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Direct Observation of the Luminescence from the $^3\delta\delta^*$ Excited State of Re_2Cl_2(*p*-OCH_3form)$_4$

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There are only a few reports on the measurement of the energy of the low-lying $^3\delta\delta^*$ state of quadruply bonded bimetallic complexes, and the direct observation of the $^1\delta^*\delta^*$ excited electronic state was only recently reported. In the quadruply bonded bimetallic complexes reported to date, luminescence arises from their $^1\delta\delta^*$ excited state, and the $^3\delta\delta^*$ state is nonemissive. Here we report the luminescence of Re_2Cl_2(*p*-OCH_3form)$_4$ [*p*-OCH_3form = (*p*-$CH_3OC_6H_4$)NCHN(*p*-$CH_3OC_6H_4$)$^-$] observed upon 400–460 nm excitation with maxima at 820 nm (CH_2Cl_2, $\tau = 1.4$ μs) and 825 nm (CH_3CN, $\tau = 1.3$ μs) at 298 K. From the large Stokes shift, the vibronic progression at 77 K, the quenching by O_2, the long lifetime, and the calculated energy of the $^3\delta\delta^*$ state, the luminescence of Re_2Cl_2(*p*-OCH_3form)$_4$ and the corresponding transient absorption signal are assigned as arising from the $^3\delta\delta^*$ ($^3A_{2u}$) excited state of the complex.

The discovery of the quadruple bond between two metal atoms revolutionized the contemporary paradigms of bonding,[1] resulting in vigorous theoretical and experimental work on metal-metal multiple bonds.[2−4] The luminescence and photochemistry of $[Re_2Cl_8]^{2-}$ and related complexes were later discovered.[5,6] Extensive investigation of the photophysical and photochemical properties of the emissive $^1\delta\delta^*$ ($^1A_{2u}$) excited states of various Mo_2(II,II), W_2(II,II), and Re_2(III,III) quadruply bonded bimetallic complexes was then undertaken.[7−12] More recently, quadruply bonded bimetallic cores have been linked together to form “dimers of dimers”,[13,14] utilized to build larger supramolecular structures,[15−17] and have been shown to organize into liquid crystalline phases.[18]

The energy of the $^3\delta\delta^*$ ($^3A_{2u}$) state of quadruply bonded complexes is predicted to be located ~10 000 cm^{-1} below

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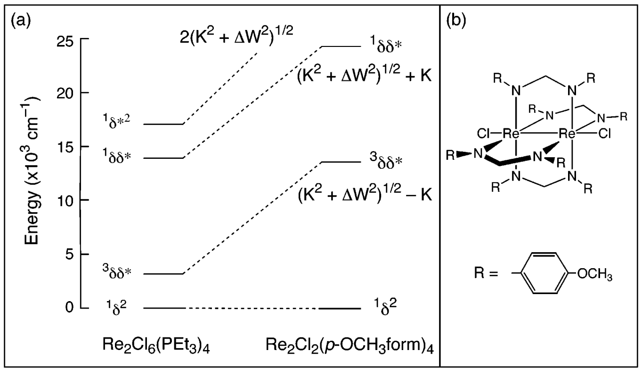

Figure 1. (a) Energies of the δ,δ^*-manifold for $Re_2Cl_6(PEt_3)_4$ (left) and Re_2Cl_2(*p*-OCH_3form)$_4$ (right) and (b) molecular structure of Re_2Cl_2(*p*-OCH_3-form)$_4$.

the corresponding $^1\delta\delta^*$ ($^1A_{2u}$) excited state, and in most cases only 1000−5000 cm^{-1} above the $^1\delta^2$ ($^1A_{1g}$) ground state.[19−21] A schematic representation showing the states that arise from the delta bonding manifold for a typical eclipsed complex, $Re_2Cl_6(PEt_3)_4$, is shown in Figure 1a. Although the energies of $^3\delta\delta^*$ and $^1\delta^*\delta^*$ excited electronic states were calculated for various quadruply bonded complexes,[19−22] only three examples of the experimental measurements of the energy of the $^3\delta\delta^*$ state using magnetic susceptibility and ^{31}P NMR spectroscopy appear in the literature,[23,24] and only recently has the $^1\delta^*\delta^*$ excited state been observed experimentally through its two-photon excitation.[25]

The luminescence reported to date for quadruply bonded Re_2(III,III), Mo_2(II,II), and W_2(II,II) complexes upon visible excitation has been assigned as arising from the $^1\delta\delta^*$ ($^1A_{2u}$) excited state.[3,4,7−9] Emission from the $^3\delta\delta^*$ ($^3A_{2u}$) state was not previously reported for quadruply bonded complexes. Since in the luminescent complexes reported to date the $^3\delta\delta^*$ state is typically close in energy to the $^1\delta^2$ ground state (Figure 1a, left), the energy gap law predicts that its nonradiative deactivation to the ground state would be efficient, likely making the triplet state weakly emissive or nonemissive.[26−28] In quadruply bonded complexes possessing formamidinate and carboxylate bridging ligands, both the $^1\delta\delta^*$ and $^3\delta\delta^*$ states are expected to lie at higher energies owing to additional mixing of the δ^* (b_{1u}) orbital with a low-lying linear combination of the ligand p-orbitals of the same symmetry (Figure 1a).[22,29,30] The greater energy difference expected between the $^3\delta\delta^*$ excited state and the $^1\delta^2$ ground state in these systems led us to explore the $^3\delta\delta^*$ luminescence from Re_2Cl_2(*p*-OCH_3form)$_4$ (*p*-OCH_3form = *p*-methoxy-formamidinate), whose structure is shown in Figure 1b.[31]

