Organometallic Networks Based on 2,2′-Bipyridine-Containing Poly(*p*-phenylene ethynylene)s

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ABSTRACT: Conjugated polymers that comprise 2,2′-bipyridine moieties as part of the macromolecular backbone represent versatile precursors for the formation of conjugated metallo-supramolecular networks, which are readily accessible via ligand-exchange reactions. Poly{2,2′-bipyridine-5,5′-diylethynylene[2,5-bis(2-ethylhexyl)oxy-1,4-phenylene]ethynylene} (BipyPPE$_1$) and a statistical copolymer comprising 5,5′-diethynyl-2,2′-bipyridine and 1,4-diethynyl-2,5-bis(alkyloxy)benzene moieties (BipyPPE$_2$) were synthesized via the Pd^0-catalyzed cross-coupling reaction of 1,4-diethynyl-2,5-bis(octyloxy)benzene, 1,4-bis[(2-ethylhexyl)oxy]-2,5-diiodobenzene, and 5,5′-diethynyl-2,2′-bipyridine. Complexation studies involving these polymers and a variety of transition metals suggest that ligand exchange leads to three-dimensional networks, which feature BipyPPE−metal−BipyPPE cross-links and display interesting optoelectronic properties. It is found that complexes with group 12 d^{10} ions (Zn^{2+} and Cd^{2+}) are emissive, while other transition metals such as Cu$^+$, Co^{2+}, and Ni^{2+} form nonradiative metal-to-ligand charge-transfer complexes with the polymers.

Introduction

Conjugated semiconducting polymers are attracting significant interest, since these materials may combine the processability and mechanical properties of polymers with the readily tailored optoelectronic properties of organic molecules.[1] Especially their (potential) use in light-emitting diodes,[2] field-effect transistors,[3] photovoltaic cells,[4] and other devices has propelled the development of conjugated polymers with unique property profiles. Our group has recently embarked to explore well-defined conjugated polymer networks.[5−7] Interestingly, materials with this structural motif have in the past received little attention,[8] possibly due to the difficulty of introducing conjugated cross-links and retaining adequate processability. Using poly(*p*-phenylene ethynylene) (PPE) derivatives[9] as an example, we have demonstrated that this problem can be overcome by synthesizing such polymers in the form of spherical particles, which can be processed from (aqueous) dispersions.[10,11] The size of the resulting particles can be readily tuned over a wide range (mm to nm) via the detailed reaction conditions, and it appears that the approach is universally applicable for many polymer systems. We have also conducted studies addressing organometallic polymer networks based on PPE derivatives and metallic cross-links. These materials are accessible through ligand-exchange reactions between the linear PPE and low-molecular-weight metal complexes. This synthetic framework relies on the formation of noncovalent bonds between the ligand sites comprised in the polymer and the metal, which are governed by the equilibrium constant of the metal−ligand interactions and—depending on the kinetic stability of the metal−ligand interaction—may be of reversible “dynamic” nature.[12] As a result, the formation of metallo-supramolecular polymer networks becomes controllable and allows for straightforward processing of these materials.[5−7] We demonstrated that such networks may exhibit substantially better charge transport characteristics than the linear parent polymers[6] and can, at least in part, overcome the problems associated with interchain charge transfer between individual macromolecules.[13] Our previous work in this arena was based on the exploitation of the ethynyl moieties comprised in the PPE backbone as ligand sites,[5−7] which can form η^2-alkyne complexes with a number of metals. While bis(η^2-diphenylethynylene)Pt^0 complexes[14] have been tremendously useful for our work, other examples of suitable bis(η^2-diphenylethynylene)metal complexes, which could provide electronic conjugation between chains, are rare.[15] We therefore considered the introduction of auxiliary ligands into the polymer backbone and opted to incorporate 2,2′-bipyridine (Bipy) moieties. This ligand has extensively been used as a chelating ligand for a broad variety of metals and was recently heralded as the “most widely used ligand”.[16] Indeed, the Bipy moiety has already been introduced into a plethora of macromolecules that form the basis of metallo-supramolecular systems.[17] Pioneering work on PPEs with Bipy groups in the polymer backbone and linear metal complexes of these polymers has been carried out by the groups of Schanze[18] and Klemm.[19] Interestingly, the metal-complexed PPEs investigated in these studies were virtually exclusively prepared by polymerizing metal-complexed monomers, rather than by complexation of the Bipy-containing polymer with metals.[20] We show here that the latter framework, which—mainly with sensor applications in mind and not under consideration of potential network formation—has been applied by a number of groups for a variety of other conjugated polymer platforms,[21−26] is formidably suited to prepare metallo-supramolecular PPE networks.

Experimental Section

Materials. 1,4-Bis[(2-ethylhexyl)oxy]-2,5-diiodobenzene (**1**),[27] 1,4-diethynyl-2,5-bis(octyloxy) benzene[27] (**2**), and 5,5′-dibromo-2,2′-bipyridine[28] were prepared as described before. All other solvents, reagents, metal complexes, and catalysts were pur-

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chased from Aldrich Chemical Co., Fisher Scientific, Strem Chemicals, or Fluka (analytical grade quality) and were used without further purification. Unless otherwise stated, spectroscopic grade $CHCl_3$ (Aldrich) was employed for all optical absorption and emission experiments and was passed through a plug of neutral Alox before use. Anhydrous toluene and anhydrous diisopropylamine used for the polymerization reactions were purchased from Aldrich Chemical Co. and were deoxygenated by sparging with Ar for at least 1 h prior to use.

Methods. All cross-coupling reactions were carried out under a dry Ar atmosphere using standard vacuum-line and glovebox techniques. Unless otherwise stated, ^1H NMR spectra were recorded in $CDCl_3$ at 22 °C on a Varian XL (300 MHz) or a Varian Inova (600 MHz) spectrometer, and chemical shifts are expressed in ppm relative to an internal TMS standard. Elemental analyses were obtained from Prevalere Life Sciences Inc. and Galbraith Laboratories Inc. UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 800 spectrometer. Photoluminescence (PL) spectra were measured under excitation at 410 nm on a SPEX Fluorolog 3 (model FL3-12) spectrometer; corrections for the spectral dispersion of the Xe lamp, the instrument throughput, and the detector response were applied.

