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Conjugated Polymer with Benzimidazolylpyridine Ligands in the Side Chain: Metal Ion Coordination and Coordinative Self-Assembly into Fluorescent Ultrathin Films

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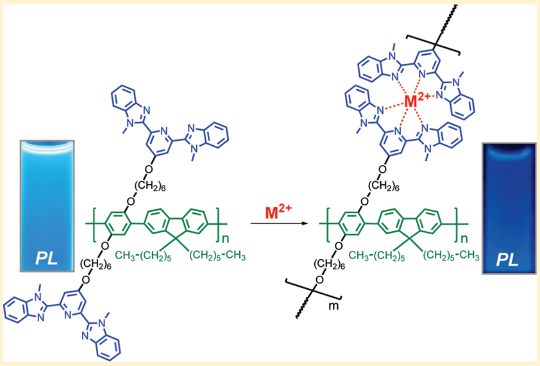
Supporting Information

ABSTRACT: The synthesis and characteristic properties of a new conjugated copolymer with poly(phenylene-*alt*-fluorene) main chain and 2,6-bis(1′-methylbenzimidazolyl)pyridine (bip) ligands attached to the main chain via flexible spacer groups are described. The copolymer was prepared upon Pd-catalyzed Suzuki coupling of the 2,7-bispinacolatoboron ester of 9,9-dihexylfluorene and a 1,4-dibromobenzene derivative carrying two ω-bip-substituted alkoxy groups in the 2- and 5-position. The yield was 88%. The polymer is readily soluble in common organic solvents and exhibits a strong blue fluorescence with maximum at 416 nm; the fluorescence quantum yield in toluene is 85%. UV/vis titration of the polymer with zinc chloride in toluene/methanol (99:1 v/v) and ferrous perchlorate in toluene/methanol (24:1 v/v) indicates formation of 2:1 ligand:metal ion (bis)complexes. Complex formation is accompanied by ion specific color changes (ionochromism) and quenching of the ligand fluorescence. The backbone fluorescence is partially retained. The coordinative interactions between the ligand-substituted polymer ("polytopic ligand") and the divalent metal ions (Zn(II), Cu(II)) can be used for layer-by-layer assembly of organized films on solid supports. Multiple sequential adsorption of metal salts and polymer leads to coordinative supramolecular assembly of the cross-linked polymer−metal ion complex on the substrate, the thickness being controlled by the number of adsorption steps applied. Since the fluorescence of the polymer backbone is not completely quenched by the ligand−metal ion interaction, the films exhibit a bluish luminescence. The new materials might be useful for metal ion sensing and for preparation of fluorescent coatings.



1. INTRODUCTION

In recent years the supramolecular organization of organic and inorganic building blocks has proven to be useful for the preparation of novel functional materials.[1−3] Especially coordinative interactions between organic ligands and metal ions facilitate the preparation of new metallopolymers and polymer network structures.[3−9] Metallopolymers with application potential in electronic and optoelectronic devices,[2a,10−14] or as sensory materials[15−17] have been described. Recently studies were reported, in which the coordinative interactions between divalent transition metal ions and di- or multitopic ligands were applied for the construction of organized films with precisely controlled thickness in the nanometer range.[17−27] For the buildup of the films a layer-by-layer adsorption strategy of alternate assembly of metal ions and ligands was used. Self-assembled films with functional properties[21−27] were obtained, among them being electrochromic polymer network films consisting of zinc, cobalt, or nickel ions and conjugated polymers with terpyridine substituent groups.[25−27] Especially polytopic ligands, i.e., polymers with ligand groups attached to the main chain, have proven useful for the preparation of stable, homogeneous films.[17,24−27] They are advantageous over ditopic ligands because no desorption or crystallization takes place, and small defects occurring during film growth can be healed. Besides the frequently used terpyridine groups, other heteroaromatic units such as 2,6-bis(1-methylbenzimidazolyl)pyridine (bip) groups are also able to coordinate transition metal ions and form octahedral ligand:metal complexes with 2:1 stoichiometry.[28] Recent studies have shown that conjugated macromonomers containing bip units at both ends can be successfully assembled into high-molecular-weight metallo-supramolecular polymers.[29,30]

In this study, for the first time the synthesis of a polymer with bip ligands in the side chain is described. The polymer consists of fluorene and phenylene units in alternating fashion introducing fluorescent properties and of bip ligands attached to the phenylene units via hexamethylene spacer groups. The aliphatic spacer groups were introduced to minimize electronic interactions between the conjugated main chain and the metal−ligand complexes such as quenching of the fluorescence.[31] Furthermore, the metal ion complexation of the polymers in solution is

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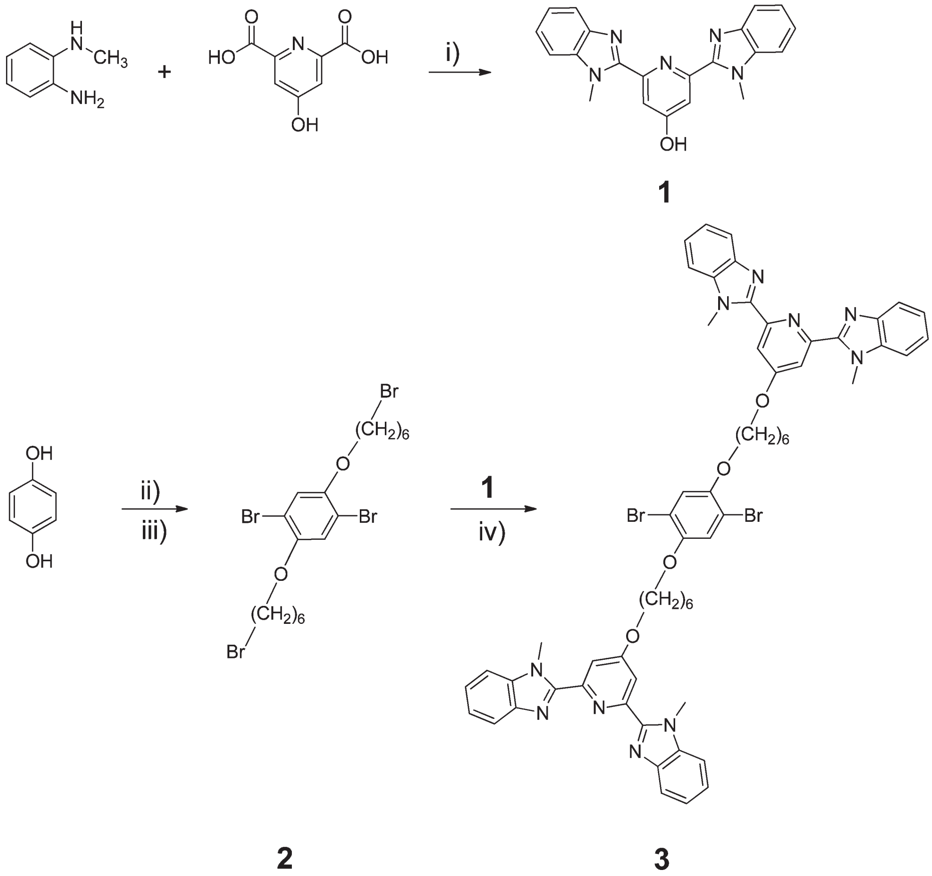
Scheme 1. Preparation of Monomer 3[a]



[a] Reagents and conditions: (i) H_3PO_4, 205 °C, 14 h, 64%; (ii) 1,6-dibromohexane, acetone, reflux, 24 h, 43%; (iii) Br_2, CCl_4, 5 °C, 2 h, 67%; (iv) KOH, DMSO, 47 °C, 24 h, 45%.

