

# Mixed Iridium(III) and Ruthenium(II) Polypyridyl Complexes Containing Poly( $\epsilon$ -caprolactone)-Bipyridine Macroligands

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**ABSTRACT:** A hydroxy-functionalized bipyridine ligand was polymerized with  $\epsilon$ -caprolactone utilizing the controlled ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of stannous octoate. The resulting poly( $\epsilon$ -caprolactone)-containing bipyridine was characterized by  $^1\text{H}$  NMR and IR spectroscopy, and gel permeation chromatography, as well as matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, revealing the successful incorporation of the bipyridine ligand into the polymer chain. Coordination to iridium(III) and ruthenium(II) precursor complexes yielded two macroligand complexes, which were characterized by NMR, gel permeation chromatography, matrix-assisted laser desorption/ionization time-of-flight MS, cyclic voltammetry, and differential scanning calorimetry. In addition, both photophysical and electrochemical properties of the metal-containing polymers proved the formation of a *trisruthenium*(II) and a *trisiridium*(III) polypyridyl species, respectively. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 4153–4160, 2004

**Keywords:** bipyridine macroligand; poly( $\epsilon$ -caprolactone); iridium(III) and ruthenium(II) polypyridyl complexes; ring-opening polymerization; luminescence.

## INTRODUCTION

2,2'-Bipyridine ligands and their symmetrical and unsymmetrical derivatives (in particular 4,4'-functionalized) have received considerable attention because of their remarkable chemistry as heterocyclic entities and their exceptional coordination chemistry.<sup>1,2</sup> Many applications benefit from the presence of metals in materials because they have a wide variety of reactivities as well as special optical, magnetic, and electrochemical properties.<sup>3</sup>

In particular, the design of luminescent and redox-active transition-metal complexes and the

study of their photochemical, photophysical, and electrochemical properties has been intensively studied in the last years because of their potential application to light-emitting devices<sup>4–18</sup> and solar cells.<sup>19–21</sup> To prevent formation of aggregates, which often leads to self-quenching and to reduced device lifetimes, incorporation of metal complexes into the polymers is helpful. Polymeric materials have the advantage of preventing aggregation of the metal–ligand complexes, as observed in polymer blends, while maintaining the characteristics of the polymer backbone and ensuring easy processing of the materials by spin coating and ink-jet printing.<sup>12</sup>

Moreover, systems exhibiting metal-to-ligand charge-transfer (MLCT) luminescence have been investigated as labeling reagents for biological

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substrates.<sup>22–30</sup> Most previous studies involved ruthenium(II), osmium(II), and rhenium(II) polypyridine complexes, which were covalently linked to different biomolecules in electron-transfer studies and other analytical applications.<sup>31</sup> Ir(III) species were far less exploited, mainly because of synthetic problems. Despite this, luminescent iridium(III) complexes are highly appealing because of their wider range of emission energies, longer lifetimes, and higher luminescence quantum yields.<sup>32</sup>

Here we describe the synthesis and characterization of luminescent iridium(III) and ruthenium(II) complexes based on a biodegradable poly( $\epsilon$ -caprolactone)–bipyridine system (bpy-PCL). These new materials were synthesized utilizing coordination of iridium(III) and ruthenium(II) precursor complexes to a prepolymer and characterized in detail utilizing NMR, IR, UV–vis spectroscopy, and cyclic voltammetry, as well as gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF MS).

## EXPERIMENTAL

### Materials and General Experimental Details

All manipulations were performed under an atmosphere of argon by employing usual Schlenk techniques. All chemicals were of reagent grade and used as received unless otherwise specified. Tin(II) 2-ethylhexanoate (stannous octoate), 2-phenyl pyridine, 2-ethoxyethanol and ammonium hexafluorophosphate were purchased from Aldrich.  $\epsilon$ -Caprolactone monomer and silver hexafluoroantimonate were purchased from Fluka and  $\text{IrCl}_3 \times n \text{H}_2\text{O}$  from ABCR. Compounds **1** and  $[\text{Ru}(\text{phen})_2\text{Cl}_2]$  (where phen stands for 1,10-phenanthroline) were prepared as published elsewhere.<sup>33</sup> The Ir(III) precursor complex was prepared according to methods in the literature.<sup>34</sup> Preparative size exclusion chromatography was performed on Biobeads S-X1 (dichloromethane).

