Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for:

Temperature Dependent Iodide Oxidation by MLCT Excited States

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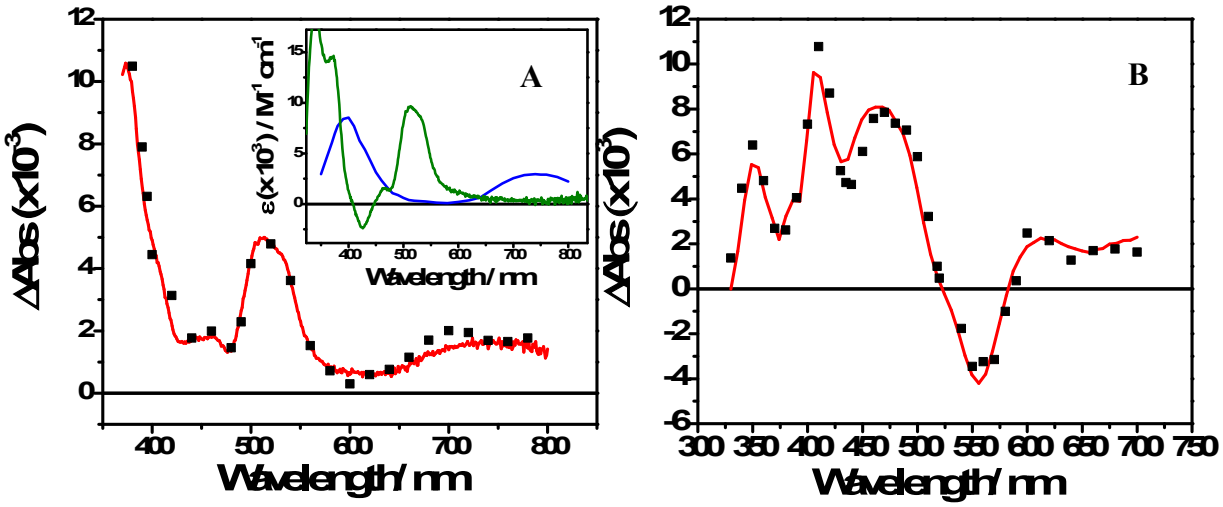

Figure S.1. A) Transient absorption spectrum (black points) observed 1 μs after pulsed 532 nm laser excitation of $[Ru(bpy)_2(deeb)]^{2+}$ in 75 mM iodide/CH_3CN solutions. The red line is a simulation based on a 1:1 mixture of $[Ru(bpy)_2(deeb)]^{+}$and $I_2^{\bullet-}$. (Inset) Extinction coefficient spectra for ($[Ru(bpy)_2(deeb)]^{+}$ - $[Ru(bpy)_2(deeb)]^{2+}$) (green) and $I_2^{\bullet-}$(blue). B) Transient absorption spectrum (black points) observed 0.5 μs after pulsed 532 nm laser excitation of $[Ru(bpy)_2(deebq)]^{2+}$ in 100 mM iodide/CH_3CN solutions. The red line is a simulation based on a 1:1 mixture of $[Ru(bpy)_2(deebq)]^{+}$and $I_2^{\bullet-}$.

