

# Optical attenuation at the 1,550-nm wavelength in a reflective mode using electrochromic ruthenium complex film

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**Abstract** Thin films of a dinuclear ruthenium complex have been prepared on a reflective electrode. The complex is redox-active in the near infrared spectral region. Electrochromic switching between the two oxidation states of the complex film gave 80% optical contrast at the telecommunication wavelength of 1,550 nm, which translates to an intrinsic attenuation of 17.5 dB/ $\mu\text{m}$  of the active material. Chronoamperometric study showed excellent stability over extended switching cycles as well as retaining high attenuation with a 5-s stepping time.

**Keywords** Optical attenuation · Ruthenium complex · Electrochromic switching

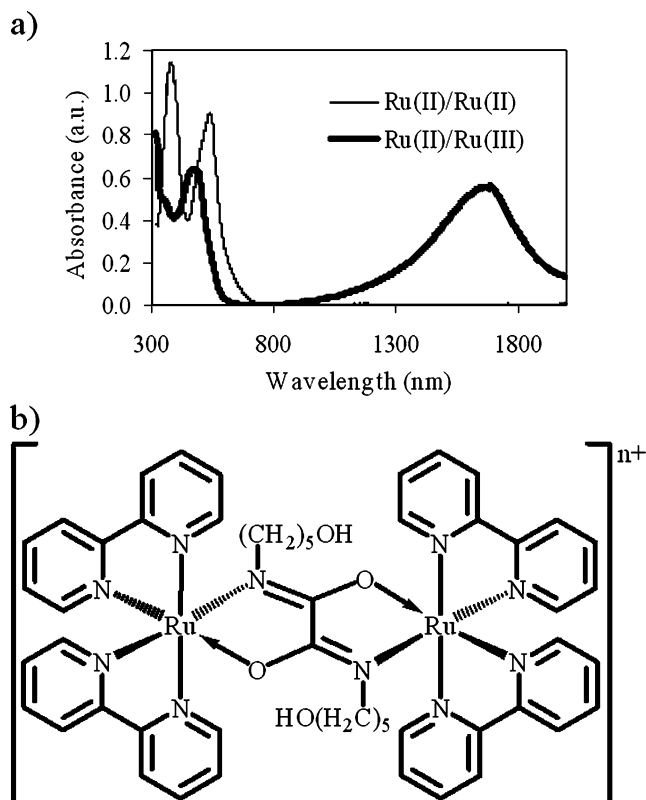
## Introduction

Electrochromic (EC) materials that show optical change in the near infrared (NIR) spectral region are subject to ever increasing attention. They are potentially useful in photonic technologies such as a variable optical attenuator (VOA), especially by the telecommunication industry, for signal transduction and switches. EC materials also find use as sensors [1–4], smart windows [5, 6], data storage [7], photovoltaics [8], as well as masking heat signatures [9, 10]. Many metal complexes, organic molecules, and conjugated polymers are electrochromic and some are NIR active [11]. In a typical VOA device, optical

attenuation with a fast response time can be achieved via microelectromechanical systems where a slit or other moveable part is used to block the incident beam [12–14]. However, the moving parts tend to be bulky and make the devices noisy [15]. In comparison, a VOA device using an EC material to absorb the light does not require the use of any moving parts and can be operated or switched on and off by applying a low voltage. One of the suitable EC materials is a dinuclear ruthenium complex (Fig. 1b), chelated by tetradentate bridging ligands, as it possesses strong NIR activity in its mixed-valence oxidation state (Fig. 1a) through an inter-valence charge transfer transition [9, 11, 16–18]. Electrochromic ruthenium complexes are also showing promise for controlling and processing light signals in linear and nonlinear optics [19–22]. McDonagh and coworkers have studied the NIR electrochromism of dinuclear molybdenum complexes in a 6-mm-thick liquid cell design for their VOA properties at 1,300 nm and achieved high attenuation [23]. Optical attenuation can also be achieved by: thermo-optic-based planar lightwave circuits [24–28], where an applied voltage generates heat that induces a drop in the refractive index of a fiber optic cable, resulting in signal loss; and through the use of liquid crystals which also relies on refractive index manipulation via an applied voltage to the liquid crystal.

