Project title: Multifunctional, Polymetallic Liquid Crystals
Supervisor name(s): Professor Duncan W. Bruce
Supervisor(s) contact email: duncan.bruce@york.ac.uk

Project Description:

There is considerable interest in multifunctional materials, that is materials with more than one exploitable physicochemical property, particularly where the effects may be coupled. Work of this type has been a subject of interest within Bruce’s group for some time in relation to the preparation of metal complexes that are both liquid crystals and triplet emitters. This work has, to date, centred on square-planar complexes of platinum(II)\(^1\) and octahedral complexes of iridium(III).\(^2\) More recently, in unpublished work in collaboration with Lynam (York), this has been extended to complexes of square-planar gold(III). The general structure of these platinum and gold complexes is shown below and in each case, neutral complexes are realised where L is an anionic ligand, for example Cl; liquid crystallinity is introduced via functionalisation of R'. However, further elaboration is possible and what this project seeks to do is to contemplate the use of derivatives of L = alkyne (and also, perhaps, R = alkyne) to build emissive, liquid-crystalline units that can act as a ligand or other modifying group to a second metal complex moiety. A very simple example of this might be a complex of the general type \(\text{trans-}[\text{Pt(com)}_2(\text{PR}_3)_2]\), where ‘com’ is an alkynyl-linked Pt\(^{II}\) or Au\(^{III}\) unit based on those in the figure below, or the linear gold(I) target \([\text{Au(com)(CN–R’’)}]\), examples of which have been described by Espinet and co-workers.\(^3\)

![Diagram of complex structure](image)

The aim of this project is then to prepare a series of multimetallic complexes with liquid crystal properties that are also triplet emitters. Furthermore, new complexes are envisaged in which both metal-based components have a photophysical response, prompting an investigation between the responses of the two components to determine the extent to which they are coupled or independent. The latter situation might allow for each emission to be tuned independently, opening up a potentially wide palette of emission characteristics.


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 proposed is truly multidisciplinary and will offer the student a very broadly based training as now outlined. In the first steps, the programme is intensely synthetic in nature. Ligands need first to be prepared followed by the related complexes. The knowledge for all of this exists within the group giving confidence that starting complexes will be readily realised, but there will be challenge in making the target complexes. In addition, some of the chemistry will require anaerobic conditions and so competency in Schlenk-line techniques will be developed.

Chemical characterisation will use the techniques of NMR spectroscopy, mass spectrometry, electronic and infrared spectroscopy, combustion analysis and, where possible, single-crystal X-ray diffraction. The student will become familiar with all of these in a hands-on fashion with the exception of crystallography, although competency will be gained in handling the cif files generated.

In terms of physico-chemical skills, multiple techniques will be brought to bear on the final products. Liquid crystal properties will be determined first using polarised optical microscopy and differential scanning calorimetry, later supported by small-angle X-ray scattering which will be done in a hands-on fashion. There will then be a need to undertake photophysical characterisation using fluorescence and lifetime spectrometers.

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 (1) the EPSRC for 3 years (2) a Department of Chemistry Teaching Studentship for 3 years or (3) a Department of Chemistry NMR Studentship for 4 years, 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/