Dendritic Mixed-Valence Dinuclear Ruthenium Complexes for Optical Attenuation at Telecommunication Wavelengths

Yinghua Qi and Zhi Yuan Wang*

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

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ABSTRACT: Novel dendritic mixed-valence dinuclear ruthenium complexes were prepared and chemically cross-linked to form thin films on ITO electrodes. The cross-linked films exhibited an excellent electrochromism in the near-infrared (NIR) region and optical attenuation of 5.4 dB/μm in thickness at 1550 nm with a switching time of 2 s. A variable optical attenuator based on these NIR electrochromic ruthenium complex materials could be envisioned.

Introduction

A variable optical attenuator (VOA) is an essential component for gaining control of optical signals in wavelength-division multiplexing networks and for dynamic channel power regulation and equalization in cross-connected nodes. Various types of VOAs have been explored, such as microelectromechanical devices, sliding-block mechanical devices, side-polished fiber devices, and thermooptic systems.[1−4] At present, a major challenge in the telecommunication industry is to develop inexpensive planar integrated VOA devices in response to the ever increasing data transmission and processing rates as well as lowering fabrication costs. Organic materials that are electrically, optically, or thermally active in the near-infrared (NIR) region, specifically at the telecommunication wavelengths (e.g., 1300 and 1550 nm), can well serve this purpose, owing to their unique electrical and optical properties, low-cost fabrication, and feasibility for use in a monolithically integrated optical device. The NIR-active organic materials are of low band gap and commonly contain an extended π-conjugation[5,6] or mixed-valence organometallic system.[7,8] Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have exhibited the most promising electrical−optical properties for use in electrochromic (EC) devices, including rapid switching speed with a high color contrast and excellent electrochemical stability upon cycling.[6] In addition, these polymers are reasonably stable at elevated temperatures and can be easily electrochemically deposited as thin films on substrates. Much research effort has been devoted to the applications of PEDOT and its derivatives in the visible region of the electromagnetic spectrum rather than at the telecommunication wavelengths. The mixed-valence metal complexes are generally difficult for use in a device, as the low molecular weight complexes do not form stable thin films by common film-making techniques such as spin coating and vapor deposition. To date, the application of organic materials in VOA has not been fully explored.[7a,9]

The early work by Kaim et al. shows that the dinuclear ruthenium complexes **1** with 1,2-dicarbonylhydrazido (DCH) and 2,2′-bipyridine (bpy) ligands (Scheme 1) are highly electrochromic in the NIR region.[10] When the dinuclear metal center is oxidized from the Ru^{II}/Ru^{II} state to the mixed-valence state (Ru^{II}/Ru^{III}), the DCH−Ru complexes display an intense NIR absorption between 1000 and 2000 nm. At the Ru^{II}/Ru^{II} state or fully oxidized Ru^{III}/Ru^{III} state, it shows no absorption in the NIR region. Complexes **1** are chemically stable in air and water at elevated temperatures (e.g., 200 °C). On the basis of the NIR electrochromism, a new electrochromic VOA or ECVOA can be envisioned using these dinuclear ruthenium complexes. ECVOA works in the same principle as electrochromic devices and employs EC materials that exhibit reversible and stable optical changes at the telecommunication wavelengths. If under one applied voltage the EC material in ECVOA exists in a redox state that is NIR absorbing, the same material should be in an opposite redox state that is NIR inactive at another voltage. When the NIR light is directed through an ECVOA device, the light will either pass through or be absorbed at two distinct redox states and thus can be attenuated variably by controlling the redox process within the EC material through the applied voltages. Accordingly, basic requirements for organic materials to be used in an ECVOA should include high coloration efficiency, fast switching speed at low voltages, good film-forming property, and stability.

Extensive studies on the novel dinuclear ruthenium complexes (DCH−Ru) have been carried out in our group in the past few years. Several synthetic routes to various ligands have been established, and a series of DCH−Ru complexes having various donor to acceptor groups and DCH−Ru linear polymers have been prepared.[11] DCH−Ru complexes with weak electron-donating strength of substituents (e.g., phenyl, alkyl, phenylene ether) are proposed to be the most promising materials for use in VOA, as they have a strong electrochromism within the telecommunication bands of 1500−1600 nm.[9]

In this paper, the synthesis and characterization of two first-generation, dendritic DCH−Ru complexes **2** and **3** are presented (Scheme 2). These ruthenium complexes contain the hydroxy groups, which allows for chemical cross-linking with an isocyanate material to form thin films on an electrode and fabrication of a concept device for ECVOA.

