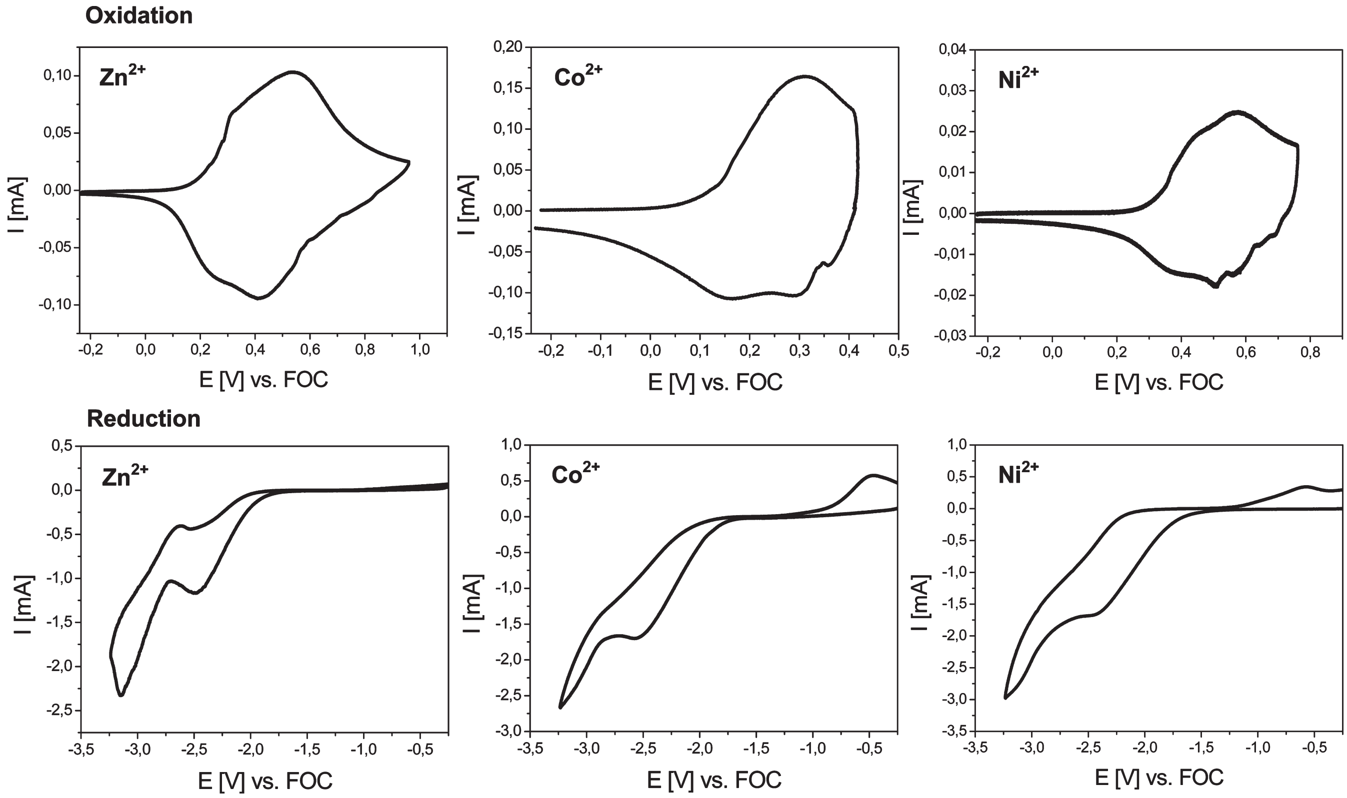


Figure 4. Oxidative (upper row) and reductive (lower row) electrochemical cycles of coordination polymer films of **P1** and various metal ions on ITO-coated glass support (12 dipping cycles).

