Me-3,2-HOPO Complexes of Near Infra-Red (NIR) Emitting Lanthanides: Efficient

Sensitization of Yb(III) and Nd(III) in Aqueous Solution

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Supporting Information

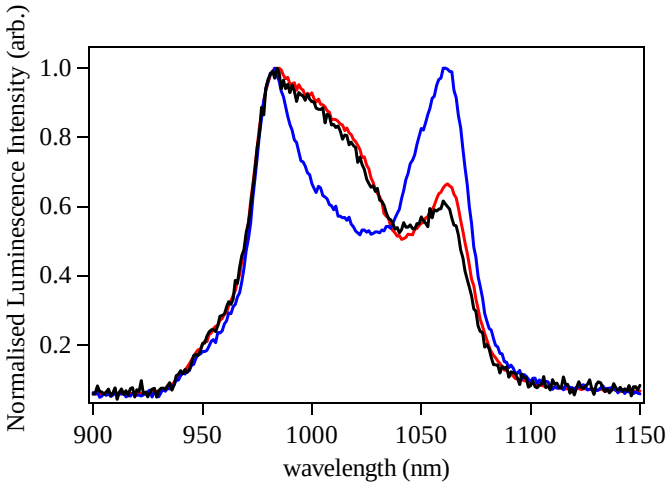

Figure S1. Observed changes in NIR luminescence from [Yb(H(2,2)-Me-3,2-HOPO)] complex in aqueous solution at pH ~ 5, (black), pH ~ 7.4 (red) and pH ~ 10 (blue).

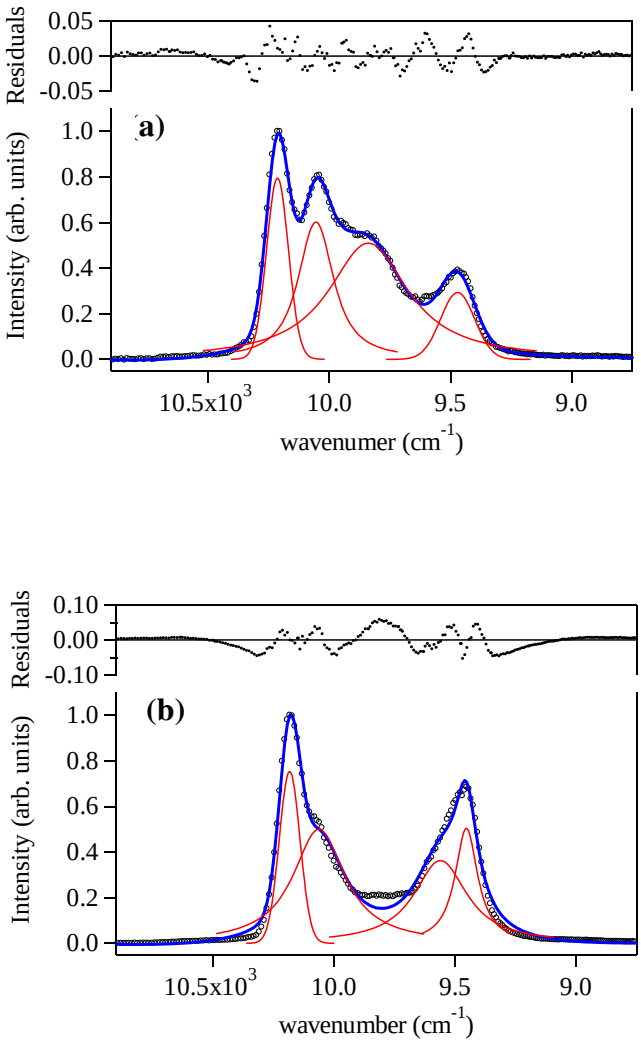

Figure S2. (a) Fitting of observed NIR luminescence from the [Yb(H(2,2)-Me-3,2-HOPO)] complex in 1:1 (v/v) MeOH:EtOH glassing solvent and **(b)** corresponding fitting in presence of 1 % piperazine (as a strong base) to four overlapping Voigt functions.

