

Faraday Discussion 155: Artificial Photosynthesis

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Faraday Discussions document a long-established series of Faraday Discussion meetings, organised by the Royal Society of Chemistry, which provide a unique international forum for the exchange of views and newly acquired results in developing areas of physical chemistry, biophysical chemistry and chemical physics. The papers presented are published in the *Faraday Discussions* volume together with a record of the discussion contributions made at the meeting. *Faraday Discussions* therefore provide an important record of current international knowledge and views in the field concerned.

The latest meeting, FD155, held at the University of Edinburgh, UK, from 5th–7th September 2011, was dedicated to the subject of artificial photosynthesis and to the specific problem of utilising solar energy as a direct supplement to our current energy supplies. The meeting attracted over 120 delegates, mostly academic researchers, from around the world and involved 22 presentations covering many different aspects of artificial photosynthesis (1). Current research follows one of two major routes: loosely speaking these can be considered to involve photo-electrochemical approaches or the construction of bio-inspired molecular devices. Photovoltaic systems, based on either organic or inorganic materials, have the advantage that they actually work under ambient light conditions but they need to be equipped with suitable electrodes in order to use the photo-generated electrical current to split water or reduce carbon dioxide. Molecular systems lag far behind in terms of practical possibilities but are highly attractive in terms of mechanistic insight, intellectual challenge and beautiful synthesis. In both areas, there is a critical need to identify effective catalysts and it is here that the platinum group metals (pgms) play an essential role.

Artificial Photosynthetic Systems

Figure 1 gives a crude indication of the essential features inherent to a bio-inspired artificial photosynthetic unit. Sunlight absorbed by an electron donor (D) causes an electron to transfer to a nearby electron acceptor (A); a reaction that does not occur in the dark. Several concerted electron-transfer reactions are needed to effect water splitting and intermediary elec-

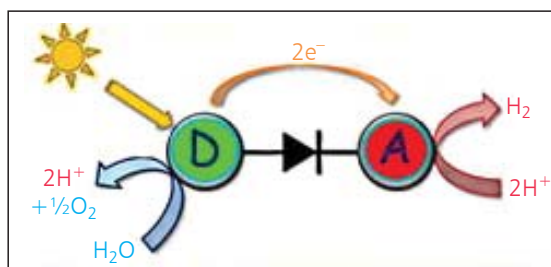


Fig. 1. Artificial photosynthetic unit. D = electron donor, A = electron acceptor (Reproduced by permission of The Royal Society of Chemistry)

trons and positive holes have to be stored for a few seconds or so at a redox catalyst. Here, we focus on the discussion relating to the use of pgms either as specific catalysts or as photon collectors. It is clear that the pgms offer unrivalled performance as redox catalysts in water splitting or as catalysts for the reduction of CO₂. Additional work relates to designing improved electron donors or acceptors based on pgms.

Water Oxidation

Tremendous progress has been made with respect to identifying new homogeneous metal-based catalysts for oxygen evolution from water under ambient conditions. This is a major challenge that must be overcome before effective photosystems can be developed for solar fuel production. A series of mononuclear ruthenium(II) pyridine complexes (Figure 2) has been synthesised by Licheng Sun *et al.* (Royal Institute of Technology, Stockholm, Sweden) and shown to be excellent water oxidation catalysts. The catalysts operate in acidic solution, under both electrochemical and chemical oxidative conditions, and have been subjected

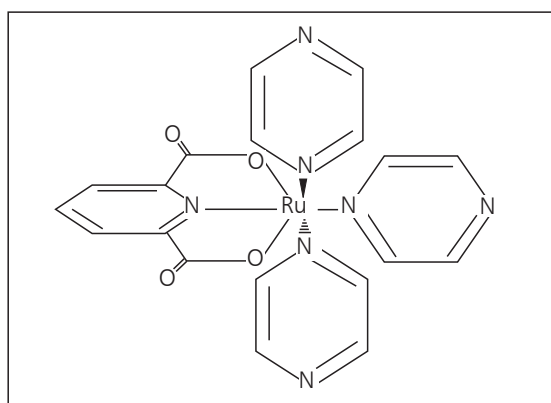


Fig. 2. An example of the series of mononuclear ruthenium(II) poly(pyridine) complexes

to detailed mechanistic examination. Interestingly, certain complexes of similar structure are poor catalysts, thereby opening the possibility to explore reactivity-structure relationships.

