Dyes and Pigments 83 (2009) 95–101

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis and characterization of near-infrared absorbing, electrochromic polyimides containing a dinuclear ruthenium complex in the polymer mainchain

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ARTICLE INFO

Article history:
Received 23 November 2008
Received in revised form
19 March 2009
Accepted 21 March 2009
Available online 9 April 2009

Keywords:
Polyimide
Dinuclear ruthenium complex
Near infrared
Electrochromic
Optical attenuation

ABSTRACT

A redox-active, near-infrared absorbing dinuclear ruthenium complex was incorporated into the mainchain of polyimides using a two-stage polymerization method. The polyimides show high thermal stability with a decomposition temperature range from 172 to 248 °C and glass transition temperature of 97–180 °C, depending on the dianhydride monomer used. The polyimides are redox active, electrochromic at 1600 nm with the ruthenium complex being in the mixed-valence state and fluorescent at 790 nm.

1. Introduction

Polyimides have been shown to be excellent structural materials for various high temperature components in microelectronic, automotive and aerospace applications. They have also been used as passive materials in optical components (e.g., optical waveguides) owing to their desirable properties such as low optical loss [1], tunable refractive index [2], high thermal stability [3] and dimensional stability [4]. To be useful as active materials, polyimides need at least to absorb or to emit the light efficiently at a specific wavelength of interest. Specifically, to make polyimides active in the near infrared (NIR) spectral region (800–2000 nm) for potential telecommunication applications such as variable optical attenuators operating at 1310 and 1550 nm [5], one can either dope (by physical mixing) or incorporate (by covalent bonding) an NIR electrochromic chromophore into a polyimide. Doping is simple but often results in phase separation or aggregation; while covalent linking of NIR chromophores to the polyimide can be synthetically challenging.

Among various NIR-absorbing materials, dinuclear ruthenium complexes (DCH–Ru, Fig. 1) with dicarbonylhydrazine (DCH) bridging ligand are a class of well-studied NIR electrochromic materials [5,6]. Previous studies on DCH–Ru complexes include the structure–property relationship between the substituents and NIR absorption [5] and incorporation into vinyl polymers as pendant groups [7]. DCH–Ru complexes can exist in three oxidation states with characteristic absorptions, Ru^{II}/Ru^{II} (550 nm), Ru^{II}/Ru^{III} (1600 nm) and Ru^{III}/Ru^{III} (800 nm), which correspond to metal-to-ligand charge transfer (MLCT), metal-to-metal charge transfer (MMCT) transitions and ligand-to-metal charge transfer (LMCT), respectively. The generic structure of DCH–Ru complexes (Fig. 1) indicates a large structural variation at the bridging ligand having the substituents (R, R′) such as alkyl, aryl, alkoxy, phenoxy, alkylamino, etc. Changing the electron withdrawing or donating ability of the ligand affects the HOMO/LUMO energy levels and thus changes the absorption wavelength.

The motivation for this study comes from the fact that polyimides are not NIR absorbing and the question of how to make polyimides NIR electrochromic for potential NIR applications while maintaining their excellent thermal, mechanical and optical properties. Polymers have the advantages of easy processing, film quality and morphology control over the small molecules. NIR emission is interesting and useful in many applications such as optical sensors and telecommunications. To date, no study has been undertaken on the incorporation of a DCH–Ru complex into the polymer backbone or in the polymer mainchain. Thus, in this work, incorporation of a DCH–Ru complex into the polyimide backbone is explored. Herein, NIR electrochromic and luminescent polyimides containing a DCH–Ru complex in the mainchain are reported. The polyimides were synthesized and characterized and all displayed an intense absorption centered at 1600 nm upon the oxidation to the mixed-valence state.

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doi:10.1016/j.dyepig.2009.03.020

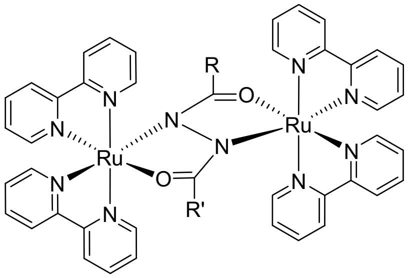


Fig. 1. Generic structure of DCH–Ru complex.

2. Experimental

2.1. Materials

4-Nitrobenzoyl chloride (ed note: combustible; incompatible with water, alcohols, strong oxidants, strong alkalis) and hydrazine hydrate (ed note: toxic; incompatible with a wide variety of materials, including oxidants, heavy metal oxides, dehydrating agents, alkali metals, rust, silver salts; combustible: contact with many materials may cause fire or explosive decomposition) solution 85% (W/V) were purchased from Aldrich and used with no further purification. Platinum oxide was purchased from Nutritional Biochemical Corporation and used as received. Ammonium hexafluorophosphate (ed note: incompatible with strong acids; combustion may generate hydrogen fluoride, phosphorus oxides or phosphine) was purchased from SynQuest Labs. Inc. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and acetonitrile (MeCN) were purchased from Caledon and used without further purification. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) purchased from ChrisKEV company, Inc. and 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) purchased from Aldrich were recrystallized from acetic anhydride and dried at 120 °C in vacuum oven. 9,9-Bis(4-aminophenyl)fluorene (BAPF) was purchased from Ken Seika Corp and purified by recrystallization from ethanol.

