Ruthenium-Chelating Poly(heteroaryleneethynylene)s: Synthesis and Properties

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Received October 1, 2001; Revised Manuscript Received December 4, 2001

ABSTRACT: A series of ruthenium(II)-chelating poly(heteroaryleneethynylene)s were synthesized by the palladium-catalyzed cross-coupling polycondensation of diethynylbenzenes and dibromobipyridine−Ru(II) chelates. The grafting of different alkoxy side chains including *n*-butoxy, (2-ethylhexyl)oxy, and *n*-octadecyloxy in the diethynylbenzene compounds enhances the solubility and processability of the new polymers. The same effect is attainable by *tert*-butyl substituents in the 2,2′-bipyridine ligands. The UV/vis absorption showed a considerable red shift of the λ_{max} from poly{bis(2,2′-bipyridine)-[2,2′-bipyridine-5,5′-diylethynylene-(2,5-dialkoxy)ethylene]ruthenium(II) bis(hexafluorophosphate)} (**5**) to the 4,4′-diylethynylene isomers **6**, suggesting an increase in the electronic delocalization between the backbone and ruthenium(II) chelate. The polymers are good photoconducting materials ($I_{Ph} = 3.7 \times 10^{-12}$ A at 18 000 cm^{-1}), exhibiting an oxidation potential of 1.24 V vs SCE. The polymers are thermostable and exhibit a good solubility in acetone, DMF, DMSO, acetonitrile, and cyclohexanone. Last, an improved method of molecular weight determination by GPC was devised.

Introduction

The introduction of metal chelates into the main chain of conjugated polymers gives access to polymers with novel properties and structures unattainable by their purely organic counterparts.[1] Particularly nonlinear optical (NLO) behavior, liquid crystallinity, redox chemistry, and luminescence properties are attractive.[2]

Tor et al. first synthesized metal-chelating poly(heteroaryleneethynylene)s by condensation of metal-containing building blocks to polymers with defined structures.[3] They used dibromophenanthroline−Ru(II) chelates for the coupling with dialkoxy-substituted 1,4-diethynylbenzenes under the classical conditions of the Heck/Sonogashira reaction. The product was a higher oligomer (with $n = 9-12$).[4]

In former publications[5,6] we reported the synthesis and characterization of high molecular weight poly(bipyridinyleneethynylenephenylene)s having the structures **1** and **2**.

Therefore, we extended our investigation to the metal chelates of these polymers. Ruthenium(II) complexes of 2,2′-bipyridine (bpy) are our favored complexes due to their rich and well-characterized photophysics.[7] Moreover, they are compatible with Pd-catalyzed coupling.

This paper reports the synthesis and properties of a series of novel ruthenium complexes of the polymers **1** and **2** with different substituents in the phenylene units and containing substituted bpy ligands. The properties are compared to those of the noncoordinated polymers.

Experimental Section

Materials. All chemicals were purchased from Fluka, Aldrich, and Merck. Acetonitrile and diisopropylamine were dried over KOH and distilled in an argon atmosphere. The solvents were degassed by sparging with argon for 2 h prior to use. All reactions, if not otherwise specified, were carried out under inert gas conditions (argon).

Methods. Melting points were measured on a Büchi 530 melting apparatus. The mass spectra were recorded using a SSQ 170 Finnigan MAT and electrospray mass spectra on a Finnigan MAT 95 XL instrument. ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX 400 (400 MHz) and a Bruker AC 250 (250 MHz). The absorption spectra were measured in acetonitrile and chloroform (HPLC grade, Baker) at a Perkin-Elmer UV/vis−NIR spectrometer Lambda 19. Fluorescence excitation and emission spectra were obtained by using a Perkin-Elmer LS 50 luminescence spectrometer in nitrogen-degassed acetonitrile. A homemade apparatus served for thermogravimetry measurements. Elemental analysis were performed on a Leco Automat CHNS-932. Molecular weight determinations by gel permeation chromatography were made at a flow rate of 0.25 mL/min in DMSO (70 °C) with 0.1 M $LiPF_6$ on Jasco UV 975 and IR 930 with NOVEMA 300 (PSS Mainz) with pullulan and dextran as standard. The electrochemical measurements were carried out with a home-built computer-controlled instrument based on the DAP-3200a data acquisition board (DATALOG Systems) as well as with the Autolab PG Stat 20 (Metrohm). Cyclic and square wave voltammograms were measured in 3 mM argon-degassed acetonitrile solutions containing 0.25 M Bu_4NPF_6 using a Ag/AgCl/CH_3CN reference electrode and Pt electrode. Ferrocene in acetonitrile was used as a standard. For comparison, all potentials were referenced to the SCE[8] (ferrocene, $E_{1/2} = 420$ mV[8] (SCE) for Fc/Fc$^+$) throughout.

Synthesis of the Monomers. *General Procedure for the Synthesis of the (Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)-ruthenium(II) Bis(hexafluorophosphate)* (**3**) *Monomers.* The monomers were prepared by refluxing of (2,2′-bipyridine)$_2$RuCl$_2$·0.5H$_2$O[9,10] (**11a**) or (4,4′-*tert*-butyl-2,2′-bipyridine)$_2$RuCl$_2$·toluene[13] (**11b**) and dibromo-2,2′-bipyridine in a mixture of ethanol/water (2:1) for 12 h. The dark red solution was evaporated to dryness, and 20 mL of water was added. Adding an excess of aqueous NH_4PF_6 precipitated the monomer. After filtration, the precipitate was collected and recrystallization from EtOH/H$_2$O (2:1) yielded the pure product.

(5,5′-Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) Bis(hexafluorophosphate) (**3a**). **11a** (1.97 g, 4.0 mmol), 5,5′-dibromo-2,2′-bipyridine[11] (1.26 g, 4.0 mmol). Yield: 3.7 g (90%) of red crystals. MS (ESI in acetonitrile): $m/z = 872.9$ ($M^+ - PF_6$,100%), 364.0 ($M^{2+} - 2PF_6$, 100%). ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 7.53$ (4H, m), 7.67 (4H, m), 7.84 (2H, d), 8.17

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10.1021/ma011712s CCC: $22.00

(4H, m), 8.46 (2H, dd), 8.81 (6H, m). ^{13}C NMR (62 MHz, DMSO-d_6): $\delta = 123.14$, 124.42, 124.52, 127.86, 138.17, 140.60, 151.33, 151.44, 151.90, 155.09, 156.26, 156.54. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 254 (29 200), 286 (74 500), 446 (14 700). Anal. Calcd for $C_{30}H_{22}N_6Br_2RuP_2F_{12}$ (1017.37): C, 35.42; H, 2.18; N, 8.26; Br, 15.71. Found: C, 35.32; H, 2.17; N, 8.22; Br, 15.62.

