

Synthesis and Characterization of an Electroluminescent Polyester Containing the Ru(II) Complex

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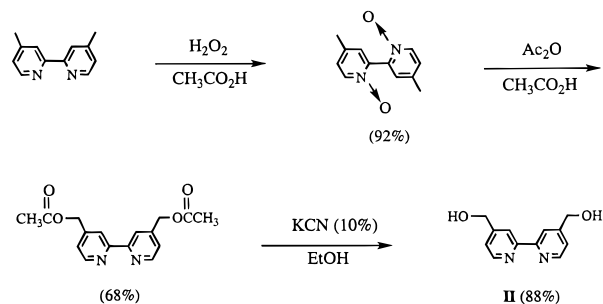
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The synthesis of macromolecules containing inorganic or organometallic structural units is of considerable interest because of their unusual physical, chemical, and electronic properties.^{1–4} Much of the early work in this area was based on the polymerization of vinyl-substituted organometallic compounds. Such polymers were found to exhibit useful catalytic properties.^{1,5–8} Ferrocene-containing polymers have been prepared via a number of different synthetic methodologies such as condensation polymerization^{3,9,10} or ring-opening polymerization (ROP).^{4,11–13} Several polymerization techniques suitable for the preparation of Ru(II) complex-containing polymers have also been reported,^{14–16} including the synthesis of conjugated polymers containing ruthenium(II) tris(bipyridine) complexes.^{17,18} Polymers containing Ru(II) complexes are of particular interest due to their potential use as emitters in thin-film electroluminescent devices. The electrogenerated chemiluminescence of these materials (primarily small-molecule systems) in liquid cells has been extensively studied;¹⁹ however, to our knowledge, there are no reports on the use of polymers containing Ru(II) com-

Scheme 1. Synthesis of Difunctionalized Bipyridine Ligand



plexes as emitters in solid-state devices. Recently we reported that an electrochemically stable polypyridyl-ruthenium(II) complex, **I**, could be used as an orange-red light emitter in solid-state electroluminescent devices (ELD).²⁰

The electrochemical stability of the electrochemically generated Ru(III)/Ru(I) species of this (and related materials) is expected to provide enhanced performance in thin film ELDs. The relatively high photoluminescent and electrochemiluminescent quantum yields of Ru(II) complexes¹⁹ should also make it possible to fabricate high-efficiency devices. The solubility of **I** in polar solvents such as water, methanol, and dimethyl sulfoxide (DMSO), allowed us to make thin-film devices using different processing techniques. A spin-coating method was used to prepare single-layer devices and a layer-by-layer sequential adsorption process^{20,21} was used to make multilayer devices.

In this communication, we describe the synthesis of a new polyester that contains the ruthenium(II) complex in the polymer main chain and report on some preliminary studies of the electroluminescent properties of this polymer in thin-film devices. Polymer-based Ru(II) complexes offer many advantages over small-molecule systems including enhanced processing capabilities and film quality, better control over morphology and molecular organization, and the ability to readily vary chemical structure. For example, the Ru(II) complex can be incorporated into a variety of polymer backbones such as conjugated or ion-conducting backbones.

To synthesize Ru(II)-based polymers, we designed a new bipyridine diol. 5,5'-Bis(hydroxymethyl)-2,2'-bipyridine (**II**) was synthesized from 5,5'-dimethyl-2,2'-bipyridine by a three-step reaction (overall yield; 55%) as shown in Scheme 1.²² There are two possible ways to make a polymer containing Ru(II) complexes from such a difunctional bipyridine ligand. One way is to first synthesize a polymer from the bipyridine diol and then react with a suitable Ru(II) compound. The bipyridine diol was easily polymerized with dodecanedioyl dichloride, ClOC(CH₂)₁₀COCl, in THF. However, the lack of solubility of the resulting polymer in methanol- and water-based solvents, common solvents