### Instrumentation

1D [ $^1\text{H}$  and  $^{13}\text{C}(^1\text{H})$ ] and 2D ( $^1\text{H}$ – $^1\text{H}$  COSY) nuclear magnetic resonance spectra were recorded on a Varian Gemini 300 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million ( $\delta$ ) downfield from an internal standard, tet-

ramethylsilane (TMS), in  $\text{CD}_2\text{Cl}_2$ . Coupling constants ( $J$  values) are reported in Hertz (Hz). MALDI–TOF MS was performed on a Voyager-DE<sup>TM</sup> PRO Biospectrometry<sup>TM</sup> Workstation (Applied Biosystems) time-of-flight mass spectrometer reflector, using dithranol as a matrix. IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. Gel permeation chromatograms were measured on a Waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photodiode array (PDA) detector, 2414 refractive index detector, 717plus autosampler, and a Styragel HT 4 GPC column with precolumn installed ( $\text{DMF}$ , 5 mM  $\text{NH}_4\text{PF}_6$ , 50 °C, flow rate of 0.5 mL/min, PEG calibration). UV spectra were recorded on a PerkinElmer Lambda-45 (1-cm cuvettes,  $\text{CH}_2\text{Cl}_2$ ). Emission spectra were recorded on a PerkinElmer LS50B luminescence spectrometer (1-cm cuvettes,  $\text{CH}_2\text{Cl}_2$ ). Electrochemical experiments were performed using an Autolab PG-STAT30 model potentiostat. A standard three-electrode configuration was used, with a platinum-disk working electrode, a platinum-rod auxiliary electrode, and a Ag/AgCl reference electrode. Ferrocene was added at the end of each experiment as an internal standard. The potentials are quoted versus the ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ). The solvent used was  $\text{CH}_2\text{Cl}_2$  (freshly distilled from  $\text{CaH}_2$ ), 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 EuroEA3000 Series EuroVector elemental analyzer for CHN. Differential scanning calorimetry (DSC) investigations were performed on a PerkinElmer Pyris-1 DSC system with a heating rate of 40 K/min ( $T_m$  and  $T_g$ ).

### Synthesis of the Macroligand Complexes

#### *Poly( $\epsilon$ -caprolactone)-Containing Bipyridine (2)*

[4-(3-Hydroxypropyl)-4'-methyl-2,2'-bipyridine] (**1**), initiator (60 mg, 0.26 mmol), and  $\epsilon$ -caprolactone, monomer (1.04 g, 9.2 mmol), were stirred under an argon atmosphere until a temperature of 110 °C was reached. Then a catalytic amount of stannous octoate was added, and the reaction mixture was stirred overnight. Precipitation from dichloromethane in methanol yielded 89% of **2** (calculated on the basis of the initiator).

IR: 3442 (OH), 2995, 2950 (CH aromatic), 1722 (C=O), 1370, 1295, 1240, 1170, 1047 ( $-\text{CH}_2-\text{O}-\text{C}=\text{O}-$ ), 962, 733.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , ppm): 1.83–1.03 (m, H, f', e', and g'),

2.04–1.87 (m, 2H, b'), 2.33–2.05 (m, H, d'), 2.36 (s, 2H, a), 2.77–2.64 (m, 2H, a'), 3.58–3.44 (m, 2H, H'), 4.29–3.44 (m, H, c', and h'), 7.07 (s, 2H, 5,5'), 8.21 (d, 2H,  $J = 5.50$  Hz, 3,3'), 8.43 (dd, 2H,  $J = 4.94, 10.98$  Hz, 6,6'). UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ): = 282 ( $9.95 \times 10^3$ ), 242 ( $7.64 \times 10^3$ ) nm ( $\text{L mol}^{-1} \text{cm}^{-1}$ ). MALDI-TOF MS (dithranol):  $\underline{M}_n = 3470 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 4340 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.25. GPC (DMF):  $\underline{M}_n = 3990 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 5610 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.4.  $T_m = 56.2$  °C.  $T_g = -56.9$  °C.