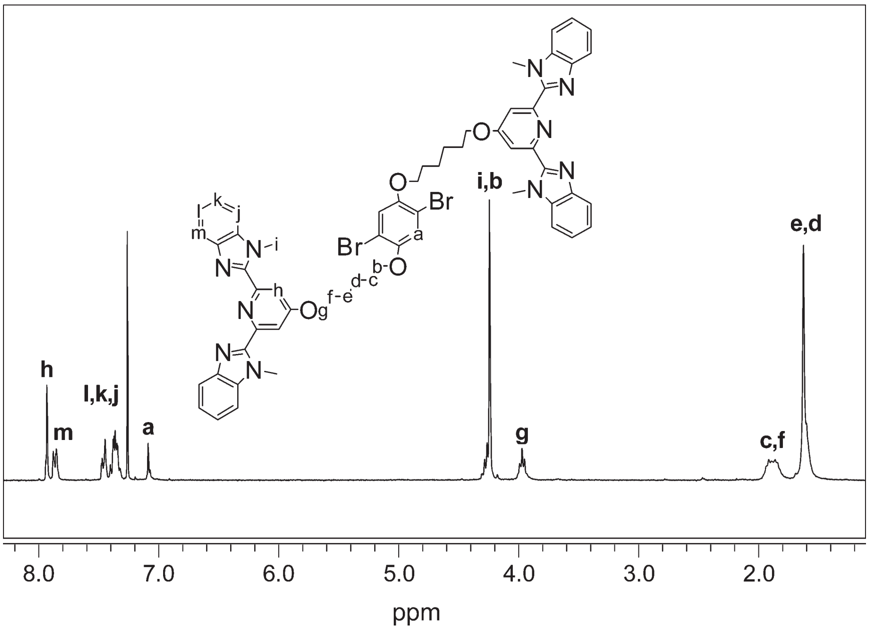


Figure 1. ^{1}H NMR spectrum of monomer **3** in deuterated chloroform.

described leading to metallo-supramolecular network structures via coordinative interactions. Finally the buildup of fluorescent ultrathin films via multiple sequential adsorption in a coordinative self-assembly process has been investigated. Studies were carried out using spectroscopic methods (UV/vis and fluorescence spectroscopy), microscopic methods (scanning electron microscopy), EDX, and thickness measurements of the films.

2. EXPERIMENTAL SECTION

2.1. Materials. The starting compounds were purchased from Aldrich, Fluka, Merck, or Acros and used without further purification. All reactions were carried out under a nitrogen atmosphere. Some of the solvents were distilled before use (e.g., toluene from sodium). 2,6-Bis(1′-methylbenzimidazolyl)-4-hydroxypyridine (**1**), 1,4-dibromo-2,5-bis(6-bromohexyloxy)benzene (**2**), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**4**) were prepared as described in the literature.[30,32−34] The syntheses of compound **3** and polymer **5** are described below, and the syntheses of compound **1** and polymer **6** are described in the Supporting Information.

*1,4-Dibromo-2,5-bis(6-(2,6-bis(1′-methylbenzimidazolyl)pyridyloxy)hexyloxy)benzene (**3**).* A suspension of freshly powdered potassium hydroxide (0.37 g, 6.60 mmol) in 40 mL of DMSO was purged with nitrogen for 30 min. To this suspension 0.94 g (2.64 mmol) of **1** was added and stirred until the mixture turned reddish. Then 0.76 g (1.28 mmol) of 1,4-dibromo-2,5-bis(6-bromohexyloxy)benzene (**2**) was dissolved in DMSO, and the solution was added to the reaction mixture. The mixture was stirred at 47 °C for 24 h and subsequently poured into ice water. The precipitate was collected by filtration and dried in vacuum at room temperature. Yield: 0.86 g (29%); mp 235 °C. ^{1}H NMR (d_1-CHCl$_3$, 300 MHz): δ (ppm) 1.63 (m, 8H), 1.89 (m, 8H), 3.98 (t, 4H), 4.26 (m, 16H), 7.11 (s, phenyl-H, 2H), 7.39 (m, phenyl-H, 12H), 7.88 (m, phenyl-H, 4H), 7.95 (m, phenyl-H, 4H). ^{13}C NMR (d_1-CHCl$_3$, 300 MHz): δ (ppm) 25.71, 28.83, 29.08, 32.68, 68.85, 70.10, 76.63, 77.05, 77.48, 110.09, 112.50, 118.51, 119.82, 123.33, 123.96, 136.77, 149.84, 166.80. Anal. Calcd for $C_{60}H_{58}Br_2N_{10}O_4$: C, 63.05; H, 5.11; N, 12.25. Found: C, 62.19; H, 5.23; N, 11.19.