(4,4′-Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) Bis(hexafluorophosphate) (**3b**). **11a** (1.38 g, 2.8 mmol), 4,4′-dibromo-2,2′-bipyridine[12] (880 mg, 2.8 mmol). Yield: 2.4 g (84%) of red crystals. ^{1}H NMR (400 MHz, acetone-d_6): $\delta =$ 7.55 (4H, m), 7.74 (2H, dd), 7.91 (2H, d), 7.96 (2H, d), 8.16 (6H, m), 8.76 (4H, m), 9.12 (2H, s). ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 124.5$, 127.9, 128.0, 128.4, 131.3, 133.9, 138.3, 138.3, 151.7, 152.1, 152.5, 157.1, 157.1, 157.4 UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 287 (81 600), 446 (14 100). Anal. Calcd for $C_{30}H_{22}N_6Br_2RuP_2F_{12}$ (1017.37): C, 35.42; H, 2.18; N, 8.26; Br, 15.71. Found: C, 35.50; H, 2.52; N, 8.18; Br, 15.57.

(5,5′-Dibromo-2,2′-bipyridine)bis(4,4′-tert-butyl-2,2′-bipyridine)-ruthenium(II) Bis(hexafluorophosphate) (**3c**). **11b** (2.79 g, 3.48 mmol), 5,5′-dibromo-2,2′-bipyridine (1.09 mg, 3.48 mmol). Yield: 3.9 g (90%) of red crystals. ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 1.40$ (18H, s), 7.57 (4H, dd), 7.82 (2H, d), 7.95 (2H, d), 8.02 (2H, d), 8.39 (2H, dd), 8.74 (2H, d), 8.86 (4H, m). ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 36.65$, 36.68, 123.00, 123.07, 124.64, 126.24, 126.78, 141.79, 152.45, 152.98, 153.42, 157.25, 158.24, 158.50, 164.15, 164.23. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 257 (34 000), 286 (78 500), 305 (59 000), 436 (16 100). Anal. Calcd for $C_{46}H_{54}N_6Br_2RuP_2F_{12}$ (1241.80): C, 44.39; H, 4.38; N, 6.77; Br, 12.81. Found: C, 44.29; H, 4.48; N, 6.89; Br, 12.74.

(4,4′-Dibromo-2,2′-bipyridine)bis(4,4′-tert-butyl-2,2′-bipyridine)-ruthenium(II) Bis(hexafluorophosphate) (**3d**). **11b** (3.0 g, 3.75 mmol), 4,4′-dibromo-2,2′-bipyridine (1.18 mg, 3.75 mmol). Yield: 4.1 g (88%) of red crystals. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 1.37$ (18H, s), 7.54 (4H, m), 7.76 (4H, m), 7.86 (2H, d), 7.98 (2H, d), 8.83 (4H, dd), 9.13 (2H, d). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 36.18$, 122.52, 122.56, 125.78, 125.87, 129.12, 132.03, 134.28, 151.76, 152.30, 153.14, 157.78, 157.82, 158.45, 163.51. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 287 (92 400), 434 (19 500), 482 (15 800). Anal. Calcd for $C_{46}H_{54}N_6Br_2RuP_2F_{12}$ (1241.80): C, 44.39; H, 4.38; N, 6.77; Br, 12.81. Found: C, 44.17; H, 4.31; N, 6.56; Br, 12.85.

Synthesis of the Model Ligand. *General Procedure for the Synthesis of the Model Ligand.* Tetrakis(triphenylphosphine)palladium (3 mol %) and copper(I) iodide (3 mol %) were given to a mixture of ethynyl-2,2′-bipyridine, 1,4-diiodobenzene, and diisopropylamine in degassed and dried toluene. The reaction mixture was stirred at 65 °C for 14 h. It was warm filtered to remove the inorganic compounds. The precipitate was washed with chloroform, and both filtrates were dried over $MgSO_4$, evaporated to dryness, and chromatographed on silica gel.

1-Iodo-4-(2,2′-bipyridine-5′-ylethynyl)-2,5-di(2-ethylhexyl)-oxybenzene (**7**). 5-Ethynyl-2,2′-bipyridine[14] (2.7 g, 14.98 mmol), 1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene,[15] diisopropylamine (40 mL), toluene (260 mL). At first chromatographed with methylene chloride to remove the side products (eluted with THF). The pure compound **7** was obtained by chromatography with hexane/ethyl acetate (v/v:1/1). Yield: 2.7 g (29.3%) of yellow oil.

MS (CI with H_2O): $m/z = 639$(M + 1/100%), 527 (80%), 414 (30%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.97-0.83$ (12 H, m, CH_3), 1.87−1.13 (16 H, 2 × m, CH_2), 1.78 (2 H, m, CH), 3.87 (4 H, m, OCH_2), 6.90 (2H, s, phenyl), 7.30 (1H, m, H5′), 7.30 (2H, s, phenyl), 7.78 (1H, dt, $^3J = 7.9$ Hz, $^4J = 1.8$ Hz, H4′), 7.88 (dd, $^3J = 8.3$ Hz, $^4J = 2.1$ Hz, 1H, H4), 8.39 (1H, d, $^3J =$ 8.2 Hz, H3), 8.66 (2H, m, H3′, H6′), 8.80 (2H, d, $^4J = 1.4$ Hz, H6). ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 11.15$, 11.21, 13.98, 14.03, 22.97, 23.92, 23.98, 29.01, 29.05, 30.49, 30.59, 39.42, 39.54, 72.11, 72.20, 88.17, 89.88, 90.95, 112.70, 115.36, 120.26, 120.47, 121.23, 123.49, 123.78, 136.82, 139.04, 149.19, 151.39, 151.87, 154.59, 154.68, 155.44. UV−vis (dioxane): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 316.8 (32 100), 352.0 (29 400). Anal. Calcd for $C_{34}H_{43}N_2O_2I$ (638.64): C, 63.95; H, 6.79; N, 4.39. Found: C, 63.98; H, 6.96; N, 4.70.

1,4-Bis(2,2′-bipyridine-5′-ylethynyl)-2,5-di(2-ethylhexyl)oxybenzene (**9a**). 5-Ethynyl-2,2′-bipyridine (870 mg, 4.83 mmol), 1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene (1179 mg, 2.01 mmol), diisopropylamine (30 mL), toluene (70 mL). Chromatography with hexane/THF (v/v:3/1). Yield: 950 mg (68.3%) of yellow crystals; mp = 145−147 °C. MS (CI with H_2O): $m/z = 691$ (M + 1/100%), 579 (40%), 466 (40%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.99-0.84$ (12 H, m, CH_3), 1.61−1.30 (16 H, 2 × m, CH_2), 1.78 (2 H, m, CH), 3.92 (4 H, m, OCH_2), 7.04 (2H, s, phenyl), 7.30 (2H, ddd, $^3J = 6.7$ Hz, $^3J = 2.7$ Hz, $^4J = 1.1$ Hz, H5′), 7.80 (2H, dt, $^3J = 7.8$ Hz,$^4J = 1.8$ Hz, H4′), 7.90 (2H, dd, $^3J = 8.3$ Hz, $^4J = 2.1$ Hz, H4), 8.40 (2H, d, $^3J = 8.4$ Hz, H3), 8.40 (2H, d, $^3J = 8.4$ Hz, H3′), 8.67 (2H, d, $^4J = 4.7$ Hz, H6′), 8.80 (2H, d, $^4J = 1.5$ Hz, H6). ^{13}C NMR (62 MHz, $CDCl_3$): $\delta =$ 11.3, 14.1, 23.1, 24.1, 29.1, 30.7, 39.6, 72.0, 90.2, 91.9, 113.8, 116.5, 120.4, 120.5, 121.3, 123.9, 136.9, 139.2, 149.3, 151.5, 154.0, 154.8, 155.5. UV−vis ($CHCl_3$): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 332.8 (51 500), 391.2 (52 100). Anal. Calcd for $C_{46}H_{50}N_4O_2$ (690.93): C, 79.97; H, 7.29; N, 8.11. Found: C, 79.66; H, 7.65; N, 8.10.