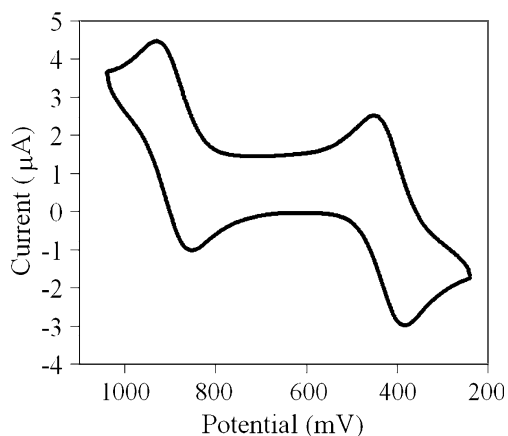
The diol oxamide ligands are readily accessible through aminolysis of ethyl oxalate using aliphatic hydroxyalkyl amines [29]. Synthesis of the complexes is performed according to a published procedure [30]. The cyclic voltammogram (CV) of the complex used in this study (Fig. 2) shows the typical redox couples at half wave potentials ( $E_{1/2}$ ) of 420 and 895 mV, representing the two consecutive one-electron oxidations of the  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  ground state. The highest oxidation state, the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$  state, as expected, does not possess NIR activity.

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**Fig. 1** **a** Absorbance spectra of the two oxidation states of the dinuclear ruthenium complex monomer and **b** its structure ( $\text{PF}_6^-$  counter anions not shown)

We have previously reported on the optical attenuation based on organic electrochromic materials in a transmissive mode of operation [31, 32]. A typical VOA device consists of the two indium-doped tin oxide (ITO) electrodes sandwiching a thin layer of redox-active material that is able to absorb the NIR light. A conductive element, such as a polymer electrolyte gel, completes the circuit. While not

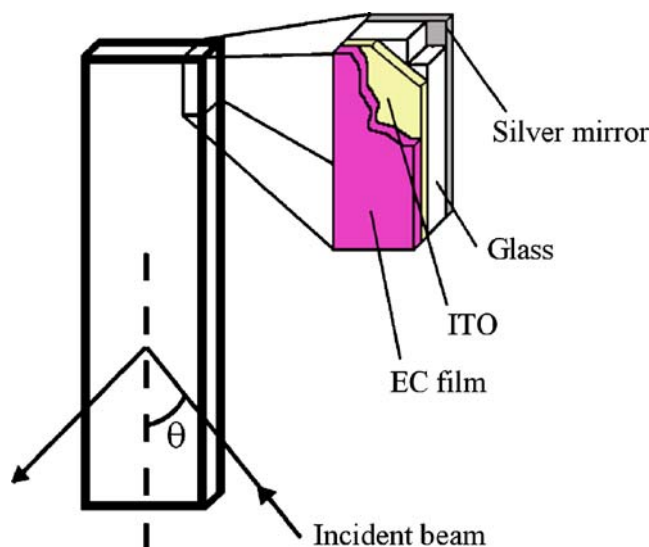


**Fig. 2** Cyclic voltammogram of ruthenium complex monomer (0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) in acetonitrile as supporting electrolyte. Scan rate of 200 mV/s. Potentials referenced to the ferrocene/ferrocenium couple against SCE)

essential for the device function, a complimentary electrochromic material and/or other suitable redox-active materials can be layered within the device assembly [33]. While ITO on glass is a suitable working electrode for visible applications, it begins to reflect the light from 1,000 nm, weakening the detected signal strength. This is especially significant for detecting the optical signal at 1,550 nm, as 35% of the light can be lost through reflection. However, this optical reflection could be harvested by working in a reflective mode for optical attenuation, where the signal beam passes through the EC material and is reflected back by the ITO electrode. As shown in Fig. 3, this device configuration offers an extra advantage that the signal passes through the EC material twice, which means that the active EC material can theoretically perform twice as well as a transmissive device containing the equivalent EC content. However, a reflective design will require more space to accommodate the incident and reflected beams than a transmissive design which can be implemented in a linear fashion. Even though transmissive designs can include multiple material layers, they offer simplicity in construction.

