

Periodical Reports: Organic and Computational Aspects

Introduction and review of the year 2015

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DOI: 10.1039/9781782626954-00003

Some aspects of photochemistry and its applications on the basis of papers published in 2015 are discussed.

1 Introduction

As in previous years, the primary aim of this introduction is that of maintaining a common background in photochemistry, while this science finds always new applications. A potentially negative aspect is that the truly chemical aspects sometimes are less apparent than physical on one hand and biological aspects on the other one. This is clearly shown by the events that have taken place during 2015, declared the official UNESCO International Year of Light and Light-Based Technologies.¹ More precisely, the year has been devoted to photonics, that is “the science and technology of generating, controlling, and detecting photons, which are particles of light”. Attention of the general public is called to the many applications of photonics that characterize “daily life from smartphones to laptops to the Internet to medical instruments to lighting technology”. It is concluded that the 21st century will depend as much on photonics as the 20th century depended on electronics. In fact, photons travel at the rate of light and this is obviously advantageous to transmit signals in a photonic rather than in an electronic circuit. Furthermore, optical interconnections cross each other with no interference, again making the introduction of photonic connections preferable to wired connections, particularly in integrated circuits, where the space available is limited.² Certainly, photochemistry is close to photonics (see further below), but the approach chosen in 2015 celebrations has been almost exclusively based on the physical aspects (and indeed the events have organized by the leading institutions of physical sciences), with little attention to the chemical aspects.³ Thus, as it frequently occurs, physics is in forefront, while chemistry seems at most to have an ancillary function. On the other hand, Kemsley in C&ENews recalled⁴ the strict relation between chemistry and light by quoting Neckers, who had remarked two decades ago that “the history of chemistry itself winds around photochemistry and spectroscopy, because it was at this interface that the nature of the chemical bond was discovered”.⁵ In a commentary, Bach further remarked that photochemistry has now established itself as a key discipline, first of all able to build in a predictable and controlled way otherwise non accessible compounds, in particular those with strained and complex structures.³ Furthermore, although at present the low price of energy discourages efforts to minimize energy consumption,

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new photocatalytic systems activated by solar light are expected to be increasingly developed and to be able to activate processes not involving any external energy supply. Appropriate photocatalysts for stereoselective reactions are likewise being developed.³

A lively portrait of the personal and scientific aspects of Michael Kasha's work,⁶ a scientific paper by him⁷ and a collection of 18 papers dedicated to him⁸ have been published in Photochemistry and Photobiology. What makes molecules exhibit such an unusual behavior upon the absorption of a photon? In some cases it would seem that a magician is operating and keeps the cards behind his back. However, the rationalization of photochemistry has rapidly advanced and the application of light-induced reactions has enormously expanded. A recently published book highlights some aspects of the history of photochemistry and attempts to connect them with the present and future role of this science.⁹

A list of the highlights published in the last volumes is available at the end of this chapter.

2 Review of the year 2015

As usual, what follows is simply a personal choice of papers, from a very large number that would have been possible. Although, as indicated above, the year of light has been dominated by physical aspects, it has also stimulated the publication of collections of chemistry papers. An excellent example is the special issue of *Angewandte Chemie* (instalment 39). This contains an essay on the unique position of light as the fastest way to transport both information and energy through the space. The possibility to convert solar light into electrical and chemical energy, and hence into mechanical energy, artificial light and valuable chemicals is illustrated by Balzani and coll.¹⁰ Furthermore, some reviews on highly topic subjects are quoted below.

Graphene based photocatalysts have been shown to be highly useful for solar fuel generation.¹¹ Activation of molecular switches by visible light allow a more extensive application of such components.¹² Advanced spectroscopic methods initially developed for photophysical targets, are being increasingly used for photochemical reactions. Thus, coherent multidimensional electronic spectroscopy has been employed for reactions such as ring opening and ring closing, *cis-trans* isomerization, coherent vibrational wave-packet motion, radical ion formation, and population relaxation. In a recent report this approach has been used for new applications, such as the spiropyran–merocianine isomerization.¹³ Precision surface functionalization in polymers is rapidly developing, as demonstrated by a review by Delaittre *et al.*¹⁴ A number (35) of exciting communications follows in the same instalment, ranging from solar cells to hydrogen and oxygen evolution from water, molecular machines, the varied uses of luminescence, photochemical gene delivery, synthesis *via* photochemical reactions, the generation of reactive intermediates, the use of luminescence for various analytic purposes. In every case, the peculiarities of photochemistry are of great advantage.

As for the relation between photonics and photochemistry, one may name a recent study of a system where large-area single layer graphene is integrated into a nanostructured silicon substrate. It has been shown that the interaction of light with graphene and substrate photonic crystals can be classified in distinct regimes, *viz* plasmonic, photonic and free-space, depending on the relation of the photonic crystal lattice constant and the relevant modal wavelengths. An appropriate choice increases the absorption of graphene in the infrared, and improves the performance of modulators, filters, sensors and photodetectors utilizing silicon photonic platforms.¹⁵

A technical note of general interest has been published by Bolton,¹⁶ who, pursuing earlier work, has highlighted that measurements of photochemical reactions should always be referred to the photons absorbed, not to the energy absorbed.