**Tetrakis(2-phenylpyridine- $C^2, N'$ ) ( $\mu$ -dichloro)diiridium (3)**

Iridium trichloride hydrate (0.388 g, 26 mmol) was combined with 2-phenylpyridine (0.76 g, 64 mmol), dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and refluxed for 24 h. The solution was cooled to room temperature, and the yellow precipitate was collected on a glass filter frit. The precipitate was washed with ethanol (60 mL) and acetone (60 mL) and then dissolved in dichloromethane (75 mL) and filtered. Toluene (25 mL) and hexane (10 mL) were added to the filtrate, which was then reduced in volume by evaporation to 50 mL and cooled to give a 72% yield (0.428 g) of  $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$  (**3**) crystals.

IR: 3058 (C=C), 1964, 1909 (CH), 1605, 1581, 1561, 1548, 1476, 1455, 1438, 1415 (C=C and C=N), 1306, 1267, 1224, 1160, 1061, 1029, 1007, 753, 734, 727, 669. MALDI-TOF MS (dithranol):  $m/z = 1040.32$   $[\text{Ir}_2\text{C}_{44}\text{H}_{32}\text{N}_4\text{Cl}_2] - \text{Cl}$ . ELEM. ANAL. Calcd for  $\text{Ir}_2\text{C}_{44}\text{H}_{32}\text{N}_4\text{Cl}_2$  (1075.82): C, 49.29%; H, 3.01%; N, 5.23%. Found: C, 49.58%; H, 3.16%; N, 5.09%.

**Ir(III) Macroligand Complex (4)**

A solution of  $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$  (**3**) (42 mg, 0.038 mmol) in methanol (10 mL) was added to a suspension of macroligand **2** (110 mg, 0.038 mmol) in dichloromethane (8 mL). Heating under reflux conditions for 12 h led to a clear yellow solution. After cooling to room temperature, a saturated solution of  $[\text{NH}_4][\text{PF}_6]$  in methanol (2 mL) was added, stirring continuously for another 12 h. Partial evaporation of the solvents under reduced pressure afforded a yellow polymer. To remove excessive  $[\text{NH}_4][\text{PF}_6]$ , the complex was redissolved in dichloromethane and extracted ( $3 \times \text{H}_2\text{O}$ ), followed by purification by preparative size exclusion chromatography and precipitation in *n*-hexane, for a yield of **4** of 123 mg (86%).

IR: 3442 (OH), 2995, 2950 (CH aromatic), 1722 (C=O), 1370, 1295, 1240, 1170, 1047 ( $-\text{CH}_2-\text{O}-$ ), 962, (CH), 837 ( $\text{PF}_6$ ), 757, 745, 736, 667.

UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 270 ( $4.58 \times 10^3$ ), 370 ( $4.85 \times 10^3$ ), 232 ( $6.36 \times 10^3$ ) nm ( $\text{L mol}^{-1} \text{cm}^{-1}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , ppm): 1.88–1.16 (m, H, f', e', and g'), 2.11–1.96 (m, 2H, b'), 2.47–2.13 (m, 2H, d'), 2.56 (s, 2H, a), 2.97–2.80 (m, 2H, a'), 3.67–3.49 (m, H, 2H'), 4.36–3.83 (m, H, c', and h'), 6.37–6.20 (m, 2H, ppy), 7.13–6.83 (m, 6H, 5,5'-bpy, ppy), 7.29–7.16 (m, 2H, ppy), 7.58–7.44 (m, 2H, ppy), 8.04–7.63 (m, 8H, 6,6'-bpy, ppy), 8.43–8.25 (m, 2H, 3,3'-bpy). MALDI-TOF MS (dithranol):  $\underline{M}_n = 3950 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 4180 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.06. GPC (DMF):  $\underline{M}_n = 5330 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 6480 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.19.  $T_m = 56.7$  °C.  $T_g = -57.3$  °C.

