Supporting Information

Molecular Mechanism of dual emission in terpyridine transition metal complexes - ultrafast investigations of photoinduced excited-state dynamics

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Detailed knowledge about the ultrafast light induced dynamics in terpyridine-based homoleptic complexes of iron(II), ruthenium(II) and osmium(II) seems to be a prerequisite to understand light conversion and energy migration in metallopolymers based on these systems. Therefore, numerous time and temperature dependent measurements were carried out to decipher the excited state relaxation pathway in such transition metal complexes.

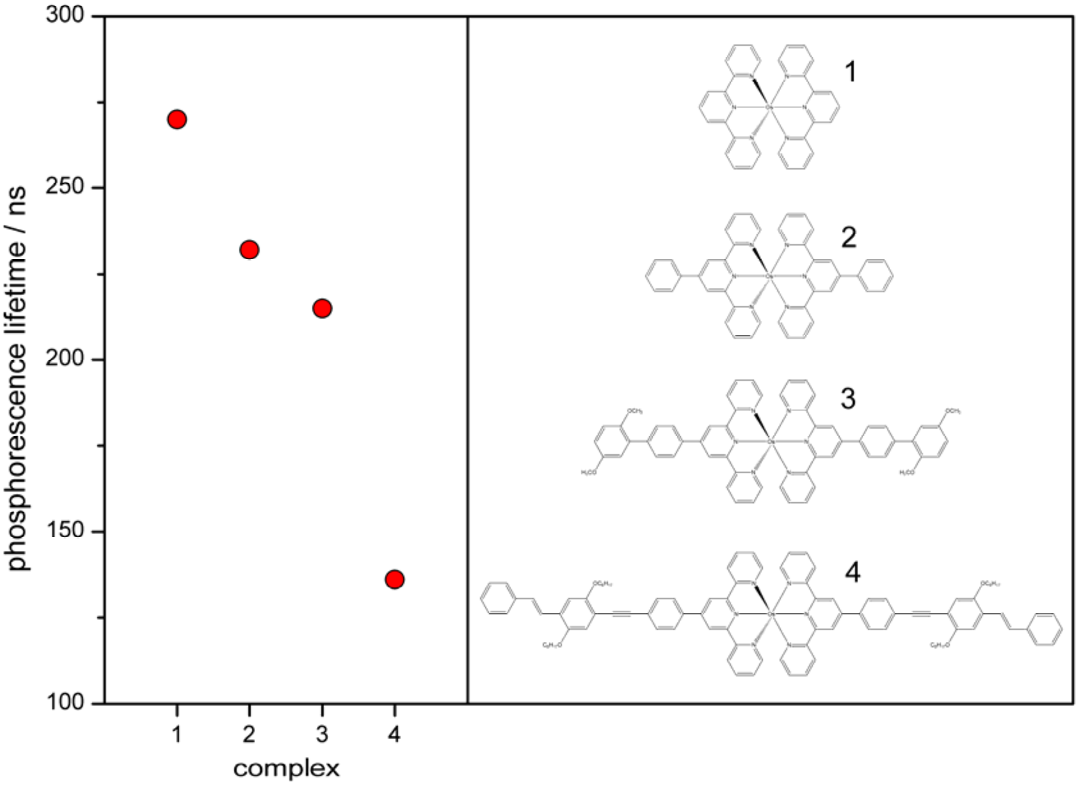

Figure S1: Comparison of the measured room temperature lifetimes of a number of osmium(II) *bis*-terpyridine complexes to their molecular structure [S1,S2]. The data reveal the trend of decreasing phosphorescence lifetime with increasing chromophore size in Os(II) *bis*-terpyridine complexes as has been reported in the literature [S1,S2] and is further observed in this study. This effect is different from the observations made in Ru(II) *bis*-terpyridine complexes as detailed in the manuscript but its origin shall not be part of the manuscript at hand.