Thus, when using a polychromatic source the measurement should be referred to the *photon fluence* over the wavelength interval chosen ($[F_{p,o}(\lambda)]$, Einstein m^{-2}), not to *fluence* ($[F_o(\lambda)]$, J m^{-2}). This is not always done, particularly when measuring the action spectrum of a substance. Thus, the fluence measured by a radiometer must be corrected by taking into account, besides geometric factors for imperfect collimation of the ray, an average function weighted by the spectral emittance of the lamp over the interval chosen. In this way, the quantum yield $\Phi_B(\lambda)$ is calculated from the (initial) reaction rate of compound B through expression (1), where V is the volume, $\chi_B(\lambda)$, the fraction of photon absorbed by B, $E_{op}(\lambda)$ the incident photon irradiance hitting the centre of the exposed vessel and the other factors take into account the geometry of the experiment, including reflected light (eqn (1)).

$$\Phi_B(\lambda) = \left[-\frac{d[B]}{dt} \right]_{t=0} \frac{V}{E_p^0(\lambda) A_H(\text{PF}) [\text{RF}(\lambda)] \chi_B(\lambda)} \quad (1)$$

Bolton further recalls that the general expression for Φ_B simplifies in two limiting cases, on one hand almost complete and constant absorption [absorbance(λ) ≈ 1] and thus apparent zero order, on the other one low absorption [absorbance(λ) < 0.02] and thus apparent first order. In a more general frame, one may remember that already Bodenstein in 1929 had remarked that such “order” had nothing to do with “what is known as the velocity constant of a chemical dark reaction; it is indeed nothing but the factor for calculating the energy absorbed in terms of the quantity of matter reacting. It is thus of course independent of external circumstances, such as temperature, addenda (if any), catalytic agents and aggregate state”. Properly speaking, there is therefore no order of photochemical reactions, as indeed it has been clearly pointed out more than a century ago.¹⁷

The mechanism of photochemical reaction is intrinsically complex and requires that all viable paths are explored. From the Franck Condon point the molecule evolves according to the topography of the surface. The excess energy available may be exchanged with the environment and any cleavage or rearrangement may occur on the same PES (adiabatic path) or after decay to another PES (nonadiabatic path) and then through direct

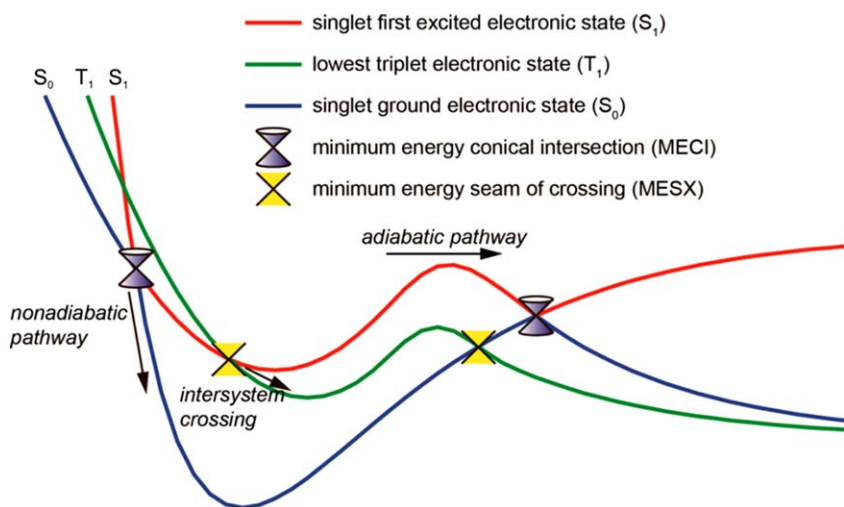


Fig. 1 Schematic of the potential energy profiles of the three states S_0 (blue), S_1 (red), and T_1 (green). Cross and cone marks represent the MESX points between the singlet and triplet states and the MECI points between the S_0 and S_1 , respectively. This is an unofficial adaptation of an article that appeared in an ACS publication.¹⁸ ACS has not endorsed the content of this adaptation or the context of its use.

and concerted paths. Despite the difficulty of the topic, advancement in theory continues at an impressive pace and, importantly, a synergy between theory and experiment develops. An efficient computational method, called the global reaction route mapping (GRRM) strategy, has been developed. This allows a theoretical exploration of ground- and excited-state PESs, their crossing seams (minimal energy conical intersections, MECI), minimal energy seams of crossing (MESX) and the location of transition states in an *automatic* manner, with no need of choosing a best-guess structure that would exclude unexpected molecular arrangements. In the case of formaldehyde, cleavage to $\text{CO} + \text{H}_2$, radical cleavage to $\text{HCO} + \text{H}$ and a path involving detachment of a hydrogen atom that migrates towards the other one (“roaming”, $\text{HCO} \cdots \text{H}$) have been characterized for singlet and triplet states (Fig. 1).¹⁸

