

Supporting Information

Interligand Electron Transfer in Heteroleptic Ruthenium(II) Complexes Occurs on Multiple Time Scales

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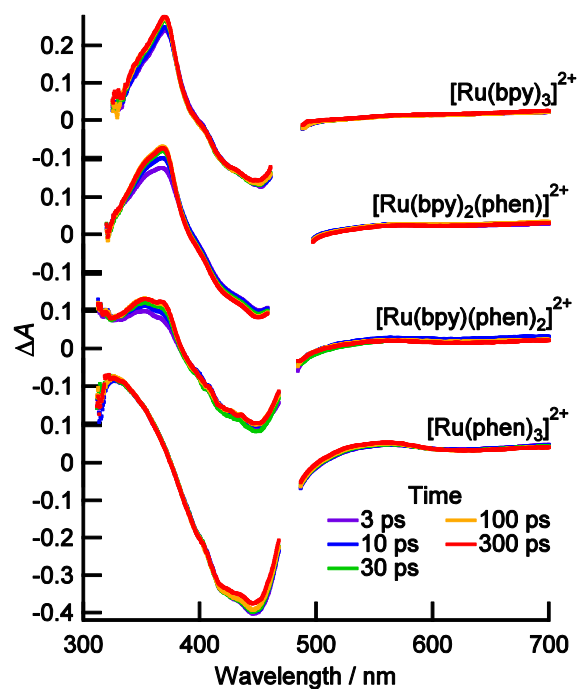


Figure S1. Transient Absorption difference spectra of each metal complex after excitation with a 480 nm pump pulse. Nearly identical kinetics are seen with excitation at 400 nm.

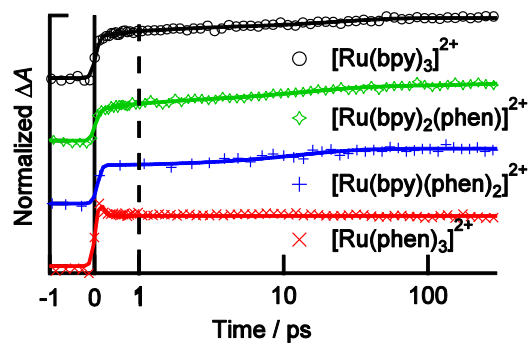


Figure S2. Normalized transient absorption signals after excitation at 480 nm. Data is collected at 370 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ (black) and $[\text{Ru}(\text{bpy})_2(\text{phen})]^{2+}$ (blue), and 350 nm for $[\text{Ru}(\text{bpy})(\text{phen})_2]^{2+}$ (green) and $[\text{Ru}(\text{phen})_3]^{2+}$ (red). Each complex is dissolved in acetonitrile solution. The vertical dashed line indicates the change from a linear to a logarithmic time axis.