Synthesis of 5,5′-Bis((trimethylsilyl)ethynyl)-2,2′-bipyridine.[12e,29] 5,5′-Dibromo-2,2′-bipyridine (1.00 g, 3.18 mmol), $Pd(P(Ph_3)_3)_2Cl_2$ (178 mg, 0.25 mmol), and CuI (48 mg, 0.25 mmol) were dissolved in a mixture of triethylamine (20 mL) and DMF (16 mL) at 55 °C, and trimethylsilylacetylene (625 mg, 6.36 mmol) was added over a period of 1 h under vigorous stirring. After the addition of trimethylsilylacetylene was completed, the reaction mixture was stirred at reflux for 1 h. The resulting suspension was cooled to RT, $CHCl_3$ (100 mL) was added, and the now clear solution was washed with a saturated aqueous EDTA solution (100 mL) for 1 h. The organic phase was separated off, and the aqueous layer, which had turned turquoise, was reextracted with $CHCl_3$ (100 mL). The combined organic layers were washed with deionized water (200 mL) and dried over $MgSO_4$, and the solvent was evaporated in a vacuum. The solid residue was purified by column chromatography (silica gel; hexanes/ethyl acetate 4:1) to yield white crystals (800 mg, 72.1%). ^1H NMR (300 MHz): δ 8.72 (d, 2H, ar), 8.34 (d, 2H, ar), 7.84 (dd, 2H, ar), 0.28 (s, 18H, $SiCH_3$).

Synthesis of 5,5′-Diethynyl-2,2′-bipyridine (3). Methanol (19 mL) and aqueous KOH (1.3 mL, 20%) were added to a stirred solution of 5,5′-bis((trimethylsilyl)ethynyl)-2,2′-bipyridine (750 mg, 2.15 mmol) in THF (38 mL), and the mixture was stirred at RT for 2 h. The reaction mixture was filtered, washed twice with deionized water (50 mL), and dried over $MgSO_4$. The organic phase was separated off, and the solvents were evaporated in a vacuum to obtain an off-white crystalline solid. The product was purified by column chromatography (silica gel, hexanes/ethyl acetate 10:1) to afford **3** in the form of off-white crystals (324 mg, 73.7%), which were stored in the dark under Ar. ^1H NMR (300 MHz): δ 8.77 (d, 2H, ar), 8.38 (d, 2H, ar), 7.88 (dd, 2H, d), 3.30 (s, 2H, C≡H). Anal. Calcd for $C_{14}N_2H_8$: C, 82.33%; N, 13.71%; H, 3.94%. Found: C, 80.23%; N, 13.17%; H, 3.75%.

Synthesis of Poly{2,2′-bipyridine-5,5′diylethynylene-[2,5-bis(2-ethylhexyl)oxy-1,4-phenylene]ethynylene} (BipyPPE$_1$). 1,4-Bis[(2-ethylhexyl)oxy]-2,5-diiodobenzene (**1**) (362 mg, 0.617 mmol), 5,5′-diethynyl-2,2′-bipyridine (**3**, 150 mg, 0.734 mmol), *p*-iodotoluene (51.2 mg, 0.234 mmol), $Pd(PPh_3)_2$ (34.1 mg, 0.0295 mmol), and CuI (6.0 mg, 0.032 mmol) were combined in a mixture of toluene (23 mL) and diisopropylamine (10 mL), and the reaction mixture was stirred under Ar at 70 °C. The formation of what appeared to be ammonium iodide salts was observed immediately after the start of the reaction, and at the same time the mixture became highly fluorescent. After 24 h the reaction was stopped by adding the mixture to a saturated aqueous EDTA solution (50 mL). After stirring for 2 h the aqueous phase had turned turquoise. The organic phase was collected, washed with deionized water (2 × 50 mL), and added dropwise to vigorously stirred methanol. The reddish polymer thus precipitated was filtered off and dried in a vacuum. The polymer was redissolved in $CHCl_3$ (50 mL) and washed with saturated aqueous EDTA solution (3 × 50 mL). The organic layer was separated off, and the aqueous phase was reextracted with $CHCl_3$ (50 mL). The combined organic layers were washed with deionized water (50 mL), concentrated in a vacuum, and introduced dropwise to vigorously stirred methanol. The solid thus precipitated was filtered off, washed with hot hexanes (50 mL), and dried in a vacuum to yield BipyPPE$_1$ as a red solid (227 mg, 62.4%). ^1H NMR (600 MHz): δ 8.82 (s, Bipy, 2H), 8.43 (s, Bipy, 2H), 7.92 (s, Bipy, 2H), 7.46, 7.17 (dd, 4H, ar/end groups), 7.34, 6.94 (2 × s, 2H, ar/end groups), 7.07 (s, 2H, ar), 3.96 (m, 4H, OCH_2), 2.39 (s, 6H CH_3/end groups), 1.81 (s, 6H, 2 × CH_2 + 2 × CH), 1.58 (m, 16H, CH_2), 1.24 (s, 20H, CH_2), 0.89 (d, 6H, CH_3); X_n = 11.

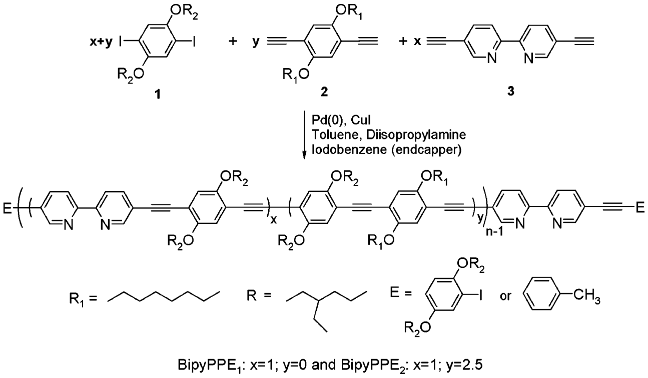
Synthesis of BipyPPE$_2$. 1,4-Bis[(2-ethylhexyl)oxy]-2,5-diiodobenzene (**1**, 548 mg, 0.934 mmol), 1,4-diethynyl-2,5-bis(octyloxy)benzene (**2**, 285 mg, 0.743 mmol), 5,5′-diethynyl-2,2′-bipyridine (50.0 mg, 0.244 mmol), *p*-iodotoluene (41.3 mg, 0.189 mmol), $Pd(PPh_3)_2$ (47.6 mg, 0.0412 mmol), and CuI (8.2 mg, 0.043 mmol) were combined in a mixture of toluene (30 mL) and diisopropylamine (12 mL), and the reaction mixture was stirred under Ar at 70 °C. The formation of what appeared to be ammonium iodide salts was observed immediately after the start of the reaction, and at the same time the mixture became highly fluorescent. After 24 h the reaction was stopped by adding the mixture to a saturated aqueous EDTA solution (50 mL). After stirring for 2 h the aqueous phase had turned turquoise. The organic phase was collected, washed with deionized water (2 × 50 mL), and added dropwise to vigorously stirred methanol. The reddish polymer thus precipitated was filtered off and dried in a vacuum. The polymer was redissolved in $CHCl_3$ (50 mL) and washed with saturated aqueous EDTA solution (3 × 50 mL). The organic layer was separated off, and the aqueous phase was reextracted with $CHCl_3$ (50 mL). The combined organic layers were washed with deionized water (50 mL), concentrated in a vacuum, and introduced dropwise to vigorously stirred methanol. The solid thus precipitated was filtered off, washed with hot hexanes (50 mL), and dried in a vacuum to yield BipyPPE$_2$ as a red solid (486 mg, 72.7%). ^1H NMR (600 MHz, 42 °C): δ 8.82 (s, Bipy, 2H), 8.43 (s, Bipy, 2H), 7.92 (s, Bipy, 2H), 7.42, 7.12 (dd, 4H, ar/end groups), 7.29, 6.91 (s, 2H, ar/end groups), 7.07 (s, 2H, ar), 3.96 (m, 4H, OCH_2), 2.39 (s, 6H CH_3/end groups), 1.81 (m, 6H, 2 × CH_2 + 2 × CH), 1.58 (m, 16H, CH_2), 1.24 (m, 20H, CH_2), 0.89 (dd, 6H, CH_3); X_n = 16.

