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Highlights from Faraday Discussion 185: Supramolecular Photochemistry, Cambridge, 2015

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In September 2015, Cambridge hosted the 185th Faraday Discussion meeting in the magnificent and historically rich surrounds of Downing College. The meeting brought together over 110 scientists from around the world to discuss the most recent advances in the wide field of supramolecular photochemistry; and also to define strategies for solving the problems of the future in this field of research.

The Faraday Division of the Royal Society of Chemistry have been organising high impact Faraday Discussions for over 100 years. These Discussions are international conferences that focus not only on emerging fields in physical chemistry, but also on the interface of physical chemistry with other scientific disciplines. Faraday Discussions are not standard conferences. They have an engaging and unusual format where research articles written by the speakers, invited by the scientific organizing committee, are distributed to the delegates before the meeting. The majority of the meeting is then devoted to discussion of the papers and all delegates, from experienced professors to new graduate students, have an opportunity to critically

contribute to the discussion. Before the first session, Tom Wilson and Sage Bowser (Royal Society of Chemistry Publishing Editors) explained the format of the Discussion to the delegates, after which they busied themselves recording the proceedings for the final publication.¹

The field of photochemistry, which is located at the intersection of chemistry, physics and biology, and at the interface between matter and light, is now more than ever accompanied by profound qualitative changes. Modern advances in synthesis, instrumentation, and theory have opened new avenues of research, and have allowed reassessment and development of older systems. In recent decades, the interest of researchers has gradually shifted from processes that occur within photo-active molecules (molecular photochemistry) to reactions that take place between molecular excited states and appropriate reaction partners (*e.g.*, intermolecular electron and energy transfer) in complex and hybrid systems. Since its inception in 1987,² the study of artificial assemblies of multiple molecular components capable of performing useful functions under light stimulus – the field of *Supramolecular Photochemistry* – has experienced impressive growth. It impacts on many topics, including artificial photosynthesis, light-activated molecular machines, molecular logic gates, and luminescence sensing and imaging, leading to applications in biomedicine, solar energy conversion, and molecular electronics

and informatics. The breadth of topics was reflected in the composition of participants who spent three days discussing the fundamentals, applications and problems that distinguish or, perhaps connect, different aspects of supramolecular photochemistry.

The meeting officially kicked off on Monday, September 20, 2015, and began with the welcoming address from the conference chair Professor Sebastiano Campagna (University of Messina, Italy), who also headed the scientific committee constituting Professor Alberto Credi (University of Bologna), Professor Luisa De Cola (University of Strasbourg), Professor Anthony Harriman (Newcastle University), Zoe Pikramenou (University of Birmingham) and Professor Antonin Vlcek, (Queen Mary, University of London).

Sebastiano Campagna (Fig. 1) presented the principal themes for discussion.

Natural and artificial photosynthesis

New information derived from the study of natural systems will be discussed and used to aid the design of artificial photosynthetic systems. Attention will be given to both synthetic light-harvesting antennae and molecular devices capable of efficacious charge-separation.

Light-activated molecular machines and logic gates

The study of multi-component systems where illumination induces controlled mechanical movements (machines) and/or

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Fig. 1 Welcoming talk by Professor Sebastiano Campagna.

definition of supramolecular chemistry given by Jean-Marie Lehn in his Nobel lecture in 1987, and then moved to the description of a Supramolecular Photochemistry System given by Balzani and co-workers as “an appropriate assembly of suitable molecular components capable of performing light-induced functions”.^{3,4}

In his amazing talk, (DOI: 10.1039/C5FD00142K) Professor Gust described how supramolecular photochemical devices consist of chromophores, donors and acceptors that are associated in such a way that the component moieties interact by mechanisms such as, but not limited to, singlet or triplet energy transfer, photo-induced electron transfer and exchange of spin information. By choosing the moieties and controlling their modes of interaction, the supramolecular photochemist can demonstrate scientifically interesting and potentially useful phenomena that are not possible in simpler systems. The association mechanisms include not only a variety of non-bonded interactions but also linkages through chemical bonds that are not part of the active components. The examples given dealt with artificial photosynthesis, molecular logic, and spin-spin interactions, thus providing an appropriate overview of the principal themes of the Discussion.

where light can be exploited as input/output information. The relevance to protein folding should not be missed.