Solvation has a key importance in determining the course of photochemical reactions. In particular, this applies to the solvation of starting excited states and of intermediates in charge transfer processes in polar solvents, a phenomenon that is usually discussed by assuming that the effect of the electrostatic fields of the solvent molecules on the internal electronic dynamics of the solute are perturbative and that the solvent–solute coupling is mainly an electrostatic interaction between the constant permanent dipoles of the solute and the solvent molecules. This model appears to be inaccurate for important classes of compounds, such as transition metal complexes, where solvent molecules are not just spectators of the electron density redistribution occurring, but significantly modulate it. Thus, an appropriate description of the dynamical changes of excited states during the solvent response demands an advanced computational method able to treat the solute and (at least) the closest solvent molecules and including the nonperturbative treatment of the interaction occurring.¹⁹

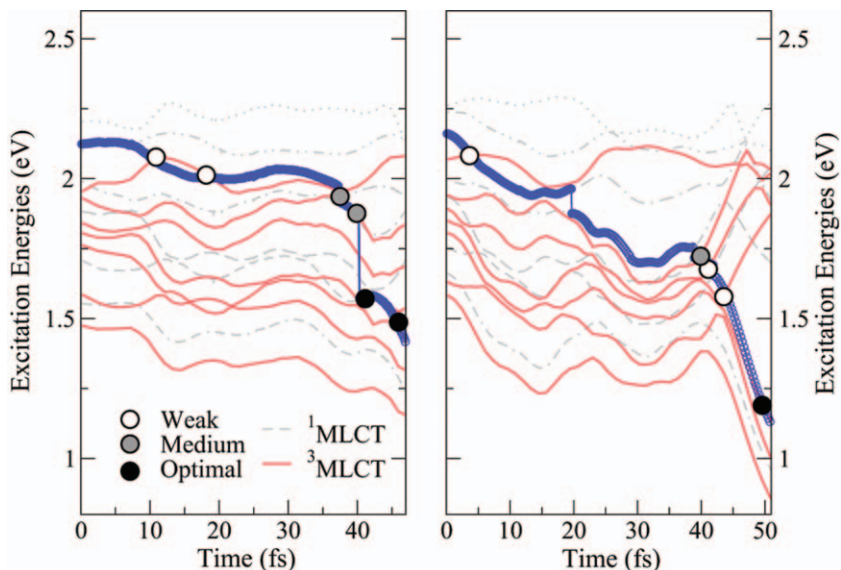


Fig. 2 Nonadiabatic molecular dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ in solution. Adapted with permission from I. Tavernelli, *Acc. Chem. Res.*, 2015, **48**, 792. Copyright 2015 American Chemical Society.

Theory is now able to offer an accurate characterization of the electronic structure of the ground and excited states and to describe the molecular dynamics in its full unconstrained configuration space, and an adequate representation of the interaction with the environment at atomistic level (using either DFT or classical molecular mechanics). As an example, the nonadiabatic molecular dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ in solution has been explored, obtaining a series of “snapshots” that represent the structure changes in the fs regime and predict possible trajectories. The stabilization due to the action of all (3298) close-lying water molecules has been determined. The panels (Fig. 2) show the time series of the relevant excited state energies corresponding to two representative trajectories. Singlet excited states (seven in total) are represented by dashed lines and triplet states (seven in total) by continuous thin lines. The system hops from one to another PES (thick line); crossings between singlet and triplet states and the largeness of spin orbit coupling (SOC, white = weak, gray = medium and black = large) are indicated.

Theory has been applied to rationalize (time-resolved) X-ray absorption spectra, as well as to the interpretation of the ultrafast relaxation dynamics of photoexcited dyes in solution and the design of specific laser pulses (capable of inducing desired chemical reactions) using local control theory.²⁰

As is well known, the assumption that the nuclear and electronic wave functions describing a molecular system can be determined independently (Born–Oppenheimer approximation) breaks down in many cases due to the important contribution of nuclear–electronic (vibronic) coupling. Spectroscopic experimental advances allows an unprecedented time and spatial resolution. As an example, different variants of

frequency-domain transient two-dimensional IR (T-2DIR) spectroscopy have been used, based on a pulse sequence combining electronic and vibrational excitations in the form of a UV-visible pump, a narrow band (12 cm^{-1}) IR pump, and a broadband (400 cm^{-1}) IR probe. The application of this approach to a donor–bridge–acceptor complex based on a Pt(II) *trans*-acetylide design motif showed that the rate of electron transfer is highly dependent on the amount of excess energy localized on the bridge following electronic excitation. Indeed, it was possible to selectively perturb bridge-localized vibrational modes during charge separation, in such a way that the donor–acceptor charge separation path was completely switched off, and all excess energy was redirected toward the formation of a long-lived intraligand triplet state. A large change in the photoproduct yield was observed only when the high-frequency bridging C≡C stretching mode was operative, suggesting that it was possible to perturb the electronic movement by stimulating a structural motion along the reaction coordinate using IR light. Controlling the pathways and efficiency of charge transfer certainly represents a breakthrough for applications such as solar energy conversion and molecular electronics.²¹

