DISCUSSIONS

Natural and artificial photosynthesis: general discussion

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Filippo Monti, John M. Kelly, Elizabeth Gibson, Marcelino Maneiro,
Anthony Harriman, Albert Ruggi, Elena Galoppini, Randolph Thummel,
Julia Weinstein, Johannes Vos, Osamu Ishitani, Devens Gust
and Alejandro Díaz-Moscoso

Qing Pan opened the discussion of the introductory lecture by Devens Gust: You mentioned that the photochemical logic gates can switch in picoseconds, does this mean they could be used for electronic systems faster than gigahertz?

Devens Gust replied: The rate constants for the photochemical reactions are indeed on the picosecond time scale, for many of the reactions. However, the actual time necessary for switching a macroscopic sample depends on the light intensity and the irradiation time. The more intense the light, the shorter the time necessary to achieve sufficient photoisomerization to switch an output ON or OFF. It would be very difficult to achieve switching times on the picosecond time scale for a macroscopic sample size.

Qing Pan said: An ensemble of molecules are needed. Would the integration of many logic gates into a circuit create a heat dissipation problem which may also affect the stability of the molecules?

Devens Gust responded: The photochemical reactions would indeed generate some heat that would need to be dissipated, just as heat dissipation is a requirement for electronic computers. Thus, mechanisms for cooling would be needed for any large, rapidly switching devices based on photochemical switches. Very high temperatures would, of course, accentuate any thermal decomposition reactions.

Jana Rohacova asked: Have you also designed a logic gate system combining photochemical and chemical or other stimuli? Would such a device find any applications besides sensing, and would there be any advantage or disadvantage?

Devens Gust answered: We have not studied many systems of this type, but others have done so and they give interesting results. We did prepare one logic gate that uses both light and magnetic inputs. Devices that have chemical inputs are excellent for sensing and perhaps tracking the history of a nanoparticle or something of that sort. Chemical inputs have a disadvantage for repetitive applications in that they require constant addition of chemicals as inputs and generate reaction products that must be removed if the system is to continue operation indefinitely.

Cornelia Bohne commented: In your logic gates changes in intensity were measured at one wavelength. Have you thought about using the additional variable of time for your logic gates since for photochromic compounds irradiation at different times will lead to solutions that could have different colors?

Devens Gust replied: The systems we have worked with have been invariant with respect to time, but you are correct that time could also be a useful variable. For example, at a given irradiation intensity, the time of irradiation will affect the amount of photoisomerization that takes place, and thus the absorption or emission amplitude at a given wavelength. In addition, some photochromes thermally isomerize, and with several of these linked, the color of a solution would change with time, and that could be useful. We have not done any experiments of that type, but they would be interesting.

A. Prasanna de Silva noted: The multi-photochromic systems described by Devens Gust show rich UV-vis spectral signatures for the various states. Using multiple wavelengths at the same time will enable quantum logic gate phenomena. A case with ion-induced variations in UV-vis spectra has been analyzed in this manner.[1]

1 A. P. de Silva and N. D. McClenaghan, *Chem.,–Eur. J.*, 2002, **8**, 4935.

Devens Gust responded: This is true, and a good point. I also pointed out that the molecule I used to illustrate molecular logic can provide different logic functions at the same time using the same two inputs but different outputs.

Gary Brudvig enquired: In natural photosynthesis, green plants are optimized to function at low light levels and utilize photoprotection mechanisms (non-photochemical quenching) to quench excess excitation energy in order to prevent photodamage at high light intensities. However, in artificial systems, it would be desirable to utilize the full solar intensity because this would enable more efficient energy conversion. Would the kinds of photoprotection systems that are in plants be useful for artificial systems?

Devens Gust answered: Analogs of pure photoprotection, such as carotenoid quenching of chlorophyll triplet states to prevent singlet oxygen sensitization, could certainly be useful for artificial photosynthesis. Regulatory systems as exemplified by NPQ in plants are not ideal for the production of solar fuels but are required because the plant is not a perfect device. Human-made devices are unlikely to be perfect as well. I could imagine that in order to make a technological device carrying out multiple-electron reductions function efficiently at lower

light intensities it might be necessary to overdrive it at high light with antennas or sunlight focusing, and thus photoregulation of some type might be needed.

Johannes Vos remarked: There was a question on whether it has been shown that molecular components do become more stable when immobilised. My comment on that is that the incorporation of ruthenium polypyridyl complexes in the Grätzel solar cell has shown that this is the case. Compounds that under irradiation are very unstable in solution are shown to be stabilised on TiO_2 since charge injection to the semiconductor prevents population of metal based excited states that promote decomposition.

Devens Gust replied: We have seen these kinds of effects as well. In addition, when sensitizers are immobilized, reactions between excited sensitizers and other sensitizer molecules are reduced or eliminated.

Dan Nocera opened discussion of the paper by Gary Brudvig: You show the interesting structural peculiarity of OEC, as compared to routine oxo complexes, of an oxygen ligand *trans* to the oxo of the dangling manganese. What can you say about this structure–function element with regard to the activity of OEC?

Gary Brudvig replied: I think this is an important structure–function element for water-oxidation catalysts. In order to activate a terminal oxo ligand of Mn for O–O bond formation, it is important to avoid a strong triple bond between Mn and the oxo, as is present for low-spin square pyramidal $Mn(v)\equiv O$ species. The oxo in these $Mn(v)\equiv O$ species is known to be unreactive. In the OEC, a μ-oxo ligand *trans* to the terminal oxo of the dangling manganese will weaken the Mn–oxo bond of the terminal oxo and help to promote reactivity. A similar motif is observed in our Mn-terpy catalyst, where the terminal water ligand that is hypothesized to form a reactive terminal oxo ligand is *trans* to a μ-oxo.

Dan Nocera remarked: We recently have prepared a manganese oxo that models the dangler in OEC (yet to be published). The oxo causes enhanced lability of the ancillary ligands of Mn and we observe an ensuing acid-base chemistry that is ultimately manifested in redox reactions of the Mn oxo. Most mechanisms of the OEC Mn oxo dangler only consider redox and do not consider an acid-base chemistry induced by ligand dissociation of the ancillary ligands on the dangler Mn oxo. Have you or anybody else considered a redox chemistry of the dangler Mn oxo kicked off by an acid-base chemistry induced by ligand dissociation from the dangling Mn oxo?

Gary Brudvig responded: Acid-base chemistry could play an important role in the mechanism of water oxidation by the OEC. For example, Pecoraro and coworkers have suggested that protonation of an oxo bridge could promote the reaction owing to the marked sensitivity of the reduction potential of the cluster to the protonation state of the ligands.[1]

1 M. J. Baldwin, A. Gelasco and V. L. Pecoraro, *Photosynth. Res.*, 1993, **38**, 303–308.

Dan Nocera commented: In our CoPi water splitting catalyst system and other synthetic OEC systems, the rate determining step of O–O bond formation occurs at the third hole equivalent. The Kok cycle implies a rate determining step of O–O bond formation on the fourth hole. Can you give any comment on the differences between the natural and synthetic OECs?

Gary Brudvig answered: I note that if the resting state of the catalyst is already partially oxidized, then O_2 formation on the first turnover would require generation of fewer than four holes. Thus, photosystem II only requires the generation of three holes for the first turnover, but four on subsequent turnovers. In other systems such as mononuclear Ru water-oxidation catalysts, the O–O bond-forming reaction results in formation of a bound hydroperoxide that requires further oxidation to release molecular oxygen.

Anthony Harriman asked: Are you able to be precise about the state of the catalyst at which oxygen evolution occurs? I refer to the number of photons and/or protons needed to activate the catalyst.

Dan Nocera responded: Yes. Our electrochemical studies have identified that the active catalyst is delivered from a one electron, one proton pre-equilibrium from a Co(III)Co(IV) state. In addition, for all electrocatalysts, we have performed extensive kinetic studies to determine the reaction order in metal, proton, and buffer for not only for oxygen evolution but self-assembly. From these data, we have provided guidelines for self-healing. With regard to the number of photons necessary to activate the catalyst, this value parallels our electrochemical studies. The catalyst is part of a buried junction. Hole and electron equivalents are delivered from the buried photovoltaic. So the redox stoichiometry for the catalysts under electrode and buried junction configurations is exactly the same.

Dario Bassani said: A considerable number of experiments involving isotope effects have been reported in an effort to understand the mechanism of the oxygen evolving complex. Are your kinetic measurements consistent with these measurements?

Gary Brudvig replied: Most of the prior experiments involving isotope effects on photosystem II have involved H/D measurements. These isotope effects are small and consistent with the S-state dependent substrate water exchange kinetics, as discussed by Hillier and Wydrzynski.[1,2]

1 W. Hillier and T. Wydrzynski, *Coord. Chem. Rev.*, 2008, **252**, 306–317.
2 W. Hillier and T. Wydrzynski, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4882–4889.

Andrea Sartorel asked: Does the electronic configuration (*i.e.* spin distribution/electron density) of the Mn4 cluster play a major role in promoting the formation of the O–O bond? Is there a significant change in electronic configuration before or after O–O bond formation?

Gary Brudvig answered: This is an interesting question, but I don't think it can be answered at this time. I think we can exclude a low-spin Mn(V)-oxo species

because such species have been synthesized and show very little reactivity, no doubt due to the very strong triple Mn–oxo bond. Computational studies suggest that a Mn(ɪᴠ)-oxyl species may be involved in formation of the O–O bond, but to date such a species has not been observed experimentally. On the other hand, a high-spin Mn(ᴠ)=O species could be involved, as recently reported by Borovik and coworkers.[1,2]

1 T. Taguchi, R. Gupta, B. Lassalle-Kaiser, D. W. Boyce, V. K. Yachandra, W. B. Tolman, J. Yano, M. P. Hendrich and A. S. Borovik, *J. Am. Chem. Soc.*, 2012, **134**, 1996–1999.
2 R. Gupta, T. Taguchi, B. Lassalle-Kaiser, E. L. Bominaar, J. Yano, M. P. Hendrich and A. S. Borovik, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 5319–5324.