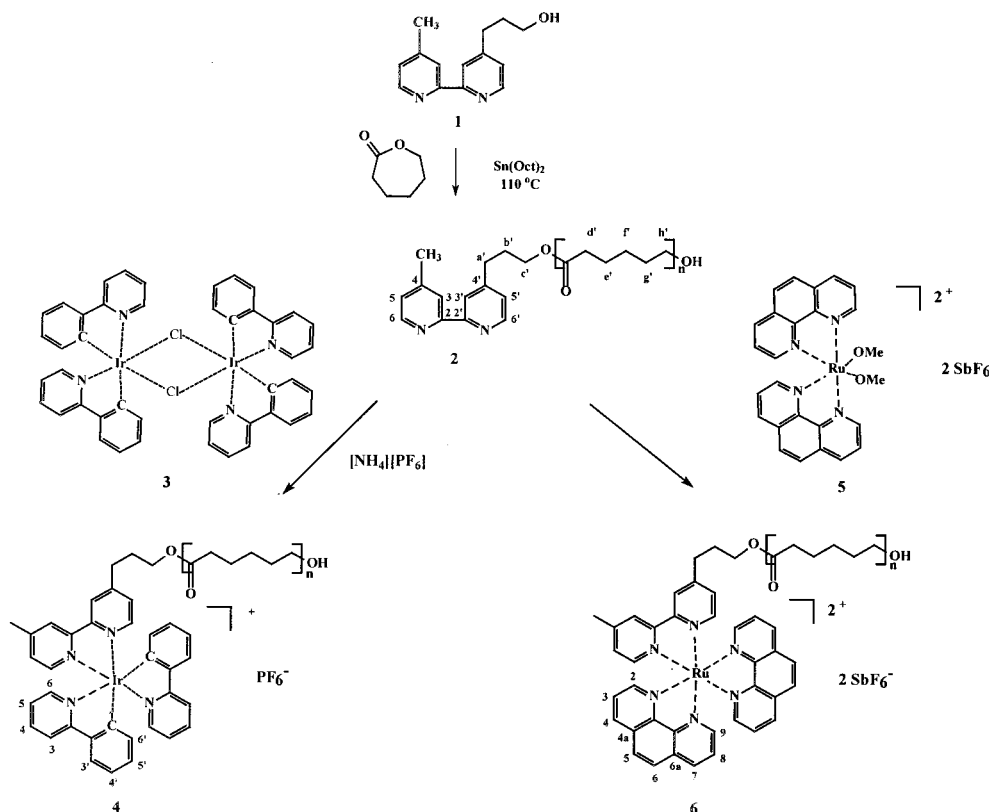
**Ru(II) Macroligand Complex (6)**

A suspension of  $[\text{Ru}(\text{phen})_2\text{Cl}_2]$  precursor (21.3 mg, 0.04 mmol) and  $\text{AgSbF}_6$  (27.5 mg, 0.08 mmol) was stirred overnight in acetone, followed by filtration of the formed  $\text{AgCl}$ . The  $[\text{Ru}(\text{phen})_2(\text{OMe}_2)_2]^{2+} 2\text{SbF}_6^-$  solution (**5**) was then added to a solution of poly( $\epsilon$ -caprolactone)-containing bipyridine **2** (80 mg, 0.02 mmol) in acetone. The reaction mixture was refluxed for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through cellite, then purified by preparative size exclusion chromatography, yielding 80 mg of **6** as an orange powder (88%).

IR: 3442 (OH), 2995, 2950 (CH aromatic), 1722 (C=O), 1370, 1295, 1240, 1170, 1047 ( $-\text{CH}_2-\text{O}-$ ), 962, 733, (CH), 657 ( $\text{SbF}_6$ ). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 454 ( $6.85 \times 10^3$ ), 267 ( $4.85 \times 10^3$ ), 232 ( $3.26 \times 10^3$ ) nm ( $\text{L mol}^{-1} \text{cm}^{-1}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ , ppm): 1.74–1.02 (m, H, f', e', and g'), 2.09–1.89 (m, 2H, b'), 2.40–2.05 (m, H, d'), 2.55 (s, 3H, a), 2.95–2.77 (m, 2H, a'), 3.65–3.50 (m, 2H, H'), 4.34–3.70 (m, H, c', and h'), 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). MALDI-TOF MS (dithranol):  $\underline{M}_n = 4040 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 4190 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.04. GPC (DMF):  $\underline{M}_n = 6490 \text{ g} \times \text{mol}^{-1}$ ,  $\underline{M}_w = 7700 \text{ g} \times \text{mol}^{-1}$ , PDI = 1.19.  $T_m = 56.9$  °C.  $T_g = -57.1$  °C.

