Project title: **Mapping the Intrinsic Photophysics of Metalloporphyrins and their Aggregates**

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**Project Description:**

There is intense current interest in the photophysical properties of metalloporphyrins (Figure 1) due to their potential applications in many key chemical areas including biomimetic and optoelectronic systems. In this proposal, we will characterize the intrinsic photophysical properties of isolated metalloporphyrins, by performing gas-phase spectroscopy and photochemistry on porphyrins and their aggregates. These experiments are of key importance as they will provide high-quality gas-phase experimental data for benchmarking state of the art theoretical calculations of metalloporphyrin photophysics. Such gas-phase measurements are currently almost entirely lacking for metalloporphyrins. A key focus of the project will be the study of aggregates of metalloporphyrins. These aggregates exhibit light harvesting and electron transfer capabilities in solution and are therefore well-known as promising candidates for device components. We will study metalloporphyrin aggregates in the gas-phase, where we will be able to map how the electronic properties (electronic spectra, photochemistry and photophysics) evolve as a function of the size of the aggregate. The proposed studies will be performed in a custom-adapted laser-interfaced commercial mass spectrometer, which has now been shown to allow the routine acquisition of gas-phase UV spectra of electrosprayed ions, along with determination of photoproducts. The proposed research has the potential to dramatically improve the current fundamental understanding of metalloporphyrin excited states, in both individual metalloporphyrins and metalloporphyrin aggregates, and hence make a critical contribution to inform the rational design of new metalloporphyrin materials. The student will be a member of both the Dessent and Perutz groups, and will perform research at the interface between inorganic and physical chemistry. The Dessent group have broad expertise in the field of gas-phase laser spectroscopy,¹ and computational chemistry, while the Perutz group has extensive experience in the field of metalloporphyrin photochemistry and photophysics, having worked on these systems as CO₂ reduction photocatalysts over recent years.²


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Figure 1: An Iron Metalloporphyrin, with a water molecule bound to the metal centre.
Training:

All research students follow our innovative Doctoral Training in Chemistry (iDTC): cohort-based training to support the development of scientific, transferable and employability skills. All research students take the core training package which provides both a grounding in the skills required for their research, and transferable skills to enhance employability opportunities following graduation. Core training is progressive and takes place at appropriate points throughout a student’s higher degree programme, with the majority of training taking place in Year 1. In conjunction with the Core training, students, in consultation with their supervisor(s), select training related to the area of their research. The project will provide a very broad range of student training in the work conducted in the CED group including mass spectrometry, (soft ionization techniques, CID, and mass spectral analysis), laser spectroscopy (use of class 4 laser systems), and also in computational chemistry techniques (ab initio and DFT). Mass spectrometry and computational chemistry are both highly-valuable, transferrable skills. The great majority of this training will be provided by CED and research group members, who have extensive experience in the techniques involved. In the RNP group, the student will gain training in the synthesis of MPs, as well as in characterization techniques (UV, IR, NMR). In addition, the student will receive training in the interpretation of photochemical measurements. The student will participate in group meetings in both groups, providing opportunities to develop scientific communication and oral presentation skills. Finally, the student will have opportunities to participate in national and international conferences, allowing the student to develop skills in dissemination of scientific research.

Equality and Diversity:

The Department of Chemistry holds an Athena SWAN Gold Award and is committed to supporting equality and diversity for all staff and students. The Department strives to provide a working environment which allows all staff and students to contribute fully, to flourish, and to excel. Chemistry at York was the first academic department in the UK to receive the Athena SWAN Gold award, first attained in 2007 and then renewed in October 2010 and in April 2015. This PhD project is available to study full-time or part-time (50%).

Funding:

Value: Studentships are fully funded either by the EPSRC or a Department of Chemistry Teaching Studentship, and cover: (i) a tax-free annual stipend at the standard Research Council rate (£14,553 for 2017-18), (ii) tuition fees at the UK/EU rate.

Eligibility: EPSRC studentships are available to UK and EU students who meet the UK residency requirements. Students from EU countries who do not meet the residency requirements may still be eligible for a fees-only award. Chemistry Teaching Studentships are available to any student who is eligible to pay tuition fees at the home rate. Further information about eligibility for Research Council UK funding can be found at the following website: http://www.bbsrc.ac.uk/documents/studentship-eligibility-pdf/

Candidate selection process:

- Applicants should submit an application for a PhD in Chemistry by **17:00 on Wednesday 10 January 2018**
- Supervisors will interview their preferred candidates either by email, telephone, web-chat or in person
- Supervisors may nominate up to two candidates to the assessment panel
- The assessment panel will shortlist candidates for interview from all those nominated
- Shortlisted candidates will be invited to a panel interview at the University of York on **13 or 15 February 2018**
- The Chemistry Graduate Awards Panel will award studentships following the panel interviews
- Candidates will be notified of the outcome of the panel’s decision by email

For more information contact chemgrad@york.ac.uk or see our web page: http://www.york.ac.uk/chemistry/postgraduate/