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Synthesis and characterization of partially crosslinked poly(*N*-vinylcarbazole-vinylalcohol) copolymers with polypyridyl Ru(II) luminophores: Potential materials for electroluminescence

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Summary

A novel difunctionalized 5,5'-dibromomethylene-2,2' bipyridine ligand was prepared and covalently bound with concurrent crosslinking by a post-polymer modification method to (N-vinylcarbazole-vinylalcohol) copolymer. The electrochemistry and UV-vis spectroscopy results both confirm the covalent attachment of ruthenium transition metal complex to the polymer backbone. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicate high thermal stability of the copolymer. The copolymer is also highly phosphorescent making it a potential polymeric material for transition metal based electroluminescent devices.

Introduction

Since the discovery of polymer-based electroluminescence from poly(phenylenevinylene) (PPV) (1), great research interest has been devoted to the use of semiconducting organic polymeric materials for the fabrication of electroluminescent devices due to their ease of processing, excellent thermal and mechanical stability, as well as their capability of providing a greater spectral range when compared to conventional inorganic semiconducting materials (2-4). Unfortunately organic polymeric materials are, in general, known to have poorer carrier mobility than their inorganic semiconductor counterparts, a paramount factor for electroluminescence. Proper selection of the organic materials, efficient carrier injection from both electrodes, and controlled electron-hole recombination within well-defined zones are the key factors in the performance of an electroluminescent device (EL). A great deal of effort has been focused on increasing charge injection efficiency, typical function metal cathode (5), and on carrier confinement by using multi-layer heterostructures (6).

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Another possible approach to enhance the electroluminescene of organic polymeric materials is by designing a marcomolecular architecture that comprises a material with both improved charge carrier mobility and efficient charge transfer to the phosphorescent center. Bipyridine complexes of ruthenium possess several especially interesting chemical and spectral properties making them suitable candidates for electroluminescent materials. For example, their strong visible absorptions arising from a metal-to-ligand charge-transfer (MLCT) transition produce long-lived excited triplets capable of affecting important redox chemistry (7-10). More importantly, these complexes are quite inert to ligand substitution and are thermally and photochemically stable. Our research group has previously observed a MLCT electrophosphorescence from $Ru(bpy)_2$ luminophore coordinated to (vinylpyridine-styrene) copolymer (11), and to our knowledge there is only one other example of electroluminescence in an organic polymeric material mediated by a ruthenium transition metal complex (12). We report here the synthesis and characterization of a phosphorescent, crosslinked copolymer, where both poly(N-vinylcarbazole), a commonly used material as hole-injecting material to the EL polymer layer (13-15), and a tris-(2,2'-bipyridyl) ruthenium (II) luminophore are covalently attached to, or are functional units forming, the polymer backbone as potential emitters for solid-state devices.

Experimental

Methods and Materials: All reagents were obtained from Aldrich Chemicals Canada, except for tetrabutylammonium hexafluorophosphate ($TBAPF_6$), which was obtained from Fluka, Inc. $TBAPF_6$ was recrystallized twice from absolute ethanol and dried in vacuum. Reagent grade solvents were obtained from BDH. Benzene and THF were refluxed over sodium/ potassium alloy in the presence of benzophenone until the characteristic blue color of the benzophenone radical anion was obtained, then distilled. 3-picoline was distilled over KOH under a N_2 atmosphere prior to use.

