

Photoinduced electron transfer in Re^I complexes with appended amino acid ligands

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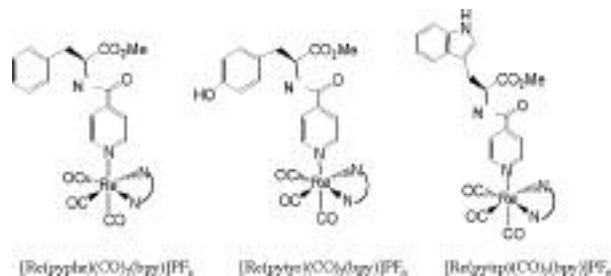
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Introduction

Unravelling the pathways involved in long-range electron transfer in biomolecules is a crucial step to obtain a complete understanding of their behaviour, and could lead to the development of important new active systems. Some metal-derivatized redox proteins, such as azurines, have shown unexpectedly fast long-range electron transfer from the metal center in the protein to a rhenium carbonyl chromophore unit on its surface. It is not completely understood if this could be due to a combination of ultrafast electron-hopping and long-range superexchange.^[1]

We were interested in investigating the possibility of an initial ultrafast electron transfer from an amino acid residue close to the surface of the azurin to the chromophore, which would later be followed by a slower electron transfer from the copper centre to the oxidized amino acid. To focus the study on the ultrafast step, we have studied a series of rhenium complexes, modeling the binding site of the chromophore to the azurine surface. Here, we present these models, [Re^I(pyaa)(CO)₃(bpy)]⁺ (py = pyridine, aa = tyrosine (tyr), phenylalanine (phe) and tryptophan (trp) methyl esters), Scheme 1. The three models have been synthesized and characterized and their behavior upon irradiation has been studied by a combination of stationary (UV-Vis absorption, fluorescence) and time-resolved (IR absorption, fluorescence) techniques.

Scheme 1



Results

[Re^I(pyphe)(CO)₃(bpy)]⁺ is used as a reference for the other two complexes, since it contains a redox inactive phenylalanine group which cannot undergo electron transfer. For the spectroscopic studies, we are exciting the absorption band at ~350 nm in all the samples, corresponding to the Re→bpy metal to ligand charge transfer (MLCT) transition. In the case of [Re^I(pytyr)(CO)₃(bpy)]⁺ and [Re^I(pytrp)(CO)₃(bpy)]⁺, we are expecting to see evidence of electron transfer from tyr and trp, respectively, to the oxidized Re^{II} center, after the MLCT excitation. This process will quench the lifetime of the excited state significantly.

The first results obtained, from emission spectroscopy, Figure 1, show quenching of the emission intensity of

[Re^I(pytrp)(CO)₃(bpy)]⁺, in relation to that of the model complex. [Re^I(pytyr)(CO)₃(bpy)]⁺, on the other hand, has the same emission profile as the model, indicating that the excited state in this complex is not quenched. Emission lifetime studies, Figure 2, also follow this trend. The lifetime of the ³MLCT state in [Re^I(pyphe)(CO)₃(bpy)]⁺ and [Re^I(pytyr)(CO)₃(bpy)]⁺ is 300 ns, whereas [Re^I(pytrp)(CO)₃(bpy)]⁺ has a much shorter lifetime of 30 ns.

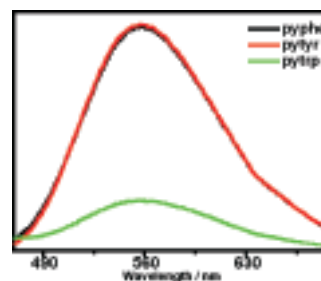


Figure 1. Emission spectra in MeCN at room temperature, excited at 350 nm.