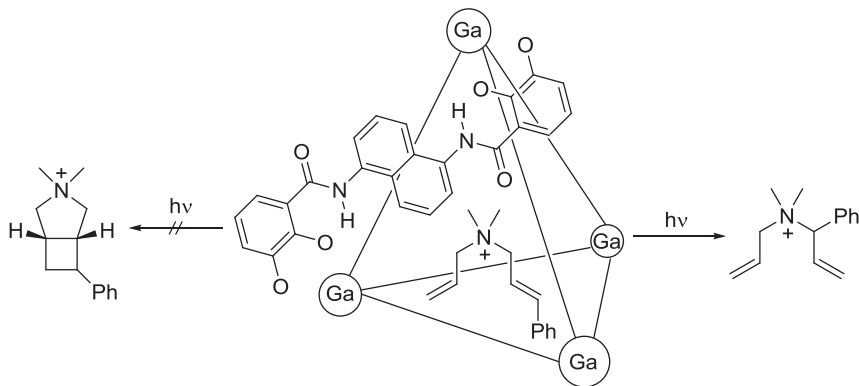
A new approach for the manipulation of photochemical processes like photoisomerization or photodissociation involves the use of short laser pulses that are intense enough to reshape the potential energy surfaces. Indeed, it has been demonstrated that chemical processes can be controlled with strong laser fields, as are properties like the molecular absorption spectrum, the state lifetimes, the quantum yields and the velocity distributions in photodissociation processes.²²

A way for characterizing non covalent interactions, such as hydrogen bonding, is matrix spectroscopy. However, this approach find limitation, *e.g.* because of a large concentration of 1 to 1 complexes that are otherwise difficult to prepare (*e.g.* $\text{H}_2\text{O}\cdots\text{O}_2$), or the reaction with mobile atoms occurring during annealing. The field has been reviewed and way for characterizing unusual complexes have been suggested.²³

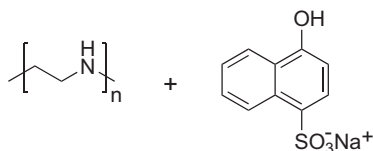
Proton coupled electron transfer is an ubiquitous phenomenon in chemistry and biology the underlying theory has been recently reviewed, pointing out the limitations still present in the currently used methods.²⁴

Supramolecular interactions in solution may guide the ensuing photochemical reactions and the variety of possibilities that it offers continue to be exploited. In a recent example, a cinnamoyl cation has been encapsulated within a $\text{Ga}_4\text{L}_6^{12-}$ (L = diamidonaphthalenebiscatecholamide) tetrahedron. Under these conditions, the 2 + 2 cycloaddition occurring in neat solvent is no more observed, and rather a 1,3-shift occurs. This process appears to involve electron transfer from the strongly donating ligand, detachment and recombination of trimethylamine (Scheme 1).²⁵

A linear polyethyleneimine, as the base, and a naphthol sulfonate, which undergoes an enhancement of the acidity upon irradiation, have been used as building blocks for a light-triggerable supramolecular assembly (Scheme 2). A ionic bond between the sulfate anion and the ammonium salt and a hydrogen bond between the phenol moiety and the non protonated amine contribute to the formation of a complex structure.²⁶



Scheme 1



Scheme 2

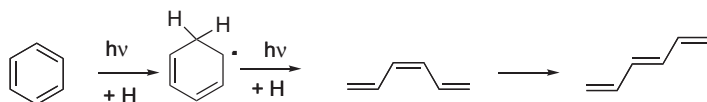
The photochemistry in the troposphere continues to attract attention because of the multitude of phenomena involved, such as inorganic bulk photolysis and radical sources, transition metal ion (mainly iron) complex photolysis, organic bulk photochemical reactions, interaction between particles and interfaces, photoinduced transformation of humic-like substances, photo-sensitized reactions in the bulk aqueous phase.^{27,28}

Further topics that have been comprehensively reviewed in the environmental field include the formation of urban particulate matter.²⁹ The atmospheric degradation of ozone depleting substances, their substitutes and related compounds and the linkage between air quality and climate change have been examined in detail.^{30,31}

