

Viewpoint on the 2019 International Conference on Photochemistry

From July 21, 2019 to July 25, 2019, a wide variety of scientists converged upon the 40th Parallel North in Boulder, CO in the United States, to discuss the latest developments within the extensive field of photochemistry. The International Conference on Photochemistry (ICP) is the oldest and most established event on the topic in the world and has provided a forum to report the effects of light on chemical, biological, and physical systems since 1962.

Returning to the United States for the first time in more than 20 years, the 2019 meeting was the 29th ICP, chaired by Prof. Gary Rumbles (National Renewable Energy Laboratory, University of Colorado, Boulder) and Prof. Gregory Scholes (Princeton University). Over time, the event and topics have evolved from the pre-laser era to today's emerging and expanding methods to understand the photochemistry and photophysics of a huge variety of systems and materials (see Figure 1, with further details discussed below). From ultrafast spectroscopy to spectroscopy at the nanoscale, from next-generation chemical reactions to device-inspired photophysics, photochemists from around the world found value and insight in conference discussions and proceedings. This meeting featured over 240 talks and 150 posters in six concurrent sessions, with a complete list available at www.colorado.edu/conference/icp2019/technical-program. Participants traveled from their institutions in over 30 countries around the world, with the global distribution of attendees illustrated in Figure 2.

To gain some insight into the broad range of topics covered within this conference, and how this has changed over time, we analyzed keywords contained within the meeting's talk and poster titles. In Figure 1, we show the most commonly occurring keywords across all titles in the 1999 ICP that was held in Durham, NC, USA (left), and the 2019 meeting in Boulder, CO, USA (right). The size of each circle indicates the relative occurrence of keywords within all conferences, normalized to the size of each meeting (in 1999, $n = 236$ contributions; in 2019, $n = 397$ contributions). For example, in 2019, the word *ultrafast* occurred in 43 separate talk and poster titles, i.e., in 11% of all contributions. The color of each circle indicates the similarity of a keyword's occurrence between the 1999 and 2019 conferences, where blue indicates a very similar proportional level of occurrence, while red indicates a word that occurs much more commonly in one meeting than the other. Common word stems were used to compile statistics (e.g., *coher** for coherence and coherent) and these stems were completed in Figure 1 for clarity.

From this visualization, it is straightforward to identify major topics that have continued as active and major areas of research over the 20 year period. The study of *excited states* and *electron or charge transfer*, and methods in *fluorescence and spectroscopy* all remain central to this research over time, having also dominated the field of photochemistry since its inception.

Further insights are given with regard to the research areas that have changed and emerged over time. In the 1999 meeting, there are very few major topics that have not continued to be represented and studied in 2019, observable

from the scarcity of brightly red colored 1999 keywords. In contrast, the 2019 chart highlights several emerging areas of research interest, which have little or no mention 20 years prior. *Hybrid*, *perovskite*, *efficient*, and *solar* all appear predominantly in 2019, related to recent interest in emerging photovoltaic and electro-optical materials, particularly in hybrid perovskites. We highlight other emerging and established topics in the context of some specific contributions below.

Ultrafast and *dynamics* were some of the most frequently occurring keywords within the 2019 ICP meeting, mentioned in ~11% of all talk and poster titles. Ultrafast time-resolved methods, made possible by developments in laser technologies beginning in the 1960s, have been significant in this field for some time. However, researchers have an increasing ability to use these techniques to look at a larger variety of systems in greater detail than ever before. This was well-reflected in the topics presented in many of the plenary lectures, these methods being leveraged to investigate a wide variety of biological, chemical, and physical systems.

