

Polymeric Ruthenium Bipyridine Complexes: New Potential Materials for Polymer Solar Cells

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ABSTRACT: Methyl methacrylate-containing bipyridine monomers were synthesized with a hydroxy-functionalized bipyridine. The 4'-methyl group of the 2,2'-bipyridine was used to introduce hydroxy-functionalized alkyl spacers of two different lengths. Two, different synthetic routes were applied for the preparation of the hydroxy-functionalized bipyridine *via* a bromo-(C₇ spacer) or a silylated-(C₃ spacer) intermediate. A copolymer of poly(methyl methacrylate) with bipyridine units in the side chains was prepared by free-radical copolymerization and characterized with ¹H NMR, ultraviolet–visible, and IR spectroscopy as well as gel permeation chromatography. The bipyridine units of the copolymer were reacted with ruthenium bipyridine precursors. The resulting graft copolymers displayed promising photophysical and electrochemical properties, opening interesting perspectives for applications in the field of solar-cell devices. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 374–385, 2004

Keywords: functionalized bipyridine ligands; poly(methyl methacrylate); ruthenium(II) polypyridyl complexes; graft copolymers; photochemical and electrochemical properties

INTRODUCTION

The research efforts in the field of bipyridine-containing ligands and their metal complexes have strongly increased within the last few years. In particular, the central focus has shifted from analytical purposes (complexation of metal ions) to the creation of new materials and polymers.^{1,2} A large portion of recent interest in this ligand stems from the very interesting photophysical and photochemical properties exhibited by several of its transition-metal complexes, especially those of ruthenium.³ Ruthenium(II) polypyridyl complexes have been exploited in nanocrystalline TiO₂-based solar cells (Grätzel-type solar

cells),^{4–6} biosensors,^{7,8} and molecular wires.⁹ The choice of this metal ion is of interest for a number of reasons. First, because of the octahedral complex geometry, specific ligands can be introduced in a controlled manner. Second, the photophysical, photochemical, and the electrochemical properties of these complexes can be tuned in a predictable way. Third, the ruthenium metal ion possesses stable and accessible oxidation states ranging from I to III.¹⁰ Grätzel and coworkers¹⁰ have developed efficient photoelectrochemical cells through the use of sensitizers based on transition-metal complexes deposited on nanocrystalline titanium dioxide electrodes. Dye-sensitized solar cells have attracted widespread academic and commercial interest for the conversion of sunlight into electricity because of their low cost, flexibility, and high-energy conversion efficiency.¹¹ The added advantages of these cells are the availability as well as the nontoxicity of the main component,

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that is, titanium dioxide, which is used in paints, cosmetics, and healthcare products.¹² The highest efficiency reported has been obtained with nanocrystalline titanium dioxide coated with *bis*(4,4'-dicarboxy-2,2'-bipyridine)-ruthenium(II) thiocyanate, for which overall solar to electrical energy-conversion efficiencies of up to 10% have been reported.^{5,13,14} The high efficiency of this cell is due to the significant overlap of the absorbance spectrum with the emission spectrum, rapid charge separation, and efficient dye regeneration.

Polymeric ruthenium(II) (polypyridyl) complexes can also undergo energy transfer and function as light-harvesting antennae.^{15,16} An interesting development in polymer chemistry has been observed regarding copolymers with supramolecular entities in the side chains. Such an approach was described by Schultze et al.,¹⁷ who reported a copolymer consisting of a coumarin-2 chromophore and a 2,2'-bipyridine ligand that was used to graft a bipyridine ruthenium complex onto the polymer chain. Furthermore, a copolymerization of the already preformed ruthenium *tris*(bipyridine) complex with the coumarin monomer has been described.^{17,18} These new polymer systems display very high energy transfer efficiencies and are therefore potentially interesting for applications in photovoltaics and luminescence-based sensors. This contribution is devoted to the selective *monoderivatization* of the 4,4'-dimethyl-2,2'-bipyridine with a functional moiety that can be polymerized. Therefore, bipyridines with methacrylate as a functional unit and different spacer lengths (C₃ and C₇) were prepared. Both monomers were synthesized in three-step reactions, starting from the 4,4'-dimethyl-2,2'-bipyridine *via* a hydroxy intermediate to the methyl methacrylate functionality. Moreover, synthesis of a poly(methyl methacrylate) (PMMA) based copolymer with bipyridine units in the side chain utilizing a free-radical polymerization process is described. Grafting of ruthenium polypyridyl complexes onto this polymer allowed the formation of a new class of graft copolymers. The photochemical and electrochemical properties were investigated to elaborate the potential application as a solar cell material.

EXPERIMENTAL

Materials and General Experimental Details

Reactions were performed under an atmosphere of argon where required and stirred magnetically.

All chemicals were of reagent grade and used as received unless otherwise specified. 2,2'-Bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenantroline, 2-bromoethoxy-*tert*-butyl-dimethyl-silane, methyl methacryloyl chloride, and methyl methacrylate were purchased from Aldrich. Diisopropylamine and *n*-butyllithium were obtained from Acros and triethylamine and 1,6-dibromohexane were purchased from Merck. Diisopropylamine and 1,6-dibromohexane were filtered through a short column of neutral aluminium oxide before use. Purified solvents were used where required. Tetrahydrofuran (THF) was distilled from molecular sieves and dichloromethane (CH₂Cl₂) was distilled from calcium hydride.

4-(7-Bromoheptyl)-4'-methyl-2,2'-bipyridine (**2**),¹⁹ the hydroxy-functionalized bipyridines **3** and **5**,^{19,20} their corresponding methacrylate monomers **4** and **6**,²¹ [Ru(bpy)₂Cl₂] (**8**), [Ru(dMbp)₂Cl₂] (**9**), [Ru(phen)₂Cl₂] (**10**),²² and bipyridine-containing PMMA (**7**)²¹ were synthesized according to modified literature methods (bpy stands for 2,2'-bipyridine, dMbp represents 4,4'-dimethyl-2,2'-bipyridine, and phen is used as an abbreviation for 1,10-phenantroline). Ligands **4** and **6** were found hygroscopic.

Column chromatography was carried out on standardized aluminum oxide 90 (Merck). The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. Size exclusion chromatography was carried out on Biobeads S-X12 or S-X1 (CH₂Cl₂) (dichloromethane). Column chromatographic separations were monitored with Merck 60 F254 (Type E) precoated alumina thin-layer chromatography (TLC) sheets. Visualization was done under UV irradiation or by subjecting the TLC plates to an aqueous solution of FeCl × 4 H₂O.