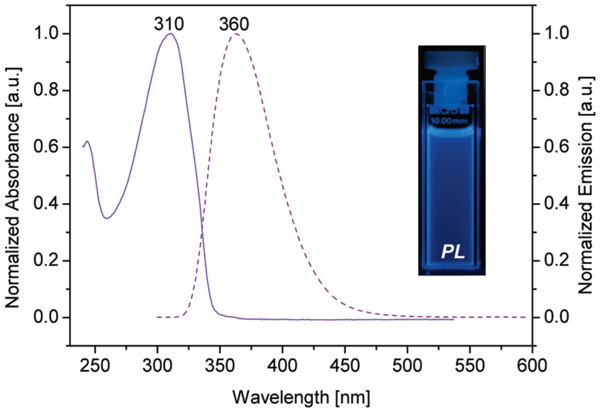
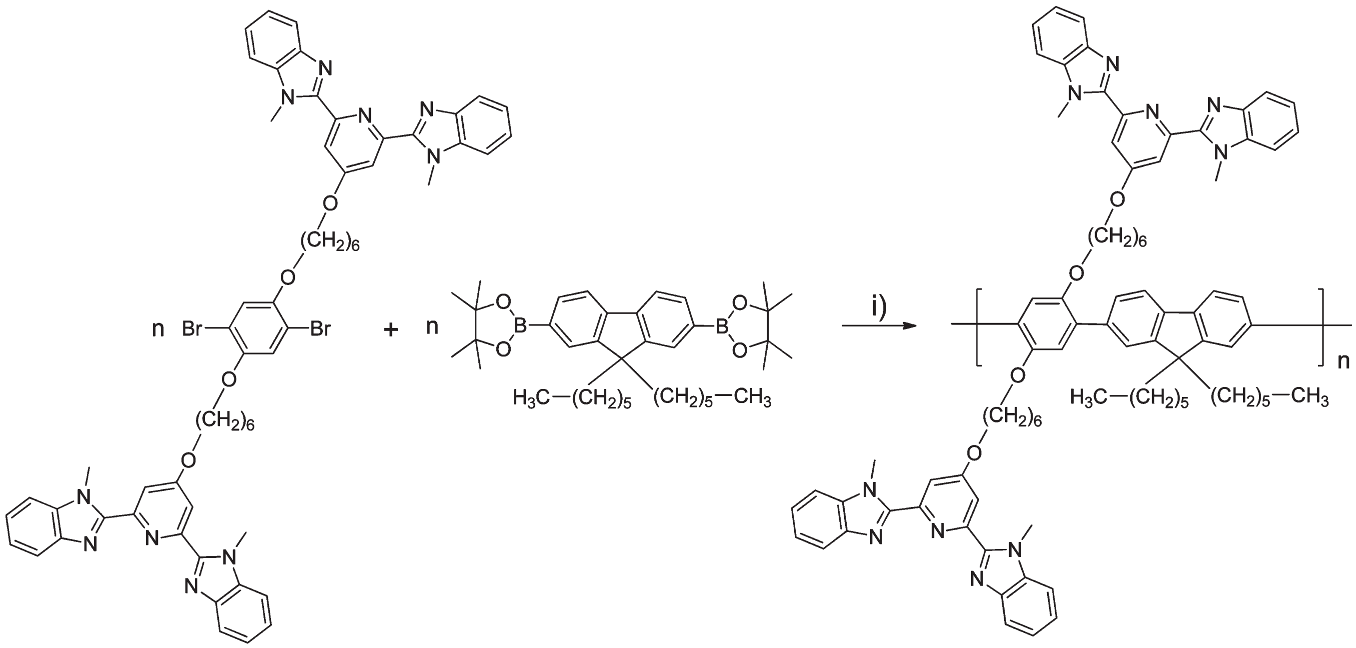


Figure 2. UV/vis and fluorescence spectra of **3** in chloroform.

*Polymer **5**.* 0.100 g (0.088 mmol) of monomer **3** was dissolved in 5 mL of a degassed toluene/dioxane (1:1) solvent mixture and stirred under nitrogen atmosphere at 110 °C for 30 min. Subsequently, 0.051 g (0.088 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**4**) in 1 mL of toluene/dioxane (1:1) was added, and the mixture was stirred for 30 min. To the mixture were added 3 mL of aqueous 10 N NaOH, 1 mL of a toluene/dioxane (1:1) solution containing 8 mol % Pd(PPh$_3$)$_4$, and 0.5 mL of 15-crown-5. The reaction mixture was heated to 95 °C and stirred for 24 h. After cooling to room temperature, the reaction mixture was diluted with 100 mL of toluene and extracted with brine. The organic phase was dried over MgSO$_4$ and filtered over Celite to remove residual palladium. After concentration in vacuum the residue was poured into ether to precipitate the polymer. The polymer was filtered off and dried under vacuum for 24 h. Yield: 0.099 g (88%); softening point: 110 °C. ^{1}H NMR (d_1-CHCl$_3$, 300 MHz): δ (ppm) 0.77 (m, 12H), 1.09 (m, 6H), 1.68 (m, 12H), 4.07 (m, 4H), 4.27 (m, 16H), 7.2 (m, 2H), 7.43 (m, 14H), 7.59 (m, 2H), 7.76 (m, 2H), 7.83 (m, 4H), 7.96 (m, 4H).

Substrates. Quartz substrates (30 × 12 × 1 mm^3) were cleaned in a fresh piranha solution (7:3 mixture of 98% H$_2$SO$_4$/30% H$_2$O$_2$; *caution: the mixture is strongly oxidizing and may detonate upon contact with organic*

Scheme 2. Preparation of Polymer 5[a]



3 **4** **5**

[a] Reagents and conditions: (i) Pd[(PPh$_3$)$_4$] (8 mol %), NaOH (10 N aqueous), 15-crown-5, toluene/dioxane, N$_2$, reflux, 24 h, 88%.

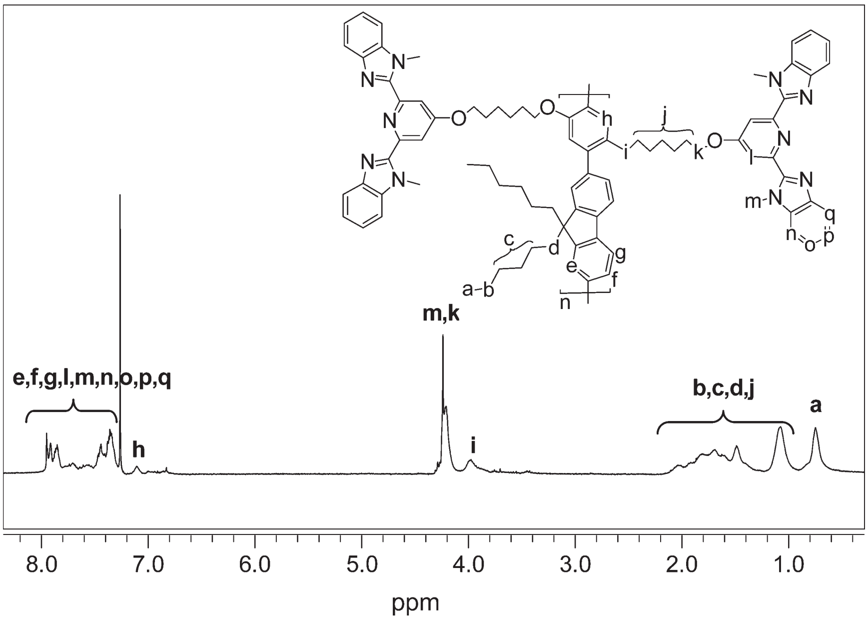


Figure 3. ^{1}H NMR spectrum of polymer **5** in deuterated chloroform.

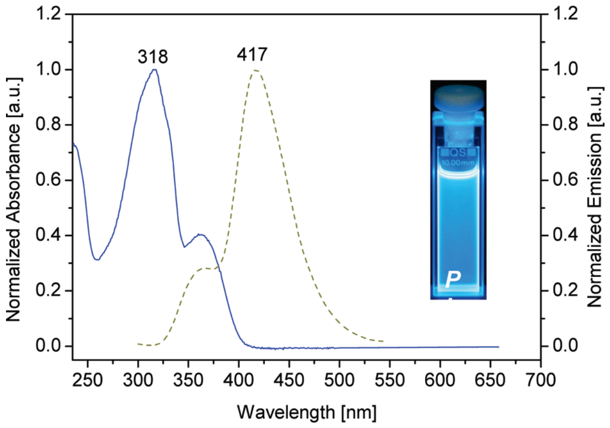


Figure 4. UV/vis and fluorescence spectra of **5** in THF.

material), washed with Milli-Q water, and successively ultrasonicated in alkaline isopropanol and 0.1 M aqueous HCl at 60 °C for 1 h each. 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), PSS as previously described.[23]

ITO-coated glass substrates were successively ultrasonicated 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.