Anthony Harriman remarked: You present your arguments in the form of a single mechanism operating for water oxidation and try to rationalize which of the two mechanisms is most likely under given circumstances. Is it not possible that both mechanisms operate simultaneously? Nature seems to be very good at adapting to specific requirements and so there seems to be a case for having multiple pathways just in case of problems.

Gary Brudvig replied: Of course, this could be possible, although we have no evidence for or against multiple pathways at the present time. I hope we will be able to answer this question in the future with new experimental results to test the mechanism.

Anthony Harriman asked: Can you provide some general information regarding the stability and turnover numbers or frequencies for photosynthetic oxygen evolution? In particular, what are the lifetimes of the intermediate states in the Kok cycle? Also, what kind of turnover is observed with respect to the manganese catalyst? This kind of information is crucial for the development of artificial analogues, where current turnover numbers are a few hundred at best.

Gary Brudvig replied: All of the intermediate S-states in the Kok cycle prior to the S_4 state are relatively stable with lifetimes on the order of tens of seconds to minutes or longer (depending on the redox poise of the sample). The slowest step in the Kok cycle is 1–2 ms, giving the manganese catalyst the capacity for a turnover frequency up to 1000 s^{-1}. However, this high rate cannot be realized because the rate-limiting step for photosystem II turnover is reduction and exchange of plastoquinone, which limits the turnover frequency to ∼50 molecules of oxygen per second. The turnover number is limited by photodamage of photosystem II, mostly due to formation of reactive oxygen species that damage the protein. Based on a measurement of the quantum yield of photodamage, one can estimate a turnover number of the photosynthetic manganese catalyst on the order of one million.

Stafford Sheehan commented: The ground state in a molecular complex is not always the same as the fully reduced state, as is seen in some man-made water oxidation catalysts. In some cases, metal complexes are partially oxidized in their resting state, which facilitates entry into the catalytic cycle for water oxidation by requiring fewer than four holes for the first turnover.

Gary Brudvig responded: This is a good point and also relates to the S-states in photosystem II, all of which are relatively stable prior to formation of the transient S_4 state that forms O_2. If a synthetic water oxidation catalyst could be stable in all of its oxidation states prior to the state that forms the O–O bond, then accumulation of the first three holes may not be so demanding. As you suggest, if the resting state of the catalyst is already partially oxidized, then O_2 formation on the first turnover would require generation of fewer than four holes. Similarly, photosystem II only requires the generation of three holes for the first turnover.

Dan Nocera opened discussion of the paper by Julia Weinstein: Why is the long-lived excited state of a Pt center needed to kick-off charge separation? In your studies the charge separated state is prepared on vibronic timescales (less than 50 ps). Why then is a long-lived MLCT excited state needed? For instance, why can't the Pt metal be substituted by first row transition metals? Is the same effect seen? Why are long-lived metal to ligand states needed?

Julia Weinstein replied: Long-lived CT states have been perceived for some time to be a requirement for, for example, DSSC. In our case, a long-lived MLCT is not required. The initial MLCT state is formed very quickly, and is short-lived, branching over several pathways on the time-scale comparable with vibrational relaxation. This is the key requirement for the effect to work. Replacing the Pt centre with a first row transition metal is definitely an exciting possibility which we must explore. One further consideration here comes from the fact that an open-shell transition metal introduces a large perturbation to the electronic structure of the molecule, leading to a very complex energy landscape. This complexity is a requirement to achieve excited-state branching to multiple products on ultrafast timescales. Moreover, having a heavy atom adjacent to the vibrations being excited is important because it helps in energetically isolating the nuclear mode, which as a result can retain its vibrational excitation for longer than in most condensed phase systems.

Villy Sundstrom commented: In our work on the Ru–Co transition metal complexes we saw a strong dependence of the Ru to Co electron transfer rate on the type of bridge. A conjugated bridge results in an approximately thousand fold faster electron transfer than a saturated aliphatic chain. We interpret this difference as a result of the aromatic bridge being involved in low lying excited states, which speeds up the electron transfer substantially. I notice that when you introduce an aliphatic group in your bridge you obtain a slow-down of the electron transfer and reduction of the IR pump effect. Could this also be a result of conjugation between the donor and acceptor, and the different bridges being involved to a different extent in the excited state?

Julia Weinstein replied: Indeed, when the $-CH_2-$ linker is removed, the donor (PTZ) becomes conjugated with the –CC– triple bond directly attached to the Pt centre. It is important that the consequences of such a change are multifold: it changes the energetics of electron transfer, the energy difference between the initially formed CT state and all other states involved.

Villy Sundstrom continued: The IR pump blocks the electron transfer to the acceptor. Can you from your data see where the excited state population goes? Is there a branched process and you see increased population of other excited state species? Can you speculate what the mechanism is to this change in excited state relaxation pathways? The IR pump is reminiscent of a coherent control experiment, do you think that such an experiment would shed light on the relaxation processes and potential energy landscape?

Julia Weinstein answered: The excited state population that is blocked from forming the full charge-separated state instead forms a π–π* long-lived intraligand triplet state localised on the acceptor (^{3}A). So indeed this is a branched process where a decrease in one product state results in an equivalent increase in another product state. The mechanism is thought to be a complex combination of effects which effectively drives the system across a conical intersection. One can speculate that the acetylide mode ($\sim$1800-1900 wavenumbers) that is excited is associated with the co-ordinate for this reaction: it could be part of a collective motion of several modes that increases and decreases coupling between different excited states. What we know for sure is that as far as our experimental setup can resolve, the effect is impulsive; *i.e.* as soon as we introduce the IR pump, we completely modify the excited state evolution prior to intramolecular vibrational redistribution from the CC ($v = 1$) mode. So we believe we are intrinsically perturbing the vibronic interactions that dictate the electron transfer pathways. The fact that the system branches to several excited states is already an indication that fluctuations in the energetics of the chromophore or its environment can alter the excited state pathways – we do this in a controlled manner with the IR pump.

Coherent control experiments would certainly be interesting! These are different experiments to those that we are able to perform at present. It can be very difficult to extract information from shaped UV-vis pulses that are optimized by learning algorithms, so it would be challenging but possible to extract detailed information on the potential energy landscape. Much information could also be inferred, especially with controlled phase modulations in the weak-field excitation regime, on the role of vibrational or vibronic coherence in the excited state dynamics.

Antonin Vlcek asked: You have demonstrated that IR excitation of the C≡C stretching vibration in a photointermediate (a CT state) changes the branching ratio between the following reaction pathways, namely inhibiting charge separation. Does it mean that the excited vibration is also the vibration active in the IR control or is it possible that the vibrational energy is first dissipated into other vibrations and/or causing some molecular distortion that affects the CT state evolution?

Julia Weinstein replied: This is an excellent question. We do know that the effect is mode-specific to pumping the bridging acetylide stretch vibration in the 1800–1900 wavenumber range. Exciting other high-frequency vibrations in the 1500–2100 cm^{-1} region *i.e.*, those attainable with our set-up, does not cause a response. However, one can not conclude that this is the vibration which is responsible for the effect, as the acetylide mode is anharmonically coupled to

many low-frequency modes. There is a little more discussion on this point in our recent Nature Chemistry article, where we consider several systems.[1]

1 M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. H. M. Meijer and J. A. Weinstein, *Nat. Chem.*, 2015, **7**, 689.

Filippo Monti inquired: You have mentioned calculations which could potentially validate the interpretation of the experimental data reported in your paper. What kind of calculations did you carry out on these systems? I assume that these molecules are too big to rigorously take into account vibronic coupling, as one would do using, for instance, CASSCF and dynamic calculations.

Julia Weinstein responded: The computational studies, conducted by Dr Anthony Meijer and Theo Keane at the University of Sheffield, used TD-DFT to investigate the properties of the excited states of these molecules. The ground and excited state potential energy surfaces were examined by scanning along the vibrational coordinate that corresponds to the vibration excited by IR pump in the experiments. These calculations showed a crossover between the MLCT state (the target of IR pumping) and the CSS (the state which is 'switched off' in the experiments) as the coordinate is extended, with the degree of extension required for crossover in agreement with the relative efficacy of the 'vibrational control' effect seen experimentally. For specific details of the methodology behind the calculations, please see our previous work[1], in particular Section 6 of the SI. We are currently investigating higher level methods to probe our hypothesis.

1 M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. H. M. Meijer and J. A. Weinstein, *Nat. Chem.*, 2015, **7**, 689.

Qing Pan noted: In your work the IR probe arrived 1 ps later than the first pump. This length of time reminds me of the very recent work done by Benjamin Dietzek, which concluded that the coherence still exists after 1 ps.[1] So I think this result might be also relevant to your work.

In addition, I think if you change the phase of the IR pump pulse, you may further actively control the population ratio/percentage in a so-called 'coherent control' manner.

1 M. Wächtler, J. Guthmuller, S. Kupfer, M. Maiuri, D. Brida, J. Popp, S. Rau, G. Cerullo and B. Dietzek, *Chem.,–Eur. J.*, 2015, **21**, 7668.

Anthony Harriman commented: There are known examples when oligothiophenes, and related polycycles, become more planar under excitation and this geometry change causes marked effects for the emission spectral properties. Do you see similar behaviour with your molecular systems?

Julia Weinstein responded: Using transient absorption spectroscopy we have monitored in detail how stimulated emission from the initial CT state evolves in the first few picoseconds following excitation.[1] This indeed revealed that there are significant conformational changes accompanying the formation of the MLCT or charge separated species. However they are very difficult to deconvolute from the more general processes such as vibrational relaxation and solvent reorganisation as all of these changes occur on similar timescales. Our DFT calculations detailed

in the aforementioned paper also provide detail on the change in geometry between the ground state and lowest excited state in these systems, but not on the intermediate states.

1 P. A. Scattergood, M. Delor, I. V. Sazanovich, O. V. Bouganov, S. A. Tikhomirov, A. S. Stasheuski, A. W. Parker, G. M. Greetham, M. Towrie, E. S. Davies, A. J. H. M. Meijer and J. A. Weinstein, *Dalton Trans.*, 2014, **43**, 17677.