Stefan Haacke (The University of Strasbourg and CNRS, IPCMS) gave a keynote presentation discussing the recent developments in understanding the ultrafast processes that occur in photosensory proteins relying on photoisomerization of their chromophore. In retinal proteins, such as Rhodopsin, the pigment of vision, this subpicosecond process allows the conversion of light into free energy via complex intermolecular coupling. This triggers vision or ion pumping on femtosecond time scales and with efficient yields. It is known that the protein environment has a large impact on the dynamics and quantum yield of this ultrafast reaction. In the framework of the French–German project “Femto-ASR”, using a combination of quantum chemistry and ultrafast spectroscopy, the Haacke group and their partners show that electrostatic properties of protein environment modulate these reaction dynamics by changes in the electronic character along the first singlet excited state potential energy surface [M. D. Marin et al., *J. Am. Chem. Soc.*, **2019**, *141*, 262–271], in addition to steric effects [P. P. Roy et al., *J. Phys. Chem. Lett.*, **2019**, *10*, 1012–1017]. Recent work in collaboration with Massimo Olivucci (University of Siena and Bowling Green) has also determined that isomerization can operate similarly to Rhodopsin in biomimetic molecular switches [J. Briand et al., *Phys. Chem. Chem. Phys.*, **2010**, *12*, 3178–3187]. Here, the observed coherent nuclear motion is critically dependent on minor chemical modifications, since these induce specific geometric and thus electronic effects [M. Gueye et al., *Nat. Commun.*, **2018**, *9* (1), 1–8]. These recent findings identify biomimetic switches as excellent model systems for experimentally addressing long-standing theoretical predictions of wavepacket dynamics and branching at conical intersections.

Helen H. Fielding (University College, London) focused her plenary session on the application of gas-phase and liquid-

Published: October 24, 2019

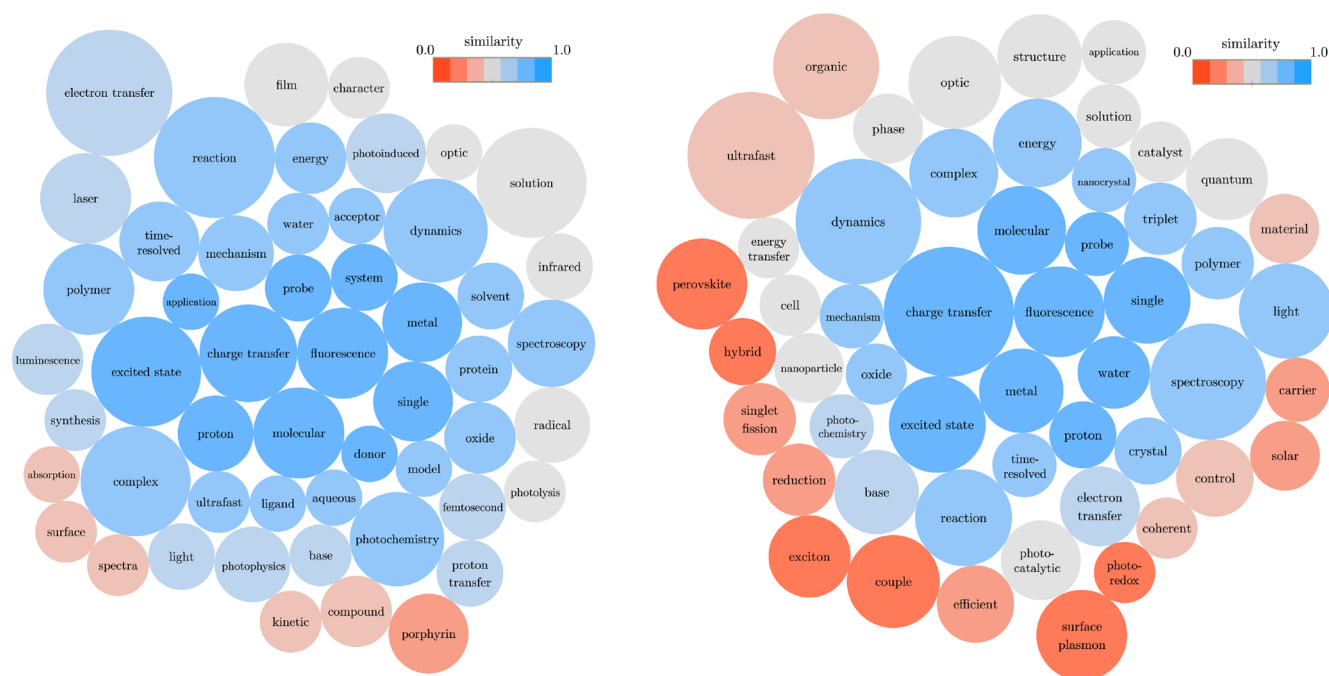


Figure 1. Keyword occurrence and difference analysis between contributed talks and posters at the International Conference on Photochemistry 1999 (left) and 2019 (right). The circle size indicates the frequency of a keyword's occurrence within all conference titles. The color of each circle indicates the similarity in occurrence between the 1999 and 2019 meetings, where blue indicates keywords that appear often in both conferences' titles, and red indicates keywords that occur much more often in one meeting than the other.