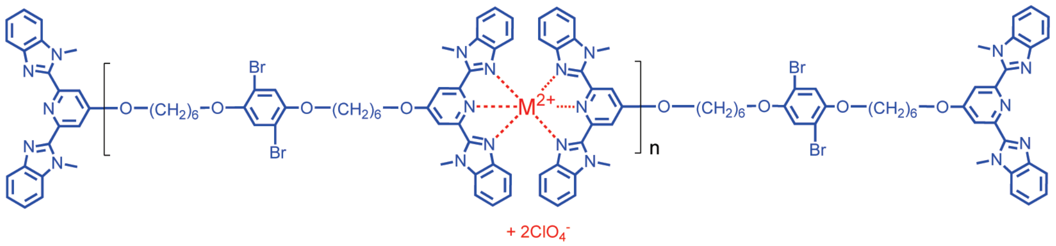
2.2. Methods. *Film Preparation.* If not especially indicated, the dipping solutions of the metal hexafluorophosphates were prepared by mixing identical volumes of a 0.02 M solution of potassium hexafluorophosphate in toluene/DMF/MeOH/*n*-hexane (12:2:4:2 v/v) and a 0.01 M solution of the corresponding metal chloride in the same solvent mixture. As dipping solution of the polytopic ligand, a 5×10^{-4} monomolar solution of polymer **5** in the same solvent mixture was used. For film preparation, the pretreated substrates were (a) dipped into the solution of the metal hexafluorophosphate, (b) washed with the toluene/DMF/MeOH/*n*-hexane solvent mixture, (c) dipped into the solution of polymer **5**, and (d) washed again with the solvent mixture. Subsequently steps a−d were repeated, etc. Immersion times were 10 min for steps a−d.

Instrumentation. ^{1}H NMR spectra were recorded using a Bruker DPX 300 spectrometer operating at 300 MHz. UV/vis absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded using a Perkin-Elmer LS50B spectrometer. For gel permeation chromatography a Waters/Millipore UV detector 481 and an SEC column combination (Latek/Styragel 50/1000 nm pore size) were used. Electrochemical experiments were performed using a PG390 potentiostat from Heka Co. (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 and counter electrodes were platinum. The experiments were carried out in acetonitrile (saturated with nitrogen) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte salt. Scanning electron microscopic (SEM) images were obtained using a Zeiss Supra 40 VP scanning electron microscope. EDX spectra were monitored using an INCA DryCool instrument coupled to the SEM (Zeiss Neon 40). The accelerating voltage was 20 kV, the area was 2500 μm^2, and 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.

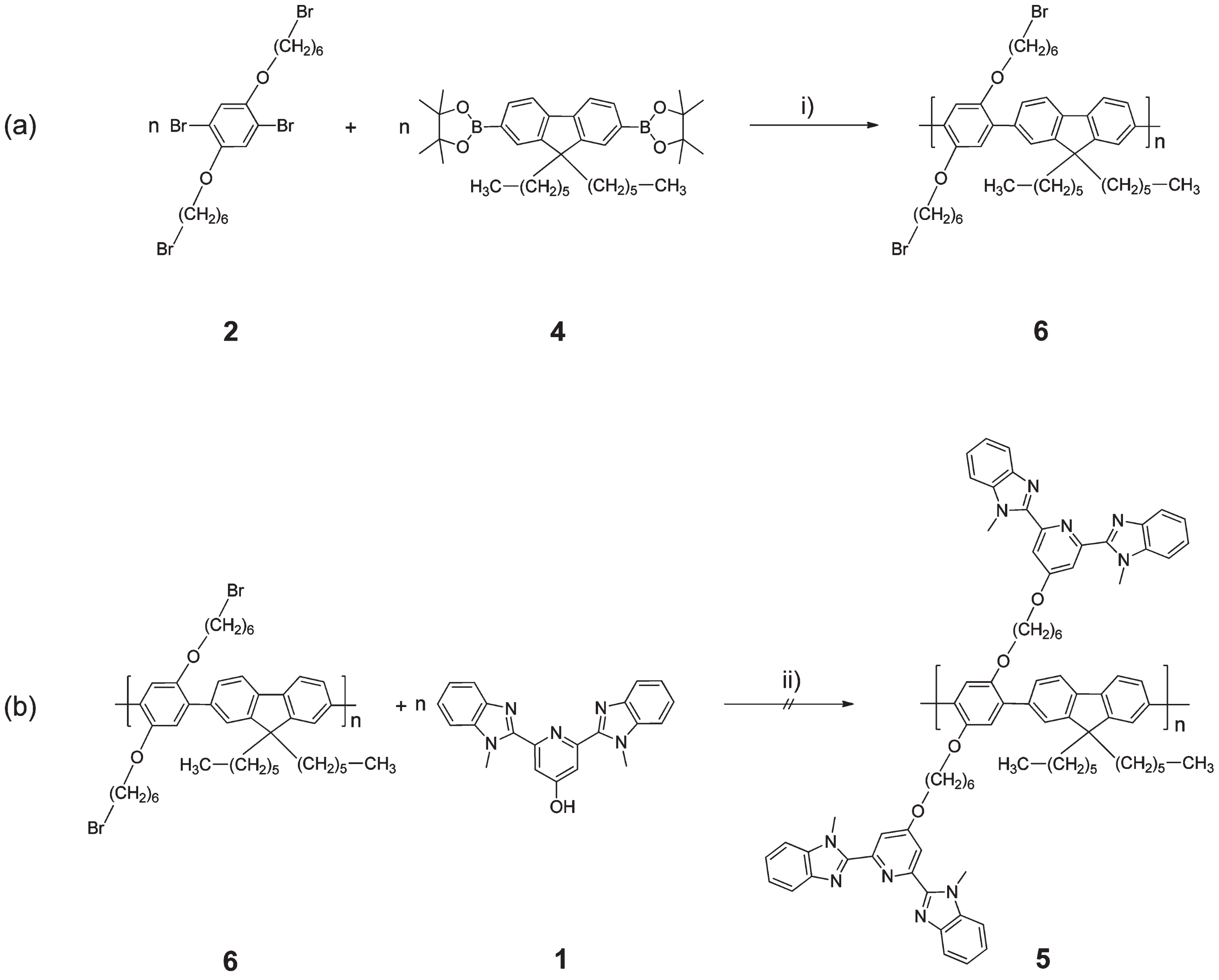
3. RESULTS AND DISCUSSION

3.1. Synthesis of Monomer and Polymer. At first the conjugated fluorescent poly(phenylene-*alt*-fluorene) carrying 2,6-bis(1-methylbenzimidazolyl)pyridine (bip) ligands as substituent groups was synthesized. The ligands were separated from the main chain via alkyl spacer groups in order to avoid or minimize quenching of the fluorescence of the main chain, which often occurs upon complex formation of the ligands with metal

