

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

REDOX ACTIVE, MULTI-CHROMOPHORE RU(II) POLYPYRIDYL-CARBAZOLE COPOLYMERS: SYNTHESIS AND CHARACTERIZATION

Abdiaziz A. Farah^a; Jonathan G. C. Veinot^a; Morey Najman^a; William J. Pietro^a

^a Department of Chemistry, York University, Toronto, Canada

Online publication date: 26 October 2000

To cite this Article Farah, Abdiaziz A. , Veinot, Jonathan G. C. , Najman, Morey and Pietro, William J.(2000) 'REDOX ACTIVE, MULTI-CHROMOPHORE RU(II) POLYPYRIDYL-CARBAZOLE COPOLYMERS: SYNTHESIS AND CHARACTERIZATION', *Journal of Macromolecular Science, Part A*, 37: 11, 1507 – 1529

To link to this Article: DOI: 10.1081/MA-100101168

URL: <http://dx.doi.org/10.1081/MA-100101168>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

REDOX ACTIVE, MULTI-CHROMOPHORE RU(II) POLYPYRIDYL-CARBAZOLE COPOLYMERS: SYNTHESIS AND CHARACTERIZATION

Abdiaziz A. Farah, Jonathan G. C. Veinot, Morey Najman, and William J. Pietro*

Department of Chemistry
York University
4700 Keele Street
Toronto, Ontario, Canada, M3J 1P3

Key Words: Metallopolymer, Carbazole, Polypyridyl Luminophore, Ruthenium Complex, Electroactive Polymer, 2-(2-Pyridyl) 4-Carboxyquinoline

ABSTRACT

A novel diimine ligand, 2-(2-pyridyl) 4-carboxyquinoline (pcq) and its corresponding polypyridyl Ru(II) complex were synthesized, characterized, and covalently attached to a carbazole based copolymer via post polymer modification. The resulting modified electroactive and multi-chromophoric polymer was readily characterized by UV-visible, FT-IR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and elemental and electrochemical analysis. Results from cyclic voltammetry and FT-IR analysis both confirmed the covalent attachment of redox active Ru(II) center into the polymer. The emission spectrum of the copolymer, in comparison to that of Ru(II) complex, demonstrated that the excited-state properties of the metal complex is maintained, in contrast to the electronic absorption spectrum, which is sensitive to the hydrophobic polymeric chain surrounding the redox sites. The thermal analysis suggested that this metallopolymer also possesses high thermal

*Author to whom correspondence should be addressed.

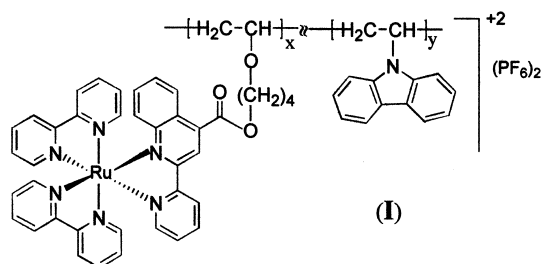
stability. The ruthenium content was also found to be 7%, which corresponds to 80% of the maximum loading, by elemental analysis.

INTRODUCTION

Transition-metal containing polymers are currently receiving much research attention due to their unique combination of the optical and electronic characteristics of transition metal complexes with structural and morphological properties typical of polymers [1]. These characteristics include their response to electric and magnetic fields, redox and catalytic properties, thermal and mechanical stability and enhanced processability. In particular, polymeric ligands containing $\text{Ru}(\text{bpy})_3^{2+}$ moieties are now attracting special research focus because of their potential application in chemically modified electrodes [2], photocatalysis in solar energy conversion [3], photoresponsive polymers based on photochemical electron transfer [4], photorefractive [5], and electronically conductive polymers [6].

One of the obvious objectives of metal ion incorporation into the polymers is to modify the essential bulk properties of these polymers with regard to possible practical application. The interaction of the metal moieties with the organic polymeric material introduces the possibility of application towards electroluminescent (EL) devices, a field demanding in-depth academic and industrial research. Although electrogenerated chemiluminescence (ECL) of both transition metal complexes and organic materials has been known for a while [7], ECL studies of solid-state light-emitting devices based on thin film ruthenium (II) complexes have only been recently demonstrated [8]. Relatively little investigation [9] into the application of conventional organic polymeric light-emitting diodes (LEDs) incorporating transition metal complexes has been reported. Thus, we have been investigating a new class of organic molecular conductors covalently bound to polypyridyl ruthenium(II) luminophores as basis of transition-metal mediated electroluminescent devices [10].

In this contribution, we describe the synthesis and characterization of a multifunctional one-component electroactive copolymer comprising of carbazole chromophore moieties covalently bound to a polypyridyl ruthenium (II) luminophore (I) for possible future application in light-emitting devices.



EXPERIMENTAL

Methods and Materials

All reagents were obtained from Aldrich Chemicals, Canada, except for tetrabutylammonium hexafluorophosphate and azo-bisisobutyronitrile (AIBN), which were obtained from Fluka Inc. and Alfa Aesar, Johnson Matthey Company, MA, respectively. Reagent grade solvents were obtained from BDH. Benzene, toluene, and THF were refluxed over sodium/potassium alloy in the presence of benzophenone until the characteristic blue color of the benzophenone radical anion was present and then distilled. Azo-bisisobutyronitrile (AIBN) and N-vinylcarbazole were recrystallized from methanol and dried in vacuum. Vinyl acetate was freshly distilled under a N_2 atmosphere prior to use. Electrochemical solvents were freshly distilled over P_2O_5 under an inert atmosphere and electrolytes were twice recrystallized from absolute ethanol and were dried in vacuum. All other chemicals were used as received. *cis*-Ru(bpy) $_2$ Cl $_2$ xH_2O was prepared as described in [11].

Infrared spectra were recorded as KBr pellets with Mattson 3000 Fourier Transform Infrared Spectrophotometer. 1H and ^{13}C NMR spectra were obtained on a Bruker ARX 400 MHz Nuclear Magnetic Resonance Spectrometer in an appropriate solvent using tetramethylsilane as an internal standard. Electronic spectroscopy was performed using a Hewlett-Packard 8452 diode array spectrophotometer. Mass spectrometry was carried out using a Kratos 902 high-resolution mass spectrometer. Fluorimetry experiments were conducted in a Shimadzu RF 551 spectrophotometer on argon deoxygenated samples. Electrospray mass spectrometry was obtained with a Sciex TAGA 6000E MS/MS system in 10 μ M sample solution in acetonitrile. Electrochemistry experiments were performed using a Princeton Applied Research Corp. 263 Potentiostat, with tetrabutylammonium hexafluorophosphate (TBAPF $_6$) as the

supporting electrolyte. Gel Permeation Chromatography (GPC) experiments were carried out in THF (1ml/min) using microstyragel columns with pore sizes of 10^3 - 10^6 Å (Waters) equipped with a dual detection system consisting of a differential refractometer (Waters model 410) and differential viscosimeter (Viscotek model H502). The molar masses were referenced to a polystyrene calibration curve. A Perkin Elmer DSC7 equipped with TAC7 instrument controller was used to study polymer thermal behavior. For DSC experiments, the instrument was calibrated with melting transitions of decane and indium, and samples were heated under N₂ atmosphere at a heating rate of 10°C/min. Thermogravimetric analyses were also obtained on the same instrument TGA7 and the temperature was calibrated with the curie transitions of Perkalloy and Nicoseal. Thermograms were obtained at a heating rate of 20°C/min under N₂ atmosphere. Galbraith Laboratories, Inc., Knoxville, TN performed elemental analyses.