2.2. Characterizations

Fourier Transform Infrared (FTIR) measurements were performed on a Bomen FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer. The onset temperatures for 5% weight loss of the polymers were determined using a TA thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen. Glass transition temperature (T_g) was determined on a TA DSC Q100 at a heating rate of 10 °C/min in nitrogen. Inherent viscosities of the polymers were measured with an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C with a concentration of 0.5 g/dL.

Cyclic voltammograms were recorded using a BAS 100B/W electrochemical station interfaced and monitored with a PC computer. A three-electrode cell configuration and 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) in acetonitrile as supporting electrolyte were used for all electrochemical measurements. The silver pseudo-reference electrode is calibrated with a ferrocene/ferrocenium redox couple. All the solutions were deoxygenated with nitrogen prior to electrochemical measurements. Spectroelectrochemical measurements were carried out by combining the electrochemical station with a Perkin Elmer Lambda 900 UV–vis–NIR spectrophotometer. Spectroelectrochemistry in solutions was conducted using an OTTLE cell or on ITO glass.

2.3. Optical attenuation measurement

In a quartz cuvette, were placed a tin-doped indium oxide (ITO) as a working electrode, a platinum counter electrode and silver reference electrode. The working electrode was coated with complex polymers or crosslinked polymer containing DCH–Ru diamine **3**. The cuvette was fitted with a Teflon cap through which the reference electrode and counter electrode were introduced to the cell via pre-drilled holes.

2.4. Ligand and monomer syntheses

2.4.1. 4-Nitro-N′-(4-nitrobenzoyl)benzohydrazide (*1*)

To a 100 mL, round-bottomed flask, 4-nitrobenzoyl chloride (1.9 g, 10 mmol) was added slowly to a solution of hydrazine hydrate (85% W/V) (0.38 mL, 10 mmol) in 30 mL of 95% ethanol at 15 °C. To this solution, sodium carbonate (1.06 g, 10 mmol) in 10 mL of water was added dropwise together with another amount of 4-nitrobenzoyl chloride (1.9 g, 10 mmol). The bright orange solution gave a fine off-white precipitate after one hour of vigorous stirring. The solution was stirred for another hour at the same temperature, then the precipitate was filtered and washed with 95% ethanol to give the desired product as off-white powders: 2.83 g (43% yield); mp 295 °C (Lit [8a] 297–298 °C, Lit [8b] 288 °C); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.0 (2H, S), 8.34 (4H, m), 8.17 (4H, m); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 164.73, 149.96, 138.36, 129.51, 124.30.

2.4.2. 4-Amino-N′-(4-aminobenzoyl)benzohydrazide (*2*)

In a hydrogenation bottle, 1 g of 4-nitro-N′-(4-nitrobenzoyl)benzohydrazide (**1**) was suspended in 60 mL of THF. Platinum oxide (0.1 g) was then added and the hydrogenation shaker switched on for 4 h at 50 psi. The mixture was then filtered and THF was evaporated to give very fine off-white powders: 0.6 g (73% yield); mp 272 °C (Lit [9] 303–304 °C); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.0 (2H, S), 8.4 (4H, m), 8.2 (4H, m), 7.8–7.9 (4H, m); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 164.79, 150.0, 138.4, 129.5, 124.30.

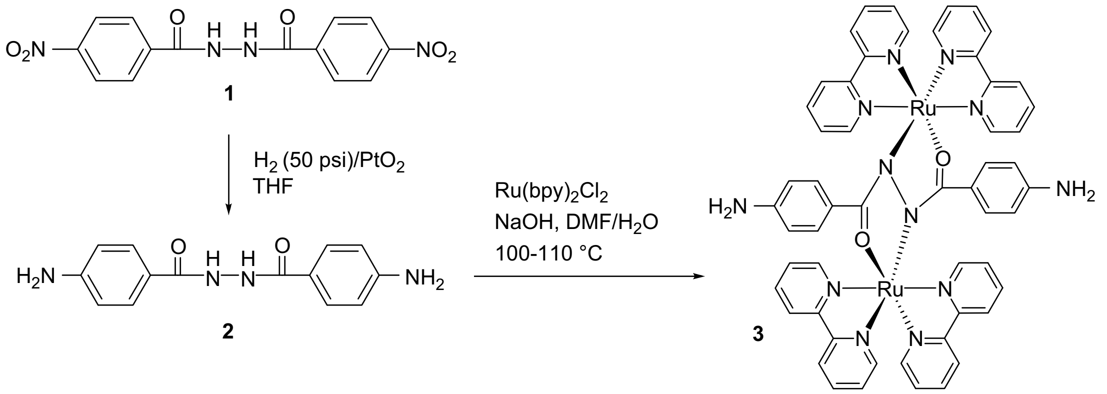
2.4.3. DCH–Ru complex monomer (*3*)

Compound **2** (0.27 g, 1.0 mmol), Ru(bpy)$_2$Cl$_2$.H$_2$O (1.03 g, 2.00 mmol) and NaOH (0.18 g, 4.50 mmol) were dissolved in DMF/H$_2$O (2:3 v/v, 25 mL). The mixture was then refluxed at 100–110 °C under argon for 24 h. After cooling to room temperature, the product was precipitated out by pouring in 300 mL of aqueous solution of NH_4PF_6 (0.75 g, 4.6 mmol). The product was then filtered, re-dissolved in acetonitrile and precipitated out from ether. Purification of the crude complex was done on neutral alumina column using 4:1 MeCN/toluene. The purple band was collected, concentrated under reduced pressure, dissolved in MeCN, precipitated out from ether and dried under vacuum overnight: 0.83 g (60% yield); MS (ESI): 1241.0 ($M-PF_6^-$).

