

## SYNTHESIS AND CHARACTERIZATIONS OF NEAR INFRARED ABSORBING POLYMERS\*

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**Abstract** A series of near infrared (NIR) absorbing dinuclear ruthenium dicarbonylhydrazine complexes (DCH-Ru),  $[\{\text{Ru}(\text{bpy})_2\}_2\mu\text{-DCH}]^{n+}$  (where bpy = 2,2'-bipyridine and  $n = 2, 3$  or  $4$ ), were prepared. The DCH-Ru complexes are electrochromic in the NIR region with a high absorption coefficient at 1550–1600 nm typically over  $10000 \text{ M}^{-1}\text{cm}^{-1}$ . DCH-Ru complex polymers with good NIR electrochromic properties were also obtained and processed to make a device for optical attenuation at a wavelength of 1550 nm. The potential of these DCH-Ru polymers for use in a variable optical attenuator has been demonstrated with an attenuating power at the 1550-nm telecommunication wavelength over 7.0 dB per micron of polymer film thickness. Other classes of NIR active materials are the pentacenediquinones and the corresponding poly(ether pentacenediquinone)s. These polymers can be electrochemically reduced to the corresponding semiquinone (radical anion) having NIR absorption within a telecom window (*e.g.*, 1310 nm).

**Keywords** Near infrared absorption, Dinuclear ruthenium complex, Poly(ether pentacenediquinone)s, Radical anion, Optical attenuation

### INTRODUCTION

Most organic materials that are either being used or being explored in optoelectronic devices (*e.g.*, organic light-emitting diode display, liquid-crystal display, electrochromic display and photovoltaic device) interact with or emit light in the ultraviolet and visible region (*ca.* 250–800 nm). Typical materials include color dyes, pentacene, dendrimers<sup>[1]</sup>, conjugated oligomers and polymers<sup>[2]</sup>, and transition metal-containing polymers<sup>[3]</sup>. On the other hand, organic materials that are electrically, optically or thermally active and responsive at wavelengths in the near infrared (NIR) region are emerging materials with interesting but less studied electrical/optical properties and foreseeable applications in photonics and telecommunications (*e.g.*, fiber optic communications at 1310 and 1550 nm). NIR-absorbing organic materials are low band-gap materials (*e.g.*, 0.75 eV or 1550 nm) and thus must contain an extended conjugation or mixed-valence system. They are difficult to prepare and process for use in a device, as most conjugated polymers are less soluble in common organic solvents and low-molecular weight organic compounds do not form thin films by coating techniques. For applications in photonics and telecommunications, there are still no photovoltaic, electrochromic, optical switching and other optoelectronic devices that are operated at wavelengths of 1310 or 1550 nm and constructed using NIR organic materials.

Several types of NIR-absorbing organic materials are reported in the literature, including (1) stacked naphthalimide anion radicals<sup>[4]</sup>, (2) fused porphyrin arrays<sup>[5]</sup>, (3) doped polythiophenes<sup>[6]</sup>, and (4) mixed-valence dinuclear metal complexes<sup>[7]</sup>. The study of symmetric  $d^5/d^6$  mixed-valence dinuclear ruthenium (II/III) species has contributed significantly to the understanding of bonding and electron transfer in and between metal complexes such as a classical example of the molecule-bridged Creutz-Taube ion<sup>[8]</sup>. However, besides soluble

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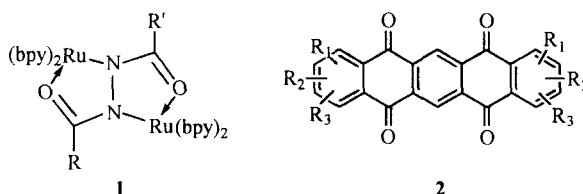
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polythiophenes, none of these known NIR materials could be processed into stable thin films on a substrate, thus precluding any possible device applications.