5,5′-(1-Ethynyl-4-(2,2′-bipyridine-5′-ylethynyl)-2,5-di(2-ethylhexyl)oxybenzene)-2,2′-bipyridine (**9b**). 5,5′-Diethynyl-2,2′-bipyridine[14] (**8**) (369 mg, 1.81 mmol), **7** (2.54 g, 3.98 mmol), diisopropylamine (30 mL), toluene (70 mL). Chromatography with hexane/THF (v/v:3/1). Yield: 1.05 g (47.3%) of yellow powder. MS (CI with H_2O): $m/z = 1225$ (M + 1/100%), 1114 (30%), 612 (80%), 388 (70%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.00−0.85 (24 H, m, CH_3), 1.69−1.33 (32H, 2 × m, CH_2), 1.80 (4 H, m, CH), 3.93 (8 H, m, OCH_2), 7.04 (4H, s, phenyl), 7.30 (2H, m), 7.80 (2H, dt, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz), 7.90 (4H, 2 × m), 8.38 (4H, d, $^3J = 8.1$ Hz), 8.43 (2H, d, $^3J = 8.0$ Hz), 8.66 (2H, d, $^4J = 4.3$ Hz), 8.80 (4H, m). ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 11.28$, 14.06, 23.04, 24.07, 29.13, 29.66, 30.68, 39.61 71.96, 90.17, 90.53, 91.95, 91.98, 113.68, 113.84, 116.43, 120.34, 120.48, 120.60, 120.69, 121.31, 123.87, 136.90, 139.14, 139.15, 149.26, 151.51, 151.60, 153.96, 153.99, 154.07, 154.79, 155.48. UV−vis (dioxane): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 329.6 (72 400), 403.3 (113 900). UV−vis ($CHCl_3$): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 332.0 (69 100), 406.4 (110 000). Anal. Calcd for $C_{82}H_{92}N_6O_4$ (1225.69): C, 80.36; H, 7.57; N, 6.86. Found: C, 80.40; H, 7.71; N, 7.00.

1,4-Bis(2,2′-bipyridine-4′-ylethynyl)-2,5-di(2-ethylhexyl)oxybenzene (**10**). 4-Ethynyl-2,2′-bipyridine (995 mg, 4.2 mmol), 1,4-dibutyloxy-2,5-diiodobenzene[15] (477 mg, 1.7 mmol), diisopropylamine (40 mL), toluene (120 mL). Chromatography with chloroform/ethyl acetate (v/v:3/1). Yield: 550 mg (54%) of yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.02$ (6H, t, $J^3 = 7.4$ Hz, CH_3), 1.60 (4H, m, CH_2), 1.86 (4H, m, CH_2), 4.07 (4H, t, $J^3 = 6.4$ Hz, OCH_2), 7.04 (2H, s, phenyl), 7.30 (2H, ddd, $J^3 = 5.8$ Hz, $J^3 = 2.7$ Hz, $J^4 = 1.0$ Hz), 7.37 (2H, dd, $J^3 = 7.5$ Hz, $J^4 = 2.8$ Hz), 7.81 (2H, dt, $J^3 = 7.7$ Hz, $J^4 = 1.8$ Hz), 8.39 (2H, d, $J^3 = 8.0$ Hz), 8.53 (2H, s), 8.65 (2H, dd, $J^3 = 5.0$ Hz, $J^4 = 0.6$ Hz), 8.67 (2H, d, $J^3 = 5.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.87$, 19.36, 31.33, 69.46, 90.41, 92.67, 113.95, 117.25, 121.12, 123.13, 123.93, 125.13, 132.48, 136.92, 149.15, 149.23, 153.93, 155.63, 156.30. UV−vis ($CHCl_3$): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 286 (38 000), 310 (39 573), 322 (35 900), 380 (31 500). Anal. Calcd for $C_{38}H_{34}N_4O_2$ (578.72): C, 78.87; H, 5.92; N, 9.68. Found: C, 79.16; H, 6.20; N, 9.74.

Synthesis of the Ruthenium Model Compounds. *General Procedure for the Synthesis of the Ruthenium Model Compounds.* The complexes were prepared by refluxing of **11a** or **11b** together with the model ligand **9** or **10** in a mixture of ethanol/water/chloroform (2:1:1) for 48−96 h. The dark red solution was evaporated until dryness, and 20 mL of water was added. The monomer was precipitated by adding an excess of aqueous NH_4PF_6. After filtration, the precipitate was collected and recrystallization twice from EtOH/H_2O (2:1), yielding the pure product.

Ruthenium Complex (**12a**). 2 equiv of **11b** (929 mg, 1.16 mmol), 1 equiv of **9a** (400 mg, 0.58 mmol). Yield: 830 g (56%) of a red powder. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.65$ (6H, m), 0.76 (6H, m), 1.27 (88H, d), 1.55 (2H, m), 3.76 (4H, m), 6.89 (2H, s, phenyl) 7.45 (10H, m), 7.74 (8H, m), 7.85 (4H, m), 8.05 (4H, m), 8.69 (12H, m). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 12.10$, 14.76, 24.09, 25.25, 31.19, 36.73, 40.70, 73.03, 91.08, 94.17, 114.76, 117.87, 122.98, 123.04, 124.97, 125.43, 126.21, 126.30, 126.35, 129.31, 139.11, 140.53, 152.54 (5 peaks), 155.42, 157.94, 158.30 (5 peaks), 163.90. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 287 (167 800), 420 (77 600). Anal. Calcd for $C_{118}H_{146}N_{12}O_2Ru_2P_4F_{24}$ (2546.56): C, 55.66; H, 5.78; N, 6.60. Found: C, 55.87; H, 5.89; N, 6.54.