Per-Arno Plötz asked: As written in your paper, it was possible to block a charge transfer process into charge separated states by IR pertubation of certain vibronic modes. Are there systems and modes where this does not work and what can be generalised from these findings?

Julia Weinstein replied: As the paper details, the effect depends on a range of parameters that must be satisfied. We have tried many systems (such as the NDI-containing complexes described in this paper) which do not exhibit the IR-control effect. The effect is very mode-specific – only when exciting the CC stretch during charge transfer can we affect the excited state pathways.

Analysing the body of the data on several series of systems (reported in this paper, as well as in the preceding Nature Chemistry and Science papers),[1,2] some essential requirements (but not necessarily all of them) have been proposed here.

1 M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. H. M. Meijer and J. A. Weinstein, *Nat. Chem.*, 2015, **7**, 689.
2 M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. H. M. Meijer, M. Towrie, and J. A. Weinstein, *Science*, 2014, **346**, 1492–1495.

Gary Brudvig inquired: Could your experiment help to differentiate whether the coherences observed in natural photosynthetic pigment–protein complexes arise from electronic or vibrational coherences?

Julia Weinstein answered: These experiments can't directly probe the difference between electronic, vibrational or mixed vibronic coherences due to the limit in time resolution. However what it does tell us is that vibronic interactions seem to play an extremely important role in charge transfer in these types of complexes, and this is adding to a growing body of evidence that vibronic coupling occupies a central role across many molecular systems – from small organic molecules through to those operating in photosynthetic organisms. Similar experiments were performed in bulk heterojunction organic photovoltaics with shorter IR pump pulses where the charge separation is thought to be aided by vibronic coherence, similarly to charge separation in photosynthetic reaction centres.

Gary Brudvig asked: Does your work help us understand quantum coherences in natural photosynthesis?

Julia Weinstein responded: The quantum coherences in PS are a really exciting area. The ~1.5 ps time resolution of our experiments does not allow us to make a conclusion whether or not a coherent mechanism being responsible for the observed modulation. Indeed we are unable to experimentally determine whether the mechanism is related to any vibrational/vibronic coherence. An analogous

experiment but with a much shorter time resolution may potentially contribute to the question.

Villy Sundstrom added: As you know, the nature of quantum coherence in photosynthetic pigment protein complexes as observed in 2D electronic spectroscopy has been intensively discussed. Two opposing pictures have been discussed in the literature, pure electronic or vibrational coherence. There is now a growing understanding that the origin in many cases is probably of mixed vibronic origin, and it is the mixing with vibrational coherence that contributes to the very long picosecond timescale dephasing times. That the coherence, whatever its nature, is present in some pigment proteins is clear, but its importance for the efficiency of photosynthesis is in my mind not at all clear. In our own work on the RuCo donor–acceptor complexes we have not observed any coherences so far, so the results do not provide much insight into this issue. Probably the electron transfer, a few hundred femtoseconds, is too slow for coherences to play a major role.

Frederick Lewis opened discussion of the paper by Villy Sundstrom: In the system with the conjugated bridge, while calculations show HOMO and LUMO orbitals localized on metal centre and not the bridge, the systems are conjugated. How do you view the interaction of the bridge with the two metal centres in the excited state? Is there ever electron density localized on the bridge?

Villy Sundstrom responded: I am not sure I fully understand the question in the way it is formulated. This is the way I see the difference between the two RuCo molecules, with the conjugated and saturated bridge. In the molecule with conjugated bridge, both calculations and optical transient absorption show that the excited state involves the bridge, *i.e.* there is electron density on the bridge in the excited state. Therefore the electron transfer from Ru to Co is very fast, on the few ps time scale. The saturated bridge lies much higher in energy and there is no sign of its involvement in the excited state, either from calculations or transient measurements. For the molecule with the saturated bridge the electron transfer is therefore a long-range electron tunneling process, which can be expected to be very slow due to the long distance between the metal centers (~1.5 nm).

Frederick Lewis asked: In the system having a saturated bridge are the bridge orbitals too high in energy to be involved in same way, or do they still play some role in mediating the electron transfer process? Since there is no through-bond coupling for the bridge consisting of two methylenes, the situation is reminiscent of the weak through-bond coupling in proteins, rather than the strong coupling between stacked bases in DNA.

Villy Sundstrom replied: As I described in the response above, this is precisely how we see it. In the molecule with the saturated bridge its energy is much too high to be involved in the lower excited states. This is apparent from the calculations and the optical TA measurements provide no evidence for involvement of the bridge.

Stafford Sheehan asked: Do the metal–ligand disassociation constants vary with the change in rigidity of the linker, and if so, could this have a greater effect on backward electron transfer than other conformational changes?

Villy Sundstrom answered: We do not observe any dissociation of the ligands in the studied complexes, thus I do not believe that this process influences the electron transfer.

Cornelia Bohne enquired: Can you comment on how much information is required from transient absorption experiments to make the assignments of the transient X-ray studies and if model studies are required? As a follow up have you encountered ambiguities in the assignments for the transient X-ray studies?

Villy Sundstrom answered: In general, it is always good to have as much information as possible from conventional transient absorption (TA) studies. TA is a powerful tool to get the dynamics of the optically bright states. The spectral information from the TA is often not very informative and that is where the X-ray studies can help. For assignment of the measured transient X-ray spectra it is key to have good reference spectra, which can be obtained by measuring ground state spectra of species corresponding to an intermediate or product of interest. For instance, if the photoinduced reaction implies the oxidation of a Ru^{2+} species to a Ru^{3+} species the measured transient X-ray difference spectrum is compared to the difference spectrum that can be constructed from a measurement of the Ru^{2+} and Ru^{3+} ground state spectra. Similarly, if a reaction sequence contains several species with different oxidation and spin states, ground state difference spectra are constructed from measurements of the relevant ground state species having the expected oxidation and spin states. This is generally a reliable method and of course depends on availability of the relevant ground state species. Measured reference spectra are generally complemented by calculated ones using, for instance, time dependent DFT.

Stafford Sheehan questioned: During X-ray measurements, how stable is the complex? Is 100 percent of the complex still there at the end of the experiment, and if not how is this mitigated?

Villy Sundstrom responded: Stability of the investigated molecules is of course a key issue and very dependent on the particular molecule. In this case of the RuCo complexes the stability was very good under inert atmosphere and there was almost no degradation during hours of measurements. The difficulty of maintaining a constant sample concentration during the course of the experiments was perhaps somewhat unexpected, to avoid/compensate for evaporation of the acetonitrile solvent. This problem was solved by monitoring the absorbance of the sample and slowly adding solvent to keep the absorbance of the main visible absorption band constant.

Christopher Lemon asked: Have you performed nitrogen X-ray absorption experiments for your systems? It would be very interesting to monitor the evolution of the charge separation over the ligands at different time delays, particularly for the construct with the tetrapyridophenazine (tpphz) bridge. In principle, you could observe the electron migration from the Ru-bound bipyridine to the tpphz bridge to the Co-bound bipyridine. Are there any practical limitations to this type of experiment?

Villy Sundstrom replied: This is a very interesting suggestion, which we have considered but not yet performed. All experiments so far are hard X-ray experiments probing the metal centers, but it would indeed be very interesting to view the migration of the electron through the molecule. In this molecule with a few nitrogen atoms, I believe this would be possible using the time resolution offered by the X-ray FELs.

Franco Scandola remarked: In your ruthenium–cobalt dyad, forward photo-induced electron transfer is followed by very fast relaxation leaving the Co(II) center in a high-spin state. Does the (slow) back reaction involve thermally activated high-to-low-spin conversion in Co(II), prior to electron transfer to Ru(III)? Have you measured the temperature dependence of this reaction?

Villy Sundstrom responded: We have not measured the temperature dependence of the recombination reaction. As you suggest, the rate limiting step could be either the electron transfer itself or the high-to-low spin conversion, and the temperature dependence could perhaps tell which. This is an experiment for the future.

Julia Weinstein noted: The excitation wavelengths used might populate several excited states. Was there any effect observed of the excitation wavelength on the X-ray data?

Villy Sundstrom replied: For the RuCo complex with the conjugated bridge there is an excitation wavelength dependence which can be explained with a model where the Franck–Condon state branches out into two parallel intra-molecular ET pathways. In the first route, the bridge-localized CT state is populated instantaneously.

John Kelly opened discussion of the papers by Frederick Lewis: My questions relate to the mechanism and energetics, which, of course, depend on the oxidation potential of the nucleobases.

Firstly could you comment on the values you have taken for both G and A? (I note, for example, that you have adopted a value of 1.44 V for A, which is lower than generally assumed.)

Your diagrams in Schemes 1 and 2 of your paper suggest that there should be activation energies in some cases. Have you tried to determine whether this is the case by carrying out temperature studies?

Have you considered whether the process could proceed by proton-coupled electron transfer? For example do we know whether the rate of reaction changes in D_2O?

Frederick Lewis answered: Your first point is an important one. Since oxidation potentials have not been directly measured within DNA, we have used potentials for the individual deoxynucleosides measured in polar aprotic solvents such as DMSO or acetonitrile. We initially used values from the literature, but later measured them ourselves so as to have a consistent set of values measured under the same conditions. Base stacking, and to a lesser extent, hydrogen bonding, certainly will change the values within duplex DNA relative to those for the

nucleosides or nucleotides. We use a lower value for adenine in duplex DNA so that it will be more similar to the value for guanine, thus avoiding having to account for the failure of G to act as a deep hole trap in an A-tract. I note that some workers have been less than rigorous in their choice of values for redox potentials, leaving a trail of self-citations that leads to a dead end. We have measured the temperature dependence of charge transport dynamics in several of our systems and find that charge transport is either weakly activated on unactivated, in agreement with current theories for charge transport.

We have not determined the dynamics of charge separation in D_2O. Since the overall charge separation process involves several steps and global analysis of the kinetic data is necessary to obtain estimates for the individual steps, I think it unlikely that we would be able to assign a small isotope effect to a specific step.