Preparative Synthesis of Bis(2,2′-bipyridine)Cu(I) Hexafluorophosphate (4). 2,2′-Bipyridine (502.7 mg, 3.218 mmol) and tetrakis(acetonitrile)Cu(I) hexafluorophosphate (599.7 mg, 1.609 mmol) were separately dissolved in anhydrous $CHCl_3$ (5 mL) and CH_3CN (6 mL), respectively. Over a period of 20 min the colorless tetrakis(acetonitrile)Cu(I) hexafluorophosphate solution was added dropwise to the stirred colorless 2,2′-bipyridine solution, and the mixture immediately turned deep red. The solvents were evaporated in a vacuum to yield **4** as a red solid (829 mg, 98.7%). UV–vis ($CHCl_3$): λ_{max} = 433 and 523 nm (shoulder).

In-Situ Synthesis of Bis(2,2′-bipyridine)Cu(I) Hexafluorophosphate (4). An aliquot of a solution of tetrakis(acetonitrile)Cu(I) hexafluorophosphate in CH_3CN (0.2 mL, 2.42×10^{-4} M) was added to a solution of 2,2′-bipyridine in $CHCl_3$ (3 mL, 3.23×10^{-5} M). The mixture was allowed to stand for 15 min before an optical absorption spectrum was recorded. UV–vis ($CHCl_3$:CH_3CN = 15:1 v/v): λ_{max} = 348, 433, and 523 nm (shoulder).

Optical Measurements of Polymer–Metal Complexes. The polymers were dissolved in $CHCl_3$ at a concentration of 1.93×10^{-5} M (BipyPPE$_1$) and 3.23×10^{-5} M (BipyPPE$_2$). (All concentrations are quoted with respect to the Bipy ligand comprised in the polymers.) The metal complexes (tetrakis(acetonitrile)Cu(I) hexafluorophosphate, cobalt tetrafluoroborate hexahydrate, nickel perchlorate hexahydrate, zinc perchlorate hexahydrate, and cadmium perchlorate hydrate were dissolved in spectroscopic grade CH_3CN (concentration range 2.16×10^{-5}–5.55×10^{-4} M). Polymer–metal complexes were produced by adding aliquots of a solution of the selected metal

Scheme 1. Synthesis and Molecular Structure of the 2,2′-Bipyridine-Containing Poly(2,5-dialkyloxy-*p*-phenylene ethynylene)s BipyPPE$_1$ and BipyPPE$_2$



complex in CH_3CN (0.2 mL) to a solution of BipyPPE$_1$ or BipyPPE$_2$ in $CHCl_3$ (3 mL); the concentration of the metal complex solution was varied to produce solutions of different [metal]:[Bipy] ratios but identical solvent composition of $CHCl_3$:CH_3CN = 15:1 v/v. The mixtures were allowed to stand for 15 min to 4 h after addition of the metal salt to the polymer solutions, before conducting optical studies on these systems.

Film Preparation. The polymers (BipyPPE$_1$ or BipyPPE$_2$) were dissolved in $CHCl_3$ at a concentration of ~2.5% w/v. Metal complexes (see above) were dissolved in CH_3CN at appropriate concentrations, and aliquots of metal solutions (0.1 mL) and polymer solution (0.2 mL) were mixed and allowed to stand for 15−20 min before thin films were produced by spin-coating onto glass substrates.

Results and Discussion

The conjugated polymers employed in the present study, poly{2,2′-bipyridine-5,5′diylethynylene[2,5-bis(2-ethylhexyl)oxy-1,4-phenylene]ethynylene} (BipyPPE$_1$) and a statistical copolymer comprising 5,5′-diethynyl-2,2′-bipyridine and 1,4-diethynyl-2,5-bis(alkyloxy)benzene moieties (BipyPPE$_2$), were designed to comprise different fractions of the Bipy moiety (BipyPPE$_1$: x:y = 1:0; BipyPPE$_2$: x:y = 1:2.5; see Scheme 1) in order to explore the influence of the latter on the electronic properties of the polymer (vide infra). These polymers were synthesized by the Pd^0-catalyzed cross-coupling reaction of 1,4-bis[(2-ethylhexyl)oxy]-2,5-diiodobenzene (**1**),[27] 1,4-diethynyl-2,5-bis(octyloxy)benzene (**2**),[27,30] and 5,5′-diethynyl-2,2′-bipyridine (**3**)[12e,28,29] (Scheme 1). Monomers **1**−**3** were synthesized according to established routes.[27−30] The polymerizations were conducted in analogy to Klemm's protocol[19a] with monomer concentrations that were slightly lower than routinely employed.[27,30,31] If the reactions were conducted at higher monomer concentrations, the mixtures gelled; in view of the facts that the molecular weight was deliberately limited by offsetting the monomer stoichiometry and using *p*-iodotoluene as an end-capper[27] and that the isolated polymers were soluble, this finding is indicative of the formation of network structures due to complexes between the Bipy moieties and the copper cocatalyst employed for the polymerization reaction. To remove the catalyst from the final product, the workup of the polymers included rigorous extraction with aqueous ethylenediamine tetraacetate (see Experimental Section for details).[12e] The isolated polymers were soluble in concentrations of at least 1% w/v in solvents such as $CHCl_3$ and toluene. ^1H NMR spectra confirm the chemical structure of the polymers, reveal 4-toluene and 2,5-bis[(2-ethylhexyl)oxy]-4-iodobenzene end groups, and put the number-average molecular weights to ca. 3100 for BipyPPE$_1$ (number-average degree of polymerization, X_n, = 11) and 6100 for BipyPPE$_2$ (X_n = 16), respectively.