Instrumentation

One-dimensional (¹H and ¹³C {¹H}) and two-dimensional (2D) [¹H-¹H correlation spectroscopy (¹H-¹H COSY)] nuclear magnetic resonance spectra were recorded on a Varian Gemini 300-MHz spectrometer at 298 K. The 2D heteronuclear spectra [¹H-¹³C heteronuclear multiple-quantum coherence experiment (HMQC)] were measured on a Varian Inova 500 spectrometer at 298 K. Chemical shifts were reported in parts per million (δ) downfield from an internal standard, tetramethylsilane (TMS), in CDCl₃ or CD₂Cl₂. Coupling constants (*J* values) were reported in Hertz (Hz). Gas chromatography mass spectrometry (GC-MS)

analysis was performed on a Shimadzu GC-MS-QP5000; the mass values were reported as the mass/charge ratio (m/z) Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems) time-of-flight mass spectrometer reflector with dithranol as a matrix. IR spectra were recorded on a PerkinElmer 1600 Fourier transform infrared spectrometer. Gel permeation chromatograms (GPCs) were measured on a Waters GPC system consisting of an isocratic pump, a solvent degasser, a column oven, a 2996 photo diode array (PDA) detector, a 2414 refractive-index detector, a 717plus autosampler, and a Styragel HT 4 GPC column with precolumn installed [dimethyl formamide (DMF), 5 mM NH_4PF_6 , 50 °C, flow rate: 0.5 mL/min, PMMA calibration]. Ultraviolet visible (UV-vis) spectra were recorded on a PerkinElmer Lambda-45 (1-cm cuvettes, CH_3CN or $\text{CHCl}_3/\text{CH}_3\text{OH}$ mixture). Emission spectra were recorded on a PerkinElmer LS50B Luminescence spectrometer (1-cm cuvettes, CH_3CN). Electrochemical experiments were performed with a Wenking POS 73 model potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode reference. Ferrocene was added at the end of each experiment as an internal standard. The potentials were quoted versus the ferrocene/ferrocenium couple (Fc/Fc^+). The solvent used was CH_2Cl_2 (freshly distilled from CaH_2), containing 0.1 M $n\text{-Bu}_4\text{PF}_6$. The scan rate was 100 mV/s. Elemental analyses were carried out on a Carlo Erba Instruments EA1108 CHNS/O Elemental Analyzer. Differential scanning calorimetry (DSC) investigations were performed on a PerkinElmer Pyris-1 DSC system with a heating rate of 40 K/min [glass-transition temperature (T_g)].

Synthesis of the Functionalized Bipyridines, Monomers, of the Copolymer, and of the Graft Copolymers

4-(7-Bromoheptyl)-4'-methyl-2,2'-bipyridine (2)

To a 50-mL, round-bottom flask equipped with a magnetic stirrer and a rubber septum, containing an anhydrous solution of diisopropylamine (187.5 μL , 1.33 mmol) in THF (2 mL) at -78 °C, 1.6 M $n\text{-butyllithium}$ in hexane (0.83 mL, 1.33 mmol) was added *via* a syringe. The resulting pale yellow solution was stirred at -78 °C for 30 min, and subsequently, 4,4'-dimethyl-2,2'-bipyridine (200

mg, 1.087 mmol) in THF (6 mL) was added dropwise. On adding the bipyridine to the amide solution, a dark orange-red solution was obtained. After 1 h at -78 °C, the dark brown solution was treated at once with 1,6-dibromohexane (663 μL , 4.35 mmol) in THF (2 mL). The resulting solution was stirred for 1 h at -78 °C and at room temperature overnight. The reaction mixture was quenched by slow addition of 2 mL of water. Subsequently, 8 mL of phosphate buffer (pH 7) were added, and the reaction mixture was extracted with diethyl ether. The organic layer was dried over magnesium sulfate, and the ether was removed under reduced pressure at room temperature. The resulting yellow-brown oil was dissolved in CHCl_3 and purified by column chromatography (neutral aluminum oxide, diethyl ether/hexane 1/1) yielding **2** as a white solid (212 mg, 56%).

^1H NMR (CDCl_3 , δ , ppm): 1.57–1.2 (m, 6H, $c'-e'$), 1.67 (bqv, 2H, $J = 7.14$, 14.28 Hz, f'), 1.82 (qv, 2H, $J = 7.14$, 13.73 Hz, b'), 2.40 (s, 3H, a), 2.67 (t, 2H, $J = 7.14$ Hz, a'), 3.39 (t, 2H, $J = 7.14$ Hz, g'), 7.11 (d, 2H, $J = 4.4$ Hz, 5,5'), 8.25 (bs, 2H, 3,3'), 8.48 (t, 2H, $J = 4.4$ Hz, 6,6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 21.1 (Ca), 28.0, 28.5, 29.1 ($Cc'-e'$), 30.3 (Cf'), 32.7 (Cb'), 33.8 (Cg'), 35.4 (Ca'), 121.2, 122.0 ($C3,3'$), 123.8, 124.6 ($C5,5'$), 148.1 (C4), 148.9, 148.9 ($C6,6'$), 152.6 ($C4'$), 156.0, 156.1 ($C2,2'$) UV-vis (CH_3CN): λ_{max} (ϵ) = 282 (53,208), 240 (45,283) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). IR: 3010, 3056, 2964, 2924, 2854 (CH aromatic), 1594, 1547 ($\text{C}=\text{C}$ and $\text{C}=\text{N}$), 1466, 1431 ($\text{C}=\text{C}$, $\text{C}=\text{N}$, CH aliphatic and $\text{CH}_2\text{-Br}$). GCMS (diethyl ether): $m/z = 347$ ($\text{C}_{18}\text{H}_{23}\text{BrN}_2^+$). MALDI-TOF MS (dithranol): $m/z = 347.36$ ($\text{C}_{18}\text{H}_{23}\text{BrN}_2^+$). ELEM. ANAL. Calcd. for $\text{C}_{18}\text{H}_{23}\text{BrN}_2$ (347.293): C, 62.25%; H, 6.68%; N, 8.07%. Found: C, 62.31%; H, 6.61%; N, 7.92%. mp: 41–42 °C.

4-(7-Hydroxyheptyl)-4'-methyl-2,2'-bipyridine (3)

2 (100 mg, 0.29 mmol) and K_2CO_3 (1.15 g, 8.1 mmol) were refluxed in an equimolar volume of dioxane/water (10 mL). After 48 h, the reaction mixture was allowed to cool to room temperature. The product was extracted with chloroform. The organic layer was washed with H_2O (3×10 mL) and dried over magnesium sulfate. Concentration under reduced pressure yielded a brown oil that was purified by column chromatography (neutral aluminum oxide, methanol/ethyl acetate 1/99), yielding **3** as a white solid (35 mg, 42%).

^1H NMR (CDCl_3 , δ , ppm): 1.44–1.36 (m, 6H, c'–e'), 1.53 (bqv, 2H, $J = 6.6$, 13.73 Hz, f'), 1.72–1.67 (bqv, 2H, $J = 7.7$, 14.28 Hz, b'), 2.44 (s, 3H, a), 2.69 (t, 2H, $J = 7.7$ Hz, a'), 3.62 (q, 2H, $J = 6.6$ Hz, g'), 7.13 (d, 2H, $J = 4.94$ Hz, 5,5'), 8.22 (bs, 2H, 3,3'), 8.54 (t, 2H, $J = 4.94$ Hz, 6,6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 21.1 (Ca), 25.5, 29.0 (Cc'–e'), 30.1 (Cf'), 32.6 (Cb'), 35.3 (Ca'), 62.8 (Cg'), 121.2, 121.9 (C3,3'), 123.8, 124.5 (C5,5'), 148.0 (C4), 148.8, 148.9 (C6,6'), 152.7 (C4'), 155.9, 156.1 (C2,2'). UV–vis (CH_3CN): λ_{max} (ϵ) = 282 (43,721), 240 (37,209) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). IR: 3318, 3068, 3031 (OH), 2916, 2850 (CH aromatic), 1597, 1548 (C=C and C=N), 1463, 1414 (C=C, C=N and CH aliphatic), 1068 (C–OH primary alcohol), 735 (C–H aromatic). GC–MS (diethyl ether): $m/z = 284$ ($\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}^+$). MALDI–TOF–MS (dithranol): $m/z = 285.28$ ($\text{C}_{18}\text{H}_{24}\text{N}_2\text{OH}^+$). ELEM. ANAL. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}$ (284.396): C, 76.02%; H, 8.51%; N, 9.85%. Found: C, 75.62%; H, 8.46%; N, 9.80%. mp: 69–71 °C.