Electrochemical solvents were freshly distilled over P_2O_5 under an inert atmosphere. All other chemicals were used as received. Infrared spectra were recorded as KBr pellets with Mattson 3000 Fourier Transform Infrared Spectrophotometer. ^1H and ^{13}C NMR spectra were performed on a Bruker ARX 400 MHz Nuclear Magnetic Resonance Spectrometer in an appropriate solvent using tetramethylsilane as an internal standard. Electronic spectroscopy was obtained using a Hewlett-Packard 8452 diode array spectrophotometer. Mass spectrometry was carried out using a Kratos profile HV4000 mass spectrometer. Fluorimetry experiments were conducted in a Shimadzu RF 551 spectrophotometer in argon deoxygenated samples. Electrochemistry experiments were performed using a Princeton Applied Research Corp. 263 Potentiostat using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as an electrolyte. A Perkin Elmer DSC7 equipped with TAC7 instrument controller was used to study the polymer thermal behavior. The instrument was calibrated with melting transitions of decane and indium. Samples were heated under N_2 atmosphere at a heating rate of 10 °C/min. Thermogravimetric analyses were also obtained on same instrument. The temperature was calibrated with the Curie transitions of Perkalloy and Nicoseal and were obtained at a heating rate of 20 °C/min under N_2. Ruthenium content analyses were performed by Galbraith laboratories, Inc., Knoxville, TN USA.

Preparation of 5,5'- dibromomethylene-2,2' bipyridine ligand (scheme 1)

5,5'-dimethyl-2,2' bipyridine (**2**). 211 g (2.27 mol) of freshly distilled 3-picoline (**1**) and 10 g of 10% weight palladium on activated carbon were refluxed for 72 hrs, followed by the addition of 100 ml of hot benzene were added and further refluxing for ½ hr. The catalyst was filtered off while still hot, then the volume of the filtrate was reduced to half and kept at 4°C overnight. The resulting white crystalline precipitate was filtered off and recrystallized from ethanol. Yield : 7.2 g (51% lit. 1.4 g/g of 10% wt Pd/C). m.p. 115°C (lit. 114-115°C) (16)

^{1}H NMR ($CDCl_3$, δ in ppm) δ: 8.39 (s, 2H, H6), 8.17 (d, 2H, H3), 7.49 (t, 2H, H4), 2.25 (s, 6H, CH3). IR (KBr pellets, ν in cm^{-1}) ν : 3050 (s, sharp, arom C-H str), 2965 (m, sharp, aliph C-H str), 1991-1677 (m, broad, arom overtone bands), 1590 (s, sharp, C=C ring str), 1363 (s, sharp, arom C-N str), 1119-1021 (m, sharp, aliph C-H in plane bend), 725 (s, sharp, arom C-H out-of-plane bend). MS-EI mode: m/z (%) 184 (100), 169 (7), 156 (12).

5,5'-dibromomethylene-2,2' bipyridine (**3**). 3.00 g (16.3 mmol) of 5,5'-dimethyl-2,2' bipyridine (**2**) were dissolved in 35 ml of dry benzene under a N_2 atmosphere and 6.10 g (34.3 mmol) of N-bromosuccinimide and 184 mg of benzoyl peroxide were added to while stirring. The reaction mixture was then refluxed for 4 hrs. The resulting yellowish solution was cooled slowly to room temperature, and the solvent was removed using a rotary evaporator. The obtained residual solid was generously washed with water, dried and twice recrystallized from ethanol. Yield: 2.51 g (45%) m.p. 174-176°C

^{1}H NMR ($CDCl_3$, δ in ppm) δ : 8.70 (s, 2H, H6), 8.42 (d, 2H, H3), 7.87 (q, 2H, H4), 4.55 (s, 4H, CH_2). IR (KBr pellets, ν in cm^{-1}) ν : 3010 (m, sharp, arom C-H str), 2965 (m, sharp, aliph C-H str), 1954-1751 (m, broad, arom overtone bands), 1587 (s, sharp, C=C ring str), 1376 (s, sharp, arom C-N str), 1247 (s, sharp, C-Br str), 1197-1019 (m, sharp, aliph C-H in plane bend), 736 (s, sharp, arom C-H out-of-plane bend), 646-560 (m, sharp, C-Br bend). MS-EI mode: m/z (%) 182 (100), 261 (88.2), 342 (13.3).