Ruthenium Complex (**12b**). 3 equiv of **11b** (623 mg, 0.78 mmol), 1 equiv of **9b** (318 mg, 0.26 mmol). Yield: 440 mg (42%) of a red powder. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.81$ (12H, m), 0.92 (12H, m), 1.26−1.85 (144H, m), 3.97 (8H, m), 7.04 (3H, s), 7.29 (1H, s), 7.63 (14H, m), 7.87 (12H, m), 8.02 (6H, m), 8.22 (6H, m), 8.85 (18H, m). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 12.10$, 14.77, 24.09, 25.24, 31.18, 36.74, 40.72, 41.01, 72.88, 73.08, 91.17, 94.21, 94.61, 114.84, 117.93, 118.13, 122.98, 125.18, 125.44, 126.19, 126.36, 129.30, 139.13, 140.48, 152.23, 152.44, 152.55, 152.72, 152.99, 153.94, 155.45, 155.62, 158.08, 158.34, 158.49, 163.95. (ESI in methyl alcohol): $m/z = 3865.7$ ($M^+ - PF_6$) 1858.7 ($M^{2+} - 2PF_6$, 15%), 1191.0 ($M^{3+} - 3PF_6$, 50%). UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 287 (243 400), 322 (135 500), 428 (154 100). Anal. Calcd for $C_{190}H_{236}N_{18}O_4Ru_3P_6F_{36}$ (4009.11): C, 56.92; H, 5.93; N, 6.29. Found: C, 57.37; H, 5.94; N, 6.24.

Ruthenium Complex (**13**). 2 equiv of **11b** (221 mg, 0.28 mmol), 1 equiv of **10** (80 mg, 0.14 mmol). Yield: 160 mg (48%) of a red powder. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.83$ (6H, m), 1.26 (76H, d), 1.69 (4H, m), 3.97 (4H, m), 7.15 (2H, s, phenyl) 7.46 (12H, m), 7.72 (6H, m), 7.87 (6H, m), 8.05 (2H, m), 8.73 (12H, m). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 14.46$, 20.28, 31.49, 32.32, 36.65, 70.39, 92.75, 95.56, 114.92, 118.39, 123.01, 125.38, 125.95, 126.25, 126.30, 126.92, 129.40, 129.81, 133.25, 139.11, 152.18, 152.27, 152.47, 152.58, 152.94, 155.42, 158.16, 158.21, 158.31, 159.09, 163.86, 163.90. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 246 (79 300), 288 (159 100), 426 (51 100), 490 (57 600). Anal. Calcd for $C_{110}H_{130}N_{12}O_2Ru_2P_4F_{24}$ (2434.34): C, 54.27; H, 5.38; N, 6.90. Found: C, 53.89; H, 5.43; N, 6.65.

Ruthenium Complex (**12c**). 2 equiv of **11b** (498 mg, 0.62 mmol), 1 equiv of **9c**[17] (180 mg, 0.31 mmol). Yield: 470 mg (63%) of a red powder. ^{1}H NMR (250 MHz, acetone-d_6): $\delta =$ 0.93 (6H, m), 1.42 (76H, d), 1.73 (4H, m), 4.02 (4H, m), 7.04 (2H, s, phenyl) 7.62 (19H, m), 7.90 (8H, m), 8.02 (4H, m), 8.21 (4H, m), 8.85 (12H, m). ^{13}C NMR (62 MHz, acetone-d_6): $\delta =$ 14.59, 20.26, 31.17, 32.24, 36.64, 70.35, 91.12, 94.11, 114.83, 116.13, 122.98, 124.96, 125.40, 126.20, 126.33, 129.28, 139.10, 140.60, 152.21, 152.41, 152.54, 152.76, 152.96, 155.19, 157.90, 158.09, 158.29, 158.49, 163.90. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 249 (84 000), 287 (209 500), 418 (93 600). Anal. Calcd for $C_{110}H_{130}N_{12}O_2Ru_2P_4F_{24}$ (2434.34): C, 54.27; H, 5.38; N, 6.90. Found: C, 54.56; H, 5.51; N, 6.58.

Polycondensation. *General Procedure for the Polycondensation*. 1.0 mmol of (dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) **(3a−d)**, 1.0 mmol of substituted 1,4-diethynylbenzene, $Pd(PPh_3)_4$ (46 mg, 4.0×10^{-2} mmol, 4 mol %), and CuI (8 mg, 4.0×10^{-2} mmol, 4 mol %) were given to a degassed solution of 30 mL of dried degassed diisopropylamine and 70 mL of dried degassed acetonitrile. The reaction mixture was degassed for further 30 min and stirred at 70−80 °C. After a total reaction time of 24 h, the viscous solution was cooled to room temperature and added dropwise to 500 mL of vigorously stirred methanol. The polymer was precipitated by adding an excess of aqueous NH_4PF_6 for exchanging the anion. The solid was collected and dissolved again in 50 mL of acetone. A small undissolved residue was filtered off, and the remaining solution was added dropwise. The polymer was purified by Soxhlet extraction with methanol. Dissolving in 50 mL of acetone and adding dropwise to 500 mL of vigorously stirred hexane.

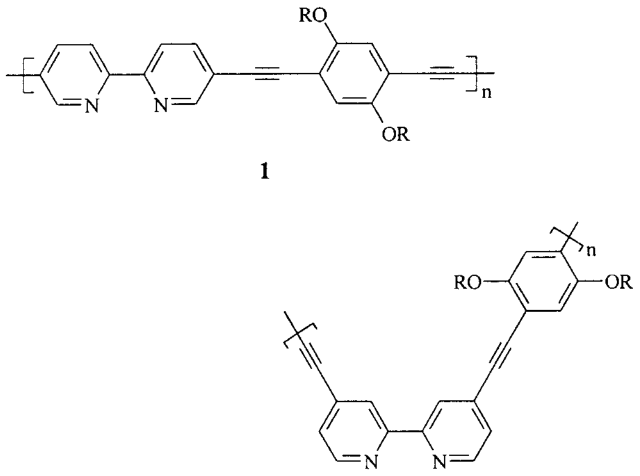
Poly{bis(2,2′-bipyridine)-[2,2′-bipyridine-5,5′-diylethynylene-(2,5-dibutyloxy-1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**5a**). (5,5′-Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3a**) (1017 mg), 1,4-diethynyl-2,5-dibutyloxybenzene[15] (**4a**) (270 mg). Yield: 1.02 g (91%) of a red polymer. ^{1}H NMR (400 MHz, acetone-d_6, 318 K): $\delta = 0.89$ (6 H, m, $-CH_3$), 1.43−1.65 (8 H, m, $-(CH_2)_2-$), 3.95 (4 H, m, $-CH_2O-$), 7.01 (2 H, s, H_{phe}), 7.57, 8.02, 8.19, 8.78 (22 H, m, H_{bpy}). ^{13}C NMR (100 MHz, acetone-d_6, 318 K): $\delta = 13.12$ (CH_3-), 18.81, 30.82 ($-(CH_2)_2-$), 69.14 ($-CH_2O-$), 89.79, 93.45 ($-C{\equiv}C-$), 113.69, 117.11, 124.60, 127.95, 138.29, 139.82, 151.82, 152.20, 152.87, 153.91, 155.78, 157.10, 157.31. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 235 (41 200), 253 (31 200), 286 (77 600), 330 (47 500), 355 (40 900), 456 (73 800). Anal. Calcd for $(C_{48}H_{42}N_6O_2F_{12}P_2Ru)_n(1125.90)_n$: C, 51.21; H, 3.76; N, 7.46. Found: C, 50.83; H, 3.78; N, 7.31; Br, 0.26.

