

Temperature and Solvent-Dependent Photoluminescence Quenching in [Ru(bpy)₂(bpy-cc-AQ)]²⁺ Supporting Information

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Variable Temperature Photoluminescence Lifetime Fitting

Fitting of the variable temperature photoluminescence lifetimes to Equation 4 in the main paper using a least squares algorithm without constraints yields the parameters presented in Table S1, with:

$$\chi^2 = \sum_i \frac{(x_i - m_i)^2}{m_i} \quad (\text{S1})$$

Where x_i is the observed value, and m_i the predicted value. It is immediately clear that the values of τ_{MLCT} for the high polarity solvents derived using this approach are not physically meaningful, despite qualitatively good fits to the data. τ_{MLCT} was therefore constrained to the value obtained for 1,2-dichloroethane (4.27 μs), which yielded the parameters reported in Table S2. Although τ_{MLCT} would be expected to exhibit some solvent dependence, the difference in magnitude between solvents should be relatively small, validating the constraint. For example, [Ru(bpy)₃]²⁺ has τ_{MLCT} range from 2.4-1.8 μs between dichloromethane and acetonitrile (ref. 47).

By comparing Tables S1-2, it can be observed that constraining τ_{MLCT} has only little effect on the other fit parameters, with butyronitrile exhibiting the greatest deviation. For acetonitrile, the deviation is almost negligible. It can therefore be surmised that the inability of the fit to accurately model τ_{MLCT} arises from the difference in magnitude between τ_{MLCT} and τ_{obs} . This limitation of the model is exemplified in Figure S1, in which it can be observed that the experimental values of τ_{obs} only represent a small fraction of the modelled τ range, and furthermore are restricted to areas close to the upper limit in 1,2-dichloroethane and the lower limit in the high polarity solvents. To accurately derive all parameters, a greater fraction of the modelled τ_{obs} range would need to be sampled. However, from the extrapolated fits in Figure S1, it is evident that the ability to sample a wide-enough temperature range to satisfactorily derive all parameters is severely restricted by solvent boiling points.

Table S1. Parameters derived from unconstrained least squares fitting of variable-temperature lifetimes of [Ru(bpy)₂(bpy-cc-AQ)]²⁺ to Equation 4 in the main paper.

Solvent	$\tau_{\text{MLCT}} / \mu\text{s}$	$\tau_{\text{CR}} / \text{ns}$	$\Delta H_{\text{ET}} / \text{eV}$	$\Delta S_{\text{ET}} / \text{meV K}^{-1}$	χ^2
Butyronitrile	1.53	135	-0.44	-1.55	0.20
Acetonitrile	5.1×10^4	1.29	-0.33	-1.24	4.7×10^{-4}
Ethanol	0.050	7.35	-0.56	-1.77	2.6×10^{-4}

Table S2. Parameters derived from least squares fitting of variable-temperature lifetimes of [Ru(bpy)₂(bpy-cc-AQ)]²⁺ to Equation 4 in the main paper, with τ_{MLCT} constrained to 4.27 μs .

Solvent	$\tau_{\text{MLCT}} / \mu\text{s}$	$\tau_{\text{CR}} / \text{ns}$	$\Delta H_{\text{ET}} / \text{eV}$	$\Delta S_{\text{ET}} / \text{meV K}^{-1}$	χ^2
Butyronitrile	4.27 ^a	89.2	-0.31	-1.15	0.42
Acetonitrile	4.27 ^a	1.31	-0.33	-1.24	4.8×10^{-4}
Ethanol	4.27 ^a	7.16	-0.48	-1.49	5.4×10^{-4}

