NIR Emission of Seven-coordinated Lanthanide Complexes with Biphenyl Frameworks

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Luminescent molecules with oxygen sensing properties have attracted attentions in the fields of aeronautical science,[1] medicine,[2] and biological engineering.[3] Among them, lanthanide complexes which show long-lived emission with high brightness are promising luminophore. In this study, we report a novel design of luminescent oxygen sensor based on delayed emission using mixed lanthanide complexes. To demonstrate the delayed emission, we designed the molecular crystal composed of non-luminescent lutetium (Lu(III)) complexes and near-infrared (NIR) luminescent ytterbium (Yb(III)) complexes (Yb(III)-Lu(III), Fig. 1(a)). Yb(III)-Lu(III) was synthesized by the chelation of Lu(tmh)$_3$(CH_3OH) and Yb(tmh)$_3$(H_2O) (tmh: 2,2,6,6-tetramethyl-3,5-heptanedionate) with dpbp ([1,1'-biphenyl]-4,4'-diylbis(diphenylphosphine oxide)) in methanol (Fig. 1(b)). Pure Yb(III) molecular crystal (pure Yb(III)) is also prepared for comparison of photophysical properties.

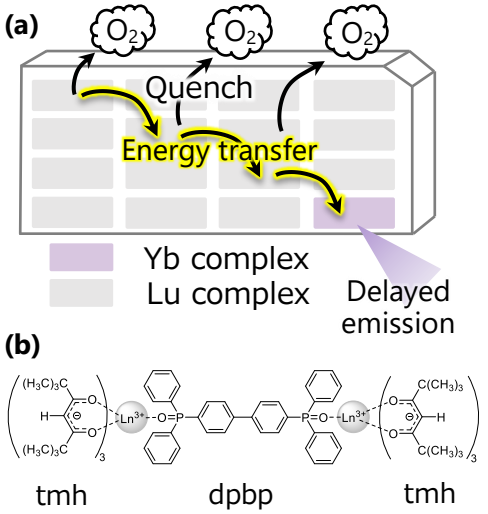

Fig. 1 (a) Luminescent oxygen sensor design. (b) $Ln_2(tmh)_6dpbp$ (Ln = Yb or Lu).

The emission bands of pure Yb(III) and Yb(III)-Lu(III) (Yb:1%, Lu:99%) were observed at 975 nm, which is assigned to $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb(III) ions (Fig. 2). Yb(III)-Lu(III) shows oxygen concentration dependent emission lifetime ($\tau_{0\%\text{-}O2}$ = 375 μs, $\tau_{20\%\text{-}O2}$ = 224 μs, $\tau_{40\%\text{-}O2}$ = 131 μs, $\tau_{60\%\text{-}O2}$ = 76.8 μs). On the other hand, pure Yb(III) was insensitive to oxygen concentration. Yb(III)-Lu(III) is the first oxygen sensor based on the emission lifetime in the Yb(III) complexes.

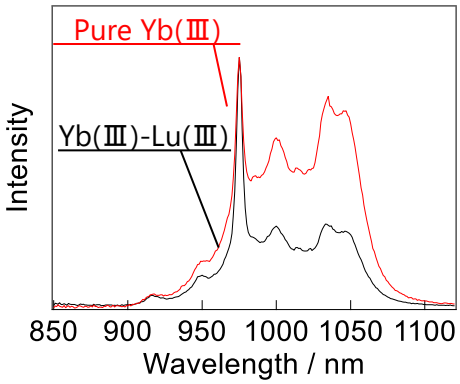

Fig. 2 Emission spectra (λ_{ex} = 356 nm) of Yb(III)-Lu(III) (black) and pure Yb(III) (red).

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