CHAPTER 22

THE HISTORICAL DEVELOPMENT OF PHOTOREDOX CATALYSIS

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INTRODUCTION

The history of photocatalysis is both interesting and, in some respects, complex. Unlike modern researchers, who design and synthesize photocatalysts and photosensitizers for particular model reactions, the early investigators had only limited knowledge of photocatalytic processes and could not rely on previous experience. Their studies were mainly of a fundamental nature, whereas practical applications remained limited. Under such conditions, the behavior of newly synthesized compounds could not be predicted. In most cases, the only way to evaluate a new molecule was to prepare it and examine its properties experimentally. Since only a small number of compounds, and sometimes only a single compound, were available, the first practical results were obtained almost entirely by experiment rather than by rational design.

1. Origins of Photoredox Catalysis (1888–1977)

Fritz Blau

The first photosensitizer that comes to the mind of most chemists is undoubtedly tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$. The history of this complex, however, began much earlier, in the nineteenth century. In 1888, the Austrian chemist Fritz Blau (1865–1929), who had received his doctoral degree at the age of twenty-one for studies on nicotine chemistry, reported the first synthesis of 2,2′-bipyridine[1] (Figure 1a). Although attempts to prepare bipyridines had been made before Blau's work, they invariably afforded mixtures of positional isomers[2]. During the same period, Weidel, who also studied the synthesis of bipyridines, probably obtained small amounts of 2,2′-bipyridine. However, it was most likely identified as the bipyridine previously reported by Anderson from the reaction of pyridine with metallic sodium. It is now known that this reaction affords predominantly 4,4′-bipyridine[3], while substituted pyridines also give mainly 4,4′-bipyridine derivatives[4].

Blau subsequently prepared and described a series of stable chelate complexes of iron. Among them were $[Fe(bpy)_3]^{2+}$ together with several cobalt(II) and copper(II) complexes containing 2,2′-bipyridine and 1,10-phenanthroline[5]. His oxidation experiments with $[Fe(bpy)_3]^{2+}$ showed that the conversion of Fe^{2+} into Fe^{3+} required a stoichiometric amount of potassium permanganate. This result demonstrated that oxidation occurred at the metal center rather than at the organic ligand. At that time, this observation provided important experimental support for Werner's coordination theory, which was being developed together with the first studies of coordination compounds.

Blau also described the resulting ferric complex as a highly reactive blue compound. Upon exposure to light, the blue solution rapidly turned red because of the reduction of iron from the +3 to the +2 oxidation state. The ferric complex was also able to oxidize metallic mercury and silver, both metals being converted into their ionic forms while the solution became red. Blau further observed that the addition of alkali caused an immediate color change from blue to red, accompanied by the evolution of ozone. He also noted that neither 3,3′- nor 4,4′-bipyridine formed analogous iron complexes, indicating that these properties were characteristic of 2,2′-bipyridine.

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[1] Fritz Blau. Die Destillation pyridinmonocarbonsaurer Salze. *Berichte der Deutschen Chemischen Gesellschaft.* 1888. Vol. 21. P. 1077–1078. DOI: 10.1002/cber.188802101201

[2] Weidel H., Russo M. Studien über das Pyridin. *Monatshefte für Chemie*. 1882. Vol. 3. P. 850–885. DOI: 10.1007/BF01516855

[3] Anderson T. Ueber die Producte der trockenen Destillation thierischer Materien. *Annalen der Chemie und Pharmacie*. 1870. Vol. 154. P. 270–286. DOI: 10.1002/jlac.18701540303
1870;154:270–286. DOI: 10.1002/jlac.18701540303

[4] Heuser A., Stoehr C. Ueber methylirte Dipyridyle; II. Abhandlung. *Journal für Praktische Chemie*. 1891. Vol. 44. P. 404–410. DOI: 10.1002/prac.18910440133

[5] Blau F. Über neue organische Metallverbindungen. *Monatshefte für Chemie*. 1898. Vol. 19. P. 647–689. DOI: 10.1007/BF01517438

Blau was also among the first investigators to study heterogeneous photochemical processes directly under the microscope. In particular, he observed the phenomenon now known as hydratochromism for tris(bipyridine)iron(III) chloroplatinate. Within a few minutes, red serrated outgrowths appeared on the surface of the original green crystals and gradually propagated along the entire crystal. Blau further demonstrated that this process was completely reversible in the solid state. Treatment of the red crystals with chlorine water immediately regenerated the original green Fe^{3+} complex without dissolution of the solid. Thus, the work published in 1898 was not limited to the preparation of the first coordination compounds but also provided one of the earliest demonstrations of a reversible light-induced redox transformation in the solid state (Figure 1b).

The life and scientific activity of Fritz Blau were later described by his friend and colleague Marcello Pirani. Pirani is best known for the invention of the Pirani vacuum gauge in 1906, an instrument that is still widely used in chemical laboratories, vacuum lines, and rotary evaporators for the measurement of low pressures. It is of interest that, at the beginning of the twentieth century, Blau left academic research and entered industry. He became the head of the newly established research department of Osram (named after the elements osmium Os and tungsten W). Pirani was responsible for studies on gas discharge and electric lamps, whereas Blau directed the chemical research, patent activities, and the metallurgy of tungsten[6].

A detailed account of the chemistry and functionalization of bipyridines has recently been presented in the review by Catherine E. Housecroft (2019)[7].

Almost fifty years later, in 1936, Francis Burstall, working at the Chemical Research Laboratory in Teddington (England), prepared the same complex that is now regarded as the classical photosensitizer, $[Ru(bpy)_3]^{2+}$. At that time, however, Burstall was not interested in its photochemical properties. His research was devoted primarily to problems of stereochemistry. According to Werner's coordination theory, the octahedral complex should exist as two optical isomers. Burstall succeeded in resolving the racemic mixture into the stable left- and right-handed enantiomers.

The replacement of iron by ruthenium, a heavier element of the same group, was later found to produce a profound change in the properties of the complex. In particular, efficient metal-to-ligand charge transfer (MLCT) became possible. Owing to the strong spin–orbit coupling of ruthenium, the complex possesses unusually long-lived triplet excited states. These properties subsequently

[6] Pirani M. Fritz Blau. *Naturwissenschaften*. 1930. Vol. 18. P. 97–101. DOI: 10.1007/BF01493015

[7] Constable E. C., Housecroft C. E. The Early Years of 2,2'-Bipyridine–A Ligand in Its Own Lifetime. *Molecules*. 2019. Vol. 24, No. 21. Art. 3951. DOI: 10.3390/molecules24213951

established $[Ru(bpy)_3]^{2+}$ as one of the most important reference compounds in both photoredox catalysis and luminescence studies[8]. Burstall also synthesized the corresponding ruthenium terpyridyl complex, which later became another reference compound in coordination photochemistry[9].

After the preparation of these complexes in pure form, they remained essentially without practical application for more than twenty years. The breakthrough came in 1959, when Paris and Brandt first observed that $[Ru(bpy)_3]^{2+}$ exhibits an unusually intense luminescence with an exceptionally long excited-state lifetime in solution at room temperature. This finding was remarkable because no comparable behavior had previously been reported for coordination compounds. They correctly suggested that the emission originated from a metal-to-ligand charge-transfer process and described it as fluorescence. However, at that time the theoretical basis of the excited-state processes was not yet established, and the nature of the emitting state remained unclear[10]. As a consequence, these results attracted little immediate attention and were met with considerable skepticism, since no satisfactory theoretical interpretation of such long-lived emission was available at that time.

In 1971, two fundamental papers were published dealing with the determination of the quantum yield of luminescence. These studies established the basis for understanding the photophysics of charge-transfer complexes[11][12]. Prior to this time, considerable discussion had existed concerning the origin of the emission from ruthenium complexes, particularly whether it should be assigned to singlet excited states or to metal-centered d–d transitions. This question had largely been clarified in 1968, when Klassen and Crosby investigated the emission spectra of nine ruthenium(II) ($4d^6$) complexes at 77 K. They demonstrated that the characteristic emission bands were remarkably similar despite substantial differences in ligand structure. Furthermore, both experimental observations and theoretical analysis showed that the excitation energies did not correlate with the values predicted by crystal field theory if the excited states were regarded as metal-centered d–d transitions. Instead, the

[8] Burstall F. H. Optical activity dependent on coordinated bivalent ruthenium. *Journal of the Chemical Society*. 1936. P. 173–175. DOI: 10.1039/JR9360000173

[9] Morgan G., Burstall F. H. Researches on residual affinity and co-ordination. Part XXXVII. Complex metallic salts containing 2:6-di-2′-pyridylpyridine (2:2′:2″-tripyridyl). *Journal of the Chemical Society*. 1937. P. 1649–1655. DOI: 10.1039/JR9370001649

[10] Paris J. P., Brandt W. W. Charge transfer luminescence of a ruthenium(II) chelate. *Journal of the American Chemical Society*. 1959. Vol. 81, No. 18. P. 5001–5002. DOI: 10.1021/ja01527a064

[11] Crosby G. A., Demas J. N. Quantum efficiencies on transition metal complexes. II. Charge-transfer luminescence. Journal of the American Chemical Society. 1971. Vol. 93, No. 12. P. 2841–2847. DOI: 10.1021/ja00741a003

[12] Crosby G. A., Demas J. N. Measurement of photoluminescence quantum yields. *Journal of Chemical Education*. 1971. Vol. 75, No. 8. P. 991–1024. DOI: 10.1021/j100678a001

observed emission spectra were found to be in good agreement with a metal-to-ligand charge-transfer (MLCT) model, in which excitation involves the transfer of an electron from a metal d orbital to an antibonding orbital of the coordinated organic ligand[13] (Figure 1c).

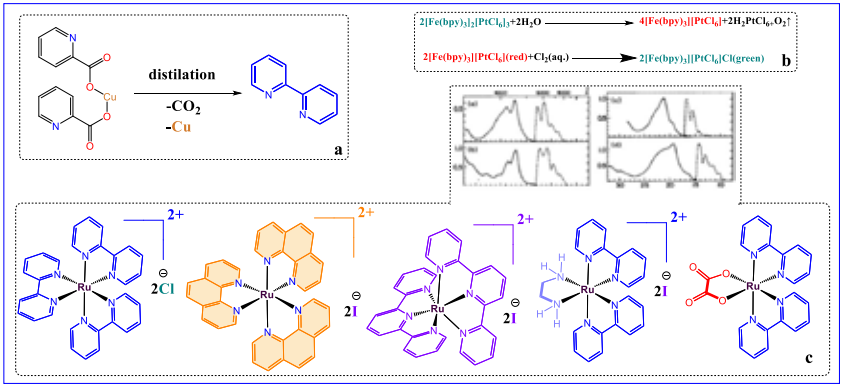


Fig. 1. Synthesis of 2,2′-bipyridine and the first metal complexes based on it

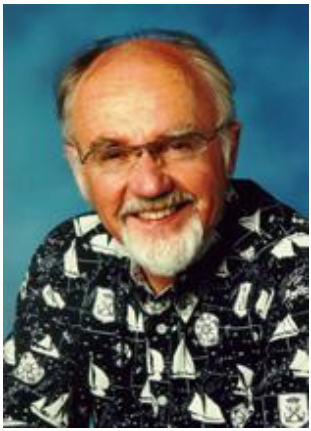
Although Klassen and Crosby demonstrated that luminescence is associated with a metal-to-ligand charge-transfer process, they had previously argued, in 1965, that charge transfer occurs only during the absorption of light. They proposed that this excited state subsequently undergoes a radiationless transition to a lower-lying state, from which the observed luminescence originates[14]. Consequently, the final emitting state was assigned to a metal-centered d–d excited state. Owing to Crosby's authority in the field, this interpretation became generally accepted.