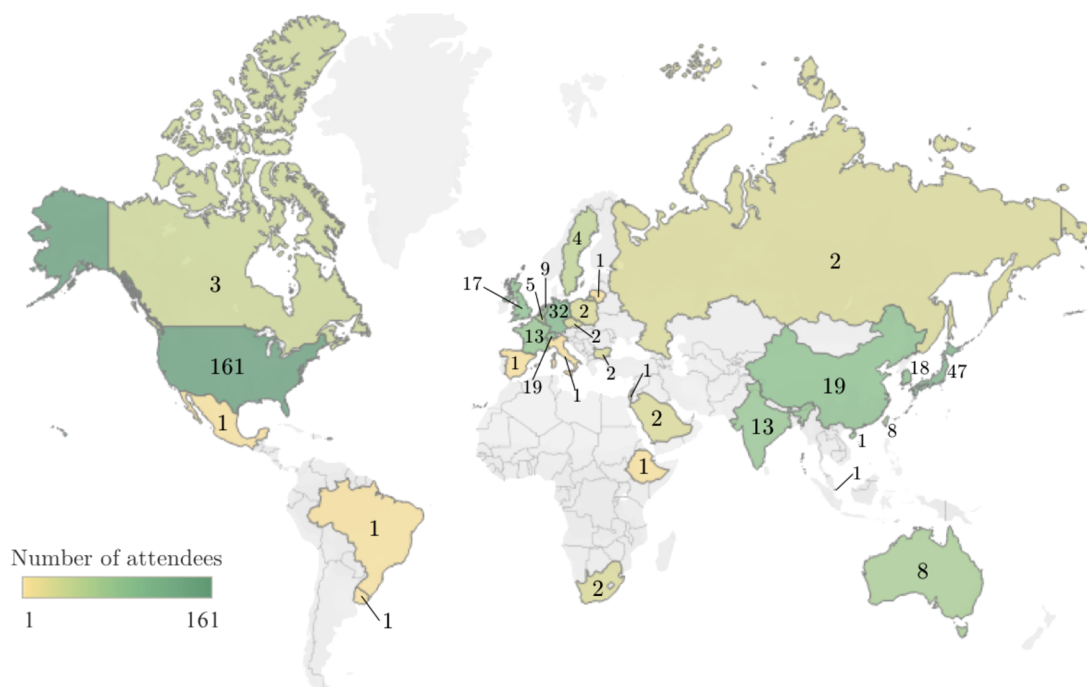


Figure 2. Countries of attendance for the 2019 International Conference in Photochemistry.

microjet photoelectron spectroscopy to isolate and study anionic forms of biomolecules, with the goal of using a bottom-up approach to improve our understanding of their photophysical properties in their natural environment. By comparing the relaxation dynamics of phenol using multiphoton ultraviolet photoelectron spectroscopy (PES) both in the gas phase and in a liquid microjet, they found that, although the dynamics in the two cases were very similar [J. Riley et al., *J.*

Phys. Chem. Lett., **2018**, *9*, 678–682], the aqueous condition also afforded the ultrafast generation of solvated electrons [A. Henley et al., *Faraday Discuss.*, DOI: [10.1039/c9fd00079h](https://doi.org/10.1039/c9fd00079h)]. Fielding then moved from a discussion of phenol to the biochromophore responsible for fluorescence emission from the green fluorescent protein (GFP). Again, using ultraviolet PES, they confirmed that, following photoexcitation, the chromophore shows signatures not only of internal conversion

to the ground electronic state but also of resonant autodetachment of the extra electron [C. R. S. Mooney et al., *J. Phys. Chem. A*, **2012**, *116*, 7943; J. Riley et al., manuscript in preparation].