## Materials and methods

Electrochromic materials were prepared by mixing a trisocyanate (derived from trimethylolpropane and xylene diisocyanate) with a diol ruthenium complex (see structure in Fig. 1b) in 500  $\mu\text{L}$  of acetonitrile and immediately used for spin-coating on ITO glass. The ratio of isocyanato group to hydroxyl group in the mixture was kept at 1.5 to 1.0. The spin-coated polymer films were cured at 150  $^\circ\text{C}$



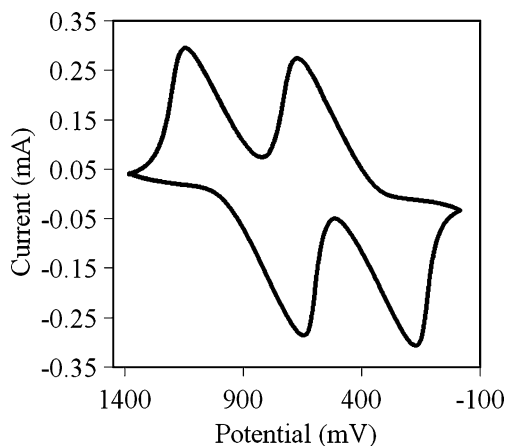
**Fig. 3** Concept construct of a reflective optical variable attenuator ( $\theta$  = incident angle)

for 2 h. The curing process was deemed complete since no complex leaching occurred by soaking the film in acetonitrile. Film thickness and ruthenium complex content were optimized to 400 nm and 48% by weight, respectively, to maximize switching speed and contrast. Higher ruthenium content resulted in phase separation in films. A portion of the film was wiped off prior to curing to expose the ITO layer, facilitating the incorporation of a copper wire lead using conductive silver epoxy paste.

For silvering of the glass side of ITO glass strips, the Rochelle Salts process was used [34]. The ITO layer was first masked using clear adhesive tape and then placed, taped side facing down, in a glass dish. A mixture of equal parts of a silver nitrate/ammonium hydroxide aqueous solution and a silver nitrate/potassium sodium tartrate aqueous solution was poured over the exposed slides to completely cover them. The silver deposition proceeded at 38 °C. Once completed, the ITO strips were taken out and washed off using distilled water. The silvering process could be repeated to obtain a thicker layer of silver. Since only the ITO surface was masked, silver was also deposited on the cross-section side of the ITO glass strips. It was necessary to remove this extra silver (using a rotary tool and polishing head) as it became apparent that an electrical contact with the ITO existed. Failure to break the contact while applying a positive potential resulted in oxidation of the silver, effectively destroying the mirror finish.

## Results and discussion

The crosslinked complex films retained their electrochemical properties relative to the complex monomer itself (Fig. 4). As expected, the redox couples ( $E_{PA}$  and  $E_{PC}$ ) of the crosslinked complex film show a larger separation than



**Fig. 4** Cyclic voltammogram of crosslinked film of ruthenium complex (0.1 M TBAH in acetonitrile as supporting electrolyte. Scan rate of 200 mV/s. Potentials referenced to the ferrocene/ferrocenium couple against SCE)

those of the monomer due to slow counter ion diffusion through the polymer network. This effect is expected to lessen with each cycle as the counter ion, once within the polymer network, will tend to remain within and be ‘available’ for the next cycle. Swelling with the electrolyte solution (e.g., acetonitrile) may also be playing a role in diffusion, since a fresh film is dry and has a slower diffusion rate than the wet film. We also noted a 65-fold increase in peak current generated from the films which can easily be explained from the much larger working electrode surface area available (1.5 cm<sup>2</sup>) compared to a 1.5-mm-diameter platinum disk electrode used for CV measurements.