We have been studying two types of NIR-absorbing organic materials: dicarbonylhydrazido ruthenium complexes (DCH-Ru) **1** and pentacenediquinones **2**. When the dinuclear metal center is oxidized from the  $\text{Ru}^{2+}/\text{Ru}^{2+}$  to  $\text{Ru}^{2+}/\text{Ru}^{3+}$  states, the complexes **1** display an intense absorption (e.g.,  $\epsilon \sim 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ) centered at 1550 nm. At the  $\text{Ru}^{2+}/\text{Ru}^{2+}$  state, it shows no absorption within 1000–2000 nm. Other unique features of this type of ruthenium complexes include the stability towards water, air and strong base (e.g., NaOH) and high thermal stability ( $> 300^\circ\text{C}$ ). In addition, these materials have been demonstrated to be useful for optical attenuation at the telecommunication wavelength of 1550 nm<sup>[9]</sup>. Upon a single-electron reduction, pentacenediquinones **2** also become NIR absorbing, typically around another telecommunication wavelength at 1310 nm. Thus, in principle using the anodically active complexes **1** and cathodically active pentacenediquinones **2**, one should be able to construct a novel electrochromic variable optical attenuator that works in a wide telecommunication window of 1300–1600 nm. However, it would be ideal to obtain a film-forming material or the polymers derived from compounds **1** and **2**. There are a number of ways to incorporate compounds **1** and **2** into a polymer. In this paper, we present a simple way to introduce the DCH-Ru and pentacenediquinone moieties into the polymer main chain.



## EXPERIMENTAL

### Measurements

Cyclic voltammograms (CV) were recorded using a BAS 100 B/W electrochemical station interfaced and monitored with a PC computer. A three-electrode cell configuration and 0.1 M of 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 potentials reported here are with respect to the normal hydrogen electrode (NHE), unless otherwise noted. All the solutions were deoxygenated with nitrogen prior to electrochemical measurements. Spectroelectrochemical measurements were carried out by combination of the electrochemical station with a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. The NMR spectra were obtained on a Varian Gemini 200. IR spectra were recorded on a Bomem Michelson-100 FTIR spectrophotometer.

### Synthesis

*cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was prepared according to the literature method<sup>[10]</sup>. The ruthenium complexes were prepared according to the literature method<sup>[11]</sup>.

### Ligand polymer 3

To 30 mL of NMP were added 1.74 g (10 mmol) of adipic dihydrazide and 1.83 g (10 mmol) of adipoyl chloride. The mixture was stirred overnight at room temperature, under  $\text{N}_2$ , followed by precipitation of the product in 300 mL of vigorously stirred  $\text{CH}_3\text{OH}$ . The product was isolated by filtration and dried overnight under vacuum. Yield of the polymer **3** was 1.7 g (61%). IR (KBr)  $\nu(\text{C}=\text{O})$   $1600 \text{ cm}^{-1}$ ,  $\nu(\text{NH})$   $3216 \text{ cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz,  $d_6$ -DMSO,  $\delta$ ) 1.5 (s, 4H), 2.1 (s, 4H), 9.7 (s, 2H).

### Poly(DCH-Ru) **4**

The synthesis was performed in the manner described previously for DCH-Ru complexes **1**<sup>[9]</sup>, using 200 mg (0.38 mmol) of  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , 35 mg (0.25 mmol) of polymer **3**, and 100 mg of  $\text{Na}_2\text{CO}_3$ . Yield was

215 mg (87% based on reacted polymer). IR (film)  $\nu(\text{C}=\text{O})$  1605  $\text{cm}^{-1}$ ,  $\nu(\text{P}-\text{F})$  830  $\text{cm}^{-1}$ .