Copolymer Preparations (Scheme 1)

Copolymer (N-vinylcarbazole-vinyl acetate) (3) [12]

100 ml of dry benzene were placed into a three-neck round-bottom flask equipped with a nitrogen inlet and reflux condenser in subdued light. After nitrogen gas was passed through the benzene for ~1.5 hours, 20 g (0.10 mol) of N-vinylcarbazole (**1**) and 44.6 g (0.520 mol) of vinyl acetate (**2**) were added and the mixture was stirred to dissolve the reagents. 154 mg of 2,2'-azobis-isobutyronitrile (AIBN) (0.15% of total mol) were added and the reaction mixture was allowed to react at 65-70°C with stirring for 48 hours. The resulting viscous solution was precipitated by the addition of 600 ml of methanol. The isolated polymer was further purified by two subsequent precipitations from chloroform using methanol, and the white polymer was dried in vacuum. Yield. 17.5 g (63%)

¹H NMR (CDCl₃, δ in ppm) δ: 8.11-7.23 (br, 8H, aromatic), 4.2-4.7 (br, 2H, CH), 1.98 (br, 2H, CH₂), 1.41 (br, 3H, CH₃). ¹³C NMR (CDCl₃, δ in ppm) δ: 170.41 (C=O), 140.41, 137.94, 125.53, 123.93, 122.44, 120.29, 119.15, 110.66, 108.48, 67.99, 66.36, 49.02, 38.62, 20.97. IR (KBr pellets, ν in cm⁻¹) 3050 (m, sharp, arom C-H str), 2928 (m, sharp, aliph C-H str), 2100-2010 (w, shoulder, arom overtone), 1736 (s, sharp, C=O ester str), 1593 (m, sharp, C=C arom ring str), 1447 (s, sharp, C=C arom ring str), 1326 (s, broad, arom C-H str), 745 (s, sharp, C-H bend), 740 (s, sharp, C=C out of plane). GPC: Mw:205,700, Mw/Mn:1.27

Copolymer (N-vinylcarbazole-vinylalcohol) (4)

16.0 g of (*N-vinylcarbazole-vinylacetate*) (**3**) were dissolved in 300 ml of tetrahydrofuran (THF) and 75 ml of 1.0 N methanolic solution of sodium hydroxide was added in subdued light. The reaction mixture was then stirred for 4 hrs at 60°C, and the resulting viscous solution was then precipitated by the addition of 800 ml of methanol. The desired polymeric material (**4**) was further purified by two subsequent precipitations from THF solution into diethyl ether. Yield: 11.0 g (81%).

¹H NMR (DMSO-d₆, δ in ppm) δ: 7.99-6.71 (br, 8H, aromatic), 3.8-4.7 (br, 2H, CH), 2.22 (br, 2H, CH₂), 1.38 (H, OH). ¹³C NMR (DMSO-d₆, δ in ppm) δ: 140.33, 137.76, 125.37, 123.18, 121.66, 120.31, 118.32, 111.61, 108.7, 67.07, 65.88, 40.07, 25.14. IR (KBr pellets, ν in cm⁻¹) 3350 (m, broad shoulder, O-H str), 3048 (m, sharp, arom C-H str), 2915 (m, sharp, aliph C-H str), 1593 (m, sharp, C=C ring str), 1448 (s, sharp, C=C str), 1324 (m, sharp, arom N-H str), 718 (s, sharp, arom C-H out of plane bend), 714 (s, sharp, C=C out of plane bend). GPC: Mw:198,300, Mw/Mn:1.35 *Copolymer (N-vinylcarbazole-vinyl-4-oxy-n-butanol) (5)* 1.07 g (4.50 mmol) of (*N-vinylcarbazole-vinylalcohol*) (**4**), (1.86 g, 140 mmol) of anhydrous potassium carbonate, (0.73 g, 6.80 mmol) of 4-chloro-1-butanol and (0.11 g, 0.68 mmol) of potassium iodide were dissolved in 25 ml of reagent grade DMF under N₂ and left refluxing for 20 hours. The resulting solution was cooled down to room temperature, diluted with 30 ml of H₂O, stirred and filtered. The volume of the filtrate was concentrated to 20 ml and the product was precipitated by the addition of methanol. The polymer (**5**) was then purified by two subsequent precipitations from the THF solution to diethyl ether and vacuum dried. Yield: 1.02 g (75%)

¹H NMR (DMSO-d₆, δ in ppm) δ: 7.99-7.11 (br, 8H, aromatic), 3.67-4.37 (br, 2H, CH), 3.34-3.40 (m, 4H, OCH₂), 1.59-2.89 (m, 12H, CH₂ chain), 1.37 (H, OH). IR (KBr pellets, ν in cm⁻¹) 3382 (m, broad shoulder, O-H str), 3050 (m, sharp, arom C-H str), 2928 (m, broad, alph C-H str), 1885 (w, broad, arom overtone), 1482 (s, sharp, C=C ring str), 1326 (s, sharp, in-plane OH bend), 1122 (m, sharp, asym C-O-C str), 749 (s, sharp, out-of plane arom C-H bend), GPC: Mw:190,450, Mw/Mn:1.36

Ligand preparation (Scheme 2)*2-(2-pyridyl) 4-carboxyquinoline Sodium Salt (8) [13]*

18 g (0.12 mol) of (2,3-indolinedione) (**6**) and 15 g (0.12 mol) of 2-acetylpyridine (**7**) were thoroughly mixed for ~30 minutes in a 500 ml beaker. 60

g (~60 ml) of 33% NaOH were added at 5°C with stirring. The solution was stirred until the contents began to harden and the temperature rose spontaneously to ~60°C. 60 ml of ice water were then added to the flask content resulting in a purple-red slurry. The slurry was allowed to cool to room temperature and was filtered. The solid was initially washed with water and further purified by a generous washing with acetone and decolorized by addition of NORIT activated carbon. Upon filtering the solid was repeatedly recrystallized from water until light-purple shining crystals were obtained. Yield: 18 g (67%)

¹H NMR (DMSO-d₆, δ in ppm) δ: 8.99 (s, H3 of quinoline), 8.78 (d, H12 of pyridine), 8.76 (d, H5 of quinoline), 8.62 (d, H9 of pyridine), 8.21 (d, H8 of quinoline), 8.05 (t, H10 pyridine), 7.88 (t, H7 of quinoline), 7.75 (t, H6 of quinoline), 7.56 (t, H11 of quinoline). IR (KBr pellets, ν in cm⁻¹). 3478 (w, shoulder, O-H str), 2064 (w, broad, arom overtone), 1695 (s, sharp, C=O str), 1586 (m, sharp, C=C ring str), 1476 (m, sharp, C=C ring str), 1283 (s, sharp, C-O str), 758 (s, sharp, C-H out of plane bend).

2-(2-pyridyl) 4-carboxyquinolic Acid (pcq) (9)

17 g (68 mmol) of 2-(2-pyridyl)-4-carboxyquinoline sodium salt (**8**) were dissolved in 300 ml of distilled water and titrated while stirring vigorously with a 10% HCl (aq.) solution to a stable pH of 7. The resulting brownish precipitate was filtered and air-dried. It was then pulverized and vacuum dried. Yield: 14 g (87%). decomp. >300 °C.

¹H NMR (DMSO-d₆, δ in ppm) δ: 8.99 (s, H3 of quinoline), 8.78 (d, H12 of pyridine), 8.76 (d, H5 of quinoline), 8.62 (d, H9 of pyridine), 8.21 (d, H8 of quinoline), 8.05 (t, H10 pyridine), 7.88 (t, H7 of quinoline), 7.75 (t, H6 of quinoline), 7.56 (t, H11 of quinoline). ¹³C NMR (DMSO-d₆, δ in ppm): 167.62, 155.20, 154.45, 149.49, 148.22, 137.59, 137.39, 130.24, 129.95, 128.37, 125.67, 125.05, 124.60, 121.08, 119.27. IR (KBr pellets, ν in cm⁻¹). 3478 (w, broad, O-H str), 2064 (w, broad, arom overtone), 1695 (s, sharp, C=O str), 1586 (m, sharp, C=C ring str), 1476 (m, sharp, C=C ring str), 1283 (s, sharp, C-O str), 758 (s, sharp, C-H out of plane bend). EI-MS (m/z) (%). 250 (55), 206 (100).

Ru(bpy)₂(2-pyridyl) 4-carboxyquinolinic Acid Ru[(bpy)₂(pcq)]²⁺ (II)
(Scheme 3)

0.35 g (0.72 mmol) of cis-Ru(bpy)₂Cl₂ xH₂O (**10**) were dissolved in 15 ml of methanol. 0.25 g (1.44 mmol) of AgNO₃ were added to the dissolved substrate and the solution was left stirring for 2 hours at room temperature. The resulting white precipitate was then filtered off and 0.18 g (0.72 mmol) of 2-(2-

pyridyl) 4-carboxyquinolic acid (**9**) in 10 ml of methanol were added to the filtrate which was then left to reflux for 16 hours. The solvent was then removed using a rotary evaporator and the resulting dark-red product was purified by column chromatography (alumina) using chloroform:methanol (1:1) as the eluant. Yield. 0.20 g (38%).