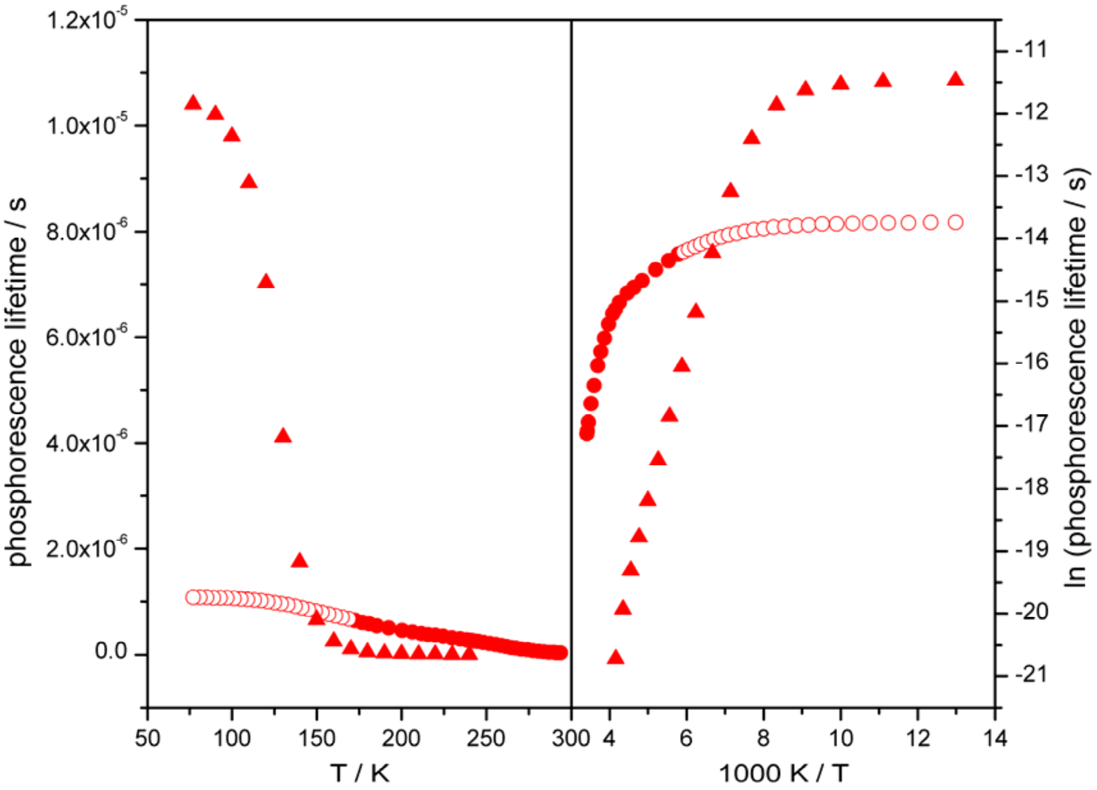

Figure S2: Comparison of the measured (full symbols) and extrapolated lifetimes (empty symbols) of **Ru** (circles) and $[Ru(bpy)_3]^{2+}$ (triangles) on a linear and logarithmic scale.[S3] Extrapolation of the lifetimes to temperature ranges not actually measured is based on the result of fitting a multiexponential decay to the data.

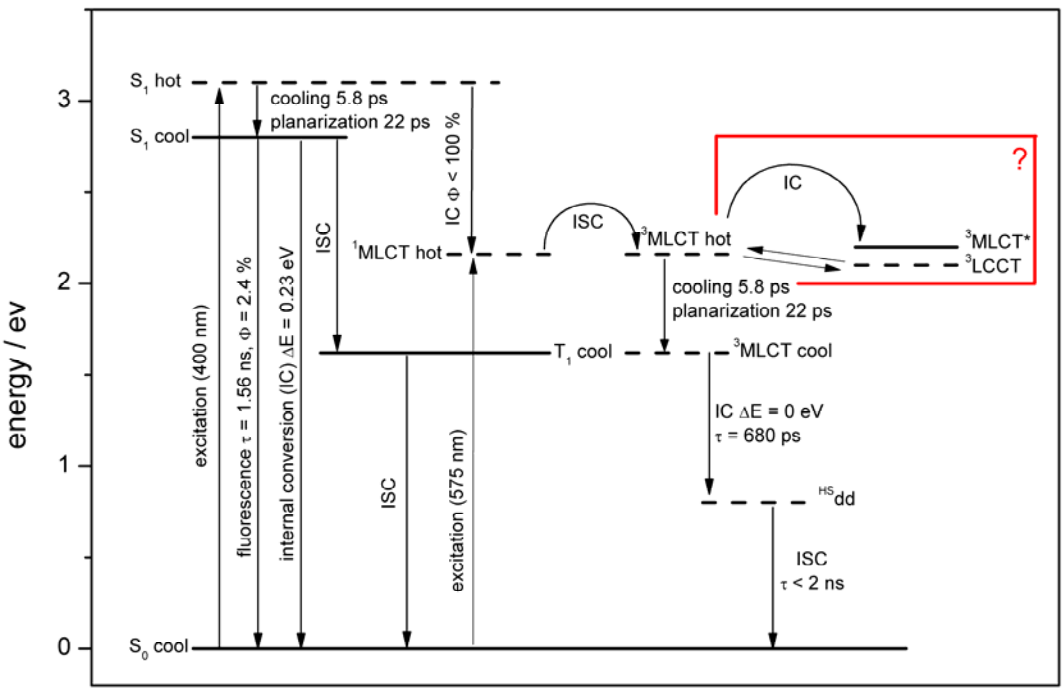

Figure S3: Representative Jablonski scheme for **Fe** reconstructed from the experimental data. Solid lines represent energy levels with defined energetic positions, while dashed ones indicate excited states, the energy of which can only be indirectly inferred or depends on excitation wavelength.

