

Sensitised Near Infrared Luminescence from Bimetallic Lanthanide Ruthenium Terpyridine Complexes

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Developing applications of Near Infra-Red (NIR) emission for biological imaging has led to an increased interest in the properties of luminescent Ln(III) complexes. In particular, complexes with Ln = Yb(III) and Nd(III) are significant since they have well-known emission bands in the NIR region.

In addition to organic ligands, photoactive *d*-block transition metal complexes have also been exploited as light harvesting antenna.^[1] For example, heterobimetallic complexes containing Ru(bpy)₃²⁺ derivatives as Ln(III) sensitisers have been well documented,^[2] and we have recently shown that Ru(tpy)₂²⁺ derivatives can also be effective in sensitising NIR luminescence from the Nd(III) and Yb(III) cations.^[3,4] Since excitation occurs via the ³MLCT excited state of the Ru(II) complex, the photophysical properties of bimetallic complexes can be readily tuned by altering the ditopic bridging ligand. As shown in Fig. 1, the distance between the 4*d* and 4*f* metal centres significantly increases going from the 6',6''-di(pyridin-2-yl)-2,2':4',4'':2'',2'''-quaterpyridine (btpy) to 4',4''''-(1,4-phenylene)-bis-(2,2':6',2''-terpyridine) (pbtpy) bridging ligand.

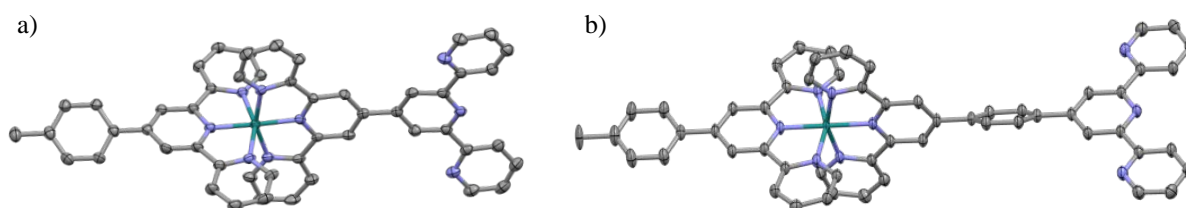


Figure 1. X-ray crystal structures of the Ru²⁺ terpy metalloligands

a) [Ru(toltpy)(btpy)]²⁺ (P2₁/n, R₁ = 7.88%) and

b) [Ru(toltpy)(pbtpy)]²⁺ (C2/c, R₁ = 4.87%).

Anion, solvent and H atoms have been omitted for clarity.

Herein, we have synthesised and characterised a series of modified bisterpyridine Ru(II) metalloligands, allowing the coordination and photophysical interactions with several Ln(III) cations (Ln = Yb, Nd) to be explored. Using a combination of steady state, time resolved, and ultrafast transient absorption experiments, the sensitisation pathway of the observed NIR luminescence has been characterised to gain a better understanding of the antenna process.

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References: [1.] Ward, M. *Coord. Chem. Rev.* 2007, 251, 1663. [2.] Sénéchal-David, K., Pope, S. J. A. Quinn, S., Faulkner, S. Gunlaugsson, T. *Inorg. Chem.* 2006, 45, 10040. [3.] Moore, E. G. Benaglia, M. Bergamini, G. Ceroni, P. *Eur. J. Inorg. Chem.* 2015, 3, 414. [4.] Sykes, D. Faulkner, S. Barbieri A. and Ward, M. D. *Chem. Eur. J.* 2008, 14, 9389.