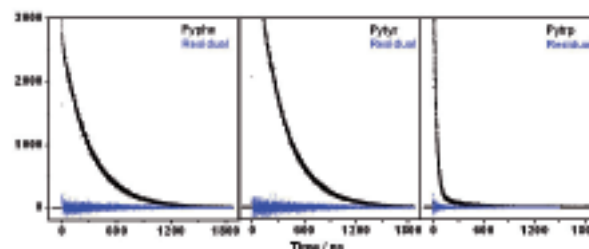


Figure 2. Time correlated single photon counting emission decay in degassed MeCN, excited at 370 nm.

It is obvious from these results that a new process is induced by trp, following MLCT excitation of [Re^I(pytrp)(CO)₃(bpy)]⁺. In order to characterize that specific process and the whole excited state behaviour of these complexes, we looked at their time resolved infrared (TRIR) spectra. The ground state spectrum of the model complex, Figure 3 top, shows two negative bands, a sharp one at ~2034 cm⁻¹ and a broad one at ~1930 cm⁻¹, corresponding to the A'(1) and the overlapping A'(2) and A'' CO vibrations respectively, and the three positive bands corresponding to those vibrations in the excited state. The shift of the CO vibrations to higher frequency confirms the MLCT character of the excited state since the movement of electron density away from rhenium decreases the backbonding from the metal to the CO π* orbital, strengthening the CO vibration.^[2] Figure 3 (bottom) shows the TRIR spectra of [Re^I(pytyr)(CO)₃(bpy)]⁺. The excited state of this complex is identical to that of the model, with no evidence of any electron transfer, even in the ns time scale.

In agreement with the previously discussed measurements, $[\text{Re}^{\text{I}}(\text{pytrp})(\text{CO})_3(\text{bpy})]^+$ shows a more complex excited state behavior than that of $[\text{Re}^{\text{I}}(\text{pyphe})(\text{CO})_3(\text{bpy})]^+$ or $[\text{Re}^{\text{I}}(\text{pytyr})(\text{CO})_3(\text{bpy})]^+$. The MLCT state is populated upon excitation as in the previous cases. On the ns time scale it is possible to see how the MLCT bands at $\sim 2071 \text{ cm}^{-1}$ and $\sim 1968 \text{ cm}^{-1}$ are decaying as a new band is formed at $\sim 1895 \text{ cm}^{-1}$, Figure 4. This band corresponds to the charge separated state, $[\text{Re}^{\text{I}}(\text{pytrp}^+)(\text{CO})_3(\text{bpy}^-)]^+$ arising from the electron transfer process, from the trp moiety to the Re^{II} . The band at $\sim 2010 \text{ cm}^{-1}$ contains two overlapping bands, the decaying MLCT A'(2) band and the charge-separated state A'(1) band increasing and then decaying. The rate constant of the electron transfer process is $3 \times 10^7 \text{ s}^{-1}$. The charge separated state bands then decay, Figure 4 inset, back to the ground state by back electron transfer from bpy^- to trp^+ . This interligand electron transfer has a rate constant estimated as $4.6 \times 10^7 \text{ s}^{-1}$. The behaviour of $[\text{Re}^{\text{I}}(\text{pytrp})(\text{CO})_3(\text{bpy})]^+$ is summarized in Scheme 2.

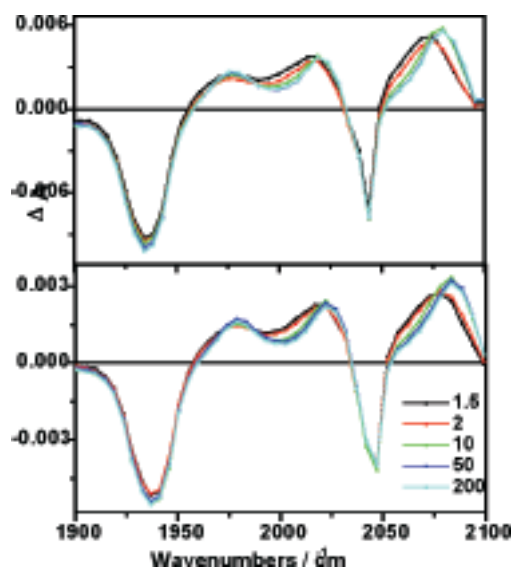


Figure 3. TRIR spectra of $[\text{Re}^{\text{I}}(\text{pyphe})(\text{CO})_3(\text{bpy})]^+$ (top) and $[\text{Re}^{\text{I}}(\text{pytyr})(\text{CO})_3(\text{bpy})]^+$ (bottom) in MeCN excited at 355 nm. Time delays are shown in ps. No new bands were observed on the ns time scale.