Proton-coupled electron transfer is very in vogue. However, there is no direct experimental evidence that it occurs on time scales that are competitive with the charge separation and recombination processes that I have described. Giese estimated a rate constant of *ca.* 10^5 s^{-1} for deprotonation of the guanine cation radical.

Dario Bassani asked: The introduction of an abasic site next to the hairpin is likely to introduce considerable conformational flexibility in the vicinity of the chromophore. Considering that the latter possess different lengths and connecting tethers, can this contribute to variations in the rates for charge injection?

Frederick Lewis answered: We were concerned about the structure of hairpins having a cyclohexane base pair analog adjacent to the hairpin linker. We relied on the structural characterization of the cyclohexane base pair carried out by the Nagoya group in our hairpin design. Hairpin structures are consistent with the observed melting temperatures and CD spectra, as well as the results of steady state fluorescence and electron transfer dynamics. While none of these by themselves constitute a proof of structure, they do eliminate structures in which the hydrophobic cyclohexanes are flipped out and not present between the hairpin linker and base pairs.

Karl Börjesson commented: In your work the sensitizer is located on the end of the DNA duplex. How would it affect the system if the sensitizer instead was located in the center of the DNA duplex?

Frederick Lewis replied: We have done such an experiment by placing a derivative of perylenediimide (PDI) within the DNA duplex. Upon excitation singlet PDI injects holes in both the 3' and 5' direction with comparable rates when A–T base pairs are located on both sides. When a G–C base pair is located near PDI then hole injection is faster in the direction of G.

Frank Würthner asked: The design of your supramolecular systems looks beautiful. In particular systems **NDI-SD-1** and even more **NDI-SD-2** with its gradient look perfect. Therefore I am wondering why the quantum yields for charge separation remain low, *i.e.* <0.2 which is much lower than those for charge separation in natural reaction centers?

Frederick Lewis responded: Even with the charge gradient in **NDI-SD-2**, charge recombination from the contact radical ion pair can compete with charge transport from the AA sequence into the G-block. Charge recombination is faster for **NDI** than for stilbenediamide because the energy gap is smaller for the stronger electron acceptor.

Frank Würthner continued: Related to my former question, could it be that conformational inhomogeneity is the reason for lower quantum yields for charge separation in your artificial systems compared to natural reaction centers? In the latter the proteins provide a quite rigid dye organization whilst small artificial self-assemblies including your DNA-derived architectures should be conformationally much more flexible.

Frederick Lewis replied: We have adopted two experimental strategies which make DNA more rigid: the use of Mg^{2+} in place of Na^+ cations and the use of "locked" nucleic acids to replace some or all of the nucleic acids in one of our hairpins. In both cases hole transport is slower and more rigid than in the more flexible DNA structures.

Dan Nocera asked: How general do you think that the effect of stacking residues may be in biology as a means to adjust energetics? You show the importance of guanine stacking in DNA. Do you think that the effect might generally extend to other types of residues, aromatic amino acids for instance?

Frederick Lewis responded: It certainly is important in shifting the absorption maxima of light harvesting antennae. I would think it would be less important in proteins, but this is just a guess on my part since I am not familiar with that literature.

Anthony Harriman addressed Dan Nocera: With reference to your stacked tyrosine-based arrays, do you see evidence for coupled proton/electron transfer? This might offer a quite different situation to what is found in DNA.

Dan Nocera answered: Indeed this is correct. The problem with tyrosine is more complex than DNA base pairs because it involves PCET, not just ET. For our tyrosine dyads with a rigid spacer, we see that the hydroxide group on the adjacent phenol moiety has an effect on modifying the electronic density (thermodynamics) within the dyad as well as coupling the two units *via* hydrogen bonding interactions (kinetics). The phenols in the dyad behave as a cooperative redox unit rather than two independent residues largely due to PCET. The first oxidation is highly proton dependent and facilitates the deprotonation of the phenol and its subsequent oxidation, while the second oxidation is proton independent.[1] You are correct, these tyrosine dyads are similar to two stacked guanine bases in DNA in form but not in specific mechanism. ET dominates for stacked base pairs whereas as PCET dominates for stacked tyrosines.

1 B. J. Koo, M. Huynh, R. L. Halbach, J. Stubbe and D. G. Nocera, *J. Am. Chem. Soc.*, 2015, **137**, 11860–11863.

Jana Rohacova opened discussion of the papers by Randolph Thummel: In your photochemical O_2-evolution system, a 470 nm light was used, however under this condition both the photosensitizer and catalyst absorb the light (although the PS is present in significant excess). Does the catalyst undergo some structural photochemical-induced changes involved in the photocatalytic cycle, or does it cause only an inner filter effect?

To overcome the water-solubility issue, would it be synthetically possible to introduce a methylsulfonate or methylphosphonate substituent or similar (but at the same time not to significantly change redox properties) instead of a simple methyl group?

Randolph Thummel responded: A potential problem with the sensitizer and catalyst absorbing in the same region is more or less nullified by the concentration difference since the sensitizer is present in large excess. This does become a problem, however, in the design of photosensitizer–catalyst dyads where both species are restricted to being equal in concentration. We have addressed this to some extent by using auxiliary ligands that red-shift the absorption of the catalyst.

Addressing solubility issues by appropriate functionalization is fairly straightforward. We can introduce acid (COOH, SO_3H) or alcohol groups. The counterion can also have a big effect on solubility.

Albert Ruggi remarked: In Fig. 5 of your paper, the MS of a $[6 + O]^{2+}$ species is shown. This peak is attributed to a Ru(IV)–O species, however on the basis of the MS it is impossible to exclude the formation of an oxidized ligand (*e.g.* N–O). How can you discriminate between these two possibilities? Do you have any data about the oxidation of the ligand?

Randolph Thummel responded: We can not readily distinguish whether the oxygen goes to the Ru center or the ligand by MS. We can detect, however, both the mass (complex + O) and the charge (+2). If it is oxidation of the ligand, should we see a +3 species? This is the same problem in Lau's paper where they isolated a Ru(III) di-N-oxo (+3) species but observe a Ru(III) di-N-oxo (+2) species in MS.[1]

1 Y. Liu, S.-M. Ng, S.-M. Yiu, W. W. Y. Lam, X.-G. Wei, K.-C. Lau and T.-C. Lau, *Angew. Chem.*, 2014, **53**, 14468.

Albert Ruggi remarked: From the Pourbaix diagram in Fig. 2 of the paper it is evident that above 1.2 V (*vs.* SHE) only the Ru(v) species are present. In your experiment ceric ammonium nitrate is used as an oxidiser (E° = +1.61 *vs.* NHE), however in the proposed catalytic cycle (Scheme 2) Ru(IV) is proposed as the resting state. How can you explain this?

Randolph Thummel replied: We do not claim that the Ru(IV) species is the "resting state". Actually, I am not very clear about the meaning of "resting state". At a thermodynamic steady state, the distribution of intermediates involved in the catalytic cycle depends on their relative energy or Gibbs free energy change (equilibrium constants) for every single step. In earlier work we have estimated that the Ru(v)=O to Ru(IV)–OO step has the greatest energy change. So I guess the Ru(v)=O is dominant. At time = 0, there is only the Ru(II) species. It may take

some time to reach the catalytic steady state, even though electron transfer is usually fast. This comes back to the induction period problem which is a kinetic issue. It corresponds to the slowest process from the initial Ru(II) state to the steady state.

Gary Brudvig asked: This question relates to the mechanism of the mono-nuclear Ru water oxidation catalysts. We and others have found that when these catalysts are immobilised on an electrode surface they have no catalytic activity. This suggests a dinuclear mechanism for the O–O bond forming reaction. In this regard, it is interesting that the *t*-butyl derivative has no lag phase, but has very slow turnover, relative to the methyl derivative. Could this be due to the steric bulk of the *t*-butyl derivative that prevents dimerization? Perhaps, the lag phase is due to the precatalyst being converted into a catalytically active dinuclear species? Have you looked at the order of the lag phase?

Randolph Thummel responded: For the type 1, 2, and 3 Ru catalysts that we have examined, they all follow first order kinetics which argues against a bimo-lecular O–O formation step. The tetra-*t*-butyl system is somewhat different in that it is slow but fairly stable. We interpret this as possibly meaning that the *t*-butyl groups may hinder a rate limiting attack by water but also inhibit oxidative degradation of the catalyst. Since there is no reaction during the "lag phase", I am not sure how to evaluate this kinetically.

Anthony Harriman commented: Is it possible to comment on the rate and/or yield of oxygen evolution from PS2? It's interesting in the context of purely arti-ficial analogues to make a critical comparison with the photosynthetic organism but data on the latter can be hard to find. Clearly, the rate of oxygen evolution is highly dependent on conditions but it would be valuable to have a crude idea of how much oxygen is produced from a square meter of green plant.

Gary Brudvig commented: In the field, the efficiency of photosynthesis is not very high because plants have adapted to function best under low light and use quenching mechanisms to dissipate most of the excitation energy absorbed under high light conditions. Thus, the rate of oxygen produced by plants in the field is far less that the maximum rate of photosystem II turnover. The short-term efficiency of solar energy utilization by plants in the rapid growth phase is 3–4%, as discussed by Blankenship *et al.*[1]

1 R. E. Blankenship, D. M. Tiede, J. Barber, G. W. Brudvig, G. Fleming, M. Ghirardi, M. R. Gunner, W. Junge, D. M. Kramer, A. Melis, T. A. Moore, C. C. Moser, D. G. Nocera, A. J. Nozik, D. R. Ort, W. W. Parson, R. C. Prince and R. T. Sayre, *Science*, 2011, **332**, 805–809.

Randolph Thummel commented: My understanding of turnover number (TON) is that it is the number of times the catalyst "turns over" before becoming inactive. In some instances this number can be very concentration dependent. Also TON should be cited with reference to a particular time framework (*i.e.* one hour).