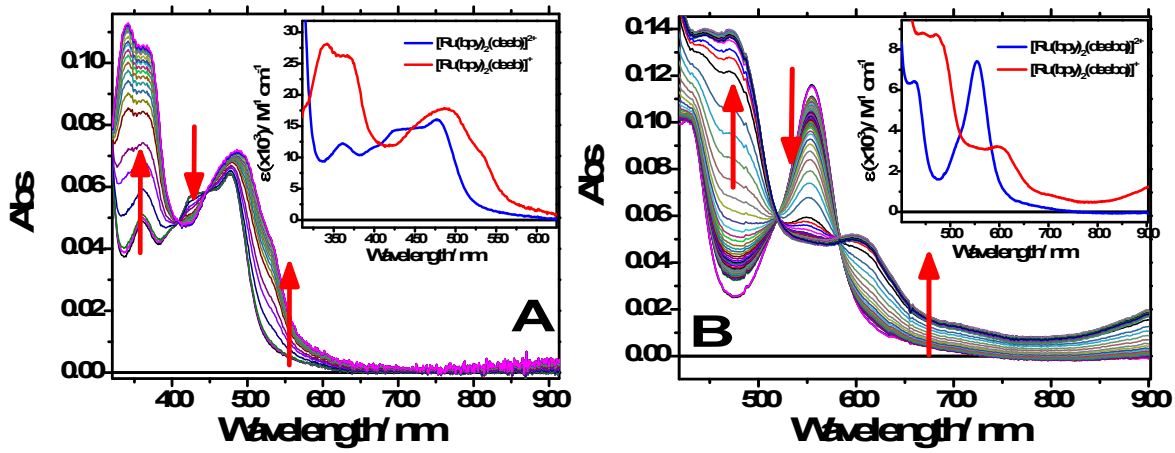

Figure S.2 Absorption spectra of A) $[Ru(bpy)_2(deeb)]^{2+}$ and B) $[Ru(bpy)_2(deebq)]^{2+}$ under steady state visible light irritation in presence of triethylamine in acetonitrile. The arrows indicate the direction of increased photolysis time. Insets) Extinction coefficient spectra of the indicated compounds in acetonitrile.

Photoluminescence Quenching at Different Temperatures (25-50°C)

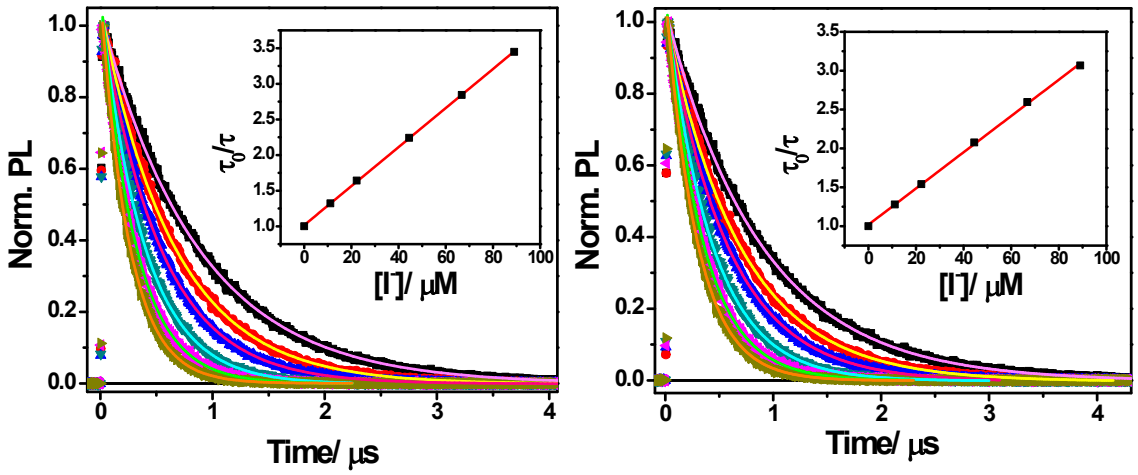

Figure S.3. Time resolved photoluminescence decays monitored at 620 nm for $[Ru(deeb)(bpy)_2]^{2+*}$ in acetonitrile at 50°C (left) and 45°C (right) as a function of increased [TBAI]. Insets show Stern–Volmer plot for lifetime quenching from which $K_{SV} = 27.4 \pm 0.2 \times 10^3$ and $23.3 \pm 0.3 \times 10^3$ M^{-1} for the mentioned temperatures respectively were abstracted.

