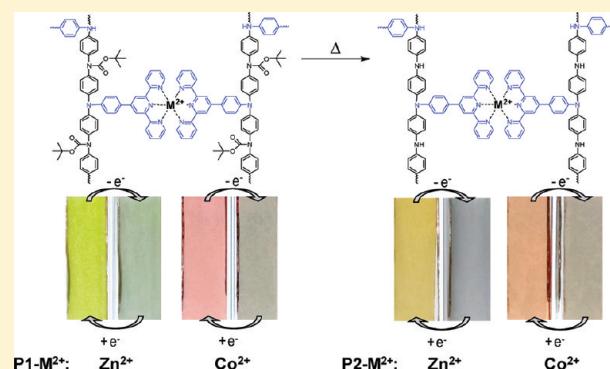


Coordinative Layer-by-Layer Assembly of Electrochromic Thin Films based on Metal Ion Complexes of Terpyridine-Substituted Polyaniline Derivatives

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ABSTRACT: Preparation, metal ion complexation, and coordinative assembly into organized electrochromic films of a polyaniline derivative **P1** substituted with *tert*-butyloxycarbonyl (boc) and terpyridine (tpy) substituent groups in alternating sequence are described. Cleavage of the boc groups after processing into thin films is also described. **P1** is prepared upon Pd-catalyzed polycondensation of *N*-*tert*-butyloxycarbonyl-4,4'-dibromodiphenylamine and 4'-(4-aminophenyl)-2,2':6,2''-terpyridine. The molecular weight is in the range of oligomers, the tetramer and pentamer being the most abundant species. **P1** is soluble in common organic solvents. Solutions are pale yellow with blue or green fluorescence depending on the solvent. Fluorescence quantum yields up to 68% are found. **P1** is able to complex divalent metal salts such as zinc(II) chloride, for example. Titration experiments indicate the formation of 2:1 tpy:metal ion complexes. Layer-by-layer (LbL) assembled films of metal ion complexes of **P1** can be prepared, if negatively charged substrates are alternately dipped into solutions of metal(II) hexafluorophosphates and **P1**. Films of the zinc and nickel ion complex of **P1** are lemon yellow in the neutral state and change color into greenish gray upon anodic oxidation, while Co-containing films are purple and change color into grayish blue upon oxidation. All color changes are reversible under ambient conditions. ATR-IR studies indicate that thermal treatment of the films at 180 °C, or acid treatment, e.g. with 5% aqueous trifluoroacetic acid solution, results in cleavage of the boc groups. **P1** is transformed into the polyaniline derivative **P2** with tpy substituent groups at every second N atom in the backbone. Films of metal ion complexes of **P2** are also electrochromic albeit the colors differ slightly from those of **P1**. For example, the absorption maximum of the Zn-**P2** film is at 456 nm, whereas it is at 446 nm for the corresponding Zn-**P1** film. Prior to cleavage of the boc group, electrochromic switching times are 1.1 to 2.0 s for 30 to 40 nm thick films, while after the cleavage 0.5 to 1.2 s are found. The contrast is 13 to 19%, and not affected by the cleavage. Because of high stability, fast switching, and high contrast, the films might be useful as active materials in electrochromic devices.



1. INTRODUCTION

The supramolecular organization of organic and inorganic compounds is a suitable method for preparation of novel functional materials. Coordinative interaction of metal ions and organic ligands can be used to prepare new metallo-polymers with interesting optoelectronic properties,^{1–6} and may also be used for the buildup of organized films with precisely controlled thickness.^{7–10} Using the strategy of layer-by-layer assembly, electrochromic,^{9,11,12} fluorescent,¹³ and photoconducting¹⁰ coordination polymer films have recently been prepared.

Polyaniline is probably the oldest conjugated polymer.^{14,15} However, it took until the 1980s that significant chemical and physical studies appeared.^{16–18} In the oxidized state the polymer is highly conducting, and anodic electrochemical cycling results in color changes, which can be used for preparation of electrochromic displays.^{19–21} However, polyaniline is usually quite insoluble in organic solvents and difficulties arise in the preparation of thin films.^{16b,18} In our study, a new and unconventional method is reported to prepare organized films containing a

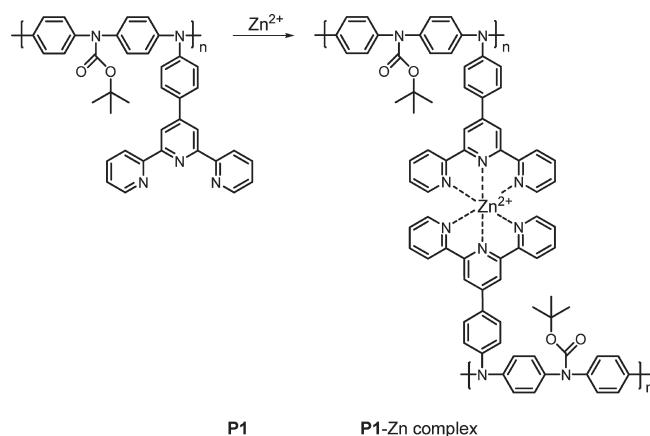
polyaniline derivative. The polymer used in this study is the soluble precursor **P1** (Scheme 1), which combines several functionalities: easily oxidizable N atoms induce donor properties and electrochromic behavior, *tert*-butyloxycarbonyl (boc)-protecting groups prevent *N*-nitroso formation²² and improve the solubility of the polymer in common organic solvents, and terpyridine (tpy) substituent groups²³ enable the coordination of di- and trivalent metal ions with formation of bis-tpy complexes of D_{2d} symmetry (see also Scheme 1). The metal ion complexation proceeds under cross-linking of the polymer and formation of a coordination polymer network structure. Upon thermal or acid treatment^{24–26} the boc-protecting groups can be removed resulting in chain ordering²⁷ and improved adhesion of the polymer. Organized coordination polymer films with polyaniline-like backbone and electronic behavior are obtained. Up to now

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Scheme 1. Molecular Structure of P1 and Its Complex with Zn(II) Ions



only a single report appeared on mono- and ditopic oligoaniline ligands functionalized with boc-groups and tpy units, and on their complexation with divalent ruthenium ions.²⁸

In the present paper, we report on the preparation of the oligomeric compound **P1**, the coordinative supramolecular assembly of **P1** and metal ions in thin films, the thermal cleavage of the boc-protecting group, the optical and electrochemical properties of the boc-protected and deprotected metal ion complex films, and their electrochromic behavior. Various analytical methods such as NMR, IR, and UV spectroscopy, cyclic voltammetry, and scanning electron microscopy were used to characterize the functional films.

