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Pinpointing the Extent of Electronic Delocalization in the Re(I)-to-Tetrazine Charge-Separated Excited State Using Time-Resolved Infrared Spectroscopy

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Using molecules to harness solar energy is generally achieved by converting light into electrical energy,[1] chemical energy,[2] or, more recently, mechanical energy through the use of molecular machines.[3] The initial step in these transformations is typically a photoinduced charge separation between electron-donor and -acceptor moieties. One effective way to initiate this separation of charge is by stimulating a metal-to-ligand charge-transfer (MLCT) transition within polypyridyl-based transition-metal complexes.[4] Such MLCT states simultaneously oxidize the metal and reduce the ligand. With this capability in mind, the MLCT state of $Re(CO)_3Cl(Me_2BPTZ)$ [Me_2BPTZ = 3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine] (Figure 1a)[5] is therefore a candidate for driving photochemical switching analogous to that displayed by a Cu(I) pseudorotaxane, which occurs by reduction of Me_2BPTZ.[6] For this purpose, it was critical to confirm that the MLCT state of $Re(CO)_3Cl(Me_2BPTZ)$ localizes an electron on the Me_2BPTZ moiety. We have done this in the present work by identifying the locations of electronic and structural changes in the excited state of the Re(I) complex.

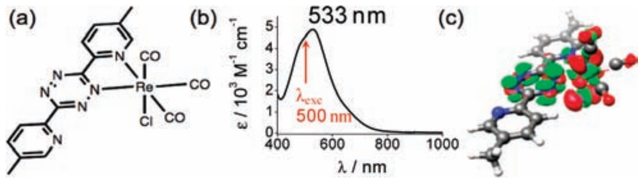

Figure 1. (a) Molecular structure and (b) UV−vis spectrum (50 μM, $CHCl_3$) of $Re(CO)_3Cl(Me_2BPTZ)$. (c) Difference density plot of the T_1 triplet excited state of $Re(CO)_3Cl(Me_2BPTZ)$ calculated using TD-DFT at the B3LYP level (red/green = depletion/accumulation of charge).

The available experimental methods capable of providing structural information on short-lived molecular excited states are generally limited to time-resolved vibrational[7,8] and X-ray[9] spectroscopic techniques. Early studies using time-resolved IR (TRIR) methods were generally restricted to the detection of strongly absorbing carbonyl and cyano ligand vibrations, thus limiting MLCT assignments to identification of oxidation alone. The current development of mid-IR detectors with improved sensitivity have now made it possible to obtain structural information on a wide range of short-lived transient intermediates.[10] For the first time, therefore, the reduction of a ligand in the MLCT state can also be identified. In this work, we report the use of femtosecond TRIR experiments and time-dependent density functional theory (TD-DFT) calculations to characterize both the formal oxidation- and reduction-state changes that take place in the MLCT excited state of $Re(CO)_3Cl(Me_2BPTZ)$.

The ground-state FTIR spectrum in the carbonyl region of $Re(CO)_3Cl(Me_2BPTZ)$ (Figure 2a) shows three absorption bands at 2034, 1953, and 1921 cm^{-1} corresponding to one symmetric and two antisymmetric vibrations of the carbonyl groups, respectively (Table 1). Upon excitation into the MLCT band at 500 nm (Figure 1b), these absorption bands shift to higher energies (2071, 2002, and 1978 cm^{-1}) (Figure 2b). This effect has been observed previously in MLCT states of other metal−carbonyl complexes[7,11,12] and can be explained by the weaker back-bonding involving the carbonyl ligands upon formal oxidation of the Re center. The early-time excited-state IR absorption spectra are broad. Within 5 ps, these absorption bands become narrower and shift to higher frequencies. Two possible processes could produce these spectral changes: either (i) intersystem crossing (ISC) from a ^{1}MLCT to a ^{3}MLCT excited state or (ii) vibrational cooling[13] from higher vibrational levels of the ^{3}MLCT state. The ISC mechanism is not likely, since the TD-DFT-calculated CO stretching frequencies of $Re(CO)_3Cl(Me_2BPTZ)$ in the singlet excited states do not match the trend observed in the experiment [see the Supporting Information (SI)]. Thus, we assign the short-time component to vibrational cooling. This process is expected to produce the observed blue shift of the vibrational frequencies on account of anharmonicity.[11,14]

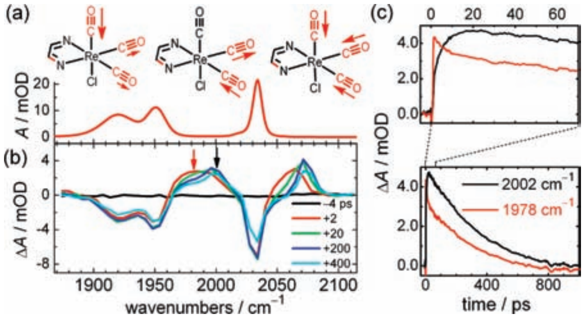

Figure 2. (a) FTIR and (b) TRIR spectra of $Re(CO)_3Cl(Me_2BPTZ)$ (5 mM, $CHCl_3$). For the TRIR measurements, the sample was excited by a 500 nm pump pulse. (c) Decay of the TRIR signal of $Re(CO)_3Cl(Me_2BPTZ)$ at (black) 2002 and (red) 1978 cm^{-1} for (top) shorter and (bottom) longer time scales, showing differences that stem from vibrational cooling.