Stafford Sheehan asked: There are reports of molecular Ru complexes degrading to ruthenium oxides and thereby becoming more active for water

oxidation. Do you know how the activity of these compounds would compare with ruthenium oxide?

Randolph Thummel answered: We have examined RuO as an oxidation catalyst and it produces O_2 but very slowly. The rate is comparable to our poorest catalysts which in fact may be decomposing to RuO. We now use DLS (dynamic light scattering) to analyze reaction solutions after O_2 evolution has ceased to verify the non-existence of RuO nanoparticles.

Dan Nocera remarked: Some researchers have reported water splitting catalysts with high activities only being achieved by chemical oxidation, not electrochemical oxidation. This always is a cause for concern because the chemical oxidants rather than the catalyst are the reason for water splitting activity. Do your compounds work equally well with chemical and electrochemical oxidation?

Randolph Thummel replied: The commonly applied sacrificial oxidant, cerium(IV) ion, oxidizes water to dioxygen only at a very slow rate. In our previous study,[1] CV of complex 3 showed salient catalytic current under moderately basic aqueous conditions (pH = 9). At pH 1.0, however, the catalytic current is suppressed and becomes insignificant. This is probably ascribed to the slow $[Ru^V(O)]^{3+} + H_2O$ to $[Ru^{IV}(OOH)]^{3+} + H^+ + e^-$ step that is not favored kinetically under acidic conditions. In other words, the time scale of a classic potential sweep measurement is not long enough to reach a steady catalytic state from the point of the $[Ru^V(O)]^{3+}$ intermediate. Therefore, specific evaluation of catalytic activity by electrochemistry was not performed in this work. This will be considered on analogue complexes under basic conditions in a future study.

1 J. T. Muckerman, M. Kowalczyk, Y. M. Badiei, D. E. Polyansky, J. J. Concepcion, R. Zong, R. P. Thummel and E. Fujita, *Inorg. Chem.*, 2014, **53**, 6904.

Dan Nocera said: In your monomer mechanism, the activity of water splitting is reduced when an equatorial ligand limits access of water to the coordination sphere. However, the Fe–O–Fe compound exhibits high activity, even though the equatorial waist is contracted, thus limiting the access to water. What is the mechanism for water oxidation by the Fe–O–Fe complex? Is it the same or different than that you propose for the monomeric catalysts?

Randolph Thummel responded: The mechanisms for the mononuclear Ru catalysts and the dinuclear Fe–O–Fe catalyst are very different. The Ru catalyst has no coordinated water but after two one-electron oxidations is then attacked by water to give a 7-coordinate species. This process is sensitive to the steric environment around the Ru center, particularly the external N–Ru–N angle. For the Fe system we suggest that water attacks a dinuclear Fe–O–Fe=O species. This process is less sensitive to the ligand environment. In the near future we will examine Fe complexes of substituted derivatives of ppq to better understand this process.

Dan Nocera commented: Per Marcus–Hush theory, usually an O atom between two redox centres results in split redox waves. In your Fe–O–Fe dimer however, you see one two-electron wave with no splitting. Why is that?

Randolph Thummel replied: The current amplitude observed for the first oxidation of the dimeric Fe–O–Fe catalyst is more than twice as great as that observed for the second oxidation process, suggesting that the first oxidation is likely a two-electron process. This process can be tentatively attributed to the simultaneous oxidation of the two Fe^{III}-centers ($Fe^{III}Fe^{III} \rightarrow Fe^{IV}Fe^{IV}$). The observation of a single two-electron wave can be explained in two ways. In one case the two Fe centers do not interact at all and thus both oxidize at the same potential but this explanation seems unlikely since the two Fe centers are separated by only one atom. More likely, the Fe^{III}(ppq) core (Cl–Fe^{III}(ppq)–O–Fe^{III}(ppq)–OH_2) could behave as a single species and undergo a two electron oxidation. This explanation would agree with electrochemical theory which states that the current passed for a one electron process is equal to $n^{\frac{1}{2}}$ which equals 1.0 when $n = 1$. Similarly, the current passed for a two electron process is equal to $n^{\frac{3}{2}}$ which is 2.82 for n = 2. The current ratio we observe is 2.71. The direct two electron oxidation would afford an $Fe^{IV}Fe^{IV}$–OH_2 species that could then disproportionate with the loss of two protons and two electrons to afford an $Fe^{III}Fe^V{=}O$.

Dan Nocera asked: Have you considered an ECE mechanism for the two-electron wave? Where the first oxidation occurs at the Fe–Cl(ax) centre, this raises the pKa of the water bound to the Fe–H_2O(ax) centre to produce an Fe–OH(ax) centre, which is more easily oxidized than the Fe–Cl(ax) centre. This might lead to a two-electron wave as you observe. Along these lines, if you add base and deprotonate the Fe–H_2O(ax) centre, do you observe an oxidation wave that occurs at a more negative potential relative to the two-electron wave?

Randolph Thummel replied: No, we have not (yet) considered an ECE mechanism. This is an interesting suggestion. We will examine this process in the presence of added base.

Elena Galoppini said: In Scheme 1 of your paper, for the synthesis of the ligands your use both the Friedlander condensation reaction and the organotin coupling. I would like to ask why the condensation was selected for the synthesis of **6**. It seems that a cross coupling between a phen and a bpy would have been equally suitable to construct the same ligand framework.

Randolph Thummel answered: To prepare many of our ligand systems we use both the Friedlander condensation and Suzuki/Stille type coupling. When the appropriate starting materials are available, we prefer the Friedlander since it is a very clean, metal-free, relatively high yield reaction that almost always works. A frequent problem with Suzuki reactions is contamination of the product with triphenylphosphine. Scheme 1 is a good illustration of both reactions.

Elena Galoppini said: This is a more general comment. In this meeting, the photochemical behavior for beautiful systems that often require a fairly complex synthetic strategy has often been reported, but the syntheses were seldom mentioned. As a synthetic chemist I would like to see a bit more emphasis on that. Should there be a "synthetic session" in this type of meeting? Or would it not be appropriate given that the emphasis is on the properties? I would like to know

your opinion on this, as your group develops beautiful synthetic approaches to new metal complexes and in your talk you often emphasize both synthetic methods and properties.

Randolph Thummel replied: I agree completely with this comment. Well conceived ligand synthesis allows us to tailor make ligands for specific coordination environments and applications. In this way we use a "synthesis driven" approach to new, more effective, photoredox catalysts. There is an enormous opportunity for synthetic chemists to make real contributions in this area. The questioner's own scientific contributions are an excellent example of how sophisticated ligand synthesis can play an important role in catalyst development.

Anthony Harriman asked: It's important to replace the sacrificial redox agent with something reversible – better still just use water. Do you have a strategy for effecting such a replacement? I know of only one molecular system that employed non-sacrificial (*i.e.*, iron(II/III) or Hg(I/II)) reagents and I worry about what will happen to your system when the persulfate is eliminated.

Randolph Thummel replied: One cannot carry out water oxidation or reduction independent of each other without some sacrificial species – chemical (Ce(IV)) or electrochemical. The whole objective is to carry out both processes simultaneously such that the electron generated on the oxidative side will be consumed on the reduction side. This is a very tall order. We are just beginning to look at some systems that might show promise in this regard.

Marcelino Maneiro commented: Several Ru(II) complexes are reported as molecular water oxidation catalysts, but there does not appear to be a correlation between the different activity of complexes **3–6** and their structural/physicochemical features. I agree that the redox potentials (in Table 2 of the manuscript) and also the N–Ru–N angles in the equatorial plane are crucial to get good catalytic systems (particularly the large external N–Ru–N angle), but the data given do not explain the different reaction rates for **3–6** in water oxidation experiments. In the case of manganese complexes, we have proposed a better catalytic behaviour when the complex is able to easily coordinate the substrate molecule,[1] and this also could explain the different catalytic behaviour for **3–6**. For our manganese complexes we have established a correlation between the factor of tetragonal elongation and catalytic behaviour. High-symmetry octahedral geometries for the model compounds make the generation of a vacancy difficult and lead to inactive complexes. On the contrary, the more distorted the octahedral geometry the more active the model compound is. This hypothesis about the relationship between the catalytic behaviour and the symmetry of the structure is in accordance with the results of our studies in solution by EPR spectroscopy, but also we have been investigating how to establish a prediction about this activity on the basis of the crystallographic data of the complexes. For the case of the Ru(II) complexes **3–6**, a higher distortion of the octahedral structure could lead to better achievement of the seven-coordinate geometry through water coordination. Thummel *et al.* could carry out CSM (Continuous Symmetry Measures) using .mol files in order to check this correlation. This point is crucial for the designing of new systems and also to understand the catalytic pathway. In absence of the .mol files, from the data taken

in Table 1 of the manuscript for **6**, and previously reported data for **3** and **5** (ref. 2 and 3), an easy alternative crystallographic approach can be done to establish an inverse correlation between the symmetry of the complexes and their catalytic activity. A simple calculation of the differences between axial, inner equatorial and outer equatorial Ru–N distances for **3**, **5** and **6** lead to results that point out that the proposed correlation exists.

1 M. A. Vázquez-Fernández, M. R. Bermejo, M. I. Fernández-García, G. González-Riopedre, M. J. Rodríguez-Doutón and M. Maneiro, *J. Inorg. Biochem.*, 2011, **105**, 1538–1547.
2 R. Zong and R. P. Thummel, *J. Am. Chem. Soc.*, 2004, **126**, 10800–10801.
3 G. Zhang, R. Zong, H.-W. Tseng and R. P. Thummel, *Inorg. Chem.*, 2008, **47**, 990–998.

Randolph Thummel replied: You are most correct. There are subtle features associated with coordination geometry, strain and steric effects that all contribute to the reactivity of various mononuclear Ru complexes as water oxidation catalysts. You might consult a recent paper of ours on that topic.[1] The bottom line is that these Ru complexes are not particularly reactive and thus differences in reactivity are not always easy to understand or explain. For this reason our current efforts are directed more towards the new more reactive earth abundant Fe(III) complexes which seem to show greater promise.