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* To whom correspondence should be addressed. E-mail: wangw@ccs.carleton.ca.

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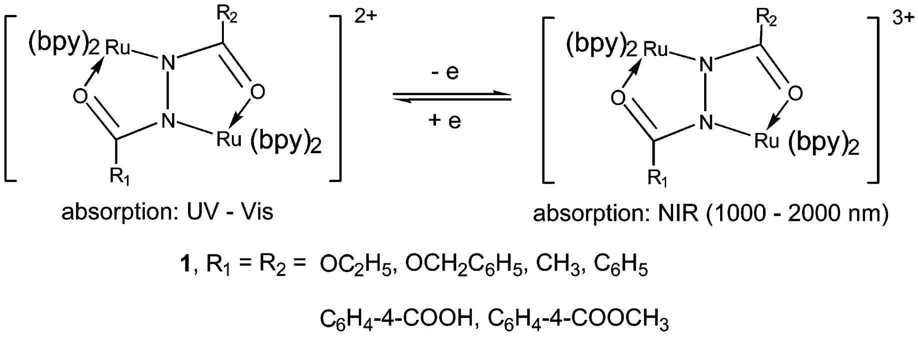
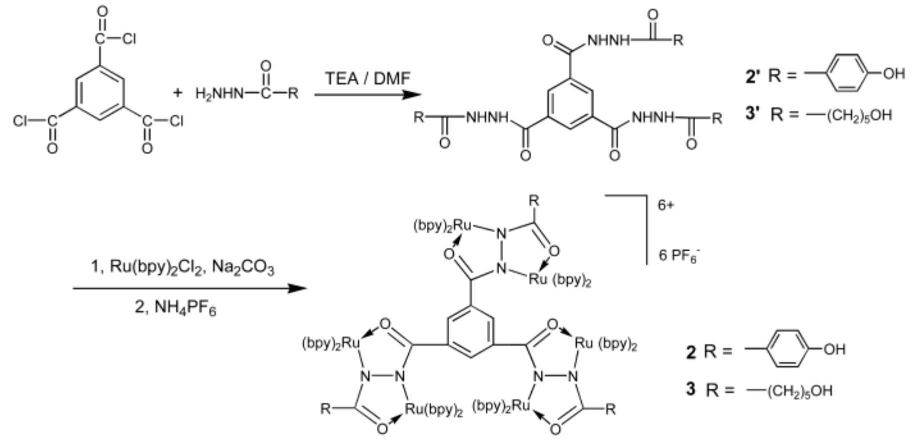
Scheme 1



Scheme 2



Experimental Section

Materials. *p*-Hydroxybenzoic hydrazide was purified by washing with tetrahydrofuran (THF). 1,3,5-Benzenetricarbonyl trichloride was distilled prior to use. *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O was prepared according to the literature method.[12] Other chemicals were purchased from Sigma-Aldrich Canada Ltd. and were used as received.

Measurements. Cyclic voltammograms (CV) were performed on a BAS 100 B/W electrochemical station interfaced and monitored with a PC using tetra-*n*-butylammonium hexafluorophosphate (TBAH, 0.1 M) as supporting electrolyte in acetonitrile. A standard three-electrode configuration was used with a platinum or tin-doped indium oxide (ITO) as working electrode, a platinum wire as counter electrode, and a silver wire as reference electrode. The silver pseudo-reference electrode was calibrated with a ferrocene/ferrocenium redox couple, and the potentials 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 using the electrochemical station together with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Spectroelectrochemical measurements in solutions were conducted using an OTTLE cell. The NMR spectra were recorded at room temperature on a Bruker AMX-400 or Varian Gemini 200. The IR spectra were performed on a Bomem Michelson-100 FT-IR spectrometer. Thermogravimetric analyses were carried out on a Seiko TG/DTA SSC 5200 under a nitrogen atmosphere. Mass spectrometry was carried out by the University of Ottawa Regional Mass Spectrometry Center. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected.

Optical switching and spectroelectrochemical studies of DCH−Ru complex films on ITO were performed using an UV quartz cuvette which contains a platinum wire as the counter electrode and a silver wire as the reference electrode and electrolyte in solution. The cuvette was fitted with a Teflon cap through which the reference electrode and counter electrode were inserted via predrilled holes.