Poly{bis(2,2′-bipyridine)-[2,2′-bipyridine-5,5′-diylethynylene-(2,5-dioctadecyloxy-1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**5b**). (5,5′-Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3a**) (1017 mg), 1,4-diethynyl-2,5-dioctadecyloxybenzene[5] (**4b**) (270 mg). Yield: 0.43 g (28%) of a red soluble polymer. Yield: 0.99 g (65%) of a red unsoluble polymer. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.88$ (6 H, m, $-CH_3$), 1.28 (60 H, m, $-CH_2-$), 1.73 (4 H, m, $-CH_2-$), 4.01 (4 H, m, $-CH_2O-$), 7.06 (2 H, s, phenyl), 7.64, 8.09, 8.26, 8.85 (18 H, m, bpy). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 14.78$ (CH_3-), 23.73, 27.05 ($-(CH_2)_2-$), 70.37 ($-CH_2O-$), 91.24, 94.85 ($-C{\equiv}C-$), 114.79, 116.07, 125.95, 129.32, 139.64, 141.14, 153.49, 154.32, 155.16, 157.01, 158.41. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 236 (42 600), 286 (74 800), 330 (45 800), 456 (66 200). Anal. Calcd for $(C_{76}H_{98}N_6O_2F_{12}P_2Ru)_n(1518.67)_n$: C, 60.11; H, 6.50; N, 5.53. Found: C, 61.04; H, 6.78; N, 5.41; Br, 0.58.

Poly{bis(2,2′-bipyridine)-[2,2′-bipyridine-4,4′-diylethynylene-(2,5-dibutyloxy-1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**6a**). (4,4′-Dibromo-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3b**) (1017 mg), 1,4-diethynyl-2,5-dibutyloxybenzene (**4a**) (270 mg). Yield: 0.93 g (83%) of a red polymer. ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 0.93$ (6 H, m, $-CH_3$), 1.51 (4 H, m, $-CH_2-$), 1.77 (4 H, m, $-CH_2-$), 4.10 (4 H, m, $-CH_2O-$), 7.32 (2 H, s, phenyl), 7.54, 8.01−8.19, 8.78−8.88 (22 H, m, bpy). ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 13.29$ (CH_3-), 18.64, 31.04 ($-(CH_2)_2-$), 68.98 ($-CH_2O-$), 91.31, 94.62 ($-C{\equiv}C-$), 113.57, 117.12, 124.48, 125.99, 127.98, 128.85, 132.04, 132.53, 138.29, 151.71, 151.89, 152.01, 154.13, 157.03, 157.17. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 242 (50 700), 287 (77 600), 426 (43 900), 494 (37 400). Anal. Calcd for $(C_{48}H_{42}N_6O_2F_{12}P_2Ru)_n(1125.90)_n$: C, 51.21; H, 3.76; N, 7.46. Found: C, 49.95; H, 3.39; N, 7.27; Br, 0.87.

Poly{bis(4,4′-tert-butyl-2,2′-bipyridine)-[2,2′-bipyridine-5,5′-diylethynylene-(2,5-dibutyloxy-1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**5c**). (5,5′-Dibromo-2,2′-bipyridine)bis(4,4′-*tert*-butyl-2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3c**) (1241 mg), 1,4-diethynyl-2,5-dibutyloxybenzene (**4a**) (270 mg). Yield: 1.20 g (89%) of a red polymer. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.90$ (6 H, m, $-CH_3$), 1.40 (40 H, m, $-CH_2-$, *tert*-butyl), 1.70 (4 H, m, $-CH_2-$), 3.98 (4 H, m, $-CH_2O-$), 7.00 (2 H, s, phenyl), 7.59, 7.82−8.19, 8.84 (18 H, m, bpy). ^{13}C NMR (62 MHz, acetone-d_6): $\delta =$ 14.58 (CH_3-), 30.86 (*tert*-butyl−C), 20.25, 32.24 ($-(CH_2)_2-$), 36.68 (*tert*-butyl−CH_3-) 70.37 ($-CH_2O-$), 91.24, 94.51 ($-C{\equiv}C-$),114.89, 118.20, 123.07, 125.95, 126.35, 140.63, 152.40, 152,87, 154.10, 155.22, 157.27, 158.24, 158.46, 164.02. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 286 (57 000), 331 (37 300), 453 (50 900), 494 (37 400). Anal. Calcd for $(C_{64}H_{74}N_6O_2F_{12}P_2Ru)_n$ $(1350.35)_n$: C, 56.93; H, 5.52; N, 6.22. Found: C, 56.28; H, 5.57; N, 6.17; Br, 0.10.

Poly{bis(4,4′-tert-butyl-2,2′-bipyridine)-[2,2′-bipyridine-4,4′-diylethynylene-(2,5-dibutyloxy-1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**6b**). (4,4′-Dibromo-2,2′-bipyridine)bis(4,4′-*tert*-butyl-2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3d**) (1241 mg), 1,4-diethynyl-2,5-dibutyloxybenzene (**4a**) (270 mg). Yield: 1.13 g (84%) of a red polymer. ^{1}H NMR (250 MHz, acetone-d_6): $\delta = 0.99$ (6 H, t, $-CH_3$), 1.43 (36 H, m, *tert*-butyl), 1.57, 1.70 (8 H, m, $(-CH_2-)_2$), 4.16 (4 H, m, $-CH_2O-$), 7.37 (2 H, s, phenyl), 7.52−7.61, 7.84, 8.04, 8.89 (18 H, m, bpy). ^{13}C NMR (62 MHz, acetone-d_6): $\delta = 14.61$ (CH_3-), 30.86 (*tert*-butyl−C), 20.28, 32.39



1

2

Figure 1. Chemical structures of polymers **1** and **2**.

(−$(CH_2)_2$−), 36.67 (*tert*-butyl−CH_3−) 70.37 (−CH_2O−), 92.69, 95.91 (−C≡C−),114.97, 118.56, 123.02, 126.31, 127.24, 130.07, 133.53, 152.21, 152.66, 152.93, 155.46, 158.25, 158.65, 164.01. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 245 (50 200), 287 (83 000), 312 (51 900), 433 (49 800), 507 (38 000). Anal. Calcd for $(C_{64}H_{74}N_6O_2F_{12}P_2Ru)_n(1350.35)_n$: C, 56.93; H, 5.23; N, 6.22. Found: C, 56.28; H, 5.85; N, 6.00; Br, 0.65.

Poly{bis(4,4′-tert-butyl-2,2′-bipyridine)-[2,2′-bipyridine-5,5′-diylethynylene-(1,4-phenylene)ethynylene]ruthenium(II) Bis(hexafluorophosphate)} (**5d**). (5,5′-Dibromo-2,2′-bipyridine)bis-(4,4′-*tert*-butyl-2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) (**3c**) (1241 mg), 1,4-diethynylbenzene^{16} (**4c**) (126 mg). Yield: 1.10 g (91%) of a red polymer. ^{1}H NMR (250 MHz, acetone-d_6): δ = 1.38 (36 H, s, *tert*-butyl), 7.47, 7.58, 7.82, 7.95, 8.00, 8.26, 8.82 (22 H, m, phenyl, bpy). ^{13}C NMR (62 MHz, acetone-d_6): δ = 30.87 (*tert*-butyl−C), 36.70 (*tert*-butyl−CH_3−) 88.04, 96.03 (−C≡C−), 123.07, 124.69, 126.36, 133.31, 140.80, 152.91, 154.50, 157.47, 158.28, 164.01. UV−vis (acetonitrile): λ_{max}/nm (ϵ/(L mol^{-1} cm^{-1})) 286 (73 300), 418 (82 400). Anal. Calcd for $(C_{56}H_{58}N_6F_{12}P_2Ru)_n(1206.13)_n$: C, 55.77; H, 4.85; N, 6.97. Found: C, 54.59; H, 5.65; N, 6.78; Br, 0.12.

