Electronic Supporting Information for

First Emission Studies of $Tc_2X_8^{2-}$ and $Re_2X_8^{2-}$ Systems (X = Cl, Br)

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EXPERIMENTAL

Materials. The commercial sources for ammonium pertechnetate and $[n\text{-}Bu_4N]Re_2Cl_8$ were Oak Ridge National Laboratory and Sigma-Aldrich, respectively. Rhodamine chloride 610 nm dye was a product of Exciton Dyes. The EPR sample tubes were products of Wilmad Glass Company.

Methods. The methods used for preparing $[n\text{-}Bu_4N]_2Tc_2X_8$ (X = Cl, Br) and $[n\text{-}Bu_4N]Re_2Br_8$ came from the literature.[1,2] After two re-crystallizations from acetone/ether, UV-visible spectroscopy confirmed the purity.

For emission-related measurements the sample container was a 3 mm quartz tube inserted into a commercial immersion dewar that fit into a normal 1 cm^2 cuvette holder. Each capped tube contained about 75 mg of powder, or a column of material about 1 cm in height. For emission measurements of the technetium compounds the excitation wavelength was 645 nm. The excitation and emission filters were a 650 nm short wave pass and a 700 nm long wave pass, respectively, and both slit settings were 20 nm because of the weak intensities. For the measurement of excitation spectra, the monitoring wavelength was 820 nm. A 750 nm short wave pass was in place on the excitation side, and an 830 nm long wave pass filter was in place between the sample and the detector.

For the emission measurements of the $[n\text{-}Bu_4N]_2Re_2Cl_8$ control, the excitation wavelength was 620 nm. To block stray light, the excitation beam passed through a 650 nm short pass filter and the emission passed through a 645 long pass filter. The slit settings were 5 nm. For the $[n\text{-}Bu_4N]_2Re_2Br_8$ control, the changes were that the excitation wavelength was 420 nm, the excitation passed through a 550 nm short wave pass filter, and the slit settings were 10 nm. For measurements of the excitation spectra, there was a 750 nm short wave pass filter between the sample and the source and an 830 nm long wave pass filter between the sample and the detector; slit widths were the same as in the corresponding emission spectra. The monitoring wavelengths were 775 nm for $[n\text{-}Bu_4N]_2Re_2Cl_8$ and 800 nm for $[n\text{-}Bu_4N]_2Re_2Br_8$.

Instrumentation. A Varian Cary Eclipse fluorimeter with a R3896 detector yielded all emission and excitation spectra. The source for the lifetime measurements was a VSL-337-NDS

nitrogen laser with a DLM-220 dye laser attachment. The equipment used to monitor the emission decay included a Hamamatsu R928 phototube connected to a Pacific Instruments Model 277 power supply, and a Tectronix TDS 520 oscilloscope.

Computational Details.

Quantum chemical calculations were performed using the multi-configurational Complete Active Space SCF (CASSCF) methods,[3] followed by second-order perturbation theory (CASPT2).[4] Relativistic all electron ANO-RCC basis sets of triple-zeta quality (VTZP) were employed on all atoms with the following contractions: 7s6p4d2f1g for Tc, 8s7p5d3f2g1h for Re, 5s4p2d1f for Cl, and 6s5p3d1f for Br.[5] Scalar relativistic effects were included using the Douglas-Kroll-Hess Hamiltonian.[6] In the CASSCF treatment, the complete active space contains twelve electrons in twelve active orbitals (12/12). This space comprises one $nd\sigma$, two $nd\pi$ and one $nd\delta$ metal-metal (M–M) bonding orbitals and the corresponding antibonding orbitals, two metal-halide (M–X) σ bonding and the corresponding antibonding orbitals. In the subsequent CASPT2 calculations, orbitals up to and including the 3d for Tc, 4d for Re, 2p for Cl, and 3p for Br were kept frozen. This approach has proven to be very successful in the studies of metal-metal bonded compounds.[7-10] A numerical CASPT2 optimization of the metal–metal (M–M) and metal–halide (M–X) bond distances was performed for both the $^1A_{1g}$ ground state and the $^3A_{2u}$ excited state of the $M_2X_8^{2-}$ species imposing D_{2h} symmetry. All calculations were performed with the MOLCAS 7.4 package.[11]

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