Self-organization of photo-active nanostructures

Identifying new and improved ways to assemble supramolecular entities with a photo-active unit, such as liquid crystals, organo-gels, dendrimers, *etc.* Although synthesis plays a crucial role in the development of such species, the discussion will deal with the synergistic features of the actual assembly.

Luminescence sensing and imaging

The *in situ* detection of changes in the local topology and in the concentration of selected substrates, including biologically relevant species.

Opening lecture

The Discussion was introduced with a brilliant lecture by Devens Gust (Arizona State), who gave a general overview of the evolution of supramolecular photochemistry from the beginning to very recent and novel results. This also provided a perspective on his outstanding

contributions to the field over the years, within the context of other developments in the field.

Professor Gust (Fig. 2) started with the question: what is supramolecular photochemistry? And during his talk he answered the question through selected examples. As a starting point, he took the



Fig. 2 Opening lecture by Professor Devens Gust.

Session 1: natural and artificial photosynthesis

The first session was chaired by Professor Antonin Vlcek and Professor Anthony Harriman, and began with a presentation by Gary Brudvig (Yale). The talk (DOI: 10.1039/C5FD00087D) dealt with the mechanism of photosynthetic water oxidation that occurs at the oxygen-evolving complex (OEC) of Photosystem II (PSII). The OEC, which contains a Mn_4CaO_5 inorganic cluster ligated by oxides, waters and amino-acid residues, cycles through five redox intermediates known as S_i states ($i = 0-4$). Professor Brudvig presented a detailed analysis of the S-state dependent substrate water binding kinetics taking into consideration data from Mn coordination complexes. The analysis presented supports a model in which the substrate waters are both bound as terminal ligands and react *via* a water–nucleophile attack mechanism. Determining the molecular mechanism of O–O bond formation in photosynthetic water oxidation remains one of the great challenges in supramolecular photochemistry and, consequently, the discussion that ensued was lively. It was established that 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 ligand which is observed, for example, in low-spin square pyramidal Mn(V)^{O} species; the oxo in these Mn(V)^{O} species is known to be unreactive.

The next paper, by Villy Sundström (Lund) and co-workers, (DOI: 10.1039/C5FD00084J) focused on the power of a combination of ultrafast optical and X-ray techniques with DFT modelling. Through this combination, our understanding of how spin, electronic and structural factors govern the photoconversion performed by photochemical molecular devices and natural systems can be greatly advanced. Sundström clarified that although it is always good to have as much information as possible from conventional transient absorption (TA) studies, the spectral information from the TA is often not very informative and that is where the X-ray studies can provide important electronic and structural information.

After that, Julia Weinstein (Sheffield) presented several new donor–bridge–acceptor charge-transfer molecular assemblies built on a *trans*-Pt(II) acetylide core, (DOI: 10.1039/C5FD00103J) which differ in the mode of attachment of the donor to the bridge. The paper discusses the molecular features necessary for the external vibronic control of the excited state processes, and highlights fundamental questions regarding the role of vibrational processes immediately

following charge transfer photoexcitation in solution. The discussion highlighted that, post electronic excitation, vibrational excitation with low energy IR light can perturb vibronic coupling in supramolecular assemblies and this “IR-control” may hopefully create a general basis for designing donor–bridge–acceptor assemblies in which reactivity can be directed by IR-light.

The field as a whole is amazingly rich, and the discussion involved many participants (Fig. 3). The discussion started by focusing on the multi-photochromic systems described by Devens Gust that show rich UV-vis spectral signatures for the various states; in particular, the opportunity to use multiple wavelengths simultaneously to enable quantum logic gate phenomena. In fact, the molecule used to illustrate molecular logic can provide different logic functions at the same time using the same two inputs but different outputs. The discussion turned to future opportunities – for example, since some photochemical logic gates can switch in picoseconds, does this mean they could be used for electronic systems faster than gigahertz? The discussion brought the answer that the more intense the light, the shorter the time available 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



Fig. 3 Discussion moments after the talks.



