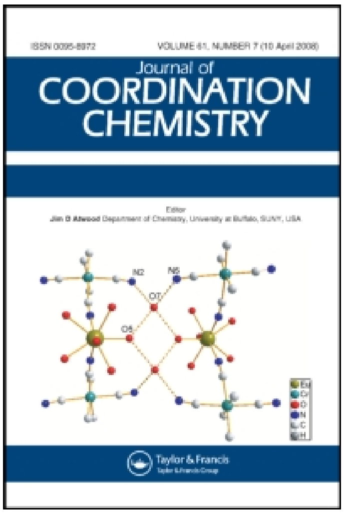

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New trends in the application of laser flash photolysis - case studies

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Review Article

New trends in the application of laser flash photolysis – case studies

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Laser flash photolysis (LFP) is a powerful tool for spectroscopic and kinetic determination of both primary photophysical transformations and rapid chemical reactions. This method is very useful in mechanistic studies of fast reactions and detection of transition states and intermediates. The main goal of the review is to point out some current applications of LFP in chemical, biological, biochemical, and environmental studies. The systems discussed spread from simple organic compounds and metal complexes to biomacromolecules and supramolecular systems.

Keywords: Laser flash photolysis; Reaction mechanisms; Supramolecular systems; Coordination compounds; Intermediates

1. Introduction

Spectroscopic techniques are among the most important methods to investigate matter and their changes. Application of lasers in spectroscopy has opened new possibilities in understanding processes of interest for atomic and molecular physics, chemistry, and biology [1–5]. One of the key steps in mechanistic studies has been the development of laser flash photolysis (LFP) [6]. Applied to various homo and heterogeneous systems, this technique has been of great importance in understanding reaction mechanisms as well as the properties of transition states or intermediates. LFP is widely and effectively used in many research areas including organic and inorganic photochemistry, chemical and biological processes, or chemical physics.

Classical time-resolved flash photolysis operating in millisecond timescale was invented in the 1950s by M. Eigen, R.G.W. Norrish, and G. Porter [7, 8]. Introduction of lasers as the source of excitation light makes it possible to look into much faster processes, occurring in nano- (in the 1960s) [9–11], pico- (in the 1970s) [12], and even femtoseconds (in the 1980s) [13]. Similar to primary flash technique, LFP takes advantage of the abilities of flash laser impulses to create short-lived transient species, possibilities for their spectrophotometrical detection, and kinetic tracing of their decay. Typical setup for LFP, shown in figure 1, consists of the source of high-intensity flash

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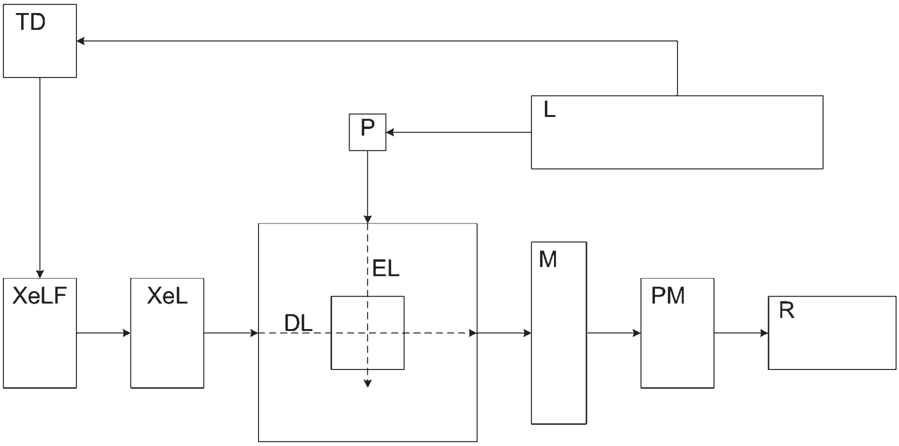


Figure 1. Schematic diagram of the LFP setup: laser (L), exciting light (EL), detecting light (DL), prism (P), xenon lamp (XeL), xenon lamp feeder, time delay (TD), monochromator (M), photomultiplier (PM), recorder (R).

light (laser) and system capable to monitor the formation and decay of excited-states and photolysis intermediates. Usually, monitoring (or detecting) system involves another source of light which inspects perpendicularly the laser-irradiated sample with appropriate delay.

Development of LFP technique made since its introduction in the 1950s concerns both exciting (L, P) and detecting systems (horizontal system XeLF – R in figure 1). Advance in laser optics and invention of new light-emitting materials provide opportunities to excite new classes of compounds thus broadening the applicability of LFP. Narrowing of the laser pulse width enabled enhancing the time resolution from micro- to nano- and picoseconds. This opened new possibilities for kinetic investigations of so far unrevealed physical and chemical processes. In general, nano- and picosecond LFP has become routine for the investigation of radicals and exited states or intermediate species [14–16]. Ultrafast femtosecond laser shots, which can be obtained now in commercially available laser flash systems, make it possible to carry out investigations of very fast physical processes [17].

Diversity of fast physical processes and chemical reactions as well as of transition states and intermediates makes application of various kinetic techniques necessary in detailed mechanistic investigations. Such fast kinetic methods as EPR, NMR, stopped-flow, T-jump, p-jump, electric-field pulse, ultrasonics, etc. are often used in complementary experiments providing comprehensive description of the overall mechanism. Proper selection of spectroscopic and kinetic techniques makes it possible to investigate both main and side processes occurring in laser-pulse-excited systems. Time-scales of the frequently used kinetic techniques are given in figure 2.

Starting from milliseconds and finishing on picoseconds, LFP technique covers the timescales of particularly important physical (i.e., radiative decay of the excited states) and chemical processes [such as photo-induced electron transfer (PET) or fast ligand-binding to metal centers], making possible investigation of protein–drug interactions, dissociation of molecules from active sites of proteins and other biologically, pharmaceutically, and environmentally relevant systems. The range of femtoseconds remains more interesting for physics than for mainstream of chemical studies.