4-(7-Heptyl methyl methacrylate)-4'-methyl-2,2'-bipyridine (4)

To a cold solution of **3** (50 mg, 0.17 mmol) in 7 mL of CH_2Cl_2 (ice bath), methacroyl chloride (22.12 μL , 0.23 mmol) and triethylamine (36.70 μL , 0.26 mmol) were added dropwise under an argon atmosphere. The reaction mixture was allowed to warm to room temperature overnight and was then washed with a saturated solution of K_2CO_3 (2×5 mL) and with H_2O (3×5 mL). The organic layer was dried over magnesium sulfate, and the dichloromethane was removed under reduced pressure (avoid heating). The crude product was purified by column chromatography (neutral aluminum oxide, ethyl acetate) and then passed over Biobeads S-X12 (CH_2Cl_2) to remove impurities. Compound **4** was isolated as a colorless and hygroscopic oil in 79% yield (49 mg).

^1H NMR (CDCl_3 , δ , ppm): 1.29–1.37 (m, 6H, c'–e'), 1.72–1.59 (m, 4H, b'–f'), 1.94 (s, 3H, k'), 2.44 (s, 3H, a), 2.69 (t, 2H, $J = 7.7$ Hz, a'), 4.13 (t, $J = 6.6$ Hz, 2H, g'), 5.54 (s, 1H, j'-olefinic), 6.08 (s, 1H, j'-olefinic), 7.13 (d, $J = 4.94$ Hz, 2H, 5,5'), 8.23 (bs, 2H, 3,3'), 8.55 (t, $J = 4.94$ Hz, 2H, 6,6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 18.6 (Ck'), 21.5 (Ca), 26.2, 28.9, 29.3, 29.4 (Cc'–e'), 30.0 (Cf'), 30.6 (Cb'), 35.8 (Ca'), 65.0 (Cg'), 121.6, 122.3 (C3,3'), 124.2, 124.9 (C5,5'), 125.5 (Cj'), 136.8 (Ci'), 148.4 (C4), 149.3 (C6,6'), 153.1 (C4'), 156.4 (C2,2'), 167.8 (Ch'). UV–vis (CH_3CN): λ_{max} (ϵ) = 281 (53,831), 241 (46,168) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). IR:

2928, 2856 (CH aromatic), 1716 (C=O), 1594, 1553 (C=C and C=N), 1459, 1180, (CH_2OCO), 822. GCMS (diethyl ether): $m/z = 352$ ($\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2^+$). MALDI–TOF–MS (dithranol): $m/z = 353.50$ ($\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2\text{H}^+$). ELEM. ANAL. Calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$ (352.340): C, 74.97%; H, 8.01%; N, 7.95%. Found: C, 74.50%; H, 7.95%; N, 7.89% (for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2 \times 0.125 \text{H}_2\text{O}$).

4-(3-Hydroxypropyl)-4'-methyl-2,2'-bipyridine (5)

A solution of diisopropylamine (1.69 mL, 11.94 mmol) in THF (10 mL) was cooled to -78 °C and was slowly treated with a solution of 1.6 M *n*-butyllithium in *n*-hexane (8.5 mL, 13.6 mmol). The resulting pale yellow solution was stirred for 20 min, and then **1** (2.0 g, 10.85 mmol) in THF (100 mL) was added dropwise. The mixture was stirred for 1 h at -78 °C, and then 2-bromoethoxy-*tert*-butyl-dimethyl-silane (2.86 g, 11.94 mmol) in THF (20 mL) was added within 10 min. The reaction mixture was allowed to warm at room temperature overnight and was then quenched by slow addition of 5 mL of water. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 , was washed with water (3×20 mL), and was dried over magnesium sulfate. The crude product was stirred overnight in HCl (1 M), and then neutralized to pH 7 with NaOH (1 M). The resulting solution was extracted with chloroform and dried over magnesium sulfate. After removal of the solvent, **5** was isolated as a yellow oil that was purified by column chromatography (neutral aluminum oxide, ethyl acetate). Yield: 1.16 g (47%).

^1H NMR (CDCl_3 , δ , ppm): 1.49 (t, $J = 4.9$ Hz, OH), 2.02–1.98 (m, 2H, b'), 2.44 (s, 3H, a), 2.81 (t, $J = 8.09$ Hz, 2H, a'), 3.70 (dt, $J = 6.6$, 4.9 Hz, 2H, c'), 7.07 (t, $J = 4.94$ Hz, 2H, 5,5'), 8.16 (d, 2H, $J = 5.50$ Hz, 3,3'), 8.47 (dd, 2H, $J = 4.94$, 10.98 Hz, 6,6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 21.2 (Ca), 31.6 (Cb'), 33.1 (Ca'), 61.8 (Cc'), 121.3, 122.1 (C3,3'), 123.9, 124.7 (C5,5'), 148.2 (C4), 148.9, 149.1 (C6,6'), 151.9 (C4'), 156.0, 156.2 (C2,2'). UV–vis (CH_3CN): λ_{max} (ϵ) = 281 (34,863), 241 (29,900) nm ($\text{L mol}^{-1} \text{cm}^{-1}$). IR: 3319, 3058 (OH), 2934, 2866 (CH aromatic, alkyl CH_2), 1594, 1553 (C=C and C=N), 1461 (CH aliphatic), 1055, 820. GC–MS (ethyl acetate): $m/z = 228$ ($\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}^+$). MALDI–TOF–MS. (dithranol): $m/z = 229.24$ ($\text{C}_{14}\text{H}_{16}\text{N}_2\text{OH}^+$). ELEM. ANAL. Calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ (228.290): C, 73.66%; H, 7.06%; N, 12.27%. Found: C, 73.68%; H, 7.39%; N, 11.03%.

4-(3-Hydroxypropyl methyl methacrylate)-4'-methyl-2,2'-bipyridine (6)

To a cold solution of **5** (400 mg, 1.75 mmol) in 12 mL of CH₂Cl₂ (ice bath), methacryloyl chloride (220.5 μ L, 2.28 mmol) and triethylamine (366 μ L, 2.63 mmol) were added dropwise under argon atmosphere. The reaction, workup, and purification procedures were performed as described in the preparation of compound **4**. Compound **6** was isolated as a colorless and hygroscopic oil in 88% yield (461 mg).