Synthesis of 6-Hydroxyhexanoic Hydrazide. ϵ-Caprolactone (5.5 mL, 0.05 mol) was added dropwise into a solution of hydrazine hydrate (5 mL, 0.1 mol) in *N*,*N*-dimethylformamide (DMF, 5 mL) at room temperature. After 1 h, the resultant white precipitate was collected by filtration and washed with hot acetone twice to give a white powder (5.8 g, 81% yield); mp 115−116 °C. ^{1}H NMR (200 MHz, DMSO-d_6): δ 8.9 (s, 1H), 4.3 (t, 1H, $J = 6.6$ Hz), 4.1 (s, 2H), 3.3 (m, 2H), 1.9 (t, 2H, $J = 7.5$ Hz), 1.4 (m, 6H). IR (KBr, cm^{-1}): 3311.3 (υ_{N-H}), 1641.6 ($\upsilon_{C=O}$), 1536.6 (υ_{N-H}). MS (ESI, *m*/*z*) for C$_6$H$_{14}$N$_2$O$_2$: 147 (M + H$^+$).

Ligand 2′. A solution of 1,3,5-benzenetricarbonyl trichloride (0.56 g, 2.1 mmol) in DMF (5 mL) was added dropwise into a solution of *p*-hydroxybenzoic hydrazide (1.2 g, 7.8 mmol) and triethylamine (0.9 mL) in DMF (15 mL). The solution was stirred at 0 °C for 1 h and then stirred at room temperature for 0.5 h. The hydrochloric salt of triethylamine was removed by filtration. The filtrate was poured into distilled water, resulting in the formation of the desired product as white solids. The crude product was recrystallized from methanol to give ligand **2′** in 64% yield; mp 298−300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.7 (s, 3H), 10.4 (s, 3H), 10.1 (s, 3H), 8.6 (s, 3H), 7.8 (d, 6H, $J = 8.8$ Hz), 7.3 (d, 6H, $J = 8.8$ Hz). IR (KBr, cm^{-1}): 3248.5 (υ_{N-H}), 1657.4 ($\upsilon_{C=O}$). MS (ESI, *m*/*z*) for C$_{30}$H$_{24}$N$_6$O$_9$: 613 (M + H$^+$).

Ligand 3′. A solution of 1,3,5-benzenetricarbonyl trichloride (0.4 g, 1.5 mmol) in DMF (5 mL) was added dropwise into a solution of 6-hydroxyhexanoic hydrazide (0.78 g, 5.3 mmol) and triethylamine (0.7 mL) in DMF (10 mL). The solution was stirred at 0 °C for 1 h and then stirred at room temperature for 0.5 h. The reaction mixture was filtered to remove the hydrochloric salt of triethylamine formed. The filtrate was evaporated under reduced pressure, and the resultant viscous yellow liquid was boiled with a mixture of ethyl acetate/hexane (4:1 v/v) for 1 h. The ethyl acetate/hexane layer was decanted, and the residual liquid was dried under vacuum to give a pale white solid. The solid was washed with distilled water to give a white powder (0.3 g, 38% yield); mp 218−219 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.6 (s, 3H), 10.0 (s, 3H), 8.5 (s, 3H), 4.4 (t, 3H, $J = 5.1$ Hz), 3.4 (dd, 6H, $J = 6.2$ Hz, 5.2 Hz), 2.2 (t, 6H, $J = 7.2$ Hz), 1.6 (m, 6H), 1.4 (m, 6H), 1.3 (m, 6H). IR (KBr, cm^{-1}): 3200.1 (υ_{N-H}), 1693.7 ($\upsilon_{C=O}$). MS (ESI, m/z) for $C_{27}H_{42}N_6O_9$: 595 (M + H$^+$).

General Procedure for the Synthesis of Dendritic DCH− Ru Complexes. A solution of *cis*-Ru(bby)$_2$Cl$_2$·2H$_2$O (0.2 g, 0.38 mmol), dendritic ligand (0.063 mmol), and sodium carbonate (50 mg, 0.5 mmol) in a mixture of water/ethanol (5/1 v:v, 80 mL) were heated to reflux for 48 h under argon. After cooling to room temperature, a solution of ammonium hexafluorophosphate (1.5 g in 60 mL of water) was added. The red dark precipitate was filtered off and redissolved in acetone (20 mL). The ruthenium complex was then precipitated out with diethyl ether and dried under vacuum at room temperature.

Complex **2**: 69% yield. IR (KBr, cm^{-1}): 1604.4 ($\upsilon_{C=N}$), 843.2 (υ_{P-F}).