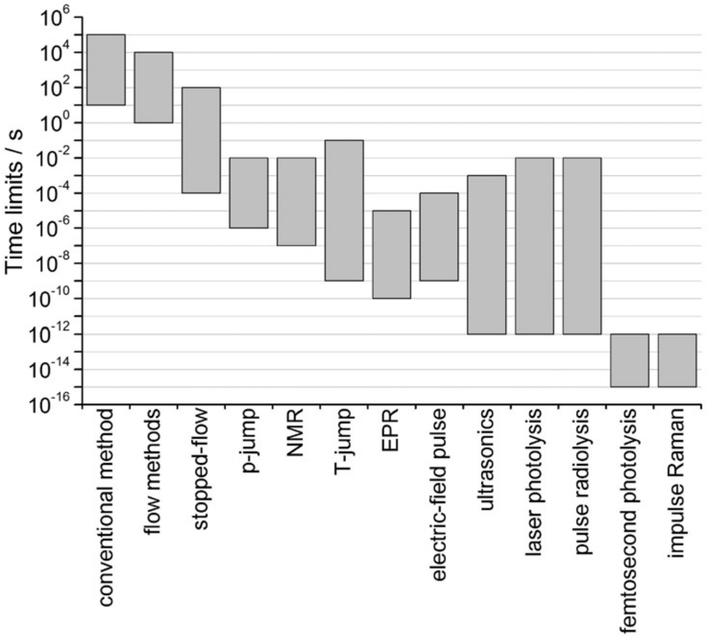


Figure 2. Time scales of various kinetic techniques [24, 110].

One of the interesting developments of LFP is its adjustment to nonclassical experimental conditions. Replacement of the standard cuvette with an optical chamber equipped with a hydraulic pump system enables LFP measurements under elevated pressure. Application of high pressure (HP) technique is of special importance for mechanistic studies as it provides kinetic and thermodynamic data for determination of activation volumes ($\Delta V^{\neq}$) as well as overall reaction volume (ΔV°) [18–21]. Hence, volume profiles can be constructed that provide visualization of the transition state changes occurring along the reaction coordinate. The activation volume is considered to be one of the most reliable kinetic parameters for the elucidation of the type of reaction mechanism [22, 23]. HP-LFP enables such studies for fast reactions. More details on the application of HP-LFP in mechanistic studies were given recently for selected hemoprotein reactions [24].

Technical advances enable broadening of the range of systems and processes investigated with LFP. Whereas, early studies were focused mainly on relatively small molecules, including simple organic compounds and metal complexes, nowadays they include far more sophisticated and complex classes of compounds such as biopolymers, supramolecular, or heterogeneous systems. Finally, current investigations are focused on various systems with fast, plausible, practical, and functional applications in environment, industry, and common life.

This short review is devoted to recent trends in the application of LFP. It focuses on both simple metalloorganic systems as well as biologically relevant macromolecules and complex supramolecular systems. Depending on the complication level of investigated systems the LFP experiments were designed either just to clarify the mechanisms of chemical reactions or to receive more specific information about photostability of drugs, photoelectrochemical properties of new supramolecular structures or photocatalytic activity of environment-friendly agents.

2. Metal complexes and organometallic systems

2.1. *LFP investigations of reaction mechanisms*

Reversible bond cleavage triggered by laser flash impulse is a typical pattern of the reaction of coordination compounds studied with LFP technique. Pulsed laser techniques are mainly well-suited for the investigation of the kinetics of ligand binding in respect of both energy required to vacate the coordination site on central ion as well as the time-resolution of the detection system, correlated with the flash-length. Unsaturated transition metal complexes make a group of particular interest as they exemplify intermediates in a variety of chemical reactions. Application of LFP enables the formation of such compounds and determination of their binding abilities. Complexes with a single labile ligand are especially useful in this scope because they make it possible to investigate specific ligand exchange. For instance, recent studies on carbonyl chromium(III) complexes showed that UV laser pulses (308 nm) enable the formation of monoarene-substituted transient species that undergo further exchange of weakly coordinated aromatic ligand to, for example, tetrahydrofuran (THF). Kinetic data obtained from LFP experiments indicated that two independent pathways, namely, dissociative (D) and interchange-dissociative (I_d), contribute in the overall mechanism of the latter transformation [25]. Similar displacement of the arene ligand with piperidine was found to proceed through a clear I_d mechanism and the rate of this process increases with the increase in electron density on the metal center [26].

Noble metal complexes are another remarkable target of recent LFP investigations among simple coordination compounds. Perspectives of diverse applications, such as catalysis, entail the requirement of detailed elucidation of their photochemical abilities. It is known that such investigations are simplified in the presence of ligands with intense charge transfer bands, for example, halide anions. Despite long-term studies, not all details in the mechanisms of light-induced ligand exchange in such complexes as $[PtBr_6]^{2-}$ have been explained, especially because the quantum yield of this transformation often exceeds unity [27]. Application of LFP [28] contributed in the clarification of the chain mechanism of photoaquation [27, 29]. It was found that this multistep process, occurring in nano and microsecond time intervals, did not involve Pt(III) intermediate species [28].

For some years LFP has been successfully applied in various stages of organometallic catalysts development. Advantage of LFP technique involves mainly the possibility of kinetic investigation of substrate binding/releasing from the metal center. Organometallic iridium complexes with iodide ligands are of particular interest as they are successfully applied in the catalysis of methanol carboxylation to acetic acid. Recently, investigations of the reaction of $[CH_3Ir(CO)_2I_3]^-$ were carried out in excess CO using time-resolved infrared (IR) detector combined with a LFP system. These studies pointed out migratory insertion leading to acyl complex (mer, trans-$[Ir(C(O)CH_3)(CO)_2I_3]^-$) formation, which proceeds *via* several isomeric decarbonylated intermediates [30]. Another organometallic iridium compound, Vaska's complex, has catalytic activity in alkane isomerization. Time-resolved IR experiments revealed some unexpected behavior of this complex. Applied laser pulses did not result in direct transformation of this compound, but initiated relatively slow generation of intermediate species occurring over the course of a few milliseconds. Such an intermediate were recognized as the dimeric Vaska's complex bridged by CO [31].