In 1966, Richard Palmer and Thomas Piper examined single crystals in polarized light and investigated their absorption spectra. Their results clearly demonstrated that the absorption bands observed in the visible region correspond to allowed metal-to-ligand charge-transfer (MLCT) transitions. Thus, their experimental observations confirmed Crosby's interpretation of the absorption process, but did not provide evidence for the nature of the emitting state. Since the intense MLCT absorption band appeared near 450 nm, Palmer and Piper

[13] Klassen D. M. Spectroscopic Studies of Ruthenium(II) Complexes. Assignment of the Luminescence. *The Journal of Chemical Physics*. 1968. Vol. 48, No. 4. P. 1853–1858. DOI: 10.1063/1.1668922

[14] Crosby G. A., Perkins W. G., Klassen D. M. Luminescence from Transition-Metal Complexes: Tris(2,2′-bipyridine)- and Tris(1,10-phenanthroline)Ruthenium(II). *The Journal of Chemical Physics*. 1965. Vol. 43, No. 5. P. 1498–1503. DOI: 10.1063/1.1696960

assumed d–d absorption bands, which according to Crosby's model should lie at slightly lower energy, were simply obscured by the much stronger MLCT transition. It was later established, however, that the crystal-field splitting places the metal-centered d–d states above the MLCT excited state rather than below it. However, the value of the crystal field splitting parameter (Δ), estimated by Palmer and Piper from their absorption spectral studies, demonstrated that the excited d–d states should lie significantly higher in energy than the MLCT state[15].



Richard Palmer

In 1973, Harrigan proposed an electronic coupling model describing the symmetry of the lowest triplet MLCT excited state, thereby establishing the theoretical framework that forms the basis of the modern interpretation of the photophysics of Ru(II) polypyridyl complexes[16] (Figure 2).

A decisive step was made in 1972, when Geoffroy and Adamson demonstrated that $[Ru(bpy)_3]^{2+}$ is capable of intermolecular electron transfer. They reported the reaction between the photoexcited ruthenium complex and $[Co(NH_3)_5Cl]^{2+}$, showing that the cobalt complex acts as a one-electron oxidant and that the excited ruthenium complex undergoes a simple single-electron-transfer process[17].

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[15] Palmer R. A., Piper T. S. 2,2′-Bipyridine Complexes. I. Polarized Crystal Spectra of Tris(2,2′-bipyridine)copper(II), -nickel(II), -cobalt(II), -iron(II), and -ruthenium(II). *Inorganic Chemistry*. 1966. Vol. 5, No. 5. P. 864–878. DOI: 10.1021/ic50039a034

[16] Harrigan R. W. Symmetry assignments of the lowest CT excited states of ruthenium(II) complexes via a proposed electronic coupling model. The Journal of Chemical Physics. 1973. Vol. 59, No. 7. P. 3468–3476. DOI: 10.1063/1.1680504

[17] Gafney H. D., Adamson A. W. Excited state $Ru(bipyr)3^{2+}$ as an electron-transfer reductant. *Journal of the American Chemical Society*. 1972. Vol. 94, No. 23. P. 8238–8239. DOI: 10.1021/ja00778a054

In the same year, Akira Fujishima and Kenichi Honda reported the first photocatalytic decomposition of water under ultraviolet irradiation. Using a titanium dioxide photoanode and a platinum cathode, they demonstrated that illumination with ultraviolet light resulted in the evolution of oxygen and hydrogen. This discovery, which later became known as the Honda–Fujishima effect, represented the first successful example of light-driven water splitting and marked the beginning of heterogeneous semiconductor photocatalysis[18] (Figure 3).

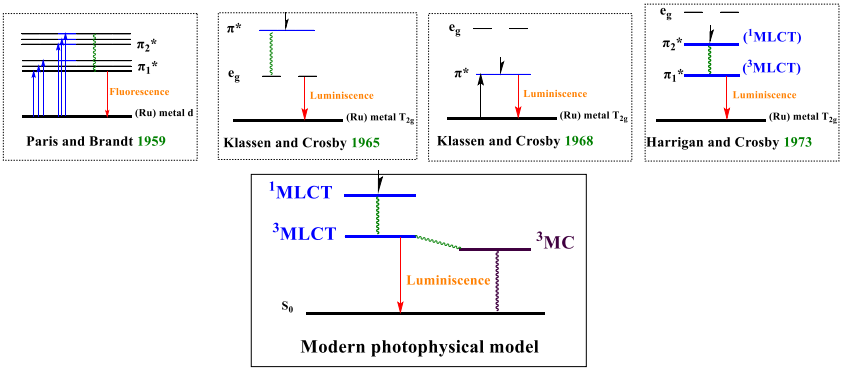

Fig. 2. Evolution of the electronic-state model for the luminescence of tris(2,2′-bipyridine)ruthenium(II), 1959–present

In 1974, Thomas J. Meyer, David G. Whitten, and Charles Bock made the next important advance by providing a detailed description of the concept of photoinduced electron transfer (PET)[19]. Using flash photolysis, they measured the rate of electron transfer from the excited state of $[Ru(bpy)_3]^{2+}$ to methyl viologen (MV^{2+}). This process resulted in the formation of the characteristic deep-blue radical cation $MV^{\bullet+}$, thereby providing direct experimental evidence for bimolecular photoinduced electron transfer (Figure 4a).

[18] Fujishima A., Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*. 1972. Vol. 238. P. 37–38. DOI: 10.1038/238037a0

[19] Bock C. R., Meyer T. J., Whitten D. G. Electron transfer quenching of the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II). Flash photolysis relaxation technique for measuring the rates of very rapid electron transfer reactions. *Journal of the American Chemical Society*. 1974. Vol. 96, No. 14. P. 4710–4712. DOI: 10.1021/ja00821a078

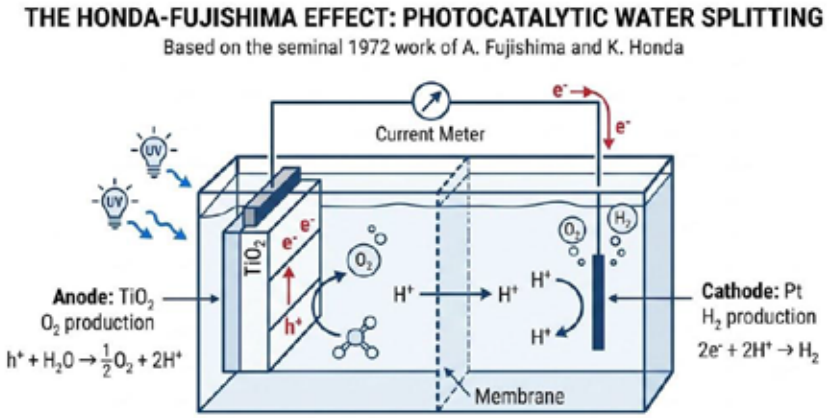

Fig. 3. The Honda–Fujishima Effect

In 1977, the future Nobel laureates Jean-Marie Lehn and Jean-Pierre Sauvage proposed the first three-component system for the photochemical production of hydrogen under visible-light irradiation[20, 21]. Almost simultaneously, in 1978–1979, Michael Grätzel and Jean Kiwi reported a series of studies in which the efficiency of hydrogen evolution was substantially improved through the optimization of colloidal noble-metal catalysts[22, 23] (Figure 4b).

Although these systems suffered from rapid deactivation, they provided the first convincing demonstration that solar energy could be utilized for the formation of chemical bonds. These investigations established the foundation for the subsequent development of artificial photosynthesis and solar fuel chemistry.

In 1978, Richard Kellogg and co-workers demonstrated that $[Ru(bpy)_3]^{2+}$ is capable of catalyzing the photoreduction of sulfonium salts in the presence of dihydropyridines as sacrificial electron donors. Although this work did not yet recognize photoredox catalysis as an independent field of organic synthesis, it

[20] Lehn J.-M., Sauvage J.-P. Chemical storage of light energy: Catalytic generation of hydrogen by visible light or sunlight irradiation of neutral aqueous solutions. Nouveau Journal de Chimie. 1977. Vol. 1. No. 14. P. 449–451

[21] Kirch M., Lehn J.-M., Sauvage J.-P. Hydrogen generation by visible light irradiation of aqueous solutions of metal complexes. An approach to the photochemical conversion and storage of solar energy. *Helvetica Chimica Acta*. 1979. Vol. 62, No. 4. P. 1345–1384. DOI: 10.1002/hlca.19790620449

[22] Kalyanasundaram K., Kiwi J., Grätzel M. Hydrogen evolution from water by visible light, a homogeneous three component test system for redox catalysis. *Helvetica Chimica Acta*. 1978. Vol. 61. P. 2720–2730. DOI: 10.1002/hlca.19780610740

[23] Kiwi J., Grätzel M. Hydrogen evolution from water induced by visible light mediated by redox catalysis. *Nature*. 1979. Vol. 281. P. 657–658. DOI: 10.1038/281657a0

is now generally regarded as the first example of the application of a ruthenium polypyridyl complex in photoredox catalysis[24] (Figure 4c).

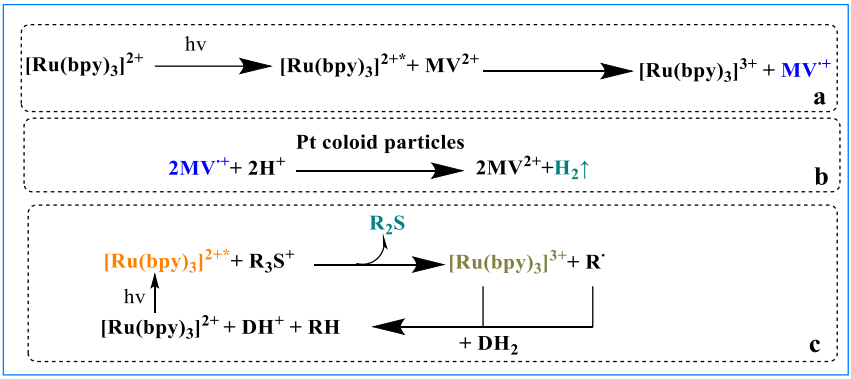

Fig. 4. Early Photophysical Reactions

2. Establishment of Photoredox Catalysis (1978–2007)

One of the earliest examples of the use of $[Ru(bpy)_3]^{2+}$ as a photocatalyst in organic synthesis is generally attributed to the work of C. Pac and co-workers, published in 1981[25]. In this study, the authors demonstrated the photocatalytic reduction of electron-deficient olefins employing the tris(bipyridine)ruthenium(II) complex as the photosensitizer. At that time, the investigation was directed primarily toward the elucidation of photochemical mechanisms and electron-transfer processes rather than toward the development of a general synthetic methodology.