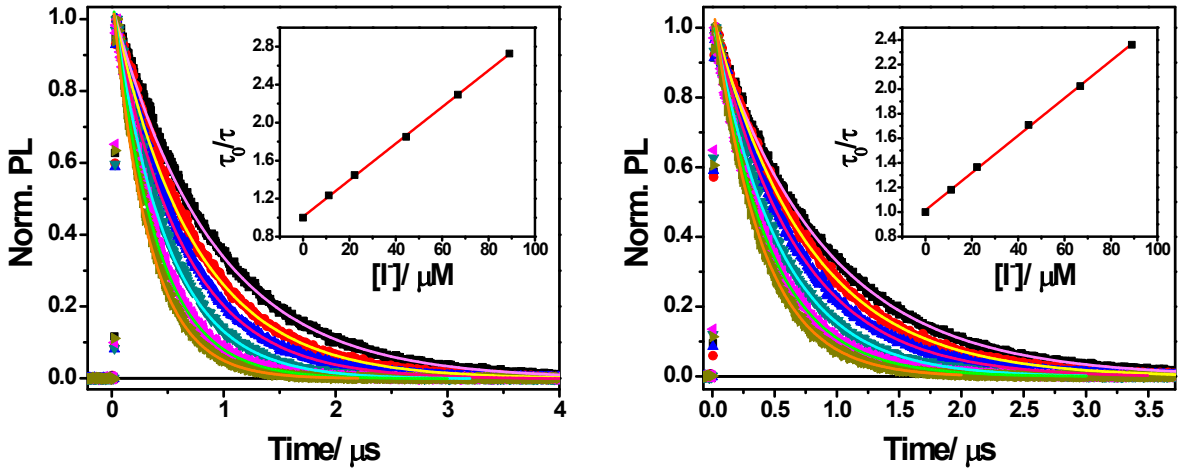

Figure S.4. Time resolved photoluminescence decays monitored at 620 nm for $[Ru(deeb)(bpy)_2]^{2+*}$ in acetonitrile at 40°C (left) and 35°C (right) as a function of increased [TBAI]. Insets show Stern–Volmer plot for lifetime quenching from which $K_{SV} = 19.2 \pm 0.2 \times 10^3$ and $15.3 \pm 0.2 \times 10^3$ M^{-1} for the mentioned temperatures respectively were abstracted.

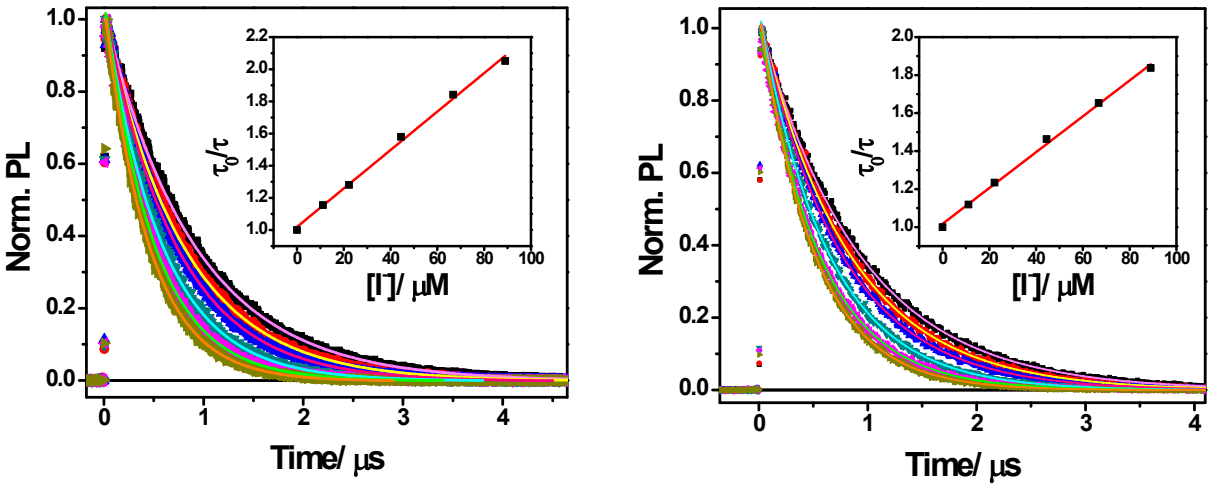

Figure S.5. Time resolved photoluminescence decays monitored at 620 nm for $[Ru(deeb)(bpy)_2]^{2+*}$ in acetonitrile at 30°C (left) and 25°C (right) as a function of increased [TBAI]. Insets show Stern–Volmer plot for lifetime quenching from which $K_{SV} = 12.0 \pm 0.3 \times 10^3$ and $9.4 \pm 0.2 \times 10^3$ M^{-1} for the mentioned temperatures respectively were abstracted.