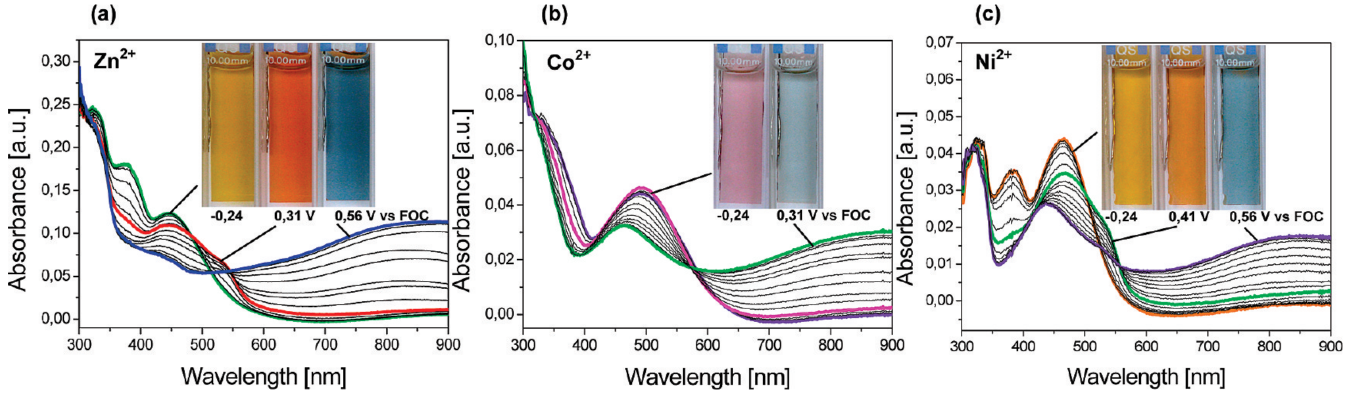


Figure 5. Spectroelectrochemistry of coordination polymer films of **P1** and different metal ions on ITO-coated glass supports (12 dipping cycles): UV/vis absorption spectra were monitored while different potentials were applied to the films. Inset pictures show color transitions (films after 24 dipping cycles). 0.1 M TBAPF$_6$/acetonitrile electrolyte/solvent couple at applied potentials (V): (a) Zn(II); (b) Co(II); (c) Ni(II).

the wavelength region shorter than 544 nm, the absorption decreases upon the oxidation.

The cobalt-containing film is purple in the neutral state. The color changes into blue, if the potential is increased to the peak potential of the broad oxidative wave at 310 mV (Figure 5). For the blue color a new absorption band with maximum at about 900 nm extending to the infrared region is responsible. Simultaneously, the absorption band at 490 nm is decreased and shifted to shorter wavelength by 30 nm. At 580 nm, an isosbestic point occurs indicating that the oxidation proceeds as a single-step transition.

The electrochromic properties of the nickel-containing film resemble those of the zinc-based film. In the neutral state, the film is pale yellow and changes color to brownish orange as soon as the potential is increased to 410 mV, the peak potential of the first oxidation step. The absorption band with maximum at 375 nm disappears completely, and the band at 460 nm strongly decreases in intensity. Simultaneously, a new band (shoulder) at about 535 nm appears. The color transition is accompanied by an isosbestic point at 502 nm. If the potential is further increased to 560 mV (the potential of the second oxidative wave), the film turns blue. A broad absorption band with maximum at about 850 nm occurs, whereas the band at 460 nm is simultaneously decreased and shifted hypsochromically to 438 nm. The orange-to-blue transition involves an isosbestic point at 554 nm.