2.2. *"Super photoacids" – photo-induced proton transfer*

The availability of flash techniques has contributed to the investigation of fast and ultrafast processes such as conformational changes, charge separation (CS) and migration, energy and electron transfer processes, etc. In the last few years, due to advanced knowledge of the excited state properties of coordination compounds, scientists have concentrated more on their applications. The unique ground and excited state properties of metal complexes made them invaluable candidates for making the components of molecular devices and machines converting light into electricity or fuel. Much work is dedicated to dihydrogen photoactivation. Currently, not only H_2 generation *via* water reduction is intensively investigated, but also research is focused on systems involving bio-inspired organometallic complexes (i.e., hydrogenases) [32–35]. Finally, many different aspects of photo-induced proton transfer (intra and intermolecular) are extensively studied, particularly with LFP application. Understanding photo-induced proton migration has fundamental significance for clarifying mechanisms of photocatalytical, environmental, synthetic, and photochemical processes.

Excited-state proton transfer (ESPT) from hydroxyarenes has been known and studied for a long time [36–38]. Extremely strong acids, commonly named "super photoacids," may be produced by photoexcitation of hydroxyaromatic compounds with electron-withdrawing groups. Widely accepted explanation of the enhanced acidity in excited state implies an intramolecular charge transfer in the excited state of the acid from the hydroxyl oxygen to the aromatic ring [39]. Apart from hydroxyarene-type photoacids, so-called photoacid generators (PAG, i.e., a compound that yields an acid as one product of photolysis) also exhibit promising activity. Since applications of so far known PAGs are limited to the exposure to UV light, visible-light active photoacids are desired. For instance, such photoacids operating upon visible irradiation may find applications in microlithographic and holographic methods, where visible-light lasers such as He–Cd, YAG, and Ar ion lasers are used as a high-power and stable light source. The detailed mechanism of the excited proton transfer in case of transition metal hydrides is still under intensive investigation. However, it is known that deprotonation occurs from the excited state of the complex. LFP is a very suitable technique for this research. Metal hydride complexes with their removable protons, in contrast to organic photoacids, have never been proved to act as photoacids. Due to the fact that hydride in metal hydride complexes is electronegative, it is believed to be difficult to be removed as protons. However, surprisingly the release of protons has been shown in some metal hydride complexes by H/D exchange reaction [40, 41].

The first example of the excited state deprotonation of a hexafluorophosphate salt of the iridium hydride complex, which absorbs in visible light ($\lambda_{max} = 430\,nm$), has been reported by Suenobu *et al.* [41] in 2003. It has been shown that deprotonation occurs in the excited state and the iridium hydride complex is an efficient photoacid.

Moreover, the H/D exchange reaction in the excited state has been proved by NMR. The photo-induced deprotonation mechanism was examined by LFP and involves the following steps: initial deprotonation of the excited state of the hydride complex; generation of the reduced form of the hydride complex and proton; and final protonation of the reduced form of the hydride complex and generation of the ground state of the hydride complex. Simple thermodynamic consideration, for both the ground and excited states of a proton-containing molecule and its conjugate base, indicates that the excited state is a much stronger acid than the corresponding ground state. The excited state of iridium hydride complex can be compared to the photoacid formation of hydroarenes. Since their enhanced acidity in the excited state is ascribed to the intramolecular charge transfer from the hydroxyl oxygen to the aromatic ring, the MLCT excitation reduces the basicity of the iridium metal center and facilitates proton release. The rate of proton recombination after the photo-induced deprotonation reaction depends significantly on the electron-withdrawing or electron-donating substituents of the diimine ligand. It is believed that iridium hydride complex represents a new class of unique candidates that exhibit promising features as a visible light-sensitive PAG.

3. Supramolecular systems based on fullerenes

Supramolecular systems based on fullerenes are indispensable models for studying intermolecular electron transfer, where fullerenes play the role of electron acceptors. LFP makes it possible to study electron transfer mechanism by monitoring the intermediate radical ions in the visible and near-IR regions. Fullerenes are excellent chromophores that extensively absorb throughout the UV and visible spectral window. They possess 3-D structures with delocalized π-electrons within the spheric carbon framework and low reduction potential. Since they exhibit small reorganization energy, systems based on fullerenes as electron acceptor entities (figure 3a–e) are characterized by relatively rapid photo-induced CS and relatively slow charge recombination (CR). Thus, fullerenes having a long-lived CS state after excitation may be applied in supramolecular artificial systems that mimic photosynthesis. Moreover, versatile photophysical and photochemical properties (i.e., low energy of the singlet (${}^{1}C_{60}^{*}$) and triplet (${}^{3}C_{60}^{*}$) electronic excited states), combined with their peculiar structural features, make them attractive compounds for optoelectronic applications, for example, artificial solar-energy-conversion devices, photosensors, etc. [42–46]. Importantly, the absorption and luminescence features of functionalized fullerenes are slightly modified compared with parent molecule, while fluorescent singlets and long-lived triplets are maintained [44, 45]. LFP enables studying electron transfer in supramolecular systems based on fullerenes due to their excited state properties such as fluorescence or triplet lifetime. The triplet lifetime is extremely sensitive to oxygen and in order to avoid triplet–triplet anihilation a weak excitation laser pulse is required.

A polycyclic aromatic hydrocarbon (e.g., fluorene) and its derivatives set up the simplest, however important, group of electron donors, mainly because of their thermal and chemical stability as well as desirable photoluminescence and electroluminescence properties and possible applications, for example, electroluminescence devices, solar cells, photodynamic therapy (PDT), etc. Recently, intermolecular electron transfer between amine-substituted fluorenes and fullerene (C_{60}) has been investigated by nanosecond laser photolysis. Transient absorption spectral method has proved photosensitized electron transfer from the ground state of fluorene derivatives to the triplet excited state of C_{60} by the radical anion of the fullerene and the radical cation of the fluorene detection. It has been concluded that fullerene is a good electron acceptor in the presence of amine-substituted fluorenes [47].