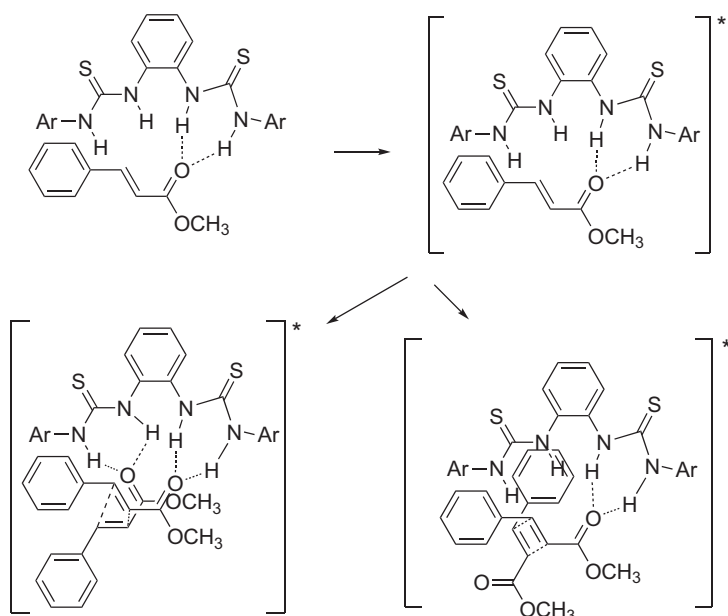
A rapidly growing topic has involved making synthetically significant long known photochemical reactions. Thus, aliphatic amines are well known electron transfer quenchers of excited states, innumerable times used for kinetic studies.

However, in the last decades it has been demonstrated that photo-sensitized oxidation (often by using visible light) and the ensuing deprotonation can be developed into a valuable synthetic method for the preparation of functionalized compound, including complex natural products.³²

The photochemistry of benzene and a number of its derivatives has been discussed in terms of aromatic *vs.* antiaromatic character, considered as a sort of Dr Jekyll, Mr Hyde contrast. The reactions occurring are viewed as arising from an attempt to alleviate the antiaromatic character of the excited states.³³ From the experimental point of view, a matrix study in solid para-hydrogen has evidenced, besides the known



Scheme 3



Scheme 4

isomerization to benzvalene and Dewar benzene, hydrogen abstraction to form a radical that further converts to hexatriene (Scheme 3).³⁴

The 2 + 2 photodimerization of cinnamates has been a major topic all along the history of photochemistry. A recent study has evidenced that carrying out the reaction in a flow system leads to a considerably larger yield and further that using a phenylendiurea allows to obtain a moderate diastereoselectivity (see the facial approach of the second molecule of cinnamate in the scheme). Studies of this type should pave the way for the next generation catalysts for highly diastereoselective and enantioselective intermolecular [2 + 2] cycloadditions (Scheme 4).³⁵

Biomolecule-compatible chemical bond-formation and bond-cleavage reactions induced by visible light have been reviewed and include electron transfer involving oxidative as well as reductive quenching and energy transfer promoted reactions.

The spatial and temporal resolution of light induced reactions combined with the decreased damage with respect to UV irradiation makes these reactions valuable for biomolecules labeling and manipulation.³⁶

Solvent-less organic fluids have developed into a new class of functional soft materials. Noteworthy, the key photochemical reactions of the molecular systems, such as photoisomerization, energy/electron transfer, photon upconversion and reversible dioxygen binding are conserved but,

differently from solutions, they are not limited by solvent, solvent polarity, the presence of oxygen *etc.*, thus challenging the established and accepted paradigms valid in solution and offering a “no worry” solution for practical application.³⁷

Photocontrollable capture and release of guest molecules from host molecules, photoresponsive rotaxanes, catenanes, and pseudorotaxanes, as well as photoresponsive supramolecular polymers and their assemblies and photoresponsive host-guest system on surfaces have been reviewed.³⁸

The biological activities in response to blue light involve three major classes of flavin photosensors, *viz.* LOV (light-oxygen-voltage) domains, BLUF (blue light sensor using FAD) proteins, and cryptochromes (CRYs). Advances in the field have been reviewed and have identified the photoexcitation of the flavin cofactor as the primary event that causes changes in redox and protonation states and ultimately lead to protein conformation remodel and molecular interactions.³⁹

The photochemistry of transition metal complexes has been exploited both for generating new complexes by ligand substitution (*via* LF states) and to sensitize or catalyze chemical processes, *e.g.* by oxygen sensitization (*via* MLCT states). As an example, a delicate tuning of the properties has been achieved in Ru²⁺ complexes by the appropriate modification of the ligands.⁴⁰

Photomedicinal applications are developing. An example is the use of photosensitizing molecules for the inhibition of β -amiloid aggregation, thus disclosing a way to rescue the post-synaptic toxicity of Alzheimer's disease in model systems.⁴¹

An informative approach in polymer photochemistry makes use of polymers that have metal-metal bonds incorporated into their backbones. In this case, irradiation in the visible leads selectively to cleavage of the metal-metal bond and then to degradation. The relatively simple degradation paths contrasts with the complex phenomenon observed with non metal containing polymers and allows a more detailed exploration of the mechanism (*e.g.*, by identifying two different environments where radicals are formed causing a double degradation kinetics).⁴²