Optical contrast between the two redox states was measured using a Harrick Scientific™ variable angle specular reflectance module and an in-house plexiglass cuvette holder. The coated ITO strip (8×40 mm) was submerged in a four-sided 1-cm quartz cuvette containing 0.1 M TBAH in acetonitrile as supporting electrolyte solution. Silver and platinum wires were used as pseudo reference and counter electrodes, respectively. The Ru<sup>II</sup>/Ru<sup>II</sup> state of the complex in the polymer film (electrochemically reduced at -0.5 V) was used as the background correction. Since the intensity of the reflected light depends on the angle of incident light, the signal strength was probed within a range of incident angles from 30° to 70°. The highest signal strength was attained with an incident angle of 56°. Thus, the reflectance was measured at this incident angle, while the polymer film was electrochemically oxidized and reduced between the two oxidation states (Ru<sup>II</sup>/Ru<sup>II</sup> and Ru<sup>II</sup>/Ru<sup>III</sup> states). The attenuation was then calculated using the equation below:

$$\text{attenuation} = 10 \times \log(T_b/T_c) \quad (1)$$

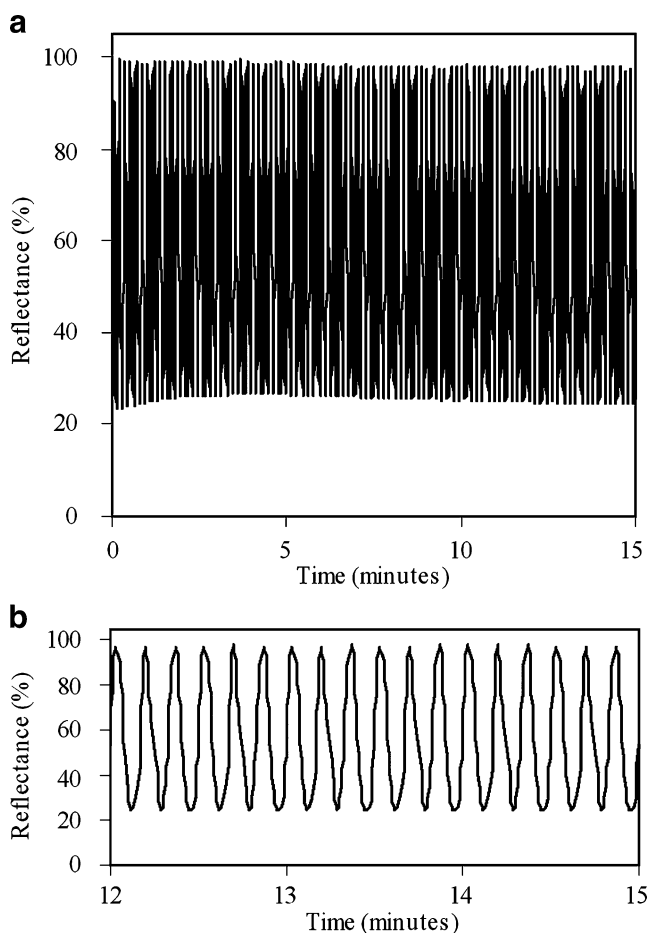
where  $T_b$  is the reflectance of the NIR-transparent state (Ru<sup>II</sup>/Ru<sup>II</sup>) and  $T_c$  is the reflectance for the NIR-absorbing state (Ru<sup>II</sup>/Ru<sup>III</sup>). The optical contrast is defined as the difference in reflectance ( $T_b - T_c$ ) between the two oxidation states considered, where  $T_b$ , using the Ru<sup>II</sup>/Ru<sup>II</sup> state, is set as 100% (without consideration of any optical loss due to absorption and/or scattering).

It was found that the polymer films coated on bare ITO glass gave only 30% optical contrast or 1.6 dB attenuation at 1,550 nm. Using the silvered ITO glass, an attenuation of 7 dB (or 80% optical contrast) at 1,550 nm was readily achieved. Considering the thickness factor of active EC layer, the intrinsic attenuation for the given polymeric EC material (with a thickness of 400 μm) in this reflective device is calculated to be 17.5 dB/μm. In comparison with the transmissive device, the similar ruthenium complex gave the attenuation values of 0.05 dB/μm in a 100-μm (path length) solution-based device assembly [32] and 4.9–5.4 dB/μm in a film-based device [31]. Also, optical