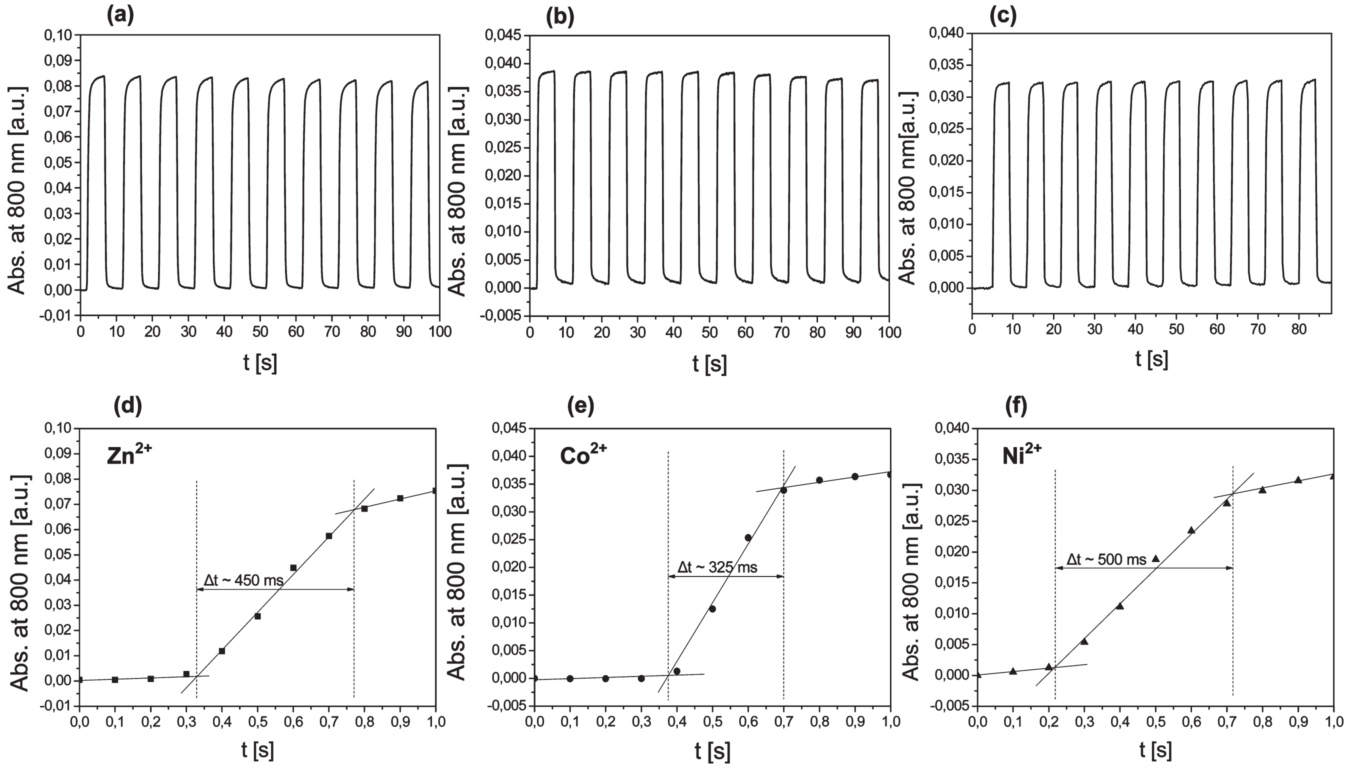


Figure 6. (a−c) Electrochromic switching of coordination polymer film of **P1** and (a) zinc(II), (b) cobalt(II), and nickel(II) on ITO-coated glass support (12 dipping cycles). Potential was switched between −240 and +560 mV (vs FOC) every 5 s, and absorption at 800 nm was monitored vs time. The first 10 cycles are shown. 0.1 M TBAPF$_6$/acetonitrile electrolyte/solvent couple. (d−f) Determination of switching time for films of **P1** and (d) zinc(II), (e) cobalt(II), and (f) nickel(II). Absorption at 800 nm is plotted vs time after increasing the potential from −240 to +560 mV (vs FOC). 0.1 M TBAPF$_6$/acetonitrile electrolyte/solvent couple.

The color changes of all films are highly reversible even if no special precautions are taken to protect the films against oxygen and humidity. The different colors of the films can be ascribed to different oxidation states, radical delocalization, and formation of a quinoid structure in the polymer backbone, and do not involve a metal ion oxidation or reduction. The cobalt-based polymer film differs from the other ones in that the two oxidation potentials E_1 and E_2 of cation radical and dication formation are so similar that only a neutral and an oxidized state (probably the dication state) can be distinguished. Although the neutral films differ in their color from the zinc- and nickel-based ones, the fully oxidized films show the same deep blue color. The ionochromism in the neutral state is based on different interactions between the d-electron of the metal ions and p-electrons of the terpyridine ligands, which affect the backbone absorption because of the π-conjugation of the side groups. In the fully oxidized state, the color is dominated by the presence of the dication state and the strong electron delocalization of the backbone, which causes all films to exhibit the same blue color no matter what kind of metal ions are present in the film.

The strong color changes between neutral and fully oxidized state were used to determine the switching time of the films. For this purpose, the potential (for zinc- and nickel-based films, 560 mV; for cobalt-based film, 310 mV) was repeatedly switched on and off for time periods of 5 s, respectively, and the absorbance at 800 nm was plotted versus the time. In Figure 6a−c, the change in absorbance of the three films is shown. By expanding the time scale of a single oxidation step the switching time could be determined (Figures 6d−f). For the zinc-containing film (12 dipping cycles) the switching time was about 450 ms, and for a thicker film (24 dipping cycles) the time was 2.2 s (see Table 2). For the cobalt- and nickel-based films (12 dipping cycles), the switching times were 325 and 500 ms, respectively (Figure 6e,f). The difference may originate from variations in the film thickness but may also reflect different morphologies (density, porosity) of the coordination polymers.