CS, electron transfer, CR, back electron transfer, as well as energy transfer have been investigated with application of LFP for polypyrrolic skeleton structures such as porphyrins, chlorines, bacteriochlorins, phtalocyanines, naphthalocyanines, which are key units for the study of photo-induced processes. The supramolecular approach of building fullerene-polypyrrolic conjugates provides challenging donor–acceptor systems for the development of solar energy harvesting and opto-electronic devices such as sensors, switches, gates, etc. [43, 44]. Recent successful functionalization of fullerene has prompted preparation of a number of multicomponent arrays assembled *via* covalent bonding (linked to both organic and inorganic moieties), supramolecular interactions and even mechanical linking (e.g., rotaxanes) [42, 45]. In particular, intermolecular electron transfer in supramolecular systems built from porphyrins, chlorophylls, phthalocyanines, naphthalocyanines, and their metal derivatives (e.g., Zn, Cu, etc.) as electron donors and fullerenes (C_{60} and C_{70}) as electron acceptors has been studied by LFP (figure 3a, c, e) [43–46].

Furthermore, multicomponent fullerene-metal complex arrays based on nanostructured donor-acceptor couples have been extensively investigated with LFP application. Fullerene hybrid assemblies with Cu(I), Ru(II), and Re(I) complexes (figure 3b) also undergo ultrafast photo-induced electron transfer upon excitation of MLCT-excited states of the metal-complexed entity. The Cu(I)-specific functionalization of the carbon sphere results in significant effect on photo-induced electron transfer by fullerene excitation. Since no sensitization of the fullerene singlet and triplet states occurs, photo-induced energy transfer is ruled out and the complex undergoes photo-induced electron transfer ($Cu \rightarrow C_{60}$). Moreover, several studies of dyes based on Ru(II) complexes and fullerene have evidenced that energy transfer is the only active photo-induced process when donor-acceptor distance is very short. Nevertheless, energy transfer has been observed in dyes with relatively long donor-acceptor distance (up to 10 Å) [44]. Remarkably, in the above-mentioned multicomponent systems, based on fullerene and coordination metal complexes with low-lying MLCT-excited levels, direct proof of electron transfer has been demonstrated, for instance by radical anions and cations transient absorption detection. Nonetheless, due to the lack of any excited state sensitization revealing energy transfer, electron transfer is compelling [44].

Unfortunately, distance and orientation between the two components are not well-defined because of lack of rigidity as porphyrins are usually attached to fullerene by a single covalent linker. To enhance and control geometrical parameters as well as to adjust electronic and light-induced properties Bourgeois *et al.* [48] attached the porphyrin to two points of the C_{60} surface resulting in so-called face-to-face porphyrin system. Since then, various similar novel examples of rigid and conformationally flexible fullerene-porphyrin systems arranged in face-to-face fashion have been investigated (figure 3c and e). The peculiar excited state properties of such complex systems can be studied by ultrafast flash photolysis. The transient absorption spectrum is generally different from that of its fullerene and porphyrin parent components exhibiting the diagnostic porphyrin radical cation fingerprint at 640 nm, with lifetime

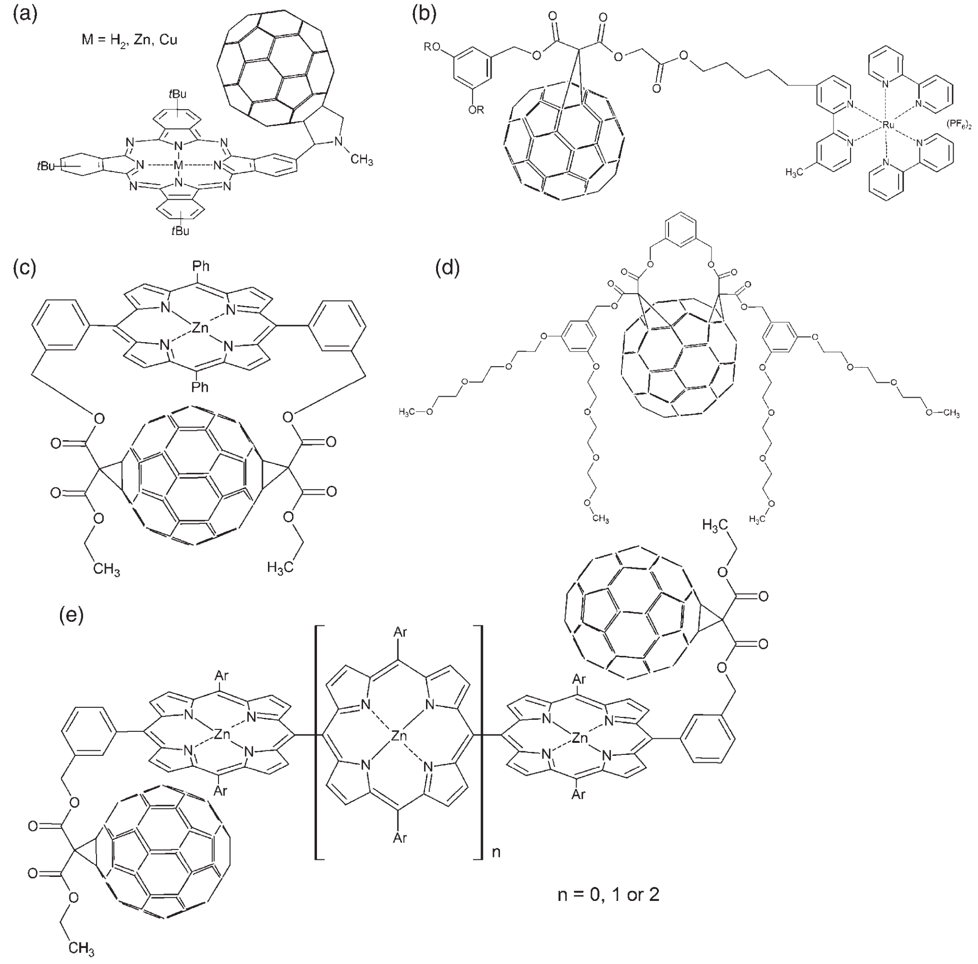


Figure 3. Examples of fullerene-based supramolecular systems [43, 44, 46].

estimated to be 630 ps in toluene. Exact confirmation of the charge transfer nature of the lowest (emitting) electronic excited state has been demonstrated for many case studies [44]. Furthermore, both nano and femtosecond LFP were applied to study intramolecular electron transfer in supramolecular complexes of bis-porphyrinyl-substituted oxoporphyrinogen and bis(4-pyridyl)-substituted fullerene. The rate of the photo-induced electron transfer from porphyrin to fullerene was found to be considerably improved by the anions attached to the pyrrole amine group. Binding of anions resulted also in significant stabilization of the charge-separated state [49].