The suggestion to carry out CSM calculations to better understand the catalytic pathway is a good one. We are primarily synthetic chemists but would be interested if such calculations might have some predictive value.

1 N. Kaveevivitchai, L. Kohler, R. Zong, M. El Ojaimi, N. Mehta and R. P. Thummel, *Inorg. Chem.*, 2013, **52**, 10615–10622.

Dan Nocera opened discussion of the paper by Andrea Sartorel: An important factor for water oxidation is to access a Co(IV) formal oxidation state at two centres of the cubane core. Have you performed electrochemistry to ascertain if a second oxidation wave is observed beyond the first oxidation wave of the cubane core? Can a two-electron oxidation be accessed electrochemically?

Andrea Sartorel answered: The cyclic voltammetry of the pristine cubane in acetonitrile shows a first one-electron oxidation at *ca.* 0.7 V *vs.* Ag/AgCl, and a second one-electron oxidation above 1.8 V *vs.* Ag/AgCl generating two Co(IV) centres. A limitation of using acetonitrile is that proton coupled electron transfers cannot occur. Concerning the "active-Co" species, formed from the pristine cubane, we performed the cyclic voltammetry in borate buffer, which shows the appearance of the catalytic wave due to water oxidation. However, electrochemical characterization of the "active-Co" is hampered by the low amount of this species in solution (*ca.* 1% with respect to the pristine cubane). Possibly, fostering the production of "active-Co" could be achieved by changing the aging conditions of the cubane (solvent, temperature).

Dan Nocera commented: I agree with you that, in the mechanism of water oxidation, it is important to remove terminal ligands to allow water access to the redox core. A possible synthetic strategy to remove the terminal ligand is to silylate off the carboxylate. Have you tried to do this? Does this produce an active water splitting catalyst?

Andrea Sartorel replied: We haven't tried yet, but this is a very good suggestion, thank you.

Christopher Lemon remarked: For an aged sample of the cobalt cubane, you observed a complete loss of catalytic activity upon the addition of EDTA. How does this result account for the loss of an acetate ligand, rather than the presence of free cobalt(II) in solution? If this is not due to cobalt(II), as you claim in the manuscript, how do you envision the interaction between the cube and EDTA to result in a loss of activity?

Andrea Sartorel responded: We excluded the presence of Co(II) aquo ions leached from the cubane on the basis of the ^{31}P-NMR line broadening test, and of the fast electron transfer to Ru(III)bpy observed by flash photolysis, while Co(II) gives a much slower electron transfer rate. Concerning the interaction of EDTA and the postulated cubane with an open coordination sphere, this can possibly occur by coordination of an EDTA arm on the apical sites of cobalt centres.

Christopher Lemon continued: With regard to the ^{31}P-NMR line broadening experiment, you report no broadening of the phosphate signal. Indeed, your fresh and aged samples both have a FWHM of 12 Hz. You exclude the presence of cobalt(II) because the sample with 25 μM Co(II) has a FWHM of 50 Hz. To make a valid comparison and exclude the presence of free Co(II), what is the FWHM of the control (Fig. 5a in the manuscript)? This value does not seem to be reported in the manuscript. As a reference, the FWHM of the phosphate control is 7.2 Hz, as reported by Nocera and co-workers.[1]

1 A. M. Ullman, Y. Liu, M. Huynh, D. K. Bediako, H. Wang, B. L. Anderson, D. C. Powers, J. J. Breen, H. D. Abruña and D. G. Nocera, *J. Am. Chem. Soc.*, 2014, **136**, 17681–17688.

Andrea Sartorel replied: The FWHM of the control is the same as the value observed for the fresh and aged samples of the cubane, around 12 Hz.

Paola Ceroni asked: In a previous work on Co(III) cubanes bearing different substituents on the pyridine ligand, you demonstrated a correlation between electronic properties and reactivity. What was the mechanism in that case? Do you observe ligand detachment as in the presently discussed cubane?

Andrea Sartorel responded: The Hammett correlations we reported were ascribed to substituent effects on the first one-electron oxidation potential of the cubane, and on the rate of primary electron transfer from Ru(III)bpy to the cubane, in the photoactivated cycle. These correlations are also maintained in the series of purified cubanes. We do not have evidence of pyridine detachment.

Villy Sundstrom opened discussion of the paper by Johannes Vos: Apparently the energetics of the ligands do not determine where the electron goes. What might be the decisive factor steering the electrons? What are the esters doing? Could you envisage a systematic manipulation of the ligands to find out the mechanism of electron redistribution among the ligands? Does the nature of the metal on the acceptor group play a role?

Johannes Vos replied: The energetics of the ligands do drive the location of the excited electron and are important, but another important factor is efficient electron coupling between the various excited states. As observed before in solar cells, introduction of the ester groupings lowers the energy of the excited state energy of these ligands. In our case that process brings the MLCT located on the peripheral ligands closer to that of the bridging ligand. What we aim do with our systematic variation of the peripheral and bridging ligand is to optimise the electron flow from the photosensitiser to the catalytic centre by manipulation of the energy and the electronic interaction of both peripheral and bridging ligands. Yes, the change of the central metal of the sensitiser is important, for example iridium type photosensitisers behave very differently.

Antonin Vlcek commented: Scheme 3 of your paper shows a 32.5 ps interligand electron transfer (ILET) from a hot bpy-based MLCT state to the bridging-ligand based MLCT state, while no ILET occurs from the relaxed state. In this case, the low ILET yield would be due to structural reorganization and an energy barrier between the two states rather than to low electronic coupling. (Vibrational excitation would help in overcoming the barrier but it would have only a small effect on coupling.) It is possible that this type of ILET acceleration is a more general effect. Fast ILET from a hot excited state was observed also in the case of a mononuclear Re(I) complex.[1,2]

1 D. J. Liard, M. Busby , I. R. Farrell, P. Matousek, M. Towrie and A. Vlček Jr., *J. Phys. Chem. A*, 2004, **108**, 556–567.
2 A. Vlček Jr., H. Kvapilová, M. Towrie and S. Záliš, *Acc. Chem. Res.*, 2015, **48**, 868–876.

Johannes Vos responded: We have no evidence that significant structural changes are occurring in this system in the excited state, but the behaviour observed may be more general in similar Ru type complexes.

Osamu Ishitani said: There are two mechanisms in supramolecular photo-catalytic reactions for water reduction, *i.e.*, intramolecular electron transfer from the excited photosensitizer unit to the catalyst unit (oxidative quenching) and reductive quenching of the excited photosensitizer unit by an electron donor. In your systems, which mechanism gave better efficiency and durability?

Johannes Vos replied: Professor Ishitani is correct and determining the mechanism associated with our systems is one of the aims in our studies. So far photocatalytic studies have shown that electron transfer from the photosensitiser to the catalytic centre is on the ps timescale in the absence of sacrificial agents and this may suggest an oxidative mechanism. However, in order to be able to compare the photocatalytic properties of different compounds, we have used only one set of catalytic conditions using TEA as a quencher and this does not allow us to identify or differentiate between the two mechanisms.

Elena Galoppini commented: This is a follow up on the discussion regarding the influence of electronic coupling of different anchor groups (COOH *vs.* phos-phonates for instance) on electron injection in the semiconductor. F. Willig and

coworkers have investigated this experimentally and theoretically,[1] along with Prof. Petter Persson of the University of Lund.[2]

1 R. Ernstorfer, L. Gundlach, S. Felber, W. Storck, R. Eichberger and F. Willig, *J. Phys. Chem. B*, 2006, **110**, 25383–25391.
2 P. Persson, M. J. Lundqvist, R. Ernstorfer, W. A. Goddard III and F. Willig, *J. Chem. Theory Comput.*, 2006, **2**, 441–445.

Johannes Vos responded: I agree.

Randolph Thummel said: Bimetallic assemblies depend upon the nature of the bridging ligand as well as the auxiliary ligands. One might consider amide substituents on the peripheral ligand as this function is more hydrolytically stable than ester groups. The electronegativity of the bridging ligand may also be important.

Johannes Vos replied: This is a very interesting option and we will try this approach.

Anthony Harriman asked: Have you considered the origin of the second electron in the reductive cycle? It is easy to imagine the first event that sends one electron to the catalytic centre but it is not straightforward to see how you get the second electron. My concern is that this arises from the sacrificial reagent and this is a serious problem in the field. A useful experiment might be to pre-reduce the catalyst by adding an electron and then checking if this interferes with the excited-state of the sensitiser.

Johannes Vos responded: At present not much is known about the origin and location of the second electron. What is known is that upon addition of water the TON values are significantly increased (see for example Rau et al.[1] vs. M. Karnahl et al.[2]) with TON numbers increasing from about 50 to 270 over 18 h, suggesting that water is the main contributor. This was also confirmed by D_2O experiments. A similar study to that suggested by Prof. Harriman, the addition of an electron, has been carried out recently, and this shows that upon electrochemical reduction of the photosensitiser a second electron is not transferred to the catalytic centre.[3]

1 S. Rau, B. Schäfer, D. Gleich, E. Anders, M. Rudolph, M. Friedrich, H. Görls, W. Henry and J. G. Vos, *Angew. Chem. Int. Ed.*, 2006, **45**, 6215.
2 M. Karnahl, C. Kuhnt, F. Ma, A. Yartsev, M. Schmitt, B. Dietzek, S. Rau and J. Popp, *ChemPhysChem*, 2011, **12**, 2101.
3 L. Zedler, J. Guthmuller, I. Rabelo de Moraes, S. Kupfer, S. Krieck, M. Schmitt, J. Popp, S. Rau and B. Dietzek, *Chem. Commun.*, 2014, **50**, 5227.

Dan Nocera asked: With multiple chromophores to drive the $2e^-$ reaction, have you performed a power dependence study? The use of two chromophores to drive redox chemistry at one metal centre should follow a power law squared dependence on intensity. Does the quantum efficiency show an intensity squared dependence?