2.5. Polymer synthesis

2.5.1. ***PRu-I***

Salicylic acid (1.77 g, 1.23 mL) was placed in a pressure glass tube, melted and maintained at 200 °C for 10 min 6FDA (0.159 mmol, 0.071 g) and DCH–Ru diamine **3** (0.159 mmol, 0.219 g) were introduced into the melt. The concentration of monomers in salicylic acid was 23 wt/v%, followed by addition of 5 drops of isoquinoline. Once all were dissolved, the reaction tube was closed tightly (with a crew cap) and the portion of the tube containing the reaction mixtures (about 1/3 in length) was immersed in an oil bath at 200 °C for 2.0 h. After cooling to about 150 °C, the tube cap was removed carefully. The red viscous polyamic acid solution was poured slowly onto Pyrex plate placed on a hot plate, which was



Scheme 1. Synthesis of DCH–Ru diamine **3**.

then heated slowly up 200 °C at a rate of 10 °C/5 min for imidization. The polymer was collected, washed with methanol/water solution and dried in vacuum oven at 120 °C.

Poly(amic acid) of PRu-I: IR (KBr, cm^{-1}): 3320 (N–H amide and OH overlapped), 1590 (C=O).

PRu-I: 62% yield. IR (KBr, cm^{-1}): 1780 (unsymmetrical C=O of imide), 1720 (symmetrical C=O of imide), 1374 (C–N of imide), 760 (C–N–C of imide).

2.5.2. *PRu-II*

A mixture of BPADA (0.253 mmol, 0.132 g) and DCH–Ru diamine **3** (0.253 mmol, 0.277 g) in 1.9 mL of DMF was placed in a dry 10 mL one-neck round-bottomed flask. The concentration of monomers in DMF was 20 wt/v%. The reaction mixture was heated at 100 °CC for 4 h under argon. After that, the viscous polyamic acid solution was poured slowly onto Pyrex plate placed on a hot plate, which was then slowly heated up 200 °C at a heating rate of 10 °C/5 min for imidization. The polymer was collected, washed with methanol/water solution and dried in vacuum oven at 120 °C. **poly(amic acid) of PRu-II**: IR (KBr, cm^{-1}): 1721 (N–H of amide and OH overlapped), 1670 (C=O).

PRu-II: 76% yield. IR (KBr, cm^{-1}): 1777 (unsymmetrical C=O of imide), 1721 (symmetrical C=O of imide), 1375 (C–N of imide), 760 (C–N–C of imide).

2.5.3. *PRu-III*

A mixture of BPADA (0.20 mmol, 0.105 g), DCH–Ru diamine **3** (0.10 mmol, 0.110 g) and BAPF (0.10 mmol, 0.035 g) and 1.5 mL of m-cresol were placed in a dry 10 mL one-neck, round-bottomed flask, followed by addition of 5 drops of isoquinoline. The concentration of monomers in m-cresol was 20 wt/v%. The reaction mixture was refluxed at 180 °C for 24 h under argon. After that, the viscous polyamic acid solution was poured slowly onto Pyrex plate placed on a hot plate, which was then heated up to 200 °C at a heating rate of 10 °C/5 min for imidization. The polymer was collected, washed with methanol/water solution and dried in vacuum oven at 120 °C.

Poly(amic acid) of PRu-III: IR (KBr, cm^{-1}): 1709 (N–H of amide and OH overlapped), 1588 (C=O).

PRu-III: 71% yield. IR (KBr, cm^{-1}): 1775 (unsymmetrical C=O of imide), 1720 (symmetrical C=O of imide), 1367 (C–N of imide), 760 (C–N–C of imide).

2.5.4. *Crosslinked polymer* ***PU-3***

The crosslinked polymer (**PU-3**) was prepared by mixing DCH–Ru diamine **3** (30 mg), tetra-n-butylammonium hexafluorophosphate (8 mg) and DABCO (1 mg) in 0.07 mL of a solution of trimethylolpropane (TMP) (prepared from 250 mg TMP in 4.75 g of a 1:1 v/v