Table 1. Optical Absorption and PL Emission Data of BipyPPE$_1$ and BipyPPE$_2$ after Complexation with Different Metal Ions[a]

	BipyPPE$_1$		BipyPPE$_2$	
	absorption λ_{max} (nm)	emission $\lambda_{max}{}^b$ (nm)	absorption λ_{max} (nm)	emission $\lambda_{max}{}^b$ (nm)
ion free	423	459	440	482
Cu^+	452	*c*	447	482
Co^{2+}	458	*c*	450	482
Ni^{2+}	458	*c*	450	482
Zn^{2+}	464	619	450	482, 646
Cd^{2+}	468	591	448	482, 646

[a] All spectra were recorded in $CHCl_3$:CH_3CN (15:1 v/v) at a concentration of polymer-bound Bipy of 1.93×10^{-5} M (BipyPPE$_1$) or 3.23×10^{-5} M (BipyPPE$_2$) and an ion concentration of 2.16×10^{-5}−5.55×10^{-4} M. [b] Excitation at 410 nm. [c] Emission is fully quenched.

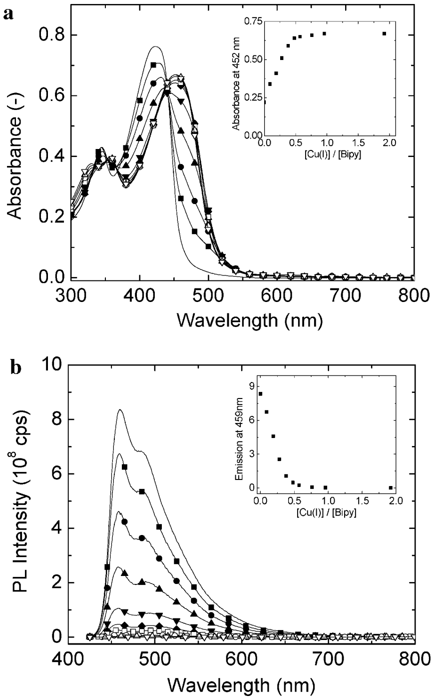


Figure 1. UV−vis absorption (a) and PL emission (b) spectra acquired upon addition of tetrakis(acetonitrile)Cu(I) hexafluorophosphate to BipyPPE$_1$ (concentration of polymer-bound Bipy = 1.93×10^{-5} M) in $CHCl_3$:CH_3CN (15:1 v/v). Shown are spectra at selected [Cu^+]:[Bipy] ratios of 0 (solid line), 0.09 (filled squares), 0.19 (filled circles), 0.28 (filled triangles), 0.38 (filled inverted triangles), 0.48 (filled rhombus), 0.57 (empty squares), 0.76 (empty circles), 0.96 (empty triangles), and 1.92 (empty inverted triangles). The insets show the absorption at 452 nm (a) and the emission at 459 nm (b) as a function of [Cu^+]:[Bipy] ratio.

The photophysical characteristics of the uncomplexed polymers were investigated in dilute solutions. A solvent mixture of $CHCl_3$:CH_3CN (15:1 v/v) was found suitable for the ligand-exchange experiments conducted (vide infra) and was therefore employed for all optical measurements conducted in this study. The results are summarized in Table 1; UV−vis absorption and photoluminescence (PL) emission spectra are shown in Figures 1 and 2 for BipyPPE$_1$ and BipyPPE$_2$, respectively. BipyPPE$_1$ exhibits essentially identical absorption and

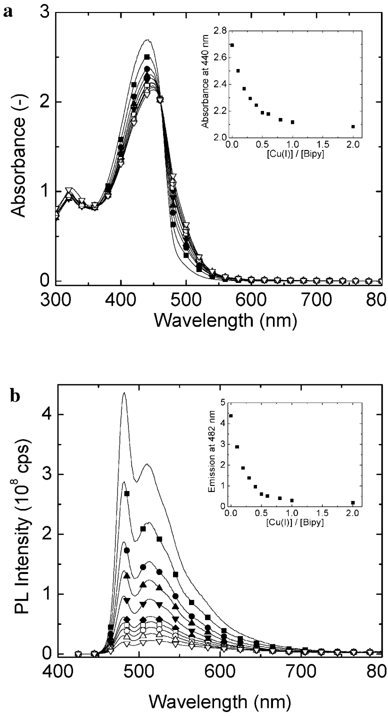


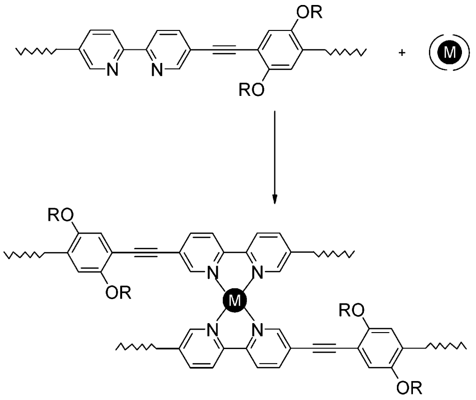
Figure 2. UV−vis absorption (a) and PL emission (b) spectra acquired upon addition of tetrakis(acetonitrile)Cu(I) hexafluorophosphate to BipyPPE$_2$ (concentration of polymer-bound Bipy = 3.23×10^{-5} M) in CHCl$_3$:CH$_3$CN (15:1 v/v). Shown are spectra at selected [Cu$^+$]:[Bipy] ratios of 0 (solid line), 0.1 (filled squares), 0.2 (filled circles), 0.3 (filled triangles), 0.4 (filled inverted triangles), 0.5 (filled rhombus), 0.6 (empty squares), 0.8 (empty circles), 1.0 (empty triangles), and 2.0 (empty inverted triangles). The insets show the absorption at 440 nm (a) and the emission at 482 nm (b) as a function of [Cu$^+$]:[Bipy] ratio.