Laser light was also discussed by Hiroshi Masuhara (National Chiao Tung University), with regard to its ability to physically manipulate particles. In optical manipulation, mechanical force is exerted on small objects by a large quantity of focused laser photons. This technique has a broad array of applications, including photopolymerization, microstructuring, photochromism, the crystallization of molecules and perovskites, and amyloid fibril formation. Masuhara discussed recent discoveries in an optically evolved assembly mechanism in which nanoparticle subjects of optical manipulation are not passively moved by the trapping laser but play a dynamic role in the system [T. Kudo et al., *Nano Lett.*, **2018**, *18*, 5846]. Nanoparticles scatter, propagate, and interfere with photons from the trapping laser, which modifies the optical potential, illuminating new phenomena and fabricating new assemblies.

Given the established expertise in renewable energy and the environment at the University of Colorado, Boulder, this meeting particularly highlighted the latest work in solar fuels and atmospheric photochemistry. Barbara J. Finlayson-Pitts (University of California–Irvine) presented ongoing investigations of photochemically driven reactions involving pollutants, including at air/water or air/solid interfaces. Photochemical reactions between primary pollutants in the environment produce secondary pollutants, many having increased toxicity. For example, the photochemical decomposition of some neonicotinoid (NN) pesticides in air generates products that have been shown by others to be more toxic than the parent NN. In addition, the greenhouse gas N_2O is formed [K. Z. Aregahegn et al., *Environ. Sci. Technol.*, **2017**, *51*, 2660]. In collaboration with B. Gerber, D. Tobias, P. Jungwirth, and M. Roeselova, Finlayson-Pitts and her group proposed that Cl^- anions are readily available for reaction at the surface of seawater, and can be involved in O_3 , OH, and particle formation [E. M. Knipping et al., *Science*, **2000**, *288*, 301]. Another example is humic acid acting as a photosensitizer in and at the surface of seawater, facilitating photochemical generation of a variety of products in the gas and aqueous phases [M. Shrestha et al., *Chem. Sci.*, **2018**, *9*, 5716; P. R. Erickson, *Environ. Sci. Technol.*, **2018**, *52*, 9170]. Photochemical reactions of pollutants in the environment at interfaces and in the bulk, and the identity and role of chromophores, remain important questions for increased understanding of these processes.

The keywords *quantum* and *coherent* comprise an existing theme in photochemical research observed more at ICP 2019 than 20 years prior. Michael R. Wasielewski (Northwestern University) in his plenary session first spoke on recent developments in observing quantum interference effects in a photoinduced electron transfer system with identical electron transfer acceptors and a single electron donor moiety. When comparing the electron transfer rate constant between molecules with only one acceptor as compared to two, Wasielewski and co-workers discovered that the rate enhancement associated with having multiple acceptors is greater than the sum of the two electron transfer rates [B. T. Phelan et al., *J. Am. Chem. Soc.*, **2019**, *141*, 12236–12239]. Importantly, this phenomenon is only apparent at cryogenic temperatures, suggesting the possibility of quantum coherence effects as a result of correlated system-bath fluctuations in frozen solutions

at low temperature. Continuing with his theme of quantum effects, Wasielewski and co-workers also showcased their most recent advances in demonstrating high-fidelity quantum teleportation. Using a molecular donor–acceptor-radical system, the organic entangled radical's spin information was transported to the donor moiety and was detected by time-resolved EPR, demonstrating prototypical quantum teleportation in an organic system [B. K. Rugg et al., *Nat. Chem.*, **2019**, DOI: [10.1038/s41557-019-0332-8](https://doi.org/10.1038/s41557-019-0332-8)].

