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A Variable Optical Attenuator Operating in the Near-Infrared Region Based on an Electrochromic Molybdenum Complex

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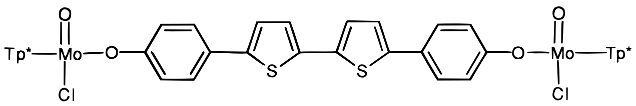
Electrochromic materials have attracted a great deal of interest due to their potential for applications such as smart windows and information display and storage devices.[1] The application of electrochromic materials in devices for optical information processing has, however, been little explored. The variable optical attenuator (VOA) is a key component in advanced wavelength division multiplexed networks.[2−4] A number of VOA devices have been designed using sliding block mechanisms (microelectromechanical systems, or MEMS)[2] and thermooptic devices using silica-[3] or polymer-based[4] materials. Although each of these techniques yields devices with desirable qualities, a VOA device that might be monolithically integrated with other optical components, as well as exhibiting low power consumption and high attenuation levels, has yet to be demonstrated. We present here a new molybdenum complex which shows strong electrochromism in the NIR region, together with experimental data illustrating its potential for use as a VOA operating in this region. The NIR region is of particular technological interest because it is used for optical data transmission through silica fibers, which have absorption minima at ca. 1300 and 1550 nm, and the development of NIR dyes[5] and NIR optical devices[6] are therefore subjects of much interest.

Structural formula of **1**:



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The new dinuclear molybdenum complex **1** was prepared by an extension of the literature procedure used for related dinuclear oxo-Mo(V) complexes.[7] Thus, reaction of the ligand 4,4′-$HOC_6H_4(2,5\text{-}C_4H_2S)_2C_6H_4OH$ (Hock et al.[8]) with excess $[MoCl_2(O)Tp^*]$ [where Tp* = hydrotris(3,5-dimethylpyrazolyl)borate] followed by chromatographic purification afforded **1** in good yield.[9]

Cyclic voltammetry measurements in dichloromethane reveal two reversible one-electron oxidations, at +0.44 and +0.69 V versus Fc/Fc^+, which may be ascribed to the successive Mo(V)/Mo(VI) couples. Splitting of the redox potentials of the two metal centers is due to significant electronic communication between the metal centers via the highly conjugated bridging ligand, an effect that has been discussed in detail elsewhere.[10] Reduction of **1** occurs at −1.1 V versus Fc/Fc^+, with two Mo(IV)/Mo(V) couples occurring nearly simultaneously to give a single symmetric double-intensity wave.

Results of UV/VIS/NIR spectroelectrochemical measurements on **1** are shown in Figure 1. The spectrum of the neutral starting complex is comparable to those of other oxo-Mo(V) complexes, with the lowest-energy transition [phenolate → Mo(V) LMCT] at 665 nm.[10] Significantly, **1** is transparent between 900 and 2000 nm. One-electron oxidation to $[\mathbf{1}]^+$ [formally, a Mo(V)/Mo(VI) complex] results in the appearance of a strong NIR absorption band centered at 1340 nm ($\epsilon = 23\,000$ M^{-1} cm^{-1}) and another, slightly weaker transition at 752 nm. These are assigned to phenolate → Mo(VI) LMCT transitions.[11] The transition at 1340 nm is the lowest-energy transition of this type we have observed to date and provides a strong and fully switchable absorbance within the 1300 nm window of silica fibers. On further oxidation to $[\mathbf{1}]^{2+}$, this transition moves to higher energy with λ_{max} at ca. 1200 nm. However, $[\mathbf{1}]^{2+}$ slowly decomposes on the measurement time scale (ca. 30 min). Upon reduction of **1** to $[\mathbf{1}]^{2-}$ in a single step, the absorption spectrum contains a weak band located at 660 nm and is transparent at wavelengths above 950 nm. With these properties in mind, a NIR optical switch may be envisaged that operates by rapid and reversible switching between **1** and $[\mathbf{1}]^+$.

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(9) Yield: 60%. FAB-MS: *m/z* 1237 [M^+], 1203 [M^+−Cl]. Anal. Found: C, 50.8; H, 5.3; N, 12.7. Calcd. for $C_{50}H_{56}B_2Cl_2Mo_2N_{12}O_4S_2$: C, 50.9; H, 6.1; N, 12.8.