Johannes Vos answered: The electronic properties of the ligands coordinated to the Ru centre are very similar and a single set of MLCT transitions is observed

around 450–470 nm, so they can therefore not really been considered to be "independent" chromophores. Upon excitation an MLCT state located on one of the ligands will be populated, depending on its energy and the electronic interaction between the different MLCT states. The $2e^-$ reaction is therefore dependent on the absorption of a second subsequent photon, while the first electron/hydrogen atom is stored on the photocatalyst.

Elizabeth Gibson addressed Johannes Vos and Anthony Harriman: Since the chemical and photophysical behaviour of molecules are different on surfaces compared to solution, is there a requirement to optimise sensitizer–catalyst systems for a sacrificial agent if they are later going to be adsorbed onto a semiconductor? For example, Professor Harriman mentioned that a potential flaw in your supramolecular system is that the rather than the required second electron transfer from the dye to the catalyst taking place, the triplet state of the ruthenium photosensitizer could cause the electron in the catalyst to return to the ruthenium centre. However, when ruthenium dyes are adsorbed on TiO_2 (or NiO), the triplet excited state is rarely observed and instead the oxidised (or reduced) dye forms rapidly. Furthermore, if the reduced species is immediately formed, decomposition reactions could be entirely different or even prevented. Diffusion/dimerisation is unlikely to occur when the system is immobilised on the surface and the stability of both the catalyst and the dye could be increased. So since the preferred electron transfer mechanism (including the driving force for each step) is likely to be entirely different on the surface, it could be preferable to optimise the system on the surface first. This would avoid spending time overcoming challenges which are present in solution (with sacrificial agents) but are avoided when a semiconductor provides the oxidising/reducing equivalents.

Anthony Harriman answered: There is a serious issue with such molecular systems in terms of charge accumulation at the catalytic centre, unless sacrificial redox agents are employed. It is not always appreciated that sacrificial reagents provide the secondary electrons (or oxidising equivalents) needed for the chemical process. You can imagine that the initial excitation causes transfer of one electron to or from the catalyst and that the sacrificial reagent restores the sensitiser to its original state. However, further excitation of the sensitiser is now followed by charge transfer with the one-electron activated catalyst to short-circuit the system. It requires bimolecular reactions to deactivate the catalyst.

Johannes Vos replied: I fully agree with Dr Gibson that the behaviour of these compounds may be very different when they are immobilised on active solid substrates as in our case NiO_x and a wide range of compounds have been reported that can already be tested. However, most of the work carried out when designing and synthesising potential photocatalysts is on the actual synthesis, characterisation and photophysical studies of these compounds, so not much time can be saved in this manner. It also needs to be stressed that is important that before clear conclusions can be drawn from surface bound systems the actual photocatalytic centre needs to be fully characterised. Furthermore, I agree with the comments made by Prof. Campagna and others about this issue that both approaches are needed and importantly in order to avoid more variables being

introduced by the immobilisation, well-defined and well-prepared NiO layers should be used for the immobilisation process.

Anthony Harriman opened discussion of the paper by Osamu Ishitani: We are still using sacrificial reagents to force fuel formation in artificial photosynthetic approaches. The first such systems were developed by Shilov in the 1970s, and I wonder if the time has not come to ban the use of such reagents. Do you have alternatives in mind? What do you feel you gain by using such reagents? Do you foresee the possibility to replace the sacrificial reagent with water or some genuine waste compound, perhaps like glycerol formed from bio-diesel production?

Osamu Ishitani replied: I completely agree with the opinion that we have to develop photocatalytic systems using water as a reductant in future for solving the problems of the shortage of energy and carbon resources and global warming. Recently, some groups, including us, have tried to develop such systems and considerable progress has been obtained for CO_2 reduction.[1–3]

If this opinion means that all the research to improve abilities and expand usable conditions is meaningless, I absolutely disagree with the opinion. We still need better photocatalysts for the reduction and oxidation of water and reduction of CO_2 in various reaction conditions. Especially, the development of photo-catalysts which can work in aqueous media as well as in organic solutions are required for coupling them with water-oxidation systems. However, most of the photocatalytic systems have been tested only in organic solutions. From this viewpoint, the most serious obstacle is the lack of a good sacrificial electron donor which can efficiently donate an electron to various photosensitizers such as excited $Ru(bpy)_3^{2+}$, and that the oxidized product does not inhibit the photo-catalytic reaction. Although most systems used ascorbate as the sacrificial donor in the aqueous solution, it was not suitable as an electron donor because it limits the suitable pH range, *i.e.*, a basic solution is required because ascorbic acid is a much worse electron donor than ascorbate and the oxidized product functions as an oxidant.[4] We recently developed a much better new sacrificial reductant which works very well in a basic aqueous solution, but it unfortunately precipi-tates in acidic aqueous solutions.[5] Therefore, we need to develop better sacrificial reductants in aqueous solution to assess the real abilities of photocatalysts in water.

1 S. Sato, T. Arai, T. Morikawa, K. Uemura, T. M. Suzuki, H. Tanaka and T. Kajino, *J. Am. Chem. Soc.*, 2011, **133**, 15240–15243.
2 G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda and O. Ishitani, *Chem. Commun.*, 2015, **51**, 10722–10725.
3 K. Sekizawa, K. Maeda, K. Domen, K. Koike and O. Ishitani, *J. Am. Chem. Soc.*, 2013, **135**, 4596–4599.
4 A. Nakada, K. Koike, T. Nakashima, T. Morimoto and O. Ishitani, *Inorg. Chem.*, 2015, **54**, 1800–1807.
5 A. Nakada, K. Koike, K. Maeda, O. Ishitani, *Green Chem.*, 2015, DOI: 10.1039/C5GC01720C

Dario Bassani inquired: Could you comment on whether the bridging ligand should be conjugated and rigid, or unconjugated and flexible? There are systems that underperform because of too much rigidity, and flexibility can be beneficial to allow the system to reach a conformation conducive for charge transfer. Did

you mean to say that, in your systems, for oxidative quenching there should be more flexibility, while for reductive systems, it should be more rigid?

Osamu Ishitani answered: Although this question is not directly related to the manuscript which we submitted for this Faraday Discussion, I will try to answer it based on our experiences which we have summarized in reviews.[1,2] Introduction of conjugation into the bridging ligand causes several drastic effects for photo-catalyses of supramolecular photocatalyts.

(1) Faster electron transfer from the excited or reduced photosensitizer unit to the catalyst unit might be expected.

(2) The energy of the π^* orbital in the bridging ligand is lowered.

(3) The rigidity of the bridging ligand causes the possibility of collisions between the photosensitizer unit and the catalyst to be lower.

Although the photocatalytic output of supramolecular photocatalysts should be affected by all of them, in some cases, one of them deals the photocatalysis a fatal blow. For example, Ru(II)–Re(I) binuclear complexes with a bridging ligand gave much lower photocatalytic abilities even compared to a mixed system with the corresponding mononuclear complexes because of effect #2. The photocatalytic reactions using these series of Ru(II)–Re(I) supramolecular photocatalysts proceed *via* reductive quenching of the excited photosensitizer unit. In the cases using a different kind of catalyst and/or proceeding *via* oxidative quenching, a different effect or effects might work strongly. Therefore, we believe that the mechanistic investigation is essentially important for developing better photocatalysts.

1 Y. Yamazaki, H. Takeda and O. Ishitani, *J. Photochem. Photobiol. C*, DOI: 10.1016/j.jphotochemrev.2015.09.001.
2 H. Takeda and O. Ishitani, *Coord. Chem. Rev.*, 2010, **254**, 346.

Cornelia Bohne commented: From your quenching studies you reached the conclusion that the quenching rate constant is above the diffusional limit and that the quenching is static. How can you account for the formation of the new 20 ns species in the system? As a follow up, I note that the curved quenching plot indicates that there are several species in solution, some for which the quenching efficiency is high and others for which the quenching is low. Understanding this diversity of species might be helpful to optimize the photochemical reactivity.

Osamu Ishitani responded: As we wrote in the manuscript, the emission decay indicated that there were at least four conformers of the hybrid (Fig. 8 and 12). In these conformers, the distances of the excited Ru unit from **POM** should be different in each conformer, which causes different quenching behaviors. Fig. 12 shows a schematic representation of this consideration. According to this consideration, we can expect that control of the relative distance between Ru units and **POM** in hybrids induces drastic change of the photochemical behaviors of the hybrids. Different positions of the phosphonate groups might be one of the possible ways to achieve this perturbation.

Andrea Sartorel asked: Do you think electrostatic interaction between the POM and the Ru(II) polypyridyl complex with zinc play a major role in the efficiency of the quenching?

Osamu Ishitani answered: Yes, we do. The very rapid quenching phenomena of emission from the excited Ru unit in **[(RuP)₂Zn]³⁺** by **Si-POM** clearly indicates that the quenching proceeded *via* static quenching even in the presence of 10 mM of $((n\text{-}C_4H_9)_4N)PF_6$ but the quenching was suppressed by addition of a much larger amount of the salt, such as 100 mM.

Sebastiano Campagna questioned: Do you see any change in absorption spectra – for example, a new absorption band arising – upon aggregation?

Osamu Ishitani replied: Fig. 4 in the manuscript shows the UV-vis absorption spectra of DMSO solutions containing **RuP**, both **RuP** and Zn^{2+} and **RuP**, Zn^{2+} and **Si-WPOM**. The peak near 465 nm is attributed to ^{1}MLCT absorption in **RuP**. As can be seen in this figure, while the addition of Zn^{2+} did not affect the absorption spectrum of **RuP**, upon addition of **Si-WPOM** to the **RuP**/Zn^{2+} solution, the **RuP** absorption maximum was slightly red-shifted and its intensity was slightly reduced.

Christopher Lemon commented: You report bimolecular quenching constants of the Ru(II) complexes by **Si-WPOM** that are approximately 10^{12}, which is above the diffusion limit. Would it be reasonable to re-analyze your data in terms of static quenching and obtain binding constants for the different Ru(II) complexes? Nocera and co-workers have used this sort of analysis for the binding of porphyrins[1] and corroles (DOI: 10.1039/c5fd00093a) to the surface of quantum dots. While there is a distribution of products in solution, an effective binding constant may be obtained. Moreover, you can use the Hill equation[1] to model the binding saturation observed for **RuP** (Fig. 7).

