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Direct Observation of a ^{1}MLCT State by Ultrafast Transient Absorption Spectroscopy in $Mo_2(O_2C\text{-}9\text{-anthracene})_4$

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The photophysical properties and photoinduced reactivity of $[Ru(bpy)_3]^{2+}$-type compounds have been investigated extensively, with these complexes being utilized as photosensitizers in the fields of solar energy conversion, photonic devices, molecular electronics, and photodynamic therapy.[1−4] In such systems, a key role is played by the long-lived ^{3}MLCT (metal-to-ligand charge transfer) excited state. Recent studies have been focused on very early times after photoexcitation.[5−7] Despite experimental efforts, direct detection of the absorption band corresponding to the precursor ^{1}MLCT has been unsuccessful, primarily due to a fast intersystem crossing process (e.g., ∼40 fs in $[Ru(bpy)_3]^{2+}$, obtained using ultrafast fluorescence upconversion experiments[8]), resulting in a very short ^{1}MLCT lifetime. Anderson et al. have inferred the presence of ^{1}MLCT state in a ruthenium derivative $[Ru(2,3\text{-dpp})_3]^{2+}$ from the complex kinetic trace at a single wavelength, with lifetime shorter than 100 fs.[9]

A recent paper by Chisholm, Turro, and co-workers reported on the photophysical properties of the metal−metal (MM) quadruply bonded complexes $Mo_2(O_2C\text{-}Ar)_4$ (Ar = phenyl, 1-naphthalene, 2-naphthalene, 9-anthracene, 1-pyrene, and 2-pyrene).[10] The emissive ^{1}MLCT state of these complexes has been proposed to be a good reducing agent, and the triplet lifetime is much longer (>40 μs) than that of $[Ru(bpy)_3]^{2+}$ (∼1 μs).

In this paper, we report on the early processes of the excited-state evolution of $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ using femtosecond transient absorption, to obtain spectral signatures of both the ^{3}MLCT and the precursor ^{1}MLCT. $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ was chosen for this study as it has been structurally well characterized and its bonding and electronic properties have been studied by DFT calculations.

In the femtosecond transient absorption experiments, a THF solution of $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ was excited at 514.5 and 347 nm (OD = 0.3) and monitored with a supercontinuum probe pulse in the spectral range of 395−655 nm. The solution was prepared in a nitrogen-filled glovebox using dry and deoxygenated THF solvent and kept under anaerobic conditions in a sealed flow cell during the measurement. The recorded spectra were time-corrected for the chirp of the supercontinuum.[11] All transient signals were linearly dependent on the excitation power. The time resolution of the system is 300 fs, as determined by the two-photon absorption of methanol in the sample cell. Laser excitation wavelengths were tuned to $(Mo_2\ \delta)^2(O_2C\text{-}Ar\ \pi^*)^0 \rightarrow (Mo_2\ \delta)^1(O_2C\text{-}Ar\ \pi^*)^1$, representing a spin-allowed MLCT transition from the bimetallic core to the aryl carboxylate ligands (514.5 nm) and the ligand-centered (LC) $^1\pi\pi^*$ transition associated with each aryl carboxylate ligand (347 nm).

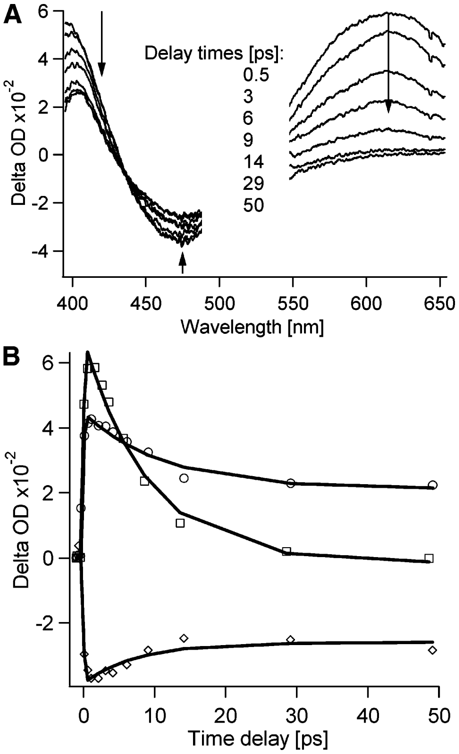

Figure 1. (A) Transient absorption spectra recorded in the 0.5−50 ps time window for $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ in THF with excitation set at 514.5 nm. A notch filter removing the excitation photons was used to record simultaneously spectra on both red and blue sides of the excitation wavelength. (B) Time dependence of the signal at selected wavelengths: 410 (○), 470 (◇), and 610 nm (□).