In perspective, fullerene-metal complex assemblies, fullerodendrimers and face-to-face porphyrin systems present challenging photoelectrochemical properties for further expansion. Supramolecular fullerene systems are an open field of research and development in sensors, smart photosensitizers, luminescent nanomaterials, solar energy conversion devices, and other optoelectronic applications. LFP is a powerful tool for the characterization of the excited state properties of the donor and acceptor moieties, the nature of the linker, the influences of the solvent and the metal ions in the cavities, etc. Owing to wide LFP accessibility above-mentioned properties of the supramolecular systems with potentially useful applications can be tuned in controlled manner.

4. Biological and biomedical systems

4.1. *Protein–drug interaction studies*

The development of better drugs for diseases without an established protocol for treatment is currently an important research area for chemists, pharmacologists, and biotechnologists. A crucial point of these studies is related to understanding the interactions between drugs and biological macromolecules, mainly proteins and nucleic acids. One technique which allows insight in such interactions is based on the determination of crystal structures for drug-biomacromolecule adducts. However, it is very often difficult to get a suitable crystal for measurements and the solid state behavior can be considerably different than in solution. Some structural information can be gained from NMR studies, however, for such measurements a high concentration of solute is required which is not always accessible. Other techniques which can be applied are IR and Raman spectroscopy, however, due to highly complex systems the interpretation can be difficult. Taking into account all these difficulties and limitations there is still a need for finding better tools for fast and efficient evaluation of drug–biomacromolecule interactions.

One useful approach to study interaction of proteins with chromophoric drugs takes advantage of their triplet exited states. Choosing the proper light energy allows the excitation of a molecule, which results in generation of a singlet excited states, which by intersystem crossing can be converted to the triplet exited state. By monitoring photophysical behavior of excited drugs, such as lifetimes of triplet excited state, which are very sensitive to medium, as well as transition absorption spectra, which give insight into the formation of new exited state species, one can get valuable information about reactivity of drugs toward proteins. Data gained from such investigations combined with those from other spectroscopic studies and computer simulations enable determination of the distribution of the drug within a protein as well as changing the internal dynamics and function of proteins [50–55]. An often used protein to study drug–protein interactions is albumin (human serum albumin, HSA, or bovine serum albumin, BSA), the most abundant blood plasma protein, which is easily accessible and relatively inexpensive. It serves as a useful model for general study of protein–drug interactions and more specific in the context of its application as a natural carrier. Interaction of drugs with albumin is also very important in relation to pharmacokinetics and the formulation of dosage pattern for treatment.

Recently several studies have demonstrated application of LFP in investigation interactions between albumin and various drugs [51–55]. After excitation of protoflavin (antibacterial and antifungal agent) [52], colchicines (alkaloid active in many type of diseases) [51], derivatives of licochalcone A (potential antibacterial, antifungal, antiviral, antiparasitic, and anticancer agent) [54, 55], or flurbiprofen (nonsteroidal anti-inflammatory drug) [56] in the presence of albumin, new bands appear in the transition spectra confirming the formation of albumin–drug complexes. This interaction has great impact on the lifetime of the triplet excited state of the drug (compare table 1). The lifetime can be either longer or shorter in comparison to drug dissolved in a buffer solution (or in other media) depending on the binding site in protein. It is often observed that the decay of drug-excited state shows biexponential behavior which points out the interaction of drug with more than one site in protein. Detailed examination of changes in photophysical behavior of a drug upon binding to protein helps in the assessment of binding sites, binding ratio, and distribution of drug between several compartments in proteins. Recent studies have shown that this technique can also be applied in the evaluation of drug distribution between different proteins in the same solution [57].

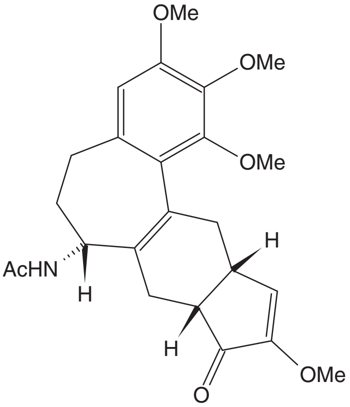
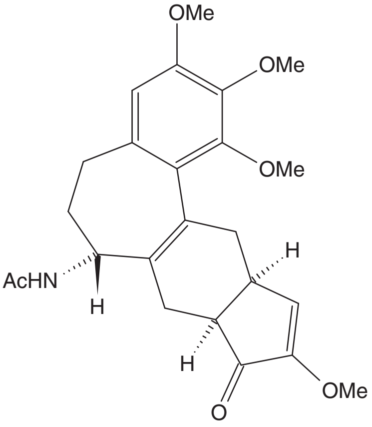
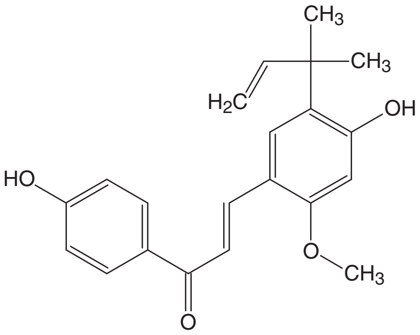
Another interesting concept is using LFP to study drug–drug interactions after binding of both species to protein [50]. Such studies are very useful when two different drug molecules share the same binding sites, or in probing of allosteric effects, which are very difficult to assess by any other technique, so LFP could become a very powerful tool for such studies. Two species, flurbiprofen (nonsteroidal anti-inflammatory drug) and carprofen (anti-inflammatory agent used in veterinary), have been covalently attached to each other and their photophysical properties after reaction with albumin have been studied [50]. The major conclusion drawn from these studies was that the examination of the behavior of the transition triplet–triplet absorption corresponding to two chromospheres by use of LFP can give information about distance between those chromophores and, thus, answer if both drugs occupied the same or different binding sites in protein. More studies are needed to verify if it is possible to apply this method for two separated drugs.