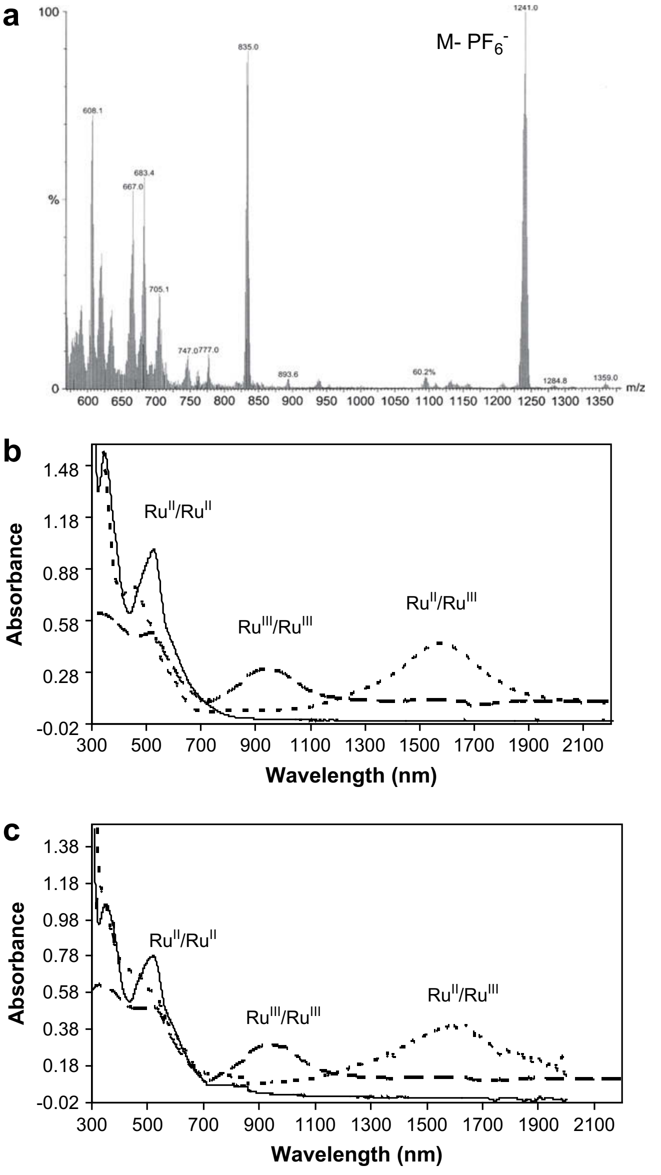
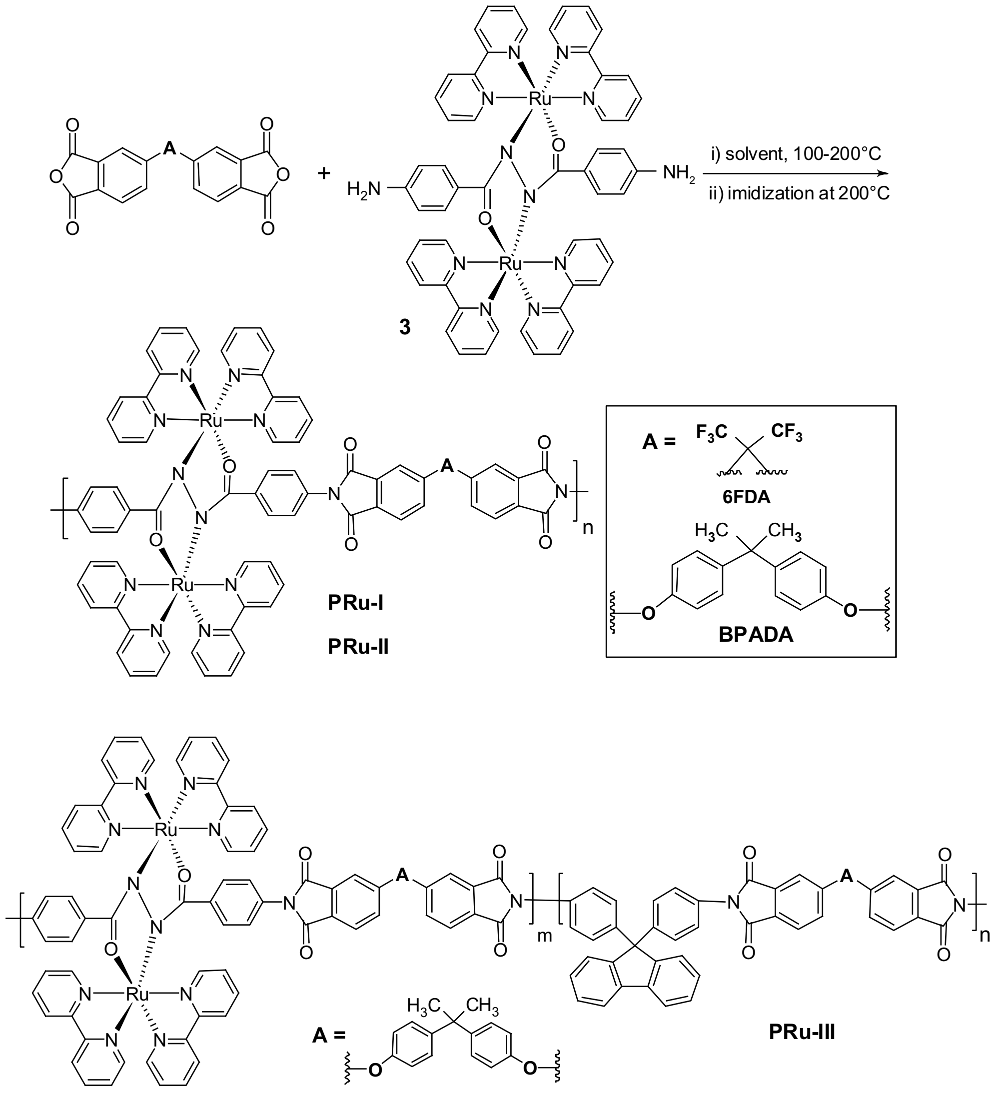


Fig. 2. (a) Mass spectroscopy spectrum of diamine **3** and UV–vis–NIR spectra of (b) diamine **3** in MeCN using OTTLE cell and (c) film of **PU-3** coated on ITO in different oxidation states.