emission characteristics as a polymer of the same structure investigated in detail before.[19d] The absorption spectrum features a strong band with $\lambda_{\max} = 423$ nm (Figure 1a), which in line with previous studies[18,19,27,30] is assigned to the $\pi-\pi^*$ transition of the polymer backbone. Optical excitation of BipyPPE$_1$ solutions at wavelengths that match this transition cause intense PL with $\lambda_{\max} = 459$ nm and features that are consistent with $\pi-\pi^*$ fluorescence of the polymer (Figure 1b). The absorption and emission spectra of BipyPPE$_1$ are significantly blue-shifted compared to poly(2,5-dialkoxy-1,4-phenylene ethynylene)s such as poly[2,5-dioctyloxy-1,4-diethynyl-phenylene-*alt*-2,5-bis(2′-ethylhexyloxy)-1,4-phenylene] ($\lambda_{\max} \approx 436$ and 474 nm for absorption and emission, respectively).[27,30] It was suggested earlier that this blue shift is related to low torsional barriers for motions of the aromatic chain segments[19d] and the nonplanar nature of the bipyridine moiety,[32] which significantly limits the conjugation.[22] BipyPPE$_2$, which comprises fewer Bipy units than BipyPPE$_1$, displays essentially identical absorption ($\lambda_{\max} = 440$ nm) and emission ($\lambda_{\max} = 482$ nm) characteristics (Figure 2) as poly(2,5-dialkoxy-1,4-phenylene ethynylene)s that comprise no Bipy.[27,30] This is consistent with the formation of sufficiently long oligo(*p*-phenylene ethynylene) segments, which exhibit optical absorption and PL emission properties that have converged to those of macromolecular chains. These segments (presumably of statistical length) are linked by Bipy moieties, which (in their uncomplexed state) appear to exert little influence on the optical properties of the PPE segments but appear to efficiently "isolate" individual chromophores (vide infra).[19]

[Cu$^{\mathrm{I}}$(Bipy)$_2$]X complexes represent a class of carefully studied, kinetically stable bis(bipyridine) complexes,[33] and we therefore elected to conduct a systematic complexation study involving BipyPPE$_1$ or BipyPPE$_2$ on one hand and Cu$^+$ on the other. Adopting the general protocol employed for the preparation of similar complexes by Müller et al.,[34] we first conducted a series of reference experiments and prepared the known [Cu$^{\mathrm{I}}$(Bipy)$_2$]PF$_6$ (**4**).[35] This complex was synthesized by combining a solution of free (i.e., not polymer-bound) 2,2′-bipyridine in anhydrous CHCl$_3$ with a solution of [Cu$^{\mathrm{I}}$(CH$_3$CN)$_4$]PF$_6$ in CH$_3$CN, using 2 equiv of ligand with respect to the metal ion. The rather concentrated mixture (~0.29 M Bipy) immediately adopted the characteristic deep red color of [Cu$^{\mathrm{I}}$(Bipy)$_2$]$^+$. The complex could be quantitatively isolated as the hexafluorophosphate by evaporation of the solvents. We also conducted this ligand-exchange reaction under more dilute conditions (~3.2×10^{-5} M Bipy) in a 15:1 v/v CHCl$_3$:CH$_3$CN mixture and characterized **4** in situ by means of UV−vis spectroscopy (see Supporting Information for spectra). The absorption spectrum of the mixture displays a maximum at 433 nm, a shoulder at 523 nm, and a feature at higher energy (348 nm) and matches the one of the isolated compound and the one published for [Cu$^{\mathrm{I}}$(Bipy)$_2$]ClO$_4$ elsewhere,[34] suggesting that under the selected conditions the ligand exchange proceeds smoothly and predominantly leads to the formation of **4**. The main absorption band centered around 433 nm is characteristic of a Cu$^+$−diimine system and is attributed to a metal-to-ligand charge transfer (MLCT) from the filled Cu 3d orbitals (3d^{10}) to the lowest empty π^* orbitals (LUMO) of the 2,2′-bipyridyl ligand.[34,36] As is the case for many other Cu$^+$−diimine systems, [Cu$^{\mathrm{I}}$(Bipy)$_2$]PF$_6$ does not display any appreciable fluorescence.

We observed that a similar exchange reaction takes place upon addition of CH$_3$CN solutions of [Cu$^{\mathrm{I}}$(CH$_3$CN)$_4$]PF$_6$ to CHCl$_3$ solutions of BipyPPE$_1$ or BipyPPE$_2$. If the polymer concentration was of the order of 1% w/v, the mixtures gelled (BipyPPE$_2$) or formed a gellous precipitate (BipyPPE$_1$), indicating the formation of metallo-supramolecular networks with Bipy−metal−Bipy cross-links. Gelation and/or formation of visible precipitation could be circumvented by reducing the absolute concentrations of the polymers (and concomitantly [Cu$^{\mathrm{I}}$(CH$_3$CN)$_4$]PF$_6$) to a level of Bipy (as comprised in the polymer) of between 1.93×10^{-5} and 3.23×10^{-5} M. In this case, the color of the polymer solutions changed instantaneously from a pale to a deep yellow upon addition of Cu$^+$. With the goal of attaining insight into the formation of the polymer−metal complexes and to elucidate their optical properties, we titrated [Cu$^{\mathrm{I}}$(CH$_3$CN)$_4$]PF$_6$ to BipyPPE$_1$.[37] UV−vis absorption and PL emission spectra acquired in CHCl$_3$:CH$_3$CN are shown in Figure 1 for selected [Cu$^+$]:[Bipy] ratios. As expected, the absorption spectrum of BipyPPE$_1$ changed significantly upon addition of Cu$^+$. The intensity of the characteristic $\pi-\pi^*$ transition associated with the conjugated polymer backbone around 423 nm systematically weakened when [Cu$^{\mathrm{I}}$(CH$_3$CN)$_4$]PF$_6$ was added, and a new band centered around 452 nm developed (Figure 1a). As can be seen from the inset in Figure 1a, the intensity of the new absorption band at 452 nm steadily intensified with increasing [Cu$^+$]:[Bipy] ratio, before