4.2. *Reaction of small molecules (O_2, NO, CO) with proteins and biologically relevant complexes*

Interactions of proteins with small molecules like O_2, NO, and CO are of particular interest because of their important role in many biochemical reactions. Even though many studies have been conducted, the mechanism of their action in living systems is not clear and remains under investigation. The discovery that NO is responsible for a broad range of physiological and pathological processes in humans has attracted considerable interest in NO chemistry [58, 59]. CO possesses also a physiological function in humans acting as a cellular signaling molecule [60] and as a byproduct of heme oxygenase having anti-inflammatory, anti-apoptotic, and anti-proliferative properties [61]. Understanding the mechanism of activation of these molecules in living systems is important not only in biology, but this knowledge can also find direct application in medicine, industrial catalysis, and environmental protection.

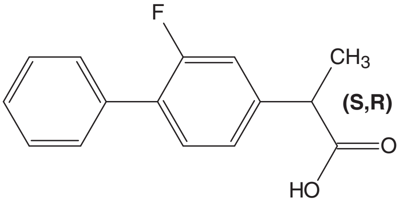
LFP is particularly useful for the study of dissociation of small molecules from active sites of proteins, mainly heme centers. Application of LFP for such studies does not cause any serious structural changes in the tested systems. In this method, LFP of an equilibrated mixture of protein with ligand bound to the heme center and ligand-free hemoprotein leads to labilization of the ligand (e.g. NO, CO, or O_2) from the metal center. Futhermore, if no permanent photoproduct is formed, the rebinding of ligand to the heme center can be followed by fast spectrophotometric techniques. Generally, the ligand photolyzed from heme–iron complex attached to protein can either rapidly

Table 1. The structure of various drugs and the values of their triplet lifetimes in the absence and presence of albumin as measured by LFP.

Drug	Structure	Medium	Triplet lifetime [μs]	Reference
β-Lumicolchicines		MeCN	2.2	[51]
		HSA	12.2	
		BSA	19.2	
γ-Lumicolchicines		MeCN	3.3	[51]
		HSA	16.3	
		BSA	11.7	
Licochalcone A		H_2O	2.4	[54, 55]
		HSA	0.9; 6	
		BSA	0.6; 3.7	

(*Continued*)

Table 1. Continued.

Drug	Structure	Medium	Triplet lifetime [μs]	Reference
Flurbiprofen		H_2O HSA BSA	1.5 11.2; 35.9^{c1} 10.2; 39.0^{c2}	[56]
			10.8; 86.5^{c1}	

rebind to the heme iron (geminate recombination which is not dependent on ligand concentration), or migrate away from the active site into the protein matrix. Further the ligand can either return to the binding pocket and rebind to the heme iron, or diffuse into bulk solution from which it also can migrate and rebind to the heme iron. The latter process is ligand concentration dependent and is called bimolecular recombination. By inspection of the rate constants and activation parameters (combining LFP with temperature and pressure studies [24, 62]) for all these steps, various information about protein–ligand interaction can be obtained. In this contribution only the latest studies in this subject will be discussed, more information can be found in our reviews [24, 62, 63].

Recently a few studies concerning examination of ligand migration (CO, O_2) inside the protein encapsulated in rigid medium (e.g., silica gel, wet sol–gel matrix) has been investigated by the use of LFP techniques [64–69]. Encapsulation of protein facilitates molecule reaching less thermodynamically stable states, which can be associated with the presence of ligand in the protein matrix [64]. This method allows the determination of factors governing ligand migration patterns, in particular, verification of the existence of temporary docking sites, and the examination of parameters that influence this process (e.g., pH, conformation state of protein, allosteric effect, and others).

The affinity of small ligands toward protein can be influenced by the presence of other metal ions in solution [70]. It has been shown that both Zn^{2+} and Cd^{2+} increase the myoglobin affinity for oxygen by conformation changes of the protein. Binding of Zn^{2+} and Cd^{2+} to protein results in the opening of the channels between distal pocket and protein interior as well as a distal pocket itself, which facilitates rapid diffusion of ligand from solvent to heme pocket. This research is very important in the context of recent examination of using nanoparticle composites based on these metals for medical purposes [70]. LFP allows for relatively fast probing how different exogenous species that could be administrated to humans as therapeutic agents can influence the reactivity of proteins toward small molecules.

A main oxidant for organic substrates in living organisms is dioxygen activated by various enzymes, for example, cytochrome P450 (cyt P450). Studies of cyt P450 with LFP have been carried out for a few decades, however, some details of the mechanism still remain unclarified. Some uncertainty concerns the electronic distribution in the cyt P450 complex with O_2, especially as the reactive species of enzyme is still not established.

Attempts to solve these problems have been made on native heme protein [71] as well as iron(III) porphyrin model complexes [72]. Nitric monoxide is often used as a model for dioxygen, especially in kinetic studies using LFP techniques at ambient and HP. Such approach provided valuable results that enable indirect characterization of the role of protein, especially the conformation of its active site. Comparison of the volume profiles determined for iron(III) model complex and native cyt $P450_{cam}$ provided with indirect evidence for NO^+ stabilization in the enzyme pocket [73]. Generation of at least three photo-induced intermediates occurring under photolytic conditions in the SR/NO reaction mixture confirmed interaction of nitric monoxide with thiolate ligands on iron(III) porphyrin [74].

Parallel to the study of O_2 activation by cyt P450, studies concerning CO binding to this protein were carried out [24, 62]. LFP can induce CO dissociation from cyt $P450_{cam}$(cam)CO (where cam is the substrate – camphor, bound to cyt P450). Rebinding CO to iron in the heme center proceeds on four different pathways. The LFP studies together with molecular dynamics simulations were applied to determine CO migration pathways in the protein [75].