The TRIR decay dynamics corresponding to the excited-state absorption bands of the CO groups (Figure 2c) can be fit to a biexponential decay function with $\tau_1 = 3.6$ ps and $\tau_2 = 225$ ps. The short-lived component is assigned to vibrational cooling. The long-lived component corresponds to the decay of the ^{3}MLCT state. This lifetime is shorter than those of most ^{3}MLCT states (which are typically in the ns to ms range) and can be explained by the

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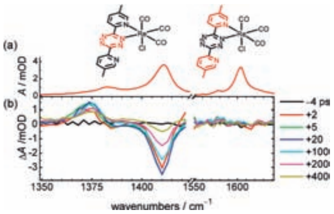

Figure 3. (a) FTIR and (b) TRIR (500 nm pump pulse) spectra of 5 mM $Re(CO)_3Cl(Me_2BPTZ)$ in $CHCl_3$.

energy-gap law.[15] Using the data from previous studies on a series of analogous Re−bipyridine complexes[16] and assuming an energy gap of 1.4 eV for $Re(CO)_3Cl(Me_2BPTZ)$, we estimate the nonradiative decay rate constant k_{nr} for the Re complex to be 3.58×10^9 s^{-1}. This value is in excellent agreement with the observed 225 ps lifetime.

Table 1. Experimental and Calculated Vibrational Frequencies (cm^{-1}) of $Re(CO)_3Cl(Me_2BPTZ)$ (the Experimental Data Were Obtained in $CHCl_3$, and the Calculations Were Performed in Vacuum)

	ground state		triplet excited state	
mode	exptl	calcd	exptl	calcd
CO symmetric	2034	2117	2071	2119
CO in-plane[a] antisymmetric	1953	2054	2002	2065
CO antisymmetric	1921	2027	1978	2059
pyridine ring vibrations	1603	1657, 1650, 1619, 1614	1603[b]	1662, 1652, 1612, 1611
tetrazine N−N[c]	1410	1487	1373	1343

[a] In the plane containing the Me_2BPTZ ligand. [b] The TRIR signal from this vibration was absent, so the frequency did not change upon excitation. [c] Consists of the entire py−TZ−py movement.

The effect of excitation on the Me_2BPTZ vibrational modes was investigated to confirm formal ligand reduction in the ^{3}MLCT state. Figure 3 presents the ground-state and transient absorption spectra of $Re(CO)_3Cl(Me_2BPTZ)$ in the 1350−1700 cm^{-1} range. The ground state absorption spectrum shows a band centered at 1603 cm^{-1} that originates from a set of vibrations localized on the two pyridine rings (Table 1). The absorption band centered at 1410 cm^{-1} is assigned to the vibrations of the central tetrazine ring. The TRIR spectrum of $Re(CO)_3Cl(Me_2BPTZ)$ shows the bleaching associated with the tetrazine vibrational mode and a corresponding excited-state absorption at 1373 cm^{-1}. The observed weakening of the tetrazine bonds is consistent with the presence of an additional electron in the antibonding orbital of the tetrazine ring in the ^{3}MLCT state.

Surprisingly, there was no transient absorption signal in the 1550−1700 cm^{-1} range, where the vibrations from the pyridine ring appear. The absence of a bleaching signal at 1603 cm^{-1} suggests that the two pyridine rings of Me_2BPTZ are not involved in the redistribution of charges associated with the ^{3}MLCT state (see the SI). Since the tetrazine ring and the two pyridine rings are coplanar in $Re(CO)_3Cl(Me_2BPTZ)$ (see the SI), one expects the electronic charge to fully delocalize over the Me_2BPTZ ligand, leading to the weakening of all the vibrational modes associated with this ligand.

In order to explain these TRIR results, TD-DFT calculations (see the SI) were performed on the ground and excited states of $Re(CO)_3Cl(BPTZ)$. Figure 1c and Figure S4 represent the difference density plot for the lowest ^{3}MLCT excited state and the ground state of $Re(CO)_3Cl(Me_2BPTZ)$. An interesting finding is that the electron density on the Me_2BPTZ moiety is restricted solely to the central tetrazine ring. Specifically, the LUMO orbital of Me_2BPTZ primarily involves the four nitrogen atoms on the tetrazine ring and does not leak into the pyridine rings. These results fully explain the absence of a TRIR signal arising from the pyridine vibrations. A similar finding was observed previously in EPR measurements and ab initio calculations of the 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (BPTZ) radical anion.[17] That study showed that BPTZ contains two close-lying LUMO orbitals: one localized on the tetrazine ring (a_u) and another delocalized over the entire molecule (b_{1u}). Which of these orbitals has the lower energy depends on the level of perturbation of the system.

In conclusion, we have verified the expected electronic charge distribution for a ^{3}MLCT excited state of $Re(CO)_3Cl(Me_2BPTZ)$ on the basis of vibrational signatures for *both* oxidation and reduction. Surprisingly, the excited electron is localized on the central tetrazine ring of Me_2BPTZ and does not involve the pyridine moieties. This finding will prove useful for further utilization of ^{3}MLCT states of complexes having Me_2BPTZ ligands.

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Supporting Information Available: Synthesis, sample preparation, TRIR laser setup, and computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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