¹H NMR (CDCl₃, δ , ppm): 1.94 (s, 3H, g'), 2.06–2.15 (m, 2H, b'), 2.44 (s, 3H, a), 2.82 (t, J = 8.09 Hz, 2H, a'), 4.21 (t, 2H, J = 6.6 Hz, c'), 5.56 (s, 1H, f'-olefinic), 6.09 (s, 1H, f'-olefinic), 7.15 (t, 2H, J = 4.94 Hz, 5,5'), 8.25 (d, J = 8.24 Hz, 2H, 3,3'), 8.55 (dd, 2H, J = 4.94, 11.54 Hz, 6,6'). ¹³C{¹H} NMR (CDCl₃, δ , ppm): 18.3 (Cg'), 21.2 (Ca), 29.24 (Cb'), 31.9 (Ca'), 63.8 (Cc'), 121.2, 122.1 (C3,3'), 123.8, 124.7 (C5,5'), 125.5 (Cf'), 136.3 (Ce'), 148.2 (C4), 148.9, 149.2 (C6,6'), 151.3 (C4'), 155.9, 156.3 (C2,2'), 167.3 (Cd'). UV-vis (CH₃CN): λ_{\max} (ϵ) = 281 (45,322), 241 (38,871) nm (L mol⁻¹ cm⁻¹). IR: 3054 (CH₂ olefinic), 2959, 2926 (CH aromatic), 1716 (C=O), 1594, 1555 (C=N and C=C), 1459 (CH₂OCO), 1159, 1034 (C—CO=C), 816. GC-MS (diethyl ether): m/z = 296 (C₁₈H₂₀N₂O₂⁺). MALDI-TOF-MS (dithranol): m/z = 297.36 (C₁₈H₂₀N₂O₂H⁺). ELEM. ANAL. Calcd. for C₁₈H₂₀N₂O₂ (296.364): C, 72.95%; H, 6.80%; N, 9.45%. Found: C, 72.41%; H, 6.75%; N, 9.38% (for C₁₈H₂₀N₂O₂ \times 0.11 H₂O).

Poly[(methyl methacrylate)-co-(methacrylic acid 4-(3-propyl)-4'-methyl-2,2'-bipyridine)] (7)

Methyl methacrylate (1.03 g, 10.12 mmol), **6** (180 mg, 0.61 mmol), and 2,2'-azobisisobutyronitrile (AIBN, 1 mol %) (16 mg, 0.10 mmol) were dissolved in 7 mL toluene and heated to 75 °C. The polymerization reaction was continued for 20 h. The reaction mixture was then poured into 15 mL of pentane, yielding 870 mg of **7** as a white solid (78%).

¹H NMR (CD₂Cl₂, δ , ppm): 0.85 (bs, 30H, CH₃-PMMA), 1.02 (bs, 16H, CH₃-PMMA), 2.14–1.59 (bm, 34H, b' and CH₂-PMMA), 2.45 (bs, 2H, a), 2.79 (bs, 2H, a'), 3.60 (s, 45H, OCH₃-PMMA), 4.01 (bs, 2H, c'), 7.16 (bs, 2H, 5,5'), 8.25 (bs, 2H, 3,3'), 8.56 (bd, 2H, J = 15.38 Hz, 6,6'). UV-vis (CH₃CN): λ_{\max} (ϵ) = 281 (286,676), 241 (245,868) nm (L mol⁻¹ cm⁻¹). IR: 2995, 2950 (CH aromatic), 1723 (C=O), 1596, 1480, 1434 (C=C and C=N), 1386, 1268, 1239, 1190 (C—O—C), 1120, 989

(CH₂), 826, 841, 750. GPC (DMF): number-average molecular weight (M_n) = 13,430 g \times mol⁻¹, weight-average molecular weight (M_w) = 31,550 g \times mol⁻¹, polydispersity index (PDI) = 2.35.

Synthesis of [Ru(bpy)₂Cl₂] (8), [Ru(dMbp)₂Cl₂] (9), and [Ru(phen)₂Cl₂] (10)

[Ru(bpy)₂Cl₂] (**8**) was prepared with an already published procedure.²² A suspension of RuCl₃ \times 3 H₂O (3.31 g, 16 mmol) and 2,2'-bipyridine (5 g, 32.01 mmol) in DMF (30 mL) was heated under reflux for 12 h. After that, most of the DMF was distilled off. The resulting reaction mixture was allowed to cool to 20 °C and LiCl (4.52 g, 106.7 mmol) as well as acetone (125 mL) were added. Finally, the mixture was stored in a refrigerator overnight to yield black-green crystals. After filtering and washing with water until the filtrate was colorless, and repeating washing with aliquots of diethyl ether (20 mL), the complex was obtained as black-green crystals. The crystals were dried under reduced pressure.

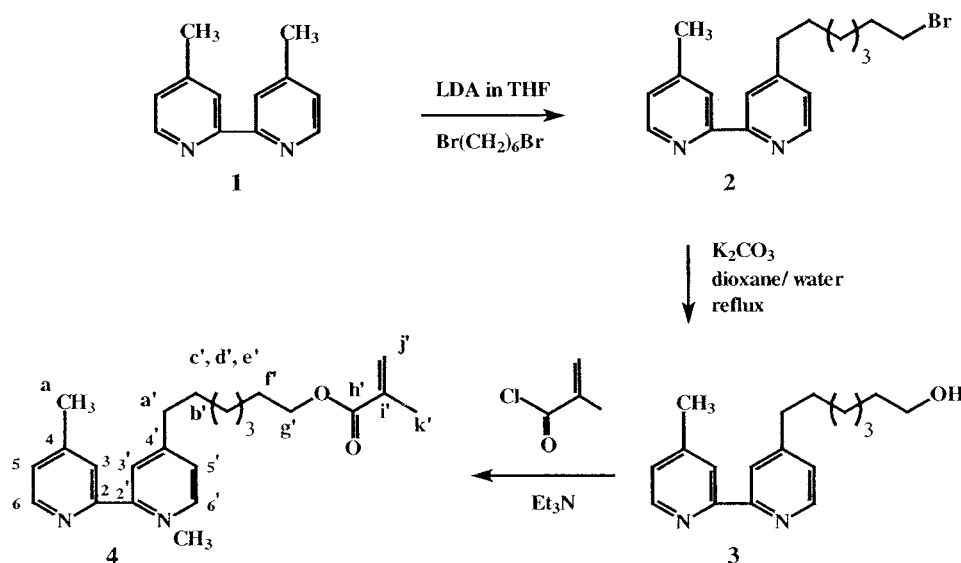
9 and **10** were prepared following the same synthetic route.

Grafting Procedure

In a general procedure, a suspension of precursor **8** (31.65 mg, 0.065 mmol) and AgSbF₆ (44.9 mg, 0.13 mmol) were stirred overnight in acetone, followed by filtration of the formed AgCl. The [Ru(bpy)₂(OMe₂)₂]²⁺ 2SbF₆⁻ solution (**11**) was then added to a solution of copolymer **7** (60 mg, 0.032 mmol) in acetone. The reaction mixture was refluxed for 60 h. After cooling to ambient temperature, the reaction mixture was filtered through paper filter and a short Biobeads S-X1 column and then purified by size exclusion chromatography (Biobeads S-X1, CH₂Cl₂), yielding **14a** as an orange powder. The same procedure was applied for **15a** and **16a**.