Scheme 2. Synthesis of DCH–Ru complex polyimides by two-step method.

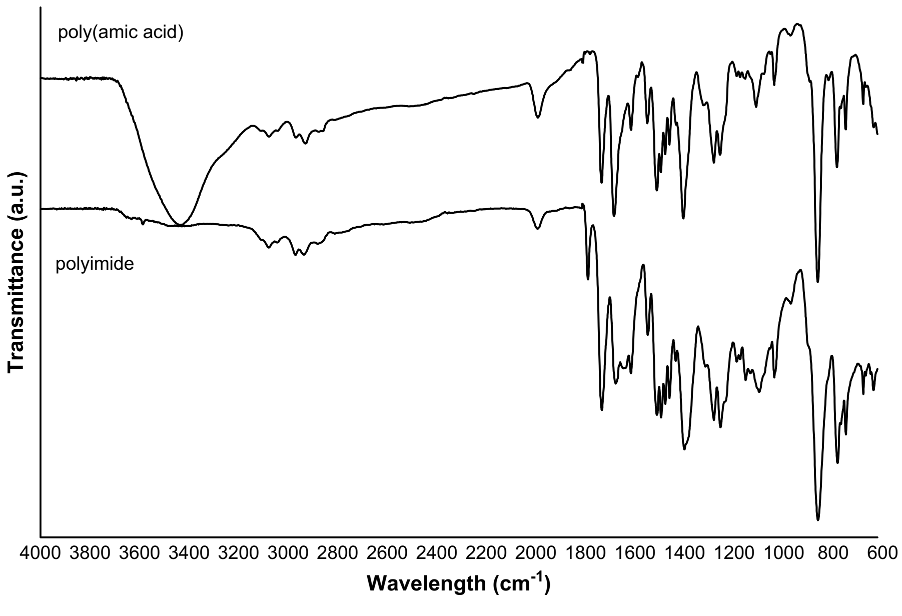


Fig. 3. IR spectra of polyimide **PRu-II** and its poly(amic acid) precursor.

Table 1
Characterization of the DCH–Ru polyimides synthesized in two-step method.

Polymer	Dianhydride	Diamine	h_{inh}[a] (dL/g)	T_d[b] (°C)	T_g[c] (°C)	λ_{max} (nm)[d]	
						Ru^{II}/Ru^{II}	Ru^{II}/Ru^{III}
PRu–I	6FDA	**3**	0.26	232	178	350, 520	1600
PRu–II	BPADA	**3**	0.16	248	180	350, 520	1600
PRu-III	BPADA	**3** + BAPF	0.23	172	97	350, 520	1600

[a] Inherent viscosity measured in DMF at 30 ± 0.1 °C with a concentration of 0.5 g/dL.
[b] Onset temperature for 5% weight loss by TGA in nitrogen with a heating rate of 10 °C/min.
[c] Glass transition temperature by DSC in nitrogen with a heating rate of 10 °C/min.
[d] Absorption measured in ACN.

Table 2
Oxidation potentials for the ruthenium complex monomer and polyimides.

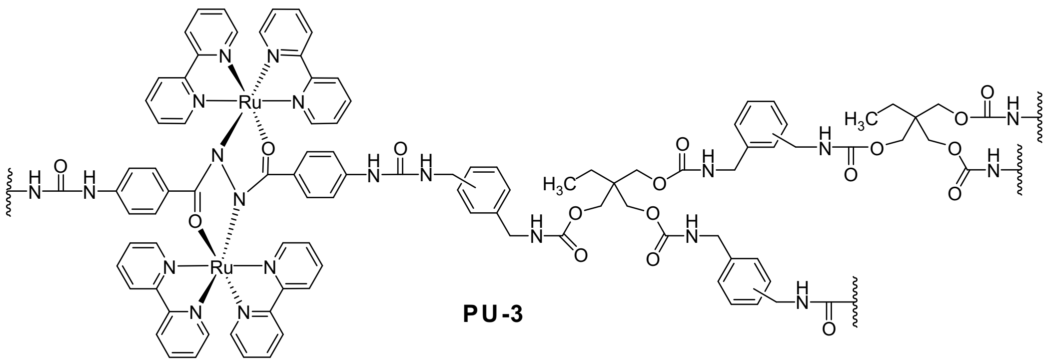
	$^1E_{Pa}$	$^1E_{Pc}$	$^1E_{1/2}$	$^2E_{Pa}$	$^2E_{Pc}$	$^2E_{1/2}$	$\Delta E_{1/2}$
3	414.0	476.0	445.0	852.0	984.0	918.0	473.0
PRu–I	252.0	596.0	424.0	851.0	1180.0	1015.5	591.5
PRu–II	565.0	689.0	627.0	1129.0	1267.0	1198.0	571.0
PRu-III	560.0	619.0	589.5	1126.0	1186.0	1156.0	566.5

mixture of THF and MeCN), followed by addition of 0.5 mL of a solution of triisocyanate (derived from trimethylolpropane and xylylene diisocyanate) as prepared from 333 mg of triisocyanate in 3.92 g of a 1:1 v/v mixture of THF and MeCN. The resulting mixture was sonicated for 10 min and immediately spin coated on ITO glass at a speed of 3000 rpm for 30 s. The film was then cured at 150 °C for 3 h. The film thickness was adjusted by the amount of polymer solution used, for either spectroelectrochemical or optical attenuation studies.

