

Excitation pathway of near-infrared luminescence in Yb³⁺ complex with tripodal Schiff base

(¹Graduate School of Environmental Studies, Tohoku University) ○ Atsuko Masuya-Suzuki,¹ Rika Nakamura,¹ Satoshi Goto,¹ Ryunosuke Karashimada,¹ Nobuhiko Iki¹

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Trivalent lanthanide (Ln³⁺) ions show luminescence with attractive features originating from the 4f electrons. So far, a sensitization of the Ln³⁺ luminescence through a light absorption by a ligand and a subsequent energy transfer to the Ln³⁺ center has been extensively studied. Among the Ln³⁺ ions, a unique sensitization path with Ln³⁺/Ln²⁺ redox has been proposed for the ytterbium (Yb³⁺) ion, which has only one excited level (²F_{5/2}: ~10350 cm⁻¹).¹ There are relatively few studies on this redox-mediated sensitization for the near-infrared Yb³⁺ luminescence. Recently, we studied luminescence property of the Yb³⁺ complex with a tripodal Schiff base (YbL^{CH3}, Figure (a)) and proposed the sensitization path with the ligand-to-metal charge transfer (LMCT) state, which acts as the intermediate state of the redox-mediated sensitization (Figure (b)).² In this work, to obtain further insight into this sensitization, we prepared Yb³⁺ complexes with ligand having Cl or Br at 5-position (YbL^{Cl}, YbL^{Br}, Figure (a)) and (YbL^R)_x(LuL^R)_{1-x} co-crystals (R = CH₃, Cl), and studied their photophysical properties.

Upon the ligand excitation, YbL^{Cl} and YbL^{Br} showed the Yb³⁺ luminescence in DMF, respectively. The values of the sensitization efficiency (η) for YbL^{Cl} and YbL^{Br} were found to be 20 and 19%, respectively. These values were significantly smaller than that of YbL^{CH3} (35%). This observation indicates that the electron-withdrawing group may increase the LMCT energy level and result in the decrease in η . The Yb³⁺ luminescence intensity of the co-crystals (YbL^R)_x(LuL^R)_{1-x} increased as x was decreased. Time-resolved profile of the Yb³⁺ luminescence ($x = 0.01$) showed growth and decay components (Figure (c)). The growth component was not observed for $x > 0.2$. From these results, we infer that the close packing of YbL^R and LuL^R in the crystal induced an excited state with long lifetime.

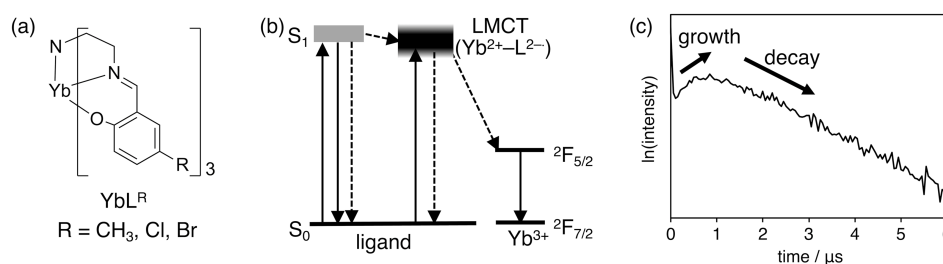


Figure (a) Structure of YbL^R, (b) proposed sensitization path for YbL^R, and (c) time-resolved profile of Yb³⁺ luminescence of (YbL^{CH3})_{0.01}(LuL^{CH3})_{0.99} co-crystal.

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