During the following years, the studies of Deronzier, Cano, and other investigators demonstrated that both oxidative and reductive transformations could be controlled by means of photoinduced electron transfer[26]. These investigations gradually established the experimental basis upon which the modern concept of photoredox catalysis was later developed[27].

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[24] Hedstrand D. M., Kruizinga W. H., Kellogg R. M. Light induced and dye accelerated reductions of phenacyl onium salts by 1,4-dihydropyridines. *Tetrahedron Letters*. 1978. Vol. 19, No. 14. P. 1255–1258. DOI: 10.1016/S0040-4039(01)94515-0

[25] Pac C., Ihama M., Yasuda M., Miyauchi Y., Sakurai H. Tris(2,2′-bipyridine)ruthenium(2+)-mediated photoreduction of olefins with 1-benzyl-1,4-dihydronicotinamide: a mechanistic probe for electron-transfer reactions of NAD(P)H-model compounds. *Journal of the American Chemical Society*. 1981. Vol. 103, No. 21. P. 6495–6497. DOI: 10.1021/ja00411a040

[26] Cano-Yelo H., Deronzier A. Photo-oxidation of some carbinols by the Ru(II) polypyridyl complex-aryl diazonium salt system. *Tetrahedron Letters*. 1984. Vol. 25, No. 48. P. 5517–5520. DOI: 10.1016/S0040-4039(01)81614-2

[27] Cano-Yelo H., Deronzier A. Photocatalysis of the Pschorr reaction by tris-(2,2′-bipyridyl) ruthenium(II) in the phenanthrene series. *Journal of the Chemical Society, Perkin Transactions 2*. 1984. Vol. 13, No. 6. P. 1093–1098. DOI: 10.1039/P29840001093

A major limitation of the classical three-component photochemical systems developed during the late 1970s was that electron transfer depended upon random diffusional encounters between the reacting species in solution. In addition, rapid back electron transfer considerably reduced the overall efficiency of the process.

To overcome these limitations, Vincenzo Balzani and Franco Scandola introduced, in the late 1980s, the concept of supramolecular photochemistry and photochemical molecular devices (PMDs). In particular, Balzani proposed that a ruthenium photosensitizer could be enclosed within a rigid three-dimensional molecular framework (a cryptand) (Figure 5b). Such encapsulation increased the rigidity of the system, prolonged the lifetime of the excited state, and protected the complex against photochemical degradation during charge transfer by nearly four orders of magnitude[28]. This concept stimulated extensive experimental work during the first half of the 1990s. Experimental confirmation was obtained following the synthesis of the first covalently linked donor–acceptor dyads and triads. Ruthenium(II) polypyridyl complexes became the classical model systems of this period and served as the basis for numerous investigations of long-range electron transfer and artificial photosynthetic assemblies.

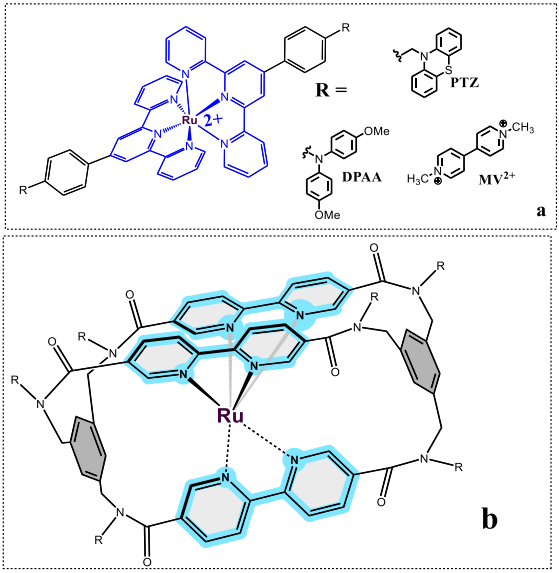

Fig. 5. Ruthenium Supramolecular Complexes

[28] Balzani V., Moggi L., Scandola F. Towards a supramolecular photochemistry: Assembly of molecular components to obtain photochemical molecular devices. In: Supramolecular Photochemistry. Dordrecht: Reidel Publishing Company, 1987. P. 1–28. DOI: 10.1007/978-94-009-3979-0_1

In the studies of Jean-Pierre Sauvage, Luisa De Cola, Lucia Flamigni, and Vincenzo Balzani, a series of donor–acceptor dyads and triads based on ruthenium bis(terpyridine) complexes covalently linked to methyl viologen, quinones, and other electron donors and acceptors was prepared[29] (Figure 5a). Investigation of these systems provided experimental confirmation of the supramolecular photochemical concept and established the foundation for the further development of photochemical molecular devices (PMDs).

During the 1990s, the concept of supramolecular photochemistry underwent rapid development. The principal efforts were directed toward the construction of increasingly sophisticated donor–acceptor dyads, triads, and multinuclear supramolecular assemblies. At the same time, considerable attention was devoted to the development of photochemical molecular devices and molecular machines, which represented an important step toward the realization of artificial photosynthetic systems[30].

Despite the remarkable progress achieved with supramolecular assemblies, their practical application remained limited owing to the extensive use of complexes of expensive noble metals. This circumstance stimulated the search for new classes of photocatalysts based entirely on organic molecules, capable of performing analogous photoinduced electron-transfer processes without the use of transition metals.

A major contribution to the modern understanding of electron-transfer reactions was made by Shunichi Fukuzumi. His research covered fundamental aspects of photoinduced and thermal electron transfer, the mechanisms of radical-ion formation, the influence of the reaction medium on electron-transfer rates, and the design of model systems that mimic the natural photosynthetic reaction center.

In one of his fundamental reviews[31], Fukuzumi summarized the mechanisms of acid- and cation-promoted electron-transfer reactions and demonstrated the general principles governing these processes (Figure 6).

In the same year (1997), Fukuzumi, together with Matthias Patz, demonstrated that many classical nucleophilic addition reactions may proceed through an initial single-electron-transfer (SET) step involving the formation of radical-ion intermediates. The factors governing the transition from conventional

[29] Collin J.-P., Guillerez S., Sauvage J.-P., Barigelletti F., De Cola L., Flamigni L., Balzani V. Photoinduced processes in dyads and triads containing a ruthenium(II)-bis(terpyridine) photosensitizer covalently linked to electron donor and acceptor groups. *Inorganic Chemistry.* 1991. Vol. 30, No. 22. P. 4230–4238. DOI: 10.1021/ic00022a026

[30] Balzani V., Credi A., Venturi M. Photochemistry and photophysics of coordination compounds: An extended view. *Coordination Chemistry Reviews.* 1998. Vol. 171. P. 3–16. DOI: 10.1016/S0010-8545(98)90005-4

[31] Fukuzumi S. Catalysis on electron transfer and the mechanistic insight into redox reactions. *Bulletin of the Chemical Society of Japan*. 1997. Vol. 70, No. 1. P. 1–28. DOI: 10.1246/bcsj.70.1

two-electron pathways to single-electron mechanisms were systematically analyzed, and particular attention was devoted to the influence of the oxidation and reduction potentials of the reactants on the course of these reactions[32].

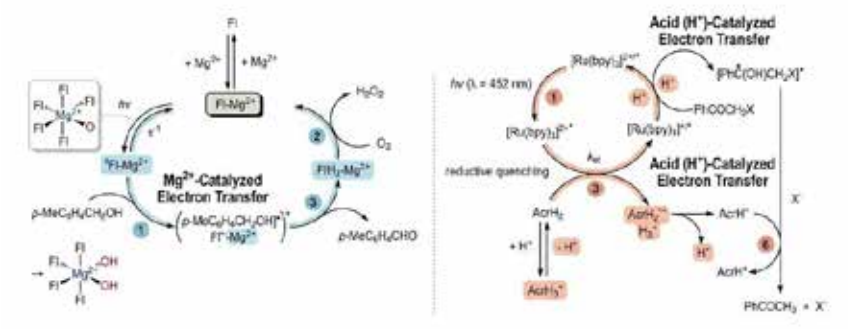

Fig. 6. Generalized Schemes of Cation and Acid Catalysis According to Fukuzumi

After a relatively short pause, Fukuzumi continued his investigations by developing a series of model systems that mimicked biological electron-transfer processes. Particular attention was devoted to artificial analogues of superoxide dismutase, hydride-transfer cofactors such as NAD^+ and $NADP^+$, and proton-transfer systems. He demonstrated that metal ions can profoundly modify the redox properties of coenzyme models, including pyrroloquinoline quinones (PQQ), tryptophan quinones, and flavins, thereby regulating both the rate and the direction of electron-transfer reactions. As one representative example, Fukuzumi described a model of bacterial methylamine dehydrogenase based on a metal complex containing a tryptophan quinone ligand. This system successfully mimicked the active site of the natural enzyme and enabled the dehydrogenation of amines under laboratory conditions[33]. It was further demonstrated that coordination of metal cations altered the redox potentials of these molecules and permitted catalytic transformations that scarcely occurred in the absence of the metal ions[34].

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[32] Patz M., Fukuzumi S. Electron transfer in organic reactions. *Journal of Physical Organic Chemistry*. 1997. Vol. 10, No. 3. P. 129–137. DOI: 10.1002/(SICI)1099-1395(199703)10:3<129::AID-POC884>3.0.CO;2-4

[33] Itoh S., Taniguchi M., Takada N., Nagatomo S., Kitagawa T., Fukuzumi S. Effects of metal ions on the electronic, redox, and catalytic properties of cofactor TTQ of quinoprotein amine dehydrogenases. *Journal of the American Chemical Society*. 2000. Vol. 122. P. 12087–12097. DOI: 10.1021/ja0020207

[34] Fukuzumi S., Itoh S. Catalytic control of redox reactivities of coenzyme analogs by metal ions. *Antioxidants & Redox Signaling*. 2001. Vol. 3, No. 5. P. 807–824. DOI: 10.1089/15230860152664993

An important stage in these studies was the experimental investigation of photoinduced electron transfer between neutral electron donors and acridinium cations. It was shown that charge-shift electron-transfer processes proceed efficiently in both polar and non-polar solvents, thus considerably extending the range of systems suitable for artificial photochemical charge separation. A further advance in the development of artificial photosynthetic systems was achieved with the construction of donor–acceptor assemblies exhibiting remarkably long-lived charge-separated states. In one such system, the lifetime of the charge-separated state reached approximately 380 ms, representing one of the longest values reported for artificial photosynthetic models at that time[35]. One of Fukuzumi's most influential contributions[36] was the development of the donor–acceptor system 9-mesityl-10-methylacridinium (Acr^+–Mes), in which the mesityl fragment served as the electron donor and the acridinium cation as the electron acceptor. The nearly perpendicular arrangement of the two aromatic units minimized π-conjugation between them and substantially reduced the reorganization energy associated with electron transfer. Upon photoexcitation, the system produced a long-lived charge-separated state, $Acr^{\bullet}$–$Mes^{\bullet+}$, with a quantum yield of approximately 98%. The energy of this state was 2.37 eV, nearly five times greater than that of the charge-separated state in the natural photosynthetic reaction center (approximately 0.50 eV). At 203 K, the lifetime of the charge-separated state reached 2 h, representing one of the longest-lived artificial donor–acceptor systems reported at that time.