3. Results and discussion

3.1. Monomer synthesis

The NIR electrochromic polyimides were synthesized by polycondensation of commercially available dianhydrides and the DCH–Ru complex diamine **3** (Scheme 1). Therefore, the NIR electrochromic and other NIR optical properties of the polyimides originate from this amine monomer. The required bridging ligand **2** was synthesized in 80% yield by the PtO_2 catalyzed hydrogenation of compound **1**, which was obtained from the reaction of 4-nitrobenzoyl chloride with hydrazine hydrate in ethanol (Scheme 1). Both compounds were obtained in quantitative yields and did not require purification. Formation of the complex **3** was accomplished by the reaction of $Ru(bpy)_2Cl_2$ dihydrate with ligand **2** in aqueous DMF at 100–110 °C under argon. The resulting complex diamine **3** was isolated by precipitation from ether and purified by column chromatography. Due to the presence of paramagnetic species that affect the NMR spectrum (ca. poorly resolved broad peaks for all the aromatic protons), the structure of diamine **3** could only be confirmed by mass spectrometry. The mass spectrum (Fig. 2a) shows a peak at 1241.0, along with multiple isotope peaks, that corresponds to the mass of the proposed structure of **3** (without one PF_6^- ion). It decomposes at 388 °C (DSC) without melting.



PU-3

The complex monomer **3** was isolated with the two ruthenium centers in the Ru^{II}/Ru^{II} oxidation state. It is expected to undergo two one-electron oxidation processes to the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{III} states consecutively. Its electrochromic response both in solution and in polymer film was assessed. The spectroelectrochemical study of **3** in MeCN reveals an intense NIR absorption at the 1600 nm for the mixed-valence Ru^{II}/Ru^{III} state due to the metal-to-metal charge transfer (MMCT) (Fig. 2b). Further oxidation to the Ru^{III}/Ru^{III} state shifts the NIR absorption to the wavelength of 950 nm, attributed to the ligand-to-metal charge transfer (LMCT) transition. Since the complex **3** has the two amino groups, it should be able to react with the isocyanates to form the urea bonds and thus to be incorporated into a crosslinked polyurea/urethane. The film of polymer **PU-3** was then prepared by mixing a triisocyanate (derived from trimethylolpropane and xylene diisocyanate) and trimethylolpropane (TMP) with **3** (39.6 wt% in the crosslinked polymer) in MeCN, followed by spin coating on ITO glass. The spin-coated film was then baked at 150 °C for 3 h. The crosslinked film retained its electrochromic properties relative to the complex monomer **3** (Fig. 2c).

3.2. Polymer synthesis

The DCH–Ru polyimides were synthesized by polymerizing the ruthenium complex diamine **3** with the corresponding dianhydrides (Scheme 2). The choice of the dianhydrides was made with consideration of the solubility of the resulting polyimides. Polymerization was first attempted in either m-cresol [10] at 200 °C or salicylic acid [11] at 200 °C, which are known media for making polyimides in one step. However, in each case, only the corresponding polyamic acids were formed as indicated by the IR analysis, which suggests the amino group in monomer **3** is weakly basic and nucleophilic. Thus, the two-step polymerization was then employed. Besides m-cresol and the melt salicylic acid, DMF was also used as a solvent [12]. The polyamic acids obtained were soluble in the reaction solvents. Imidization was then carried out by heating the poly(amic acid) films gradually up to 200 °C under the flow of argon. The resulting homopolyimides, **PRu-I** and **PRu-II**, were not soluble in common organic solvents but could be slowly dissolved in DMF. More soluble polyimides could be obtained by

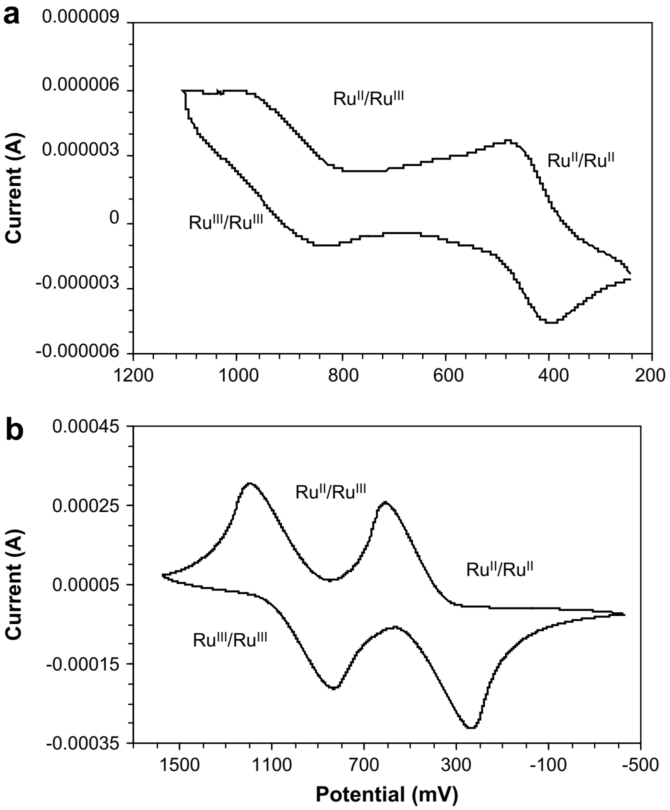


Fig. 4. Cyclic voltammograms of (a) DCH–Ru diamine **3** and (b) **PRu-I** at a scan rate of 200 mV/s.

copolymerization using another diamine or dianhydride monomer. As an example, copolymer **PRu-III** was obtained by polymerization of BPADA with **3** and BAPF (1:1 molar ratio) and found to be readily soluble in DMF and slightly in MeCN.