Complex **3**: 66% yield. IR (KBr, cm^{-1}): 1606.4 ($\upsilon_{C=N}$), 841.8 (υ_{P-F}).

Determination of the Ruthenium Content in Complexes 2 and 3. The quantitative analysis of the ruthenium content in complexes **2** and **3** was carried out according to a method reported by Balcerazk et al.[13] Because of the absence of other interfering metals such as osmium, UV−vis absorption spectra were used directly for the determination of ruthenium. The reported extinction coefficient ($\epsilon_{445\ nm} = 2.7 \times 10^3$ L mol^{-1} cm^{-1}) of the analyte solutions with the ruthenium concentration in the range 0.5−45 μg/mL was used for calculation. A typical method is described as follows: A 50 mL, two-neck, round-bottomed flask equipped with a nitrogen inlet and a distillation head was charged with complex **2** (13.4 mg) and HClO$_4$/H$_2$SO$_4$ (1/3 v/v, 20 mL). A gentle stream of nitrogen gas was introduced into the flask and bubbled out at the distillation end into two connected traps, each containing 20 mL of aqueous HCl solution (2 N) at a speed of 2−3 bubbles/s. The sample solution was heated at 120 °C until it turned into colorless. The aqueous HCl solution in two traps were combined and diluted to the volume of 100 mL in a volumetric flask. A small portion (2 mL) of this solution was taken out from the volumetric flask into another flask, followed by addition of 0.5 mL of SnCl$_2$ (1 M) in 2 M aqueous HCl solution and 7.5 mL of 6 M aqueous HCl solution. The resulting solution in the flask was heated on a boiling water bath for 45 min, and a sample solution was taken out for UV−vis analysis. The ruthenium content was calculated from the given ϵ value and the measured absorbance at 445 nm.

Complex **2**: Ru % found: 14.0 ± 0.3%; calcd: 15.3%.

Complex **3**: Ru % found: 13.7 ± 0.4%; calcd: 15.4%.

Preparation of Cross-Linked DCH−Ru Films on ITO for Optical Attenuation Studies. Complex **2** (0.06 g, 0.015 mmol) and triisocyanate (trimethylolpropane, carbamate with xylylene diisocyanate) (0.01 g, 0.015 mmol) were dissolved in 0.7 mL of acetonitrile that contained 1,4-diazabicyclo[2.2.2]-octane (DABCO, 1 wt % relative to **2**). The prepared solution was immediately filtered through a syringe filter with a pore size of 0.2 μm, and the filtrate was used to spin-coat the films on ITO. The film on ITO was dried at room temperature for 0.5 h and then thermally cured under nitrogen at 120 °C for 2 h.

The cross-linked film based on complex **3** was prepared by the same procedure as for complex **2**, except that the cure temperature was at 140 °C.

Fabrication of a Prototype ECVOA Device. The sandwich-type test devices were assembled using two ITO glass plates coated with two different EC materials and a gel electrolyte based on poly(ethylene oxide) (PEO). The composition of gel electrolyte was LiClO$_4$:PEO:propylene carbonate: ethylene carbonate in a ratio of 9:20:30:41 by weight. The working electrode was coated with the cross-linked DCH−Ru complex **2**. The counter electrode was coated with tungsten oxide by electrochemical deposition according to the literature method.[14] The gel electrolyte was cast onto the counter electrode and dried in air for 15 min, before it (ca. 0.1 mm in thickness) was covered with the working. The devices were then placed in a glovebox to allow a complete gelation for 3 days before testing.

Table 1. Electrochemical Data for Dendritic DCH−Ru Complexes

complex	$^1E_{1/2}{}^a$ (Ru^{II}/Ru^{II}→Ru^{II}/Ru^{III})	$^2E_{1/2}{}^a$ (Ru^{II}/Ru^{III}→Ru^{III}/Ru^{III})	ΔE^b
2	780	1431	651
3	817	1451	634

[a] From cyclic voltammetry performed at 100 mV/s scan rate. Potentials E in mV vs NHE. [b] $\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$.

Results and Discussion

Synthesis of Dendritic DCH−Ru Complexes. It is known that the branched molecular structure of dendrimers provides well-defined surface functionality and specific geometrical sizes, which give rise to some unique properties not accessible in linear polymers.[15] In our case, the dendritic ruthenium complexes should have a larger free volume than the linear analogue, which favors a rapid ion transportation and thus may result in rapid response time with a high optical attenuation. Furthermore, they should have better solubility in common organic solvents than the linear analogue, thus allowing for easy film fabrication by spin coating or casting. For the ECVOA application, the dendritic ruthenium complexes can also be readily cross-linked with a cross-linker, if an appropriate reactive group is introduced into the dendrimers. Thus, DCH−Ru complexes **2** and **3** with reactive hydroxy groups rather than linear polymers were designed and prepared in this study.