^1H NMR (DMSO- d_6 , δ in ppm) δ : 8.64 (s, H3, quinoline), 8.42 (d, H5, quinoline), 7.56 (q, H6, quinoline), 7.21 (t, H7, quinoline), 7.48 (q, H8, quinoline), 7.47 (q, H9, quinoline), 8.00 (t, H10, quinoline), 7.48 (q, H11, quinoline), 8.18 (m, H12, quinoline), 8.80 (d, H13, bpy), 8.20 (t in m, H14, bpy), 7.50 (t in m, H15, bpy), 7.74(d, H16, bpy), 8.20(d in m, H17, bpy), 7.40(t in m, H18, bpy), 8.20 (t in m, H19, bpy), 8.50 (d, H20, bpy), 7.84 (d, H21, bpy), 7.60 (t in m, H22, bpy), 8.20 (t in m, H23, bpy), 8.93 (d, H24, bpy), 8.59 (d, H25, bpy), 7.60 (t in m, H26, bpy), 8.20 (t in m, H27, bpy), 8.81(d, H28, bpy). IR (KBr pellets, ν in cm^{-1}). 3407 (m, broad shoulder, O-H str), 3066 (m, broad, arom C-H str), 1607 (s, sharp, C=O str), 1382 (s, sharp, C-O str), 767 (m, sharp, out-of-plane C-H bend). UV-Vis (DMF) ϵ_{max} : 290 ($\epsilon=53381 \text{ mol}^{-1} \text{ L cm}^{-1}$), 440 ($\epsilon=10163 \text{ mol}^{-1} \text{ L cm}^{-1}$) and 504 nm ($\epsilon=9627 \text{ mol}^{-1} \text{ L cm}^{-1}$). ES-MS. $\text{C}_{35}\text{H}_{26}\text{N}_6\text{O}_2\text{Ru(II)}$. 329.0, 329.5, 330.0, 330.5, 331.0, 331.5, 332.0, 332.5, 333.0, 333.5, 334.0

*Covalent Attachment of $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ (**11**) to (N-vinylcarbazole-vinyl-4-oxy-n-butanol) Copolymer (**5**) (Scheme 3)*

0.12 g (0.16 mmol) of $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ (**11**) were dissolved in 15 ml of thionyl chloride containing a catalytic amount of DMF. The reaction was allowed to reflux with constant stirring under nitrogen for ~ 3 hours. Following removal of the excess thionyl chloride, the obtained solid material was reacted *in situ* by refluxing it with 24.50 mg (0.36 mmol) of imidazole in 10 ml of dry toluene for 1 hour. After cooling to room temperature the solvent was removed under vacuum. 73.40 mg (0.25 mmol) of (N-vinylcarbazole-vinyl-4-oxy-n-butanol) (**5**) in 15 ml of DMF were added and the reaction mixture refluxed with constant stirring for 3 hours. The mixture was allowed to cool slowly to room temperature, then a ten fold excess of aqueous potassium hexafluorophosphate was added producing an orange precipitate which was filtered and washed generously with water, methanol and finally dissolved in THF and precipitated by addition of methanol. The resulting polymeric (**I**) product was dried under vacuum. Yield. 20 mg (11%)

IR (KBr pellets, ν in cm^{-1}) 3086 (w, broad, arom C-H str), 2929 (w, broad, aliph C-H str), 1999 (w, broad, arom, arom overtone), 1713 (s, sharp, C=O ester str), 1255 (s, broad, arom C-N str), 831 (s, broad, out-of-plane arom C-H str), 763

(s, sharp, ring C=C out-of-plane bend) UV-Vis (DMF) ϵ_{max} : 292 ($\epsilon=17182 \text{ mol}^{-1} \text{ L cm}^{-1}$), 458 nm ($\epsilon=3682 \text{ mol}^{-1} \text{ L cm}^{-1}$).

RESULTS AND DISCUSSION

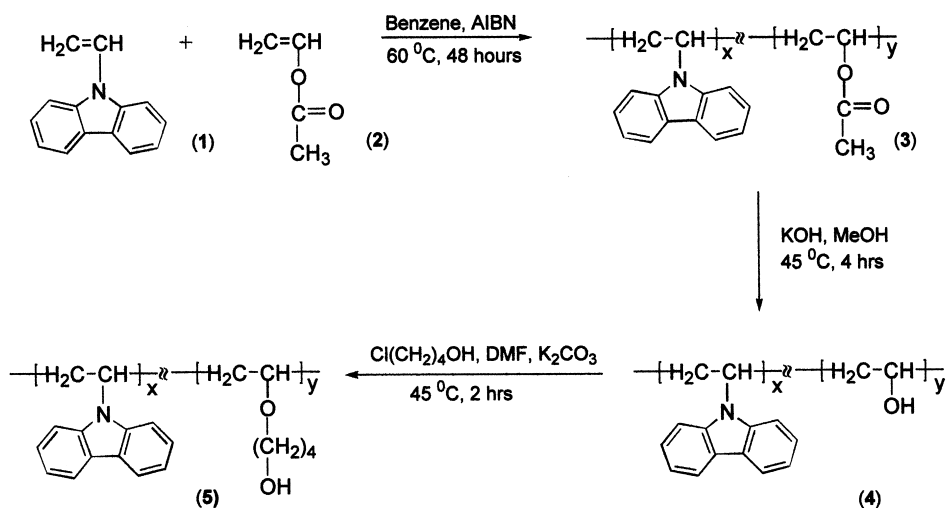
Reactions Schemes and Characterizations

Copolymer Synthesis

There are two popular approaches towards synthesizing new polymeric materials in which the ruthenium complex is covalently bound to the polymer chain. The first approach, involves the synthesis of polymers bearing the bipyridyl type ligands, followed by coordination of the transition metal complexes [14]. The second one, involves the synthesis of monomers containing ionic transition metal complexes following the polymerization/or copolymerization with related monomers [9(b), 15]. We have chosen an alternative method based on post-polymer modifications, in which chemically active functional polymers were reacted with well-characterized ionic ruthenium complexes through common polymeric reactions [16].

The design of our polymers starts with poly (N-vinylcarbazole), because of its good hole-conducting characteristics under applied electric field [17]. Poly(N-vinylcarbazole) homopolymer is, however, stiff and fragile substance and copolymerization with suitable monomers, where applicable, could result in materials with an enhanced film property [18]. Thus, we copolymerized 9-vinylcarbazole (**1**) with vinylacetate (**2**) in 1:5 monomer feed ratio in benzene under N_2 atmosphere for 48 hours in subdued light using AIBN as a radical initiator (Scheme 1). The resulting poly(N-vinylcarbazole-vinylacetate) (**3**) was hydrolyzed to poly(N-vinylcarbazole-vinylalcohol) (**4**) with methanolic potassium hydroxide at 60°C for 4 hours. In order to allow the hydroxyl functionality of the copolymer (**4**) to further react with sterically bulky transition metal complex while maintaining copolymer integrity, we extended the functionality away from the polymer chain by reacting the alcohol with 4-chloro-butanol, thus yielding the copolymer (**5**).

Copolymers (**3**), (**4**), and (**5**) were characterized using ^{13}C NMR, ^1H NMR, FT-IR and gel permeation chromatography (GPC). ^{13}C NMR of the copolymer (**3**) revealed the presence of C=O carbon at 170 ppm corresponding to carbonyl group of the vinylacetate. In addition, signals in the range of 108-140 ppm characteristic of aromatic carbons, corresponding to the carbazole moiety in the polymer chain, were observed. For copolymers (**4**) and (**5**) no signals were detected at 170 ppm,



Scheme 1. Synthesis of the copolymers

which clearly supports the lack of ester functionality in the copolymers. It was also found in the ^1H NMR that these copolymers comprise 20:80 vinylcarbazole/vinylalcohol in composition. More interestingly, The ^1H NMR of all copolymers revealed broad overlapping peaks centered at 7.42-8.10 ppm for the carbazole aromatic protons and 1.20-4.4 ppm for aliphatic chain protons with no observable peaks at 5.0 ppm. This particular large upfield shift to 5.0 ppm of one of the aromatic protons is generally attributed to the shielding effects of neighboring carbazole groups on the polymer chain with restricted internal rotation [19]. The absence of this peak presumably indicates that in our copolymers the carbazole chromophores are not in close proximity to one another. The FT-IR exhibited an intense absorption at 1736 cm^{-1} for copolymer (3) corresponding to $\text{C}=\text{O}$ ester stretch of the acetate group, which was no longer detected for copolymers (4) and (5). FT-IR also confirmed the presence of the carbazole aromatic entity with absorptions at 3050 cm^{-1} characteristic of the aromatic C-H stretch, and broad multiples centered at $2100\text{-}1950\text{ cm}^{-1}$ corresponding to aromatic overtone bands. An intense broad signal was also observed at 1320 cm^{-1} for the C-N aromatic stretch of the carbazole groups for all copolymers.

