

Charge Density Studies of Photo-redox Metal Complexes: An Experimental Comparison of the Ground and Lowest Excited States.

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The photo-induced transfer of electrons (PET) forms the basis for biological and environmental processes fundamental to life, including photosynthesis and atmospheric ozone generation.[1] It also underpins a range of vital technologies[2] such as photocatalysis,[3] which has key applications in environmentally sustainable chemical manufacturing, and a global market expected to reach AU \$ 6.64 billion by 2025.[4] A thorough understanding of PET and the species involved will be of great benefit to the Australian chemicals industry.

Owing to their rich physical and chemical properties, metal complexes are widely applicable for PET processes, and accordingly account for the vast majority of available photocatalysts. As their functions arise through their ability to accept or donate electrons upon absorption of light, knowledge of the distribution of electronic charge over their structures in both the ground and in excited states is critical for understanding their behaviour.

While significant theoretical efforts have been made to model their electronic structures,[5] experimental data is rare. The collection of experimental data that reveals the distribution of electronic charge on photo-redox metal complexes is of paramount importance for the development of a more complete understanding of their PET behaviour.

Charge-density X-ray experiments combined with in situ photo-excitation provide a method of obtaining this experimental data in both ground and excited states. High-quality single crystal neutron diffraction studies, such as those possible using the KOALA beamline at the Australian Centre for Neutron Scattering, are required for these measurements to establish the nuclear coordinates, particularly the position of hydrogen atoms.

Our current interest in this research is focused on elucidating the charge density structures of well-known photocatalysts such as tris-2,2'-bipyridineruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$)[6] and tris[2-phenylpyridinato-C₂,N]iridium(III) ($[\text{Ir}(\text{ppy})_3]$).[5a] Experiment design and preliminary data in this avenue of research will be presented.

1. B. Eliasson, M. Hirth, et al., *J. Phys. D: Appl. Phys.*, 1987, 20, 1421-1437.
2. (a)T. D. Ashton, K. A. Jolliffe, et al., *Chem. Soc. Rev.*, 2015, 44, 4547-4595; (b)A. Listorti, B. O'Regan, et al., *Chem. Mater.*, 2011, 23, 3381-3399; (c)A. Periasamy, *Fluorescence resonance energy transfer microscopy: a mini review*, SPIE, 2001.
3. K. L. Skubi, T. R. Blum, et al., *Chem. Rev.*, 2016, 116, 10035-10074.
4. Grand View Research, 2017.
5. (a)B. J. Powell, *Coord. Chem. Rev.*, 2015, 295, 46-79; (b)I. N. Mills, J. A. Porras, S. Bernhard, *Acc. Chem. Res.*, 2018, 51(2), 352-364.
6. (a)P. S. Braterman, A. Harriman, G. A. Heath and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1983, 1801-1803; (b)G. A. Heath, L. J. Yellowlees and P. S. Braterman, *J. Chem. Soc., Chem. Commun.*, 1981, 287-289

Speakers Gender

Male

Travel Funding

Yes

Level of Expertise

Early Career <5 Years since PdD

Do you wish to take part in the poster slam

Yes

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