*Crosslinking of 5,5'-dibromomethylene-2,2' bipyridine (**3**) to (N-vinylcarbazole-vinylalcohol) copolymer* (**4**). 0.21 g (0.88 mmol) of copolymer (N-vinylcarbazole-vinylalcohol) (**4**) were dissolved in 15 ml of dry tetrahydrofuran under a N_2 atmosphere and the reaction flask kept cooled in an ice bath. After complete dissolution of the copolymer, 2 ml of butyllithium (2M in pentane) were added and the resulting solution stirred for 15 min. 0.15 g (0.44 mmol) of 5,5'-dibromomethylene-2,2' bipyridine (**3**) in 10 ml of tetrahydrofuran were then added dropwise and the reaction mixture left stirring at room temperature for 3 hrs. The volume of the obtained solution was then reduced to half using a rotary evaporator and the product precipitated from methanol and vacuum dried. Yield. 275 mg (91%)

^{1}H NMR ($CDCl_3$, δ in ppm) δ: 9.20-7.10 (br, 22H, arom), 4.80-5.29 (br, CH-N, chain), 3.37-3.78 (br, CH_2-arom), 2.10-2.42 (br, CH_2 aliph chain), 1.34 (br, 1H, OH).

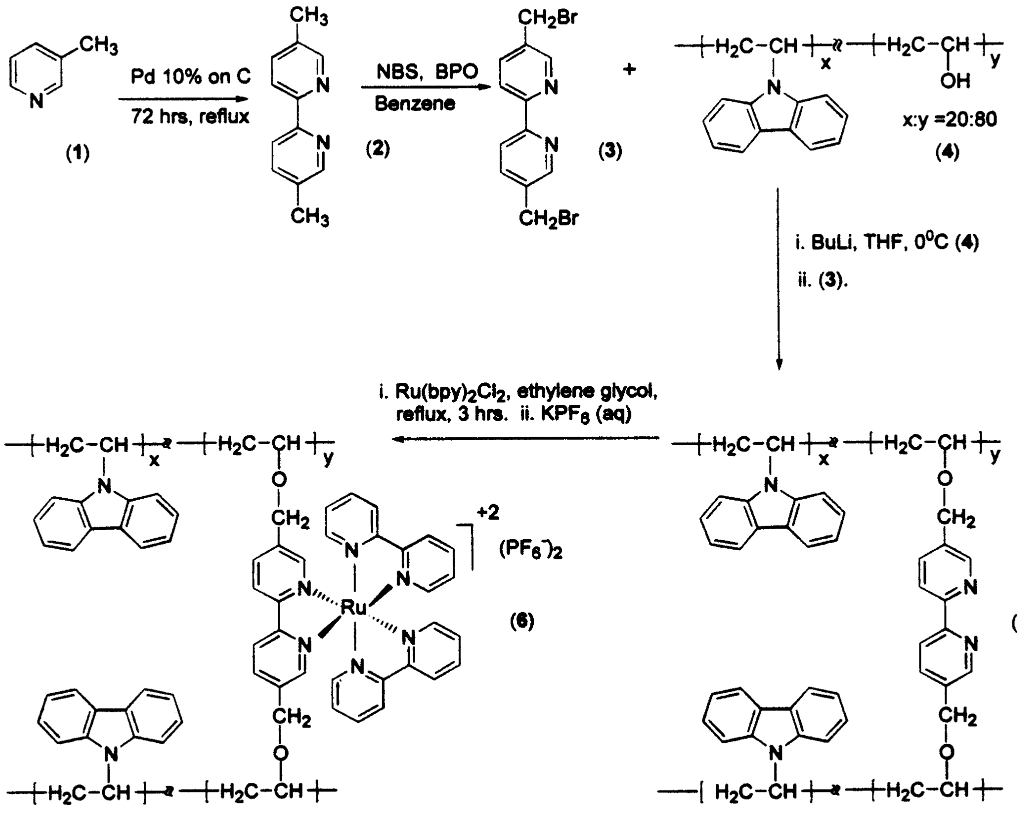
IR (KBr pellets, ν in cm^{-1}) ν : 3341 (m, weak shoulder, OH str), 3038 (m, sharp, arom C-H str), 2907 (m, sharp, aliph C-H str), 1880-1694 (m, arom overtone bands), 1589 (s, sharp, C=C ring str), 1324 (s, sharp, arom C-N str), 1150-1117 (m, sharp, aliph in plane bend), 1084 (m, sharp, C-O-C str), 732 (s, sharp, arom C-H out-of-plane bend).