3.3. *Polymer characterization*

The poly(amic acid) was characterized by FTIR and then converted to polyimides. The imidization of the poly(amic acid) was verified by observing the disappearance of the characteristic peaks for amides and appearance of the imide's carbonyl peaks. For example, in Fig. 3 the broad peak at 3320 cm^{-1} and 1500–1650 cm^{-1} for the poly(amic acid) of **PRu-II** disappeared and those of the imide ring appeared near 1780 cm^{-1} (unsymmetrical C=O), 1720 cm^{-1} (symmetrical C=O) 1380 cm^{-1} (C–N of imide) and 720 cm^{-1} (C–N–C of imide) after thermal imidization.

The DCH–Ru complex polyimides have rather poor solubility in many common solvents but a good solubility in DMF, which enabled viscosity to be measured. The viscosity data provide an estimate of the molecular weight of the polymer (Table 1). The obtained polyimides had an inherent viscosity ranging from 0.16 to 0.26 dL/g, indicating a low molecular weight but sufficient for the formation of thin films on a substrate.

The thermal properties of these polyimides were determined by TGA and DSC. The glass transition temperatures (T_g) for the DCH–Ru polyimides ranged from 97 to 180 °C, depending on the chemical structures of the dianhydrides and diamines used. All the polyimides were thermally stable up to 172.0 °C in nitrogen, as assessed by TGA for the onset temperatures for 5% weight loss (Table 1), indicative of maintaining the high rigidity of the polymer backbone containing the DCH–Ru complex unit.

The electrochemical property of the DCH–Ru complex diamine and polyimides were studied by cyclic voltammetry (CV) using a platinum electrode. It was done using platinum electrode against silver pseudo-reference electrode in nitrogen purged solution of 0.1 M TBAH in MeCN for the complex monomer **3**, while the polymers were measured as a thin film on ITO and calibrated with ferrocene/ferrocenium redox couple. The DCH–Ru complex, either in monomer or in polyimide, undergoes two successive one-electron oxidation steps in the positive potential region due to the oxidation of Ru^{II}/Ru^{II} to the Ru^{II}/Ru^{III} state (first oxidation wave $^1E_{1/2}$) and oxidation to the Ru^{III}/Ru^{III} state (second oxidation wave $^2E_{1/2}$). Indeed, the complex diamine **3** underwent two reversible oxidation steps. The $^1E_{1/2}$ and $^2E_{1/2}$ appear at 445 mV and 918 mV, respectively, similar to the other known DCH–Ru complexes. The DCH–Ru polyimides also underwent two successive one-electron oxidations. The half wave potentials for the first and second oxidation steps ranged from 424 to 627 mV and 1015–1198 mV, hence giving a potential window of 571–591 mV. The electrochemical data for the diamine and polyimides are listed in Table 2.

Fig. 4 shows the CV of diamine **3** and one selected polyimide, **PRu-I**. The redox cycles are reversible over time, indicating the suitability for use as an electrochemical switch. The CV trace of **PRu-I** appears to be quite sharp, implying a good mobility for ions going through the polyimide film to the electrode.

The photoluminescence (PL) of the complex monomer and polyimides as thin films was examined under the excitation of

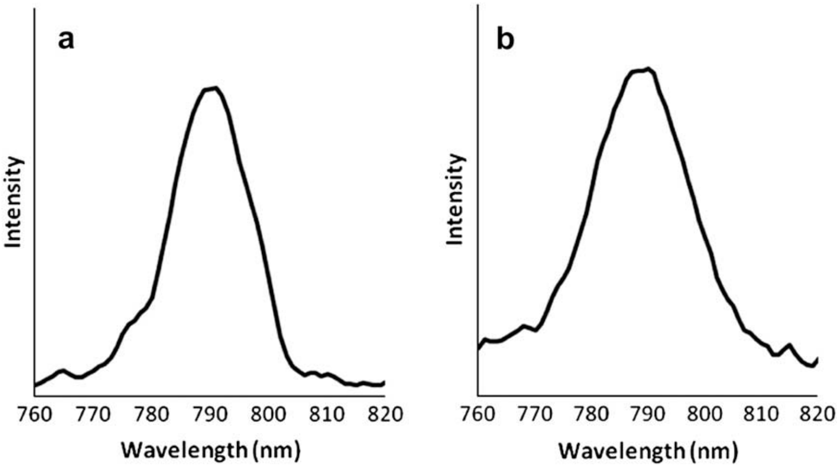


Fig. 5. PL spectra of thin films of (a) **PU-3** and (b) **PRu-I** (excitation at 520 nm).