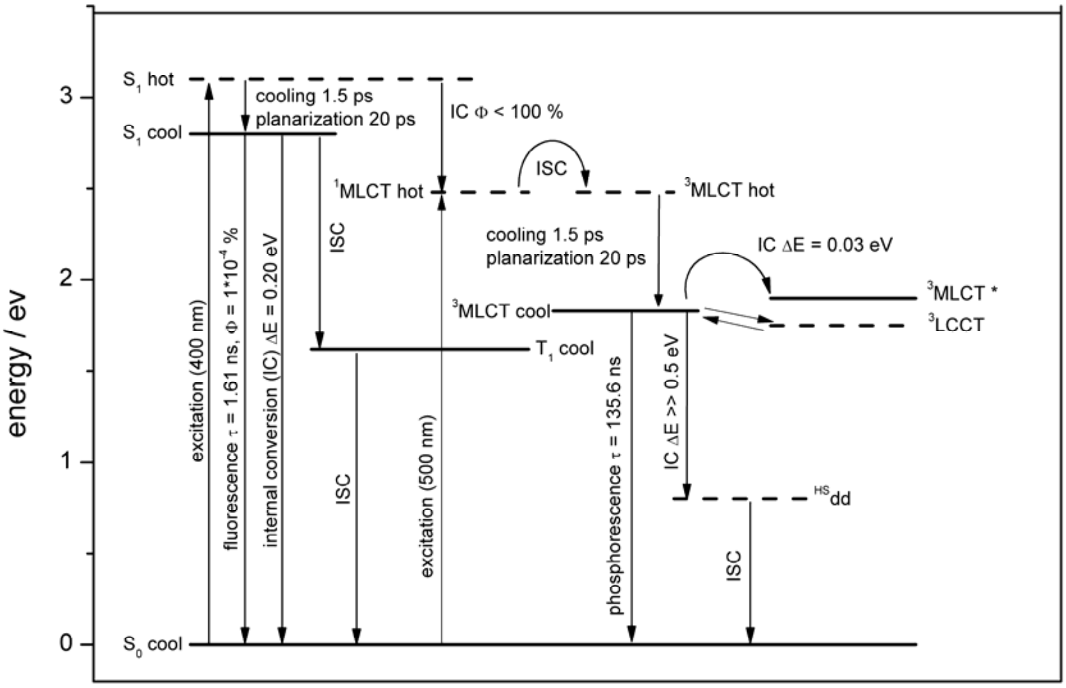

Figure S4: Representative Jablonski scheme for **Os** reconstructed from the experimental data. Solid lines represent energy levels with defined energetic positions, while dashed ones indicate excited states, the energy of which can only be indirectly inferred or depends on excitation wavelength.