Results and Discussion

The structures of these new polymers were spectroscopically and analytically characterized and in comparison with monodispers low molecular model compounds. Figure 5 outlines the approach to the model compounds. The model compounds **12a**−**d** and **13** were synthesized by complexation of the ruthenium-free model ligands **9a**−**c** and **10** with $Ru(bpy)_2Cl_2$ (Table 2). The model ligands were synthesized in toluene/diisopropylamine similar to the polycondensation using $Pd(PPh_3)_4$ and CuI as catalyst (Sonoghashira reaction) (Figure 4).

The new polymers **5** and **6** were synthesized by the Sonogashira cross-coupling reaction of (4,4′- or 5,5′-dibromo-2,2′-bipyridine)bis(2,2′-bipyridine) or (4,4′-*tert*-butyl-2,2′-bipyridine)ruthenium(II) complexes (**3a**−**d**) and 1,4-diethynylbenzenes (**4**) in a step growth polymerization mechanism (Figure 2). The typical reaction conditions used for the synthesis of the polymers involved stirring the argon-degassed mixture of the monomers and catalyst (4 mol % of $Pd(PPh_3)_4$ and 4 mol % of CuI) in acetonitrile/diisopropylamine for 72−96 h at a temperature of 75 °C. The polymers were isolated by dropping into methanol and further precipitation with NH_4PF_6. Soxhlett extraction with methanol, dissolving in 50 mL of acetone, and adding dropwise to 500 mL of vigorously stirred *n*-hexane gave the pure red polymer with yields above 85%, pointing at a very high conversion.

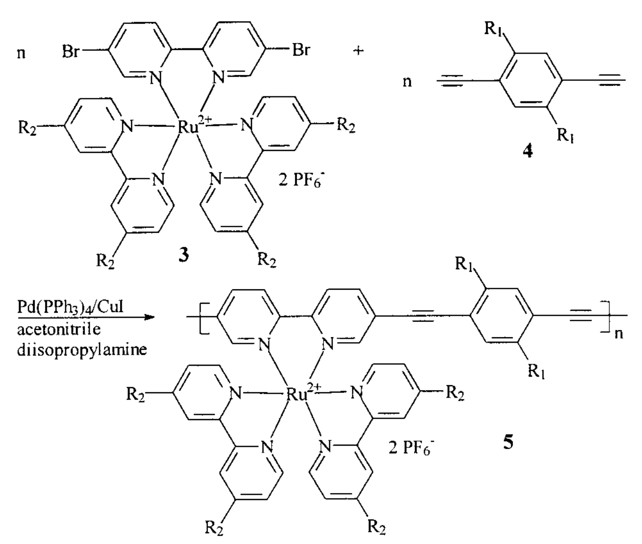
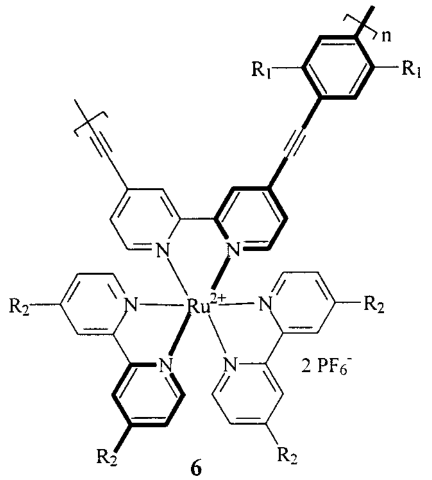


Figure 2. Synthesis and chemical structure of polymer **5**.



6

Figure 3. Chemical structure of polymer **6**.

The polymers **5** and **6** are soluble in acetone, acetonitrile, DMF, and DMSO. Moreover, it is remarkable that the simple change of the substituents in the ligands (*tert*-butyl instead of H) leads to a significant modulation of the solubility of the polymers. Whereas the polymer **5e** ($R_1 = R_2 =$ H) for example is absolutely insoluble in all common organic solvents, the polymer **5d** (R_1 = H, $R_2 = C(CH_3)_3$) is completely soluble in acetone, acetonitrile, and DMSO. The polymers substituted with *tert*-butyl groups are also soluble in cyclohexanone, which is a suitable solvent to process the polymers into transparent films. All polymers are able to be converted into transparent thin films (thickness between 150 nm and 3 μm). This is important for application in optical devices.

The chemical structures of the polymers and of the model compounds were confirmed by ^{1}H NMR and elemental analysis. Figure 6 depicts the ^{1}H NMR spectrum of polymer **5a** measured in deuterated acetone. The proton shift of the aliphatic region of the polymer are nearly the same shift like in the model compound. The overlap of the chemical shift of the protons of 2,2′-bipyridyl ligands complicates the proton assignment in the aromatic region. However, the peak areas confirmed the expected numbers of protons in this downfield region.

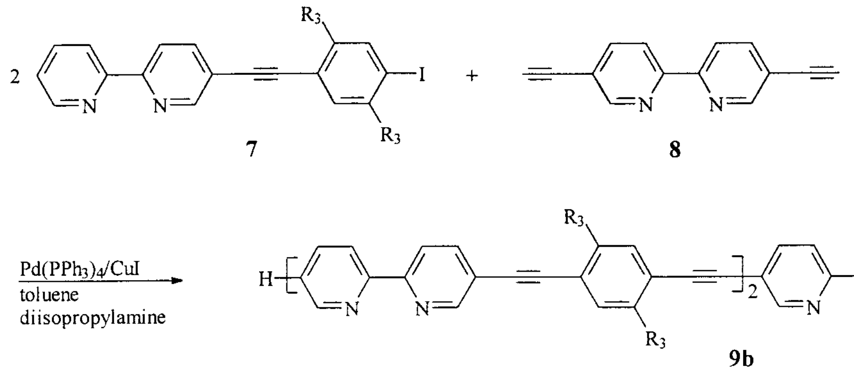


Figure 4. Synthesis and chemical structure of model compounds **7**–**9**.