The synthesis of dendritic ligands **2′** and **3′** was achieved via a nucleophilic substitution reaction of 1,3,5-benzenetricarbonyl trichloride with the corresponding hydrazides at low temperatures (Scheme 2). It is critical to control the reaction temperature in order to avoid the side reaction of the hydroxy group with acyl chloride. The dendritic ruthenium complexes **2** and **3** were prepared by reacting the ligands **2′** and **3′** with a ruthenium exchange agent and obtained in the Ru^{II}/Ru^{II} state as purple solids. The ruthenium content in complexes **2** and **3** was determined according to a method reported by Balcerazk et al.[13] and was found to be in a reasonably good agreement with the calculated values. The other methods such as NMR and mass spectroscopy (by electron, chemical, and electrospray ionizations) were found to be futile in quantification of the ruthenium content. Complexes **2** and **3** in the Ru^{II}/Ru^{II} state are found to be stable to the air, water, and strong bases and exhibit good thermal stability as assessed by thermogravimetry for the onset temperature for 5% weight loss (ca. 348 °C for complex **2** and 315 °C for complex **3**). The orange-colored complexes **2** and **3** in the mixed-valence state can be obtained by chemical (e.g., H$_2$O$_2$) or electrochemical oxidation and have good stability in air. However, the complexes in the Ru^{III}/Ru^{III} state are highly labile and cannot be obtained in high purity.

Electrochemical and Spectroelectrochemical Studies. The electrochemical and electronic absorption data for the DCH−Ru dendrimers are summarized in Tables 1 and 2. Figure 1 (trace a) shows the cyclic voltammogram of complex **2**. As expected, there are two quasi-reversible, one-electron oxidation processes in the positive potential region vs NHE, associated with the successive Ru^{II}/Ru^{III} couples. The first oxidation wave

Table 2. Absorption Data for Dendritic DCH−Ru Complexes

complex	oxidation state	λ_{max} (log ϵ)[a]
2	Ru^{II}/Ru^{II}	354 (4.60); 518 (4.49)
	Ru^{II}/Ru^{III}	434 (4.34); 1593 (4.26)
	Ru^{III}/Ru^{III}	476 (4.17); 804 (4.01)
3	Ru^{II}/Ru^{II}	348 (4.64); 515 (4.54)
	Ru^{II}/Ru^{III}	434 (4.39); 1549 (4.15)
	Ru^{III}/Ru^{III}	479 (4.00); 806 (4.16)

[a] Wavelength in nm; molar extinction coefficient ϵ in $M^{-1}\ cm^{-1}$.

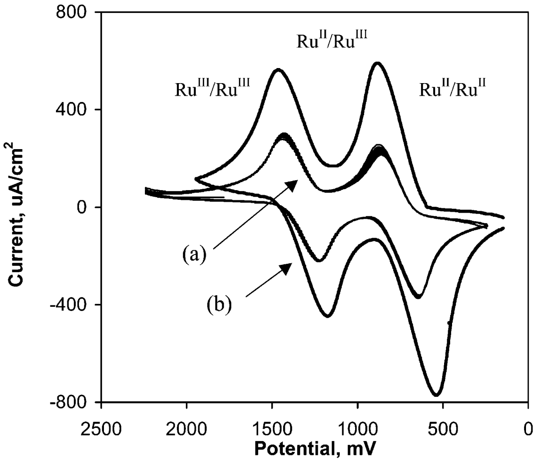


Figure 1. Cyclic voltammograms of (a) complex **2** and (b) cross-linked film of complex **2** on ITO in acetonitrile/0.1 M TBAH (in reference to NHE).