Fig. 4 Poster session.

sample size. The discussion continued informally during the tea break, and then proceedings continued with the exploration of photocatalysts for water splitting.

John Kelly introduced the paper by Randolph Thummel (Houston) that focused attention on a new series of Ru(II) complexes that behave as water oxidation catalysts (DOI: 10.1039/C5FD00051C). His results demonstrate how substitution with *tert*-butyl subunits on a tetradentate equatorial ligand increases the stability of the catalyst but depresses the catalytic efficiency. A detailed investigation of the coordination circumstances during catalysis provided evidence to understand the relationship between the structure and activity of these new species.

Frederick Lewis (Northwestern) described how insertion of an artificial base pair composed of cyclohexyl base surrogates in the interior of a synthetic duplex slows charge separation and recombination in hairpin duplexes capped with donor/acceptor pairs (DOI: 10.1039/C5FD00043B). These systems efficiently generate long-lived charge separated states in DNA, if appropriate design principles are followed.

Immediately following a series of invited lightning presentations, delegates made their way to the poster session, Fig. 4.

The number of posters, at 60, was impressive, so two different poster sessions were organized. This allowed

almost every delegate to contribute to the novel aspects presented in all four subtopics: natural and artificial photosynthesis; luminescence sensing and imaging; light-activated molecular machines and logic gates; and self-organization of photo-active nanostructures. The arguments were so stimulating that discussions continued over dinner.

The first session on Wednesday morning continued the artificial photosynthesis theme and was chaired by Frank Würthner who introduced the work presented by Andrea Sartorel (Padova). The presentation focused on the very hot topic of designing and expending synthetic effort for the development of Co(III) cubane water oxidation catalysts (DOI: 10.1039/C5FD00076A). The author demonstrated how the design of molecular species should still be relevant, in order to optimize the interface of the catalyst/ photosensitizer modules within an artificial photosynthetic architecture. For instance they demonstrated that an important factor for water oxidation is the access to a Co(IV) formal oxidation state at two centres of the cubane core.

Presentations continued with the other side of the artificial photosynthesis coin with the second speaker, Johannes Vos (Dublin City University) talked about photocatalytic hydrogen generation from water (DOI: 10.1039/C5FD00068H). In this contribution, examples of intramolecular photocatalytic assemblies for solar fuel

generation in solution were described. Particular attention was devoted to hydrogen generating assemblies with the aim of identifying and optimising pathways for light driven intramolecular electron transfer in multinuclear assemblies.

The presentations for this topic ended with the very inspiring work of Osamu Ishitani (Tokyo Institute of Technology). He presented the development of supramolecular hybrids composed of polyoxometalates and photofunctional metal complexes for applications in artificial photosynthesis (DOI: 10.1039/C5FD00080G).

The animated discussion that followed these papers quickly got to the heart of the topic (DOI: 10.1039/C5FD90089A). The argument centred on a serious drawback of molecular systems, in that charge accumulation at the catalytic centre relies on the use of sacrificial redox agents. The question was: is the molecular approach worth studying if it is not a reflection of processes in devices? After considerable debate, participants maintained their respective views, whilst acknowledging the different phenomena under examination. Regarding the direction of the field, some very interesting results have already been obtained in the last five years; some using molecules, others using materials. The general opinion is that one direction or approach should not limit research in other directions, even if at the moment it looks like the most effective one, it is too early to select just one direction or approach, and it is important that all options are explored.

Session 2: luminescence sensing and imaging

The presentations on the new theme began after morning tea with contributions by two younger speakers, chaired by Cornelia Bohne. Shani Osborne (Birmingham) presented her latest results on the photophysical studies of gold nanoparticles, AuNPs, coated with surface-active ruthenium complexes (DOI: 10.1039/C5FD00108K). The results demonstrated that the ruthenium luminescent centre show an enhancement in luminescence lifetime when attached to the AuNP,

providing an insight into the design of functionalised nanoparticles.

Following this, Filippo Monti (Bologna) described the synthesis, structural characterisation, and detailed photophysical study of three cationic cyclometalated iridium(III) complexes bearing a chelating diisocyanide as the ancillary ligand (DOI: 10.1039/C5FD00064E). The presentation demonstrated that a combination of structural and electronic features enables tuning of the emission colour by suitable modifications of the CN ligands, going from blue to orange upon extension of the π -conjugation.