The average molar mass and the degree of polymerizations of these copolymers were investigated by gel permeation chromatography (GPC). These analyses showed that the copolymer (4) has $M_w=198,000$ and $M_n=145,000$, and for copolymer (5) $M_w=190,000$ and $M_n=137,000$, which corresponds to a high average degree of polymerization of approximately 600 monomer units for both copolymer [20].

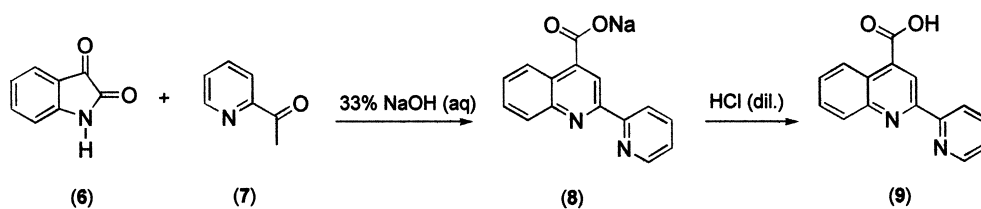
Ligand Synthesis

2-(2-pyridyl) 4-carboxyquinoline (PCQ) (**9**) was prepared from the reaction of 2,3-indolinedione (**6**) and 2-acetylpyridine (**7**) [10] (Scheme 2). The two reactants were stirred in the presence of concentrated aqueous sodium hydroxide in a two-step reaction with an overall yield of 77% (Scheme 2). This acid ligand (**9**) was characterized using ^1H NMR, ^1H - ^1H COSY, FT-IR and mass spectrometry. A first order spectrum was revealed in its ^1H NMR where a pair of doublets represented each proton and a distinguishable shift at 9.00 ppm was also observed (Figure 1). The intense singlet peak at 9.00 ppm corresponds to the uncoupled protons (H3) of quinoline. In addition, another eight protons corresponding to the correct number of hydrogen atoms in the product (excluding the acid proton) were observed. The FT-IR spectrum also indicated all characteristic vibrational absorptions of the desired product. A weak OH stretch was observed at 3470 cm^{-1} , as well as a strong C=O absorption at 1695 cm^{-1} . The carbonyl stretch of the acid ligand is relatively low in energy compared to the typically reported values for aromatic carbonyls, however, it is characteristic of quinolic systems [21].

The electron impact mass spectrum of 2-(2-pyridyl) 4-carboxyquinoline (PCQ) (**9**) is shown in Figure 2. This spectrum reveals two major features. First, the lack of large background from the presence of impurities which would have obscured the facile recognition of the ligand peaks, and secondly, the presence of two main intense peaks at ($m/z = 250$) and ($m/z = 206$) which correspond to the parent molar mass of the 2-(2-pyridyl) 4-carboxyquinoline (PCQ) ligand and the molar mass of the molecular ion after loss of CO_2 , respectively.

$\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ Complex Synthesis

The ruthenium complex containing the 2-(2-pyridyl) 4-carboxyquinoline (PCQ) ligand $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ (**11**) was prepared in two-step reaction with an overall yield (38%) as shown in (scheme 3). $\text{cis-Ru}(\text{bpy})_2\text{Cl}_2$ (**10**) was dissolved



Scheme 2. Synthesis of 2-(2-pyridyl) 4-carboxyquinoline (pcq) ligand (**9**).

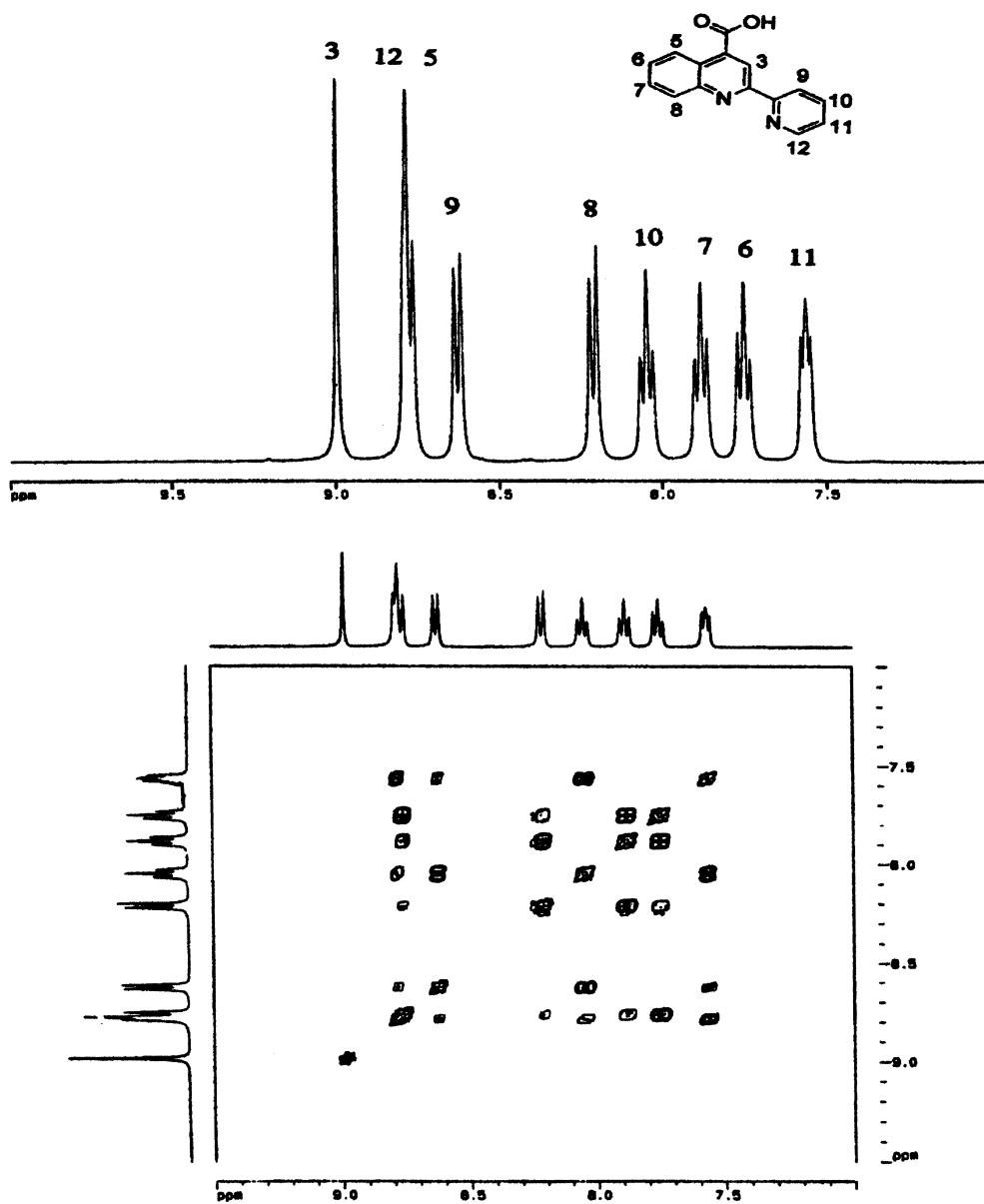


Figure 1. ^1H NMR and ^1H - ^1H COSY of 2-(2-pyridyl) 4-Carboxyquinoline (PCQ) ligand (9) in DMSO- d_6 .