Early in 2004, Fukuzumi reported the preparation of this exceptionally long-lived charge-separated system. Later in the same year, he demonstrated for the first time its practical application as a photocatalyst for the photooxidation of anthracene and tetramethylethylene by molecular oxygen. This work marked the beginning of acridinium photoredox catalysis as a distinct area of organic photocatalysis[37].

During the following years, Fukuzumi further expanded the scope of acridinium photoredox catalysis by investigating the mechanisms of photoinduced electron transfer, the activation of molecular oxygen, the formation of reactive

[35] Imahori H., Guldi D. M., Tamaki K., Yoshida Y., Luo C., Sakata Y., Fukuzumi S. Charge separation in a novel artificial photosynthetic reaction center lives 380 ms. *Journal of the American Chemical Society*. 2001. Vol. 123, No. 27. P. 6617–6628. DOI: 10.1021/ja004123v

[36] Fukuzumi S., Kotani H., Ohkubo K., Ogo S., Tkachenko N. V., Lemmetyinen H. Electron-transfer state of 9-mesityl-10-methylacridinium ion with a much longer lifetime and higher energy than that of the natural photosynthetic reaction center. *Journal of the American Chemical Society*. 2004. Vol. 126, No. 6. P. 1600–1601. DOI: 10.1021/ja038656q

[37] Kotani H., Ohkubo K., Fukuzumi S. Photocatalytic oxygenation of anthracenes and olefins with dioxygen via selective radical coupling using 9-mesityl-10-methylacridinium ion as an effective electron-transfer photocatalyst. *Journal of the American Chemical Society*. 2004. Vol. 126, No. 49. P. 15999–16006. DOI: 10.1021/ja048353b

oxygen species, and the influence of Lewis acids on photocatalytic efficiency. These studies established the foundations for his subsequent contributions to artificial photosynthesis and the photocatalytic conversion of solar energy.

In the following years, Fukuzumi continued to develop acridinium photoredox catalysis by investigating the mechanisms of photoinduced electron transfer, the activation of molecular oxygen, the formation of reactive oxygen species, and the influence of Lewis acids on the efficiency of photocatalytic processes. These studies provided the foundation for his subsequent work in the fields of artificial photosynthesis and photocatalytic conversion of solar energy.

Beginning in the second half of the 2010s, Fukuzumi gradually shifted his research from the development of individual organic photocatalysts toward the design of integrated artificial photosynthetic systems. In particular, he reviewed contemporary approaches to the photocatalytic production of hydrogen as a clean and sustainable fuel. Special attention was also given to the problems of hydrogen storage and transportation, which remain among the principal challenges of the hydrogen economy[38].

Shunichi Fukuzumi

After 2015, one of the major directions of Fukuzumi's research became the use of hydrogen peroxide as an alternative solar fuel. He demonstrated the possibility of photocatalytic synthesis of H_2O_2 directly from water and molecular oxygen under solar irradiation and further showed its potential application in fuel cells for the direct generation of electrical energy. In contrast to molecular hydrogen, hydrogen peroxide is a liquid under ambient conditions, which greatly simplifies its storage, transportation, and practical use[39].

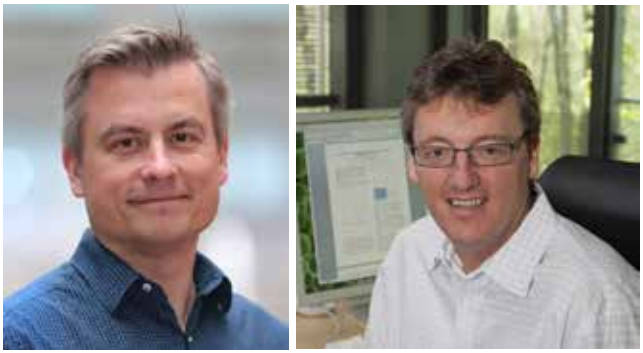
[38] Fukuzumi S. Artificial photosynthetic systems for production of hydrogen. *Current Opinion in Chemical Biology.* 2015. Vol. 25. P. 18–26. DOI: 10.1016/j.cbpa.2014.12.008

[39] Fukuzumi S. Artificial photosynthesis for production of hydrogen peroxide and its fuel cells. *Biochimica et Biophysica Acta.* 2016. Vol. 1857, No. 5. P. 604–611. DOI: 10.1016/j.bbabio.2015.08.012

3. Modern Development of Photoredox Catalysis (2008–2026)

Tehshik Yoon

While Fukuzumi was engaged in the synthesis of new acridinium systems and in the study of their application in photocatalysis, the field of photoredox catalysis entered a new stage of development at the end of 2008. In September of that year, Tehshik P. Yoon and co-workers demonstrated that the complex $Ru(bpy)_3^{2+}$ could promote visible-light-induced [2+2] cycloaddition reactions of enones, thereby revealing the considerable synthetic potential of such transformations[40].



David Nicewicz and David MacMillan

Only one month later, David W. C. MacMillan and David A. Nicewicz published in Science the first example of combining photoredox catalysis

[40] Ischay M. A., Anzovino M. E., Du J., Yoon T. P. Efficient visible light photocatalysis of [2+2] enone cycloadditions. *Journal of the American Chemical Society.* 2008. Vol. 130, No. 39. P. 12886–12887. DOI: 10.1021/ja805387f

with organocatalysis for the asymmetric α-alkylation of aldehydes. This work demonstrated that photoredox catalysis could serve as a general platform for complex organic transformations and is now widely regarded as the beginning of the modern era of visible-light photoredox catalysis[41].

A further advance followed in 2009, when Corey R. J. Stephenson demonstrated the broad applicability of ruthenium polypyridyl complexes in radical reactions of organic synthesis. The contributions of Yoon, MacMillan, Nicewicz, and Stephenson established the modern concept of visible-light photoredox catalysis, which during the following decade became one of the most rapidly developing areas of synthetic organic chemistry[42].

Following these pioneering studies of 2008–2009, photoredox catalysis rapidly evolved into an independent field of modern organic synthesis. Between 2010 and 2012 numerous new photocatalytic transformations were reported, including alkylation, fluoroalkylation, cycloaddition, and radical functionalization of organic molecules. At the same time, the theoretical foundations of the field were established, and the mechanisms of photoinduced electron transfer were systematically reviewed. As a result, photoredox catalysis came to be regarded not as a specialized branch of photochemistry, but as a general synthetic strategy applicable to a wide range of organic reactions[43].

An important step in the further development of the field was the combination of photoredox catalysis with organocatalysis. Soon after the first report of MacMillan and Nicewicz, methods for the asymmetric trifluoromethylation of aldehydes were developed, considerably expanding the scope of radical functionalization of carbonyl compounds.

At approximately the same time, the efficient introduction of trifluoromethyl groups into arenes and heteroarenes under visible-light irradiation was demonstrated. These transformations proved to be of considerable value for the synthesis of biologically active molecules and pharmaceutical compounds. Collectively, these studies demonstrated that photoredox catalysis was applicable not only to model reactions but also to synthetically important transformations[44].

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[41] Nicewicz D. A., MacMillan D. W. C. Merging photoredox catalysis with organocatalysis: the direct asymmetric alkylation of aldehydes. *Science*. 2008. Vol. 322. P. 77–80. DOI: 10.1126/science.1161976

[42] Narayanam J. M. R., Tucker J. W., Stephenson C. R. J. Electron-transfer photoredox catalysis: development of a tin-free reductive dehalogenation reaction. *Journal of the American Chemical Society*. 2009. Vol. 131, No. 25. P. 8756–8757. DOI: 10.1021/ja9033582

[43] Narayanam J. M. R., Stephenson C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chemical Society Reviews*. 2011. Vol. 40, No. 1. P. 102–113. DOI: 10.1039/B913880N

[44] Pham P. V., Nagib D. A., MacMillan D. W. C. Photoredox catalysis: a mild, operationally simple approach to the synthesis of α-trifluoromethyl carbonyl compounds. *Angewandte Chemie International Edition*. 2011. Vol. 50. P. 6119–6122. DOI: 10.1002/anie.201101861

Corey Stephenson

The early studies in modern photoredox catalysis were based primarily on the $Ru(bpy)_3^{2+}$ complex. It soon became evident, however, that its reducing power was insufficient for the activation of many organic substrates. This limitation was overcome by the use of the fac-$Ir(ppy)_3$ complex, originally synthesized in 1985[45] but first introduced into photoredox catalysis on a broad scale by Corey Stephenson in the early 2010s[46]. Owing to its more negative excited-state reduction potential, this complex enabled transformations that were inaccessible to ruthenium photocatalysts and initiated the rapid development of iridium-based photocatalytic systems. Compared with $Ru(bpy)_3^{2+}$, iridium complexes possess longer-lived triplet excited states, a broader range of redox potentials, and higher photostability[47]. These properties make them effective in reactions requiring stronger photooxidants or photoreductants, and they rapidly became one of the principal classes of photocatalysts in modern organic synthesis.

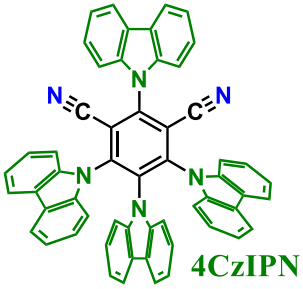
[45] King K. A., Spellane P. J., Watts R. J. Excited-state properties of a triply ortho-metalated iridium(III) complex. *Journal of the American Chemical Society*. 1985. Vol. 107, No. 5. P. 1431–1432. DOI: 10.1021/ja00291a064

[46] Nguyen J., D'Amato E., Narayanam J. et al. Engaging unactivated alkyl, alkenyl and aryl iodides in visible-light-mediated free radical reactions. *Nature Chemistry.* 2012. Vol. 4. P. 854–859. DOI: 10.1038/nchem.1452

[47] Condie A. G., Gonzalez-Gomez J. C., Stephenson C. R. J. Visible-light photoredox catalysis: aza-Henry reactions via C–H functionalization. *Journal of the American Chemical Society*. 2010. Vol. 132, No. 5. P. 1464–1465. DOI: 10.1021/ja909145y

Burkhard König

In 2011, the groups of Burkhard König and Kirsten Zeitler published one of the first studies comparing the performance of organic dyes with that of the classical photocatalyst $Ru(bpy)_3^{2+}$. They demonstrated that eosin Y afforded results comparable to those obtained with the ruthenium complex in a number of representative transformation. This work provided important experimental evidence that organic dyes could serve as inexpensive and readily available alternatives to photocatalysts based on precious metals[48]. Although eosin- and fluorescein-derived dyes did not become the principal photocatalysts of the field, they represented the first important step toward the development of metal-free organic photocatalysis.