Tom Mallouk and coworkers (The Pennsylvania State University, USA) are following a quite different approach. Here, a photo-electrochemical device has been engineered based on a porous titanium dioxide anodic film equipped with a Ru(II) poly(pyridine) sensitizer that collects photons across much of the visible spectrum. A key feature of this system is the provision of iridium(IV) oxide hydrate (IrO₂·*n*H₂O) nanoparticles that function as the catalyst for water oxidation. The quantum yield is low because of fast charge recombination between the primary charges but the system is amenable to detailed mechanistic examination that should assist optimisation of the overall device. At present, this is one of the most effective systems available for artificial photosynthesis. Furthermore, Erwin Reisner (University of Cambridge, UK) has proposed a complementary system wherein a related Ru-based dye is coated onto TiO₂ particles and subsequently equipped with a cobalt-based reduction catalyst. Illumination of the Ru(II)-based dye leads to fast charge injection into the conduction band of the TiO₂. The promoted electron is then trapped at the Co(III)-based catalyst and used to reduce water to molecular hydrogen in neutral solution. Performance of this system is highly promising but it must be noted that hydrogen evolution occurs at the expense of consuming an added organic material.

Several researchers introduced water-splitting photosystems based on the use of a Ru(II) poly(pyridine) complex as the light absorbing unit. This species, apart from collecting incident photons, enters into light-induced electron transfer with added substrates and thereby initiates the oxidation or reduction of water. Thus, Sebastiano Campagna and colleagues (University of Messina, Italy) have used a conventional photochemical reaction to oxidise Ru(II) *tris*(2,2'-bipyridine) in aqueous solution. The resultant oxidant is used subsequently to oxidise water *via* a tetra-cobalt(III) cubane cluster: [Co₄O₄(O₂CMe)₄(py)₄] (py = pyridine). The novelty here lies with trying to mimic the oxygen-evolving catalyst found in natural photosynthetic organisms with the Co cluster. Haruo Inoue *et al.* (Tokyo Metropolitan University, Japan) have considered an alternative oxidative scheme. The idea is to employ a Ru(II) porphyrin, which has superior light-harvesting performance, as a sensitizer for epoxidation of alkenes. The critical feature of this system relates to

using water as the source of the added oxygen. This, in turn, introduces some interesting mechanistic concerns. In many cases, the photochemical reaction occurs in surprisingly high quantum yield and results in formation of a valuable product.

Photochemical Carbon Dioxide Reduction

Osamu Ishitani and coworkers (Tokyo Institute of Technology, Japan) have worked for many years on developing photochemical systems capable of the reduction of CO₂. This is an extremely difficult reaction to realise, especially in aqueous solution, and has been a major bottleneck for the successful introduction of an artificial photosynthetic system; hence the focus on production of hydrogen from water as a simpler alternative. The main problem for CO₂ reduction relates to the high overpotential associated with most catalysts. Ishitani *et al.* have investigated several classes of rhenium(I) complexes as effective CO₂ catalysts. Here, a novel photosystem is introduced whereby a Ru(II) poly(pyridine) sensitiser is covalently linked to a Re(I) complex (Figure 3) to form an integral unit. Illumination into the Ru(II)-based sensitiser results in electron transfer to the nearby Re(I) complex. Transfer of a second electron, fuelled *via* an added sacrificial reagent, leads to reduction of CO₂ to CO in reasonably high quantum yield. The reaction is carried out in *N,N*-dimethylformamide, not water, and requires high pressures of CO₂. Nonetheless, this system represents the state of the art in the field.

Electron Transfer

Without doubt, the biggest problem associated with the successful development of a bio-inspired form of artificial photosynthesis relates to the need to accumulate multiple charges at a redox site. This situation arises because all photochemical electron-transfer reactions are necessarily single-electron events whereas fuel formation involves a minimum of two electrons. Most systems stop at the one electron stage due to short-circuiting. The bottleneck is removed by the use of sacrificial reagents but this is a very short-sighted approach. Leif Hammarström and colleagues (Uppsala University, Sweden) have searched for ways around the problem and, at FD155, described an interesting series of molecular dyads able to undergo light-induced charge accumulation. Here, a Ru(II) poly(pyridine) sensitiser is covalently linked to an oligo-triarylamine residue (Figure 4). Illumination into the Ru(II)-based sensitiser causes electron transfer from the nearest amine residue but, due to thermodynamic arguments, the resultant positive hole moves to one of the peripheral amines, thereby slowing the rate of charge recombination. Linking the Ru(II)-based chromophore to the surface of TiO₂ allows the promoted electron to be discharged, leaving the accumulated positive holes on the terminal oligo-triarylamine unit. Such research offers promise for the development of multi-electron storage systems.