2. EXPERIMENTAL PART

Materials. Zinc acetate, $Zn(OAc)_2 \cdot 2H_2O$, cobalt acetate, $Co(OAc)_2 \cdot 4H_2O$, nickel acetate, $Ni(OAc)_2 \cdot 4H_2O$, and zinc chloride, $ZnCl_2$, were obtained from Merck, and potassium hexafluorophosphate was purchased from Aldrich. The 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), trifluoroacetic acid and tetrabutylammonium hexafluorophosphate were obtained from Acros and Aldrich and used without further purification. 4'-(4-Aminophenyl)-2,2':6,2''-terpyridine and *N*-*tert*-butyloxycarbonyl-4,4'-dibromodiphenylamine were prepared according to the literature.^{29,30}

Synthesis of P1. First, 0.070 g (0.216 mmol) of 4'-(4-aminophenyl)-2,2':6,2''-terpyridine²⁸ and 0.092 g (0.216 mmol) of *N*-*tert*-butyloxycarbonyl-4,4'-dibromodiphenylamine³⁰ are dissolved in 5 mL of toluene under inert conditions using the Schlenk tube technique. To this solution are added 0.00494 g (5.39 μ mol) of $Pd_2(dba)_3$ and 0.00647 g (0.0326 mmol) tri-*tert*-butylphosphine in toluene, and finally 0.062 g (0.647 mmol) of sodium *tert*-butoxide. The reaction mixture is filtered under nitrogen at 95 °C for 21 h. After cooling to room temperature, the reaction is quenched by the addition of 10 mL of aqueous ammonia. The organic phase is washed several times with saturated solution of sodium chloride and then dried over magnesium sulfate. After concentration in vacuo the residue is poured into hexane to precipitate the polymer, which is filtered

off, washed with hexane, and dried under ambient conditions to yield 0.112 g of the product as a beige powder. Yield: 88%.

¹H NMR (300 MHz, C_6D_6), δ (ppm): 1–1.5 (alkyl group); 6.81 (phenylene H); 6.97 (phenylene H); 7.08 (phenylene H); 7.23 (phenylene H); 7.38 (phenylene H); 7.57 (tpy arom. H); 8.65 (tpy arom. H); 8.78 (tpy arom. H); 9.2 (tpy arom. H).

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 *i*-propanol, 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 (polystyrenesulfonate), PEI (polyethylenimine), and PSS as previously described.³¹

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. The PSS coating provided a high density of negative charges at the substrate surface for adsorption of the metal ions in the next deposition step.

Dipping Solutions. 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/methanol/*n*-hexane (1: 0.1: 0.5: 1 v/v) with a 0.01 M solution of the corresponding metal acetate in THF/DMF/methanol/*n*-hexane (1: 0.1: 0.5: 1 v/v). The dipping solution of the ligand was a 5×10^{-4} monomolar solution in THF/*n*-hexane (1:1 v/v).

Methods. *Film Preparation. Films with P1.* The pretreated substrates were dipped sequentially into (a) the THF/DMF/methanol/*n*-hexane (1: 0.1: 0.5: 1 v/v) solution of metal hexafluorophosphate, (b) THF/methanol/*n*-hexane (1.5: 0.5: 1 v/v), (c) THF/methanol/*n*-hexane (1.5: 0.5: 1 v/v), (d) the THF/*n*-hexane (1:1 v/v) solution of **P1** in THF/*n*-hexane (1:1 v/v), (e) THF/*n*-hexane (1:1 v/v), (f) THF/*n*-hexane (1:1 v/v), and the sequence a–f is repeated. Immersion times are 5 min each for steps a and d and 5 s for steps b, c, e, and f.

Removal of Boc-Protecting Groups upon Thermal and Acid Treatment of Films

- (a) **Thermal treatment:** the substrate coated with **P1** and metal hexafluorophosphate was annealed in a drybox at 180 °C for 40 min.
- (b) **Acid treatment:** the substrate coated with **P1** and metal hexafluorophosphate was dipped once into a 5% toluene solution of trifluoroacetic acid (TFA) for a few seconds.

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. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B spectrometer. Photoluminescence quantum yields were measured in toluene, THF and dichloromethane, the values were calculated by comparing with Rhodamine 6G in ethanol ($\Phi_r = 0.95$). 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

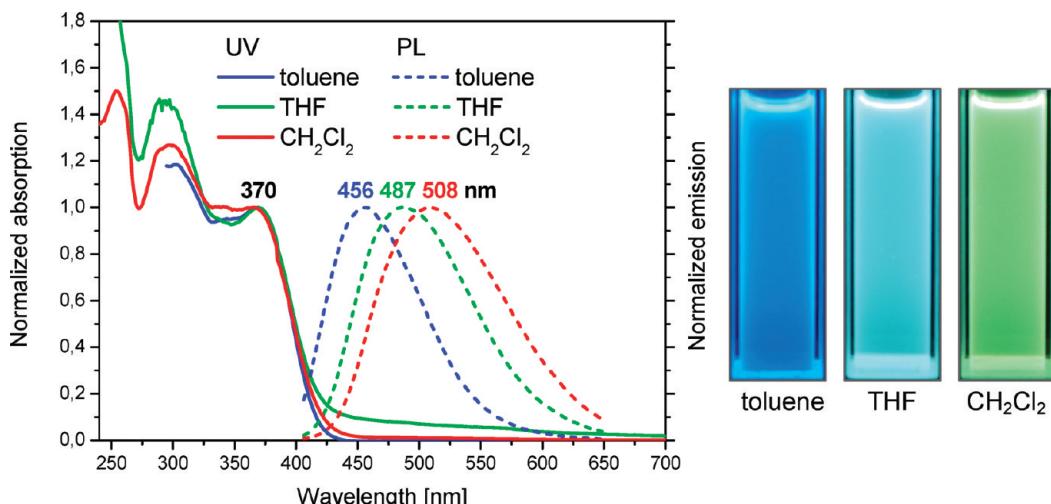


Figure 1. Normalized UV–vis absorption and fluorescence spectra of P1 in toluene, THF and dichloromethane ($\lambda_{\text{ex}} = 370 \text{ nm}$). Photographic images of the fluorescent polymer solutions are also shown.

Table 1. Optical Properties of P1

	solvent	absorption λ_{max} [nm]	emission λ_{max} [nm]	quantum yield Φ_f [%]
P1	toluene	367	456	68
	THF	370	487	55
	CH ₂ Cl ₂	367	508	40