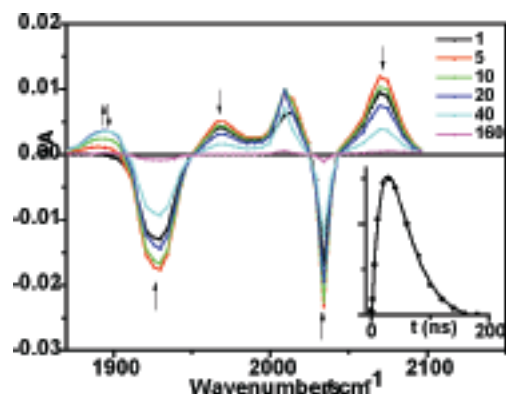
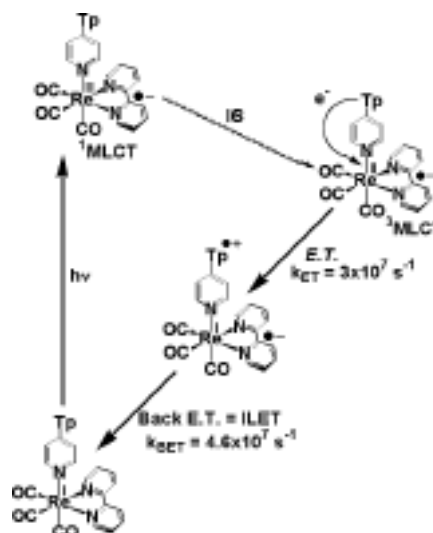


Figure 4. TRIR spectra of $[\text{Re}^{\text{I}}(\text{pytrp})(\text{CO})_3(\text{bpy})]^+$ in MeCN excited at 355 nm. Time delays are shown in ns. The arrows indicate spectral evolution. Inset: kinetic plot of the charge separated state in the ns time scale.

Conclusions

These studies have shown that optical excitation of the three complexes leads to a typical $\text{Re} \rightarrow \text{bpy}$ $^3\text{MLCT}$ excited state. The model complex, $[\text{Re}^{\text{I}}(\text{pyphe})(\text{CO})_3(\text{bpy})]^+$, which is not expected to undergo electron transfer since it contains a redox inactive phenylalanine group, exhibits a long-lived $^3\text{MLCT}$ with a lifetime of 300 ns. The $^3\text{MLCT}$ state of $[\text{Re}^{\text{I}}(\text{pytrp})(\text{CO})_3(\text{bpy})]^+$ has a much shorter lifetime ($\sim 30 \text{ ns}$) as it undergoes an electron transfer process, from the trp moiety to the Re^{II} , to produce a charge separated state, $[\text{Re}^{\text{I}}(\text{pytrp}^+)(\text{CO})_3(\text{bpy}^-)]^+$. The rate constant of this process is $3 \times 10^7 \text{ s}^{-1}$. The ground state is then recuperated by a $\text{bpy}^- \rightarrow \text{trp}^+$ interligand electron transfer whose rate constant is estimated as $4.6 \times 10^7 \text{ s}^{-1}$. In contrast, $[\text{Re}^{\text{I}}(\text{pytyr})(\text{CO})_3(\text{bpy})]^+$ shows an excited state identical to that of the model, so it follows that no electron transfer occurs in this complex.

Scheme 2



These results show that it is possible to have fast electron transfer from an amino acid residue to the excited rhenium unit. This is a good basis for the elucidation of the electron transfer process in metalloproteins and the development of electron transfer dyads.

References

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