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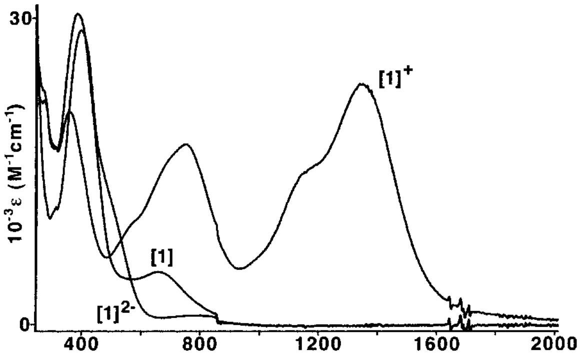

Figure 1. Electronic spectra of [**1**], [**1**]$^+$, and [**1**]$^{2-}$ measured at −30 °C in dichloromethane. Experimental details for the spectroelectrochemistry have been published elsewhere.[10]

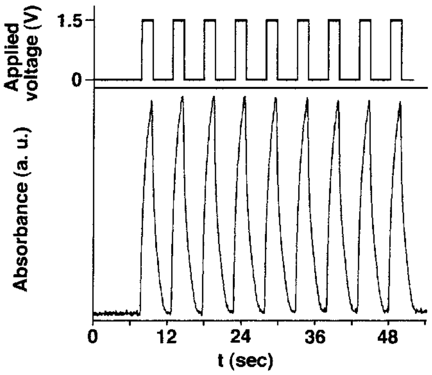

Figure 2. Reversible optical absorption of **1**/[**1**]$^+$ at $\lambda = 1160$ nm with an applied voltage cycled between 0 V (3 s) and +1.5 V (2 s).

To investigate the performance of this material in an optical switching device, experiments were performed using a home-built two-electrode optically transparent thin-layer electrode (OTTLE) cell based on two ITO-coated glass slides. The absorption of the cell containing an acetonitrile solution of **1** was monitored at a wavelength of 1160 nm while a stepped potential was applied to the electrodes.[12] An absorption increase was observed when a potential ≥1.0 V was applied although significant decomposition of the material occurred when the applied potential was greater than 1.6 V, resulting in formation of unstable [**1**]$^{2+}$. Experiments performed by repeated stepping of the applied potential between 0 and 1.5 V showed reversible optical switching; Figure 2 illustrates the change in absorption with the applied voltage. This process was repeatable over several thousand cycles. By varying the higher potential step during these experiments within the range of 1.0−1.5 V, the maximum absorbance of the material at a given wavelength could be changed. That is, the degree of attenuation of the incident light beam can be controlled by adjusting the applied potential.

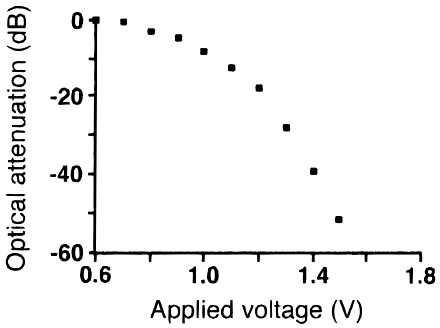

Figure 3. Optical attenuation of a 1300 nm laser as a function of applied voltage in a cell based on **1**/[**1**]$^+$.

Experiments were performed to evaluate this material in a VOA device. By use of an acetonitrile solution of **1** in a cell with a 6 mm optical path length[13] and a 1300 nm Fabry−Perot laser as a light source, light was injected into the cell via a standard single mode optical fiber. The variation in optical power out of the sample for differing applied voltages was measured (Figure 3), and the attenuation reaches a maximum of 50 dB at an applied potential of 1.5 V. This degree of attenuation is comparable to the best that is currently available from alternative attenuator technologies.[2−4]

Although the response time in this cell is a few minutes, it is proposed that containment of the electrochromic material in a single-mode waveguide structure with the optical path length along the plane of the electrodes, combined with a greatly reduced electrode separation, should afford sub-millisecond response times. Such experiments are currently underway.

In summary, we have prepared a new electrochromic molybdenum complex which exhibits a strong NIR absorption band upon one-electron oxidation. This material may be reversibly switched between neutral and oxidized forms with the attenuation of incident light dependent on the applied voltage; compared to other optical attenuator devices, a high degree of attenuation is available for a low voltage. This voltage-dependent attenuation of an incident light beam forms a functional basis for a VOA device.

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(12) The OTTLE cell consisted of two indium-doped tin oxide-coated glass slides separated by 0.2 mm thick glass spacers and fixed together with a wax sealant. The cell was filled with a 0.9×10^{-3} M solution of **1** in acetonitrile with 0.1 M [n-Bu_4N]PF_6 as electrolyte. No attempt was made to exclude air.

(13) The cell used for VOA measurements consisted of two indium-doped tin oxide-coated glass slides separated by a 6 mm thick Teflon spacer. The cell was filled with a 3×10^{-4} M solution of **1** in acetonitrile with 0.1 M [n-Bu_4N]PF_6 as electrolyte. No attempt was made to exclude air.