

Transient infrared and emission spectroscopy of selective ion-sensors

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Introduction

The development of luminescent sensors for the detection of oxoanions attracts attention as an efficient means of selective analysis^[1]. Our studies address oxometalates^[2] since there are no selective chemosensors available for molybdate, tungstate or vanadate. The analysis of molybdate is important for environmental, biochemical and medical analysis. Oxometalates must not only complex successfully for the sensor with other oxoanions, such as SO_4^{2-} and HPO_4^{2-} , but also with metal cations, such as Fe^{3+} and Cu^{2+} .

Rhenium carbonyl bipyridine complexes have been the subject of intensive study by TRIR spectroscopy and it is now well established that MLCT excited states exhibit high frequency shifts of $\nu(\text{CO})$ whereas photoinduced electron transfer from ligands to $\text{Re}(\text{bpy})$ causes low frequency shifts^[3]. TRIR spectroscopy is the method of choice for mechanistic studies of such complexes.

We have recently reported a complex that acts as a molybdate sensor via luminescence quenching^[4]. The complex includes a catechol binding unit capable of electron transfer to rhenium. Our sensor molecules are designed to signal the presence of molybdate by a change in the emission intensity. We based the selectivity on a combination of co-ordinative bonding and electrostatics, choosing catecholamide ligands as receptors and $\text{Re}(\text{diimine})(\text{CO})_3$ lumophores. Fig. 1 shows the sensors $[\text{Re}(\text{bpy})(\text{CO})_3(\text{H}_2\text{-L}^1)]^+$ and $[\text{ReBr}(\text{CO})_3(\text{H}_2\text{-L}^2)]$. The electron withdrawing effect of the positively charged lumophores lowers the pK_a values (4.5 to 5.5) of the *ortho*-phenolates, increasing the affinity of the sensor systems for molybdate at low pH. The crystal structures reveal that the catecholamide units and the phenanthroline units are nearly coplanar. Therefore, π -overlap and through-bond electronic coupling allow rapid electron transfer between the catechol quenchers and the lumophores.

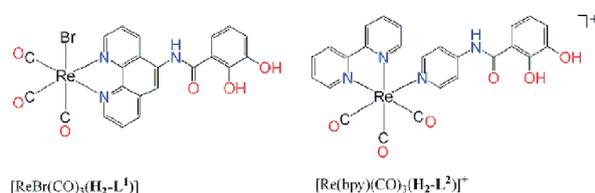


Figure 1. Structures of sensor molecules

Almost complete quenching of luminescence is observed in the presence of molybdate down to pH values as low as 0.1. Vanadate and tungstate may also be detected by this sensor system^[4]. Absorption spectra reveal a change in the spectrum both with pH and with molybdate binding that is consistent with catecholate-to-bipyridine charge transfer. This process is abbreviated as a ligand-to-ligand charge transfer (LLCT). The photochemical mechanism of

this sensor system remained uncertain, so long as our measurements were confined to the steady state and nanosecond time-resolved absorption/emission. The rhenium bound CO-ligands provide reporters for the investigation of the photophysical properties of the systems by time resolved infrared-spectroscopy. We set out to establish the basis of the selectivity for oxometalates by time-resolved infrared spectroscopy and also by time-correlated single photon counting.

Results

The results from the experiments on the *PIRATE* system provided a clear guide to the different excited states involved in the sensors' responses and to their dynamics.

(a) **pH Response of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{H}_2\text{-L}^1)]^+(\text{OTf})^-$.** We collected excellent ps ($\lambda_{\text{ex}} = 400$ and $\lambda_{\text{ex}} = 355$ nm) and ns ($\lambda_{\text{ex}} = 355$ nm) data on $[\text{Re}(\text{bpy})(\text{CO})_3(\text{H}_2\text{-L}^1)]^+(\text{OTf})^-$ in DMF + 5% D_2O as a function of pH. Baseline data sets were also collected on the protected sensors. These experiments revealed MLCT excitation at low pH with a high frequency shift in $\nu(\text{CO})$. As the pH was increased, MLCT excitation was gradually supplanted by direct excitation into the LLCT excited state characterised by low frequency shifts in $\nu(\text{CO})$ (Fig. 2). The substantial low