Attachment of ruthenium moiety to the copolymer (**5**). 0.19 g (0.38 mmol) of bis-2,2' bipyridine ruthenium dichloride and 0.25 g (0.38 mmol) of the crosslinked copolymer (**5**) in 30 ml of reagent grade ethylene glycol were heated to reflux under a N_2 atmosphere for 2 hrs. The reaction mixture was allowed to cool to room temperature in which 0.90 g (6.2 mmol) of potassium hexafluorophosphate in 15 ml of water were added producing an orange precipitate, which was filtered off and generously washed with water, then with isopropyl alcohol, and dried. The polymer was then soxhlet extracted with tetrahydrofuran and, after concentrating the volume of the solution, the product was precipitated by the addition of diethyl ether and vacuum dried. Yield: 180 mg (35%).

IR (KBr pellets, ν in cm^{-1}) ν : 3419 (m, weak shoulder, OH str), 3032 (m, sharp, arom C-H str), 2956 (m, sharp, aliph C-H str), 1890-1730 (m, broad, arom overtone bands), 1598 (s, sharp, C=C ring str), 1447 (m, sharp, arom C-N str), 1097 (s, broad, C-O-C str), 722 (s, sharp, arom out-of-plane bend). UV-Vis (in DMF) λ_{max}: 292 nm (ε=11625 mol g^{-1} cm^{-1}), 454 nm (ε= 1805 mol g^{-1} cm^{-1}).

Results and discussion

Bis-2,2' bipyridine ruthenium dichloride $Ru(bpy)_2Cl_2$, with minor modification to the method of Meyer (17), and (N-vinylcarbazole-vinylalcohol) copolymer of (x:y:20:80) composition and with Mw=198,300 and Mw/Mn=1.35 were obtained as indicated in (18). 5,5'-dibromomethylene-2,2' bipyridine ligand (**3**) was prepared in a two-step reaction with an overall yield (48%) as outlined in scheme 1. 5,5'-dimethyl-2,2' bipyridine was obtained from the coupling reaction of 3-picoline catalyzed by the palladium on activated carbon as previously described (16). 5,5'-dimethyl-2,2' bipyridine (**2**) was then converted to the dibromo product (**3**) by reaction with N-bromosuccimide in benzene using benzoyl peroxide as a radical initiator. Both products were completely characterized by ^{1}H NMR, FT-IR and mass spectrometry. The ^{1}H NMR of 5,5'-dimethyl-2,2' bipyridine revealed singlet methyl protons at 2.25 ppm along with the characteristic aromatic bipyridine protons, which, when brominated as in the 5,5'-dibromomethylene- 2,2' bipyridine (**3**), shifted downfield at 4.55 ppm. FT-IR analysis also indicated all of the characteristic vibrational peaks of both products, in particular 5,5'-dibromomethylene-2,2' bipyridine revealed absorptions at 1247 cm^{-1} and 646-560 cm^{-1} corresponding to C-Br stretching and bending respectively. The electron impact mass spectrum of the 5,5'-dibromomethylene-2,2' bipyridine (**3**) ligand revealed the lack of polysubstituted dibromo or tribromo byproduct impurities from the radical reaction that would have obscured the facile recognition of the desired ligand peaks, and indicated the presence of three main intense peaks centered at (m/z=342), (m/z=261) and (m/z=182) corresponding to the parent molar mass of 5,5'-dibromomethylene-2,2' bipyridine molecular ion and the molar mass of the molecular ions after loss of the first and second bromine ion, respectively.