Scheme 2. Schematic Representation of the Formation of Metallo-Supramolecular Networks via the Formation of Metal−Bis(ligand) Complexes with 2,2′-Bipyridine-Containing Poly(2,5-dialkyloxy-*p*-phenylene ethynylene)s BipyPPE$_1$ and BipyPPE$_2$



leveling off at a [Cu$^+$]:[Bipy] ratio of about 0.5. Similarly, the polymer's PL was gradually quenched upon addition of [Cu^I(CH$_3$CN)$_4$]PF$_6$ (Figure 1b). Also, this effect scaled with the [Cu$^+$]:[Bipy] ratio, and the PL was completely suppressed beyond a [Cu$^+$]:[Bipy] ratio of about 0.5. Scatchart plots[38] of the data presented in Figure 1 (see Supporting Information) are curved and characteristic of positive cooperative binding.[39] Control experiments in which [Cu^I(CH$_3$CN)$_4$]PF$_6$) was added to poly[2,5-dioctyloxy-1,4-diethynyl-phenylene-*alt*-2,5-bis(2′-ethylhexyloxy)-1,4-phenylene] (EHO−OPPE,[27] a PPE derivative lacking the Bipy recognition site) under similar conditions showed no optical changes. Thus, these results are consistent with the formation of BipyPPE$_1$−Cu$^+$−BipyPPE$_1$ cross-links between the conjugated macromolecules (Scheme 2) and point to relatively large binding constants. In view of the similarities to the optical characteristics of the low-molecular-weight model compound **4**, we tentatively interpret the optical properties of the Cu$^+$−BipyPPE$_1$ networks with the formation of a nonradiative metal-to-ligand charge-transfer complex between the metal's 3d and the BipyPPE$_1$ π^* orbitals. The absorption maximum of the polymeric metal complex is red-shifted by 19 nm when compared to **4**, presumably as a result of the extended conjugation of the polymeric ligand. The fact that the partially metalated BipyPPE$_1$ retained a significant extent of PL emission (Figure 1b) is indicative of limited exciton migration along the polymer to the nonradiative low-band-gap sites. This unusual feature was reported before[18,19d] and appears to be related to the "deconjugated" nature of uncomplexed, twisted Bipy moieties. These groups cause efficient "optical insulation", which allows the coexistence of multiple chromophores on the same macromolecule. The fact that they display weak electronic coupling is in marked contrast to the PPE-based polymer systems reported by Swager and coworkers, which act as "molecular wires" and display energy migration over up to ~50 repeat units.[30,40]

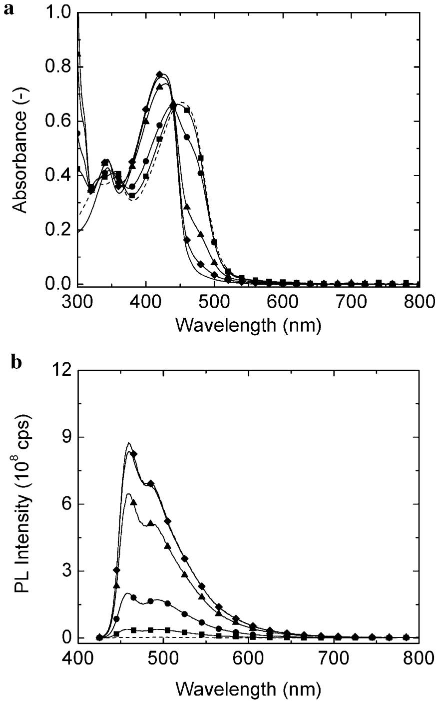


Figure 3. UV−vis absorption (a) and PL emission (b) spectra acquired upon addition of free 2,2′-bipyridine to a mixture of BipyPPE$_1$ (concentration of polymer-bound Bipy = 1.93×10^{-5} M) and tetrakis(acetonitrile)Cu(I) hexafluorophosphate (ratio of [Cu$^+$]:[Bipy comprised in the polymer] = 1:0.96) in CHCl$_3$:CH$_3$CN (15:1 v/v). Shown are spectra for ratios of [free Bipy]:[polymer-bound Bipy] of 0:1 (dashed line), 1:1 (filled squares), 2:1 (filled circles), 5:1 (filled triangles), and 10:1 (filled rhombus). The spectra of neat BipyPPE$_1$ (solid line) are included for reference.

The titration of [Cu^I(CH$_3$CN)$_4$]PF$_6$ to BipyPPE$_2$ in CHCl$_3$:CH$_3$CN caused optical changes (Figure 2) that were qualitatively similar to those observed for the Cu$^+$−BipyPPE$_1$ complexes. The shift of the main absorption band from 440 to 447 nm (Figure 2a) was less pronounced than in the latter case ($\Delta\lambda_{max} = 29$ nm) due to the smaller band-gap of the uncomplexed BipyPPE$_2$. In contrast to the Cu$^+$−BipyPPE$_1$ complexes, the BipyPPE$_2$'s luminescence was not fully extinguished upon addition of more than stoichiometric amounts of Cu$^+$ (Figure 2b). This feature reflects the absence of dominant intermolecular energy transfer processes and significant internal absorption and is consistent with the statistical product distribution dictated by the nature of the polymerization reaction; the number-average degree of polymerization and the Bipy concentration in the polymer are both low, and due to the statistical incorporation of the Bipy monomer, a small fraction of the macromolecules does not comprise any Bipy moieties and therefore remains emissive upon addition of [Cu^I(CH$_3$CN)$_4$]PF$_6$. Similar to BipyPPE$_1$, the optical changes caused by titration of BipyPPE$_2$ with Cu$^+$ leveled off at a [Cu$^+$]:[Bipy] ratio of about 0.5, but minor spectral changes can be discerned upon further addition of Cu$^+$ (Figure 2). Scatchart plots of the data presented in Figure 2 (see Supporting Information) are almost linear and indicate the absence of cooperative binding. Thus, while these results also point to the formation of BipyPPE$_2$−Cu$^+$−BipyPPE$_2$ cross-links, the driving force for their formation appears to be less pronounced than in the case of BipyPPE$_1$. This may reflect the fact that in contrast to BipyPPE$_1$, which features a regular structure of alternating 1,4-diethynyl-Bipy and 2,5-bis(2-ethylhexyl)oxy-1,4-phenylene moieties, the Bipy moieties comprised in BipyPPE$_2$ are statistically distributed, stifling the formation of BipyPPE$_2$−Cu$^+$−BipyPPE$_2$ moieties at higher Cu$^+$ concentrations due to geometric constraints and limitations with respect to chain mobility.