The unique ability of spatial and temporal control photochemistry offers makes contributions to medicinal chemistry more and more important. New applications of photodynamic therapy based on oxidative photocatalytic paths, promoted by titania nanoparticles, carbon nanomaterials (fullerenes, carbon nanotubes and graphene), liposomes and polymeric nanoparticles.⁴³ Among the most recently developed PDT catalysts are metal complexes of the natural polyphenol curcumin.⁴⁴ On the other hand, the high rate of photochemical processes makes this mode of reaction the preferred choice for understanding fast biological processes, *e.g.* how do proteins work. A suitable method is time-resolved X-ray solution scattering (TRXSS) that utilizes a pump-probe scheme employing an optical pump pulse to initiate photoreactions of proteins and an X-ray probe pulse to monitor ensuing structural changes. Indeed, the technical advances in both ultrafast lasers and X-ray sources make now possible to bring temporal resolution down to femtoseconds.

As an example, in the case of hemoglobin the dynamics of complex allosteric transitions among transient intermediates has been unraveled by applying structural refinement analysis based on rigid-body modeling. It has been found that the allosteric transition of hemoglobin accompanies the rotation of quaternary structure and the contraction between two heme domains. This kind of studies suggest that TRXSS can be used to probe the structural dynamics of various proteins and clarifying the working mechanisms of their physiological operation. When combined with femtosecond X-ray pulses generated from X-ray free electron lasers, TRXSS will allow to explore ultrafast protein dynamics on sub-picosecond time scales.⁴⁵

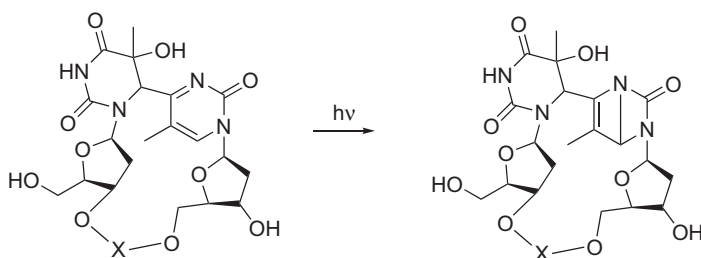
In the field of photoinduced damage to DNA (compare this year Nobel Prize), an investigation on thymidine dimers has shown that, although unconstrained, these compounds isomerizes quantitatively to the corresponding Dewar benzene (Scheme 5).⁴⁶

The work on the photochemical activation of proteins by inserting tetrazine derivatives has been further expanded. Thus, the tetrazine ring has been introduced between two SH groups in protein thioredoxin (*i.e.*, the chain has been stapled) and then the starting material has been regenerated (unstapling) (Scheme 6).⁴⁷

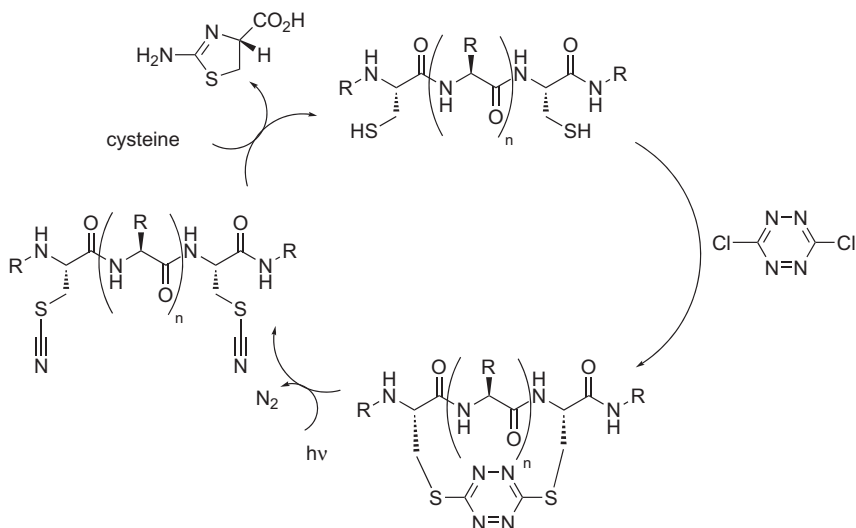
Multidentate lipoic acid (LA)-modified ligands have been used for transferring ZnS-overcoated quantum dots to the aqueous phase. The photoactive moiety is the deformed dithiolane present in the skeleton that originates a characteristic band in the UV as well as various reactions. Irradiation of the ligand alone, whether by a UV lamp or by using solar light prior to mixing with hydrophobic QDs is sufficient to promote ligand exchange. Ligation onto the QDs selectively favors oligomers, presumably due to their higher coordination onto the metal-rich QD surfaces. The use of mixed ligands allowed the preparation of reactive nanocrystals. These are useful for cellular staining after coupling to proteins and peptides further for developing fluorescent platforms for the application in imaging and sensor design.⁴⁸

An updated review on the photochemical fate of pharmaceuticals, including a discussion of the factors that affect the photolability of drugs, the choice of formulation in order to improve photostability and the guidelines of photostability tests has been published.⁴⁹