Scheme 1. Synthesis of the partially crosslinked (N-vinylcarbazole-vinylalcohol) ruthenium (II) containing copolymer (6)

As in common in functionalized polymer reactions (19), the reactive hydroxyl functionality of the copolymer (**4**) was activated with BuLi and subsequently reacted with the 5,5'-dibromomethylene-2,2' bipyridine ligand (**3**) scheme 1. The resulting partially crossslinked polymer (**5**) was soluble only in high boiling point polar solvents such as ethylene glycol, dimethylsulfoxide, and pyridine. Conversely, after reacting with Ru(bpy)$_2$Cl$_2$, the resulting bulky, ionic Ru (II) containing copolymer (**6**) was readily soluble in most common organic solvents. This improved solubility property has allowed the facile thin film formation of the polymer as well as its full characterization by conventional analytical methods. The ruthenium content of the copolymer was found to be 4.3 % by the elemental analysis which corresponds to 50% of maximum theoretical loading.

The cyclic voltammogram of the copolymer (**6**) containing the Ru (II) metal complex as shown in (figure 1 (top)), revealed three reversible one-electron reduction peaks at -1.30, -1.47, and -1.58 V (vs. SCE), corresponding to the reductions of the bipyridine ligands; the third reduction peak is broadened due to electrode passivation by the adsorption of the twice-reduced (per Ru) polymer onto the surface of the electrode as previously seen in similar systems (20). A reversible one-electron oxidation wave at 1.18 V was also observed for the Ru(II)/Ru(III) couple.

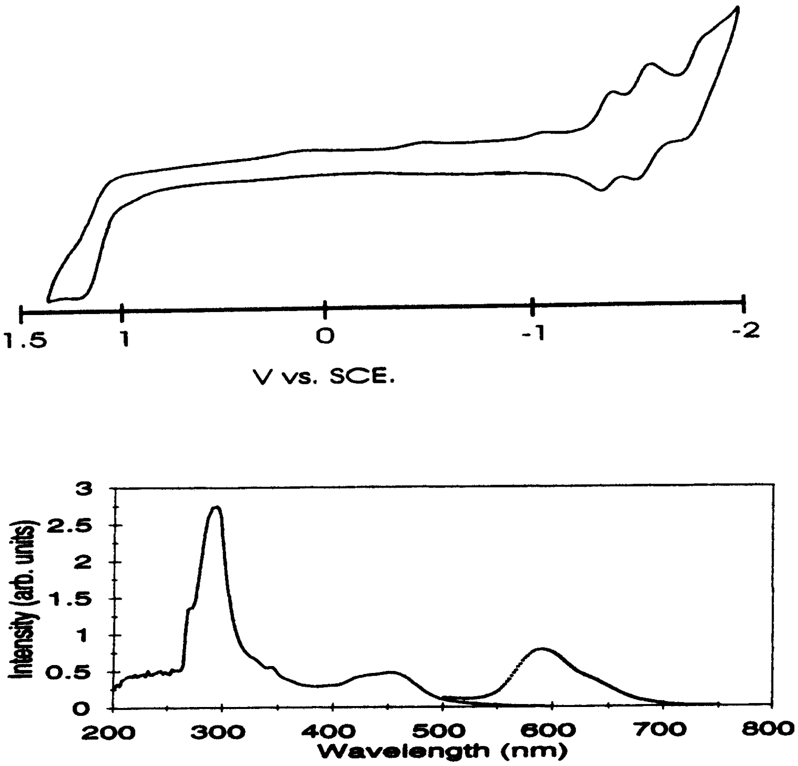


Figure 1. Cyclic voltammogram of copolymer (6) in DMF/N$_2$; 0.1M TBAPF$_6$; scan rate 100V/s Pt. disc. (Top), Absorption (solid lines) and emission spectrum (dotted lines) of the same copolymer (6) in DMF (bottom).