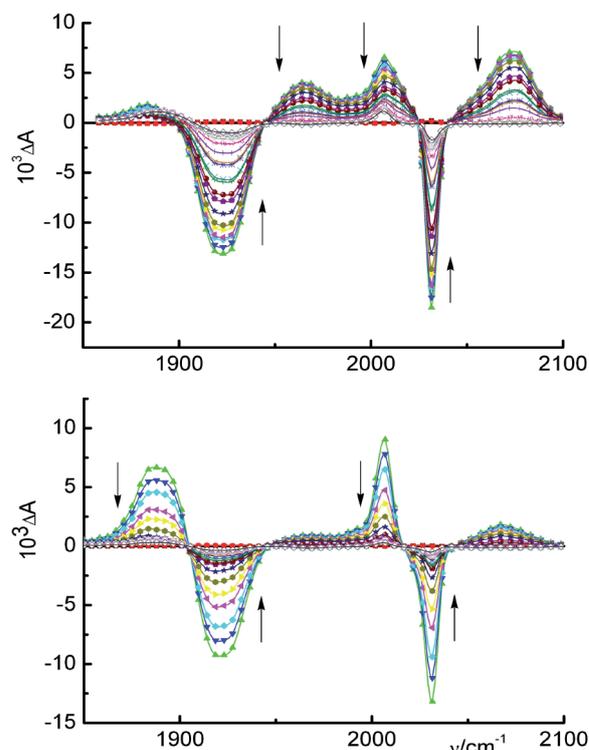


Figure 2. Free sensor $[\text{Re}(\text{bpy})(\text{CO})_3(\text{H}_2\text{-L}^1)]\text{PF}_6$ in DMF/ D_2O (20: 1), ns timescale. $\lambda_{\text{ex}} 400$ nm. Above: pH 4. Below: pH 8.

frequency shift of the LLCT state arises because an electron is transferred from the remote catecholamide ligand to the bipyridine ligand which is adjacent to rhenium. Excited state lifetimes of the MLCT state varied remarkably little: 70 ns for the protected sensor, 53 ns for the deprotected sensor at pH 4, decreasing to 22 ns at pH 8. The LLCT state exhibited three decay processes: (i) an ultrafast process of ca. 5 ps, assigned as 1 [LLCT] to ground state, (ii) a decay of ca. 4 ns, assigned as 3 [LLCT] to ground state (iii) a small proportion with a lifetime exceeding 1 μ s.

(b) pH Dependence of $[\text{ReBr}(\text{CO})_3(\text{H}_2\text{-L}^2)]$. Similar data sets were collected for $[\text{ReBr}(\text{CO})_3(\text{H}_2\text{-L}^2)]$ in THF + 10% D_2O and qualitatively similar behaviour was observed. In this case, the catecholate to phenanthroline charge-transfer results in intra-ligand charge-transfer (ILCT) states.

(c) Effect of oxometallates. The effect of added molybdate, vanadate or tungstate was investigated with each of the two sensors. The spectra revealed the striking result with molybdate that the LLCT state is formed by two mechanisms: both directly and at the expense of the MLCT state. Moreover, both mechanisms are detected even at low pH. The MLCT state converts to the LLCT state with a time constant of ca. 180 ps both in Mo:Re = 1:1 and 1:2 solutions but the rate changes significantly with pH (Fig. 3). This electron transfer process accounts for ca. 50% of the LLCT state. The results with tungstate were qualitatively similar, but there was no evidence that vanadate affected the photophysics significantly.

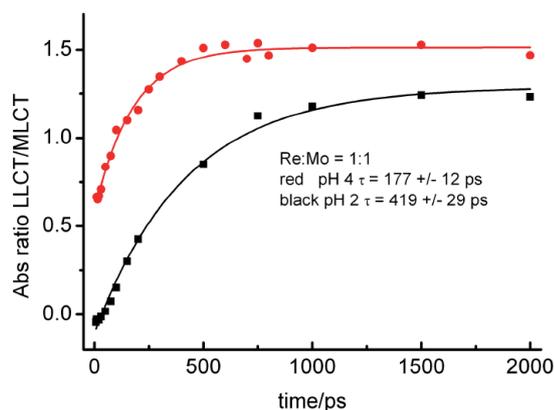


Figure 3. Kinetics of PeT conversion of MLCT to LLCT states, Re:Mo = 1:1, showing pH dependence of rate.