Chihaya Adachi

One of the most significant advances in metal-free photocatalysis was the introduction of a new class of donor–acceptor organic photocatalysts based

[48] Neumann M., Füldner S., König B., Zeitler K. Metal-free, cooperative asymmetric organophotoredox catalysis with visible light. *Angewandte Chemie International Edition.* 2011. Vol. 50, No. 4. P. 951–954. DOI: 10.1002/anie.201002992

on carbazole and dicyanobenzene. In 2012, Adachi and co-workers prepared 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) as an emitter for organic light-emitting diodes (OLEDs). Owing to the phenomenon of thermally activated delayed fluorescence (TADF), this compound exhibited a long-lived excited state, excellent photostability, and favorable redox properties. These characteristics subsequently made 4CzIPN one of the most efficient organic photocatalysts, capable of replacing ruthenium and iridium[49] complexes in many photoredox transformations.

The introduction of 4CzIPN stimulated the rapid development of TADF photocatalysts and demonstrated that highly efficient visible-light photoredox catalysis could be achieved without the use of precious metals. Since that time, numerous donor–acceptor organic photocatalysts have been developed, greatly expanding the scope of metal-free photoredox catalysis.

Despite the rapid development of donor–acceptor TADF photocatalysts, acridinium salts have retained their importance. The further development of this class is closely associated with the work of David A. Nicewicz, who considerably expanded the synthetic applications of acridinium photocatalysts. In contrast to ruthenium and iridium complexes, acridinium salts possess exceptionally high excited-state oxidation potentials (typically exceeding +2.0 V vs SCE), allowing the activation of unfunctionalized arenes, alkenes, and other electron-rich substrates through single-electron oxidation[50].

In 2014, the group of Nicewicz published a series of papers demonstrating the use of 9-mesityl-10-methylacridinium salts as efficient organic photocatalysts, particularly for the photocatalytic functionalization of alkenes[51]. Acridinium photocatalysts did not replace Ru(II)- and Ir(III)-based systems; instead, they occupied a distinct position owing to their substantially higher excited-state oxidation potentials, the absence of precious metals, the relative simplicity of their synthesis, and their lower cost. These properties enabled transformations that were inaccessible to most ruthenium- and iridium-based photocatalysts.

By the period 2015–2017, photoredox catalysis had become established as an independent discipline within modern organic chemistry. Attention gradually shifted from the discovery of new reactions toward the consolidation of accumulated knowledge, the development of new classes of photocatalysts,

[49] Uoyama H., Goushi K., Shizu K., Nomura H., Adachi C. Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature*. 2012. Vol. 492, No. 7428. P. 234–238. DOI: 10.1038/nature11687

[50] Nicewicz D. A., Nguyen T. M. Recent applications of organic dyes as photoredox catalysts in organic synthesis. *ACS Catalysis*. 2014. Vol. 4, No. 1. P. 355–360. DOI: 10.1021/cs400956a

[51] Romero N. A., Nicewicz D. A. Mechanistic insight into the photoredox catalysis of anti-Markovnikov alkene hydrofunctionalization reactions. *Journal of the American Chemical Society*. 2014. Vol. 136, No. 49. P. 17024–17035. DOI: 10.1021/ja506228u

and the expansion of their synthetic applications. During this period, two comprehensive review articles published in Chemical Reviews summarized nearly a decade of progress in modern photoredox catalysis.

Another major advance occurred in 2014 with the emergence of dual metallaphotoredox catalysis. The group of David W. C. MacMillan demonstrated that the combination of an iridium photocatalyst with a nickel catalyst enabled the decarboxylative cross-coupling of alkyl carboxylic acids with aryl halides under remarkably mild conditions. The photoexcited iridium complex generated alkyl radicals through single-electron transfer, whereas the nickel catalyst mediated the conventional cross-coupling cycle. This strategy successfully combined the advantages of photoredox catalysis with transition-metal catalysis and established a new direction in modern organic synthesis[52]. Shortly thereafter, the concept was extended to numerous C–C, C–N, C–O, and C–S bond-forming reactions, making dual nickel/photoredox catalysis one of the most rapidly expanding areas of synthetic chemistry.

The review by Tehshik P. Yoon, Dual Catalysis Strategies in Photochemical Synthesis (2016), focused on the development of dual catalytic systems in which photoredox catalysis was combined with organocatalysis, transition-metal catalysis, Lewis acid catalysis, and other catalytic strategies[53].

In the same year, David A. Romero and David A. Nicewicz published the review «Organic Photoredox Catalysis»[54], in which the principal classes of organic photocatalysts were systematically summarized for the first time. This review established the modern view that photoredox catalysis had evolved along two major directions: transition-metal photoredox catalysis, based primarily on ruthenium and iridium complexes, and organic photoredox catalysis, represented by a broad range of metal-free photocatalysts.

Following the introduction of 4CzIPN, studies published during 2016–2017 demonstrated that this organic photocatalyst could efficiently replace ruthenium- and iridium-based complexes in a variety of photoredox transformations. The work of the groups of Gary A. Molander[55] and Burkhard König[56] showed that the combination of a long-lived excited state, high photostability, and favorable

[52] Zuo Z. et al. Merging photoredox with nickel catalysis: Coupling of α-carboxyl sp3-carbons with aryl halides. *Science*. 2014. Vol. 345. P. 437–440. DOI: 10.1126/science.1255525

[53] Skubi K. L., Blum T. R., Yoon T. P. Dual catalysis strategies in photochemical synthesis. *Chemical Reviews*. 2016. Vol. 116, No. 17. P. 10035–10074. DOI: 10.1021/acs.chemrev.6b00018

[54] Romero N. A., Nicewicz D. A. Organic photoredox catalysis. *Chemical Reviews*. 2016. Vol. 116, No. 17. P. 10075–10166. DOI: 10.1021/acs.chemrev.6b00057

[55] Patel N. R., Kelly C. B., Siegenfeld A. P., Molander G. A. Mild, redox-neutral alkylation of imines enabled by an organic photocatalyst. *ACS Catalysis*. 2017. Vol. 7. P. 1766–1770. DOI: 10.1021/acscatal.6b03665

[56] König B. Photocatalysis in organic synthesis – past, present, and future. *European Journal of Organic Chemistry.* 2017. P. 1979–1981. DOI: 10.1002/ejoc.201700420

redox properties enabled 4CzIPN to achieve catalytic efficiencies comparable to those of many Ru(II) and Ir(III) photocatalysts, while eliminating the need for precious metals[57].

Gary Molander

Following 2016, one of the most rapidly developing areas became the application of donor–acceptor organic molecules exhibiting thermally activated delayed fluorescence (TADF). In many photoredox transformations these photocatalysts proved to be efficient alternatives to ruthenium and iridium complexes.

At the same time, new applications of photoredox catalysis were actively explored. Considerable progress was achieved in electrophotocatalysis, continuous-flow photochemistry[58], and in the photocatalytic conversion of CO_2, nitrogen, water, and molecular oxygen. Current research is increasingly directed toward the development of energy-efficient and environmentally sustainable photocatalytic processes.

The emergence of efficient organic photocatalysts also stimulated the development of new synthetic methods for their preparation. At the end of 2017, Christoph Sparr reported a convenient one-step synthetic approach to acridinium, xanthylium, and silicon-rhodamine (SiR) fluorophores. Silicon-rhodamine dyes had originally been introduced in 2008[59] and rapidly found

[57] Huang H., Li X., Yu C., Zhang Y., Mariano P. S., Wang W. Visible-light-promoted nickel- and organic-dye-cocatalyzed formylation reaction of aryl halides and triflates and vinyl bromides with diethoxyacetic acid as a formyl equivalent. *Angewandte Chemie International Edition*. 2017. Vol. 56, No. 6. P. 1500–1505. DOI: 10.1002/anie.201610108

[58] Politano F., Oksdath-Mansilla G. Light on the horizon: current research and future perspectives in flow photochemistry. *Organic Process Research & Development*. 2018. Vol. 22. P. 1045–1062. DOI: 10.1021/acs.oprd.8b00213

[59] Fu M., Xiao Y., Qian X., Zhao D., Xu Y. A design concept of long-wavelength fluorescent analogs of rhodamine dyes: replacement of oxygen with silicon atom. *Chemical Communications*. 2008. No. 15. P. 1780–1782. DOI: 10.1039/B718544H

widespread application in fluorescence microscopy and bioimaging[60]. Owing to their absorption and emission in the red and near-infrared region of the spectrum, these compounds remain attractive candidates for the development of photocatalytic systems operating under long-wavelength irradiation.

Christoph Sparr

In 2019, Sparr further demonstrated that acridinium photocatalysts are capable of competing with the most widely used organic photocatalysts. Comparison with 4CzIPN revealed that while 4CzIPN afforded superior results in certain transformations, modified acridinium salts were more efficient in others. The authors concluded that the principal advantage of acridinium photocatalysts lies in their broad structural tunability, which is largely unavailable for 4CzIPN. Such structural flexibility permits systematic adjustment of their photophysical and redox properties, making it possible to optimize the photocatalyst for a particular transformation[61].

The continued development of photoredox catalysis has also led to the emergence of a new class of photoactive materials, namely organic semiconductor photocatalysts. In 2019, the groups of Burkhard König and Markus Antonietti demonstrated that carbon nitride can serve as an efficient heterogeneous photocatalyst for the functionalization of arenes and heteroarenes[62].

[60] Grimm J. B., Klein T., Kopek B. G., Shtengel G., Hess H. F., Sauer M., Lavis L. D. Synthesis of a far-red photoactivatable silicon-containing rhodamine for super-resolution microscopy. *Angewandte Chemie International Edition.* 2016. Vol. 55, No. 5. P. 1723–1727. DOI: 10.1002/anie.201509649

[61] Fischer C., Kerzig C., Zilate B., Wenger O. S., Sparr C. Modulation of acridinium organophotoredox catalysts guided by photophysical studies. *ACS Catalysis*. 2020. Vol. 10, No. 1. P. 210–215 DOI: 10.1021/acscatal.9b03606

[62] Ghosh I., Khamrai J., Savateev A., Shlapakov N., Antonietti M., König B. Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science*. 2019. Vol. 365, No. 6451. P. 360–366. DOI: 10.1126/science.aaw3254

Bart Pieber

The next stage in the development of this field was the combination of organic semiconductor photocatalysts with transition-metal catalysis. In 2020, the group of Bartholomäus Pieber demonstrated that the use of carbon nitride in combination with nickel catalysis overcomes one of the principal limitations of dual photoredox catalysis, namely the deactivation of the nickel catalyst. This approach provided more stable C–N cross-coupling reactions, improved catalytic efficiency, and further demonstrated the potential of heterogeneous organic photocatalysts in dual catalytic systems[63].

