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Effect of the chlorine substituent of 3-chloroacetylacetone in the Eu^{3+} tetrakis complexes: Connecting vibrational and luminescence spectroscopies

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Lanthanide (Ln^{3+}) tetrakis(β-diketonate) complexes are widely studied due to their high luminescence intensities properties. However, some Ln compounds exhibit poor performance due to luminescence quenching through the ligand-to-metal charge transfer (LMCT) states, that effectively suppressing the radiative energy from excited states[1]. Herein, we report on the photoluminescence and vibrational spectroscopies of two Eu^{3+} tetrakis(β-diketonate) complexes (fig. 1a), connecting experimental and theoretical approaches. In this way, the spectroscopic properties were determined using infrared absorption, Resonance Raman, diffuse reflectance, and photoluminescence, further supported by computational calculations at the Density Functional Theory (DFT) level, such as vibrational Local Mode Analysis (LMA), Characterization of Normal Mode (CNM), and Natural Bonding Orbitals (NBO) calculations. Interestingly, the α-chlorinated compound presents an unusually lower energy LMCT state for tetrakis(β-diketonate) complexes, which leads to an almost total quenching of the luminescence (Figure 1).

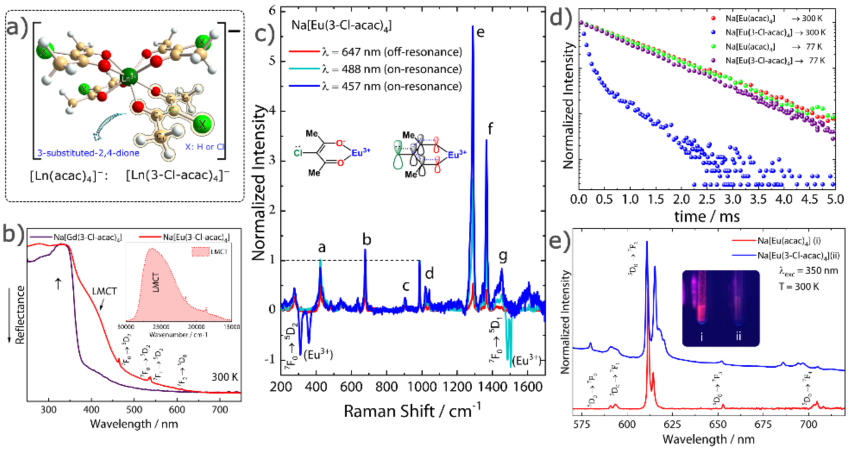

Figure 1. a) Representative structure of the $[Eu(3\text{-}X\text{-}acac)_4]^-$ anion, b) Reflectance spectra for the $Na[Ln(3\text{-}Cl\text{-}acac)_4]$ complexes, c) Resonance Raman spectra of the $Na[Eu(3\text{–}Cl\text{–}acac)_4]$ complex; d) decay curves and e) Photo-luminescence spectra for the $Na[Eu(acac)_4]$ and $Na[Eu(3\text{-}Cl\text{-}acac)_4]$ registered in the solid state.

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References

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