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Transient absorption spectroscopy reveals the excited state dynamics of the tetrakis(2-thenoyltrifluoroacetonato)europate(III) complex anion

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The intense luminescence of lanthanide(III) complexes, enolates included, is intrinsically related to the phenomenon of ligand-to-metal energy transfer. However, the efficiency of such energy transfer processes is directly dependent on the lifetime of the excited states of the organic ligands. Nonetheless, such lifetimes can be difficult to measure at room temperature, especially when the energy transfer process is highly operative such as in europium(III) compounds, where the 4f excited states quench any possible emission from the organic excited triplet state. In this context, femtosecond transient absorption spectroscopy (fs-TAS) is a powerful technique that can probe the organic ligands excited states, including the so-called dark excited states. To fill this gap in the area of lanthanide diketonates, we have chosen the tetraethylammonium salts of $[La(tta)_4]^-$ and $[Eu(tta)_4]^-$ to study the dynamics of the excited states of the 2-thenoyltrifluoroacetonate (tta) ligands. Our transient absorption measurements revealed a singlet lifetime in the order of 300 fs that decays into a triplet state which outlived the duration of the experiment (3 ns). Furthermore, in the presence of europium(III) ions, this long-lived triplet state was quenched, and the measured lifetime was reduced to 320 ps, experimentally showing the energy transfer process with an inferred efficiency of 98%
. Rate-equations modelling was also performed to have the full dynamics of the excited states.

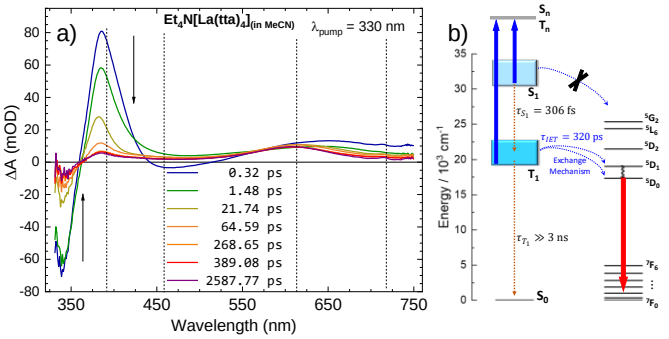

Figure 1: **(a)** Time slices of the Transient Absorption spectrum of the $Et_4N[La(tta)_4]$ complex in acetonitrile solution. **(b)** Energy diagram showing the measured dynamics of the $Et_4N[Eu(tta)_4]$ system.

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