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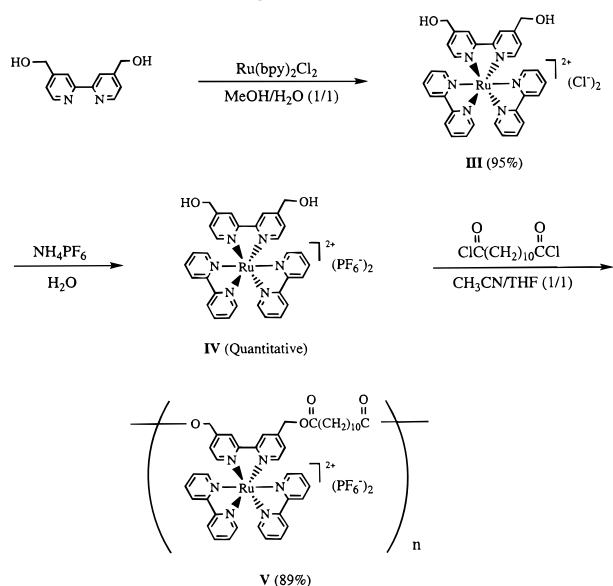
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(22) **II**: ¹H NMR (DMSO-*d*₆) δ 8.60 (dd, 2H, aromatic H(6)), 8.39 (m, 2H, aromatic H(3)), 7.37 (m, 2H, aromatic H(4)), 5.53 (t, 2H, OH), 4.63 (d, 4H, CH₂OH); ¹³C NMR (DMSO-*d*₆) δ 155.2 (s, C(1)), 152.8 (s, C(5)), 148.9 (d, ¹J = 172 Hz, C(3)), 121.4 (d, ¹J = 161 Hz, C(4)), 117.8 (d, ¹J = 163 Hz, C(6)), 61.7 (t, ¹J = 142 Hz, CH₂).

Scheme 2. Preparation of the Polyester Containing Ru(II) Complexes



for the coupling reaction with $\text{Ru(bpy)}_2\text{Cl}_2$ ($\text{bpy} = 2,2'$ -bipyridine), hindered the introduction of the Ru complex into the polymer. The other approach is to first synthesize the Ru complex and then polymerize it with a suitable diacyl chloride such as dodecanedioyl dichloride. A ruthenium complex having one difunctionalized ligand, **III**, was prepared with high yields from the reaction of $\text{Ru(bpy)}_2\text{Cl}_2$ with **II**. The counteranion was changed from Cl^- to PF_6^- by a metathesis reaction in order to obtain an organic-soluble complex **IV**.²³ **IV** was reacted with $\text{ClOC(CH}_2\text{)}_{10}\text{COCl}$ to give the desired polyester containing Ru complexes, **V**, as shown in Scheme 2.²⁴ This polymerization turned out to be very sensitive to the polymerization solvent system. In a THF solution, no polymerization occurred probably due to the low solubility of **IV** in THF. Even in a CH_3CN solution where the monomer **IV** is very soluble, no polymerization was detected. In a 1:1 mixture of CH_3CN and THF, the polymerization proceeded giving good yields of polyester **V**. The molecular weight of polymer **V** could not be measured by GPC due to the ionic

(23) Cl^- was changed to PF_6^- by treating with a 10-fold excess amount of NH_4PF_6 in water: the resulting precipitate was filtered and dried in vacuo (yield 88–90%).