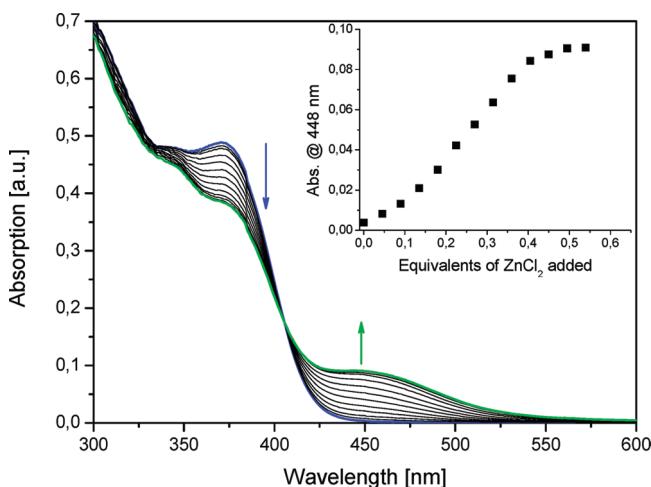
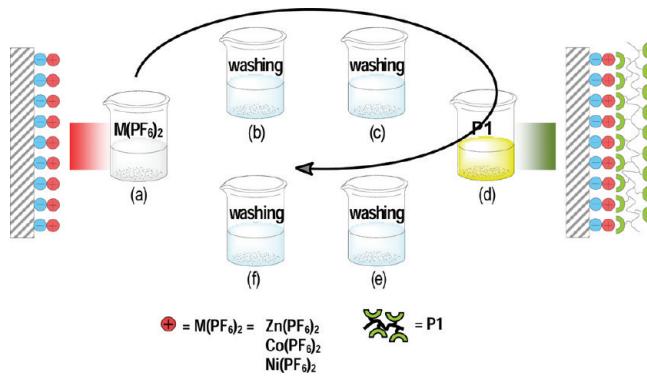


Figure 2. UV–vis absorption spectra of P1 (concentration: $1.69 \times 10^{-5} \text{ monomol} \cdot \text{L}^{-1}$) in toluene/methanol (99:1 v/v) monitored before and after stepwise addition of 7 μL aliquots of ZnCl₂ solution (concentration: $2.93 \times 10^{-4} \text{ monomol} \cdot \text{L}^{-1}$). The inset shows the change in absorbance at 448 nm versus the equivalents of ZnCl₂ added.

employing the polymer film on an ITO-coated glass substrate; reference and counter electrodes were platinum. The experiments were carried out in acetonitrile (saturated with N₂) containing 0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF₆) as electrolyte salt. SEM images were obtained using a Zeiss Neon 40 scanning electron microscope. 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 $\pm 2.5 \text{ nm}$.

Scheme 2. Supramolecular Sequential Assembly of Metal Ions and P1 Resulting in the Formation of a Coordination Polymer Network Film on a Solid Support



3. RESULTS AND DISCUSSION

3.1. Synthesis and Optical Properties of P1. P1 was prepared upon polycondensation of *N*-*tert*-butyloxycarbonyl-4,4'-dibromodiphenylamine and 4'-(4-aminophenyl)-2,2':6,2''-terpyridine using the Pd₂(dba)₃/tri-*tert*-butylphosphine system as catalyst and sodium *tert*-butoxide as the base. The synthesis followed procedures reported by Buchwald,³² Hartwig,³³ and Kanbara,³⁴ and it was already used in our group for preparation of polyiminofluorenes,¹¹ polyiminocarbazolylenes,¹² and other conjugated polymers with nitrogen atoms in the main chain.³⁵ The product was obtained as a beige powder, which was readily soluble in common organic solvents such as toluene, chloroform, dichloromethane, or tetrahydrofuran (THF). Solutions were pale yellow and showed a blue, light blue or green fluorescence depending on the nature of the solvent. A MALDI-TOF study of the molecular weight distribution indicated that oligomers were formed, the tetra- and pentamer in equimolar ratio being the most frequent species.

In Figure 1 normalized UV–vis absorption and fluorescence spectra of P1 in different solvents are shown. The absorption

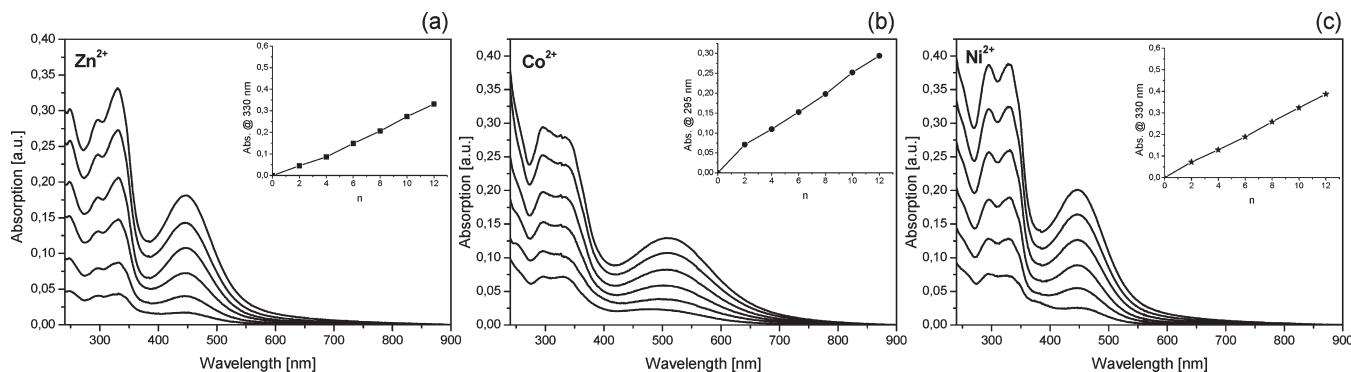


Figure 3. UV-vis absorption spectra of coordination polymer films of **P1** and (a) zinc(II), (b) cobalt(II), and (c) nickel(II) ions monitored after n different numbers of dipping cycles. The insets show plots of the absorbance at 330 nm (a), 295 nm (b), and 330 nm (c) vs n .

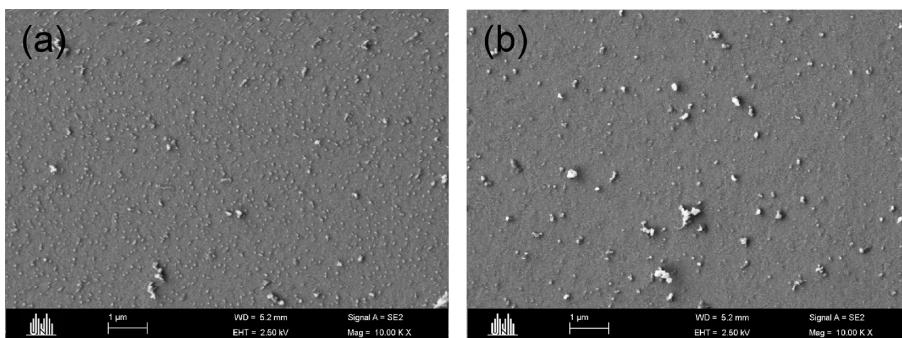


Figure 4. SEM pictures of Zn-**P1** film (12 dipping cycles) (a) and after thermal conversion into Zn-**P2** film (b).

spectra in THF and dichloromethane indicate three bands at about 250, 290, and 370 nm, the maxima being slightly dependent on the solvent used (Table 1). In THF the absorption is slightly red-shifted because it exhibits the largest dipole moments among the solvents used in our study and the dipolar interactions with the π -conjugated structure of **P1** are strongest.