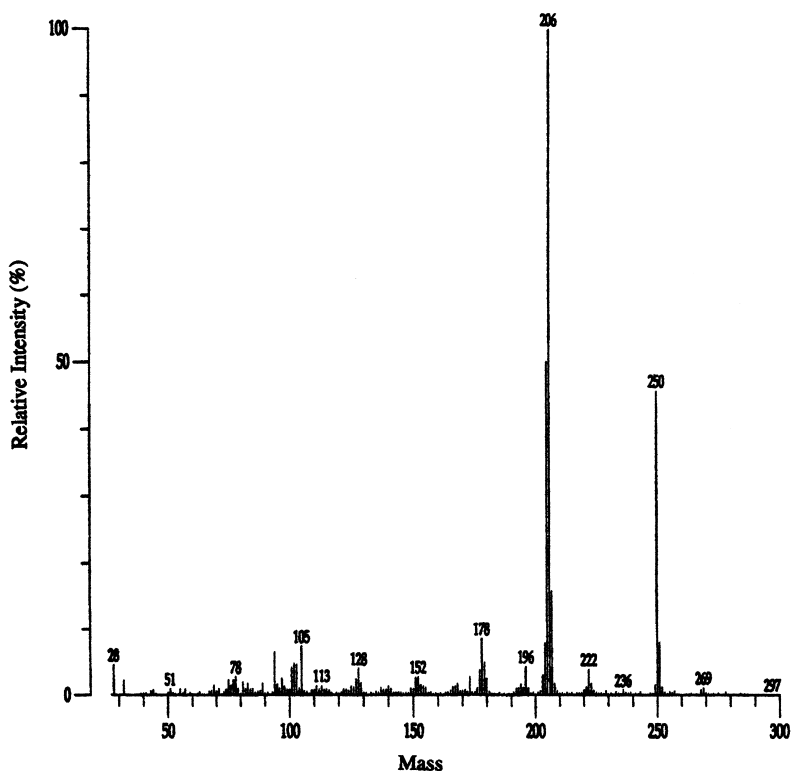


Figure 2. Electron impact mass spectrum of 2-(2-pyridyl) 4-Carboxyquinoline (PCQ) ligand (9).

in methanol and reacted with AgNO_3 in order to precipitate out AgCl . Upon removal of the chloride ion, the solvated ruthenium species were then allowed to react with 2-(2-pyridyl) 4-carboxyquinoline (pcq) acid ligand (9) for attachment.

The crude complex, after the removal of the solvent, was purified by column chromatography on alumina using a 1:1 mixture of chloroform: methanol as an eluant.

The purified ruthenium complex (11) was analyzed and characterized using the ^1H NMR, ^{13}C NMR, ^1H - ^1H COSY, FT-IR, electrospray mass spectrometry and ruthenium elemental analysis. ^1H NMR and ^1H - ^1H COSY spectra indicated that the coordination of the acid ligand to the ruthenium center was achieved Figure 3. Both spectra have the distinguishable signal appearing at ~ 9.00 ppm corresponding to the uncoupled (H3) proton of the acid ligand. Furthermore, the number of protons assigned correspond to the correct number of protons of the desired ruthenium complex, which clearly supports the suc-

cessful attachment of the ligand to the metal center. FT-IR spectroscopy provided further evidence of the incorporation of the ligand to the metal center. An absorption band corresponding to the acid, C=O stretch at 1607 cm^{-1} , and a broad shoulder O-H stretch at 3407 cm^{-1} were detected. The electrospray mass spectrum obtained in the positive-ion mode for the complex $\text{C}_{35}\text{H}_{26}\text{N}_6\text{O}_2\text{Ru}$ (II) (**11**) is illustrated in Figure 4. It gives a clean parent-ion envelope centered at m/z 332, and it is obvious from the half-mass unit separation of the peaks in the isotope pattern that it is a dication with a mass of 665 Daltons as expected. The inset also shows that the agreement between the experimental and the calculated isotopic distribution pattern is excellent, within (± 1) Dalton supporting the above assignment.

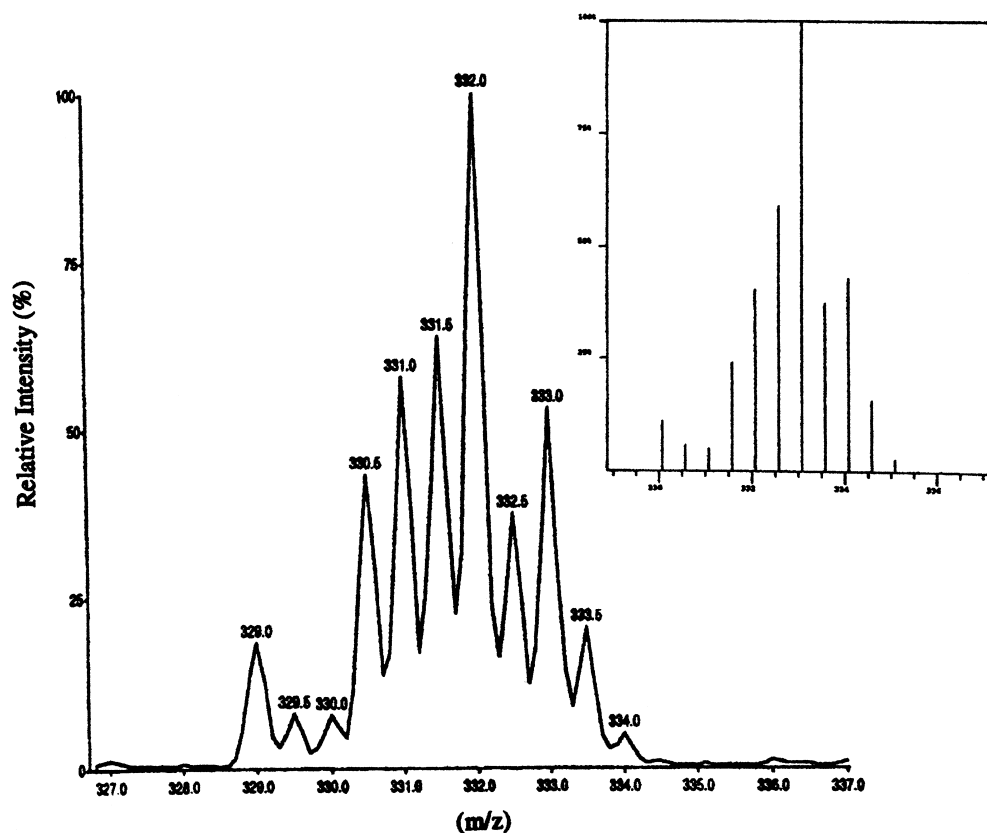
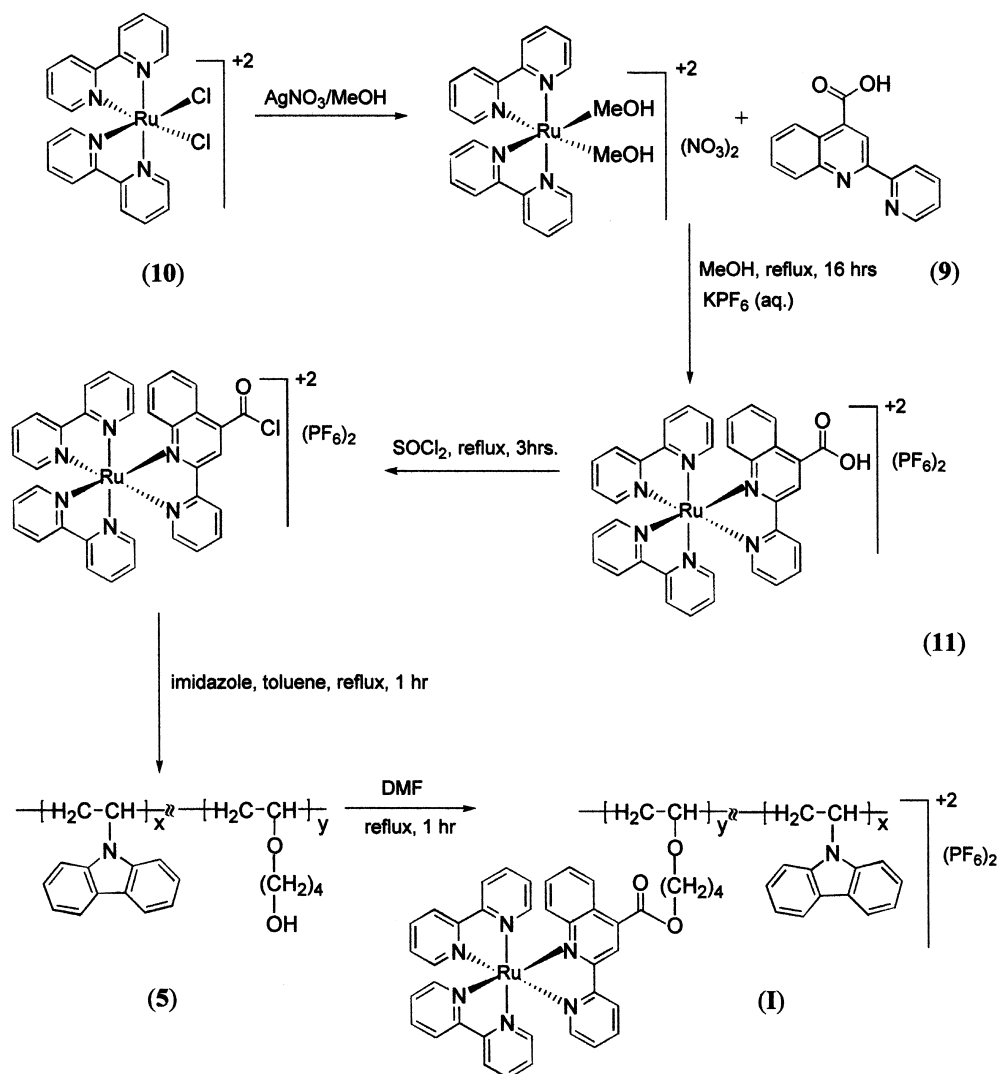


Figure 4. Electrospray mass spectrum of $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex (**11**) in acetonitrile. The inset shows the comparison between the observed traces and calculated (sticks) of isotopic distributions for the base peaks of the complex.