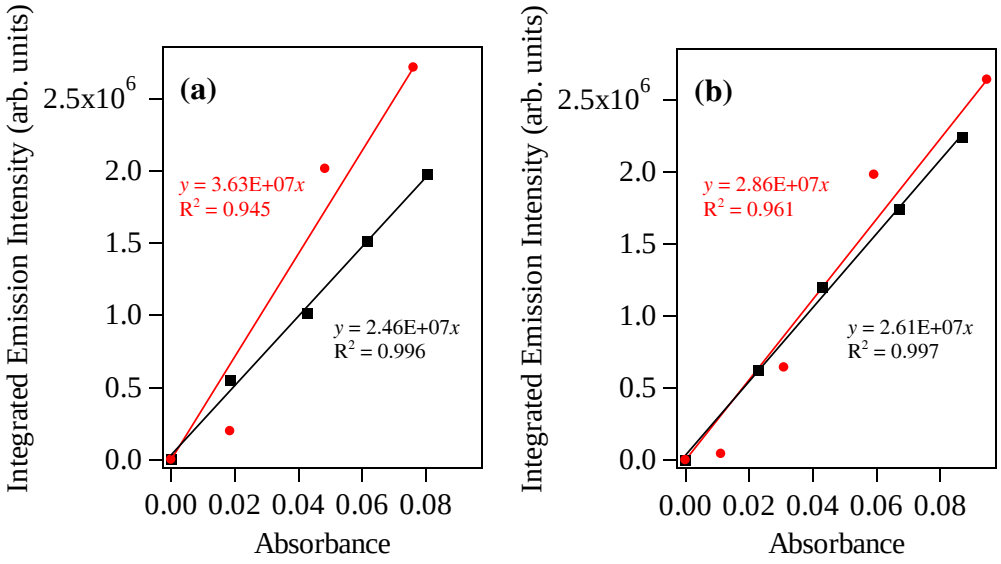

Figure S3 Relative quantum yield determination (shown in duplicate, (a) and (b)) for [Yb(5LIO-Me-3,2-HOPO)$_2$] (black squares) in 0.1 M TRIS buffered aqueous solution at pH 7.4 versus [Yb(TTA)$_3$(H$_2$O)$_2$] (red circles) (where TTA = thenoltrifluoromethylacetylacetonate) in toluene solution as the reference (Φ_{ref} = 0.35 %. see Tsvirko, M. P., *et al*, *Opt. Spectrosc.*, **1999**, *87*, 866 and Meshkova, S. B., *et al*, *Acta Physica Polonica*, *A.*, **1999**, *6*, 983). Red and black lines are linear fits of the absorption versus emission data, with fit parameters as summarised in each figure. The quantum yield can be calculated using the equation;

$$\frac{\Phi_x}{\Phi_r} = \left[\frac{A_r(\lambda_r)}{A_x(\lambda_x)}\right] \times \left[\frac{I(\lambda_r)}{I(\lambda_x)}\right] \times \left[\frac{\eta_x^2}{\eta_r^2}\right] \times \left[\frac{D_x}{D_r}\right]$$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the same wavelength, η is the refractive index and D is the integrated emission intensity. The subscripts 'x' and 'r' refer to the sample and reference respectively. This equation which simplifies to;

$$\Phi_x = \Phi_r \times \left[\frac{slope\ \text{of}\ x}{slope\ \text{of}\ r}\right] \times \left[\frac{\eta_x^2}{\eta_r^2}\right]$$

when used graphically as above and a common excitation wavelength is used. Refractive indices of η_x = 1.33 and η_r = 1.49 were taken for aqueous and toluene solutions respectively, resulting in an overall quantum yield of Φ_{tot} = 0.22 % ± 0.05 for [Yb(5LIO-Me-3,2-HOPO)$_2$].

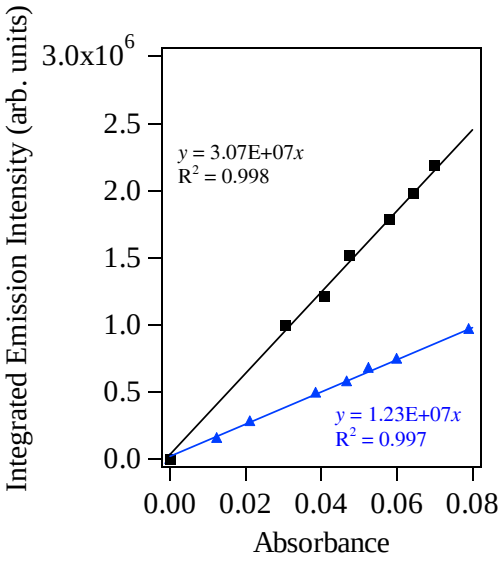

Figure S4. Relative quantum yield determination for [Yb(H(2,2)-Me-3,2-HOPO)] (blue triangles) in 0.1 M TRIS buffered aqueous solution at pH 7.4 versus [Yb(5LIO-Me-3,2-HOPO)$_2$] (black squares) in 0.1 M TRIS buffered aqueous solution at pH 7.4, used as a secondary reference (Φ_r = 0.22 %). Blue and black lines are linear fits of the absorption versus emission data, with fit parameters as summarised in the figure. Again, the quantum yield was calculated using the equation;

$$\Phi_x = \Phi_r \times \left[\frac{slope\ \text{of}\ x}{slope\ \text{of}\ r}\right] \times \left[\frac{\eta_x^2}{\eta_r^2}\right]$$

where the subscripts '*x*' and '*r*' refer to the sample and reference respectively, and taking the refractive index as 1.33 for both η_x and η_r, which results in an overall quantum yield of Φ_{tot} = 0.09 % ± 0.02 for [Yb(H(2,2)-Me-3,2-HOPO)].