Fluorescence spectra and quantum yields were strongly dependent on the polarity of the solvent. With increasing polarity, the fluorescence maximum was bathochromically shifted, the maximum in toluene being at 456 nm, in THF at 487 nm, and in dichloromethane at 508 nm. In toluene, the fluorescence was blue, in THF it was light blue, and in dichloromethane, the fluorescence was green (Figure 1). The reason might be a photoinduced charge transfer from the nitrogen atoms of the main chain to the adjacent aromatic units inducing a dipole moment in the polymer, which is best stabilized in a polar solvent.^{36,37} Consequently the fluorescence is bathochromically shifted. Simultaneously the fluorescence quantum yield Φ decreased with increasing polarity of the solvent. In toluene, Φ was 0.68, in THF 0.55, and in dichloromethane 0.40.

3.2. Complexation of P1 with Zn(II). The metal ion complexation of **P1** was studied quantitatively by titrating polymer solutions in toluene/methanol (99:1, v/v) with zinc chloride in the same solvent mixture. Upon stepwise addition of zinc(II) chloride, the low energy $\pi-\pi^*$ transition of the diphenylamine unit in **P1** at 370 nm was gradually diminished (Figure 2). Simultaneously a new band with maximum at 448 nm appeared, which can be ascribed to an MLCT (metal-to-ligand charge transfer) band indicating complex formation between the zinc ions and the tpy ligands. The color change from pale yellow to

orange involves an isosbestic point at 405 nm indicating that only a single equilibrium between metal-free and complexed tpy groups exists. The end point of the titration was reached when 0.5 equiv of zinc ions with regard to the repeat units of **P1** were added. This indicates the formation of the 2:1 complex (bis-complex) between the tpy ligands and the zinc ions. The process of complex formation is represented in Scheme 1. Although the complexation most likely proceeds as an interchain reaction accompanied by cross-linking, we did not observe a precipitation. Possible reasons are the low molecular weight of **P1**, and the low concentration in solution preventing efficient cross-linking. Instead a colloidal solution of aggregates may have formed.

3.3. Sequential Assembly and Optical Properties of Films. For the film preparation we used pretreated quartz supports (for pretreatment see Experimental Part) and indium–tin–oxide (ITO) coated glass substrates. First the substrates were dipped into the solution of the metal salt so that the metal hexafluorophosphate was adsorbed at the substrate surface (Scheme 2, step a). After washing twice in a solvent mixture of THF/methanol/*n*-hexane (1.5: 0.5: 1 v/v) (steps b and c) in order to remove nonadsorbed ions, the substrate was dipped into the solution of **P1** in THF/*n*-hexane (1:1 v/v) (step d). Subsequently nonadsorbed material was removed upon dipping into THF/*n*-hexane (1:1 v/v) (steps e and f). Dipping times in steps a and d were 5 min, while for b and d only short dips were applied.

In Figure 3, UV-vis absorption spectra of Zn-, Co- and Ni-containing films subjected to different numbers of dipping cycles are compiled. The Zn-containing films exhibit absorption maxima at 248, 296, 330, and 445 nm (Figure 3a), the color of the film being lemon yellow. The absorption maxima of the

Co-based films occur at 296, 335, and 510 nm (Figure 3b). The films are purple in color. The Ni-based films are lemon yellow and exhibit maxima at 295, 328, and 447 nm (Figure 3c). The different colors indicate a pronounced ionochromism of the coordination polymer films. Profilometry indicates a thickness of the Zn–P1 film of 40 nm, and 30 nm for films of the Co and Ni ion complex. All films were subjected to 12 dipping cycles.

Scanning electron microscopy (SEM) indicates a rather smooth and homogeneous surface structure of Zn–P1 film (Figure 4a) with few aggregates distributed statistically over the substrate. Holes or larger defects are clearly missing.

3.4. Elimination of the Boc-Groups. The cleavage of the boc-group was comprehensively studied for films of the Zn–P1 complex. As a result, films of the corresponding Zn–P2 complex should be formed. From the cleavage we expected that the structure of the backbone becomes more polyaniline-like, the oxidation potential and the electrochromic properties being changed. Furthermore, the NH group formed upon the cleavage might induce hydrogen bonding, which renders desorption of the oligomer chains more difficult, and the film becomes more stable.

The boc-groups were removed upon thermal and acid treatment of the films (see also Scheme 3). For UV–vis spectroscopy, films were deposited on glass slides, and for ATR-FTIR spectroscopy, they were deposited on germanium crystals. Films were always prepared by application of 12 dipping cycles.

3.4.1. Thermal Cleavage. For thermal cleavage of the boc-group the samples were heated to 180 °C for different time

periods and directly after cooling they were investigated at room temperature. During heating, isobutene and carbon dioxide are set free from the boc group, and an NH group is formed in the backbone. UV–vis spectra recorded after heating for 10 min indicate a decrease of the main absorption band, the maximum being shifted from 446 to 456 nm (Figure 5). The color of the lemon yellow film turns pale orange, possibly due to chain ordering and formation of π – π -interactions between adjacent chains. After 30 min heating no further change in the UV spectra is detectable.

IR spectra were recorded from a film of Zn–P1 prior and subsequent to heating at 180 °C for 30, 40, and 60 min (Figure 6). The disappearance of the C=O stretching modes at 1706 and 1640 cm^{-1} indicates the cleavage of the boc groups. Both methods show in agreement that the boc groups are nearly completely removed after heating at 180 °C for 30 min.

The influence of the heating on the film morphology was studied using scanning electron microscopy. As shown in Figure 4b, the influence is only poor. After heating the finely porous surface is

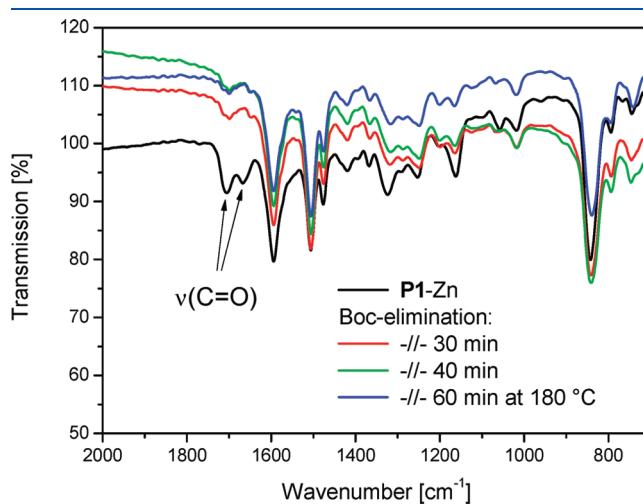


Figure 6. ATR–FTIR spectra of coordination polymer film of Zn–P1, and after thermal treatment for different time periods.