The UV-vis spectrum exhibits mainly the characteristic features of ruthenium polypyridyl compounds. It revealed two bands centered at 290 nm and 454 nm which are to be attributed to bipyridine ligand π-π* transition and metal-to-ligand charge transfer transition (MLCT) respectively. The polymer also emitted at 590 nm upon excitation of the maximum absorption at 400 nm as shown in (figure 1 (bottom)). To evaluate the thermal stability of polymers (**6**), (**5**) and (**4**), thermogravimetric analyses were carried out under N_2 atmosphere from ambient temperature up to the total degradation temperature of the polymers at a heating rate of 20 °C /min. Two successive degradation stages were observed, the first beginning at 300 °C and the second at 450 °C due to the relative rigidity of the polymer backbone arising from the multiple presence of aromatic rings and the ionic bulky Ru(II) metal center. In all cases, (see Figure 2) the weight loss was 10% at about 250 °C, and there were differences in the loss pattern for the polymers in terms of degradation onset temperatures depending upon the difference of chemical structure of the polymer backbone. For the DSC thermograms, there were no detectable thermal transitions and the polymers decompose before they melt.

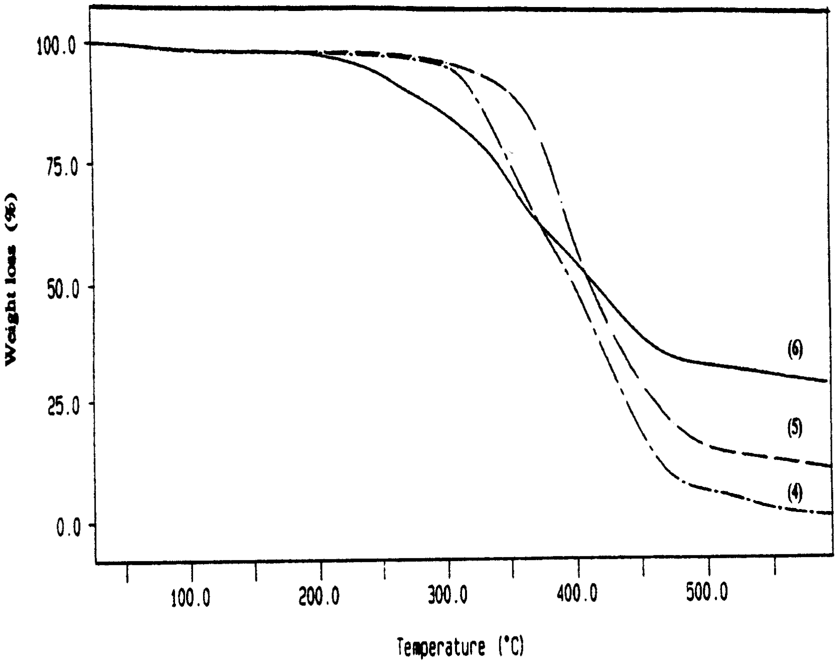


Figure 2. Thermogravimetric analysis (TGA) of copolymers (4), (5), and (6) under N_2 atmosphere, heating rate 20^0C/min.

Conclusion

We have synthesized and characterized a novel difunctionalized diimine ligand and easily incorporated it to a polypyridyl ruthenium entity. Electrochemical and electronic absorption spectroscopy results both confirm the covalent attachment of the ruthenium moiety into the polymer backbone. The resulting partially crosslinked copolymer not only has an excellent thermal stability but also promising electro and optical properties making it potential transition metal mediated electroluminescent device. The electroluminescence studies of this copolymer are in progress and will be reported in future.

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