Among applications, a review of gel nail technologies may be mentioned.⁵⁰



Scheme 5



Scheme 6

3 Highlights in volumes 37 to 44

- Azobenzene photoisomerization, 2017, **44**, 294–321.
 Cultural heritage, and photochemistry, 2011, **39**, 256–284.
 Cyclodextrins, photoresponsive, 2016, **43**, 226–269.
 Exiton fission, 2016, **43**, 270–285.
 Flow photochemistry, 2016, **43**, 173–190.
 Fluorescence Imaging, nanoscale, 2011, **39**, 191–210.
 Global artificial photosynthesis, 2017, **44**, 259–282.
 Industrial applications, of photochemistry, 2010, **38**, 344–368.
 Interfacial electronic processes, on the surface of nanostructured semi-conductors, 2009, **37**, 362–392.
 History of photochemistry, IAPS, 2013, **41**, 269–278.
 History of photochemistry, EPA, **40**, 197–229.
 History of photochemistry, APA, 2012, **40**, 230–244.
 Human skin, photoprotection of, 2012, **40**, 245–273.
 Nitric oxide photorelease, 2013, **41**, 302–318.
 Nucleic acids, caged, 2013, **41**, 319–341.
 Organic solid-state luminescence, 2016, **43**, 191–225.
 OLEDs, 2009, **37**, 393–406.
 Photochromic, nanoparticles, 2011, **39**, 211–227.
 Photocatalysis for depollution, 2017, **44**, 346–361.
 Photolithography materials, 2010, **38**, 369–387.
 Photon–molecule coupling fields, 2011, **39**, 228–255.
 Photo-induced water oxidation, 2012, **40**, 274–294.
 Photoluminescence sensors, 2017, **44**, 322–345.
 Photo-oxygenation, 2010, **38**, 307–329.
 Polymerization, 2015, **42**, 215–232.
 Prebiotic atmosphere, 2013, **41**, 342–359.

Prebiotic photochemistry, 2010, **38**, 330–343.
Proton transfer, in flavonols, 2012, **40**, 295–322.
Reactive oxygen species, 2013, **41**, 279–301.
Solar energy conversion, 2017, **44**, 283–293.
Singlet oxygen, in biological media, 2015, **42**, 233–278.
Solid-state, photoreactions, 2016, **43**, 286–320 and 2016, **43**, 321–329.
TiO₂ photoredox catalysis, 2017, **44**, 362–381.
UV spectra, calculated, 2015, **42**, 197–214.

References

- 1 <http://www.light2015.org/Home.html>.
- 2 C. Yeh, *Applied Photonics*, Academic Press, S. Diego, 1994.
- 3 T. Bach, *Angew. Chem.*, 2015, **54**, 11294.
- 4 J. Kemsley, *C&EN*, 2015, **93**, 13.
- 5 D. C. Neckers, *Selected Papers on Photochemistry*, SPIE Press Books, 1993.
- 6 J. Saltiel, *Photochem. Photobiol.*, 2015, **91**, 574.
- 7 D. McMorro, M. I. Wyche, P. T. Chou and M. Kasha, *Photochem. Photobiol.*, 2015, **91**, 576.
- 8 *Photochem. Photobiol.*, 2015, **91**, 576–759.
- 9 A. Albini, *Photochemistry. Past, Present and Future*, Springer, Heidelberg, 2015.
- 10 V. Balzani, G. Bergamini and P. Ceroni, *Angew. Chem., Int. Ed.*, 2015, **54**, 11320.
- 11 Q. Xiang, B. Cheng and J. Yu, *Angew. Chem., Int. Ed.*, 2015, **54**, 11350.
- 12 D. Bléger and S. Hecht, *Angew. Chem., Int. Ed.*, 2015, **54**, 11338.
- 13 P. Nuernberger, S. Ruetzel and T. Brixner, *Angew. Chem., Int. Ed.*, 2015, **54**, 11368.
- 14 G. Delaittre, A. S. Goldmann, J. O. Mueller and C. Barner-Kowollik, *Angew. Chem., Int. Ed.*, 2015, **54**, 11388.
- 15 T. Gu, A. Andryeuskii, Y. Hao, Y. Li, J. Hone, C. W. Wong, A. Lavrinenko, T. Lowand and T. F. Heinz, *ACS Photonics*, 2015, **2**, 1552.
- 16 J. R. Bolton, I. Maior-Smith and K. G. Linden, *Photochem. Photobiol.*, 2015, **91**, 1252.
- 17 M. Bodenstein and C. Wagner, *Z. Phys. Chem.*, 1929, **3(B)**, 456.
- 18 S. Maeda, T. Taketsugu, K. Ohno and K. Morokuma, *J. Am. Chem. Soc.*, 2015, **137**, 3433.
- 19 A. Rondi, Y. Rodriguez, T. Feurer and A. Cannizzo, *Acc. Chem. Res.*, 2015, **48**, 1432.
- 20 I. Tavernelli, *Acc. Chem. Res.*, 2015, **48**, 792.
- 21 M. Delor, I. V. Sazanovich, M. Towrie and J. A. Weinstein, *Acc. Chem. Res.*, 2015, **48**, 1131.
- 22 I. R. Sola, J. Gonzalez-Vazquez, R. de Nalda and L. Benares, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13183.
- 23 L. Khriachtchev, *J. Phys. Chem. A*, 2015, **119**, 2735.
- 24 S. Hammes-Schiffer, *J. Am. Chem. Soc.*, 2015, **137**, 8860.
- 25 D. M. Dalton, S. R. Ellis, E. M. Nichols, R. A. Mathies, F. D. Toste, R. G. Bergman and K. N. Raymond, *J. Am. Chem. Soc.*, 2015, **137**, 10128.
- 26 C. Cardenas-Dawand and F. Gröhn, *J. Am. Chem. Soc.*, 2015, **137**, 8660.
- 27 H. Herrmann, T. Schaefer, A. Tilgner, S. A. Styler, C. Weller, M. Teichand and T. Tobias, *Chem. Rev.*, 2015, **115**, 4259.
- 28 C. George, M. Ammann, B. D'Anna, D. J. Donaldson and S. A. Nizkorodov, *Chem. Rev.*, 2015, **115**, 4218.