Graham R. Fleming (University of California, Berkeley) gave his keynote talk centering on the application of two-dimensional electronic vibrational spectroscopy, or 2DEV, to track the photophysical dynamics in photosynthetic systems. As opposed to two-dimensional electron spectroscopy (2DES), 2DEV is a technique that can directly correlate electronic transitions of a chromophore with its vibrational motion by using a combination of visible and mid-IR pulses. Utilizing the influence of local protein structure on the energies of various chlorophyll high-frequency modes in light-harvesting complex II (LHCII), Fleming and co-workers demonstrated the ability to track energy transfer and elucidate relaxation pathways in this photosynthetic protein on the picosecond time scale [N. H. C. Lewis et al., *J. Phys. Chem. Lett.*, **2016**, *7*, 4197–4206]. Utilizing data from ultrafast spectroscopy, Fleming went on to describe a model for energy flow in the thylakoid membrane and the regulation of photosynthetic light harvesting [D. I. G. Bennett et al., *Proc. Natl. Acad. Sci.*, **2018**, *115*, E9523–E9531]. He further demonstrated his group's dedication to elucidating the photophysical processes in photosynthetic organisms by performing ultrafast transient absorption spectroscopy on live cells of *Nannochloropsis oceanica*, in an effort to identify the presence and physiological triggering factors of nonphotochemical quenching in wild-type and mutant systems [S. Park et al., *Proc. Nat. Acad. Sci.*, **2019**, *116*, 3385–3390].

While major themes emerged from our keyword analysis, it was also evident that the huge diversity of topics covered within the umbrella of photochemistry are not adequately represented in Figure 1. An excellent example of this is the work presented in the lecture of Christy Landes (Rice University). She presented strategies to leverage super-resolution microscopic techniques in order to quantify protein adsorption/desorption events and transport. She explained that, while chemical separation uses as much as 15% of U.S. domestic energy consumption, the science of this separation at nanostructured interfaces has remained largely empirical. Adsorption and desorption events can be modeled within the framework of statistical thermodynamics, providing a physical connection to the underlying chemistry that has been lacking in previous methods. Fluorescence superlocalization coupled with kinetic analysis makes it possible to distinguish between specific, repeat protein adsorption at ligand sites. In addition, Landes' group combined these super-resolved techniques with improvements in temporal resolution facilitated by the use of rotating phase masks in the optical detection path during data acquisition. This method of supertemporal-resolved microscopy was applied to the quantification of adsorption–desorption dynamics, protein unfolding, and nanoconfined transport, revealing previously unresolvable dynamics in this reinvigorated field of research [N. A. Moringo et al., *Annu. Rev. Phys. Chem.*, **2018**, *69* (1), 353–375].

Surface plasmons are a topic with a rich scientific history, yet this topic was completely absent in our 1999 ICP title keyword

analysis. In contrast, *surface plasmon* appeared in ~6% of 2019 ICP contributions, including the plenary lecture of Professor Paul Mulvaney (The University of Melbourne). He spoke about his group's recent advances on the surface plasmon spectroscopy of gold nanoparticles. These metal nanostructures offer a unique sensitivity to changes in their electron density in the form of their surface plasmon resonance. These effects can be exploited by examining plasmon spectra in high-pressure environments, where they can report on both the change in solvent refractive index and the mechanical properties of the nanostructure itself [C. Martín-Sánchez et al., *J. Phys. Chem. Lett.*, **2019**, *10*, 1587–1593; C. Martín-Sánchez et al., *ACS Nano*, **2019**, *13*, 498–504]. Similarly, the surface plasmon of a particle can be modified by adding even modest numbers of electrons. Through the integration of nanostructures into ion gel devices, rapid charging and detection of as few as 110 electrons was possible using a single gold rod as a sensor. Quite unlike a macroscopic conductive object, here, a color change will indicate that a particle is charged [S. S. E. Collins et al., *Nano Lett.*, **2016**, *16*, 6863–6869]. Another emerging technique developed by the group allows for the directed assembly of evenly spaced gold particles into ordered arrays, opening up new avenues in single nanocrystal spectroscopic sensing.