#### 2,9-; 2,10-Difluororopentacenediquinone (5)

Pyromellitic dianhydride (4.00 g, 0.018 mol) was placed in a flame-dried flask equipped with a magnetic stirrer and a reflux condenser. To the flask were added 30 mL of anhydrous fluorobenzene and  $\text{AlCl}_3$  (9.600 g, 0.072 mol). The suspension was heated at reflux for four hours. The excess fluorobenzene was distilled off and the obtained residue was carefully decomposed on ice and hydrochloric acid. The chunky solid was filtered off and dissolved in a solution of  $\text{NaHCO}_3$ , which was filtered to remove insoluble solids. The clear filtrate was acidified with concentrated hydrochloric acid, to give a white precipitate which was collected by suction filtration, and dried in a vacuum oven overnight at 100°C. Yield was 6.0 g (81%). The white solid (1.00 g) was placed in a mortar and ground together with 7 g of  $\text{AlCl}_3$  and 1 g of  $\text{NaCl}$  until a homogenous fine powder was obtained. The powder was transferred into a flame dried round-bottomed flask that was fitted with an air condenser. The mixture was heated at 200°C and the melt became purple. After 4 hours, the melt was allowed to cool to room temperature and a mixture of ice and  $\text{HCl}$  was carefully added to the flask. The solid was allowed to decompose overnight. The solid was isolated by suction filtration and stirred for four hours in a solution of  $\text{NaHCO}_3$  to remove the unreacted precursor acid. The precipitate was then filtered and finally stirred in acetic acid. After filtration, the product was dried in a vacuum oven at 200°C for 24 h. After recrystallization from hot nitrobenzene and sublimation at 450°C under  $10^{-5}$  mmHg, 0.430 g (47 % yield) of compound 5 as a yellow solid was obtained. mp > 400°C; IR (KBr  $\text{cm}^{-1}$ ): 1682, 1587, 1472, 1401, 1277, 1090, 994, 943, 849, 714, 690. HRMS calcd. for  $\text{C}_{22}\text{H}_8\text{F}_2\text{O}_4$ : 374.0379, found 374.0379.

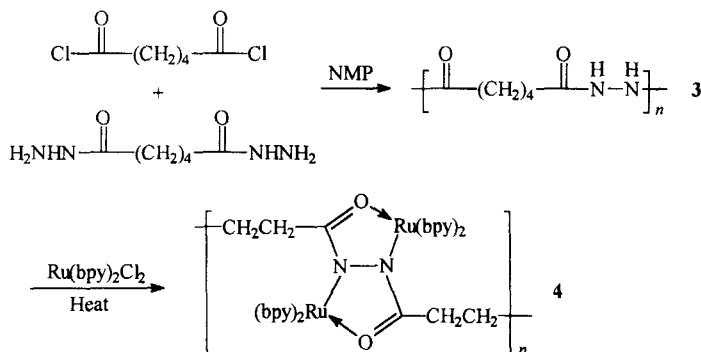
#### Poly(ether pentacenediquinone) 6

In a three-neck, round-bottomed flask equipped with a magnetic stirring bar, Dean-Stark trap, reflux condenser and argon inlet/outlet, were added difluoride (2 mmol), 9,9-bis(4-hydroxyphenyl)fluorene (2 mmol),  $\text{K}_2\text{CO}_3$  powder (4 mmol), toluene (2 mL) and 3 mL of tetramethylenesulfone (3 mL). The reaction mixture was gradually heated to 180°C during 30 min with the water being distilled off together with toluene. Afterwards the temperature was raised to 200°C and held for 7 h. As the solution viscosity increased during polymerization, additional tetramethylenesulfone (1 mL) was added. The reaction mixture was then poured into acidic water (1 mL of conc.  $\text{HCl}$  in 200 mL of water). Polymer 6 was isolated as dark purple powders and dried in a vacuum oven at 100°C. Yield varied between 80 and 100%. Inherent viscosity was 0.2 dL/g, as measured in NMP at 25°C; the glass transition temperature was determined by DSC to be 180°C.

## RESULTS AND DISCUSSION

We established a viable synthetic route to the DCH-Ru polymers 4 based on the use of the polymeric dicarbonylhydrazido (DCH) ligand 3 (Scheme 1). The ligand polymer 3, as synthesized from equimolar amounts of each monomers in NMP using the method of Frazer *et al.*<sup>[12]</sup>, was found to be sparingly soluble in DMF, acetonitrile and DMSO. Its inherent viscosity was measured in DMSO and was found to be 0.26 dL/g, indicative of low molecular weight. The synthesis of polymer 4 was performed in the same manner as that of the comparable DCH-Ru complexes previously reported, since experimentation revealed that the ligand polymer 3 was freely soluble in weak aqueous base solutions. The polymer 4 was thus obtained as brilliantly purple colored solids.