Scheme 4. Metal Ion Coordination of Monomer 3 Leading to Linear Metallopolymer Chain



Scheme 3. Preparation of Polymer 6[a]



[a] Reagents and conditions: (i) Pd[$(PPh_3)_4$] (3 mol %), K_2CO_3 (2 M aqueous), toluene/dioxane, N_2, reflux, 24 h; (ii) K_2CO_3, DMSO, 47 °C, 24 h, 45%.

ions. Bip-ligand **1** was synthesized similar to a previously described method.[30] Details are given in the Supporting Information. For preparation of monomer **3** we started from hydroquinone. First, the OH-groups of hydroquinone were etherified with surplus 1,6-dibromohexane, and subsequently the resulting 1,4-disubstituted phenylene was brominated in the 2- and 5-position to yield compound **2** (Scheme 1). Both steps were carried out as described in the literature;[32,33] the yields were 43 and 67%, respectively.

Monomer **3** was obtained upon reaction of **2** with bip-ligand **1** in a yield of 45%. The ^{1}H NMR spectra of intermediates **1** and **2** are shown in the Supporting Information. The spectrum of monomer **3** is shown in Figure 1. All signals could be assigned. Signals of the aromatic protons appear between 7 and 8 ppm, and

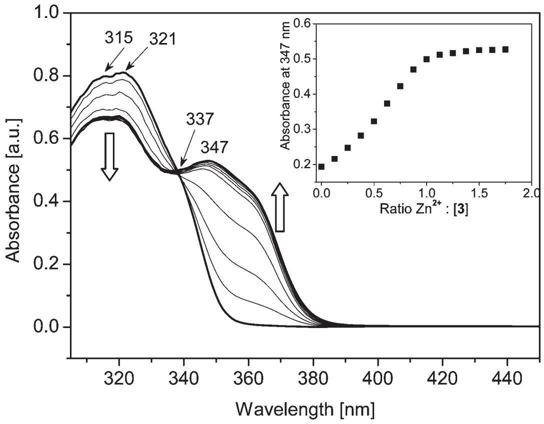


Figure 5. UV/vis absorption spectra of monomer **3** (concentration: 4.46×10^{-4} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v) before and after addition of 1 μL aliquots of zinc perchlorate (concentration: 1.24×10^{-3} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v). The inset shows the absorbance at 347 nm versus the molar ratio of zinc ions and **3**.

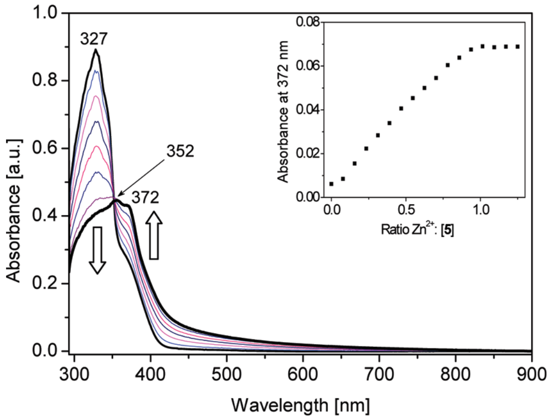


Figure 6. UV/vis absorption spectra of polymer **5** (concentration: 1.82×10^{-4} mol L^{-1}) in toluene/methanol (99:1 v/v) before and after addition of 1 μL aliquots of zinc chloride (concentration: 1.37×10^{-3} mol L^{-1}) in toluene/methanol (99:1 v/v).

signals of the methylene protons of the hexyl chain appear between 1.5 and 2 ppm. The signals of the O$-$CH$_2$ groups of the alkyl chains appear at 3.9 and 4.3 ppm; the signal of the *N*-methyl group of the imidazole moiety is also found at 4.3 ppm. In chloroform solution, monomer **3** shows an intense absorption at 310 nm and a blue fluorescence with maximum at 360 nm. The fluorescence spectrum and a picture of the fluorescing solution are also shown in Figure 2.

Polymer **5** was prepared upon Suzuki coupling of **3** and the known[34] 9,9-dihexylfluorene-2,7-bispinacolatodiboron ester **4** as shown in Scheme 2. A light yellow powder was obtained in a yield of 88%, which was well soluble in tetrahydrofuran (THF) and toluene. The polymer is fluorescing in the solid state and in solution. The quantum yield in toluene is 85%. The ^{1}H NMR spectrum (Figure 3) in deuterated chloroform exhibits broad signals. Compared with the spectrum of **3**, additional signals appear between 7 and 8 ppm, which can be ascribed to the fluorene unit. The signals of the methylene groups of the dihexylated fluorene and the spacer units connecting the bip ligands and the main chain are situated between 0.5 and 2.5 ppm.

The optical properties of polymer **5** were studied using UV/vis and fluorescence spectroscopy. As shown in Figure 4, the polymer exhibits two absorption maxima at 318 and 360 nm originating from $\pi-\pi^*$ transitions of the ligand (318) and the backbone chromophore (360). Fluorescence maxima appear at 365 and 417 nm, again originating from the ligand (365) and the backbone chromophore (417). A picture of the fluorescing solution is also shown in Figure 4. The band assignment is based on polymer **6**, which was obtained upon Suzuki coupling of compounds **2** and **4** as shown in Scheme 3a (for details of the synthesis of **6** see Supporting Information). Polymer **6** contains the same backbone chromophore as **5**, but the ligand chromophore in the substituent groups is missing. Consequently, the polymer only exhibits a single absorption band with maximum at 355 nm and a single fluorescence maximum at 417 nm. Unfortunately, all attempts to convert polymer **6** into **5** upon etherification of the ω-bromoalkyl side chains with the phenolate of **1** (see Scheme 3b) failed.