Another topic with increasing popularity at this year's ICP was *photoredox catalysis*. David W. C. MacMillan (Princeton University), as a pioneer in this field, presented several examples of photoredox catalysis helping access traditionally challenging organic transformations. Merging photocatalysis with transition-metal catalysis, new nickel and copper catalyzed cross-coupling reactions to form C–C, C–N, C–O, and C–S bonds can be accomplished under much milder conditions with various photocatalysts and blue light-emitting diode (LED) light. This approach takes advantage of the enhanced redox properties of photocatalysts to generate high-valence metal states to promote otherwise thermodynamically prohibitive elementary steps, such as reductive elimination and oxidative addition. The enhanced redox properties can also be exploited to promote facile generation of organic radicals to achieve C–H bond activation and selective isotopic substitution. For example, after photo-oxidation by an iridium photocatalyst, the α -H becomes extremely acidic and can exchange with deuterated and tritiated protic solvents [Y. Y. Loh et al., *Science*, **2017**, *358*, 1182–1187]. These new reactions altogether contribute to a more complete toolkit for large molecule synthesis for pharmaceutical as well as energy-related applications.

Poster prizes were awarded for 10 excellent contributions across a broad variety of session topics. Singlet fission, first reported in 1965, has enjoyed a recent research renaissance (see [Figure 1](#)), due to new materials, methods, and applications in the area of photovoltaics. The research of Michelle Chen (Northwestern University) reflected this, with her poster, *State Mixing Determines the Fate of the Multiexciton State in Singlet Fission*. Science with applications to light harvesting by solar cells was further highlighted by Andressa Vidal Müller (Universidade Federal do ABC and University of North Carolina at Chapel Hill) in the poster, *Tuning the Electron Transfer Rates in DSSCs with Ru(II) Dyes Having N-Heterocyclic Aromatic Substituents*. Muazzam Idris (University of Southern California) presented work entitled *Phenanthro[9,10-d]imidazole as Hosts and Fluorescent Emitters for Hybrid*

White Organic Light-emitting Diode Application, exploiting singlet and triplet energy levels in new LED materials.

New spectroscopic techniques were applied in the award-winning posters of Kathryn Ledbetter (Stanford University), *Time-Resolved X-ray Diffuse Scattering as a Probe of Site-Specific Solvation*, and Daria Blach (Purdue University) contributing to *Ultrafast Imaging of Energy Transport in CdSe/CdS Lateral Heterostructures*. Nancy Awwad (North Carolina State University) presented *Photochemical Upconversion Induced Polymerization* in the “Photochemistry and Photoredox session”, and Kylie Couch (University of Colorado, Boulder) won the session on “Atmospheric and Environmental Chemistry” with her poster, *Investigation of the Production of Hydroxylating Species from Dissolved Organic Matter Photolysis*.

Solar photochemistry remained a prevalent topic, with excellent contributions from Yuchun Wang (Hokkaido University) with *In-Situ Surface Enhanced Raman Scattering Observations of Water Oxidation Reactions Enhanced by the Modal Strong Coupling*; Maria Wächter (Leibniz Institute of Photonic Technology, Jena) with *Charge-Separation in Ni-tipped CdSe@CdS Nanorods for Hydrogen Evolution*; and Abdulaziz Alherz (University of Colorado, Boulder) with *Organic Hydrides for the Photoelectrochemical Catalytic Reduction of CO₂*.

The 2019 International Conference on Photochemistry has continued to explore important and established topics in the field and has illuminated new avenues of fascinating and useful light-induced phenomena across physics, biology, and chemistry. We would like to recognize the past and present conference chairs, as well as the large number of student volunteers, led in 2019 by NREL graduate student Justin Earley, for their efforts toward crafting an excellent meeting. The 30th International Conference on Photochemistry was recently announced and will be held July 18–23, 2021 in Geneva, Switzerland, chaired by Prof. Eric Vauthey. This meeting will undoubtedly continue the tradition of bringing together a wide variety of scientists to discuss and explore many different topics within the rich world of photochemical research. Interested participants are encouraged to visit www.icp2021.ch for further information.

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■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpca.9b09156](https://doi.org/10.1021/acs.jpca.9b09156).

Full list of conference talk and poster titles ([PDF](#))

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank Prof. Clifford Kubiak, Prof. David Phillips, Prof. Ken Ghiggino, and Prof. Garry Rumbles for their help in providing past conference data and information for this publication. We would also like to thank the speakers mentioned within this manuscript for feedback regarding their presentation summaries.