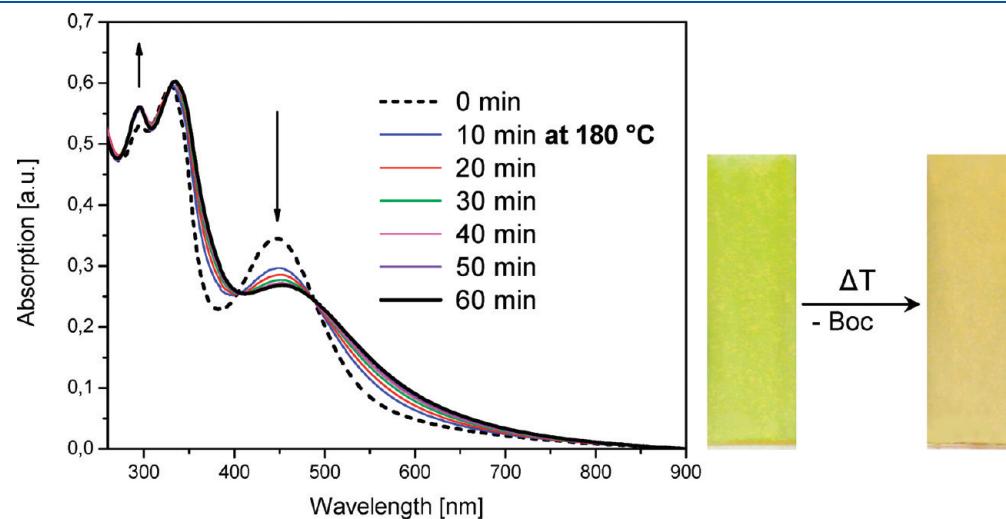


Figure 5. UV–vis absorption spectra of coordination polymer film of Zn–P1, and after annealing at 180 °C in a drybox for different time periods. The pictures show the color transition of the polymer film upon thermal elimination of the boc-groups.

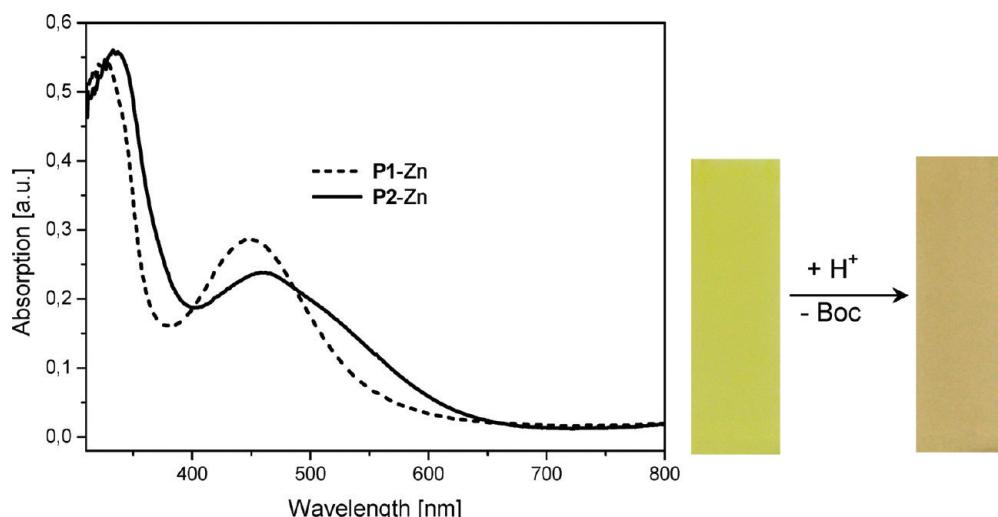


Figure 7. UV-vis absorption spectra of Zn–P1 coordination polymer film monitored before and after dipping into 5% solution of trifluoroacetic acid in toluene. The pictures show the color transition of the polymer film upon acid elimination of the boc groups.

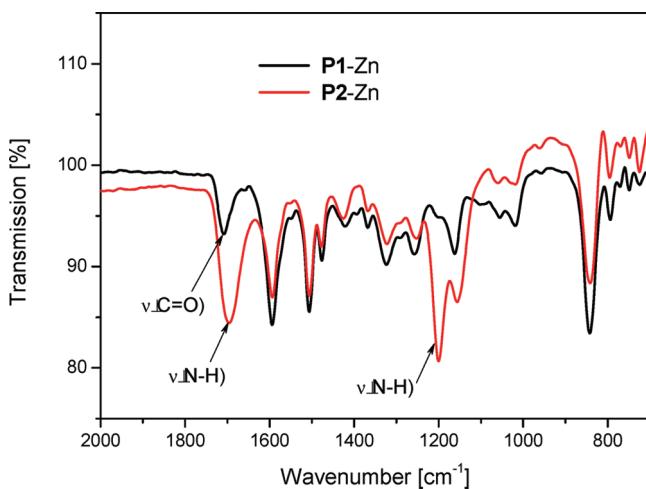


Figure 8. ATR-IR spectra of Zn–P1 coordination polymer films, prior and subsequent to acid elimination of the boc groups.

smoothed, while larger aggregates embedded in the film remain unchanged. The thickness is not changed.

3.4.2. Acid Cleavage. Treatment with trifluoroacetic acid (TFA) also results in elimination of the boc protecting group leaving behind an NH group in the main chain. A single dipping of the film into a 5% solution of TFA in toluene is sufficient for a cleavage of the groups. Subsequently the substrate is immersed in pure toluene or a 5% solution of triethylamine in toluene in order to remove residual TFA from the film.

Similar to the thermal treatment, the acid cleavage is accompanied by a color change from lemon yellow to pale orange. UV-vis spectra prior and subsequent to acid treatment are shown in Figure 7. Because of the cleavage of the boc group the absorption spectrum at 446 nm is bathochromically shifted by 12 nm. Infrared spectra taken prior and subsequent to acid treatment are shown in Figure 8. It can be seen that two new bands at 1699 and 1202 cm⁻¹ occur, which can be ascribed to the N–H deformation mode of secondary amines indicating the cleavage of the boc group.

Further studies of the electrochemical and electrochromic properties of Zn–P2 films, and films of P2 with other metal ions, were carried out with samples annealed at 180 °C for 30 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 9, upper row, oxidative cycles of films containing zinc, cobalt, and nickel complexes of P1 are shown. The oxidative cycles of all films are similar. Only a single broad oxidative wave occurs. The mid potentials are 0.76 V for the zinc- and nickel-containing films, and 0.89 V for the cobalt-containing film. The electrochemical oxidation of the films is highly reversible.

The similarity of the oxidative cycles suggests that in the three films the same electron transfer reactions of the main chain take place. As recently discussed,^{11,12} a two step oxidation of nitrogen atoms in the backbone is likely. We believe that the oxidation potentials of the two differently substituted N atoms in the main chain are similar because the electron withdrawing effect of the t-boc group is comparable in its strength with the mesomeric effect of the tpy ligand. Therefore, the oxidation of the two N atoms will occur at a similar potential and only a single broad wave occurs. In Scheme 4a, a possible mechanism of the oxidation is indicated. Since the oxidation of the two N atoms is equally likely, it is hard to decide in which position the cation radical will be located. In the second oxidation step, a dication with quinoid structure between adjacent oxidized N atoms will be formed.