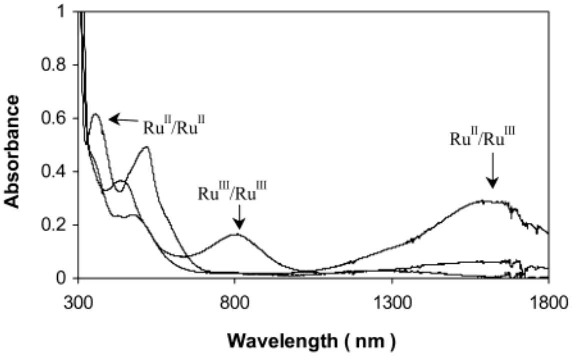


Figure 2. UV−vis−NIR spectra of complex **2** in three oxidation states.

corresponds to the oxidation of the Ru^{II}/Ru^{II} metal center to the Ru^{II}/Ru^{III} state, while the second corresponds to the further oxidation of the Ru^{II}/Ru^{III} state to the Ru^{III}/Ru^{III} state. The gap between the two oxidation potentials (ΔE) is 0.65 V. This value is larger than those of other dinuclear metal complexes,[8−11] offering a better control in voltage for the ECVOA application. Multisweep experiments showed a negligible change after 20 cycles of scanning, which indicates a good reversibility of the electrochemical process of these dendritic ruthenium complexes.

Complexes **2** and **3** in the Ru^{II}/Ru^{II} state display two intense absorptions around at 350 and 520 nm associated with the MLCT transition (metal-to-ligand charge transfer). Oxidation to the Ru^{II}/Ru^{III} state results in the appearance of a strong and broad intervalence transition band centered at 1593 nm for complex **2** (Figure 2) and at 1549 nm for complex **3**. These bands are attributed to the MMCT transition (metal−metal charge transfer) formed in the mixed-valence state. Compared to small DCH−Ru complexes like **1**,[9b] complexes **2** and **3** show a larger MMCT extinction coefficient (ϵ) at 1550 nm (Table 2). Upon further oxidation to the Ru^{III}/Ru^{III} state, a new band at 800 nm appears, which is assigned to a ligand-to-metal charge-transfer (LMCT) transition.

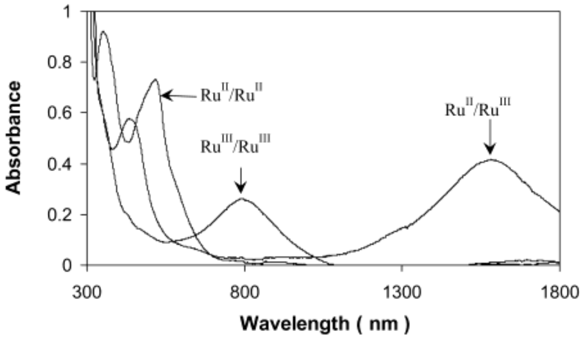


Figure 3. UV−vis−NIR spectra of cross-linked film of complex **2** on ITO glass.

Optical Attenuation Studies. To fabricate a test cell for optical attenuation study, thin films of DCH−Ru complexes need to be formed on ITO-coated glass. Since complexes **2** and **3** contain a hydroxy group, a triisocyanate compound was used as a cross-linker to form a polymer network via the urethane bonds. The cross-linking or cure reactions for complexes **2** and **3** were carried out under nitrogen at 120 and 140 °C, respectively, and monitored by IR. The characteristic IR band of the isocyanate group (2260 cm^{-1}) decreased with the increase of cure time and completely disappeared after 2 h. The cured films tightly adhered to the ITO surface even after being soaked in organic solvents such as DMF, acetone, acetonitrile, and chloroform over days. The electrochemical and spectroelectrochemical behaviors of the cross-linked films are almost identical to those of DCH−Ru complexes in solution (Figures 1−3).

The studies on dynamic attenuation or optical switching were performed using a quartz cuvette cell, which contained an ITO plate coated with a layer of cured DCH−Ru film with a thickness of 400 nm, a solution of TBAH in acetonitrile, a silver reference electrode, and a platinum counter electrode. The film can be switched on and off in less than 2 s, and optical attenuation was recorded at 1550 nm. The films of complexes **2** and **3** displayed optical attenuation of 2.2 and 2.0 dB at 1550 nm with a switching time of 2 s, respectively. Accordingly, their attenuation powers are 5.4 and 4.9 dB/μm of film in thickness.