^a Value constrained

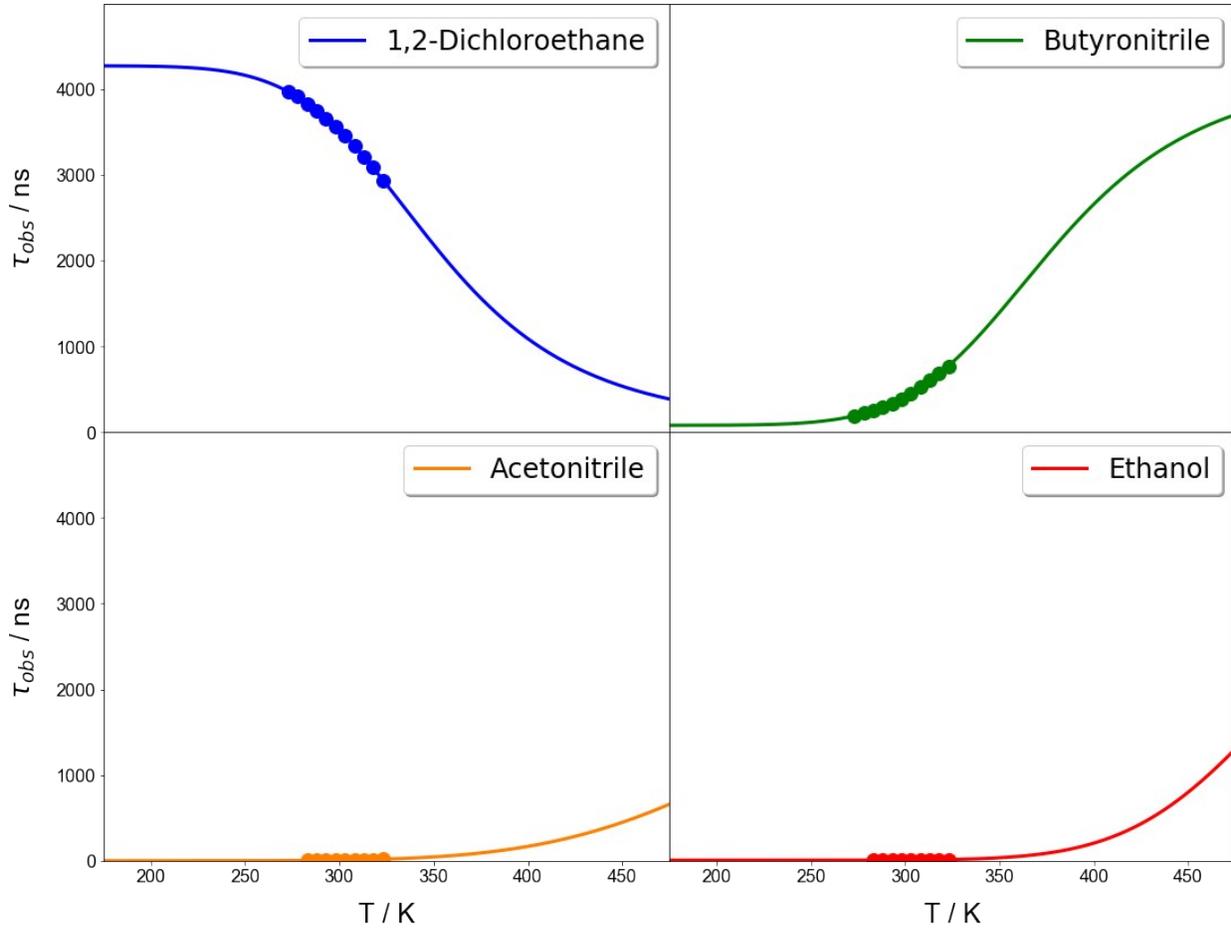


Figure S1. Extrapolated fits of the variable temperature photoluminescence lifetimes in 1,2-dichloroethane, butyronitrile, acetonitrile and ethanol to Equation 4 in the main paper, with τ_{MLCT} constrained to 4.27 μ s (corresponding to the parameters derived in Table S2).

Marcus Theory Considerations

Merging Equations 3 and 6 from the main paper yields Equation S2a.

$$k_{obs} = \frac{k_{MLCT} + \sqrt{\frac{\pi}{\hbar^2 \lambda k_B T}} \cdot H_{DA}^2 \cdot e^{-\left(\frac{\Delta G_{CR}^\ddagger}{k_B T}\right)} \cdot e^{-\left(\frac{\Delta G_{ET}}{k_B T}\right)}}{1 + e^{-\left(\frac{\Delta G_{ET}}{k_B T}\right)}} \quad (S2a)$$

Where the activation energy for charge recombination is defined by Equation S2b.

$$\Delta G_{CR}^\ddagger = \frac{(\lambda + \Delta G_{CR})^2}{4\lambda k_B T} \quad (S2b)$$

Treating the pre-exponential terms as a constant, Equation S2a can be rearranged to Equation S3.

$$k_{obs} = \frac{k_{MLCT} + \frac{A}{\sqrt{T}} \cdot e^{-\left(\frac{\Delta G_{ET} + \Delta G_{CR}^\ddagger}{k_B T}\right)}}{1 + e^{-\left(\frac{\Delta G_{ET}}{k_B T}\right)}} \quad (S3)$$

Assuming no temperature-dependence of ΔG_{ET} , Equation S3 is unable to even qualitatively reproduce the variable temperature behaviour of the photoluminescence lifetimes in the higher polarity solvents. It is therefore evident that any temperature-dependence of k_{CR} alone cannot account for the observed variable temperature photoluminescence lifetime behaviour.