The knowledge gained from studies on activation of small molecules by proteins have motivated researchers to search for synthetic systems which could mimic the enzymatic activity of proteins. One such system was based on μ-oxo bridged heme/non-heme diiron(III) complexes as models for the active site of nitric oxide reductase. Photochemical studies performed in various media showed that in the presence of an O-atom acceptor or in a solvent with reactive C-H bonds, both Fe(III) ions are reduced to Fe(II). LFP experiments were performed in order to elucidate the mechanism of photoreduction. Disproportionated (heme)Fe^{II}–O–Fe^{III}(non-heme) species are suggested to be the reactive intermediates in this reaction [76]. Not only iron ions can be utilized in the design of bio-inspired catalysts, but also other metalloderivatives of tetrapyrrolic compounds are commonly used. Chromium(III) porphyrins can be given as an example since they are used in organic synthesis, acting as Lewis acids. Probing the labilization effect of the axial position in such complexes is of great importance since it is postulated that substitution of the axial ligand plays a key role in the catalytic process. The LFP technique has been applied to produce coordinatively unsaturated intermediate *via* axial ligand (H_2O, py, $OPPh_3$) release and to study subsequent rebinding. This methodology produces the *in situ* active intermediate to follow its decay and thus helps in understanding of the mechanisms involved in catalytic action [77]. Recently a cytochrome *c* oxidase-inspired system based on tetrakis(2,6-difluorophenyl) porphyrinate^{2-} (F_6TPP) complex of iron(II) was synthesized for catalytic purposes. In the studies performed on [Fe^{II}(F_6TTP)(CO)(THF)] the rebinding of CO after photodissociation induced by LFP was monitored to get insight into the mechanism of this process. The CO–porphyrin complexes of iron are often used to study transient oxygenation, which occurs after photolytic dissociation of CO generating a free coordination site for O_2 [78]. Cobalt(III) tetraphenylporphyrin (TPP) with nitro ligand in the axial position has been designed and characterized as a model complex for nitrite reductase. Similar to CO and O_2 complexes of metalloporphyrins, exposure of $Co^{III}(NO_2)$(TPP) to a flash of light causes photodissociation of NO_2 and formation of Co^{II}(TPP). For some derivatives the recombination of NO_2 and Co^{II}TPP can occurr *via* formation of the long-lived transient intermediate which was recognized as (ONO)Co^{III}TPP [79]. An interesting model for nitrite reductase has been described by Isoda *et al.* [80]. They designed dinuclear Ru(II)–Cu(II) complex in which Ru(II) acts as the photosensitizer of the Cu(II) moiety. This complex is able to reduce nitrite to NO in a photochemical reaction in the absence of any sacrificial electron-donor reagent. To get better insight into primary photochemical processes in the system, LFP was applied to study the photo-induced intramolecular electron transfer between both metal centers [80].

Diversity in biological activities of small gaseous molecules, particularly NO or CO, means they can be both necessary and harmful for living organisms. Therefore a strict control of their concentration and distribution is crucial for contemporary medicine. As a result, searching for exogenous agents to scavenge NO is of particular interest due to their possible competition with proteins for binding with this molecule. One example is $[\mathrm{Ru^{III}(edta)H_2O}]^-$ [(ethylenediaminetetraacetic acid (edta)], which is an efficient NO scavenger. Recent reports indicate considerable difficulties in the kinetic studies of NO binding to this complex due to the occurrence of side reactions. The primary product of the reaction between ruthenium complex and NO was $[\mathrm{Ru^{II}(edta)(NO^+)}]^{2-}$, however, under specific conditions (excess of NO and the presence of $\mathrm{NO_2^-}$ impurities) $[\mathrm{Ru^{II}(edta)(NO^+)(NO_2^-)}]^{2-}$ is formed. The assignment of this side product has been feasible by use of laser flash experiments, which revealed the formation of two photoproducts after exposing $[\mathrm{Ru^{II}(edta)(NO)}]^+$ to flash light, namely, $[\mathrm{Ru^{II}(edta)(NO)}]^{2-}$ and $[\mathrm{Ru^{III}(edta)(NO_2^-)}]^{2-}$ [81]. These studies are important also due to the possible application of $\mathrm{Ru^{III}}$ complexes with EDTA as antisepsis and antitumor therapeutic agents.

4.3. *Other biological applications of LFP*

There are many other examples of application of LFP to study fast photophysical and photochemical processes of biologically and medically relevant systems. One field where LFP is particularly useful comprises studies of photosensitizers in application in PDT [82]. LFP can be used in studies on parameters such as lifetime and quantum yield of fluorescence, lifetime of triplet state or quantum yield of singlet oxygen generation. Many synthetic photosensitizers have been investigated and recent data have been summarized in reviews and books [62, 83]. Current studies also include some nature-based compounds as potential photosensitizers for PDT. Pheophorbide, chlorophyll *a* derivative with hydrolyzed phytyl chain and removed magnesium ion, is of particular interest as it shows considerable solubility in water and, hence, in body fluids. Excited by visible light, it undergoes efficient intersystem crossing to the lowest triplet state with quantum yield of *ca* 0.65 and relatively long lifetime (9.1 μs). Pheophorbide having such photophysical properties is capable to transfer energy to triplet oxygen and generate singlet oxygen [84]. The excited photosensitizers can also be quenched by endogenous biomolecules, particularly proteins. For example LFP studies performed for thioxantones have shown that the excited molecule can be quenched by some aminoacids, such as tryptophan and tyrosine, *via* an electron transfer pathway leading to protein photodegradation [85]. On the other hand, excited tryptophan can be quenched by natural nucleotides, AMP, CMP, GMP, and UMP. The latter is responsible for radical formation [86]. In general, energy transfer processes receive considerable interest due to their participation in photosensitized degradation of biomolecules as well as in antioxidant defense of living organisms. Hydroxycinnamic acid (HCA) can be given as an example of a compound which scavenges radicals and repairs protein damage. Recent LFP investigations indicated that it can inhibit radiation-mediated damage *via* both scavenging radicals and quenching oxidative triplet states, as HCA was found to be capable of $SO_4^{\bullet -}$ reduction and facilitation of benzophenone triplet state deactivation, respectively [87].

Many drugs and pharmaceutical agents are subjects of photochemical tests to check their photostability. LFP can be utilized to study the primary photoproducts and help to understand the mechanism of photodecomposition of drugs. One can mention Norfloxacin, an antibiotic belonging to the fluoroquinolones, which is successfully applied in infection therapy. LFP studies of this drug enabled characterization of the species formed during photodecomposition [88]. Such undesired intermediates formed in biological systems can cause serious side-effects and hence require careful examination of their chemical and biochemical activity.