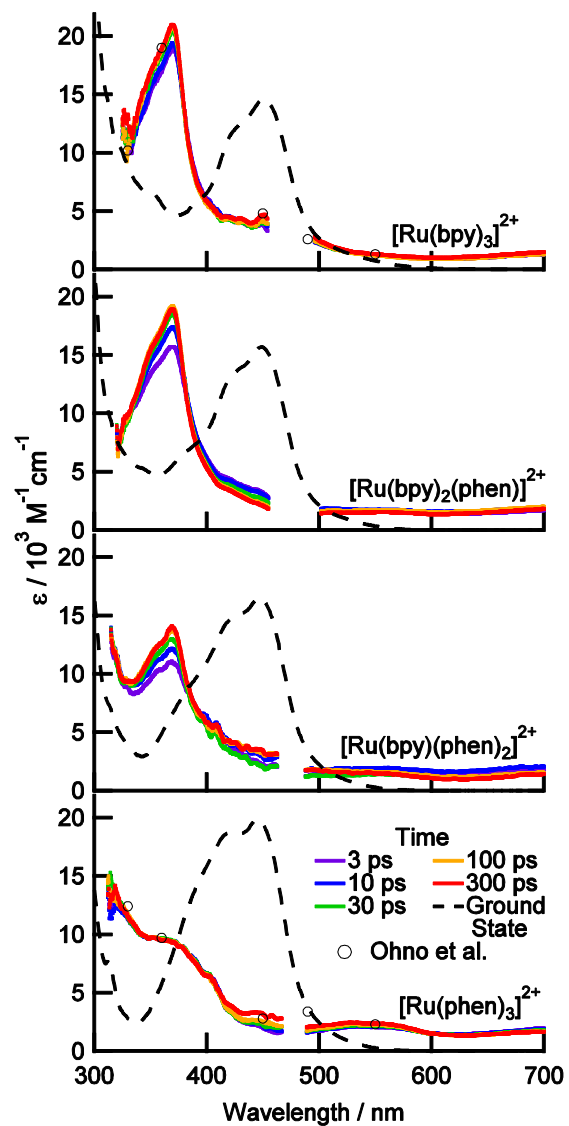


Figure S3. Excited State Absorption Spectra of each metal complex after excitation with 480 nm pump pulses. The ground-state absorption spectra are shown for comparison (black dashed curves).

Kinetic Model for Emission Lifetimes

States A, B, and C in Figure S4 represent the ³MLCT excited states of a ruthenium(II) diimine complex like the ones in this study. The blue arrows and first-order rate constants k_1 through k_6 describe hopping of a given ³MLCT excited state to either of the two other ligands, while k_A , k_B , and k_C represent the total rate of radiative and nonradiative decay to the ground state.

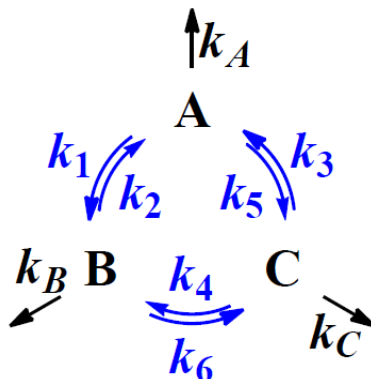


Figure S4. The kinetic model used to describe the hopping of ³MLCT states among three ligands.

The differential equations describing the kinetics of this system are,

$$\begin{aligned} \frac{dA}{dt} &= k_2B + k_3C - (k_1 + k_5 + k_A)A \\ \frac{dB}{dt} &= k_1A + k_4C - (k_2 + k_6 + k_B)B \\ \frac{dC}{dt} &= k_5A + k_6B - (k_3 + k_4 + k_C)C \end{aligned} \quad (1)$$

The rate of change of the total excited state population is obtained by summing all three of the above differential equations,

$$\frac{d(A+B+C)}{dt} = -(k_A A + k_B B + k_C C) \quad (2)$$

When $k_A, k_B, k_C \ll k_i$, $i = 1 \dots 6$ equilibrium will be maintained among the excited state populations, and all excited states will decay at the same rate at long times after initial transients have died out. This follows because the ratio of any two of the three excited state populations is constant at all times so the populations must have identical first-order decay constants. Each

excited state population thus decays according to,

$$\frac{dA}{dt} = -\lambda A, \quad \frac{dB}{dt} = -\lambda B, \quad \frac{dC}{dt} = -\lambda C \quad (3)$$

where λ is the common decay rate constant. Substituting eq. 3 into eq. 2 yields,

$$\lambda = \frac{k_A A + k_B B + k_C C}{A + B + C} \quad (4)$$

Because populations in states A, B, and C are in equilibrium, eq. 4 can be written as,

$$\lambda = \frac{k_A + k_B K_{BA} + k_C K_{CA}}{1 + K_{BA} + K_{CA}} \quad (5)$$

where the following equilibrium constants have been used,

$$K_{BA} = \frac{B}{A} = \frac{k_1}{k_2}, \quad K_{CA} = \frac{C}{A} = \frac{k_5}{k_3} \quad (6)$$

These equilibrium constants are related to the energy differences between pairs of ligands,

$$K_{ij} = e^{-\Delta E_{ij}/k_B T} \quad (7)$$

where $\Delta E_{ij} = E_i - E_j$. Assuming that the $k_{A/B/C}$ rate constants are unaffected by the nature of the other ligands, then each is given by the decay rate of the corresponding homoleptic complex. When only two types of ligands are present (bpy and phen), eq. 5 can be used to express the emission decay rate, k_n , of the complex having n phen ligands as,

$$k_n = \frac{(3-n)k_0 + nk_3 \exp(-\Delta E / k_B T)}{3-n + n \exp(-\Delta E / k_B T)} \quad (8)$$

where ΔE is the energy splitting between the phen- and bpy-localized ³MLCT states. Eq. 8 shows that the excited-state decay rates of the mixed-ligand complexes, k_1 and k_2 , are weighted averages of the rates of the tris complexes, k_0 and k_3 .