Photoexcitation of $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ at 514.5 nm at ambient temperature produces the transient absorption spectra shown in Figure 1A. In these spectra, transient absorption features at 410 and 610 nm are observed at early times, which we attribute to the ^{1}MLCT state. This is the first direct observation of a ^{1}MLCT spectrum obtained via transient absorption spectroscopy. The signal rise is instantaneous, as expected, since the ^{1}MLCT state is directly photoexcited (see Figure 1B). The positive band at 610 nm decays with a time constant of ∼10 ps, while decay of the band at 410 nm achieves an offset, corresponding to the population of the ^{3}MLCT state. Indeed, the final spectrum at the delay of 50 ps can be assigned to ^{3}MLCT on the basis of nanosecond time-resolved studies.[10] We conclude that the main deactivation path of the ^{1}MLCT state is an intersystem crossing process to the ^{3}MLCT manifold. In Figure 1A, the negative band at 470 nm is assigned to ground-state depletion and corresponds to the steady-state absorption band ($\epsilon \approx 10.9 \times 10^3$ M^{-1} cm^{-1}).[10] Triplet formation efficiency is high and was estimated by comparing the bleaching bands of $Ru(bpy)_3^{2+}$ at 480 nm, following excitation at 532 nm, with $Mo_2(O_2C\text{-}9\text{-anthracene})_4$. From the ground-state recovery kinetic trace at 470 nm, shown in Figure 1B, we estimate that the triplet formation

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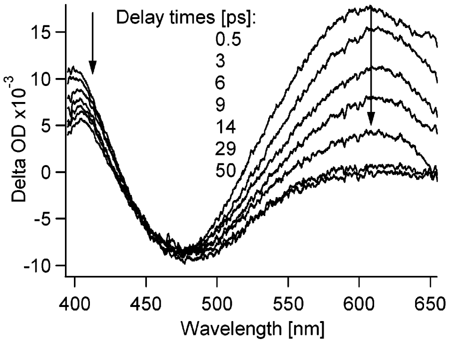

Figure 2. Transient absorption spectra recorded in the 0.5−50 ps time window for $Mo_2(O_2C\text{-}9\text{-anthracene})_4$ in THF with excitation set at 347 nm.

efficiency is ~80%. The presented transient absorption spectra (Figure 1A) are not affected by stimulated emission from ^{1}MLCT, as fluorescence occurs outside the recorded probe spectrum, at 743 nm. [10]

Excitation at 347 nm leads to a LC state of $Mo_2(O_2C\text{-}9\text{-anthracene})_4$. The transient absorption spectra and kinetic traces recorded with 347 nm excitation, shown in Figure 2, are very similar to those acquired at 514.5 nm. Since the rise of the ^{1}MLCT band at 610 nm is almost instantaneous, we can estimate that the lifetime of the precursor LC excited state is shorter than 1 ps. The time constant of singlet ^{1}MLCT decay is again ~10 ps, attributed to the intersystem crossing process leading to the triplet ^{3}MLCT.

Two small differences in the spectra acquired at 347 and 514.5 nm are observed: the ratios between the two bands at 410 nm ($^1\text{MLCT} \rightarrow S_m$) and 610 nm ($^1\text{MLCT} \rightarrow S_n$, $n < m$) are not the same, while no dynamics in the band at 470 nm is observed in the spectra excited at 347 nm. In the case of 347 nm excitation, the ^{1}MLCT state formed following excitation to the LC state can be assigned to a hot state, in which case the transient absorption band should be broader compared to those of the directly excited ^{1}MLCT (with 514.5 nm). Unfortunately, the region 395−490 nm is difficult to interpret, owing to the strong overlap of the ^{1}MLCT, ^{3}MLCT, and ground-state depletion bands.

The Jablonski diagram presented in Figure 3 summarizes our results obtained from the femtosecond transient absorption experiments on the MM quadruply bonded complex, $Mo_2(O_2C\text{-}9\text{-anthracene})_4$. The unique ability of these complexes to exhibit emission from the ^{1}MLCT state is consistent with the finite lifetime determined in this work. In contrast to $[Ru(bpy)_3]^{2+}$-type compounds, the MM quadruply bonded complexes exhibit longer-lived ^{1}MLCT and ^{3}MLCT states. The nature of the coupling between the metal and ligand electronic states in the MM quadruply bonded complexes is fundamentally different from those observed in $[Ru(bpy)_3]^{2+}$-type compounds. Our interpretation of the transient absorption spectra is supported by the observation of stimulated emission (negative absorption) in the region from 705 to 740 nm (data not shown). The stimulated emission band and the transient absorption band at 610 nm have an isosbestic point at ~705 nm. Both bands decay with a similar dynamics. We also note that, in complexes of the type $Mo_2(O_2CR)_4$, where R is an aliphatic group, we do not observe the transient absorption feature we assign to the ^{1}MLCT state. Our preliminary data on related MM quadruply bonded compounds with aromatic ligands indicate that longer excited-state lifetimes of these complexes, relative to mononuclear complexes, is a general phenomenon.

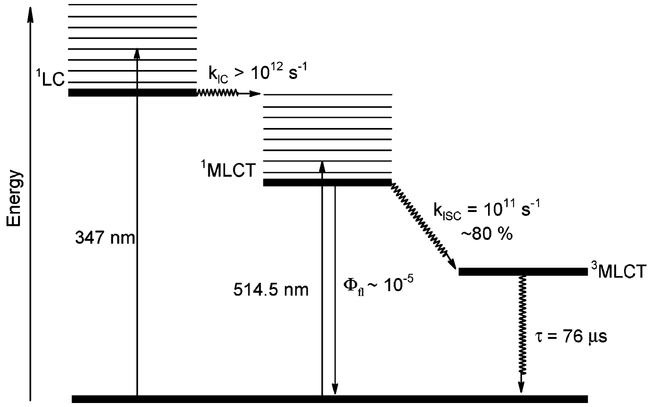

Figure 3. Jablonski diagram showing the photophysical processes in $Mo_2(O_2C\text{-}9\text{-anthracene})_4$.

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