Recently, in several studies, LFP was used to characterize sensors for biologically relevant anions. The binding properties and selectivity of Zn-salophen toward some inorganic phosphates (PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$) and nucleotides (AMP^{2-}, ADP^{3-}, ATP^{4-}) were tested with various spectroscopic methods, including LFP, which provided information about the type of host–guest intermediate formed [89]. The other marker used for biological anion recognition, namely, ninhdrin, is known for many years, however its photochemistry is still a subject of investigation. It is important to get information how light can change the compounds and how it can influence the analytical measurements. To elucidate the mechanism underlying the photoinstability of this compound, LFP was applied for determination of the rate constants of electron and energy transfer, as well as hydrogen abstraction [90].

5. Environmental systems

5.1. *Natural and bio-inspired photosystems*

Operation of any photosystem is based on light-induced electron transfer processes. Therefore, both natural and bio-inspired photosystems are rewarding subjects of LFP studies. Such studies have been frequently reported during last decades [91–97] making it impossible to summarize in the present review. Hence, only some interesting examples of the latest research in this field are presented below.

Functional systems that mimic the crucial stages in bacteria and plant photosynthesis, that is, solar to chemical energy conversion and CS, have been reproduced not only in functionalized semiconducting materials but also in systems consisting of relatively simple organic compounds and metal complexes. LFP is utilized in examination of the activity of single compounds as well as complex systems. PET processes are the main goals of such studies. Investigations performed on individual entities of the electron transfer chain [12, 98, 99] have been carried out for better understanding of the mechanism of electron acceptor–donor system operation. Recent LFP investigations of a quinone derivative, namely, 1,8-dihydroxyanthraquinone, showed that laser pulses cause generation of its triplet state. Such excited state was found to be efficiently quenched by triphenylamine *via* PET [100].

Significance of LFP studies on light-induced CS processes is twofold: elucidation of the mechanisms of reactions occurring in bacteria and plants as well as help in construction of artificial photosynthetic systems capable of solar energy conversion. Ruthenium(II) complexes with bipyridine (bpy) and tyrosine are often used in model photochemical studies on photosystem II. Some evidence for such photoactivity of $[Ru^{II}(bpy)_3]$ was recently reported by Xu *et al.* [101]. As a result of exposure to laser flash pulse, Ru(II) releases an electron which is transferred to the acceptor, such as methyl viologen, and then is reduced back by tyrosine. Such redox cycle was observed in LFP experiments performed for the series of Ru(II) complexes [101]. Some variation of this system can be recognized in dinuclear Ru(II) complex with 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz)-bridging ligand, which secures efficient electronic coupling between metal centers. As a result of laser flash, mononuclear intermediates were formed. Moreover, bptz was found to induce metal to ligand delocalization of electron. This effect was halfway between the effect of bpy and 2,2′-bipyrazine (bpz) ligands observed in analogous tetracyanoruthenium complexes [102].

Since excited states of transition metal complexes featuring metal-to-ligand charge transfer have long lifetimes of photoluminescence occurring after visible light absorption, they have been utilized for several years for solar energy conversion and other photoelectronic purposes. Recent studies performed on cyclometallated Pt(II) complexes indicate that intraligand triplet state is the main intermediate in laser-pulse-induced processes. This state reveals the lifetime matched with the luminescence lifetime of the complex [103].

5.2. *Photocatalytic systems in environmental processes*

Coordination compounds of transition metals are involved in various photo-induced environmental processes. For many years LFP has been successfully applied in the investigations of fast photocatalytic processes occurring in aqueous solutions. Considerable attention is currently paid to the role played by iron(III) complexes in environmental systems. Carboxylate complexes are of special interest, as they take responsibility for O_2 consumption as well as CO and CO_2 production in natural waters. Recent LFP investigations contributed to the elucidation of the photocatalytic cycle involving Fe(III) complex with sulfosalicylic acid (SSA). They indicated that, depending on laser pulse energy, excitation can be followed either by fast relaxation occurring in the picosecond timescale or by electron transfer from ligand to the triplet state of the FeSSA complex [104]. Reduction of Fe(III) to Fe(II) was observed during LFP experiments on iron complex with tartaric acid carried out in the presence of methyl viologen. This PET transfer process was accompanied by the formation of organic radical [105]. Similar effect was observed in the case of $[Fe^{III}(C_2O_4)_3]^{3-}$. Photoreduction of Fe(III) entails release of ligands that are transformed to oxalate radical species [106].

Light-induced facilitation of axial ligand dissociation is one of the main features that makes iron complexes with macrocyclic ligands both essential in biochemical cycles in living organisms and useful in photocatalytic systems. By analogy to well-known catalytic properties of porphyrins, iron phthalocyanines (Pc) find application, for example, in hydrogen peroxide degradation. LFP investigations confirmed their considerable photostability which makes them less prone to undergo oxidative decay. Studies performed on FeO_2Pc built into layered double oxide matrix pointed to formation of long-lived transient species and high activity of the solid in photodegradation of aqueous phenol [107].

Photocatalysis can also occur in environmental systems not involving transition metal ions. Humic acids can be given as an example as they participate in the photodegradation of phenols, amines, and heterocyclic compounds. LFP investigation showed that reactivity of their excited states is strictly correlated with the types of the side substituents [108]. Triplet states generated in LFP experiments were quenched by molecular oxygen with rates ($7–8 \times 10^8\,s^{-1}$) comparable with those obtained for fulvic acids [109].

6. Conclusions and perspectives

In this brief review we attempted to highlight new trends in recent applications of LFP technique. Current development of laser flash techniques makes them a promising tool for studying complex mechanisms of chemical and biochemical reactions as well as for the determination of the properties of new materials. Applications of LFP increase rapidly in evolving new interdisciplinary research areas integrating inorganic and organic chemistry with biological, medical, environmental, and material sciences. LFP also gives many perspectives in nanotechnology, particularly in development of new materials useful in molecular photonics and construction of electronic devices.

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