1 C. M. Lemon, E. Karnas, M. G. Bawendi and D. G. Nocera, *Inorg. Chem.*, 2013, **52**, 10394–10406.

Osamu Ishitani responded: Although we tried to simulate the quenching experimental result (Fig. 7) using a static quenching model (1 : 1 association between **[(RuP)₂Zn]³⁺** and POM) where the emission quantum yield of the hybrid is lower than that of free **[(RuP)₂Zn]³⁺**, the experimental result was not fitted well; saturation of the quenching was observed even in the case of a much smaller amount of POM compared to **[(RuP)₂Zn]³⁺**. It should be understandable if the ratio between **[(RuP)₂Zn]³⁺** and POM in the hybrid when an added amount of POM was different from that of **[(RuP)₂Zn]³⁺**; for example, in the lower concentration of POM, 2 : 1 and/or 3 : 1 **[(RuP)₂Zn]³⁺**–**POM** hybrids might form. However, we wish to emphasize that the ratio in the hybrid was mostly 1 : 1 in the solution containing **[(RuP)₂Zn]³⁺** and **POM** with a 1 : 1 ratio, as shown in the manuscript.

Clémence Allain remarked: Have you tried different POMs with different charges, and if so do you observe stronger association with more negative charges?

Osamu Ishitani replied: Yes, we have. We checked the emission quenching of **[(RuP)₂Zn]³⁺** in the presence of $[W_6O_{19}]^{2-}$, $[PW_{12}O_{40}]^{3-}$, $[W_{10}O_{32}]^{4-}$, or $[SiMo_{12}O_{40}]^{4-}$ The emission quenching ratios were 24%, 78%, 78%, and 81%,

respectively (in the case of **Si-POM** with 4+ charge, 78%). A lower charge than 3+ should lower the association constant between $[(RuP)_2Zn]^{3+}$ and **POM**.

Silvia Marchesan opened a general discussion of the papers by Andrea Sartorel, Johannes Vos, and Osamu Ishitani: During this Faraday Discussion, we have heard a lot about the advantages, also in terms of stability, of spraying a photo-catalytic system on a surface, as opposed to having a (supra)molecular photo-catalyst in solution. Do you see a scope for confining catalysts in supramolecular hydrogels, in bulk or as thin coatings on a surface, or for having switchable and reversible sol-gel systems?

Gary Brudvig replied: I think it will be essential to confine molecular water-oxidation catalysts because water is more difficult to oxidize than organic C–H bonds. Thus, a freely diffusing water-oxidation catalyst in solution will degrade by ligand oxidation. Your suggestions for confining catalysts are good directions for future research.

Stafford Sheehan replied: Just as important as the stability of the photo-catalytic system itself is the stability of its linkage to a surface or otherwise confined system. We have to keep in mind the advantages and disadvantages of different linking schemes, which are based on the conditions required for catalysis. For example, in caustic or acidic solutions that are required for efficient large-scale water electrolysis, certain metal–oxo bonds possess exceptional stability and may be the best (or only) option.

Johannes Vos commented: The use of hydrogels as electrochemically useful matrices on electrode surfaces was proposed, but comments have been made on the problems with strongly reduced charge transport rates.

The advantage of hydrogels is that they provide the opportunity to immobilise larger amounts of active ingredients such as electrocatalysts on electrode surfaces. As the downside of this approach reduced charge transport may be observed. This issue can however be addressed by a careful control of the layer thickness as well as manipulation of the structure of the polymer backbone, electrolyte and the solvent used.

Andrea Sartorel asked Dan Nocera: Regarding the proposal of using a triple junction PV module to evaluate HECs/OECs, do you think that reference cathodic and anodic compartments should be used to "rank" OECs and HECs, respectively? Can you indicate a benchmark catalyst for HER and for OER?

Dan Nocera responded: We don't like the concept of benchmarking for heterogeneous based catalysts. Everyone wants to "rank" their catalyst or system to say that it is "the best", but it's very difficult to ensure that valid comparisons are made. To begin with, most do not know the structure of the catalyst. For instance, many have benchmarked metal oxides on "volcano" plots. But many, including us using HRTEM, have shown that the surface of the oxide becomes hydrous and porous under OER conditions. Thus the catalyst is not the oxide. In the case of Co_3O_4, authors have benchmarked the oxide against our CoPi catalyst. But we have shown that the surface of Co_3O_4 is transformed to the CoPi catalyst.

Thus they are naïvely benchmarking CoPi against CoPi! Indeed different activities are observed but that has nothing to do with the catalyst *per se*. It has to do with the mesostructure of the catalyst and the other factors. The lack of rigorous comparison methodologies, along with the unknown intrinsic activity of many catalyst systems, renders it impossible to accurately benchmark heterogeneous catalysts.

For homogeneous catalysts, the task is more manageable, as Jean-Michel Savéant has recently established.[1]

1 C. Costentin, G. Passard, M. Robert and J. M. Savéant, *Proc. Natl. Acad. Sci. U.S.A.*, 2014, **111**, 14990–14994.

Sebastiano Campagna made the general comment: Regarding the direction of the field, some very interesting results have already been obtained in the last five years. Some have been obtained using molecules, others using materials. There are several options. My opinion is that one direction or approach, even if at the moment it looks like the most effective one, should not limit research in other directions. It is too early now to select just one direction or approach. It is important to continue to explore all directions. Although, obviously, resources can really be a serious limitation. Sacrificial reagents maybe not practical but give useful information, and we need information on the mechanisms if we wish to progress. Clearly, we should be aware that working in solution can be different than working on surfaces or with electrodes and so on. However, the progress made in the last 5–7 years on photo-assisted water splitting (photo-electrochemical methods on electrodes decorated with molecules, for example) and CO_2 photoreduction with sacrificial agents in solution are impressive and belong to different realms and use different approaches. This would be enough to suggest that we need to explore all the directions and possibilities.

Devens Gust added: I agree that it is too early to choose a final approach to solar fuel generation. It would be a mistake to focus too soon on a single technology, and possibly eliminate some that could later turn out to be advantageous. Indeed, it may well be that different technologies may turn out to be suitable for different purposes. For example, society currently uses several technologies for generating electricity, and each technology has its own best area of application.

Elena Galoppini responded: I also agree with Sebastiano that we should explore all the directions and possibilities, even if may not appear to be immediately successful for a technology or an application. Important fundamental questions may be answered or the research will generate more fundamental questions that need to be answered. This is also very, very important, to satisfy our curiosity. It is probably the point of view of someone who always worked in academia!

Osamu Ishitani commented: I agree with Sebastiano, too. I think that nobody can select the "best" system for the usage of solar energy at this stage and possibly there are several useful combinations of such technologies. However, we must not tell lies which will mislead people, and should always point out the importance and the "reality" levels of these technologies.

Johannes Vos replied: I fully agree with these comments.

Villy Sundstrom responded: I fully agree with Sebastiano, it is too early to choose track. I think very interesting work has been performed by combining different types of materials. Exactly which combinations will be the winners, only the future will tell.

Anthony Harriman remarked: We continue to see a variety of wonderful molecular architectures designed on the basis of natural photosynthesis. These are highly imaginative and demand some really challenging synthesis and compound characterisation. Many such supermolecules have been critically examined by electrochemical and photochemical methods in order to elucidate the energy- and/ or electron-transfer pathways. However, there are few cases, if any, where these beautiful materials have found applications for artificial photosynthesis. While great progress has been realised in terms of photoelectrochemical approaches, we are no nearer finding a solution for purely molecular approaches. While it is true that Nature uses a molecular approach, this knowledge doesn't help us – you could say the same about nuclear fusion on certain stars. Perhaps the harsh conditions inherent to water splitting are too severe.

Devens Gust responded: It is true that water oxidation and fuel generation using molecules have some significant challenges, but we have to remember that photosynthesis uses molecules to make essentially all fuel for life, and is responsible for all the fossil fuels that we depend on today. Thus, it can be done.

Alejandro Díaz-Moscoso answered: Following your comparison with nuclear fusion in stars, well, reproducing star conditions in a controlled way on the Earth, that is a huge challenge! And we (mankind) are still optimistic about employing such a source of energy in the "near" future. So, shouldn't we stay optimistic about mimicking Nature in supramolecular water splitting when we already have the same starting conditions? I agree with the previous comment, it can be done. We just need interdisciplinary knowledge and imagination to find our way, although the work of billions of years of evolution must not be underestimated.

Gary Brudvig replied: I agree that water oxidation using molecular catalysts is challenging, but Nature has shown that it is possible in photosystem II which can carry out a million turnovers without degradation of the manganese-based catalyst. A key lesson that can be learned from Nature is that it is important to confine the water-oxidation catalyst to avoid intermolecular degradation processes. We have found that our molecular iridium water-oxidation catalyst is stable for long-term catalytic turnover when anchored to a metal oxide surface .[1]

1 S. W. Sheehan, J. M. Thomsen, U. Hintermair, R. H. Crabtree, G. W. Brudvig and C. A. Schmuttenmaer, *Nature Comm.*, 2015, **6**, 6469.

Villy Sundstrom replied: A purely molecular system may have problems doing the final job, but organic–inorganic combinations, where molecular systems mimic some key part of photosynthesis, may very well do the job. The dye sensitized solar cell is a nice example.

Stafford Sheehan commented: Throughout this meeting the stability and, as a consequence, practical applicability of molecular systems were brought up a number of times. Nature tackles these issues by embedding molecular catalysts within enzymes to increase their stability, analogous in some ways to binding molecules to robust surfaces. Such surface-binding and encapsulating methods have now been used in quite a few commercial products that employ molecular systems (*i.e.* catalysts and chromophores), and that are long-lived and durable. Examples such as these demonstrate that molecular catalysts can possess the stability required for large-scale applications, provided they are designed and evaluated properly.