**RESULTS AND DISCUSSION**

Because of their variable structures, physical properties, and reactivity, metal complexes often

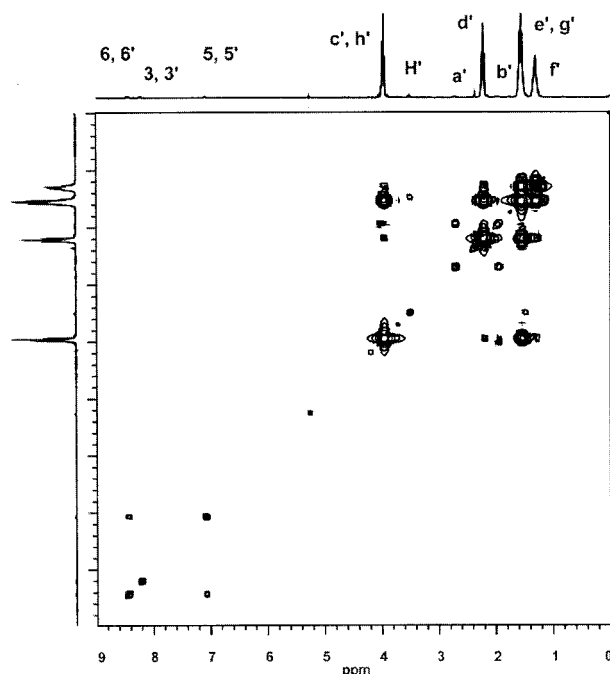


**Scheme 1.** Schematic presentation of the synthesis of macroligand complexes **4** and **6**.

play key roles in macromolecular chemistry. In particular, novel polymeric materials based on ruthenium(II) and iridium(III) complexes are under investigation because of their potential applications in organic light-emitting devices and solar cells,<sup>4,7,10,13,19,35</sup> as well as in biochemical and biomedical areas.<sup>21–29</sup> They offer a range of remarkable advantages such as high quantum efficiencies, long luminescence lifetimes (ruthenium complexes), and short phosphorescence lifetimes, as well as color-tuning ability from metal-to-ligand-based radiation (iridium complexes).

With the appropriate catalyst and reaction conditions, the ring-opening polymerization of  $\epsilon$ -caprolactone proceeds in a controlled fashion, giving rise to well-defined polymer products with low polydispersity indices (PDIs) and adjustable molecular weights determined as by reaction stoichiometry.<sup>36</sup> The synthesis of poly( $\epsilon$ -caprolactone)-containing bipyridine **2** is outlined in Scheme 1. The reaction was performed in bulk monomer using the hydroxy-functionalized bipyridine **1** as initiator and  $\text{Sn}(\text{Oct})_2$  as the catalyst. Precipitation in methanol from dichloromethane yielded 89% of the macroligand **2**.

$^1\text{H}$  NMR spectroscopy proved that the bipyridine ligand was incorporated into the poly( $\epsilon$ -caprolactone) backbone: no shift in the aromatic resonances of the parent bipyridine **1** was detected. Well-resolved, discrete signals were observed for the bipyridine protons as well as for the terminal methylene of the polymer chain (denoted  $\text{H}^t$  as they “belong” to the protons  $\text{h}^t$  of the polymer backbone). The assignments were also confirmed by two-dimensional  $^1\text{H}$ - $^1\text{H}$  correlation spectroscopy (Figure 1). Using this method, the cross peaks corresponding to the coupling of aromatic protons  $\text{H}^6$  and  $\text{H}^{6'}$  with  $\text{H}^5$  and  $\text{H}^{5'}$ , respectively, but also the coupling of the terminal methylene group of the polymer chain ( $\text{H}^t$ ) with its neighboring protons,  $\text{H}^{t'}$ , can be identified. In addition,  $\text{H}^{b'}$ - $\text{H}^c$  coupling could be observed even though  $\text{H}^c$  protons are hidden under the polymer backbone ( $\text{H}^t$ ). Moreover, NMR spectroscopy was used to determine the molecular weight of the polymer. Specifically, the molecular weight was calculated by comparing the integration of the main-chain methylene groups to that of their respective end-group methylene protons ( $\text{H}^t$ ). However, a molecular weight higher than mono-



**Figure 1.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of macroligand **2** in  $\text{CD}_2\text{Cl}_2$ .

mer-to-initiator loading was obtained ( $M_{n,\text{NMR}} = 5540 \text{ g} \times \text{mol}^{-1}$  vs  $M_{n,\text{th}} = 3680 \text{ g} \times \text{mol}^{-1}$ ). This might be caused by performing the polymerization reaction on a rather small scale, leading to inaccuracy in weighing. GPC characterization showed a monomodal distribution for the obtained polymer. Finally, end-group modification was confirmed by MALDI-TOF MS. Both techniques showed controlled polymerization and the expected molecular weight distribution.