Covalent Attachment of the Ru(II) Complex to the Copolymer

Ru[(bpy)₂(pcq)]²⁺ complex (**10**) was converted to an acid chloride by refluxing with thionyl chloride and then converted into the more reactive acylimidazole adduct as shown in Scheme 3. The acylimidazole complex adduct was then reacted *in situ* with copolymer (**5**). The reaction progress was monitored by FT-IR spectroscopy for the continuous decrease of the 3350 cm⁻¹ of O-H stretch-



Scheme 3. Synthesis of Ru[(bpy)₂(pcq)]²⁺ complex (**11**) and its attachment to the copolymer (**5**).

ing absorption band of the copolymer, and subsequent formation of 1713 cm^{-1} of C=O, ester stretch in the final copolymer. The reaction product was then precipitated with a large excess of aqueous potassium hexafluorophosphate giving an orange solid material, which is readily soluble in common organic laboratory solvents. The ruthenium content of the copolymer was found to be 7.10% by elemental analysis, which corresponds to 81% of the maximum theoretical amount.

Electrochemical, Thermal and Electronic Spectroscopic Analysis

Electrochemical studies of these ruthenium-containing compounds, yielded unambiguous information about the ligand environment, and verified the covalent attachment of the complex to the polymer main chain. For $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex (**11**) three reversible reduction peaks at -1.28, -1.60, and -1.88 V, corresponding to the reduction of the coordinated ligands, and a reversible Ru(II)/(III) oxidation wave at 1.27 V were observed in DMF (all versus SCE) as shown in Figure 5 The copolymer (**I**) exhibited two reversible ligand reduction

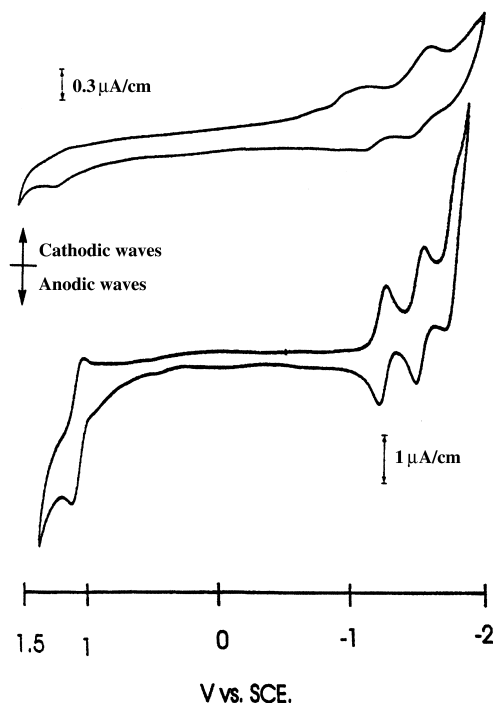


Figure 5. Cyclic voltammograms of derivatized Ru(II) containing copolymer (**I**) (top) and $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex (**11**) (bottom) in DMF/ N_2 , 0.1 M TBAPF_6 , Scan rate 100mV/s; Pt disc.

peaks at -1.30, -1.60, and a reversible oxidation of the metal center at 1.33 V. The third ligand reduction peak of the copolymer was broadened due to electrode passivation arising from the adsorption of the twice-reduced (per Ru) polymer as previously encountered in similar systems [22]. It is also reasonable that the hydrophobic environment created by the high local concentration of the polymeric chain may affect the redox behavior of $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex. In this poorly solvated polymeric surrounding, the differences in solvation of electrochemically generated radicals may create non-homogeneous sites along the polymer chain, giving rise to the observed broadened waves in the voltammogram.

Carbazole itself, as an electroactive moiety [23], seems a major contributor to the observed surface broadening waves in analogy to polymers having redox-reversible pendant groups [24]. This has been attributed to various factors, such as a difference in the spatial distribution of the redox centers [25], a distribution of species with different redox potentials for the electroactive units [26], and repulsive interactions [27], depending on the particular system. Once the electroactive groups become coated onto the electrode surface, the possibility of further reaction is reduced, making the material more insulating. The $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex (**11**) shows well-defined oxidation/reduction waves which remain unchanged even after multiple scans, but complete electro-inactivity is observed for the copolymer in subsequent cycles due to electrode passivation. Nevertheless, the observed slight variations in the values of the reduction and oxidation peaks between the $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex and the copolymer may indicate interactions between the electronic structures of the ruthenium complex and the copolymer as predicted.

Thermogravimetric (TGA) analyses were carried out under N_2 atmosphere from ambient temperature to total degradation of the polymer. The TGA thermograms revealed, as shown in Figure 6, multiple degradation processes, where the onset of the first degradation process is around 240°C , the second at 375°C , the third and the fourth at 475°C and 500°C , as can be seen from the differential curve (dotted curve). This observed multiple degradation pattern presumably arises from the relative rigidity of the polymer imparted by the high density of aromatic rings and the bulk ionic Ru (II) center. The polymer demonstrated high thermal stability with less than 3% weight loss at around 300°C . For the DSC thermograms, there were no detectable thermal transitions as the polymers decompose before melting.

UV-vis spectra show some interesting features of the $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ complex (**11**) and the copolymer (**I**) to which it is attached, as shown in Figure 7. The absorption spectrum of the $\text{Ru}[(\text{bpy})_2(\text{pcq})]^{2+}$ (**11**) showed three bands. An absorption around 290 nm is attributed to polypyridyl $\pi-\pi^*$ transition, and two metal-to-ligand charge transfer bands (MLCT) at 440 nm and 504 nm, respec-