(24) **III**: $^1\text{H NMR}$ ($\text{DMSO-}d_6$) δ 8.39 (d, 4H, H(6) of bpy), 8.78 (s, 2H, H(6) of bpy), 8.16 (dd, 4H, H(5) of bpy), 7.74 (dd, 4H, H(3) of bpy), 7.64 (d, 2H, H(3) of bpy), 7.55 (m, 4H, H(4) of bpy), 7.51 (d, 2H, H(4) of bpy), 6.05 (t, 2H, OH), 4.73 (d, 4H, CH_2OH); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$) δ 156.6 (s, C(1) of bpy), 156.0 (s, C(1) of bpy'), 154.5 (s, C(5) of bpy), 151.1 and 151.0 (d, $^1J = 187$ Hz, C(3) of bpy), 150.6 (d, $^1J = 184$ Hz, C(3) of bpy'), 137.8 (d, $^1J = 170$ Hz, C(5) of bpy), 127.8 (d, $^1J = 171$ Hz, C(6) of bpy), 125.1 (d, $^1J = 168$ Hz, C(6) of bpy'), 124.5 (d, $^1J = 172$ Hz, C(4) of bpy), 121.5 (d, $^1J = 170$ Hz, C(4) of bpy'), 61.0 (t, $^1J = 140$ Hz, CH_2). **IV**: $^1\text{H NMR}$ ($\text{DMSO-}d_6$) δ 8.83 (d, 4H, H(6) of bpy), 8.69 (s, 2H, H(6) of bpy), 8.16 (dd, 4H, H(5) of bpy), 7.74 (dd, 4H, H(3) of bpy), 7.65 (d, 2H, H(3) of bpy), 7.52 (dd, 4H, H(4) of bpy), 7.46 (d, 2H, H(4) of bpy), 5.73 (t, 2H, OH), 4.73 (d, 4H, CH_2OH); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$) δ 156.6 (s, C(1) of bpy), 156.0 (s, C(1) of bpy'), 154.2 (s, C(5) of bpy), 151.2 and 151.0 (d, C(3) of bpy), 150.6 (d, C(3) of bpy'), 137.7 (d, C(5) of bpy), 127.8 (d, C(6) of bpy), 125.0 (d, C(6) of bpy'), 124.4 (d, C(4) of bpy), 121.2 (d, C(4) of bpy'), 61.1 (t, CH_2). Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{F}_{12}\text{N}_6\text{-O}_2\text{P}_2\text{Ru}$: C, 41.80; H, 3.07; N, 9.14. Found: C, 41.84; H, 3.10; N, 9.22. **V**: $^1\text{H NMR}$ ($\text{DMSO-}d_6$) δ 8.84 (d, 4H, H(6) of bpy), 8.77 (s, 2H, H(6) of bpy), 8.17 (dd, 4H, H(5) of bpy), 7.73 (m, 6H, H(3) of bpy and bpy'), 7.53 (m, 6H, H(4) of bpy and bpy'), 5.32 (s, 4H, $\text{CH}_2\text{-OC(O)}$), 2.43 (br, 4H, C(O)CH_2), 1.55 (br, 4H, $\text{C(O)CH}_2\text{CH}_2$), 1.22 (br, 10H, CH_2); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$) δ 172.6 ($\text{C}_{\text{carbonyl}}$), 156.5, 156.1, 151.1, 147.6, 137.9, 127.8, 125.6, 124.4, and 122.3 ($\text{C}_{\text{aromatic}}$), 63.0 (CH_2O), 33.2, 28.9, 28.7, 28.5, and 24.3 (C_{alkyl}).

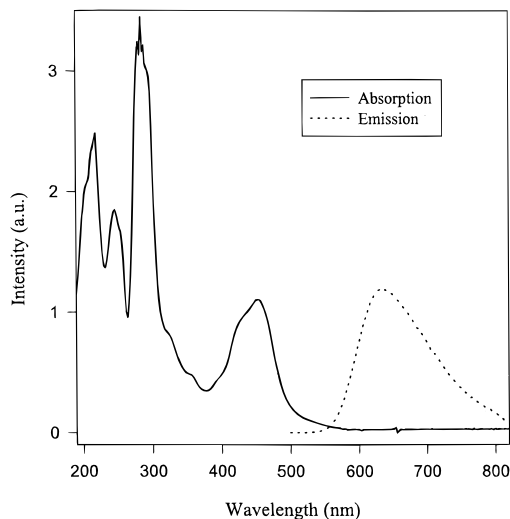


Figure 1. Absorption and emission spectra of Ru polyester **V**.

interaction of the polymer with the stationary phase material in the column. From an end-group analysis carried out with polymer encapped with terminal hydroxymethyl groups (by reaction with excess acetyl bromide), the average number of repeat units was estimated to be about 5. The calculated number average molecular weight of **V** is about 5500 g/mol. Polymer **V** is therefore essentially an oligomer. It turns out, however, that this molecular weight is high enough to form high-quality films via spin-casting methods. Further efforts to increase the molecular weight of **V** have not as of yet been made, although we anticipate that this will be possible. One interesting feature of **V** is the change in solubility that occurs when the counterion of the Ru complex is changed. **V** is very soluble in CHCl_3 , THF, and acetone, but when the PF_6^- counterion is changed to Cl^- , the new polymer is soluble only in very polar solvents such as water and methanol.²⁵ This versatility makes it possible to prepare thin-film devices by either spin-coating from organic solutions or by layer-by-layer self-assembly from water solutions.

$^1\text{H NMR}$ spectra of the polymer revealed a change of the chemical shift of the $-\text{CH}_2\text{O}-$ peak of the Ru(II) diol from 4.73 to 5.32 ppm after the formation of the ester linkage as well as the disappearance of the $-\text{OH}$ peak of **IV** at 5.73 ppm. All of the aromatic peaks corresponding to the bipyridine ligands of the Ru(II) complex were observed from the $^1\text{H NMR}$ spectrum of polymer **V** along with the aliphatic peaks from the dodecanedioyl moiety. The absorption and emission spectra of monomer **IV** and polymer **V** both displayed the same peaks (see Figure 1); $\lambda_{\text{max,abs}} = 454$ nm and $\lambda_{\text{max,em}} = 636$ nm. The photoluminescent quantum yields were determined to be 3.6% and 4.9%, respectively. These results confirm that Ru(II) complexes are incorporated into the polymer backbone. FT-IR spectra showed further evidence for the incorporation of Ru(II) complexes into the polymer. A new vibrational peak corresponding to the ester linkage, $\nu(\text{C}=\text{O})$, was detected at 1740 cm^{-1} , and the OH peak at 3580 cm^{-1} disappeared after polymer formation. Several reversible