To probe the effect of the applied potential on the redox process and optical attenuation, optical attenuation of complexes **2** and **3** was measured at various potentials. Figure 4 depicts the optical attenuation as a function of applied potential. The film-coated ITO electrode was stepped between its reduced (−100 mV vs silver electrode) and oxidized state with a switching time of 2 s. At the same time, the transmittance at 1550 nm was monitored with UV−vis−NIR spectroscopy in order to determine the optical attenuation. Both films underwent 200 switching cycles for each stepping potential and displayed an excellent reproducibility of attenuation during the repeated redox switching. For complex **2**, optical attenuation increased dramatically with the increase of applied potential. It reached a plateau at a potential of 850 mV until a potential of 1200 mV. In the more positive range, optical attenuation gradually decreased due to the partial oxidation of the

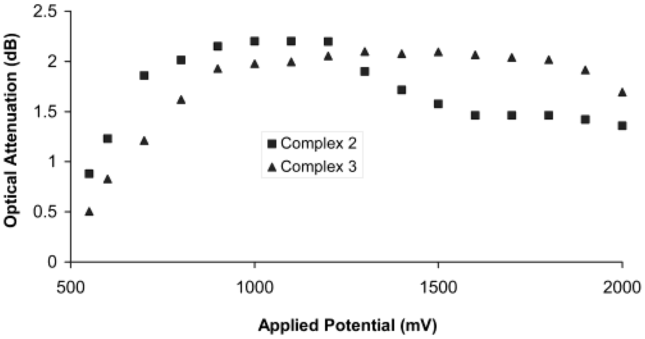


Figure 4. Optical attenuation of films of complexes **2** and **3** on ITO glass as a function of applied potential with a switching time of 2 s and a stepping potential (−100 mV vs silver electrode).

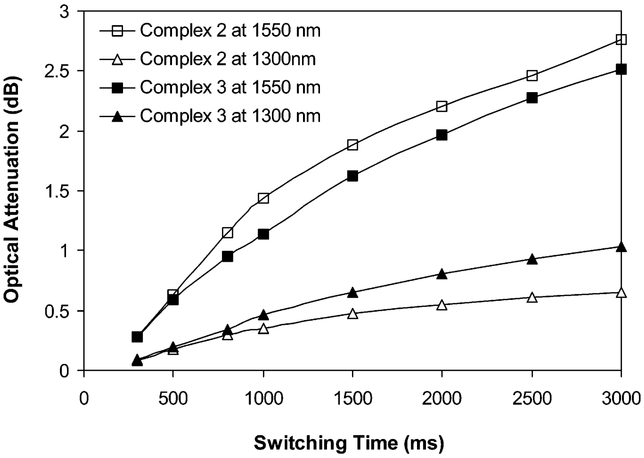


Figure 5. Dependence of optical attenuation on switching time for films of complexes **2** and **3** on ITO glass.

$\mathrm{Ru^{II}/Ru^{III}}$ state to the $\mathrm{Ru^{III}/Ru^{III}}$ state. The optical attenuation of complex **3** reached a maximum value at about 900 mV. However, unlike complex **2**, the attenuation of complex **3** did not decrease until the potential was higher than 1900 mV, which may be attributed to the slow oxidation reaction of complex **3** to the $\mathrm{Ru^{III}/Ru^{III}}$ state. Clearly, variable optical attenuation could be achieved and corresponded almost linearly to the applied voltage within the range 500−2000 mV vs a silver electrode.

To study the effect of switching time on optical attenuation at two telecommunication wavelengths, the film on ITO was switched between −100 and +1100 mV vs silver electrode with different switching time. Both complexes **2** and **3** exhibited a gradual increase in attenuation with the longer switching time (Figure 5). In comparison with complex **2**, complex **3** displayed a lower optical attenuation at 1550 nm but a higher optical attenuation at 1300 nm.

Coloration efficiency (CE) is an important wavelength-dependent parameter for evaluating electrochromic materials. It is determined as the variation of optical density as a function of injected/ejected charge per unit electrode area. The ideal EC material or device for the ECVOA application should show a large transmittance variation with a small amount of charge or has a high CE. The CE values of cross-linked films of complexes **2** and **3** were assessed in solution according to the known method.[6c,16] The relatively high CE values of 206 and 238 $\mathrm{cm^2/C}$ were obtained at 1550 nm for complexes **2** and **3**, respectively.

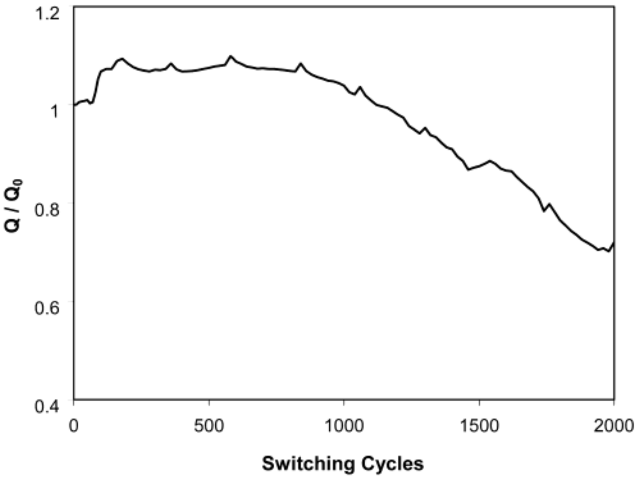
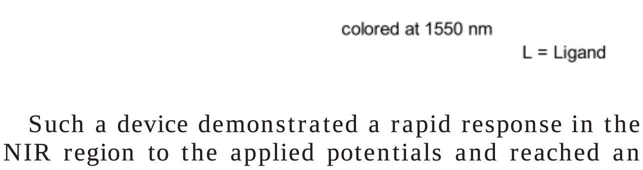