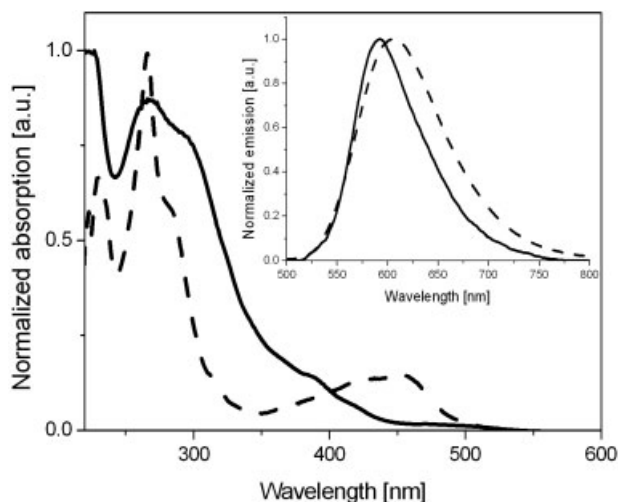
In 1999 Neve et al.<sup>37</sup> introduced a general synthetic strategy for the synthesis of mixed ligand orthometallated iridium(III) complexes in high yield and of high purity. Complexation of the orthometallated dimer  $[\text{Ir}(\text{N}^{\wedge}\text{C})_2\text{Cl}]_2$  (where  $(\text{N}^{\wedge}\text{C})$  is ppy = 2-phenylpyridine) yielded the monomeric mixed-macroligand iridium(III) complex **4**  $[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{bpy-PCL})]^+$  via a bridge-splitting reaction exploiting the chelating polymeric bipyridine **2**. The reaction was carried out in a refluxing dichloromethane/methanol mixture (6:4, v/v). Macroligand complex **4** was precipitated with a saturated methanolic  $[\text{NH}_4][\text{PF}_6]$  solution while performing counter-ion exchange. Excess ammonium hexafluorophosphate was extracted with water, then the polymeric complex was purified by preparative size exclusion chromatography, followed by precipitation in *n*-hexane yielding 86% of macroligand complex **4**. The yellow monocationic com-

plex **4** is soluble in organic solvents of medium to high polarity.

A  $[\text{Ru}(\text{phen})_2(\text{OMe})_2]^{2+} 2 \text{ SbF}_6^-$  synthon (**5**) was obtained by stirring the corresponding ruthenium chloride ( $\text{Ru}(\text{phen})_2\text{Cl}_2$ ) with twofold excess  $\text{AgSbF}_6$  in acetone overnight.<sup>33,38</sup> The filtrate was then added to a suspension of macroligand **2** in acetone in a 2:1 excess (mol %, on the basis of the bipyridine content of the macroligand **2**). After 48 h of reflux, the reaction mixture was filtered, concentrated, and purified by preparative size exclusion chromatography. The resulting macroligand complex **6** was dried under reduced pressure to yield 88% of an orange polymer.

The main infrared vibration features of the macroligand complexes **4** and **6** were intense bands at 3442 (OH), 1722 (C=O), and  $1170 \text{ cm}^{-1}$  ( $-\text{CH}_2-\text{O}-\text{C}=\text{O}-$ ), characteristic of the PCL backbone. Moreover, the characteristic bands of hexafluoroantimonate and hexafluorophosphate counter ions at 658 and  $837 \text{ cm}^{-1}$ , respectively, were visible.

Figure 2 shows the UV-vis spectra data of complexes **4** and **6** in dichloromethane solutions. For iridium(III) macroligand complex **4**, the strong absorption band at about 270 nm was addressed to the ligand-centered  $\pi^* \leftarrow \pi$  transitions on the 2-phenylpyridine. The broad absorption bands at lower energy were a result of typical spin-allowed metal-to-ligand charge-transfer (MLCT) transitions. The shoulder at around 370 nm was assigned to spin-allowed CT transitions. For the polymeric ruthenium(II) complex, the presence of