The contrast was determined by measuring the change in transmission at 800 nm, Δ%T, if a potential of 560 mV was applied. For the zinc-containing film, Δ%T was 18 and 54%, respectively, depending on whether 12 or 24 dipping cycles were applied. For the cobalt-based film (12 dipping cycles) the contrast was only 8.5% because of the lower thickness of the film. All data regarding switching time and contrast of the various films are compiled in Table 2. A comparison of switching time and contrast with previously reported electrochromic films prepared upon layer-by-layer techniques is rendered difficult because of different device structures and geometries. Multilayered films (always 10 bilayers) of polyaniline (PANI) and Prussian Blue (PB) exhibited a coloring time of 0.66 s and a contrast Δ%T (transmission at 750 nm) of 15.4,[15] films of linear

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(15) Delongchamp, D. M.; Hammond, P. T. *Chem. Mater.* **2004**, *16*, 4799.

polyethylenimine and PB a coloring time of 0.63 s and $\Delta\%T$ of 16.5 (at 700 nm),[16] and multilayered films of poly(3,4-ethylenedioxythiophene) (PEDOT) and polyallylamine hydrochloride (PAH) a switching time of less than 2.5 s and a contrast $\Delta\%T$ of 10% (at 530 nm).[17] This suggests our electrochromic films exhibit a fast switching time and the contrast is similar to the previous films.

Potential switching only had a minor effect on the film morphology. A scanning electron micrograph of a zinc-based film subjected to 100 potential cycles exhibits a smoother surface than the pristine film (see the Supporting Information). Profilometry indicates that the thickness decreased from 46.7 to 45.6 nm. Absorption spectra monitored prior and subsequent to 100 cyclovoltammetric cycles indicate a decrease of the optical absorption by a few percent. This points to desorption of some loosely bound aggregates from the surface, whereas most of the film is retained.

4. Conclusions

Our work indicates that polyiminofluorenes with conjugated phenylterpyridine substituent groups are suited for supramolecular sequential assembly of ultrathin coordination polymer films with divalent metal ions on solid supports. Electronic interactions between the metal ions and the polymer chains are responsible for different colors of the coordination polymer films in the neutral state and for differences in the oxidation potential. The ionochromism is advantageous for tuning the color of electrochromic devices and for ion sensing.

It was possible to prepare electrochromic ultrathin films of a coordination polymer upon a supramolecular self-assembly process. Previous studies of electrochromic ultrathin films prepared upon a layer-by-layer (lbl) procedure were based on polymers with redox-active viologen[18] and triphenylamine groups,[19] conjugated polyelectrolytes such as polythiophene derivatives[17,20] and polyaniline,[15] or colloidal solutions of Prussian Blue nanoparticles.[15,16] In most cases, films were prepared upon alternating electrostatic assembly of electroactive components and nonactive counter-polyelectrolytes using the lbl-technique reported by Decher and co-workers.[21]

In our contribution, a different method of multiple sequential assembly was used. Metal ions and the polytopic ligand **P1** were alternately immobilized on a solid support via coordinative interactions. No counter-polyelectrolyte was needed, which would "dilute" the functional properties of the film. As a result, electrochromic films with fast switching times, high contrast ratio, and high stability could be prepared. After optimizing the conditions, film preparation was found to be a fast and easy process. Twelve dipping cycles and a time period of less than five minutes were sufficient to obtain a film of 100 nm in thickness.

The use of the polyiminofluorene backbone is advantageous because of good solubility in common solvents, reversible oxidation behavior, and high contrast in transmission, if switched between the neutral and the oxidized state. The sequential assembly of films is favored by the polyfunctional character of the polymer chains acting as polytopic ligands. After immobilization, the highly functionalized polymer chains provide a high concentration of tpy groups at the substrate surface, which again favors the immobilization of metal ions in high concentration and so on. Furthermore, the metal ion coordination of the polymer chains leads to a cross-linked structure and desorption of individual polymer chains becomes highly unlikely. This is especially advantageous for electrochromic switching.

As a result of the aromatic character of the polymer backbone and the substituent groups, the coordination polymer network is rather rigid and highly porous, comparable with metal−organic frameworks (MOF), which enable rapid ion transfer and fast switching times. Especially a variation of the arylene groups in the backbone might lead to films of different colors and oxidation potentials but similar architecture and switching characteristics. A variation of the ligand units and the small counterions or further variation of the metal ions might also influence the functional properties.

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Supporting Information Available: EDX spectrum of blank ITO support, EDX spectrum of **P1** (solution cast film) on ITO support, and EDX spectrum of zinc complex of **P1** (lbl assembled film) on ITO-support. SEM pictures of lbl assembled film of zinc complex of **P1** before and after 100-fold cyclovoltammetric cycling. This material is available free of charge via the Internet at http://pubs.acs.org.

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