Two papers of direct interest to pgm chemistry were presented at the follow-on Post Faraday Meeting that

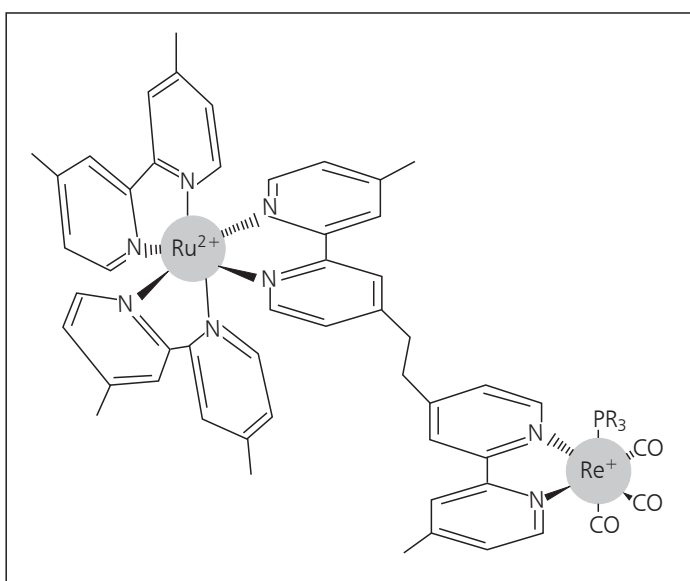


Fig. 3. A ruthenium(II) poly(pyridine) sensitiser is covalently linked to a rhenium(I) complex

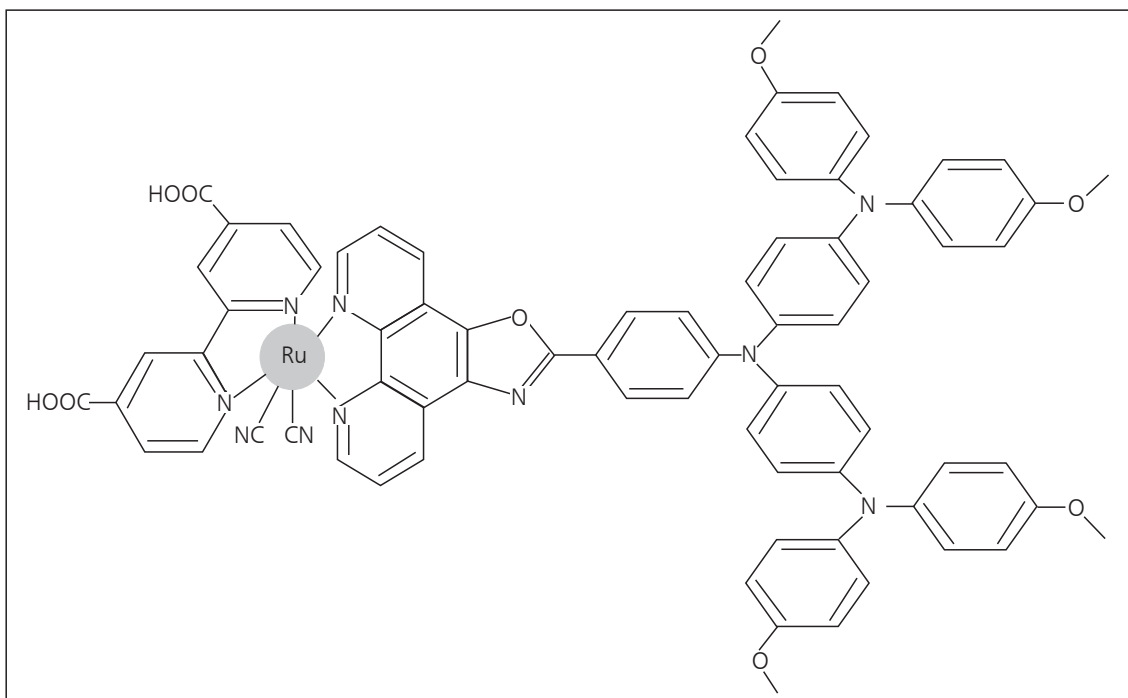


Fig. 4. A ruthenium(II) poly(pyridine) sensitizer is covalently linked to an oligo-triarylamine residue