14a: 44 mg (46%)

¹H NMR (CD₂Cl₂, δ , ppm): 0.74 (bs, 30H, CH₃-PMMA), 0.92 (bs, 16H, CH₃-PMMA), 1.62–2.07 (bm, 34H, b' and CH₂-PMMA), 2.50 (bs, 2H, a), 2.86 (bs, 2H, a'), 3.50 (s, 45H, OCH₃-PMMA), 3.95 (bs, 2H, c'), 7.10–7.28 (m, 2H, 5,5'), 7.31–7.54 (m, 6H, 6,6' and 6,6'-bpy), 7.59–7.70 (m, 4H, 5,5'-bpy), 7.93–8.05 (m, 4H, 4,4'-bpy), 8.28 (s, 2H, 3,3'), 8.39 (s, 4H, 3,3'-bpy). UV-vis (CH₃CN): λ_{\max} (ϵ) = 245 (3,700,398), 286 (432,383), 455 (687,883) nm (L mol⁻¹ cm⁻¹). Emission (CH₃CN): λ_{\max}



Scheme 1. Synthesis of methyl methacrylate-functionalized bipyridine **4** via a bromo intermediate.

= 616 (λ_{ex} = 456 nm). IR: 2995, 2950 (CH aromatic), 1722 (C=O), 1604, 1435 (C=C and C=N), 1242, 1190 (C—O—C), 986, 842, 764 (C—H aromatic), 657 (SbF_6^-).

15a: 45 mg (75%)

^1H NMR (CD_2Cl_2 , δ , ppm): 0.74 (bs, 30H, CH_3 -PMMA), 0.91 (bs, 16H, CH_3 -PMMA), 1.46–2.11 (bm, 34H, b' and CH_2 -PMMA), 2.47 (bs, 2H, a), 2.80 (bs, 2H, a'), 3.50 (s, 45H, OCH_3 -PMMA), 3.95 (bs, 2H, c'), 7.38–7.12 (m, 4H, 5,5'-dMbpY and 2H, 3,3'-bpyPMMA), 7.38–7.6 (m, 4H, 6,6'-dMbpY), 8.10–8.40 (m, 2H, 6,6'-bpy-PMMA and 4H, 3,3'-dMbpY), 8.45–8.65 (b, 2H, 5,5'). UV-vis (CH_3CN): λ_{max} (ϵ) = 258 (389,434), 287 (433,207), 462 (697,358) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). Emission (CH_3CN): λ_{max} = 621 (λ_{ex} = 460 nm). IR: 2995, 2951 (CH aromatic), 1986, 1723 (C=O), 1620, 1480, 1435, (C=C and C=N), 1242, 1191 (C—O—C), 987, 841, 751 (C—H aromatic), 657 (SbF_6^-).

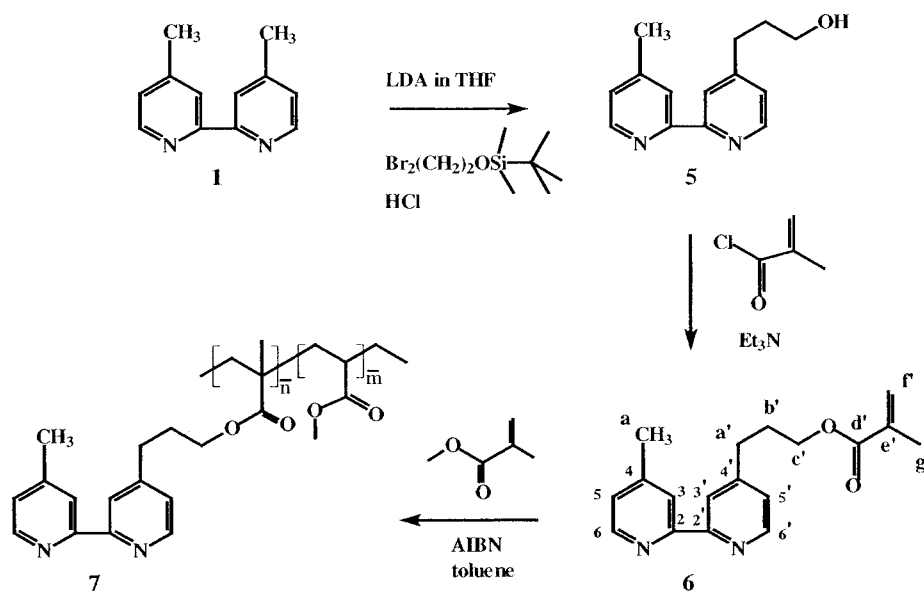
16a: 38 mg (62%)

^1H NMR (CD_2Cl_2 , δ , ppm): 0.74 (bs, 30H, CH_3 -PMMA), 0.91 (bs, 16H, CH_3 -PMMA), 1.49–2.07 (bm, 34H, b' -bpy and CH_2 -PMMA), 2.49 (bs, 2H, a-bpy), 2.83 (bs, 2H, a' -bpy), 3.50 (s, 45H, OCH_3 -PMMA), 3.95 (bs, 2H, c' -bpy), 7.02–7.26 (m, 2H, 5,5'-bpy), 7.36–7.77 (m, 2H, 3-phen and 1H, 8-phen and 2H, 6,6'-bpy), 7.78–7.94 (m, 1H, 8-phen and 2H, 2-phen), 8.08–8.52 (m, 2H, 3,3'-

bpy and 4H, 5,6-phen and 2H, 9-phen), 8.52–8.66 (bd, 4H, 4,7-phen). UV-vis (CH_3CN): λ_{max} (ϵ) = 264 (397,590), 284 (427,711), 449 (676,204) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). Emission (CH_3CN): λ_{max} = 603 (λ_{ex} = 450 nm). IR: 2962 (CH aromatic), 1977, 1725 (C=O), 1619, 1483, 1434 (C=C and C=N), 1259, 1191 (C—O—C), 1088, 1016, 842, 798 (C—H conjugated system), 657 (SbF_6^-).

RESULTS AND DISCUSSION

The synthesis of bipyridine metal complex containing polymers, which combine both the features of metal complexes and polymers, has been explored extensively in the last years.^{23,24} Here, we describe several synthetic strategies to prepare monofunctionalized 2,2'-bipyridines and a copolymer with bipyridine units in the side chain. The respective Ru(II) polypyridyl complexes were obtained utilizing a grafting approach. For the preparation of the hydroxy-functionalized bipyridines, two different routes were used starting from the same 4,4'-dimethyl-2,2'-bipyridine **1**, via a bromo-(C_7 spacer, **2**) or a silylated-(C_3 spacer, **5**) intermediate (Schemes 1 and 2). Reaction of equimolar amounts of **1** with lithium diisopropylamide (LDA) in THF generates the monolithiated species, which is efficiently quenched with alkyl dibromides (Scheme 1). Slow addition of the dibromoalkane has to be avoided as it yields linked bipyridines. Specifically, treatment of the di-



Scheme 2. Synthesis of bipyrindine-containing poly(methyl methacrylate) **7** via a silylated intermediate ($\bar{n} = 3$, $\bar{m} = 33$, based on GPC results).

methyl compound **1** with LDA in THF at $-78\text{ }^{\circ}\text{C}$ for 1 h resulted in the dark brown monolithiated compound.¹⁹ Addition of a THF solution of the appropriate dibromide to the carbanion species yielded the crude product, which was purified by column chromatography on neutral alumina. The obtained bromo-functionalized bipyrindine **2** was characterized by NMR, mass spectrometry (GC-MS and MALDI-TOF-MS), IR, UV-vis, and elemental analysis.