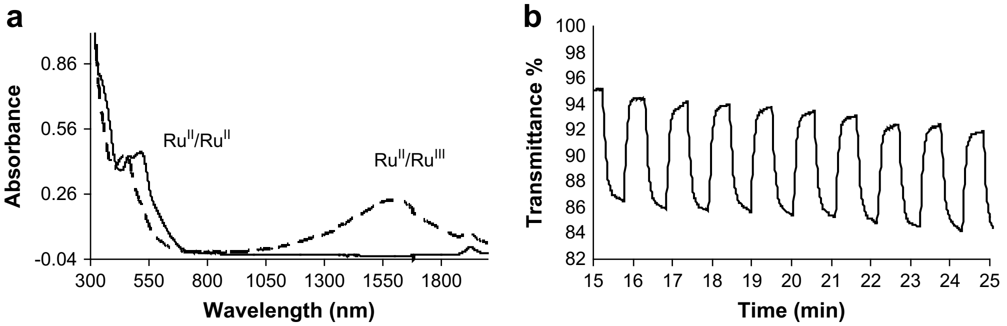


Fig. 6. (a) UV–vis–NIR spectra of **PRu-I** in MeCN in the two oxidation states. (b) Modulation of optical attenuation at 1550 nm of the film of **PRu-I**.

520 nm light at room temperature. The PL spectra of the complex monomer and polyimides are very similar and showed a peak centered at about 790 nm (Fig. 5). The NIR PL observed in both the monomer and polymers is mainly due to the excitation of the metal-to-ligand charge transfer (MLCT) transition of the DCH–Ru complex moiety.

3.4. Spectroelectrochemical and electrochromic switching studies

The spectroelectrochemical measurements of the complex diamine **3** and polyimides were performed by applying different potentials. The UV–vis–NIR absorption spectra for the complex monomer and polymers show two intense absorption bands at 350 and 520 nm, assigned to the MLCT transition of the Ru^{II}/Ru^{II} state of the complex moiety, while the broad NIR absorption at 1600 nm corresponds to the MMCT band of the Ru^{II}/Ru^{III} mixed-valence state. Upon further oxidation to the Ru^{III}/Ru^{III} state, a new band at 800 nm was only observed for monomer **3** and **PU-3** (Fig. 2) but not for the other polyimides (Fig. 6a). These results indicate that the complex monomer and polymers are NIR electrochromic at the telecommunication wavelength of 1550 nm. Thus, **PU-3** can be switched between the Ru^{II}/Ru^{II} and Ru^{II}/Ru^{III} or Ru^{II}/Ru^{III} and Ru^{III}/Ru^{III} oxidation states, while polyimides (e.g., **PRu-I**) can only be electrochemically switched between the Ru^{II}/Ru^{II} and Ru^{II}/RuI^{II} states.

Since the DCH–Ru polyimides show a good electrochemical stability and strong NIR electrochromism, NIR optical attenuation can be realized by utilizing the electrochromic switch between the Ru^{II}/Ru^{II} and Ru^{II}/Ru^{III} states and an intense absorption of the mixed-valence state in the NIR region. The crosslinked polyurea/urethane film of **PU-3** shows a rapid response in the NIR region to the applied potentials and reaches a dynamic range of optical attenuation of 5.3 dB/μm at 1550 nm with a stepping time of 5 s (Table 3). The polyimide film shows however a slower switching speed, mainly due to the diffusion-controlled process for ions going through the polyimide film coated on the electrode (Fig. 6b). The dynamic range for optical attenuation depends on the content of NIR chromophore, film thickness and polymer structure, and as well the redox process. The attenuation value per film thickness may provide a practical measure for a given material to attenuate the light at 1550 nm. However, the light-attenuating ability clearly relates to the nature of polymer structure, which can significantly affect the redox process. Depending on the molecular weight of the monomers used and the ratio of diamine monomer **3**, the DCH-Ru content in polyimides (**PRu-I** to **PRu-III**) and polyurea/urethane (**PU-3**) varies from 72.8% to 39.6% (Table 3). Although having the lowest NIR chromophore content, **PU-3** film shows the largest attenuation range (3.2 dB or 5.3 dB/μm), while **PRu-I** with the highest content of DCH–Ru (72.8 wt%) had only 1.5 dB/μm attenuation (Table 3). Such a difference is believed to be due to the nature of polymer structure. The urea/urethane bonds in **PU-3** are much more polar than the imide bonds in the DCH–Ru polyimides and thus allow for faster ion transport through the film, which lead to a faster and more complete oxidation and reduction of the DCH–Ru moiety. In comparison, the relatively lower attenuation observed in DCH–Ru polyimides is the consequence of incomplete electrochemical redox reaction of the DCH–Ru moiety. The results imply that further improvement on the polyimide structure requires incorporation of some polar bonds such as urea and urethane groups.

Table 3
Attenuation values of complex monomer and polymers.

	PU-3	**PRu-I**	**PRu-II**	**PRu-III**
DCH–Ru content (wt%)	39.6	72.8	69.3	48.5
Attenuation (dB) at 1550 nm	3.2	0.46	0.22	0.08
Film thickness (μm)	0.60	0.30	0.43	0.70
Attenuation/thickness (dB/μm)	5.3	1.5	0.51	0.11

4. Conclusion

Near-infrared electrochromic polyimides containing a dinuclear ruthenium complex with good electrochemical properties, thermal stability and film forming ability have been prepared and characterized. All the complex polyimides are NIR absorbing at 1600 nm in the mixed-valence state and emit at 790 nm, making them potentially useful for variable optical attenuation at the telecommunication wavelengths.

Acknowledgment

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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