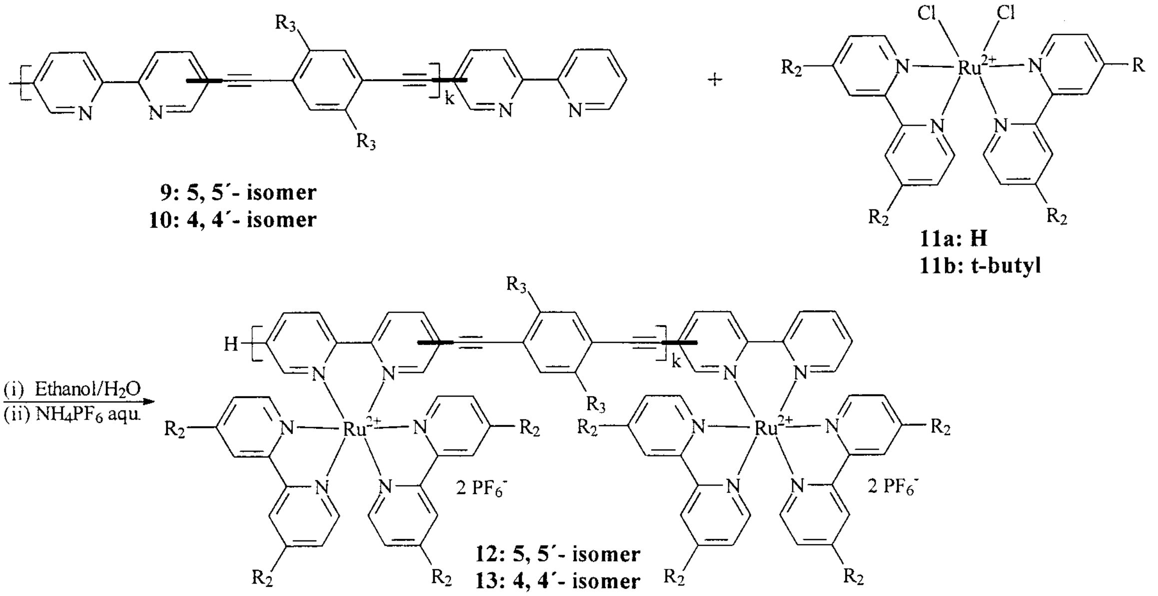


Figure 5. Synthesis and chemical structure of model compounds **9**–**13**.

Table 1. Substitution of Polymers 5 and 6

polymer	R_1	R_2	bpy-Br_2[a]
5a	OC_4H_9	H	5,5′
5b	$OC_{18}H_{37}$	H	5,5′
5c	OC_4H_9	*tert*-butyl	5,5′
5d	H	*tert*-butyl	5,5′
5e	H	H	5,5′
6a	OC_4H_9	H	4,4′
6b	OC_4H_9	*tert*-butyl	4,4′

[a] Substitution of bpy in the main chain.

Table 2. Substitution of Model Compounds 7, 9, 10, and 11

model	R_3	R_4	bpy-subst[a]	*k*
9a	OC_8H_{17}(EH)		5	1
9b	OC_8H_{17}(EH)		5; 5,5′	2
9c	OC_4H_9		5	1
10	OC_4H_9		4	1
12a	OC_8H_{17}(EH)	*tert*-butyl	5	1
12b	OC_8H_{17}(EH)	*tert*-butyl	5; 5,5′	2
12c	OC_4H_9	*tert*-butyl	5	1
12d[17]	OC_4H_9	H	5	1
13	OC_4H_9	*tert*-butyl	4	1

[a] Substitution of the bpy in the main chain.

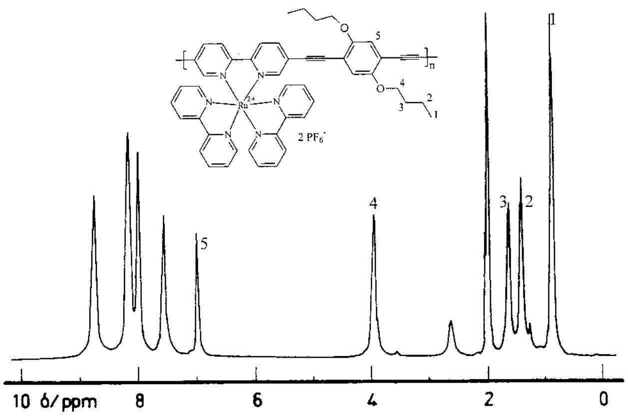


Figure 6. ^{1}H NMR spectrum of polymer **5a** in acetone-d_6.

The molecular weight determination of the rigid polymers such as poly(aryleneethynylene)s is not trivial. It is still more complicated if metal ions are present in such polymers. GPC vs polystyrene however is so far the most commonly used method for determination of molecular weight and molecular weight distribution.[18] We tested the method by using our model compounds and found unreasonable and nonreproducible results. A good correctness can be obtained with a NOVEMA 300 (PSS) column and pullulan and dextran standards. The GPC curves of the model compounds are shown in Figure 7. We observed well-resolved signals. Figure 8 shows for example the GPC curves of the polymer **5c** and of the model compound **12b**. We compared the real molecular weight with the molecular weights obtained by GPC (Tables 3 and 4). We figured out that the molecular weights are underestimated by GPC with a

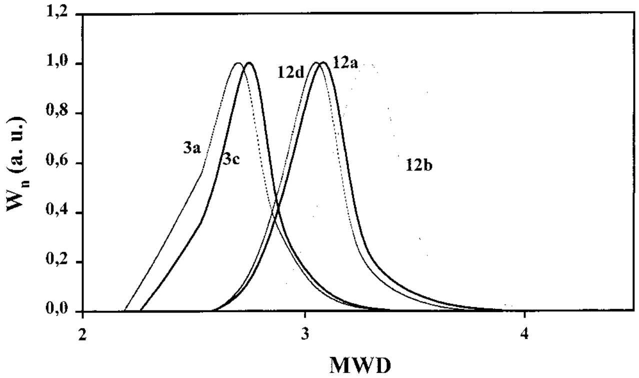


Figure 7. GPC curves of model compounds **3a**,**c** and **12a**,**b**,**d**.

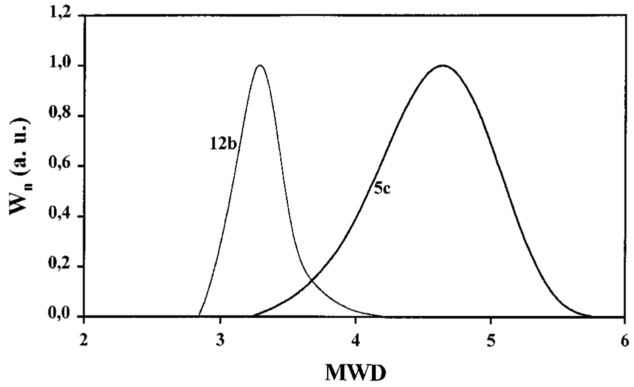


Figure 8. GPC curves of polymer **5c** and of model compound **12b**.

Table 3. GPC Data of Model Compounds 3 and 9

model	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	*D*	*M* (g/mol)	$\bar{M}_n/M$
3a	420	503	1.20	1017	0.41
3c	488	570	1.17	1242	0.39
12d	1036	1200	1.16	1985	0.52
12a	1113	1324	1.19	2547	0.44
12b	1799	2175	1.21	4009	0.45

factor of 2−2.4. Moreover, we performed end group determination (Table 4). In comparison to those results the GPC with pullulan standards shows overestimated molecular weights by a factor of approximately 2.7.