From Figure 3 in the main paper, it can be observed that:

$$\Delta G_{CR} = - (G_{MLCT} + \Delta G_{ET}) \quad (S4)$$

Where G_{MLCT} is the energy of the MLCT excited state, previously determined as 1.97 eV (ref. 43). Using the parameters derived for butyronitrile from Table 1 in the main paper, and a hypothetical λ of 1.5 eV, the values reported in Table S3 are obtained. Of particular note is the difference in thermal sensitivity between ΔG_{ET} and ΔG_{CR}^\ddagger , which elicit a 670% and 20% increase in K_{eq} and k_{CR} (defined by the exponential term in Equations S2a and S3 – as the pre-exponential term is treated as a constant), respectively, across the investigated temperature range. It is therefore evident, based on Equations 4, S2a and S3, that the observed rate constant for photoluminescence (τ_{obs}) is dominated by the thermal sensitivity of K_{eq} as opposed to that of k_{CR} .

Table S3. Temperature-dependent parameters obtained from Equations 4 and 5 (from the main paper), S2, S3 and S4 for butyronitrile, with $\Delta H_{ET} = -0.31$ eV, $\Delta S_{ET} = -1.15$ meV K⁻¹, $G_{MLCT} = 1.97$ eV, and $\lambda = 1.5$ eV.

T / K	ΔG_{ET} / meV	ΔG_{CR} / eV	ΔG_{CR}^\ddagger / meV	K_{eq}	$\frac{e^{-\left(\frac{\Delta G_{CR}^\ddagger}{k_B T}\right)}}{\sqrt{T}} (\times 10^{-3})$
273	3.95	-1.97	37.4	0.85	12.3
278	9.70	-1.98	38.4	0.67	12.1
283	15.5	-1.99	39.3	0.53	11.9
288	21.2	-1.99	40.2	0.43	11.7
293	27.0	-2.00	41.2	0.34	11.4
298	32.7	-2.00	42.1	0.28	11.2
303	38.5	-2.01	43.1	0.23	11.0
308	44.2	-2.01	44.1	0.19	10.8
313	50.0	-2.02	45.1	0.16	10.6
318	55.7	-2.03	46.1	0.13	10.4
323	61.5	-2.03	47.1	0.11	10.3

Dielectric Continuum Model Solvent Effects

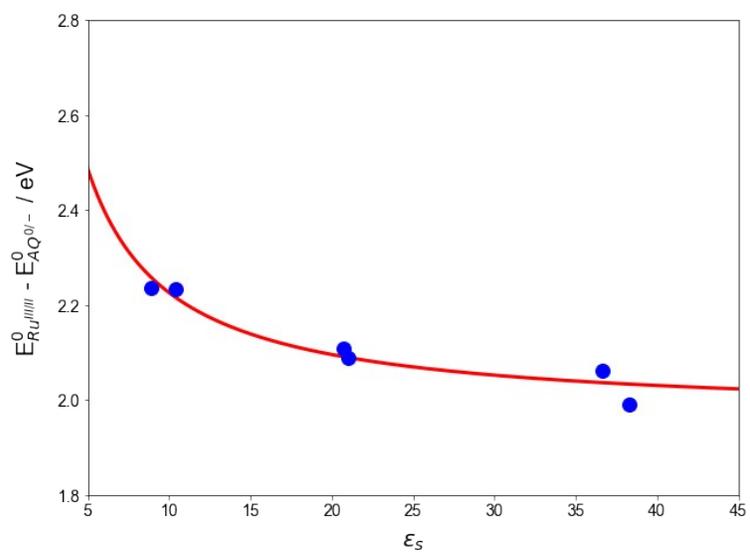


Figure S2. Fit of electrochemical data of $[Ru(bpy)_2(bpy-cc-AQ)]^{2+}$ from ref. 43 to Equation 7 in the main paper, with $a_1 = a_2 = 4 \text{ \AA}$, and $r_{DA} = 12.8 \text{ \AA}$, yielding ΔG_{vac} of 4.57 eV.