took place immediately after the conclusion of FD155 (2). Etsuko Fujita (Brookhaven National Laboratory, New York, USA) reported detailed mechanistic studies relating to the mode of action of a mononuclear Ru complex (Figure 5) able to bring about the 4-electron oxidation of water to molecular oxygen. Using a battery of sophisticated experimental techniques, aided

by quantum chemical calculations, several key intermediates in the redox cycle have been identified. Separately, Oluwafunmilola Ola (University of Nottingham, UK) described her research into pgm-promoted reduction of CO₂ on the surface of TiO₂ under illumination. Palladium and rhodium appear to be the promising metal deposits for such challenging reduction pro-

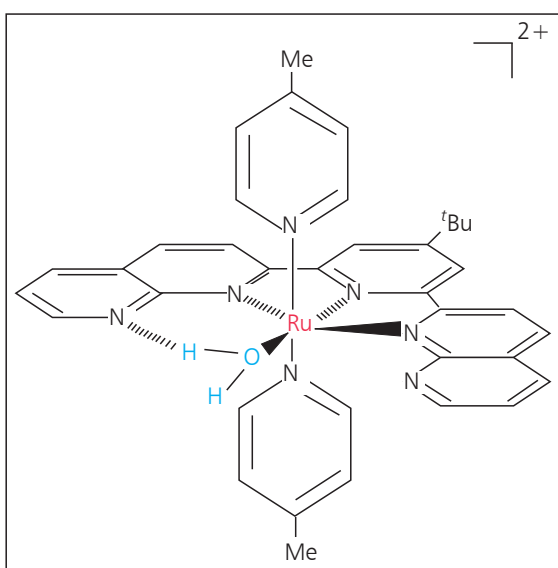


Fig. 5. The mode of action of a mononuclear ruthenium complex able to bring about the 4-electron oxidation of water to molecular oxygen

cesses, although the nature of the TiO₂ host plays a very important role in deciding overall efficiency.

Concluding Remarks

This review has focused on those presentations dealing with the pgms. The remaining presentations demonstrated that considerable research activity has been carried out on the search for cheaper and more plentiful alternatives to the pgms as redox catalysts. Iron and manganese have often been presented as logical replacements for Ru or Ir as catalysts for water oxidation but their performance does not justify such optimism. At present, the pgms are much the better catalysts, especially in terms of reductive chemistry. The challenge for the immediate future, therefore, is to equip these catalysts with high levels of selectivity, as found in natural enzymes.

Copies of all the presentations and the subsequent discussion will be published as *Faraday Discussions* 155 and may be obtained from the Royal Society of Chemistry (3).

References

- 1 Artificial Photosynthesis: *Faraday Discussions* 155: <http://www.rsc.org/FD155> (Accessed on 15th November 2011)

- 2 Post Faraday Meeting: <http://www.rsc.org/ConferencesAndEvents/RSCConferences/FD155/satellite.asp> (Accessed on 15th November 2011)
- 3 *Faraday Discuss.*, 2012, in press

The Reviewer



Anthony Harriman started his career in artificial photosynthesis at the Royal Institution in London in 1974, working under Sir George Porter. He spent a total of 14 years at the Royal Institution, including terms as Dewar Research Fellow, 1977–1988, and Assistant Director of the Davy-Faraday Research Laboratory, 1982–1988. He moved to the University of Texas at Austin in 1988 to become Director of the Center for Fast Kinetics Research. This was followed by a short stay at the Université Louis Pasteur in Strasbourg. In 1999, he took up the position of Professor of Physical Chemistry at Newcastle University. He has maintained a strong interest in artificial photosynthesis. Among his many awards are the Corday-Morgan Medal and Prize, 1984, the first Prix Grammaticakis-Neumann en Photochimie, 1985, and the RSC Chemical Dynamics Award, 2011. He has published more than 400 papers in the areas of molecular photophysics, artificial photosynthesis and electron/energy transfer.