The UV/vis spectra of the chelating polymers (**5c**, **6b**) and of the model compounds (**12c**, **13**) are presented in Figure 9.

UV/vis absorption spectra of the polymer **5a** and the model complexes **12a**,**b** showed four absorption maxima in acetonitrile. The absorption maximum in the visible region (ca. 450 and 420 nm, respectively) is similar[4] to those of $Ru(bpy)_3{}^{2+}$ and therefore corresponds to the metal-to-ligand charge-transfer (MLCT) band of ruthenium(II) complex units. The larger red-shifted absorption maximum of the polymer relative to the model is a result of the extended conjugation. The model complex gives an additional absorption band at 310 nm due to the overlapping $\pi-\pi^*$ transition of the bpy ligand.

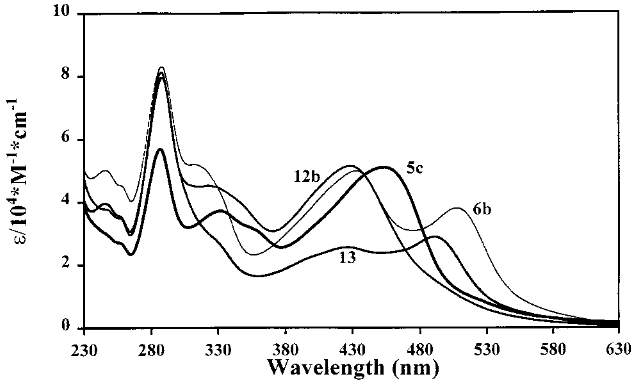


Figure 9. UV−vis spectra of polymers **5c** and **6b** and model compounds **12b** and **13** in acetonitrile.

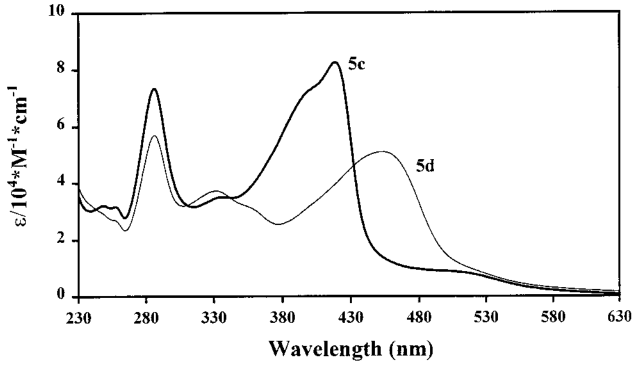


Figure 10. UV−vis spectra of polymers **5c** and **5d** in acetonitrile.

Although the band of the bpy appears to remain largely unchanged, extending the conjugation of the ligand in the polymer results in the appearance of a lower energy band above (330) 350 nm.

It is remarkable that the polymers of the 4,4′-diethynylbipyridylene structure (polymer **6b** and model **13**) give a significant red shift in the MLCT absorption spectra compared to the linear polymer. A possible explanation of this behavior might be the longer conjugation than in the 5,5′-isomer (including the ligands in the conjugation) (Figure 3). The same properties can be found for the model compounds (**12c** and **13**). The absorption maximum of the 4,4′-bipyridine compound **13** is red-shifted in comparison to the linear 5,5′-bipyridine (**12c)** compound.[3]

The alkoxy side groups lead to a small bathochromic shift of the absorption maximum with respect to their unsubstituted counterparts (R_1 = H), λ_{max} = 425 (Figure 10 shows **5c** in comparison to **5d**).

Figure 11 shows the excitation and emission spectra of polymer **6a** and model compound **12b** in deaerated (with N_2) acetonitrile. When excited at 494 nm (428 nm for **12b**), the polymer showed an emission peak at 676 nm (714 nm for **12b**). This peak is attributed to the MLCT states. A similar interpretation is given for

Table 4. GPC Data of Polymers 5 and 6

polymer	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	*D*	P_n	$\bar{M}_n$ (g/mol)^a max	P_n	Br content	$\bar{M}_n$(Br)	P_n
5a	16 600	47 500	2.9	15	38 500	34	0.26	61 000	53
5b	18 800	62 800	3.3	12	40 700	27	0.58	28 000	18
5c	22 600	57 700	2.6	17	43 400	32	< 0.10	160 000	117
5d	19 400	74 800	3.9	16	31 700	26	0.12	132 000	108
6a	6 900	15 700	2.3	6	11 700	10	0.87	19 000	16
6b	25 300	84 900	3.4	19	53 300	39	0.65	25 000	18

[a] Maxima of the GPC curves.

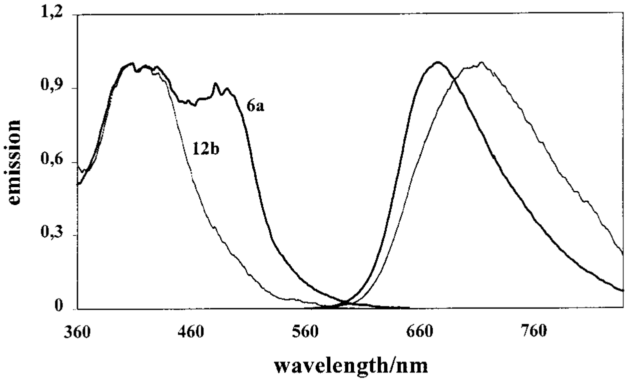


Figure 11. Excitation and emission spectra of polymer **6a** and of model compound **12b** in acetonitrile.

phenanthroline-based conjugated polymers containing the Ru(II)bpy$_2$ metal complex.[4]

Cyclic- and square-wave voltammetry of the polymers shows a typical Ru$^{2+/3+}$ couple exhibiting an oxidation potential of 1.27 V (**5a**) and 1.23 V (**6b**) vs SCE.

The new polymers are good photoconducting materials, even without any sensitizer. The maximal photocurrent, I_{Ph}, was found at 3.7 × 10^{-12} A (**6b**) at $\nu_{\max} =$ 18 000 cm^{-1} and $U = 400$ V.

Thermogravimetric analysis carried out at a heating rate of 10 K/min under air indicates high thermal stability of the polymers. Thermal decomposition starts around 290 °C. As revealed by differential scanning calorimetry, the polymers have no glass transition temperature; the heating was carried out up to 200 °C at a rate of 10 K/min.

Conclusion

Our work resulted in the preparation of a novel family of multi-Ru(II)-chelating polymers. The solubilities of the polymers increased by adding a *tert*-butyl substituent in the bpy ligands.

The polymers have a molecular weight ($\bar{M}_n$) of about 2 × 10^4 g/mol as determined by GPC (pullulan, dextran standard). In comparison to end group determination, the GPC method overestimates the molecular weights by a factor of approximately 2.7.

The polymers exhibit an oxidation potential of 1.27 V vs SCE; they are good photoconducting materials.

Acknowledgment. This research has been supported by the Deutsche Forschungsgemeinschaft (SFB 196). We gratefully thank Dr. E. Birckner for carrying out the photoluminescence analysis and Dr. M. Rudolph for the electrochemical measurements.

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MA011712S