The morning session was wrapped up with a presentation by Daniel Nocera (Harvard). Professor Nocera demonstrated, in a very stimulating talk, that micelle encapsulation represents a scalable method of synthesizing quantum dot nanosensors and circumvents the laborious multi-step polymer syntheses required for coating QDs for covalent conjugation to a chemosensor (DOI: 10.1039/C5FD00093A). These results highlighted micelle encapsulation as an ideal vehicle to implement sensing *via* FRET signal transduction pathways of QD-donor/acceptor assemblies.

The subsequent discussion focused on different arguments ranging from the use of iridium materials (very rare elements) in the construction of LEDs, to the basics of photophysical deactivation pathways of metal complex excited states in hybrid materials. Particular interest was shown in the use of quantum dots for bio-imaging because of their possible toxic effects as well as their interaction with molecular oxygen. Other discussion concerned the methodology used for structural and dimensional characterization of these materials.

After lunch, Session 2 continued with Daniel Nocera and Zoe Pikramenou as chairs.

The first talk in the afternoon was delivered by Cécile Moucheron (Bruxelles) and demonstrated how photoinduced electron transfer between a photo-oxidizing ruthenium complex and a tryptophan residue incorporated in short peptide sequences could be strongly influenced by several parameters (DOI: 10.1039/C5FD00059A). Professor Moucheron

reported for the first time the formation of intramolecular bi-adducts between a Ru-TAP complex and tryptophan residues, despite the rigid geometry of octahedral ruthenium(II) complexes.

The second talk moved attention to purely photophysical studies. Gilles Lemerrier (Reims) described how a phenanthroline-ethynyl-aminobenzene species displays a solvent-tuned dual emission with a newly-described charge transfer model (DOI: 10.1039/C5FD00054H). The results presented showed that the effects of polarity and hydrogen bonding lead to a more evident dual emission associated with a large multi-emission band in some solvents like methanol, highlighting this species as a promising candidate for white light emission.

Moving into the biomedical realm, Luca Prodi (Bologna), in his very interesting talk, spoke about the use of analytical techniques such as electrochemiluminescence (ECL) to monitor prostate cancer (DOI: 10.1039/C5FD00096C). The results described for the first time the application of an innovative approach for the selective and sensitive detection of the PCa biomarker sarcosine, obtained using a synergistic ECL supramolecular approach, in which the free base form of sarcosine acts as co-reagent in a $[\text{Ru}(\text{bpy})_3]^{2+}$ -ECL process.

After useful discussion in the session room (DOI: 10.1039/C5FD90090E) and during afternoon tea, the meeting switched to the third theme.

Session 3: light activated molecular machines and logic gates

The next session was chaired by Willy Sundström and John Kelly, and started with a spectacular talk (Fig. 5) by A. P. de Silva (Belfast). Molecular logic-based computation continues to throw up original applications in sensing and switching, the newest being the edge detection of objects (DOI: 10.1039/C5FD00056D). Professor De Silva explained how structure-activity relationships in edge-detecting molecular logic systems help to delineate the scope of this new phenomenon in molecular computation. A general mechanism emerges, which is based on the photoproduction of protons in written regions, followed by the slow diffusive encroachment across the boundaries into unwritten regions. To clarify, a proton-induced switching 'on' of fluorescence then occurs in these areas. Subsequent erasure of the fluorescence takes place in the irradiated areas as a product gradually accumulates.

