TRANSIENT ABSORPTION AND TIME-RESOLVED FLUORESCENCE STUDIES OF SOLVATED RUTHENIUM DI-BIPYRIDINE PSEUDO-HALIDE COMPLEXES

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Time-resolved IR and fluorescence measurements were performed to probe the vibrational and electronic properties, respectively, of ruthenium di-bipyridine pseudo-halide ($Ru(Bpy)_2(X)_2$ (where X = CN, N_3 or NCS)) complexes. Vibrational energy relaxation (VER) times were determined for the complexes dissolved in dimethyl sulfoxide (DMSO) with a trend in VER time of NCS $>$ CN $>$ N_3. A similar trend and comparable absolute rates for NCS^- and $N3^-$ were previously observed by our group and others for simple inorganic anions in solution, suggesting a minimal contribution due to complexation. Measurements of the VER time of the CN complex in various solvents provide VER times in ethanol (42.3 ps) and DMSO (53.3 ps), which shows that protic solvents promote the relaxation. Time-resolved fluorescence measurements indicate a strong ligand dependence, with a factor of five decrease in the excited electronic state decay time from the CN (215 ns) to the NCS (39 ns) complex. A solvent dependence of the CN complex reveals a nearly 3-fold increase in the fluorescence decay time from acetonitrile (70 ns) to DMSO (215 ns).