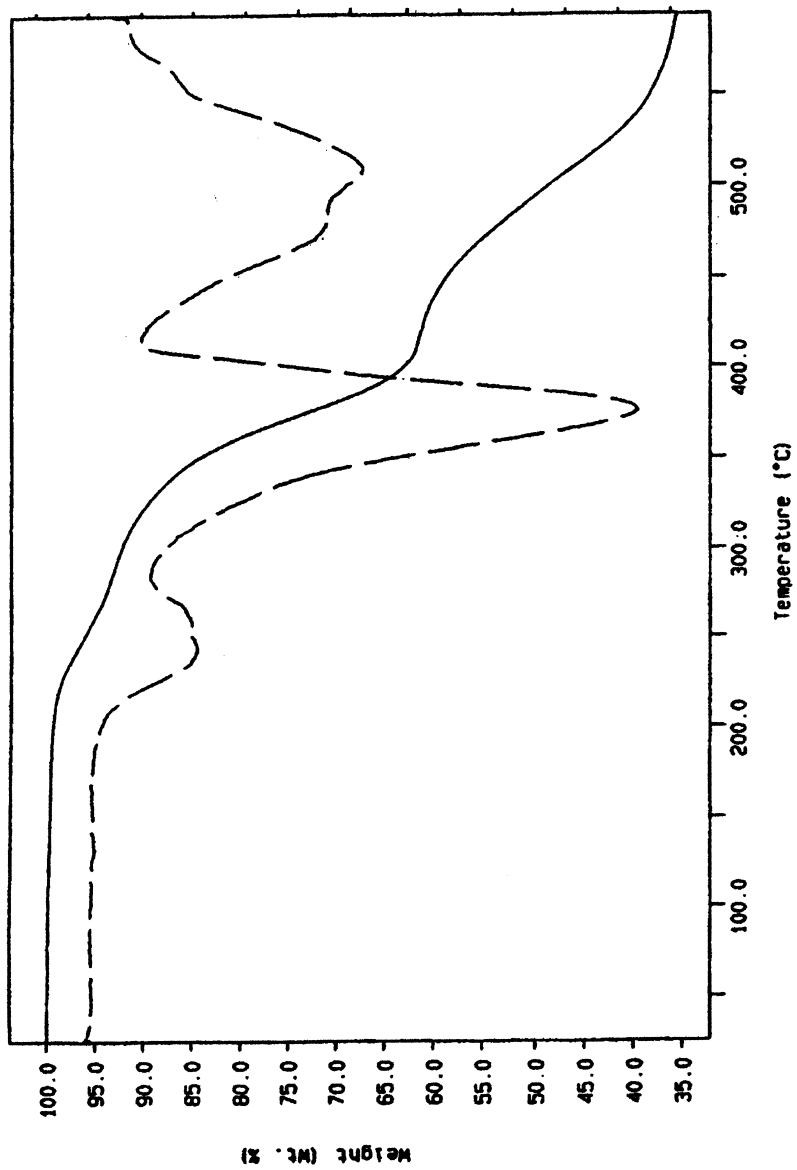


Figure 6. TGA thermogram (solid) and differential curve (dotted) of derivatized Ru(II) containing copolymer (I), under N_2 atmosphere, scan rate $20^\circ C/min$.

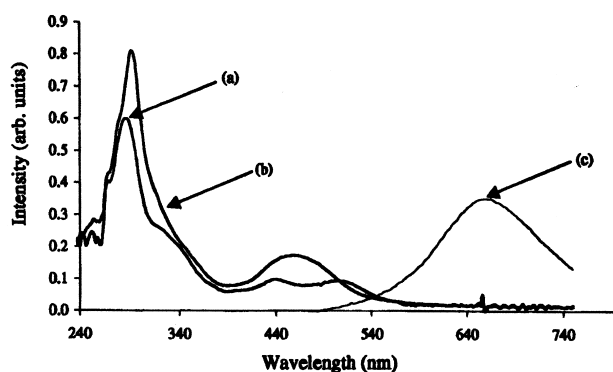


Figure 7. Absorption spectra of Ru[(bpy)₂(pcq)]²⁺ complex (a) and copolymer (11) (b)

tively, were also observed. We tentatively assigned the MLCT band centered at 440 nm to involve the bipyridine ligand and the band at 504 nm to the 2-(2-pyridyl) 4-carboxyquinoline (pcq) ligand, presumably red-shifted due to the more extended π -electron orbitals in this conjugated benzoid ring. In the copolymer (I) the situation is different; the UV-vis spectrum showed that the ligand centered π - π^* transition still exists at around 290 nm along with one broad MLCT peak at around 458 nm. There may be two absorptions under the broad peak, however, in a polymeric environment, it is difficult to assess. Preliminary ZINDO calculations revealed a 494 nm MLCT transition, which we assigned to the 2-(2-pyridyl) 4-carboxyquinoline (pcq) ligand, and a 457 nm MLCT transition assigned to the bipyridine ligand in a very good agreement to UV-vis analysis. These results suggest two important points. First, the ruthenium complex is indeed incorporated into the polymer chain and second, more important, the MLCT transition energy is lowered. The second point is crucially important not only for designing these polymers for electroluminescent application with systems that undergo fast charge transfer process, but also in controlling the polymers optical properties. The fluorimetric analysis of the complex and its polymer after excitation at the maximum absorption peak of 400 nm, both displayed the same emission peak centered at 655 nm.

CONCLUSION

In conclusion, we have successfully synthesized and fully characterized a novel 2-(2-pyridyl) 4-carboxyquinoline (pcq) diimine ligand and easily incorpo-

rated it onto a polypyridyl ruthenium entity. Furthermore, we have demonstrated its covalent attachment via post-polymer modification to poly(N-vinylcarbazole-vinyl alcohol) copolymer. The resulting multifunctional derivatized copolymer shows interesting electrochemical, thermal and optical properties making it a potential candidate for electroluminescent (EL), transition metal mediated, polymeric based devices. The electroluminescence studies of this copolymer are in progress and will be reported shortly.

ACKNOWLEDGMENTS

We express our gratitude to Dr. A. B. P. Lever and his research group for their valuable comments and discussions, to Dr. Ian Manners and his research group for assistance in gel permeation chromatography and Lisa Nelson for mass spectrometry. We also thank to the Natural Science and Engineering Research Council (NSERC) of Canada for financial support.

REFERENCES

- [1] For a general review of metal-containing polymers see: (a) *Organometallic Polymers*, C. E. Carraher, Jr., J. E. Sheats, and C. U. Pittman, Jr. (Eds., Academic Press, NY, 1978); (b) *Metal Containing Polymeric Systems*, J. E. Sheats, C. E. Carraher, Jr., and C. U. Pittman, Jr., Eds., Plenum, NY, 1985; (c) *Inorganic and Metal-Containing Polymeric Materials*, J. E. Sheats, C. E. Carraher, Jr., C. P. Pittman, Jr., M. Zeldin, and B. Currel, Eds., Plenum, NY, 1985; (d) *Inorganic and Organometallic Polymers*, M. Zeldin, K. J. Wynne, and H. R. Allcock, Eds., ACS Symp. Ser., 360, (1988); (e) B. M. Cullbertson and C. U. Pittman, Jr., *New Monomers and Polymers*, Plenum, NY, 1984; (f) E. W. Neuse and H. Rosenberg, *Metallocene Polymers*, Marcel-Dekker, NY, 1970; (g) J. E. Sheats, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Ed., Vol. 15, Wiley and Sons, NY, 1981; (h) I. Manners, *Adv. Organomet. Chem.* 37, 131 (1995).
- [2] (a) P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, 102, 5543 (1980), (b) A. Fujishima, K. Honda, *Nature*, 37, 238 (1972); (c) A. Fujishima and K. Honda, *Bull. Chem. Soc. Jpn.*, 44, 1148 (1971); (d) M. S. Wrighton,

- D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Liwz, *Proc. Natl. Acad. Sci. USA*, **72**, 1518 (1975).
- [3] (a) J. S. Connolly, Ed., *Photochemical Conversion and Storage of Solar Energy*, Academic, New York, (1981); (b) M. Kaneko and A. Yamada, *Adv. Polym. Sci.*, **55**, 1, (1984).
- [4] (a) Y. Kurimura, M. Shinozaki, F. Ito, Y. Uratani, K. Shigehara, E. Tsuchida, M. Kaneko, and A. Yamada, *Bull. Chem. Soc. Jpn.*, **55**, 380 (1982); (b) J. M. Kelly, C. Long, C. M. O'Connell, J. G. Vos, and A. H. A. Tinnemans, *Inorg. Chem.*, **22**, 2818 (1983); (c) M. Kaneko, A. Yamada, E. Tsuchida, and H. Nakamura, *J. Phys. Chem.*, **88**, 1061 (1984); (d) K. Sumi, M. Furue, and S. I. Nozakura, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 3059 (1985); (e) X. H. Hou, M. Kaneko, and A. Yamada, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2749 (1986); (f) P. M. Ennis, J. M. Kelly, and C. M. O'Connell, *J. Chem. Soc., Dalton Trans.*, 2485 (1986); (g) M. Kaneko, and H. Nakamura, *Macromolecules*, **20**, 2265 (1987); (h) J. Olmsted III, S. F. McClanahan, E. Danielson, J. N. Younathan, and T. J. Meyer, *J. Am. Chem. Soc.* **109**, 3297 (1987); (i) P. M. Ennis and J. M. Kelly, *J. Phys. Chem.*, **93**, 5735 (1989); (j) J. N. Younathan, S. F. McClanahan, and T. J. Meyer, *Macromolecules*, **22**, 1048 (1989); (k) G. F. Strouse, L. A. Worl, J. N. Younathan, and T. J. Meyer, *J. Am. Chem. Soc.* **111**, 9101 (1989); (l) L. A. Worl, G. F. Strouse, J. N. Younathan, S. M. Baxter, and T. J. Meyer, *J. Am. Chem. Soc.* **112**, 7571 (1990); (m) J. N. Younathan, W. E. Jones, Jr., and T. J. Meyer, *J. Phys. Chem.*, **95**, 488 (1991); (n) S. M. Baxter, W. E. Jones, Jr., E. Danielson, L. A. Worl, G. F. Strouse, J. N. Younathan, and T. J. Meyer, *Coord. Chem. Rev.*, **111**, 47 (1991); (o) W. E. Jones, Jr., S. M. Baxter, G. F. Strouse, and T. J. Meyer, *J. Am. Chem. Soc.*, **115**, 7363 (1993); (p) R. M. Leasure, T. Kajita, and T. J. Meyer, *Inorg. Chem.*, **35**, 5962 (1996); (q) L. M. Dupray and T. J. Meyer, *Inorg. Chem.*, **35**, 6299 (1996); (r) T. Nakahira, Y. Inoue, K. Iwasaki, H. Tanigawa, Y. Kouda, S. Iwabuchi, and K. Kojima, *Makromol. Chem., Rapid Commun.*, **9**, 13, (1988).
- [5] Q. Wang, L. Wang, and L. Yu, *J. Am. Chem. Soc.*, **120**, 12860 (1998).
- [6] S. S. Zhu and T. M. Swager, *Adv. Mater.*, **8**, 497 (1996).
- [7] *Principles and Recent Developments of Solid State Light-Emitting Electrochemical Cells (LEC)*, see: a) Q. Pei, G. Yu, C. Zhang, Y. Yang, and A. J. Heeger, *Science*, **269**, 1086 (1995); b) A. J. Bard, *Science*, **270**,