-
- 29 R. Zhang, G. Wang, S. Guo, M. L. Zamora, Q. Ying, Y. Lin, W. Wang, M. Hu and Y. Wang, *Chem. Rev.*, 2015, **115**, 3803.
 - 30 J. B. Burkholder, R. A. Cox and A. R. Ravishankara, *Chem. Rev.*, 2015, **115**, 3704.
 - 31 E. von Schneidmesser, P. S. Monks, J. D. Allan, L. Bruhwiler, P. Forster, D. Fowler, A. Lauer, W. T. Morgan, P. Paasonen, M. Righi, K. Sindelarova and M. A. Sutton, *Chem. Rev.*, 2015, **115**, 3856.
 - 32 J. W. Beatty and C. R. J. Stephenson, *Acc. Chem. Res.*, 2015, **48**, 1474.
 - 33 R. Papadakis and H. Ottosson, *Chem. Soc. Rev.*, 2015, **44**, 6472.
 - 34 S. Y. Toh, P. Djuricanin, T. Momose and J. Miyazaki, *J. Phys. Chem. A*, 2015, **119**, 2683.
 - 35 R. Telmesani, S. H. Park, T. Lynch-Colameta and A. B. Beeler, *Angew. Chem., Int. Ed.*, 2015, **127**, 11683.
 - 36 C. Hu and Y. Chen, *Tetrahedron Lett.*, 2015, **56**, 884.
 - 37 S. S. Babu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3950.
 - 38 Q. Da-Hui, Q.-C. Wang, Q.-W. Zhang, X. Ma and H. Tian, *Chem. Rev.*, 2015, **115**, 7543.
 - 39 K. S. Conrad, C. C. Manahan and B. R. Crane, *Nat. Chem. Biol.*, 2014, **10**, 801.
 - 40 J. D. Knoll, B. A. Albani and C. Turro, *Acc. Chem. Res.*, 2015, **48**, 2280.
 - 41 B. I. Lee, S. Lee, Y. S. Suh, J. S. Lee, A. Kim, O. Y. Kwon, K. Yu and C. B. Park, *Angew. Chem., Int. Ed.*, 2015, **54**, 11472.
 - 42 D. R. Tyler, *Inorg. Chim. Acta*, 2015, **424**, 29.
 - 43 R. Yin, T. Agrawal, U. Khan, G. K. Gauravi, H. Vikrant, Y. Ying and M. R. Hamblin, *Nanomedicine*, 2015, **10**, 2379.
 - 44 S. Banerjee and A. R. Chakravarty, *Acc. Chem. Res.*, 2015, **48**, 2075.
 - 45 J. G. Kim, T. W. Kim, J. Kimand and H. Ihee, *Acc. Chem. Res.*, 2015, **48**, 2200.
 - 46 T. Douki, S. Rebelo-Moreira, N. Hamon and P.-A. Bayle, *Org. Lett.*, 2015, **17**, 246.
 - 47 S. P. Brown and A. B. Smith III, *J. Am. Chem. Soc.*, 2015, **137**, 4034.
 - 48 F. Aldeek, D. Hawkins, V. Palomo, M. Safi, G. Palui, P. E. Dawson, I. Alabugin and H. Mattoussi, *J. Am. Chem. Soc.*, 2015, **137**, 2704.
 - 49 B. Vinod, V. Budhwaar and A. Nanda, *Int. J. Pharm. Res. Bio-Sci.*, 2015, **4**, 54.
 - 50 F. C. Pagano, *Cosmet. Toiletries*, 2015, **130**(40), 42.