Oxidative cycles of P2 films containing zinc, cobalt or nickel ion complexes are shown in Figure 9, lower row. The cleavage of the boc group leads to a change of the electrochemical properties of the films. The Zn– and Ni–P2 films exhibit two anodic waves, the new wave occurring at very low potential. The cleavage of the electron-withdrawing boc units is responsible for the new anodic wave at 0.14 to 0.21 V. A two step oxidation mechanism of P2 with formation of the cation radical and dication state is shown in Scheme 4b. Films of the cobalt complex even show a third anodic wave after boc removal. The third wave might indicate further oxidation of the backbone from the emeraldine to the pernigraniline state.¹⁶ The mid potentials are 0.16 and 0.86 V for the Zn

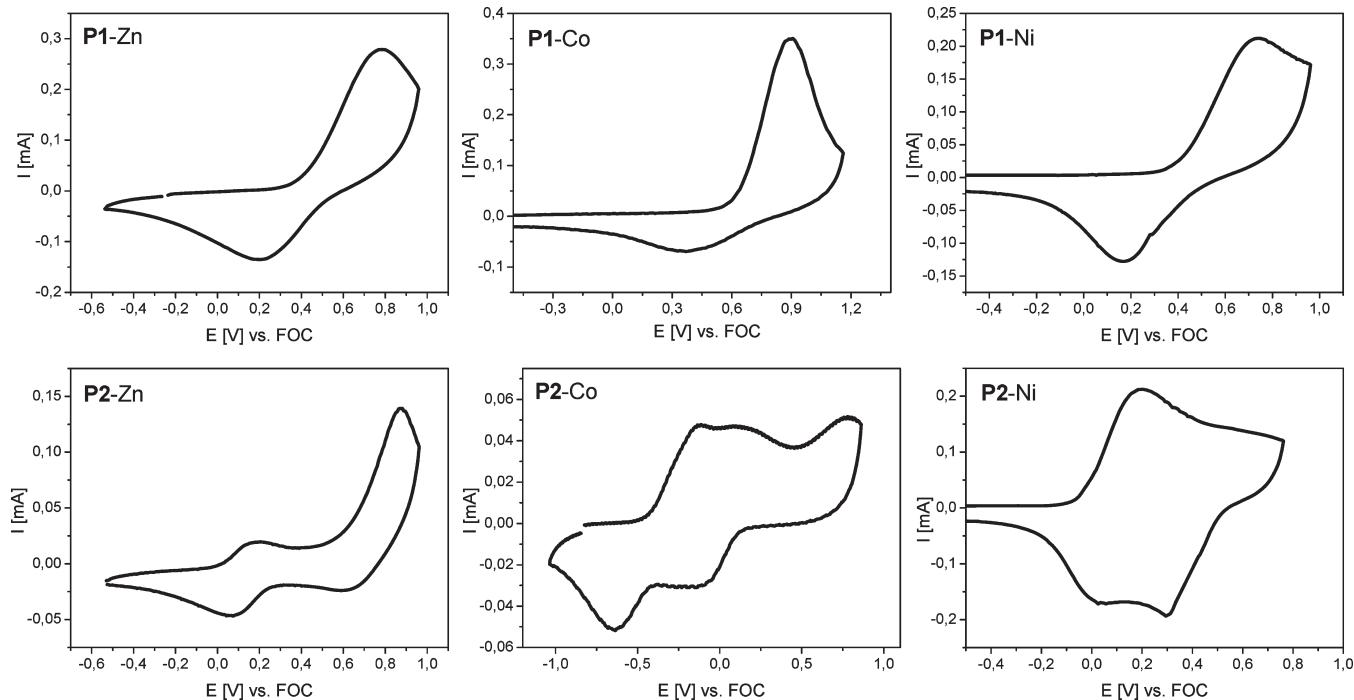
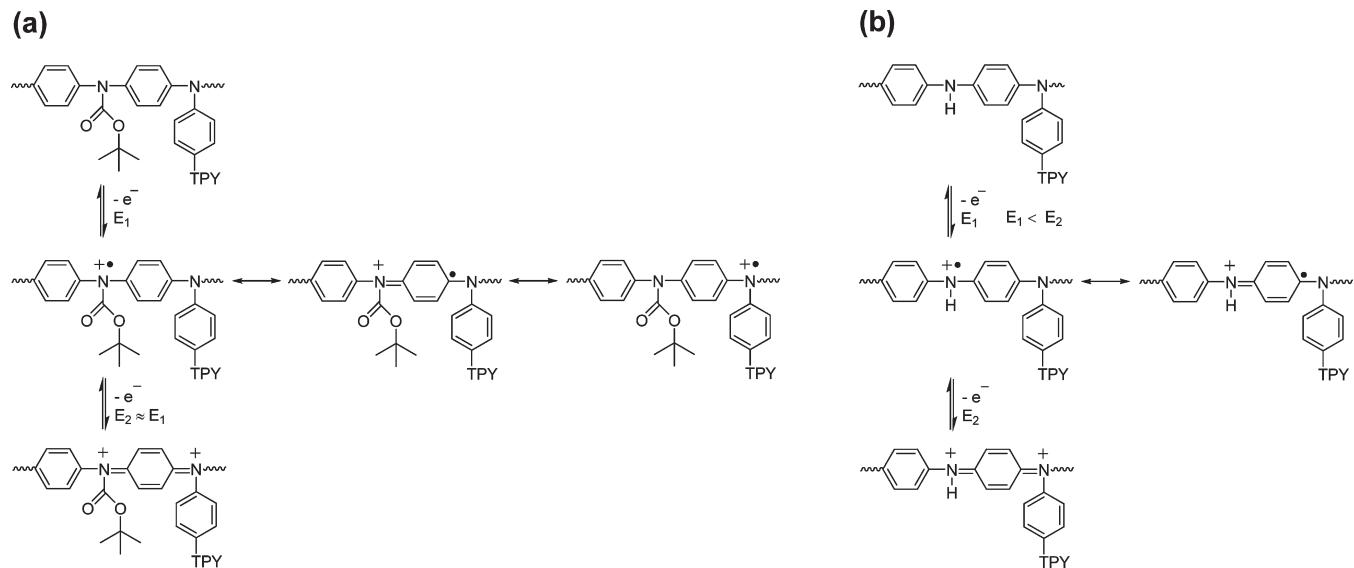


Figure 9. Oxidative voltammetric cycles of coordination polymer films of **P1** (upper row) and **P2** (lower row) with different metal ions. Support: ITO-coated glass substrate (12 dipping cycles).

Scheme 4. Electrochemical Oxidation States of P1 (a) and P2 (b)



complex, -0.14 , 0.21 , and 0.76 V for the Co complex, and 0.2 and 0.61 V for the Ni-containing films. In all cases the oxidative cycles are highly reversible.

3.6. Electrochromic Properties. Films based on **P1** and **P2** exhibit pronounced electrochromic effects. Spectroelectrochemical studies and photographic images of the films in the neutral and oxidized states are compiled in Figure 10.