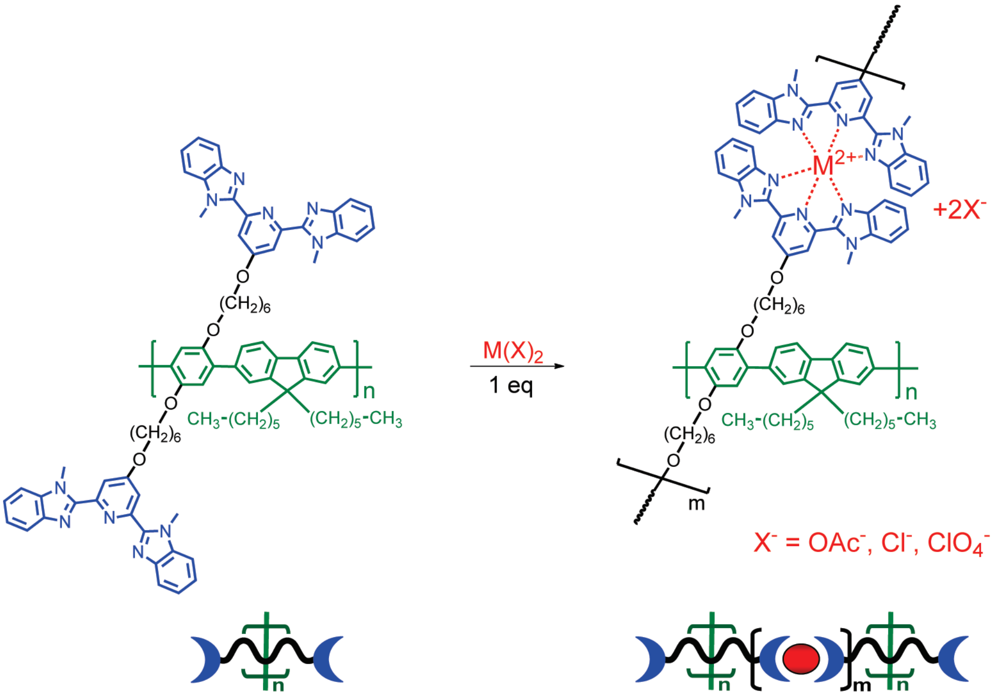
3.2. Metal Ion Complexation in Solution. Before studying the metal ion complexation of polymer **5**, we investigated the corresponding reaction of monomer **3**. **3** not only represents a monomer for the synthesis of conjugated polymers via palladium-catalyzed coupling reactions but also is a ditopic ligand for the formation of nonconjugated metallopolymers as shown in Scheme 4. The formation of the metallopolymer was followed upon UV/vis titration of **3** in a 9:1 (v/v) mixture of acetonitrile/chloroform with a zinc(II) salt in the same solvent mixture. UV/vis absorption spectra monitored after stepwise addition of small amounts of zinc perchlorate are shown in Figure 5. **3** behaves like other ditopic ligands with nonconjugated spacers between the bip units,[30] which initially show an intense absorption with maxima at 315 and 321 nm originating from a $\pi-\pi^*$ transition of the bip unit. Upon addition of zinc perchlorate a new band forms, which exhibits a maximum at 347 nm and a shoulder at 365 nm. The end point of titration is reached, if 1 equiv of zinc ions with regard to compound **3** is added. The complex formation involves an isosbestic point at 337 nm, indicating the existence of a single equilibrium between metal ion complexing and noncomplexing ligands.

Using the same solutions as used for the UV/vis titration, a fluorescence titration of compound **3** was also carried out. The addition of the zinc salt led to a gradual decrease of the fluorescence with maximum at 368 nm until at a molar ratio zinc(II)/**3** of 1.0 a weak and constant fluorescence with maximum at 400 nm was left. Again the behavior is similar to other ditopic bip ligands with nonconjugated spacer groups[30] (spectra are shown in the Supporting Information). Our experiment shows that the zinc complex of **3** is fluorescent although the fluorescence is weaker than for the metal-free ligand.

UV/vis titration was also used to study the complexation of polymer **5**. In this case, a toluene/methanol 99:1 (v/v) mixture served as solvent for the polymer, and small amounts of zinc chloride in the same solvent mixture were successively added. As shown in Figure 6, the absorption maximum at 327 nm gradually decreases in intensity and a new maximum at 352 nm with shoulder at 372 nm appears. The spectral changes are accompanied by an isosbestic point at 350 nm. The color transition was complete as soon as a 1:1 ratio of zinc ions and monomoles of polymer **5** was reached in the solution. This indicates the formation of the bis-complex consisting of one metal ion per two ligand groups (see Scheme 5).

The titration of the polymer was also carried out in an acetonitrile/chloroform solvent mixture (9:1 v/v) using zinc perchlorate for complex formation. Again, the end point of

Scheme 5. Metal Ion Coordination of Polymer 5 Involving Cross-Linking of Side Chains



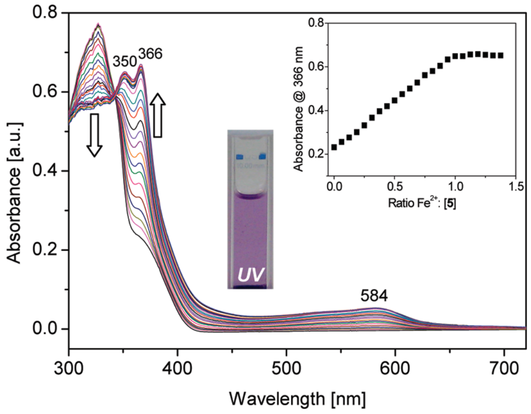


Figure 7. UV/vis absorption spectra of polymer **5** (concentration: 7.82×10^{-4} mol L^{-1}) in toluene/methanol (24:1 v/v) before and after addition of 8 μL aliquots of iron perchlorate (concentration: 5.22×10^{-4} mol L^{-1}) in toluene/methanol (24:1 v/v).

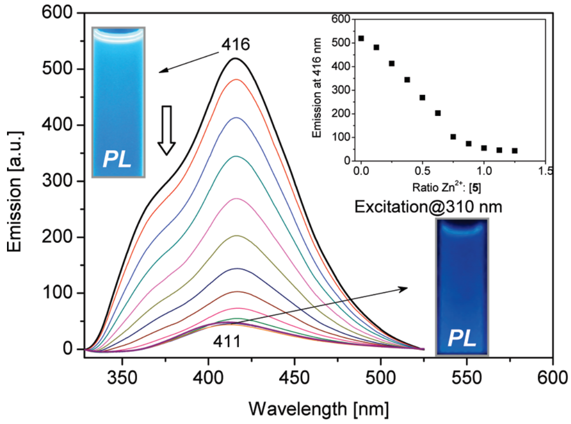
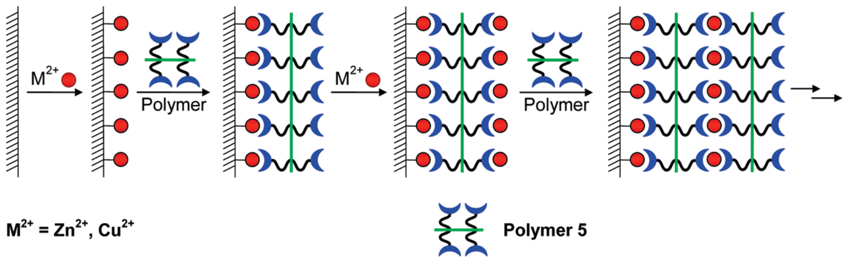


Figure 8. Change of fluorescence of polymer **5** (concentration: 1.09×10^{-4} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v) before and after addition of 1 μL aliquots of zinc perchlorate (concentration: 1.24×10^{-3} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v).