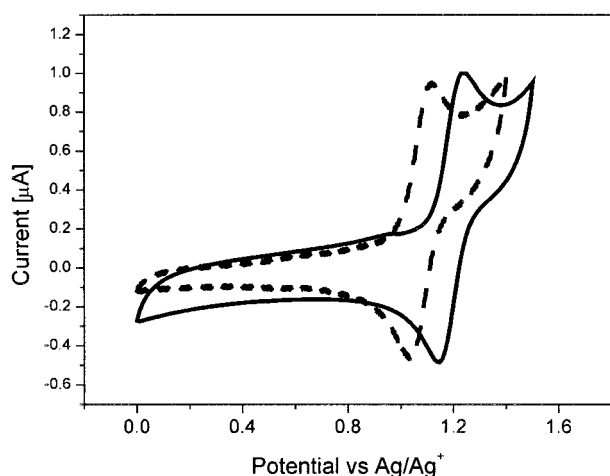
**Figure 2.** Absorption and emission (inset) spectra of macroligand complexes **4** (solid line) and **6** (dashed line). All spectra were recorded in  $\text{CH}_2\text{Cl}_2$ .

**Table 1.** Photophysical and Electrochemical Properties of Macroligand Complexes **4** and **6**

Compound	Oxidation Potentials $E_{\text{ox}}$ (vs. $F_c/F_c^+$ ) (eV)	Absorption $\lambda_{\text{max}}$ (nm)	Emission $\lambda_{\text{max}}$ (nm)
Macroligand complex <b>4</b>	1.19 (0.25)	370	591
Macroligand complex <b>6</b>	1.06 (0.26)	454	605

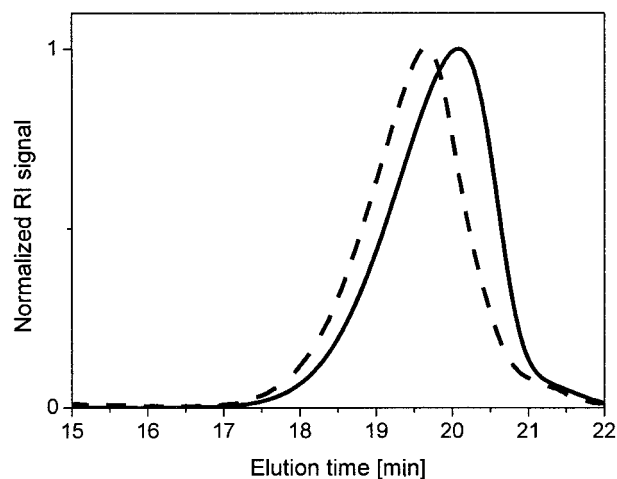
the MLCT band, ranging from 445 to 465 nm, confirmed a successful incorporation of the phenantroline precursor into the polymer backbone but also that the PCL backbone was not influencing the absorption properties of a Ru(II) polypyridyl species. Excitation at 370 nm on the iridium-containing polymer revealed a broad emission band with a maximum at 605 nm (Fig. 2, inset). The emission spectrum of the polymeric Ru(II) complex in dichloromethane at room temperature was recorded upon excitation at 456 nm (Fig. 2, inset); a maximum at 591 nm was exhibited. Redox properties of the macroligand complexes were determined by cyclic voltammetry (Fig. 3) and are summarized in Table 1. The oxidation potentials were in agreement with literature data.<sup>22,39</sup> Only one active species was formed throughout the chelation reaction. An overview of the photophysical and electrochemical properties of the macroligand complexes **4** and **6** is given in Table 1.