Polymer 4 showed no glass transition temperature by DSC and had the onset temperature for 5% weight loss in nitrogen at 202°C. Electrochemistry was performed on polymer 4 as a thin film on a Pt disk electrode in chloroform containing 0.1 M TBAH. The CV trace showed two quasi-reversible couples attributable to the two one-electron couples per dinuclear DCH-Ru fragment in the polymer (Fig. 1). The first  $E_{1/2}$  potential was found to be 310 mV (versus silver pseudo-reference electrode at 10 mV/s scan rate) and the second one appeared at 920 mV. The peak-to-peak separations for both couples ranged between 75 and 272 mV. The magnitude of this separation was generally higher versus the DCH-Ru complexes 1 and can be attributed to lower kinetics due to the uptake and expulsion of electrolyte from the film.



**Scheme 1** Synthesis of DCH-Ru complex polymer **4**

In order to measure long term switching stability, the polymer (**4**) film on a Pt disk electrode (1.6 mm diameter) in chloroform (with 0.1 M TBAH) was subjected to repeated switching between the reduced  $\text{Ru}^{2+}/\text{Ru}^{2+}$  state and the mixed-valence  $\text{Ru}^{2+}/\text{Ru}^{3+}$  state at a frequency ranging from 1.2 to 2.4 s. After 50000 cycles (or 16.7 hours), the total charge per unit area of electrode taken from the integration, with respect to time of the current trace initially, at the middle and finally the end of the experiment, was found to be  $184 \mu\text{C}/\text{cm}^2$ ,  $241 \mu\text{C}/\text{cm}^2$  and  $258 \mu\text{C}/\text{cm}^2$ , respectively. The results show an increase of nearly a factor of two for polymer **4**. The UV-vis-NIR spectra for polymer **4** in its reduced, mixed-valence and oxidized form were taken in-situ with the polymer mounted on ITO coated glass (Fig. 2). In its mixed-valence state, a peak was found to be centered around 1530 nm. This is consistent with the presence of isolated DCH-Ru fragments within a saturated polymer where no electronic interaction between the DCH-Ru fragments exists.

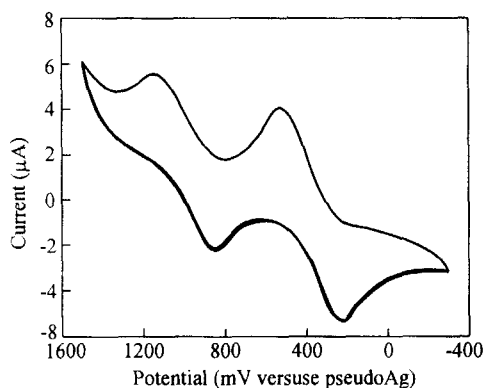


**Fig. 1** Cyclic voltammogram of polymer film **4** on a Pt disk electrode in chloroform at a scan rate of 20 mV/s (with 0.1 M TBAH)