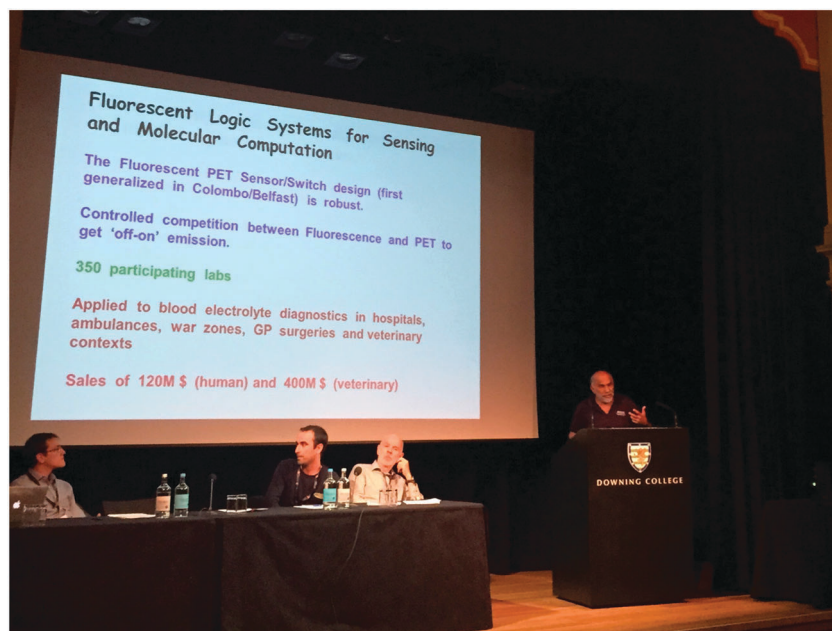


Fig. 5 First talk of the third session by Professor A. P. de Silva.

The second talk in the evening was from Lapo Bogani (Stuttgart) who presented a report on the synthesis, and magnetic and photomagnetic behaviour of a novel valence tautomeric cobalt complex (DOI: 10.1039/C5FD00088B).

The authors demonstrated how its use in the rational design of novel molecular magnets opens the path to molecular photoswitchable systems and multifunctional materials.

The final talk from Nuno Basilio (Universidade Nova de Lisboa) presented the pH dependence of a multistate molecular dyad containing flavylium and viologen units, and the pseudorotaxane it forms with cucurbit[7]uril (DOI: 10.1039/C5FD00078E). The approach was based on the pH-dependent kinetics of the chalcone/flavylium molecular switching abilities rather than on the steric hindrance and/or electrostatic repulsion approaches used in other interlocked systems.

Adding further information on these interesting inclusion complexes, Cornelia Bohne (Victoria) presented results on the role of pK_a shifts in the binding dynamics of a 2-aminoanthracenium cation with the ring of cucurbit[7]uril (DOI: 10.1039/C5FD00095E). This highlighted how not only thermodynamics, but also kinetics, are important when designing pH probes.

A general discussion followed which covered ground from details of photo-physics in the edge-detecting system, through cucurbituril insertion and pH effects, to deliberation of light-driven molecular machines and complex systems (DOI: 10.1039/C5FD90091C). This was followed by the second poster session and wine reception, leading on to the conference meal. A long day of exciting talks and discussions created a friendly atmosphere among the conference attendees, which permeated throughout the evening dinner that followed. The fun culminated in a

hilarious but always fascinating rendition of the Loving Cup⁵ Ceremony (see Fig. 6). Participants drifted away to bed, dreaming of A. P. de Silva's pink elephants.

Session 4: self-organization of photoactive nanostructures

The final set of discussions, chaired by Cecile Moucheron and Fred Lewis, began on Thursday morning with contributions covering a diverse range of topics from chiral assembly of lanthanide containing hydrogels to self-assembled multichromophoric architectures.

The opening paper was by Thorfinnur Gunnlaugsson (Trinity College Dublin) and described the preparation and photo-physical behaviour of lanthanide-directed



Fig. 6 Snapshots of the social dinner time.

self-assembled structures of water-soluble chiral ligands (DOI: 10.1039/C5FD00105F). In particular, the probing of the chiroptical properties of Ln(III)-directed assembly in solution was highlighted as a powerful method, complementing routine achiral spectroscopy, to allow both stoichiometric speciation and binding affinities to be determined reliably from spectroscopic data.

In the field of multichromophoric architectures, George Pistolis (Demokritos) contributed a presentation on the coordination-driven supramolecular synthesis and photophysics of a [4+4] and a [2+2] assembly, constructed from donor-acceptor chromophoric boron dipyrromethane (BODIPY) and perylene bisimide dye (PBI) building blocks (DOI: 10.1039/C5FD00083A). By combining theoretical calculations and spectroscopy, fast excitation energy hopping leading to a rapid excited state equilibrium among the low energy perylene bisimide was demonstrated.