To investigate the reversibility of the complexation of the Bipy-containing PPEs with Cu$^+$, we have titrated

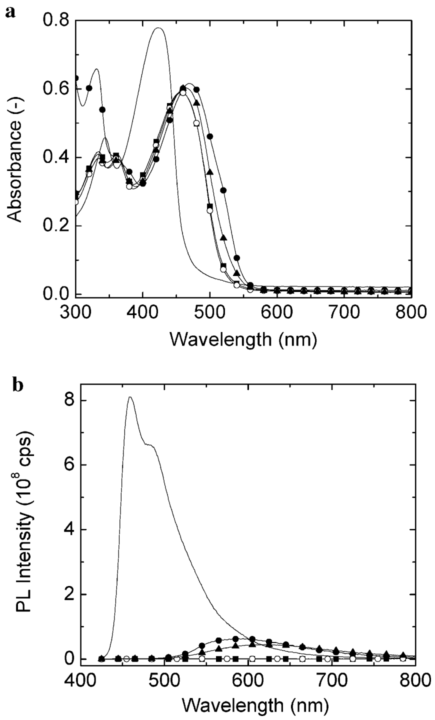


Figure 4. UV−vis absorption (a) and PL emission (b) spectra acquired upon addition of cobalt(II) tetrafluoroborate hexahydrate (filled squares), nickel(II) perchlorate hexahydrate (empty circles), zinc(II) perchlorate hexahydrate (filled triangles), and cadmium(II) perchlorate hydrate (filled circles) to BipyPPE$_1$ (concentration of Bipy comprised in the polymer in solution = 1.93×10^{-5} M) in $CHCl_3$:CH_3CN (15:1 v/v). Shown are spectra for [M^{2+}]:[Bipy] ratios of 0.5:1. The spectra of neat BipyPPE$_1$ (solid line) are included for reference.

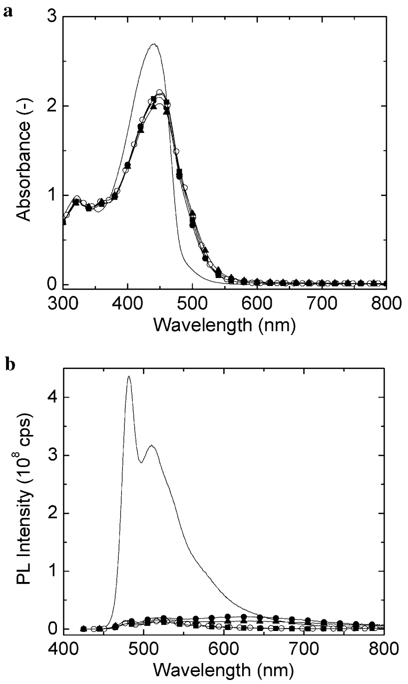


Figure 5. UV−vis absorption (a) and PL emission (b) spectra acquired upon addition of cobalt(II) tetrafluoroborate hexahydrate (filled squares), nickel(II) perchlorate hexahydrate (empty circles), zinc(II) perchlorate hexahydrate (filled triangles), and cadmium(II) perchlorate hydrate (filled circles) to BipyPPE$_2$ (concentration of polymer-bound Bipy = 3.23×10^{-5} M) in $CHCl_3$:CH_3CN (15:1 v/v). Shown are spectra for [M^{2+}]:[Bipy] ratios of 0.5:1. The spectra of neat BipyPPE$_2$ (solid line) are included for reference.

a $CHCl_3$:CH_3CN solution comprising equimolar amounts of BipyPPE$_1$ and [$Cu^I(CH_3CN)_4$]PF_6 with free (i.e., not polymer-bound) 2,2′-bipyridine. Gratifyingly, upon addition of Bipy, the UV−vis absorption (Figure 3a) and PL emission (Figure 3b) spectra converged back to those of the uncomplexed polymer. At a [free Bipy]:[polymer-bound Bipy] ratio of 10:1 the optical properties of BipyPPE$_1$ were fully restored. Thus, the experiment unequivocally demonstrates that decomplexation of the polymer−metal system occurs upon addition of a competing ligand and that the ligand exchange reaction is fully reversible.

With the objective to explore the influence of the metallic cross-linker on the optical properties of the polymers at hand, we have conducted complexation experiments involving BipyPPE$_1$ or BipyPPE$_2$ and perchlorates of Co^{2+}, Ni^{2+}, Zn^{2+}, or Cd^{2+}. With reference to the above-summarized complexation study with Cu^+ and with the objective to form [M(II)(Bipy)$_2$]$^{2+}$ complexes that function as cross-links between the macromolecules, the [M^{2+}]:[Bipy] ratio was kept constant at a level of 0.5:1. UV−vis absorption and PL emission spectra acquired in $CHCl_3$:CH_3CN are shown for BipyPPE$_1$ and BipyPPE$_2$ in Figures 4 and 5, and the results are summarized in Table 1. The addition of $Co(ClO_4)_2$ or $Ni(ClO_4)_2$ led to very similar optical changes as were observed before for [$Cu^I(CH_3CN)_4$]PF_6 at the same [M^{2+}]:[Bipy] ratio. Complexation with Co^{2+} or Ni^{2+} shifted the maximum of the absorption band of BipyPPE$_1$ (Figure 4a) from 423 to 458 nm (Cu^+: 452 nm) and that of BipyPPE$_2$ (Figure 5a) from 440 to 450 nm (Cu^+: 447 nm). The PL of BipyPPE$_1$ was completely quenched upon addition of Co^{2+} or Ni^{2+} (Figure 5a), while BipyPPE$_2$ displayed the weak residual emission (Figure 5b) that appears to be associated with the Bipy-free fraction of macromolecules (vide supra). These results are consistent with the formation of Bipy−M^{2+}−Bipy moieties and reflect the fact that also Co^{2+} and Ni^{2+} both exhibit a strong tendency for the formation of metal-to-ligand charge-transfer complexes with imine ligands.[41] Interestingly, the addition of $Zn(ClO_4)_2$ or $Cd(ClO_4)_2$ caused a somewhat different response. Complexation with these metals shifted the maximum of the absorption band of BipyPPE$_1$ from 423 to 464 (Zn^{2+}) and 468 nm (Cd^{2+}) (Figure 4a) and that of BipyPPE$_2$ from 440 to 450 (Zn^{2+}) and 448 nm (Cd^{2+}) (Figure 5a). Thus, the changes were somewhat more pronounced than in the case of the other metals investigated here. The characteristic PL band of BipyPPE$_1$ was completely quenched upon addition of Zn^{2+} or Cd^{2+}, while BipyPPE$_2$ displayed the weak residual emission associated with the Bipy-free macromolecules (vide infra). In the case of both metals, however, new, broad, structureless emission bands centered at 619 (BipyPPE$_1$−Zn^{2+}), 591 (BipyPPE$_1$−Cd^{2+}), and 646 nm (BipyPPE$_2$−Zn^{2+} and BipyPPE$_2$−Cd^{2+}) developed (Figures 4b and 5b). These results reflect the fact that Zn^{2+} and Cd^{2+} both exhibit a fully occupied d-orbital (Zn^{2+}: $3d^{10}$; Cd^{2+}: $4d^{10}$), which frequently displays a weak tendency for the formation of metal-to-ligand charge transfer.[42] Hence, the complexation of these metals with Bipy-containing polymers does not usually lead to MLCT complexes.[25] Rather, the optical changes appear to be related to a significant reduction of the polymers' $\pi-\pi^*$ transition on account of a planarization of the Bipy moiety[22,23] as well as electron density variation upon complexation with the electron-poor metals.[25] In view of the fully occupied d-orbital of the metal, the observed emission cannot be