The bromo-alkyl-substituted 2,2'-bipyridine **2** was subsequently converted into the corresponding alcohol **3**, as shown in Scheme 1. The hydroxy functionality was chosen because it can easily be used for a variety of chemical transformations or reactions. Here, we chose the ester-type coupling with methacryloyl chloride in the presence of a base (triethylamine) at $0\text{ }^{\circ}\text{C}$ to prepare the bipyrindine-functionalized methacrylate **4** in 79% yield.

The proton and carbon chemical shifts for the bromo- (**2**), hydroxy- (**3**), and methacrylate- (**4**) functionalized bipyrindines were assigned based on 2D techniques (^1H - ^1H COSY and ^1H - ^{13}C HMQC). The ^1H - ^1H COSY spectrum (Fig. 1) reveals a slightly complicated coupling pattern in the aliphatic region (1.82–1.2 ppm) because of the relatively long alkyl spacer between the ring and the functional moiety. The cross peaks corresponding to the three-bond correlation $\text{H}-\text{C}-\text{C}-\text{H}$ (multiple-bond coupling) were exemplified for the case of aromatic protons H^3 and

$H^{3'}$. Thus, one can identify the cross peaks corresponding to their couplings with protons H^5 and $H^{5'}$, respectively, as well as with the aliphatic protons $^a\text{CH}_3$. The IR spectra (Fig. 2) also confirmed the successful modifications of the side chain. The formation of the characteristic bands for the hydroxy-derivatized bipyrindine **3** as com-

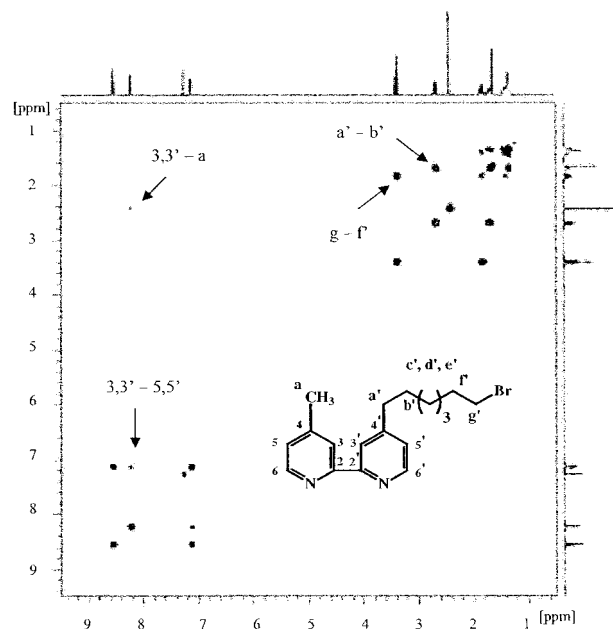


Figure 1. ^1H - ^1H COSY spectra of compound **2** in CDCl_3 .

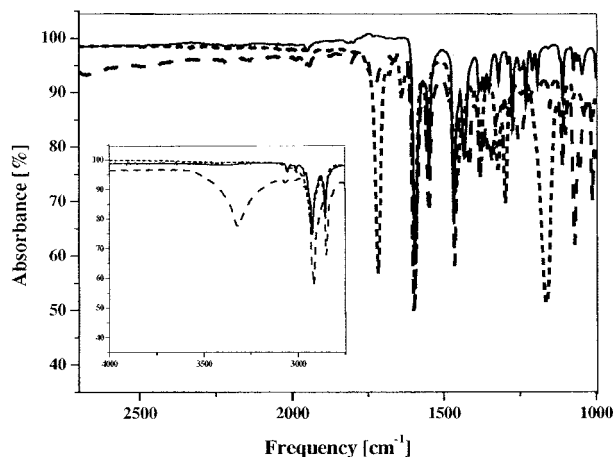


Figure 2. IR spectra of **2** (solid line), **3** (dashed line), and **4** (dotted line).

pared to the bromo-functionalized bipyridine **2** can be easily observed: 3318 cm^{-1} (OH intramolecular) and 1068 cm^{-1} (significant for the C—OH of a primary alcohol). Furthermore, the disappearance of the bands corresponding to the alcohol **3** and the appearance of new bands at 1716 cm^{-1} (C=O), 1459 and 1180 cm^{-1} ($\text{CH}_2\text{—O—C=O}$) confirmed the successful methacrylate functionalization. Similarly, a bipyridine-modified methacrylate **6**, differing in the spacer length (C_3), was synthesized in a two-step reaction (Scheme 2). The hydroxy intermediate **5** was obtained by the reaction of the monolithiated 4,4'-dimethyl-2,2'-bipyridine with 2-bromoethoxy-*tert*-butyl-dimethyl-silane, followed by the cleavage of the Si—O bond in a strong acidic medium. In a second step, an ester coupling was performed with methacryloyl chloride to yield the bipyridine-functionalized methacrylate **6** in 88% yield. NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$), and ^1H - ^1H COSY, IR, GC and MALDI-TOF-MS and elemental analyses confirmed the proposed structure as well as the purity for compounds **5** and **6**.

The straightforward approach *via* the silylated intermediate drastically reduced the overall preparation time and generated products in higher yields. Moreover, the reaction could be performed on relatively large scale. This was the reason for choosing the C_3 -spaced bipyridine ligand **5** for the copolymerization followed by a grafting approach.

A copolymer based on PMMA with a methyl methacrylate (MMA)-modified bipyridine moiety as a functional unit (short spacer C_3) was prepared. Free-radical polymerization with AIBN as an initiator (1 mol %) was then used for the copo-

lymerization of **6** with MMA (Scheme 2). The obtained polymer **7** was characterized by means of ^1H NMR, UV-vis, IR, as well as GPC, revealing an M_n of $13,430\text{ g} \times \text{mol}^{-1}$ (GPC, DMF), a PDI of 2.35, and a bipyridine content of 6.2% (NMR). Therefore, an average number of .7 bipyridine units per polymer chain was calculated. Figure 3 depicts the NMR spectra of compounds **5**, **6**, and **7**. A characteristic shift of the $^c\text{CH}_2$ protons toward a low magnetic field could be observed for the methacrylate monomer **6** as compared to the $^c\text{CH}_2$ protons of the hydroxyl-functionalized bipyridine **5**, proving the formation of the MMA derivative. Furthermore, resonances in the aromatic region remained unshifted, indicating that the bipyridine monomer was successfully incorporated into the PMMA chain. DSC was used to investigate the thermal properties of material **7**, revealing a T_g of $83\text{ }^\circ\text{C}$.