(25) PF_6^- was changed to Cl^- by treating with a 4-fold excess amount of Bu_4NCl in acetone: the resulting precipitate was filtered and dried in vacuo (quantitative yield).

reduction peaks at -1.50 , -1.68 , and -1.91 V and a reversible oxidation peak at 1.09 V were observed from a cyclic voltammogram of monomer **IV** in CH_3CN (all versus SCE). As expected, polymer **V** exhibits essentially the same electrochemical properties as monomer **IV** with reversible reduction peaks at -1.46 , -1.72 , and -1.96 V and a reversible oxidation peak at 1.15 V.

Single-layer ELDs were prepared by spin coating a polymer solution of **V** onto glass substrates coated with a patterned indium tin oxide (ITO) anode. The polymer solution was 3% (w/w) in 2-methoxyethanol. Film thicknesses were measured to be about 650 \AA via profilometry. Aluminum electrodes were used as the cathode contact in these thin film devices. Figure 2 shows a typical light-voltage ($L-V$) and current-voltage ($I-V$) curve for a ITO/**V**/Al device fabricated from the Ru(II) polyester **V**. This device showed an orange-red emission under a forward bias with a maximum measured luminance level of about 80 cd/m^2 (2400 nW) at a current density of 750 mA/cm^2 . The external quantum efficiency of this device was estimated to be about 0.01% (photons per electron). To date, our best spin-coated devices have exhibited luminance levels near 300 cd/m^2 with external quantum efficiencies of about 0.08%. Thin films of this material were also fabricated via the layer-by-layer electrostatic self-assembly technique.^{20,21} This was accomplished with an aqueous solution of the Ru(II) polyester in which the counteranions were exchanged to Cl^- . Multilayer thin films were fabricated with the Ru(II) polyester as the polycation and poly(acrylic acid) (PAA) as the polyanion. Preliminary results show that it is possible to create thin-film devices with external quantum efficiencies close to 1% (ratio of nW/mA in the $6000/1$ range). These remarkably high efficiencies are comparable to some of the best devices based on conjugated polymers or small-molecule systems. Details concerning the fabrication of the self-assembled films and device characteristics will be published shortly.

In conclusion, we have demonstrated that polymers containing Ru(II) complexes can be prepared by a

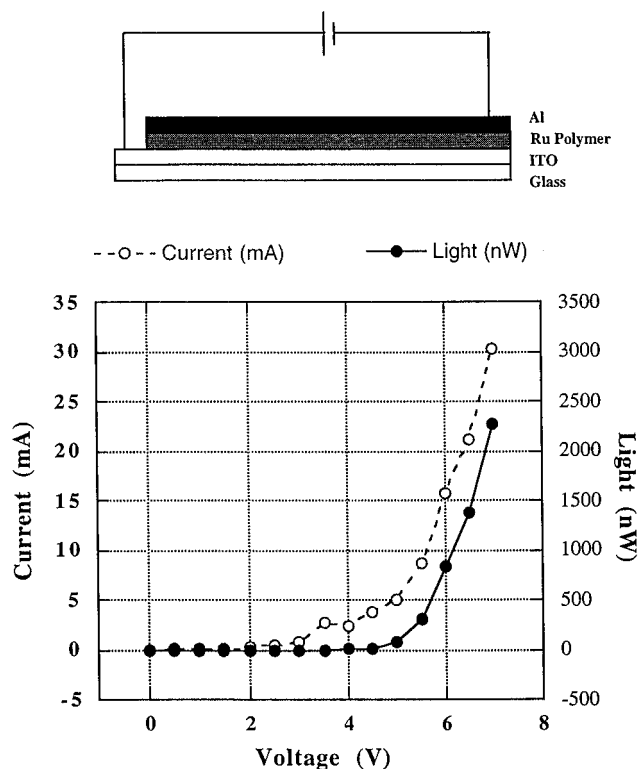


Figure 2. $I-V$ and $L-V$ characteristics of EL devices of Ru polyester **V**.

condensation polymerization and that this new type of light-emitting polymer shows very promising electroluminescent properties.

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