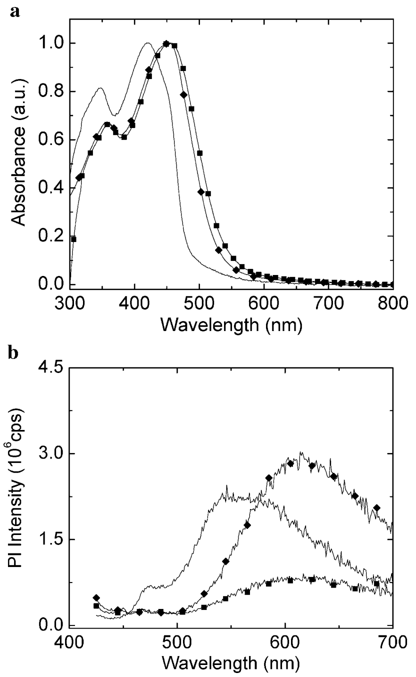


Figure 6. (a) UV–vis absorption and (b) PL emission spectra of spin-coated films of complexes produced by ligand-exchange reactions between BipyPPE$_1$ and zinc perchlorate hexahydrate (filled rhombus) or cadmium perchlorate hydrate (filled squares). Shown are spectra for [metal]:[Bipy] ratios of 0.5:1. The spectra of neat BipyPPE$_1$ (solid line) are included for reference.

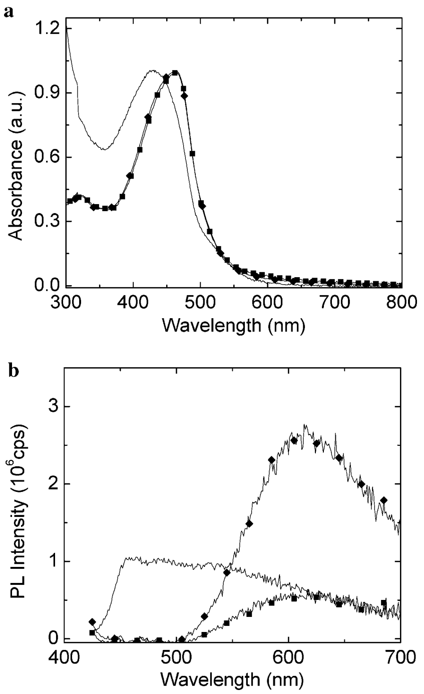


Figure 7. (a) UV–vis absorption and (b) PL emission spectra of spin-coated films of complexes produced by ligand-exchange reactions between BipyPPE$_2$ and zinc perchlorate hexahydrate (filled rhombus) or cadmium perchlorate hydrate (filled squares). Shown are spectra for [metal]:[Bipy] ratios of 0.5:1. The spectra of neat BipyPPE$_2$ (solid line) are included for reference.

related to a d–d transition but appears to be caused by intraligand $\pi-\pi^*$ transitions.

Homogeneous thin films of good optical quality could be produced by spin-coating solutions of the polymer–metal complexes (see Experimental Section for details). The films thus produced were insoluble in $CHCl_3$, which is a good solvent for the uncomplexed polymers, consistent with the formation of cross-linked BipyPPE$_1$–metal and BipyPPE$_2$–metal networks. On the other hand, if free (i.e., not polymer-bound) 2,2′-bipyridine was added to the solvent, the films readily redissolved, demonstrating again that the complexation reactions are reversible. The metal-complexed films show similar absorption spectra as in solution, with absorption maxima that range from 420 nm (uncomplexed film) to 454 nm (Zn^{2+}) in the case of BipyPPE$_1$ (Figure 6a) and from 427 nm (uncomplexed film) to 462 nm (Zn^{2+}) in the case of BipyPPE$_2$ (Figure 7a). The emissive characteristics of the Zn(II) and Cd(II) complexes of BipyPPE$_1$ and BipyPPE$_2$ were retained after processing these materials into thin films (Figures 6b and 7b), and these films displayed orange-red emission with maxima at 612 and 609 nm, respectively. While the development of red solid-state emitters was clearly beyond the original focus of our work, the relatively intense emission, in particular of the Zn-coordinated PPEs, appears to represent an interesting byproduct of our work.

Conclusions

In summary, we have presented a new synthetic framework that allows for the synthesis and processing of conjugated organometallic polymer networks. We have shown at the example of poly(*p*-phenylene ethynylene) derivatives that the introduction of 2,2′-bipyridine moieties leads to conjugated polymers, which are formidable precursors for metallo-supramolecular PPE networks that are accessible via ligand-exchange reactions. The resulting three-dimensionally cross-linked, conjugated BipyPPE$_1$–metal and BipyPPE$_2$–metal networks display interesting optoelectronic properties. As expected, the coordination of the metal markedly influences the photophysical characteristics of the polymer. It is obvious that the approach is broadly applicable to other conjugated polymer platforms and also to other ligands. We are aware of the fact that the (pseudo)-tetrahedral coordination of four-coordinated metals (as in the case of some of the complexes explored here) might ultimately not represent the most desirable geometry from a charge-transfer point of view and that the ionic nature of the ions used here might lead to charge trapping.[6,7] After having employed these complexes in the present study to demonstrate the possibility to prepare a new family of π-conjugated organometallic polymer hybrid systems, we envision to extend the present concepts to the use of square-planar complexes and conduct experiments related to the charge-carrier transport in such systems.

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Supporting Information Available: UV–vis absorption spectra of model compound **4** and Scatchard plots of the data presented in Figures 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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