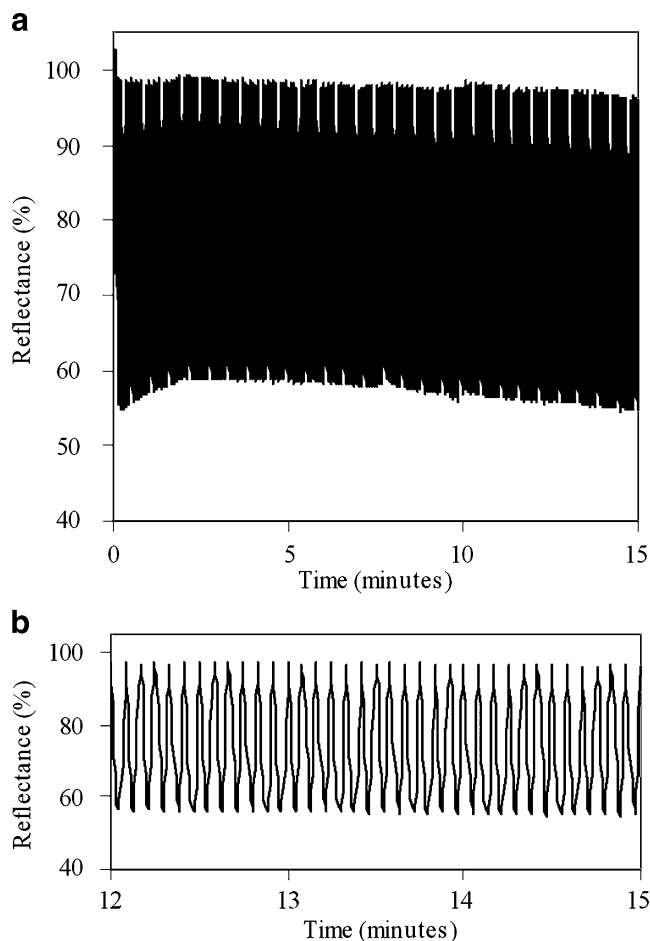
attenuation of the dinuclear molybdenum complex, when thickness is taken into consideration, becomes 0.01 dB/ $\mu\text{m}$  [23]. While some variation can be accounted by the differences in molar extinction coefficients of the complexes used, it is clear that the device configuration also plays a role in performance.

To further investigate the attenuation dynamics and switching stability, chronoamperometry was performed using a stepping time of 5 s and cycling potentials from  $-0.5$  to  $0.8$  V. Under these conditions, 70% optical contrast was achieved (Fig. 5), which translates to a dynamic range of attenuation of 14.9 dB/ $\mu\text{m}$  of EC polymer film thickness. The attenuation value is about 15% lower than the maximum that was recorded in a static mode, which signifies that 85% of the ruthenium complex is oxidized or converted to the NIR-absorbing state in 5 s. The dynamic range drops down to 4.0 dB/ $\mu\text{m}$  (or 31% optical contrast) when a stepping time of 2.5 s is applied (Fig. 6).

Higher potentials could be used to increase the response time, as a common practice [35], but these dinuclear ruthenium complexes can be further oxidized to the  $\text{Ru}^{\text{III}}$ /



**Fig. 5** **a** Chronoamperometry of a silvered film cycling from  $-0.5$  to  $0.8$  V with a 5-s stepping time; **b** last 4-min expansion



**Fig. 6** **a** Chronoamperometry of a silvered film cycling from  $-0.5$  to  $0.8$  V with a 2.5-s stepping time; **b** last 4-min expansion

$\text{Ru}^{\text{III}}$  specie which, in this case, forms at potentials above 850 mV (based on Fig. 4) and does not express NIR activity. Since the redox process must pass through the mixed-valence state, it is probable that faster stepping time and higher potentials could generate the NIR active state exclusively. Also, the EC films coated on ITO are fairly large (about  $1.5 \text{ cm}^2$  in size); miniaturization should improve switching time drastically. Further improvement can be expected by modifying the gap between the working and counter electrodes.

In conclusion, we have shown that a three-fold increase in optical attenuation is achieved for EC ruthenium complex polymer films when operating in a reflective mode and cycling from  $-0.5$  to  $0.8$  V compared to a transmissive device based on similar EC materials. Faster response time could be achieved by using higher oxidation potentials only if the mixed-valence state ( $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ ) can be generated selectively. Larger dynamic range in optical attenuation and faster switch can be expected for an electrochromic VOA with a well-designed reflective configuration.

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