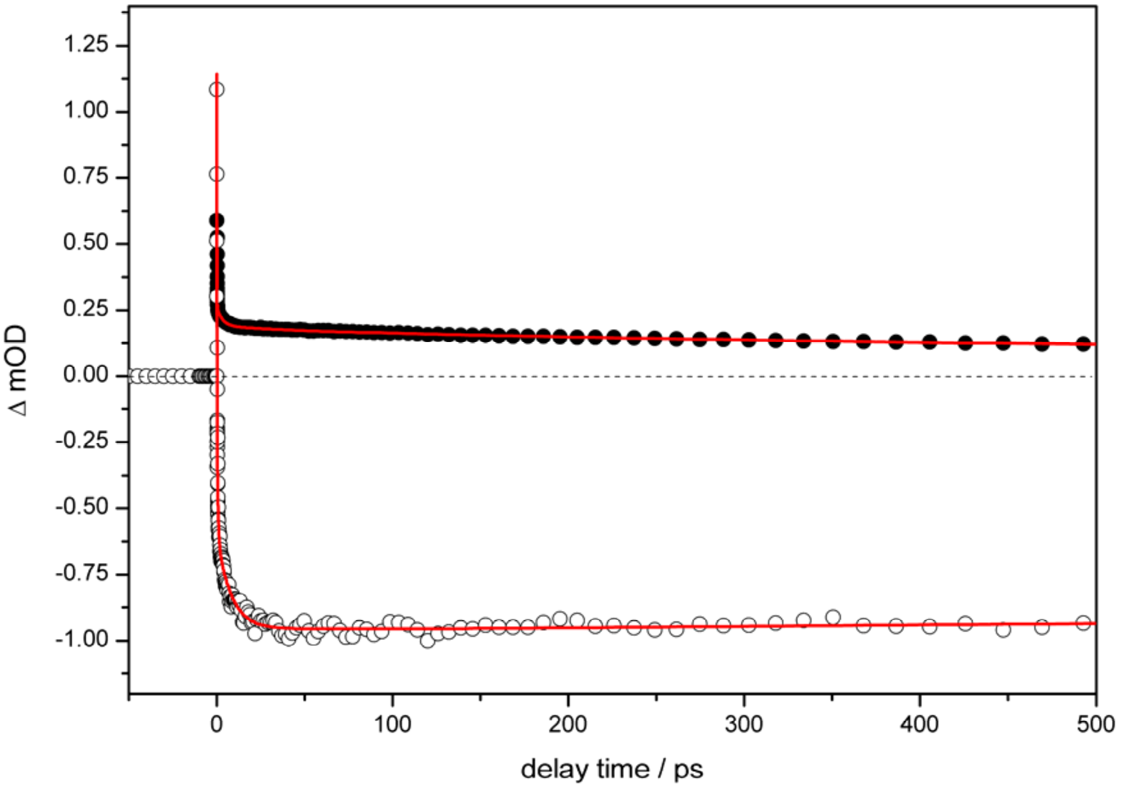

Figure S5: Differential absorption kinetics of **Fe** recorded at 750 nm upon photoexcitation of the S_1 state at 400 nm (solid symbols) and at 575 nm (open symbols). The data indicates that upon excitation of the S_1 state residual excited-state absorption can be detected (positive ΔOD signal) which follows the characteristic decay behaviour observed for the photoinduced dynamics of the free ligand.[S4] The results of fitting a multiexponential decay function to the data are shown as solid lines. The results of the fit of the 400-nm pump data agree with the data obtained for the isolated ligand [S4].

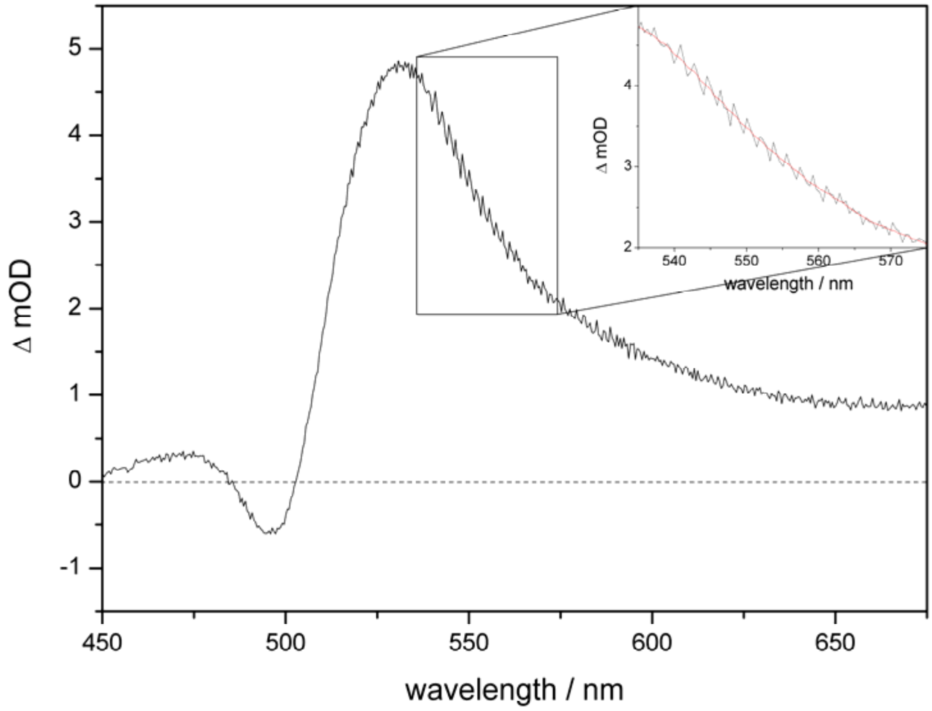

Figure S6: Correction of the measured transient spectra (black line) by a five-point smoothing average (red line) to eliminate the noise from the spectrometer.

References

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