- 719 (1995); c) Q. Pei, Y. Yang, G. Yu, C. Zhang, and A. J. Heegar, *J. Am. Chem. Soc.*, *118*, 3922 (1996); d) F. Huang, H. L. Wang, M. Feldstein, A. G. MacDiarmid, B. R. Hseih, and A. J. Epstein, *Synth. Metals*, *85*, 1283 (1997); e) Q. Pei, Y. Yang, G. Yu, Y. Cao, and A. J. Heegar, *Synth. Metals*, *85*, 1229 (1997).
- [8] *Examples of ECL Ru(II) Based Systems*, see: (a) C. M. Elliott, F. Pichot, C. J. Bloom, and L. S. Rider, *J. Am. Chem. Soc.*, *120*, 6781 (1998); (b) C. H. Lyons, E. D. Abbas, J. K. Lee, and M. F. Rubner, *J. Am. Chem. Soc.*, *120*, 12100 (1998); (c) J. K. Lee, D. S. Yoo, E. S. Handy, and M. F. Rubner, *Appl. Phys. Lett.*, *69*, 1686 (1996); (d) D. S. Yoo, A. Wu, J. K. Lee, and M. F. Rubner, *Synth. Met.*, *85*, 1425 (1997).
- [9] *Examples of Conventional Polymeric LEDs Ru(II) Based Systems*, see (a) W. Y. Ng, X. Gong, and W. K. Chan, *Chem. Mater.*, *11*, 1165 (1999); (b) J. K. Lee, D. Yoo, and M. F. Rubner, *Chem. Mater.*, *9*, 1710 (1997).
- [10] J. G. C. Veinot, A. A. Farah, and W. J. Pietro, *Makromol. Chem. Rapid Commun.* (to be submitted) (1999).
- [11] B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, *17*, 3334 (1978).
- [12] D. M. Chang, S. Gromelski, R. Rupp, and J. E. Mulvaney, *J. Polym. Sci. Polym. Chem. Ed.*, *15*, 571 (1977).
- [13] Y. Bass, R. J. Morgan, R. J. Donovan, and A. D. Baker, *Synthetic Commun.*, *27(12)*, 2165 (1997).
- [14] J. N. Younathan, S. F. McClanahan, and T. J. Meyer, *Macromolecules*, *22*, 1048 (1989)
- [15] Z. Peng and L. Yu, *J. Am. Chem. Soc.*, *118*, 3777 (1996).
- [16] A. Akelah and D. C. Sherrington, *Chem. Rev.*, *81*, 557 (1981).
- [17] *Poly(N-vinylcarbazole) as a Hole-Conducting Material* see: (a) *Organic Electroluminescent Materials*, S. Miyata, H. S. Nalwa, Eds., Gordon and Breach Publishers, Chap. 5, 1997; (b) S. Y. Song, M. S. Jang, H. K. Shim, D. H. Hwang, and T. Zyung, *Macromolecules*, *32*, 1482 (1999); (c) S. Maruyama, X-T.Tao, H. Hokari, T. Noh, Y. Zhang, T. Wada, H. Sasabe, H. Suzuki, and T. Watanabe, *Chem. Lett.*, 749 (1998); (d) K. Kim, M. K. Ryu, D. K. Kim, and S. M. Lee, *Macromolecules*, *31*, 1114 (1998); (e) Z. Peng, Z. Bao, and M. E. Galvin, *Chem. Mater.*, *10*, 2086 (1998); (f) S. Wang, W. Hua, F. Zhang, and Y. Wang, *Synth. Metals*, *99*, 249 (1999); (g) X. Z. Jiang, Y. Q. Liu, X. Q. Song, and D. B. Zhu, *Synth. Metals*, *91*, 311 (1997); (h) Y. Yang, H. Jiang, S. Liu, X. Zhou, F. Wang, F. Wu,

- W. Tian, Y. Ma, and J. Shen, *Synth. Metals*, *91*, 335 (1997); (i) H. Kusano, S. Hosaka, N. Shiraishi, S. Kawakami, K. Sugioka, M. Kitagawa, K. Ichino, and H. Kobayashi, *Synth. Metals*, *91*, 337 (1997); (j) S. Berlab, W. Brüttig, M. Schwoerer, R. Wehrmann, and A. Elschner, *J. Appl. Phys.*, *83*, 4403 (1998); (k) W. Brüttig, S. Berlab, G. Egerer, M. Schwoerer, R. Wehrmann, and A. Elschner, *Synth. Metals*, *91*, 325 (1997); (l) D. D. Gebler, Y. Z. Wang, S. W. Jessen, J. W. Blatchford, A. G. MacDiarmid, T. M. Swager, D. K. Fu, and A. J. Epstein, *Synth. Metals*, *85*, 1205 (1997).
- [18] R. Z. Greenley, in *Polymer Handbook*, 4th Ed., by J. Brandrup, E. H. Immergut, and E. A. Grulke, John Wiley & Son, 1999, p. 181.
- [19] (a) D. J. Williams, *Macromolecules*, *5*, 602 (1972); (b) S. Yoshimoto, Y. Akana, A. Kimura, H. Hirata, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, 987 (1969).
- [20] G. G. Odian, *Principles of Polymerization*, 3rd Ed., John Wiley & Sons, 1991, p. 54.
- [21] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectroscopic Identification of Organic compounds*, 5th Ed., John Wiley & Sons, 1991, p. 125.
- [22] (a) H. D. Abruna, A. Y. Teng, G. J. Samuels, and T. J. Meyer, *J. Am. Chem. Soc.*, *101*, 6745 (1979); (b) A. A. Farah and W. J. Pietro, *Polymer Bulletin*, *43*, 135 (1999); (c) A. A. Farah and W. J. Pietro, *Polymer Journal (to be submitted)* (1999).
- [23] (a) B. R. Hsieh, M. H. Litt, and K. Abbey, *Macromolecules*, *19*, 521 (1986); (b) J. W. Park, J. H. Lee, J. M. Ko, H. N. Cho, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, *32*, 2789 (1994).
- [24] A. J. Bard and P. J. Peerce, *J. Electroanal. Chem.*, *114*, 89 (1980).
- [25] K. Itaya and A. J. Bard, *J. Anal. Chem.*, *50*, 1487 (1978).
- [26] M. S. Wrighton, M. C. Pallazzotto, A. B. Bocarsly, J. M. Bolts, A. B. Fisher, and L. Nadjo, *J. Am. Chem. Soc.*, *100*, 7264 (1978).
- [27] (a) J. R. Lenhard and R. W. Murray, *J. Am. Chem. Soc.*, *100*, 7870 (1978); (b) K. Kuo, P. R. Moses, J. R. Lenhard, D. C. Green, and R. W. Murray, *Anal. Chem.*, *51*, 745 (1979); (c) D. F. Smith, K. William, K. Kuo, and R. W. Murray, *J. Electroanal. Chem.*, *95*, 217 (1979).

Received September 29, 1999

Revision received June 1, 2000