

Shedding New Light on the Design of Polyaromatic Coordination Complexes as Triplet Photosensitisers

Yue Lu¹, Junsi Wang¹, Colin Caverly¹, Sylvia Draper¹, Jinzhang Zhao²

¹Trinity College Dublin, School of Chemistry, Dublin 2, Ireland.

²Dalian University of Technology, State Key Laboratory of Fine Chemicals, Dalian 11602, China

E-mail: smdraper@tcd.ie

As an energy transfer process Triplet-Triplet Annihilation Upconversion (TTA-UC) has drawn much attention due to its potential application in photodynamic therapy, artificial photosynthesis, photocatalysis, photovoltaics and luminescent oxygen sensing. There are many upconverting materials but those based on single molecules need to undergo efficient intersystem crossing (ISC), show intense absorption in the visible region, and have relatively long-lived triplet excited state lifetimes. While these criteria are widely recognised, the design of potential triplet photosensitisers has proven to be a considerable challenge. Feeding into existing synthetic strategies within the group, the Draper team set about generating a library of mono substituted, homo and hetero bi-substituted ethynylaryl-1,10-phenanthroline complexes (Fig.1).^[1,2,3]

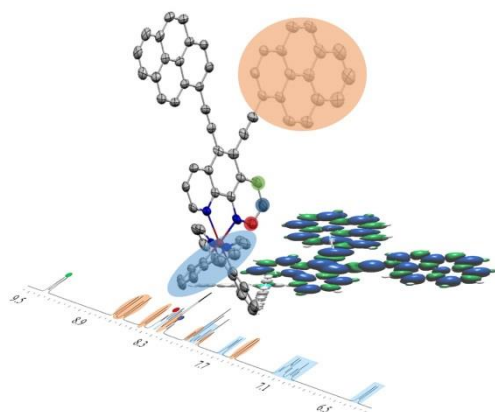


Figure 1: Solution/solid-state characterization and spin density distribution in a 5,6-bisubstituted Ir(III) phenanthroline complex

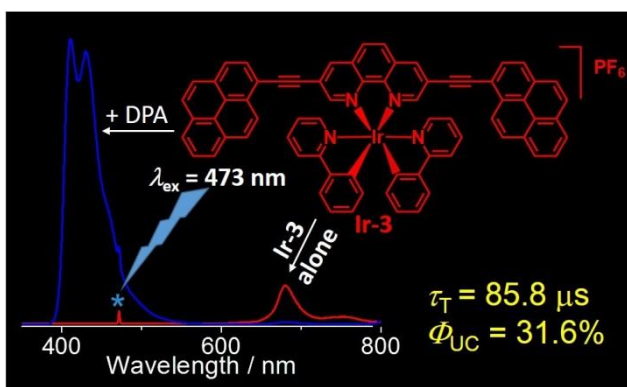


Figure 2: TTA upconversion of the 3,8-bisubstituted isomer in the presence of DPA as annihilator ($\lambda_{\text{ex}} = 473$ nm).

In appending triphenylamine, pyrene, naphthalene, naphthalamide, and bodipy (boron-dipyrromethene) moieties to a series of Ir(III) and Ru(II) complexes, the team has been able to shed some light on how to access intense absorption spanning from the UV region, right across to the near-IR (NIR). The systems possess long-lived triplet lifetimes (up to 1.3 ms), and exhibit exceptionally high UC quantum yield (up to 31%) (Fig. 2)^[2]. Further to this, near unity singlet oxygen quantum yields and cytotoxicity under light exposure have been demonstrated^[3]. As a spin-off result, the NIR UC materials have yielded positive results

on testing against certain cell lines (photodynamic therapy). This paper hopes to give an overview of our research toward optimizing the designs of these materials.

Funding: Science Foundation **Ireland** (15/IA/3046, 15/TIDA/2952)

References:

- [1] Y. Lu, N. McGoldrick, F. Murphy, B. Twamley, X. Cui, C. Delaney, G. M. Máille, J. Wang, J. Zhao, S. M. Draper. *Chem. Eur. J.* **2016**, 22, 11349
- [2] Y. Lu, J. Wang, N. McGoldrick, X. Cui, J. Zhao, C. Caverly, B. Twamley, G. M. Máille, B. Irwin, S. M. Draper. *Angew. Chem. Int. Ed.* **2016**, 55, 14688
- [3] J. Wang, Y. Lu, N. McGoldrick, C. Zhang, W. Yang, J. Zhao, S. M. Draper. *J. Mater. Chem. C.* 2016, 4, 6131