Figure 6. Electroactivity of film of complex **2** on ITO as a function of switching cycles.

Long-term stability of complexes **2** and **3** as films on ITO was further determined by probing the ratio of Q/Q_0. The ratio of Q/Q_0 represents the charge involved in the redox process after a given number of switching cycles to the initial switching charge. Figure 6 shows a representative graph of electroactivity of complex **2** with a switching time of 2 s. An initial increase of the electroactivity was observed. Like some conjugated polymers, this phenomenon is not surprising as more electroactive sites of the film were activated after the short break-in period.[17] After 2000 switching cycles, the film of complex **2** displayed a retention of 73% of its original electroactivity. The drop of electroactivity was found to be mainly due to the film delamination from ITO in the electrolyte solution. Thus, a preliminary test using 3-aminopropyltrimethoxysilane as the first layer on the ITO electrode before coating complex **2** or **3** indicated an improvement in switching stability. The films of complexes **2** and **3** on the treated ITO electrode reached 19 000 cycles with a 15% drop of attenuation and 18 000 cycles with a 19% drop of attenuation, respectively.

Prototype ECVOA Device. Since the cross-linked DCH−Ru films exhibited good attenuating properties at 1550 nm, a prototype ECVOA device was fabricated for further evaluation using anodically NIR-coloring complex **2** and cathodically NIR-coloring tungsten oxide ($\mathrm{WO_3}$). A gel electrolyte based on poly(ethylene oxide) was sandwiched in between two ITO glass plates coated with complex **2** and $\mathrm{WO_3}$ films. The overall electrochemical process of this device may be written as follows:



$$x\{[(\mathrm{Ru^{II}/Ru^{II}} - \mathrm{L})_3]^{+6}(\mathrm{PF_6^-})_6\} + 3\,\mathrm{WO_3} + 3x\,\mathrm{LiClO_4} \rightleftharpoons x\{[(\mathrm{Ru^{II}/Ru^{III}} - \mathrm{L})_3]^{+9}(\mathrm{PF_6^-})_6(\mathrm{ClO_4^-})_3\} + 3\,\mathrm{Li}_x\mathrm{WO_3}$$

Such a device demonstrated a rapid response in the NIR region to the applied potentials and reached an attenuation of 5.4 dB at 1550 nm with a switching time of 3 s (Figure 7). However, an increase in the switching time (up to 10 s) did not further expand the attenuation range.

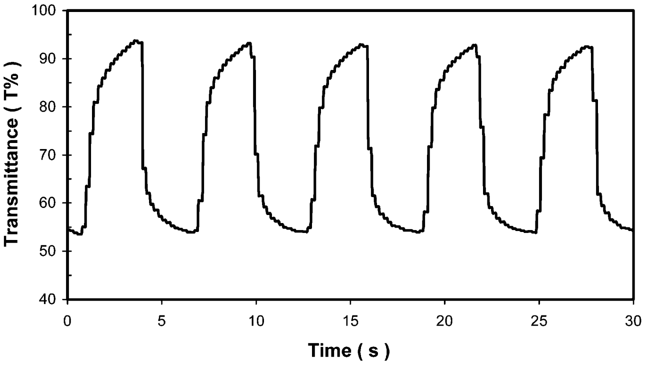


Figure 7. Variation of transmittance for a prototype ECVOA device based on complex **2** and WO_3.

Conclusion

The cross-linked films of two mixed-valence dendritic ruthenium complexes exhibit strong absorption around at 1550 nm at low oxidation potentials, high coloration efficiency, fast switching speed, and good electrochemical stability, making them potential candidates for use in a device for optical attenuation at telecommunication wavelengths. The concept of an electrochromic variable optical attenuator has been demonstrated with the use of organic and inorganic NIR electrochromic materials.

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