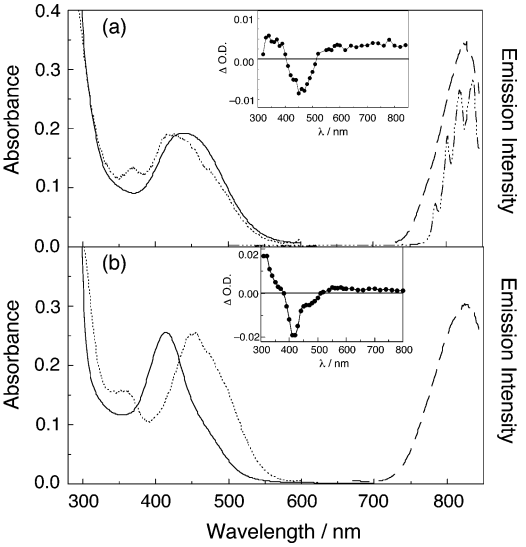

Figure 2. Room temperature absorption (—), excitation (λ_{em} = 800 nm, · - -), and emission (λ_{exc} = 420 nm, − − −) spectra of Re_2Cl_2(*p*-OCH_3-form)$_4$ in (a) CH_3CN and (b) CH_2Cl_2; emission of the solid at 77 K (λ_{exc} = 420 nm, − - - - −). Inset: transient absorption spectrum after 200 ns (298 K, CH_2Cl_2, λ_{ex} = 532 nm, fwhm ~ 8 ns, 5 mJ/pulse).

The room temperature electronic absorption, emission (λ_{ex} = 420 nm), and excitation (λ_{em} = 800 nm) spectra of Re_2Cl_2(*p*-OCH_3form)$_4$ in CH_3CN and CH_2Cl_2 are shown in Figure 2, along with the emission spectrum of the solid (λ_{ex} = 420 nm) collected at 77 K.[32] The absorption spectra are consistent with those previously reported for dirhenium(III,III) tetra-formamidinates,[29] possessing maxima at 414, 413, and 438 nm in CH_2Cl_2, THF, and CH_3CN, respectively, with $\epsilon \sim 12\,000$ M^{-1} cm^{-1}. This peak was previously assigned to the $^1\delta^2 \rightarrow {}^1\delta\delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) transition.[3,5a,29,33] The position of the shoulder at ~465 nm ($\epsilon \sim 4000$ M^{-1} cm^{-1}) remains constant in these solvents.

The luminescence from Re_2Cl_2(*p*-OCH_3form)$_4$ exhibits a large Stokes shift, with maxima at 820, 837, and 825 nm in CH_2Cl_2, THF, and CH_3CN, respectively. The excitation spectrum in CH_3CN shows good overlap with the absorption spectrum in the same solvent; however, in CH_2Cl_2 a greater emission intensity is observed from excitation of the low-energy shoulder than the peak maximum at 414 nm.

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The emission ($\lambda_{ex} = 532$ nm, fwhm ~8 ns, ~5 mJ/pulse) could be fit to a monoexponential decay with $\tau = 1.4$ μs in CH_2Cl_2 and $\tau = 1.3$ μs in CH_3CN at 298 K.[34] The transient absorption signal from CH_2Cl_2 and CH_3CN solutions of Re_2Cl_2(p-OCH_3form)$_4$ at 298 K (Figure 2) resulted in difference spectra with bleaching of the ground state absorption and a strong positive signal at $\lambda < 370$ nm, both of which decay with lifetimes of 1.4 and 1.3 μs in CH_2Cl_2 and CH_3CN, respectively.[34] These results show that the emission and transient absorption originate from the same excited state and are inconsistent with the luminescence arising from an impurity, since the observation of the transient absorption signal would require the impurity to make up a large portion of the sample. Such impurity is not observed in the ^{1}H NMR spectrum in CD_2Cl_2.

The emission spectrum of solid Re_2Cl_2(p-OCH_3form)$_4$ at 77 K exhibits a vibronic progression with $\Delta\nu = 259$ cm^{-1} (± 4 cm^{-1}), similar to the ground state ν(ReRe) of 275−295 cm^{-1} for $Re_2X_8^{4-}$ and $Re_2(O_2CR_4)_2X_2$ (X = Cl, Br; R = CH_3, C_2H_5, C_3H_7, C_6H_{11}, C_6H_5),[3,35] leading to an assignment of the luminescence as arising from the $\delta\delta^*$ manifold. The dynamic Stern−Volmer quenching of the emission lifetime by O_2 in CH_2Cl_2 results in $k_q = 1.0 \times 10^9$ M^{-1} s^{-1}. This value is consistent with an emissive triplet state, since O_2 quenching by singlet excited states typically proceeds with $k_q \geq 10^{10}$ M^{-1} s^{-1}.[36] The independence of the emission maximum on solvent, long lifetime, rate constant for O_2 quenching, large Stokes shift, and the 77 K vibronic progression leads to the assignment of the luminescence as arising from the $^3\delta\delta^*$ excited state.

