Ultrafast dynamics of boron porphyrin/porphyrinoid complexes that push the limits of porphyrin flexibility

 $\frac{Nina Novikova^{1,2,4}}{M. Cather Simpson^{1,2,3,4}}, Penelope J. Brothers^{1}$ 1 MacDiarmid Institute for Advanced Materials and Nanotechnology 2 The Dodd-Walls Centre for Photonic and Quantum Technologies 3 The University of Auckland, Department of Physics, 23 Symonds Street, Bldg 301, Auckland 1010, New Zealand

4 The University of Auckland, Photon Factory, 23 Symonds Street, Bldg 301, Auckland 1010, New Zealand

Photophysical and photochemical properties of photoactive compounds are often determined by the ultrafast dynamics that occur immediately after irradiation with light. The initial interaction with light is very fast, on a femtosecond $(10^{-15}s)$ time scale and many processes that follow occur on a similarly fast time scales, between tens of femtoseconds to a few nanoseconds $(10^{-9}s)$. A detailed understanding of the dynamical processes that a photoactive compound undergoes directly after irradiation is therefore essential in order to understand their overall properties and potential applications. A study of those processes in real time is possible using such pump/probe techniques as transient absorption (TrA) spectroscopy and time resolved fluorescence/phosphorescence spectroscopies with further information that is obtained using laser induced acoustic spectroscopy, quantum chemical calculations and static spectroscopy methods. The efficiency and timescales of photophysical processes were determined for a library of boron porphyrin and boron porphyrinoid complexes with unique structural features.¹ The versatility and unusual coordination motifs available to boron porphyrin complexes as well as structural similarity to the BODIPY dyes used in fluorescent labelling offers intriguing possibilities for the application of these complexes.² Special attention was paid to the effect of structural changes on the photosensitising properties important in photodynamic therapy applications.



Figure 1. An example of a Jablonski diagram showing relaxation pathways possible for a porphyrin (left), ultrafast pump/probe transient absorption spectroscopy setup (right).

- 1. Weiss, A.; Hodgson, M. C.; Boyd, P. D. W.; Siebert, W.; Brothers, P. J., Chem. -Eur. J. 2007, 13 (21), 5982-5993
- 2. Belcher, W. J.; Boyd, P. D. W.; Brothers, P. J.; Liddell, M. J.; Rickard, J. Am. Chem. Soc. 1994, 116 (18), 8416-17