Let us first discuss the film of the Zn–**P1** complex. At the first anodic wave, the intensity of the absorption bands at 300 and 443 nm decreases, and simultaneously a new broad band with maximum at 880 nm appears (Figure 10a). The color of

the film changes from lemon yellow to greenish gray. The transition is accompanied by two isosbestic points at 410 and 520 nm. At the second wave, the just formed band at 880 nm partially decreases in intensity, a new band with maximum at 405 nm appears, and the absorption between 500 and 700 nm slightly increases in intensity. The greenish gray color of the film is retained.

The spectroelectrochemical study of the Ni–**P1** film exhibits a similar behavior. At the first anodic wave the band at 447 nm decreases in intensity and is shifted to 412 nm, the absorption at 870 nm is increased (Figure 10 c). At the second wave the band at

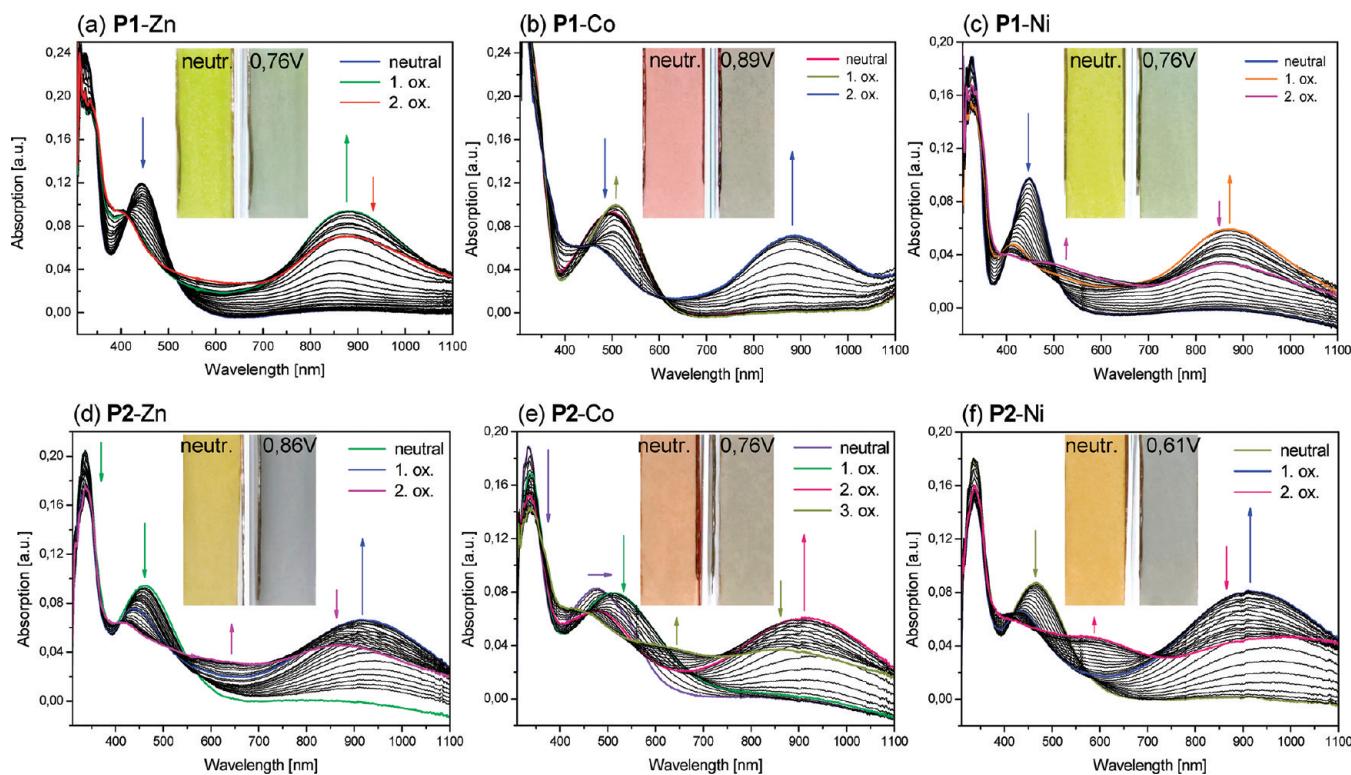


Figure 10. Spectroelectrochemistry of coordination polymer films of **P1** (a–c) and **P2** (d–f) with different metal ions on ITO-coated glass supports (12 dipping cycles); UV-vis absorption spectra were monitored while different potentials were applied to the films. Inset pictures show color transitions (24 dipping cycles). 0.1 M (TBA) PF_6 /acetonitrile/solvent couple at applied potentials (V).

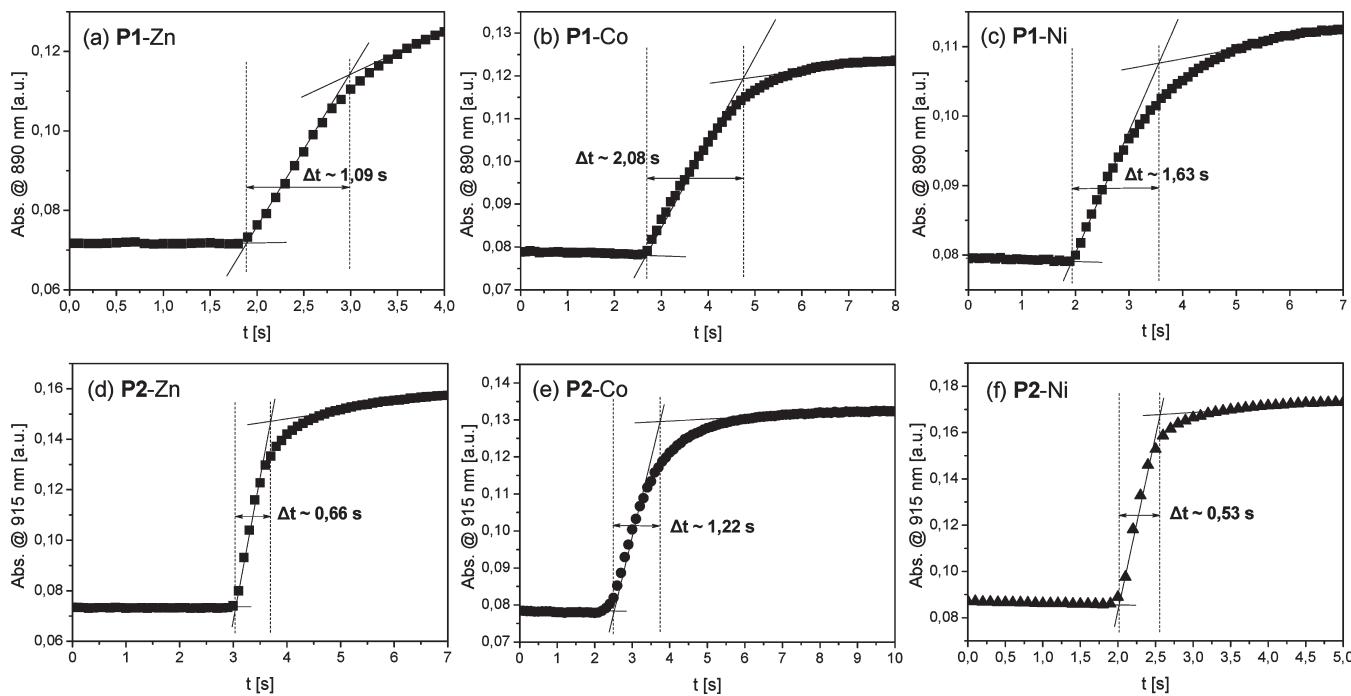


Figure 11. Determination of switching time of coordination polymer films of **P1** (a–c) and **P2** (d–f) with different metal ions. Potential is switched between -240 mV and $+1$ V or 900 mV (vs FOC), and absorption at 890 or 915 nm is monitored vs time.