An electronic structure calculation on Re_2Cl_2(p-OCH_3form)$_4$ results in similar orbital ordering as that previously reported for Re_2Cl_2(HNC(H)NH)$_4$.[29] However, the calculation with the additional p-methoxyphenyl groups for Re_2Cl_2(p-OCH_3form)$_4$ results in a low energy allowed LMCT ($^1A_{1g} \rightarrow {}^1E_u$) transition, π (p-OCH_3form, e_g) $\rightarrow$ δ^* (b_{1u}), at approximately the same energy as the $^1\delta\delta^*$ transition.[37] The solvent dependence and the molar absorptivity of the 414 nm peak (CH_2Cl_2) is consistent with a ^{1}LMCT transition. This assignment is also supported by the shift of this peak to higher for Re_2Cl_2(p-Cl-form)$_4$ ($\lambda_{max} = 400$ nm, CH_2Cl_2), for which the formamidinate ligand is harder to oxidize.[31] Similarly, a shift in the absorption maximum from 409 nm for Re_2Cl_2(m-OCH_3form)$_4$ to 392 nm for Re_2Cl_2(m-Cl-form)$_4$ is observed in CH_2Cl_2,[31] which also correlates with the ease of ligand oxidation. In all complexes, a shoulder is observed at ~465 nm (ϵ ~4000 M^{-1} cm^{-1}), whose position is invariant to solvent or the substituent on the formamidinate. This shoulder, which may arise from a peak which lies under the LMCT transition, can be assigned to possess significant $^1\delta^2 \rightarrow {}^1\delta\delta^*$ parentage. The excitation spectra with maximum at 452 nm in CH_2Cl_2 is indicative of the luminescence arising from the low-energy shoulder ($^1\delta\delta^*$ excitation), showing that there must be poor communication between the LMCT state and MC manifold.

Typically, a relatively small Stokes shift (2000−3000 cm^{-1}) of the luminescence from the $^1\delta\delta^*$ excited states of quadruply bonded complexes with lifetimes shorter than 200 ns in fluid solution at room temperature is observed.[3,6−12] In contrast, the luminescence of Re_2Cl_2(p-OCH_3form)$_4$ exhibits an energy difference between the absorption and emission maxima of ~13 000 cm^{-1} and a significantly longer lifetime than those previously reported. The energy of the $^3\delta\delta^*$ excited electronic state can be estimated from the measured energy of the $^1\delta\delta^*$ excited state, the one-electron energy difference between the δ and δ^* levels, ΔW, and the electron exchange, K (Figure 1a).[22] The $^1\delta\delta^*$ and $^3\delta\delta^*$ energies and the value of ΔW are sensitive to both the torsional angle (overlap of the d_{xy} orbitals), χ,[23,24] and the mixing of the δ and δ^* orbitals with linear combinations of ligand orbitals.[22]

Since the value of K is rather invariant to the ligand system, an average of the values reported or calculated by us for nine different Re_2(III,III) complexes, 5080 cm^{-1}, was used here for Re_2Cl_2(p-OCH_3form)$_4$.[22,38−40] Using the experimentally determined energy of the $^1\delta\delta^*$ state, $E(^1\delta\delta^*)$, of 22 124 cm^{-1} in CH_2Cl_2 (excitation maximum), ΔW was calculated to be 16 269 cm^{-1}.[22] Using these values and $E(^3\delta\delta^*) = [(K^2 + \Delta W^2)^{1/2} - K]$, the energy of the $^3\delta\delta^*$ excited state of Re_2Cl_2(p-OCH_3form)$_4$ was calculated to be 1.20×10^4 cm^{-1} (846 nm).[22] This energy is consistent with the observed emission of the complex shown in Figure 2 ($\lambda_{em} = 820$ nm, CH_2Cl_2), and comparable to those calculated for $Re_2Cl_2(O_2CR_3)_4$ (R = alkyl) complexes.[22,38,39]

From the large energy difference between the absorption and emission maxima, its insensitivity to the solvent, the vibronic progression at 77 K, the quenching by O_2, the long lifetime of the emission, and the calculated energy of the $^3\delta\delta^*$ state, the luminescence of Re_2Cl_2(p-OCH_3form)$_4$ in the 700−850 nm range is assigned as arising from the $^3\delta\delta^*$ ($^3A_{2u}$) excited state of the complex. To our knowledge, this report represents the first example of luminescence from the $^3\delta\delta^*$ excited state of a quadruply bonded complex.

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Note Added after ASAP: The version of this paper posted ASAP on October 16, 2003, contained an incorrect footnote 31. The version posted on October 29, 2003, contains the correct footnote 31.

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