We have recently isolated the red crystalline Mo:Re = 2:1 complex. Data collected from this crystalline material proved to be identical to those collected by molybdate addition to $[\text{Re}(\text{bpy})(\text{CO})_3(\text{H}_2\text{-L}^1)]^+$ (Fig. 4). The molecular structure, determined by X-ray diffraction of $[\text{MoO}_2\{\text{Re}(\text{bpy})(\text{CO})_3(\text{L}^1)\}_2]$ shows two rhenium catecholamide units bound to the molybdate via chelating oxygen ligands from the catecholamide. Figure 5 illustrates the charge transfer processes superimposed on the structure.

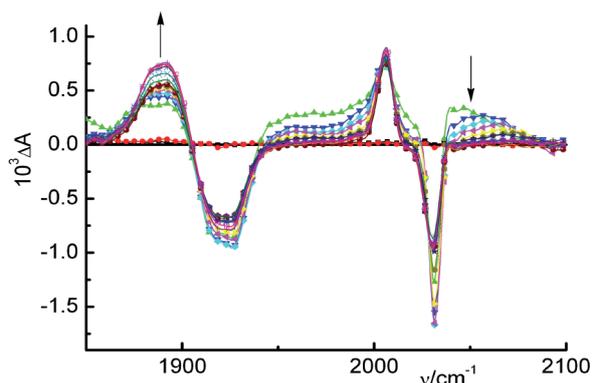


Figure 4. TRIR spectra of $[\text{MoO}_2\{\text{Re}(\text{bpy})(\text{CO})_3(\text{L}^1)\}_2]$ at pH 4 in DMF/ D_2O (20:1) time range 0-250 ps, λ_{ex} 400 nm.

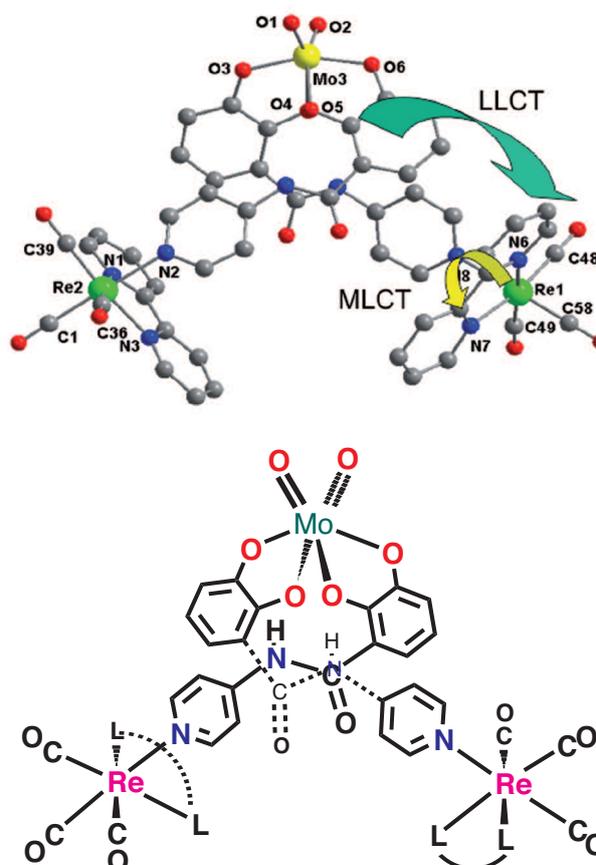


Figure 5. Molecular structure of $[\text{MoO}_2\{\text{Re}(\text{bpy})(\text{CO})_3(\text{L}^1)\}_2]$. Above: Structure with superimposed arrows showing MLCT and LLCT processes. Below: chemical formula with 2,2'-bipyridine ligands abbreviated as L-L.

(d) Time-correlated single photon counting. We also attempted to study the luminescence of these systems by time-correlated single photon counting. Although we obtained comparable data to the literature on standard rhenium tricarbonyl complexes, we were unable to obtain satisfactory data on the sensor systems.

Conclusions

The rhenium sensors are excited to two electronic states. The MLCT state dominates at low pH and in the absence of molybdate. The LLCT state is observed at high pH or on molybdate binding. Photo-induced electron transfer from catcholate to rhenium can interconvert the states in the presence of molybdate with time constants of the order of 10^{-10} s.

References

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