The next talk returned to the DNA theme, where John Kelly (Trinity College Dublin) described studies of purine photo-oxidation by intercalated $[\text{Ru}(\text{TAP})_2(\text{dppz})]^{2+}$. The talk showed how the replacement of guanine with the less oxidisable inosine base can be used to understand the mechanism of electron transfer processes (DOI: 10.1039/C5FD00085H). The study demonstrated that the use of inosine substitution as a control experiment for guanine photo-oxidation should be performed with care, especially where the photosensitiser of interest binds from the minor groove.

This group of talks was closed with a contribution on photoactive templating structures for the design of porous frameworks with built-in optical functionalities, given by Fabio Cucinotta (Newcastle). The presentation showed how it is possible to obtain hybrid materials with modulated photoactivity, depending on the aggregation properties of the chromophoric templates (DOI: 10.1039/C5FD00081E). In particular, by varying the content of an amphiphilic dye (for instance BODIPY) in the templating micelles, different systems can be obtained with specific emission properties.

Following the refreshing morning tea, the session continued with Han Vos and Eimer Tuite as chairs. The first paper,

presented by Paola Ceroni (Bologna) investigated the photophysical properties of silicon nanocrystals functionalized with tetraphenylporphyrin Zn(II) chromophores at the periphery (DOI: 10.1039/C5FD00098J). These systems perform as light-harvesting antennae in which visible excitation results in long-lived NIR emission. These authors stress the potential applications in the bioimaging field, taking advantage of stronger light-absorption in the red with respect to porous silicon nanomaterials: long-lived emission enables time-gated detection, meaning that sample autofluorescence is eliminated, and NIR emission allows for a deeper penetration length.

Elena Galoppini (University of Massachusetts Boston) contributed with a presentation on the electrochemical and photoelectrochemical properties of the rigid-rod porphyrins with or without an intramolecular dipole in the bridge. These were studied in solution and bound to nanostructured nanoparticles (DOI: 10.1039/C5FD00082C). The experiments demonstrated how the presence or direction of the bridge dipole does not change the electronic properties of the porphyrin ring in nanostructured films, whereas a small effect is observed in monolayers on single crystal semiconductors.

The final paper of the session, and of the meeting, by Frank Würthner (Würzburg)

focused on the electronic and structural factors that govern photoinduced electron transfer processes in supramolecular assemblies (DOI: 10.1039/C5FD00052A). This contribution elucidated how, in a conjugated oligomeric electron donor with appended perylene bisimide (PBI) acceptor dyes, the transition from an open conformation with non-interacting PBI dyes to a conformation with π -stacked PBI dyes influences the photophysical behaviour of the donor-acceptor dyad system. The photophysical study showed that for a situation similar to that found in heterojunction organic solar cells – *i.e.* a low thermodynamic driving force for charge separation – an initially very efficient PET process for non-aggregated molecules (open conformation) may be completely suppressed upon dye aggregation due to a thermodynamically favoured and kinetically fast relaxation channel into excimer trap states. The author highlighted how relevant such relaxation pathways are for other planar π -systems, and therefore should be given due consideration in research that aims to replace globular fullerene acceptors by organic semiconductor molecules in organic photovoltaics.

A final discussion session covered different aspects of these talks (DOI: 10.1039/C5FD90092A), with focus on the photophysics and surface properties of nanostructured materials and silicon



Fig. 7 Closing remarks by Professor Dario Bassani.

quantum dots, electron transport mechanisms at different surfaces, and photo-physics in stacked systems.

Concluding remarks

The Faraday Discussion was finally concluded by Dario Bassani (Fig. 7), who highlighted in a lively manner and with inimitable style some of the topical

points that arose during the meeting, and proposed possible future directions for the field (DOI: 10.1039/C5FD00146C).

The concluding remarks were followed by well-deserved acknowledgements to the hosts and organisers, before one final lunch brought a very successful and enjoyable Faraday Discussion to a close. The delegates went their separate ways with plenty to think about following an intense but stimulating three days of discussion.

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