Sukbok Chang

Another important contribution made in 2020 was reported by the group of Sukbok Chang, who synthesized a rhodium complex incorporating

[63] Gisbertz S., Reischauer S., Pieber B. Overcoming limitations in dual photoredox/nickel-catalysed C–N cross-couplings due to catalyst deactivation. *Nature Catalysis*. 2020. Vol. 3, P. 611–620. DOI: 10.1038/s41929-020-0473-6

an acridinium chromophore. This catalyst enabled efficient light-driven C–H arylation and C–H methylation reactions. The study demonstrated the feasibility of integrated photocatalytic systems in which the photosensitizer and the transition-metal complex operate as a single catalytic entity[64]. During the period 2021–2023, considerable attention was devoted to the preparation of new acridinium photocatalysts possessing modified redox properties, enhanced photostability, and improved selectivity[65]. At the same time, the development of dual metallaphotoredox catalysis, particularly nickel-based systems[66], continued rapidly. During these years, acridinium salts became firmly established as one of the most important classes of organic photocatalysts. Numerous new C–C, C–N, C–O, and C–S cross-coupling reactions, together with methods for direct C–H functionalization, were reported, considerably expanding the synthetic scope of modern photoredox catalysis[67].

A further development of the integrated metallaphotoredox concept was reported in 2024. A bifunctional photocatalyst was prepared in which a donor–acceptor organic photosensitizer structurally related to 4CzIPN was covalently linked to a bipyridine ligand capable of coordinating nickel ions. This molecular design combined the functions of the photosensitizer and the metal ligand within a single structure[68].

Unlike previous systems, where the semiconductor photocatalyst and the metal complex were employed as separate components, a different strategy was introduced in 2025. In this case, a MnSalen complex was covalently immobilized on the surface of graphitic carbon nitride. Besides improving catalytic efficiency, this approach also allowed repeated recovery and reuse of the catalyst[69].

During 2025–2026, research on graphitic carbon nitride (g-C_3N_4) became increasingly focused on controlling its crystallinity and defect structure in

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[64] Kim J., Kim D., Chang S. Merging two functions in a single Rh catalyst system: Bimodular conjugate for light-induced oxidative coupling. *Journal of the American Chemical Society*. 2020. Vol. 142, No. 45. P. 19052–19057. DOI: 10.1021/jacs.0c09982

[65] Yan H., Zhu S., Xu H.-C. Integrating continuous-flow electrochemistry and photochemistry for the synthesis of acridinium photocatalysts via site-selective C–H alkylation. *Organic Process Research & Development*. 2021. Vol. 25, No. 12. P. 2608–2613. DOI: 10.1021/acs.oprd.1c00038

[66] Palkowitz M. D., Emmanuel M. A., Oderinde M. S. et al. A paradigm shift in catalysis: electro- and photomediated nickel-catalyzed cross-coupling reactions. *Accounts of Chemical Research*. 2023. Vol. 56, No. 20. P. 2851–2865. DOI: 10.1021/acs.accounts.3c00479

[67] Singh P. P., Singh J., Srivastava V. Visible-light acridinium-based organophotoredox catalysis in late-stage synthetic applications. *RSC Advances*. 2023. Vol. 13, No. 16. P. 10958–10986. DOI: 10.1039/d3ra01364b

[68] Dolcini L. et al. Bifunctional photocatalysts display proximity-enhanced catalytic activity in metallaphotoredox C–O coupling. *ACS Catalysis*. 2024. Vol. 14, No. 24. P. 18651–18659. DOI: 10.1021/acscatal.4c05893

[69] Shi X. et al. Enhanced three-component chloro-/azido-fluoroalkylation of unactivated alkenes via the proximity effect in a heterogeneous metallaphotocatalyst. *ACS Catalysis*. 2025. Vol. 15, No. 3. P. 2180–2191. DOI: 10.1021/acscatal.4c06960

order to improve its photophysical properties in the photocatalytic production of hydrogen peroxide, hydrogen, the oxidation of biomolecules, and a variety of organic transformations[70]. At the same time, the concept of photocharged carbon nitride received considerable attention. In these systems, graphitic carbon nitride is capable of storing photogenerated charge and subsequently utilizing the accumulated charge to promote catalytic reactions even after irradiation has ceased. In parallel, elemental sulfur (S_8) was shown to be a more selective oxidant than molecular oxygen and an efficient sulfur source for the sulfurization of organic compounds. Since carbon nitride is a heterogeneous photocatalyst, its separation from the reaction mixture is straightforward, providing an additional practical advantage[71].

Thus, the modern development of photoredox catalysis is increasingly directed not only toward the discovery of new photocatalysts but also toward the construction of integrated catalytic systems, in which the photosensitizer and the transition-metal complex function as a single molecular or material architecture. Such an approach provides new opportunities for controlling electron-transfer processes, reaction selectivity, and catalytic efficiency, and represents one of the principal directions of contemporary photocatalytic chemistry (Figure 7).

4. Development of Mesityl-Acridinium Photosensitizers in Photocatalysis

Photocatalysis is based on the ability of a photosensitizer to absorb light, reach an excited state, and undergo single-electron transfer (SET). The rate and efficiency of this process determine whether a given catalyst is suitable for a particular photochemical transformation.

The theoretical basis of electron-transfer reactions was established by Rudolph A. Marcus in 1956[72]. According to the Marcus theory, the rate of electron transfer depends not only on the thermodynamic driving force of the reaction (ΔG, Gibbs free energy), but also on the reorganization energy (λ), which reflects the structural rearrangement of both the reacting molecules and their solvent shells accompanying electron transfer. The maximum electron-transfer rate is achieved when the driving force is close to the reorganization energy. In other words, when the reaction becomes excessively exergonic (i.e., ΔG becomes much more negative than λ), the rate of electron transfer decreases

[70] Zheng Y., Liang X., Qu J., Zhang Y., Liu Y., Li Y., Guo X. Crystal phase engineering of carbon nitride: Advances in regulation strategies and photocatalytic applications. *Chemistry – A European Journal*. 2025. Vol. 31. Art. e02011. DOI: 10.1002/chem.202502011

[71] Wang C., Zhuang J., Savateev O. Organic synthesis mediated by carbon nitride photocatalysis and photocharged carbon nitrides. *Accounts of Chemical Research*. 2026. Vol. 59, No. 2. P. 246–257. DOI: 10.1021/acs.accounts.5c00687

[72] Marcus R. A. On the theory of oxidation-reduction reactions involving electron transfer. I. *The Journal of Chemical Physics.* 1956. Vol. 24, No. 5. P. 966–978. DOI: 10.1063/1.1742723

rather than increases. For the development of this theory, Marcus was awarded the 1992 Nobel Prize in Chemistry[73].

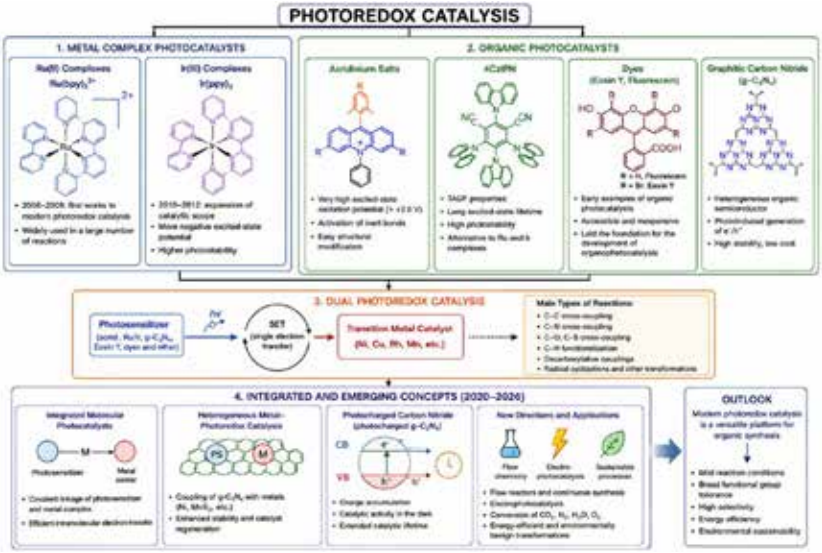

Fig. 7. Modern Photoredox Catalyst

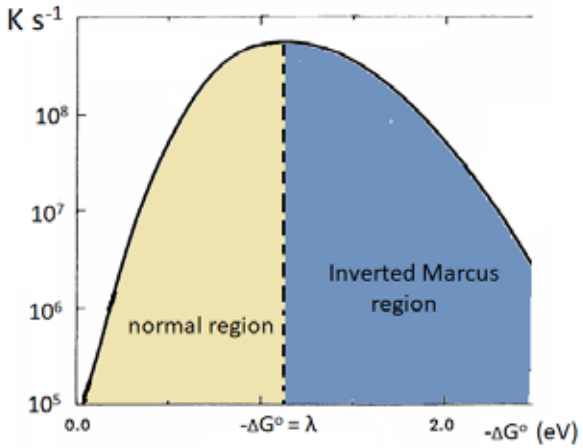

Fig. 8. Electron Transfer Rate in the Normal and Inverted Marcus Regions

[73] The Nobel Prize in Chemistry 1992. NobelPrize.org. Nobel Prize Outreach. 2026. Available at: https://www.nobelprize.org/prizes/chemistry/1992/summary/ (accessed 29.07.2026).

In photoredox catalysis, the electron-transfer ability of a photocatalyst is generally evaluated from its oxidation and reduction potentials, which describe its photooxidizing and photoreducing power after photoexcitation. For this reason, the literature usually reports two sets of electrochemical data, namely E_{ox} and E_{red}, together with the corresponding excited-state potentials E^*_{ox} and E^*_{red}, which are directly used to predict the feasibility of a given photoredox process.

On the basis of the Marcus theory, Fukuzumi described the kinetics of back electron transfer (BET) from the photoinduced charge-separated state [Mes•⁺–Acr•] to the ground-state species [(Mes–Acr)⁺] (Equation 1). Upon photoexcitation, the charge-separated state [Mes•⁺–Acr•] is formed with a quantum yield of approximately 98%. The energy of this state was found to be 2.37 eV (−0.49 − +1.88 eV), which is nearly five times greater than that of the charge-separated state found in the natural photosynthetic reaction center (approximately 0.50 eV). At 203 K, the lifetime of the charge-separated state reached two hours, representing one of the longest-lived artificial donor–acceptor systems reported at that time.

$$\ln(k_{BET}T^{-1}) = \ln\left(\frac{k_B}{h}\right) - \frac{(\Delta G^0_{BET} + \lambda)^2}{4\lambda k_B T}$$

Equation 1

The reorganization energy, λ, consists of two contributions: an external and an internal component. In solution, the external contribution corresponds to the energy required for solvent reorganization around the molecule, whereas the internal contribution reflects structural changes within the molecule itself, including variations in bond lengths and bond angles.

Based on these considerations, Fukuzumi designed the 9-mesityl-10-methylacridinium system in such a way that the mesityl group remains nearly perpendicular (approximately 90°) to the acridinium ring. As a consequence, the molecular geometry changes very little upon photoexcitation, leading to a remarkably small reorganization energy. At the same time, the molecule retains a large energy difference between its oxidized and reduced states, resulting in a very high excited-state redox potential.