titration was reached as soon as a 1:1 molar ratio of Zn(II) and polymer **5** was present in the solution. However, in this case the color change during titration did not involve a clear isosbestic point (see also Supporting Information). In a further experiment, a polymer solution in toluene/methanol (24:1 v/v) was titrated with ferrous perchlorate. Upon addition of Fe(II) the solution attained a deep purple color originating from a metal-to-ligand charge transfer (MLCT). As shown in Figure 7, the color change was complete at a 1:1 ratio of metal ions and monomoles of polymer. The polymer—Fe(II) complex exhibits maxima at 350, 366, and 584 nm, the latter one originating from MLCT. The complex formation involves an isosbestic point at 340 nm (see Figure 7). A solution of polymer **5** in acetonitrile/chloroform (9:1 v/v) was also titrated with copper(II) acetate in the same solvent mixture. Again the polymer absorption with maximum at 324 nm decreased and a shoulder at 371 nm appeared. The complex formation involved an isosbestic point at 344 nm (see Supporting Information). Different from the addition of Zn(II) or Fe(II) ions, the change in absorbance of the complex already slowed down after about 0.3 equiv of copper(II) was added, and further salt addition had only little effect on the absorbance. We believe the copper complexation proceeds more rapidly so that a colloidal solution of the complex is formed in which a further copper ion complexation is slowed down.

We also carried out a fluorescence titration of polymer **5** with zinc perchlorate. A 9:1 (v/v) mixture of acetonitrile and chloroform was used as solvent for polymer and metal salt. As shown in

Scheme 6. Supramolecular Sequential Assembly of Coordination Polymer Films Containing Metal(II) Salts and Polymer 5 (Small Counterions Are Omitted for Clarity)



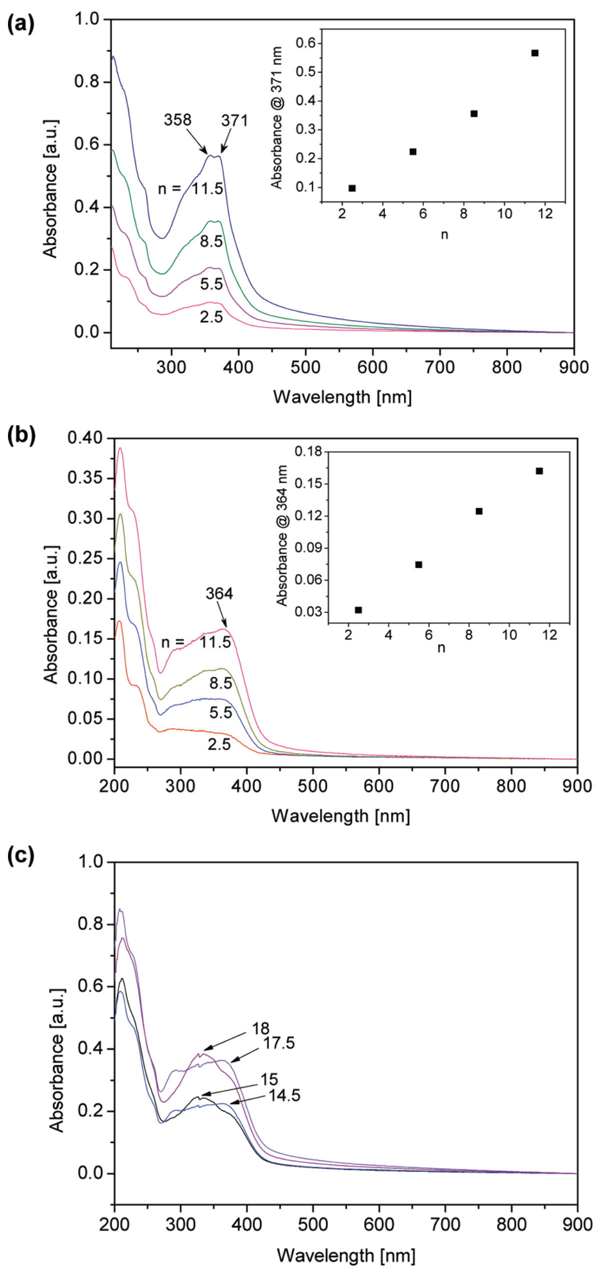


Figure 9. UV/vis absorption spectra of layer-by-layer assembled films of polymer **5** and different metal ions monitored after different numbers n of dipping cycles: (a) Zn(II), (b) Cu(II). In (c) the effect of the last dipping step on the spectra in shown (last dip into polymer solution: *n* = 15 or 18; last dip into Cu(II) solution: *n* = 14.5 or 17.5).

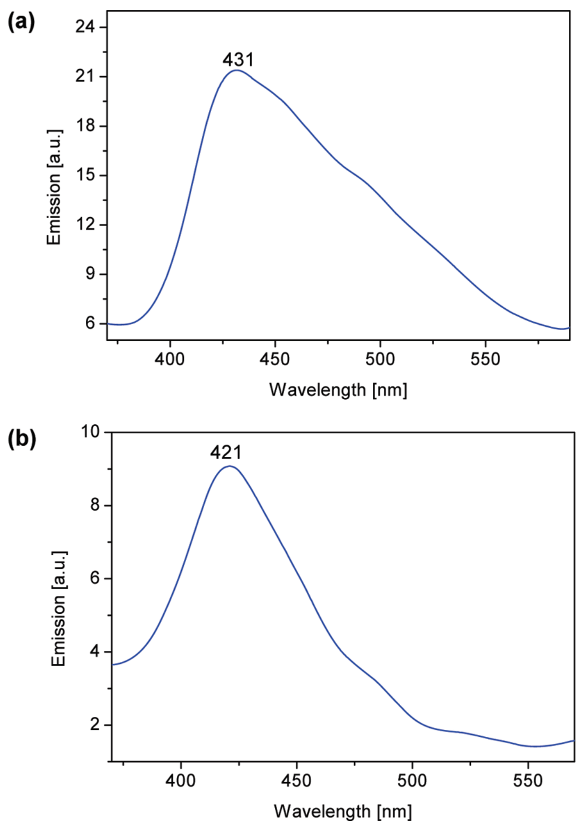


Figure 10. Fluorescence spectra of layer-by-layer assembled films of polymer **5** and different metal ions (12 dipping cycles): (a) Zn(II); (b) Cu(II).

Figure 8, the broad polymer fluorescence with shoulder at 370 and maximum at 416 nm decreases upon salt addition but does not disappear completely. If a 1:1 ratio of Zn(II): monomoles of **5** is reached, no further changes occur. The residual fluorescence with maximum at 410 nm can be ascribed to the backbone chromophore, whereas the fluorescence of the bip units (the shoulder at 370 nm) is completely quenched by the complex formation. The same fluorescence titration was carried out with copper acetate. Again, the fluorescence of bip was quenched, and the polymer fluorescence decreased until a weak emission at 416 nm remained. As for the change in absorbance, the change in fluorescence intensity was largely complete after addition of only 0.3 equiv of copper(II), and further salt addition only had a small effect (see Supporting Information).