870 nm is decreased again and a broad shoulder with maximum at 495 nm is formed. The colors of the film are very similar to the Zn-containing film.

The Co-containing film exhibits a color change from purple to grayish blue. At the first anodic wave, the absorption band with maximum at 500 nm is slightly shifted to 508 nm (Figure 10b).

Table 2. Characteristic Data of Electrochromic Films of P1 and P2 and Various Metal Ions (12 Dipping Cycles)

polymer	metal ion	film thickness [nm]	switching time Δt [s]	contrast Δ%T at 890 nm	contrast Δ%T at 915 nm
P1	Zn	37	1.09	19.0	
	Co	30	2.02	15.0	
	Ni	28	1.63	13.3	
P2	Zn	37	0.66		14.4
	Co	30	1.22		13.5
	Ni	28	0.53		16.6

There is no visible color change involved in this transition. Upon further oxidation the band at 508 nm is decreased and a new absorption band with maximum at 885 nm is formed. The transition is accompanied by a color change from purple to grayish blue. The spectroelectrochemical study clearly indicates that the oxidation proceeds in two steps, while with the naked eye only a single color change is observed.

Because of the cleavage of the boc group, the electrochromic properties of the films are changed. During oxidation the pale orange films of the zinc and nickel ion complexes of P2 change their color into dark gray. The pinkish brown film of the cobalt ion complex turns into gray. The spectroelectrochemical study and photographic images are compiled in Figure 10d–f.

Anodic oxidation of the Zn–P2 film first is accompanied by a decrease of the absorption bands at 335 and 460 nm, and the formation of a new broad band with maximum at 920 nm (Figure 10d). The color of the film is changed from light orange to dark gray. If the potential is further increased, the new band at 920 nm is slightly decreased and shifted to 865 nm. The band with maximum at 460 nm is further decreased and shifted to 415 nm. In the range from 550 to 700 nm the absorption slightly increases. In the second oxidation step, the dark gray color of the film is retained.

The cobalt–P2 film is pinkish brown in the neutral state. If a potential of -0.14 V is applied, the absorption band at 335 nm decreases in intensity and the band at 475 nm is shifted to 512 nm (Figure 10e). In the second oxidation step the absorption band at 512 nm is decreased and shifted to 475 nm, the absorption at 913 nm is increased, the film turns gray. In the third step the absorption at 913 nm is decreased again and two shoulders at 445 and 625 nm become apparent. The color of the film is retained.

The spectroelectrochemical study of the Ni–P2 film indicates that the oxidation behavior is very similar to the Zn-based film. The only difference is that in the first oxidation step an absorption band at 915 nm is formed (Figure 10f). In the second step, the intensity of the 915 nm band is decreased again and a new band with maximum at 580 nm is formed. The colors of the film are very similar to those of the Zn-containing film.

For the films containing zinc, cobalt, and nickel ion complexes of P1 (12 dipping cycles) switching time and contrast were determined. For this purpose, the time needed for the entire change of absorption at 890 nm after switching the potential from the neutral (-0.24 V vs FOC) to the fully oxidized state (0.9 V vs FOC) was measured (Figure 11a–c). The switching times of the P1-based films are rather long. For the zinc ion complex it is 1.09 s, for cobalt 2.02 s, and for nickel 1.63 s. We believe that the presence of the boc group in the film increases the density and thus lowers the permeability of the counterions. The contrast was determined from the change in transmission, $\Delta\%T$, at 890 nm observed upon the switching from the neutral to the fully oxidized state. The values for

the Ni- and Zn-containing films, i.e., 13.3 and 19%, respectively, are comparatively high. Characteristic data of the electrochromic P1- and P2-based films are compiled in Tab. 2.

Switching times and contrasts of the P2-based films were measured at 915 nm for switching between -0.24 and 0.9 V vs FOC (Figure 11d–f). For the zinc ion complex the switching time is 0.66 s, for cobalt 1.22 s, and for nickel 0.53 s. This indicates that the removal of the boc group is accompanied by a decrease of the switching time. It is likely that a more porous and less dense film structure is formed through which the counterions can permeate more rapidly. The contrast of the Zn- and Co-containing films is slightly lower (14.4 and 13.5%, respectively), while the contrast of the Ni-based film is higher (16.6%).

4. CONCLUSIONS

Our study indicates that tpy- and boc-substituted polyaniline derivatives can be prepared upon palladium catalyzed amination reactions. Oligomers with an interesting combination of properties become accessible. First, due to presence of the boc group, the compounds are well soluble in common organic solvents and exhibit a strong fluorescence in solution. Second, because of the presence of the tpy ligand groups they are able to form 2:1 ligand: metal ion complexes with a variety of divalent transition metal ions. Because of the pronounced color changes accompanied by ion complexation (ionochromism) the compounds are suitable as sensor materials. Third, the coordinative interactions between the tpy-groups and metal ions can be used for coordinative layer-by-layer (LbL) assembly on solid substrates leading to organized films of coordination polymer networks. Films with smooth surface and thickness control in the nanometer range are obtained showing interesting electrochromic properties. Fourth, the thermal or acid treatment of the films allows for cleavage of the boc groups from the oligomer chains. The removal of the boc groups results in a change of the electronic structure of the backbone indicated by a decrease of the oxidation potential, and the change of color and electrochromic behavior of the films. Moreover, the films become more porous and permeable resulting in faster switching times. The high stability of the coordination polymer films is striking. Films can be annealed at 180 °C for several hours, treated with acid, and electrochemically switched repeatedly under ambient conditions without decomposition of the organic material (except for the cleavage of the boc group).

Our work also shows that the variation of the aromatic units in the backbone is an efficient method to change color, oxidation potential and electrochromic effects of the coordination polymer films. With fluorene units, yellow-to-red-to-blue transitions dominate¹¹ whereas with carbazole units yellow-to-olive and yellow-to-green-to-blue transitions occur,¹² and with the oligoaniline units of the present study yellow-to-grayish blue (in thicker films: yellow-to-black) transitions dominate. As pointed out in previous papers, contrast and switching time of the LbL-assembled coordination polymer network films compare well with those of electrostatically adsorbed LbL-films of conjugated polymers,³⁸ Prussian Blue–polymer composites,³⁹ and others.^{40,41} In further work the ligand group will be varied and effects on the film formation and electrochromic film properties will be studied.

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