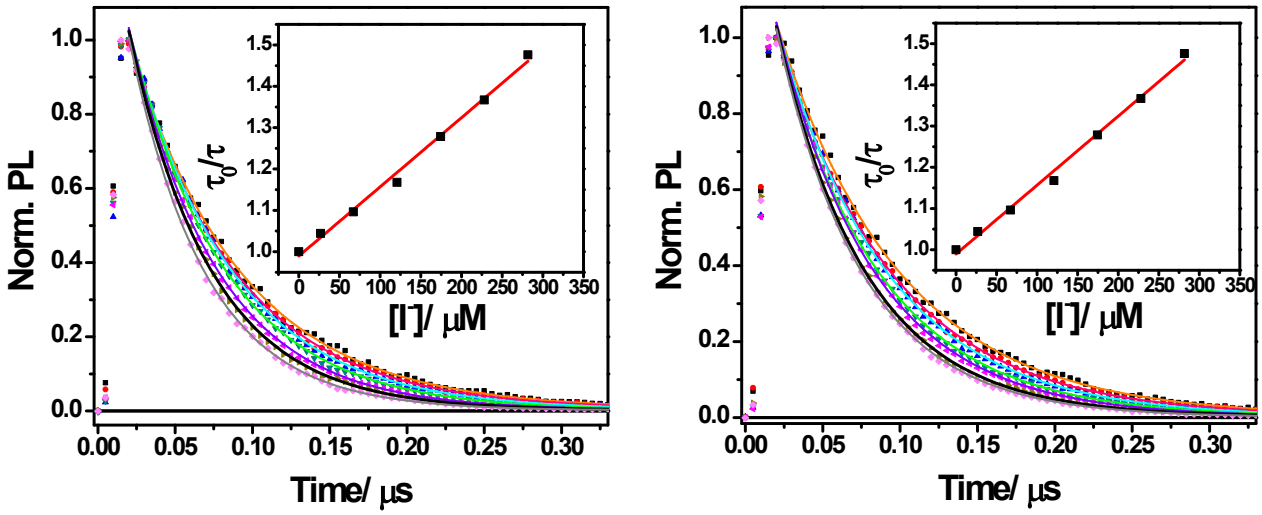

Figure S.6. Time resolved photoluminescence decays monitored at 700 nm for $[Ru(deebq)(bpy)_2]^{2+*}$ in acetonitrile at 40°C (left) and 35°C (right) as a function of increased [TBAI]. Insets show Stern–Volmer plot for lifetime quenching from which $K_{SV} = 27.4 \pm 0.2 \times 10^3$ and $23.3 \pm 0.3 \times 10^3$ M^{-1} for the mentioned temperatures respectively were abstracted.

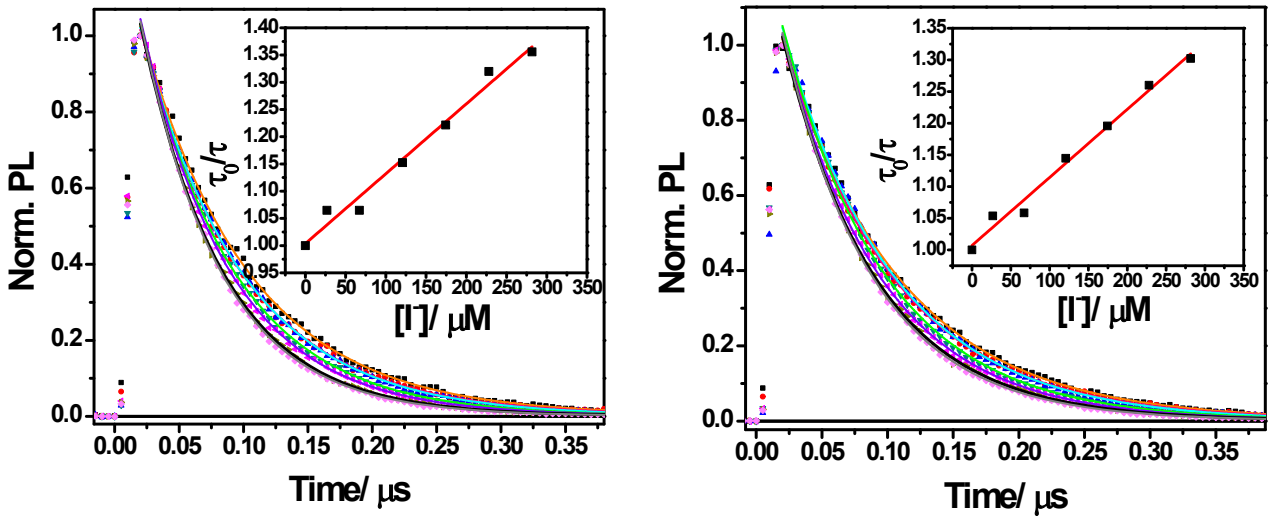

Figure S.7. Time resolved photoluminescence decays monitored at 700 nm for $[Ru(deebq)(bpy)_2]^{2+*}$ in acetonitrile at 30°C (left) and 25°C (right) as a function of increased [TBAI]. Insets show Stern–Volmer plot for lifetime quenching from which $K_{SV} = 27.4 \pm 0.2 \times 10^3$ and $23.3 \pm 0.3 \times 10^3$ M^{-1} for the mentioned temperatures respectively