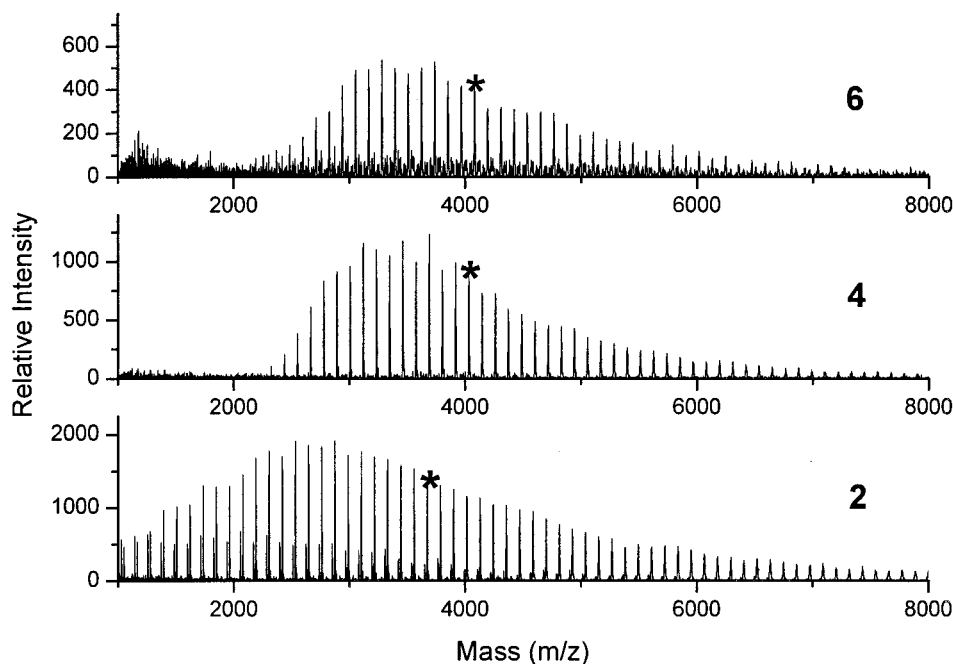
In the  $^1\text{H}$  NMR spectra of the two polymeric complexes the integration of the aromatic protons

**Figure 3.** CV results of macroligand complexes **4** (solid line) and **6** (dashed line). All spectra were recorded in  $\text{CH}_2\text{Cl}_2$  (freshly distilled from  $\text{CaH}_2$ ) containing 0.1 M  $n\text{-Bu}_4\text{PF}_6$  vs.  $\text{Ag}/\text{Ag}^+$  reference electrode.

clearly revealed, as expected, the presence of one bpy-PCL macroligand and two phenantroline and two phenyl-pyridine ligands, respectively. GPC characterization utilizing an optimized eluent<sup>40</sup> showed the purity and stability of macroligand complexes **4** and **6** (Fig. 4). No fragmentation of the metal-to-ligand bonds was observed during elution on the chromatographic column. The slight shift of the elution bands might be an effect of the different hydrodynamic volumes of the investigated materials (different counter ions and ligands).

Polymers **2**, **4**, and **6** were also characterized by MALDI-TOF MS. Figure 5 shows the MALDI mass spectrogram of macroligand **2** and of their corresponding complexes **4** and **6**. The molecular weight distributions are shifted toward higher molecular weights on complexation of polymer **2** with the phenyl-pyridine (**3**) and phenantroline (**5**) precursor complexes. For both macroligand complexes only one distribution was observed in the MALDI spectrum. From this result together with NMR spectroscopy as well as gel permeation chromatography data, it can be concluded that polymer **2** is fully complexed. Therefore, MALDI-

**Figure 4.** GPC elution bands for macroligand complexes **4** (solid line) and **6** (dashed line).



**Figure 5.** MALDI-TOF MS spectra for bipyridine-PCL **2** and for PCL-based polymers **4** and **6**. The marked peaks (\*) correspond to  $n = 30$ .

TOF MS is a valuable supplementary tool for the characterization and identification of polypyridyl-based polymers **4** and **6**.

Preliminary thermal analysis using DSC was performed on the poly( $\epsilon$ -caprolactone)-containing bipyridine **2** as well as on macroligand complexes **4** and **6**, revealing similar behavior ( $T_m$  and  $T_g$  values around 56 °C and -57 °C, respectively, for bipyridine-PCL **2** and PCL-based polymers **4** and **6**). This demonstrates that the polymer properties are not influenced by the incorporation of the metal complexes and thus the processing features are maintained.

## CONCLUSIONS

We have described the synthesis of a bipyridine macroligand and its corresponding polymeric iridium(III) and ruthenium(II) polypyridyl complexes via a hydroxy-functionalized bipyridine ligand. The ring-opening polymerization of  $\epsilon$ -caprolactone using a hydroxy-functionalized 2,2'-bipyridine as initiator was performed in a controlled fashion. Coordination of iridium(III) and ruthenium(II) precursor complexes onto the macroligand allowed the preparation of functional materials with valuable properties and the

potential for applications in device technology or for biomedical purposes. Characterization by NMR, GPC, and MALDI-TOF MS confirmed the full complexation of the macroligand with both metal precursors. These metal-containing polymers displayed favorable photophysical and electrochemical properties as well as good processability because of the film-forming properties of the PCL backbone. Future work will include morphology studies on these functional materials with a view to their potential application in displays.

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