An important consequence of this molecular design is that photoexcitation occurs within the normal Marcus region, whereas the back electron-transfer process takes place in the Marcus inverted region. Under these conditions, the larger the difference between the driving force and the reorganization energy, the slower the back electron transfer becomes, thereby substantially increasing the lifetime of the excited charge-separated state.

This concept became the fundamental principle underlying the molecular design of acridinium-based photosensitizers and enabled the preparation of photocatalysts possessing exceptionally long-lived excited states.

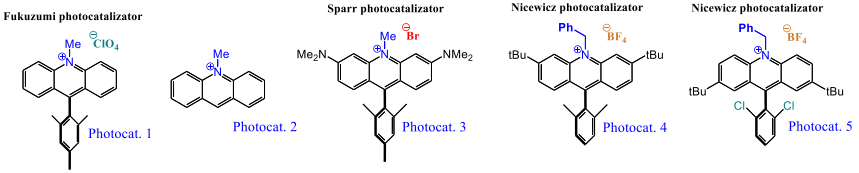

Table 1

Photophysical Properties of Selected Widely Used Photosensitizers[74, 75, 76]

PC	λ abs, nm	τ,ns	$E_{1/2}(P^*/P^-)$, V
Photocat. 1 (MesAcr$^+$Me)	430	6–10	+2.08
Photocat. 2 (Acr$^+$Me)		34 – 37	+2.32
Photocat. 3	503	2.2	+1.25
Photocat. 4	422	23.7	+2.13
Photocat. 5	--------	25.7	+2.20
4CzIPN	435	Pf-18.7, df-1390[a]	+1.35
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	380	2300	+1.21
$[Ru(bpy)_3](PF_6)_2$	452	1100	+0.77
Eosin Y	520	S-2.1, T-160000[b]	+0.83
Rose Bengal	558	S-2.38, T-2400[c]	+0.81

a) For 4CzIPN, values are given for prompt fluorescence and delayed fluorescence.
b) S – measured in methanol; T – measured in H_2O.
c) Measured in 10^{-4} M NaOH solution saturated with air

Despite their considerably shorter excited-state lifetimes compared with Ru and Ir complexes, organic photocatalysts exhibit comparable catalytic activity in many reactions owing to their significantly higher excited-state oxidation potentials (Table 1).

5. Synthesis of N-Alkyl and N-Aryl Acridinium Salts

At present, the Reaxys database contains approximately 2,500 reported syntheses of N-alkyl and N-aryl acridinium salts, of which about 500 compounds

[74] Zilate B., Fischer C., Sparr C. Design and application of aminoacridinium organophotoredox catalysts. *Chemical Communications*. 2020. Vol. 56, No. 12. P. 1767–1775. DOI: 10.1039/C9CC08524F

[75] Bryden M. A., Zysman-Colman E. Organic thermally activated delayed fluorescence (TADF) compounds used in photocatalysis. *Chemical Society Reviews*. 2021. Vol. 50, No. 13. P. 7587–7680. DOI: 10.1039/d1cs00198a

[76] White A. R., Wang L., Nicewicz D. A. Synthesis and characterization of acridinium dyes for photoredox catalysis. *Synlett*. 2019. Vol. 30, No. 7. P. 827–832. DOI: 10.1055/s-0037-1611744

have been commercialized. Among these, 90 are tetrafluoroborate derivatives, and 24 are commercially available compounds. Derivatives of N-methylamines have frequently been employed as starting materials, with approximately 130 reported examples (Figure 9).

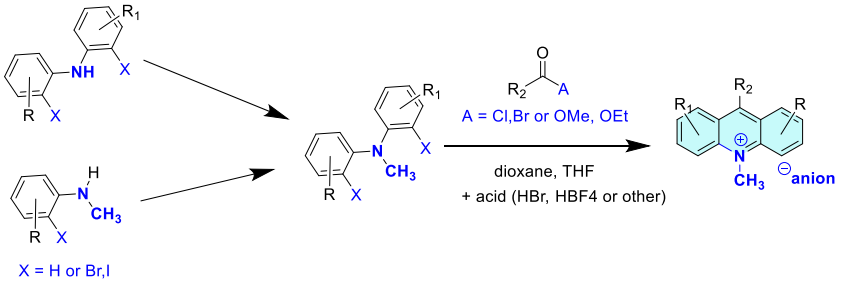

Fig. 9. Synthesis of Methylacridinium Salts from Methylamines

N-Methylacridones (approximately 218 examples) have also been widely used as starting materials. Another common synthetic approach involves N-alkylation using alkylating agents, for which approximately 1,100 examples have been reported (Figure 10).

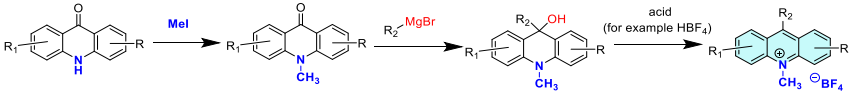

Fig. 10. Synthesis of Methylacridinium Salt Derivatives from Acridones

A convenient modern synthetic method is based on the condensation of xanthylium salts with amines. The corresponding xanthylium derivatives were described in the work of Nicewicz[52] (Figure 11).

These reactions are, in fact, an extension of the classical studies of Alan Katritzky, who, in the late 1970s and early 1980s, demonstrated that pyrylium salts could be converted into the corresponding pyridinium salts by condensation with amines[77].

Several examples of acridinium-containing coordination systems have also been reported. The first studies on the coordination chemistry of acridinium derivatives appeared in the late 1980s[78] and were later reproduced and further

[77] Katritzky A. R., Marson C. M. Pyrylium mediated transformations of primary amino groups into other functional groups. New synthetic methods. *Angewandte Chemie International Edition*. 1984. Vol. 23, No. 6. P. 420–429. DOI: 10.1002/anie.198404201

[78] Jonker S. A., Ariese F., Verhoeven J. W. Cation complexation with functionalized 9-arylacridinium ions: possible applications in the development of cation-selective optical probes. *Recueil des Travaux Chimiques des Pays-Bas*. 1989. Vol. 108. P. 109–115. DOI: 10.1002/recl.19891080307

developed in more recent publications[79]. However, the vast majority of these investigations were devoted to the photo-physical properties of the resulting systems, whereas their application in photoredox catalysis has remained largely unexplored. An interesting synthetic example is represented by bis-acridinium derivatives, which have mainly been investigated because of their ability to induce oxidative stress and to destroy malignant cells[80].

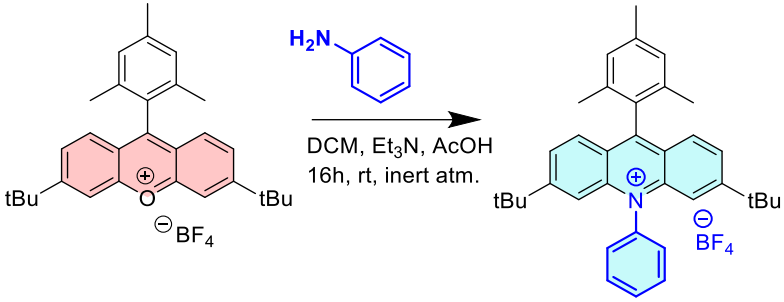

Fig. 11. Synthesis of Acridinium Salts from Xanthylium Salts (according to Nicewicz)

6. Potential Application of the New Acridinium Photocatalyst

Analysis of the literature and the Reaxys database has shown that a large number of N-methyl, N-aryl, and other N-alkyl acridinium salts have been described. In contrast, no examples of N-propyl acridinium salts were found in the Reaxys database. This observation prompted the synthesis of an N-propyl acridinium salt and the investigation of its physicochemical properties as a new representative of this class of compounds.

Because of the considerable synthetic potential of acridinium photocatalysts and our own interest in this field, we decided to prepare a new N-alkyl acridinium photocatalyst.

The designed compound represents a homolog of the Fukuzumi catalyst containing a longer alkyl substituent, which may influence the overall electronic properties of the molecule.

The proposed photocatalyst is expected to participate in organophotoredox reactions similar to those describe for related acridinium salts.

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[79] del Giacco T., Carlotti B., De Solis S., Barbafina A., Elisei F. Steady-state and time-resolved investigations of a crown thioether conjugated with methylacridinium and its complexes with metal ions. *Physical Chemistry Chemical Physics*. 2011. Vol. 13. P. 2188–2195. DOI: 10.1039/c0cp01411g

[80] US2008119492A1. [Compositions and methods for treating cancer and other diseases characterized by abnormal cell proliferation]. 2008. Available at: https://worldwide.espacenet.com/patent/search/family/039417684/publication/US2008119492A1?q=pn%3DUS2008119492

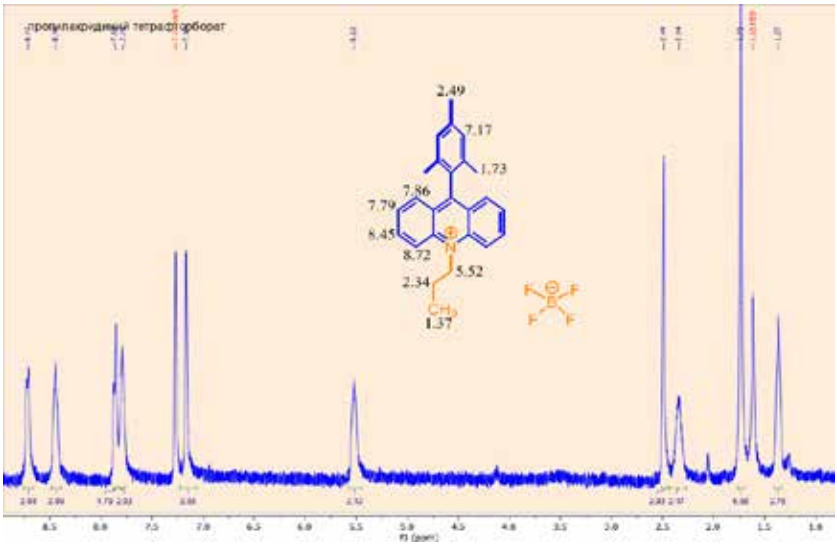

Fig. 12. ^{1}H NMR spectra of 9-mesityl-10-propylacridinium tetrafluoroborate in CDCl^{3}

^{1}H NMR (400 MHz, cdcl$_3$) δ 8.72 (br, 2H, acr-H^{1},H^{8}), 8.45 (br, 2H, acr-H^{2},H^{7}), 7.86 (br, 2H, acr-H^{4},H^{5}), 7.79 (br, 2H, acr-H^{3},H^{6}), 7.17 (s, 2H, mes^{CH}), 5.52 (br, 2H, Pr$^{N\text{-}CH2}$), 2.49 (s, 3H, mes^{CH3}), 2.34 (br, 2H, Pr^{CH2}), 1.73(s, 6H, mes^{CH3}), 1.37 (br, 3H,Pr^{CH3}).