To perform the grafting of the ruthenium complexes, a modified method originally reported by Wu and Fraser²⁵ was followed. A series of *bis*-ruthenium(II) precursor complexes was used to construct a class of graft copolymers based on copolymer **7**: **8**, **9**, and **10**. The $[\text{Ru}(\text{bpy})_2(\text{OMe}_2)_2]^{2+} 2\text{ SbF}_6^-$ (**11**), $[\text{Ru}(\text{dMbp})_2(\text{OMe}_2)_2]^{2+} 2\text{ SbF}_6^-$ (**12**), and $[\text{Ru}(\text{phen})_2(\text{OMe}_2)_2]^{2+} 2\text{ SbF}_6^-$ (**13**) synthons were obtained by stirring the corresponding ruthenium chlorides with a twofold excess of AgSbF_6 in acetone overnight (Scheme 3). The filtrates were then added to a suspension of copolymer **7** in acetone in a 2:1 excess (mol %, on the basis of the bipyridine content of copolymer **7**). Scheme 4 shows a schematic synthesis of the graft copolymers. After

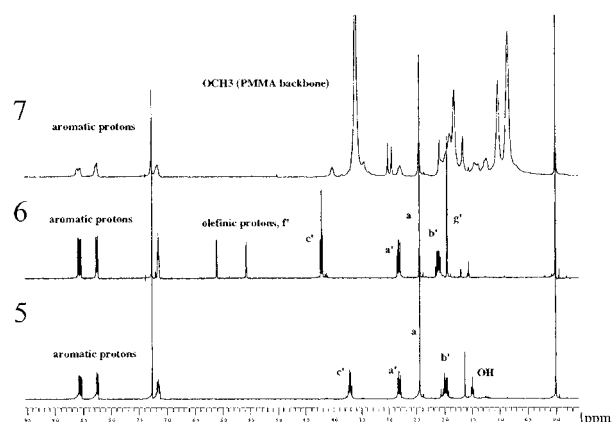
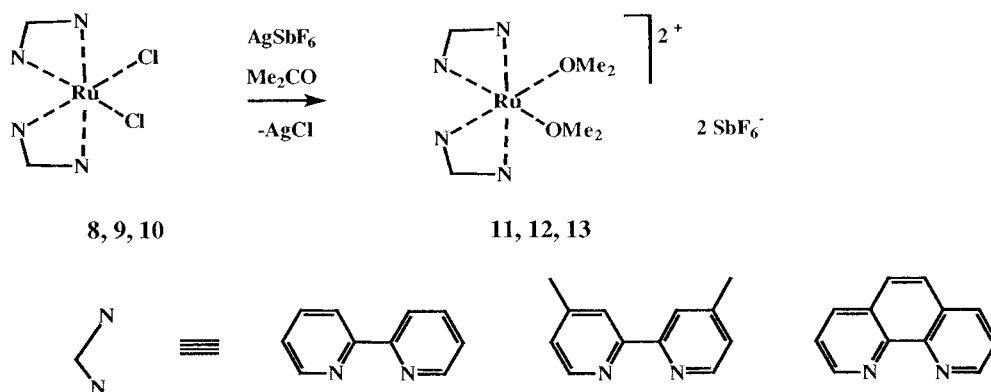


Figure 3. ^1H NMR spectra of 4-methyl-4'-(3-hydroxypropyl)-2,2'-bipyridine **5** (bottom), the corresponding methacrylate monomer **6** (middle), and poly(methyl methacrylate) copolymer **7** (top). **5** and **6** were recorded in CDCl_3 and **7** was recorded in CD_2Cl_2 .



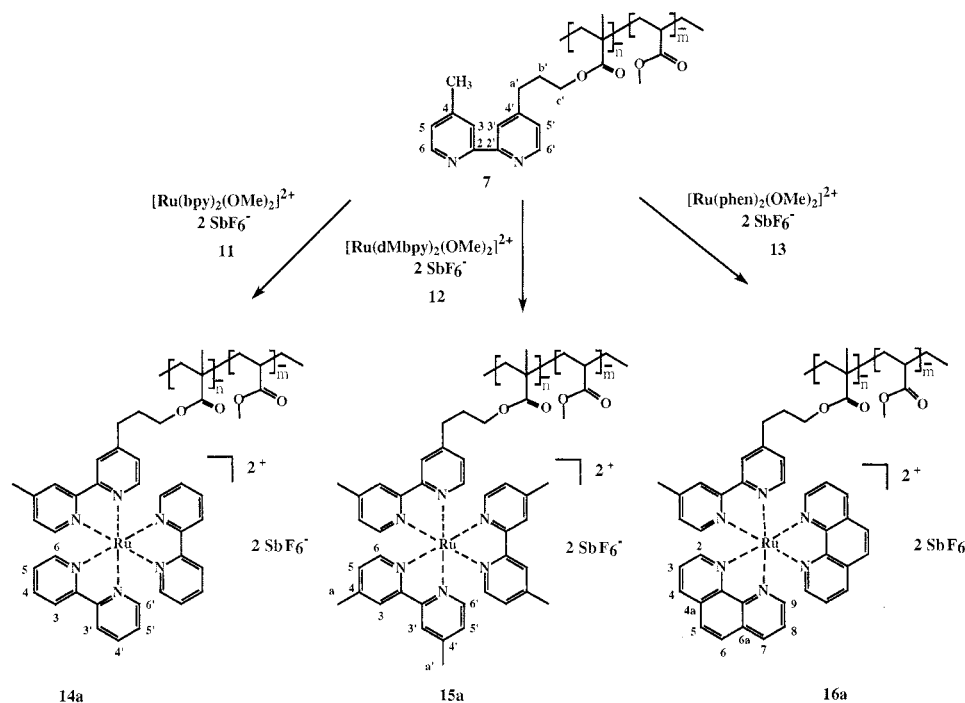
Scheme 3. Schematic synthesis of the Ru(II) precursor complexes **11**, **12**, and **13** used in the grafting procedure.

60 h of reflux, the reaction mixture was filtered, concentrated, and purified by size exclusion chromatography (Biobeads S-X1, CH_2Cl_2). The resulting graft copolymers **14a**, **15a**, and **16a** were dried under reduced pressure to yield orange powders.

To prove that the photophysical properties of the *tris*-Ru(II) bipyridine complexes were not influenced by the incorporation into copolymer **7**, three modified *tris*-Ru(II) model complexes were prepared with **5** (L) and the three different Ru(II) precursor complexes used in the grafting approach (**8**, **9**, and **10**): $[\text{Ru}(\text{bpy})_2\text{L}](\text{SbF}_6)_2$ (**14b**), $[\text{Ru}(\text{dMbpy})_2\text{L}](\text{SbF}_6)_2$

(**15b**), and $[\text{Ru}(\text{phen})_2\text{L}](\text{SbF}_6)_2$ (**16b**).²⁶ For comparison, their spectroscopic data (NMR, UV-vis, and emission) were collected. In addition, their compositions were verified by MALDI-TOF MS revealing the expected molecular mass peaks.

The proton assignments of the graft copolymers were solved with the aid of ^1H - ^1H COSY spectra of their corresponding model complexes (**14b**, **15b**, and **16b**). No shift of the aromatic protons was detected for the grafted copolymers when compared to their corresponding model complexes, but the resonances were broader and



Scheme 4. Synthesis of the graft copolymers **14a**, **15a**, and **16a**.