3.3. Coordinative Assembly of Ultrathin Films. For the preparation of ultrathin films we used quartz supports, which

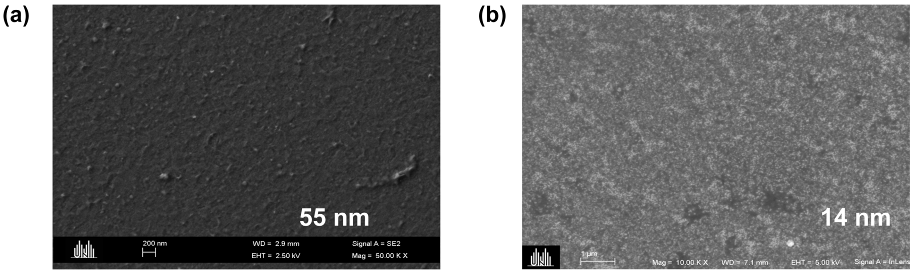


Figure 11. SEM pictures of films (a) of polymer/zinc ion complex and (b) of polymer/copper ion complex. Samples were subjected to 12 dipping cycles. The film thickness is also indicated.

were pretreated as described in the Experimental Section. The films were built up on the substrates upon alternate dipping into solutions of the metal salt and polymer **5** as outlined in Scheme 6. In order to remove surplus salt or polymer and to avoid contamination of the dipping solutions, additional washing steps in pure solvent were applied. Films were prepared using zinc(II) and copper(II) chloride dissolved in a mixture of toluene/DMF/MeOH/*n*-hexane (12:2:4:2 v/v). Potassium hexafluorophosphate was added to the solutions in order to decrease the solubility of the polymer−metal ion complexes and to favor the adsorption on the substrate. In order to further decrease the solubility, small amounts of the nonsolvent *n*-hexane were also present in the dipping solution. Dipping times in the individual solutions were 10 min.

3.4. Optical Properties of Films. The buildup of the films was followed by monitoring UV/vis absorption spectra of the coated supports after 2, 5, 8, and 11 dipping cycles and an additional dipping into the metal salt solution. Films of the polymer−zinc ion complex are colorless exhibiting absorption maxima at 358 and 371 nm (Figure 9a). The maxima are consistent with the maxima found for UV titration in solution. They indicate that the zinc ion complex of **5** has formed on the substrate. As shown in the inset, the maximum absorption increases nearly linearly with the number of dipping cycles indicating homogeneous film growth; i.e., in each dipping cycle the same amount of the polymer complex is deposited. Using copper(II) instead of zinc(II), it was also possible to build up films on the substrate. Corresponding spectra are shown in Figure 9b. An absorption band with maximum at 364 nm is found, which indicates the formation of the copper complex on the substrate. From the plot of the absorbance at 364 nm vs the number of dipping cycles *n*, a linear relation is found; i.e., equal amounts of the complex are adsorbed in each dipping cycle. It should be mentioned that spectra of substrates last dipped into the polymer solution were different from those last dipped into the metal salt solution. As shown in Figure 9c, the absorption maximum is bathochromically shifted by about 50 nm after dipping into the Cu(II) salt solution, and the shift is reverted after dipping into the polymer solution. This indicates a partial reversibility of the complex formation depending on whether the substrate is exposed to an excess of metal ions or polymer in the solution. However, prolonged exposure to the polymer salt solution for up to a week did not lead to a dissolution of the film.

Since the fluorescence titration in solution (section 3.2) indicated that the zinc ion complex of the polymer exhibits a weak fluorescence with maximum at 414 nm, it was also of interest to study the fluorescence of the films. Not surprisingly, a film of the zinc ion complex of **5** was fluorescent (Figure 10a). The fluorescence with maximum at 426 nm can be ascribed to the poly(phenylene-*alt*-fluorene) backbone chromophore. A corresponding film of the copper complex also shows a weak fluorescence with maximum at about 424 nm originating from the backbone chromophore (Figure 10b).

3.5. Film Morphology and Composition. In further studies morphology and metal ion content of self-assembled films of the zinc and copper complexes of **5** were investigated. Typical SEM pictures of the morphology are shown in Figure 11. Films of the zinc and copper complex exhibit a rather smooth surface with only few inhomogeneities distributed over the whole surface. The thickness of the films prepared upon 12 dipping cycles were 55 and 14 nm for the zinc and copper complex, respectively, as determined using profilometry. The metal ion content of the film was analyzed using EDX. Since an ITO-coated glass substrate was used as support, the most frequent elements were silicon, oxygen, indium, and tin. Zinc (1.14 wt % of inorganic material) was also found. For a corresponding film of the copper complex of **5**, a copper content of 0.59 wt % was found (for details see Supporting Information).

4. CONCLUSIONS

A new conjugated polymer with poly(fluorene-*alt*-phenylene) backbone and 2,6-bis(1′-methylbenzimidazolyl)pyridine substituent groups was synthesized. The polymer is able to form complexes with metal ions such as zinc(II) or copper(II) which exhibit a 2:1 ligand:metal ion stoichiometry. The polymer is ionochromic; i.e., the color changes from colorless to yellow, orange, or even purple depending on the metal ion used for complexation. Because of presence of an alkyl spacer between ligand and main chain the electronic properties of the two conjugated parts of the molecules are decoupled, and two absorption and fluorescence maxima occur. Upon addition of the metal ions, the fluorescence of the ligand is quenched, whereas the backbone fluorescence is only decreased in intensity, but not completely quenched. Elongation of the spacer unit may help to decouple the electronic interactions more efficiently and increase the fluorescence of the main chain. The formation of the metal ion complex proceeds under cross-linking of the polymer, but neither a precipitation nor a gel formation was observed. Because of the low polymer concentration and a proper choice of the solvent and the counterion of the metal salt, the formation of a gel or a precipitate are prevented and a colloidal solution is formed instead.

Our study also shows that a proper choice of the solvent (or solvent mixture) causes that the coordination polymer network becomes insoluble and is deposited on the substrate. Fluorescent films of the coordination polymer network are formed, the thickness being controlled by the number of dipping cycles. The supramolecular assembly is driven by coordinative interactions between the ligand groups and the metal ions. Variation of the aromatic groups in the main chain and exchange of the bip ligands for other ligands such as bisbenzothiazolyl- or bisbenzoxazolylpyridine will alter the ionochromic properties, and other coordination polymer network structures may become accessible.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis of ligand **1** and polymer **6**; ^{1}H NMR spectra of **1**, **2**, and **6**; UV/vis titration of polymer **5** with zinc perchlorate and copper acetate in acetonitrile/chloroform (9:1 v/v); EDX spectra of layer-by-layer assembled films of zinc and copper complex of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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