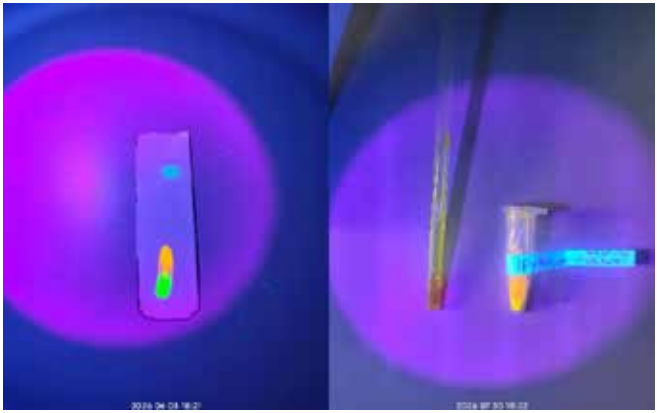

Fig. 13. Experimental photographs: (a) reaction mixture TLC in EtoAc 100%; (b) isolated sample; (c) sample prepared for NMR analysis

For example, the present photocatalyst may be applied to decarboxylative arylation reactions analogous to those catalyzed by 9-mesityl-10-methylacridinium salts (Figure 14), which provide an attractive alternative to conventional cross-coupling methods[81].

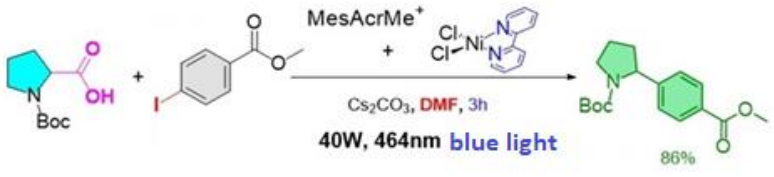

Fig. 14. Decarboxylative Arylation Mediated by Mes-Acr^{+}Me

The high redox potential of acridinium salts also makes them suitable for oxidative aromatization of heterocyclic compounds. One example is the oxidation of the indoline ring to the corresponding indole, a transformation employed during the synthesis of the antiviral drug Elbasvir[82] (Figure 15a). This reaction represents the final aromatization step of a heterocyclic framework prepared through a multistep synthetic sequence and illustrates a practical application of acridinium photocatalysts in organic synthesis. In this case, the transformation leads to the formation of Elbasvir, a pharmaceutical agent used in the treatment of hepatitis C virus infection.

Cyclization reactions constitute another important field of application. Under visible-light irradiation, photocatalysts, including acridinium salts[58], promote a variety of cycloaddition processes. Among these, [3+2] cycloaddition between alkenes and aromatic substrates has attracted particular attention. In this transformation the acridinium photocatalyst[83] replaces the previously employed ruthenium complex while maintaining high reaction efficiency. Such methodology provides convenient access to dihydrobenzofuran derivatives, structural motifs frequently encountered in biologically active compounds and pharmaceutical intermediates (Figure 15b).

The combination of transition-metal complexes with metal-based photosensitizers has been extensively developed in the pioneering studies of Molander and MacMillan. Their catalytic systems promoted the coupling of aryl

[81] Fischer C., Sparr C. Direkte Umwandlung von Estern in heterocyclische Fluorophore. *Angewandte Chemie International Edition*. 2017. Vol. 130, No. 9. P. 2461–2465. DOI: 10.1002/anie.201711296

[82] Yayla H. G. et al. Discovery and mechanistic study of a photocatalytic indoline dehydrogenation for the synthesis of elbasvir. *Chemical Science*. 2016. Vol. 7, No. 3. P. 2066–2073. DOI: 10.1039/C5SC03350K

[83] Blum T. R., Zhu Y., Nordeen S. A., Yoon T. P. Photocatalytic synthesis of dihydrobenzofurans by oxidative [3+2] cycloaddition of phenols. *Angewandte Chemie International Edition*. 2014. Vol. 53, No. 41. P. 11056–11059. DOI: 10.1002/anie.201406393

halides with α-amino acids or secondary amines[84], as well as amidoarylation[85] reactions (Figure 16).

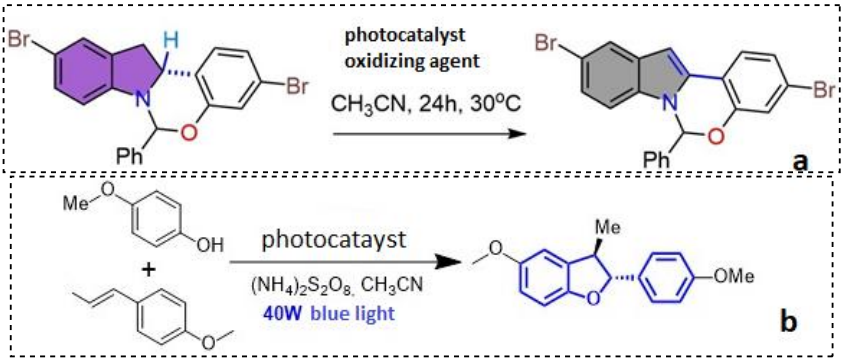

Fig. 15. One of the Key Steps in the Synthesis of Elbasvir and Photoinduced [3+2] Cycloaddition in the Synthesis of Dihydrobenzofuran

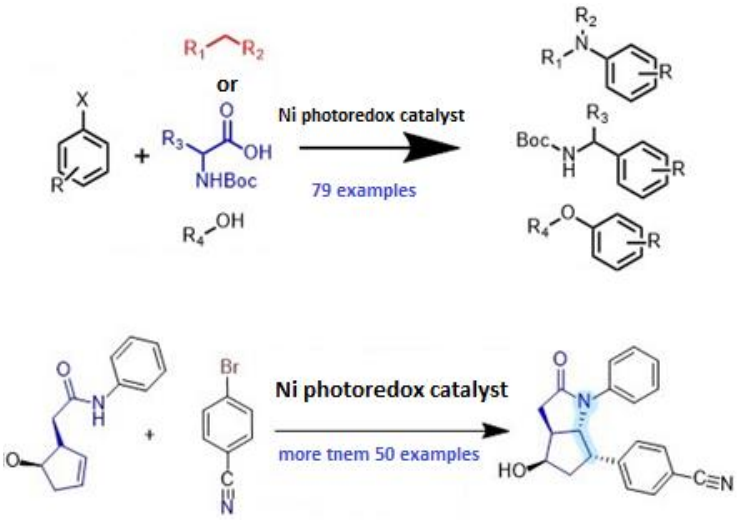

Fig. 16. Nickel-Catalyzed Photocatalytic Amidoarylation

[84] Marchi M. et al. The nickel age in synthetic dual photocatalysis: A bright trip toward materials science. *ChemSusChem*. 2022. Vol. 15, No. 18. DOI: 10.1002/cssc.202201094

[85] Zheng S., Gutiérrez-Bonet Á., Molander G. A. Merging photoredox PCET with Ni-catalyzed cross-coupling: Cascade amidoarylation of unactivated olefins. *Chem*. 2019. Vol. 5, No. 2. P. 339–352. DOI: 10.1016/j.chempr.2018.11.014

Another classical example of modern photoredox catalysis is represented by the Minisci reaction, which enables the direct functionalization of electron-deficient heteroarenes under mild conditions[86,87].

CONCLUSIONS

Over the past decades, photoredox catalysis has become one of the leading fields of modern chemistry. The development of this area has been driven by studies of electron-transfer mechanisms, the design of new photocatalysts, and the expansion of their practical applications.

A special role in the development of organic photoredox catalysis belongs to the work of Shunichi Fukuzumi, who established the foundations for the use of acridinium photosensitizers, formulated the principles of their molecular design, and demonstrated the possibility of efficiently controlling photoinduced electron-transfer processes. The subsequent development of this field led to the emergence of new organic photocatalysts, dual photoredox catalysis, and integrated photocatalytic systems.

The literature analysis conducted in this work demonstrated the considerable potential of acridinium salts as organic photocatalysts. Based on the analysis of modern synthetic approaches, an N-propylacridinium photocatalyst was synthesized, which may potentially be applied in organic photoredox catalysis and in further studies of photoactive systems.

SUMMARY

This monograph summarizes the development of photoredox catalysis from the earliest photochemical systems to modern organic photocatalysts. The main stages in the evolution of the field are discussed, with particular attention given to the contribution of Shunichi Fukuzumi to the development of acridinium-based photosensitizers and the principles of their molecular design. The development of transition metal, organic, and dual photoredox catalysis, as well as current trends in integrated photocatalytic systems, is analyzed. The principal synthetic approaches to N-alkyl and N-aryl acridinium salts are reviewed. Based on the literature analysis, a new N-propylacridinium salt was synthesized, and its potential application in photoredox catalysis was considered. The presented results may be useful for further research in organic photoredox catalysis and the development of new photoactive systems.

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[86] Sun A., McAtee R., McClain E., Stephenson C. Advancements in visible-light-enabled radical C(sp2)–H alkylation of (hetero)arenes. *Synthesis.* 2019. Vol. 51, No. 5. P. 1063–1072. DOI: 10.1055/s-0037-1611658

[87] Jin J., MacMillan D. W. C. Direct α-arylation of ethers through the combination of photoredox-mediated C–H functionalization and the Minisci reaction. *Angewandte Chemie*. 2015. Vol. 127, No. 5. P. 1585–1589. DOI: 10.1002/ange.201410432

The following figure illustrates the historical and chemical development described in this monograph (Figure 17).

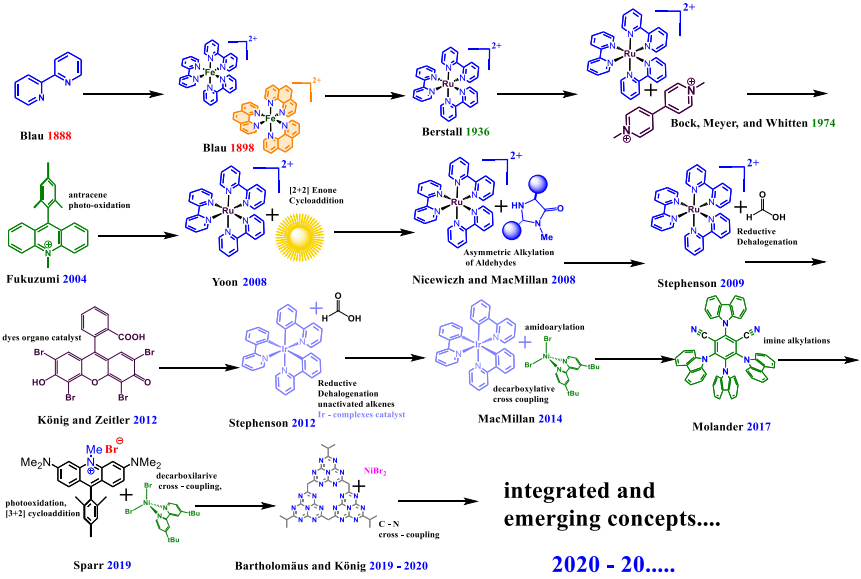

Fig. 17. The historical and chemical development of photoredox catalysis

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