

Sensitised Ln (III) Emission and Excited State Dynamics of Cofacial ‘Pacman’ Porphyrin Terpyridine Complexes

Jane Y. Liew,¹ Matthias Schwalbe,² Evan G. Moore¹

¹ School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, 4072, Australia.

² Institute of Chemistry, Humboldt Universität zu Berlin, Berlin, 12489, Germany.

E-mail: egmoore@uq.edu.au

Luminescence from trivalent lanthanide cations has received significant interest due to their characteristically sharp emission bands and long-lived excited states.^[1] However, since direct *f-f* absorptions are Laporte forbidden, a strongly absorbing organic chromophore is often required, acting as an antenna to absorb light and transfer this energy to the 4*f* excited states.

The use of various porphyrin derivatives as sensitisers for Ln(III) emission is well documented,^[2,3] in particular since their excited state energy levels are well matched with those of Near-Infra-Red (NIR) emitting cations such as Yb(III) and Nd(III), which have applications in advanced display technologies,^[4] telecommunications,^[5] and biological imaging.^[6]

In this work, we have prepared^[7] a cofacial Zn^{II} porphyrin derivative covalently anchored to a terpyridine chelate using a rigid xanthene moiety, [Zn(PXT)], and its interactions with several trivalent Ln(III) cations (Ln = Nd, Yb and Lu) have been examined. Solution stability constants determined via UV-Vis titration demonstrate exclusive 1:1 ML complex formation, which is also evidenced using NMR and MS techniques.

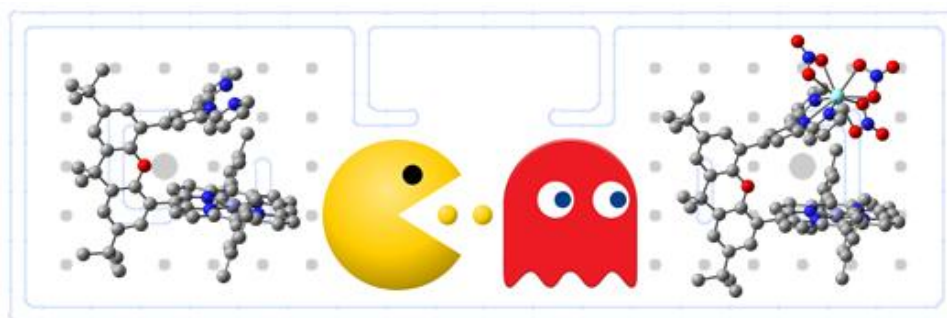


Figure 1. Illustration of 1:1 [Zn(PXT)Ln(NO₃)₃] complex formation.

The resulting [Zn(PXT)Ln(NO₃)₃] complexes with Ln = Yb and Nd display characteristic metal centered emission in the NIR region, which has been quantified. Moreover, the kinetics of the energy transfer processes from the Zn(II) porphyrin donor to Ln(III) acceptor have also been investigated using ultrafast transient absorption techniques, allowing an insight into the mechanism and efficiency of the antennae effect.

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