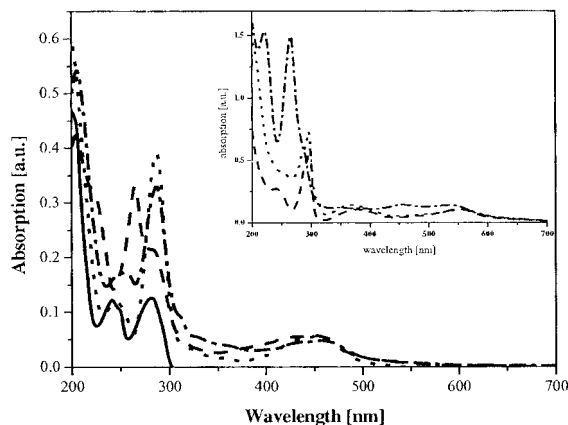


Figure 4. UV-vis spectra of copolymers **7** (solid line), **14a** (dashed line), **15a** (dotted line), and **16a** (dashed dotted line) before and after grafting. The inset shows the absorption spectra for the ruthenium precursors **8** (dashed line), **9** (dotted line), and **10** (dashed dotted line). The spectra of the precursor complexes were recorded in methanol, and the copolymer and the graft copolymers were monitored in CH_3CN .

not well resolved because of the polymeric character of the materials. The integration of the aromatic protons clearly revealed the presence of one bpy-PMMA ligand and two bpy ligands from the precursors, confirming the complete grafting of the *bis*-bipyridine ruthenium complexes to the polymer chain. For the graft copolymers **14a**, **15a**, and **16a**, the observed IR bands showed only few significant changes when compared with the starting copolymer **7**. The appearance of a new band at 657 cm^{-1} was characteristic for the hexafluoroantimonate counterion. Unfortunately, the GPC method could not be applied to the ruthenium containing polymers **14a**, **15a**, and **16a** because of strong interactions with the column material. Similar problems have already been reported in the literature.^{18,27}

The successful incorporation of the ruthenium precursor complexes into the copolymer could be easily checked with UV-vis spectroscopy. In all cases, the disappearance of the two bands corresponding to a *bis*-Ru(II) complex and the appearance of the characteristic metal-to-ligand charge-transfer band for the *tris*-ruthenium(II) complexes between 445 and 465 nm could be detected (Fig. 4). The emission spectra of the three graft copolymers showed the expected emission bands of a Ru(II) *tris*-bipyridine complex at 616 nm for compound **14a** ($\lambda_{\text{ex}} = 456\text{ nm}$), 621 nm for compound **15a** ($\lambda_{\text{ex}} = 460\text{ nm}$), and 603 nm for compound **16a** ($\lambda_{\text{ex}} = 450\text{ nm}$), respectively (Fig. 5).

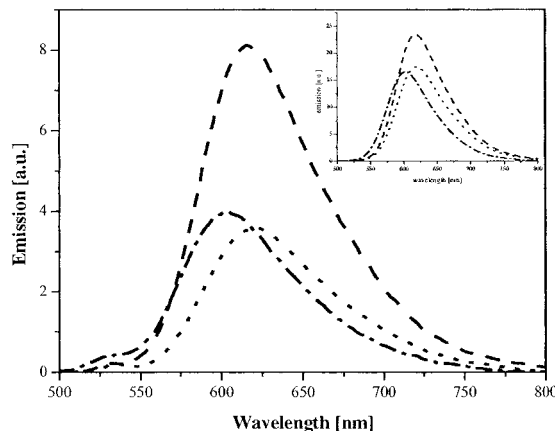


Figure 5. Emission spectra of graft copolymers **14a** (dashed line), **15a** (dotted line), and **16a** (dashed dotted line). The inset shows the absorption spectra for their corresponding model ruthenium complexes: **14b** (dashed line), **15b** (dotted line), and **16b** (dashed dotted line). All spectra were recorded in CH_3CN .

For comparison, the emission spectra of the model complexes **14b**, **15b**, and **16b** are also depicted in Figure 5.

Redox properties of the model complexes and the respective graft copolymers were determined by cyclic voltammetry (Fig. 6) and are summarized in Table 1. The oxidation potentials and the shapes of the cyclic voltammograms did not differ much between the graft copolymers and their cor-

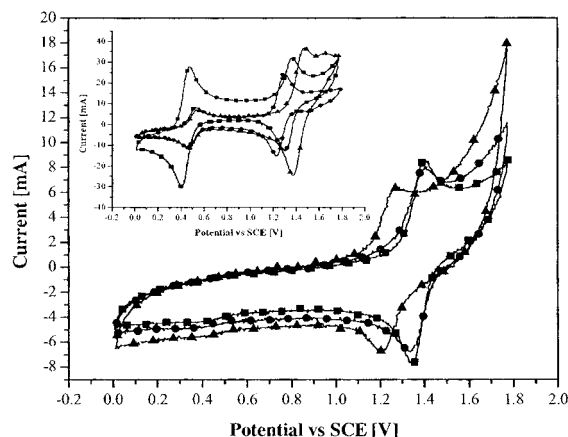


Figure 6. Overview of the electrochemical properties of the graft copolymers **14a** (squares), **15a** (circles), and **16a** (triangles). The inset shows the CV results for their corresponding model ruthenium complexes: **14b** (squares), **15b** (circles), and **16b** (triangles). All spectra were recorded in CH_2Cl_2 (freshly distilled from CaH_2) containing $0.1\text{ M } n\text{-Bu}_4\text{PF}_6$.

Table 1. Electrochemical and Photophysical Data for Graft Copolymers **14a**, **15a**, and **16a** and for Their Corresponding Model Complexes **14b**, **15b**, and **16b**. The Oxidation Potential of the Ferrocene/Ferrocenium Couple (Fc/Fc^+) Is Given in Brackets.

Compound	Oxidation Potentials F_{ox} (vs Fc/Fc^+) (eV)	Absorption λ_{max} (nm)	Emission λ_{max} (nm)
Graft copolymer 14a	1.37 (0.49)	455	616
Graft copolymer 15a	1.26 (0.49)	462	621
Graft copolymer 16a	1.42 (0.50)	449	603
Model complex 14b	1.33 (0.44)	455	617
Model complex 15b	1.25 (0.46)	462	618
Model complex 16b	1.37 (0.48)	449	602

responding model complexes, proving that the PMMA backbone did not modify the properties of a *tris*-Ru(II) species and that only one active species was formed throughout the grafting process. An overview of the photophysical and electrochemical properties of the graft copolymers **14a**, **15a**, and **16a** and of their corresponding model complexes **14b**, **15b**, and **16b** is given in Table 1. The results agreed with the literature data.²⁸ In summary, the new polymeric materials **14a**, **15a**, and **16a** displayed similar photophysical and electrochemical properties as compared to the complexes **14b**, **15b**, and **16b**. Thus, starting from the mother copolymer **7** with the introduced grafting procedure, a straightforward synthetic approach is accessible to gain defined materials with tunable as well as predictable properties. The advantages of the novel graft copolymers are their film-forming PMMA backbone that does not influence the complex characteristics. However, PMMA increases the quantum efficiency in the range of 2–3%.²⁹ The study of the polymers **14a**, **15a**, and **16a** in photoelectrochemical cells and the investigation of the resulting electron-transfer properties in polymeric materials will be part of further investigations.

CONCLUSIONS

The described selective *monofunctionalization* of 4,4'-dimethyl-2,2'-bipyridine allows the introduction of different reactive groups. The hydroxy-functionalized bipyridine proved to be a versatile starting material for the synthesis of bipyridine derivatives bearing methacrylate functionalities. Subsequently, a PMMA-based copolymer with bipyridine units in the side chain was prepared

with free-radical polymerization. Characterization with NMR and GPC indicated the successful incorporation of the bipyridine moieties into the PMMA polymer chain. The introduced grafting procedure opens the way to a straightforward synthetic methodology to gain defined materials with tunable as well as predictable properties. The grafting approach led to polymers that display favorable absorption and luminescence as well as electrochemical properties for photovoltaic device applications. Use of these polymeric Ru(II) complexes as solar-cell devices will be part of future work.

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