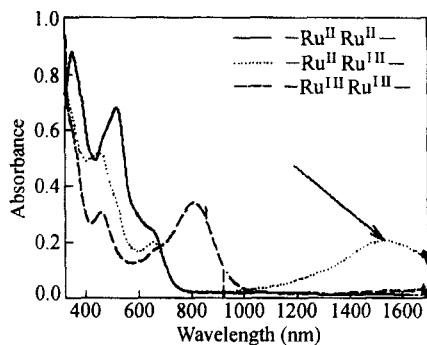
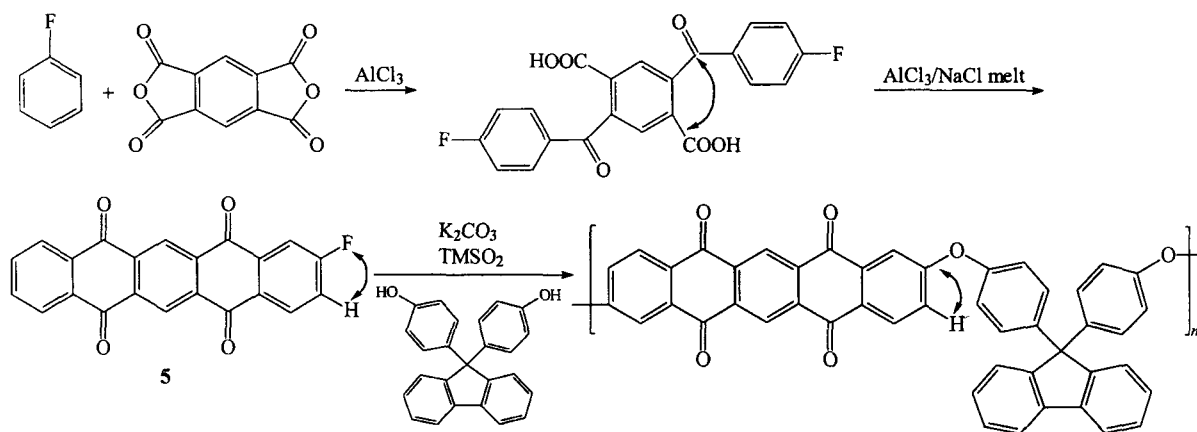


**Fig. 2** Spectroelectrochemical spectra for polymer film **4** on ITO electrode in chloroform (with 0.1 M TBAH)

The pentacenediquinone moiety was introduced into a polymer main-chain via nucleophilic displacement polymerization of a functionalized pentacenediquinone (*ca.* difluoride **5**) and a bisphenol such as 9,9-bis(4-hydroxyphenyl)fluorene (Scheme 2). The difluoride **5** was obtained as a regioisomeric mixture, which afforded the corresponding poly(ether pentacenediquinone) **6** that was found to be more soluble than the one derived from the single isomeric **5**. The polymer **6** was soluble in NMP and could be cast into a tough film on substrates such as ITO.



Scheme 2 Synthesis of poly(ether pentacenediquinone) 6

The cyclic voltammogram of compound 5 showed two reversible couples (first  $E_{1/2}$  at 200 mV and second  $E_{1/2}$  at 642 mV versus NHE) attributable to the two one-electron couples for its radical anion and dianion intermediates. Accordingly, the radical anion species showed a strong absorption at 1360 nm and the dianion species had a peak at 890 nm. In comparison, pentacenediquinone 5 shows absorbance at 335 nm, due to the  $\pi-\pi^*$  transition. In the case of semiquinone or radical anion, its NIR band is postulated to originate from a  $\pi^*-\pi^*$  transition, SOMO-LUMO from a delocalized ground state<sup>[13]</sup>. The SOMO-LUMO represents the difference in energy between the two lowest unoccupied molecular orbitals. The polymer 6 had similar electrochemical behavior to compound 5. The radical anion (or semiquinone) of the polymeric film (6) on ITO was prepared electrochemically in a solution of 0.1 M  $\text{LiClO}_4$  as the supporting electrolyte, which also showed a broad NIR band (Fig. 3). Interestingly enough, this semiquinone polymer alone on ITO was found to be stable in air over months.

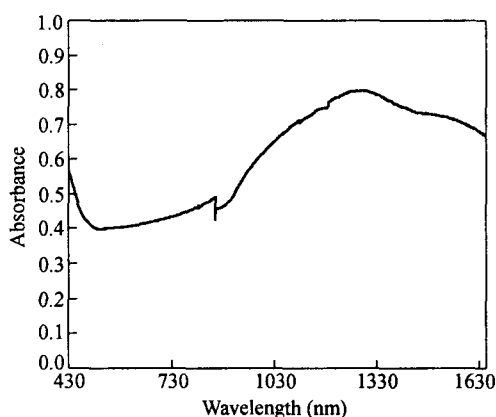


Fig. 3 NIR absorption of the radical anion of polymer 6 on ITO electrode

## CONCLUSION

Both anodically and cathodically NIR-active polymers (4 and 6) were prepared and were shown to be able to form a thin film on ITO electrode. Their NIR electrochromic properties suggested a potential use in the development of an electrochromic variable optical attenuator.

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