Photoinduced Electron Transfer Reactions: From the Elucidation of Old Problems in Bulk Solutions Towards the Exploration of Interfaces

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Abstract: The activities of our research group in the field of photoinduced electron transfer reactions are discussed and illustrated by several examples.

Keywords: Liquid interfaces · Nonlinear spectroscopy · Photoinduced charge transfer · Ultrafast reaction dynamics

Introduction

Electron transfer (ET) can be considered as the simplest chemical reaction and as such it is a benchmark for theories of the chemical reactivity. ET is ubiquitous in chemistry, most reactions involving some electronic redistribution if not a full charge transfer, as well as in biology.[1,2] Many ET reactions that are totally inefficient when the reactants are in the electronic ground state become operative upon photoexcitation. These photoinduced ET reactions are particularly interesting because their phototriggering allows the study of their dynamics with ultrafast laser spectroscopy. Additionally, they represent a key step in the conversion of solar energy into electrical or chemical energy.

Although photoinduced ET is one of the most investigated photochemical processes, there are still several important problems that remain unsolved.[3] In the following, we will discuss some of them and present our efforts to elucidate them. In parallel, we are also exploring new directions, *e.g.* photoinduced ET in complex molecular systems and at liquid–liquid interfaces, that will also be presented here.

Some Old Problems

One of the most successful theories of ET reactions is that developed by Marcus in the 50s–60s and refined later by Marcus himself and others.[4,5] The most important outcome of this theory is the relationship between the ET driving force, $-\Delta G_{ET}$, and its rate constant, k_{ET}. It predicts an increase of k_{ET} with increasing driving force up to a maximum where the process is barrierless, followed by a decrease of k_{ET} with a further augmentation of the driving force. The latter regime, called *the inverted region,* is equivalent to the energy gap law of nonradiative transitions. The first attempts to detect this region were unsuccessful and one had to wait until 1984 for its first observation using a series of anionic donor-bridge-acceptor systems produced by pulse radiolysis.[6] Since this breakthrough, the inverted regime has been found with many different types of ET, such as the charge recombination (CR) of ion pairs.[7–9] However, there is still no convincing report of an inverted regime for intermolecular photoinduced charge separation (CS). As found more than 40 years ago,[10] the rate constant of intermolecular CS measured by fluorescence quenching increases with increasing driving force until the process becomes diffusion controlled and the observed quenching rate constant remains equal to the diffusion constant even at very high driving force, where the inverted region is expected. Several hypotheses have been proposed to explain this strong discrepancy. The two prevailing ones are related to the nature of the primary product:

Hypothesis 1) Highly exergonic CS could result in the population of the ionic product in an electronic excited state, making the effective driving force substantially smaller.[10]

Hypothesis 2) According to a dielectric continuum description of the solvent, highly exergonic CS should be faster when the reactants are not in contact. The lack of inverted regime could thus be due to remote ET.[11]

Despite considerable efforts, none of these hypotheses could be either confirmed or dismissed and photoinduced bimolecular CS in polar solvents is usually discussed in terms of the scheme depicted in Fig. 1.

Over the past years, we have been applying ultrafast spectroscopy to get a deeper insight into these reactions.[3,9,12–18] According to the second hypothesis, highly exergonic CS should yield two ions at remote distance, and thus CR should be relatively slow. Our measurements using a donor/acceptor (D/A) pair with $\Delta G_{CS} = -2.2$ eV reveal that more than 90% of the ion pairs undergo CR in less than 1 ps.[15] This clearly points to a strong electronic
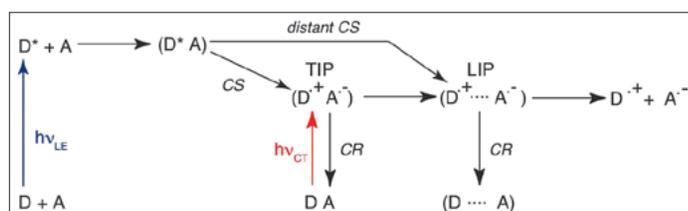
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Fig. 1. Conventional scheme of photoinduced bimolecular electron transfer reactions in polar solvents.

coupling of the ion pairs, that can be considered as tight ion pairs (TIPs, Fig. 1). Thus CS occurs mostly at contact. In fact, the coupling is so strong that CR occurs before the ion pair has reached thermal equilibrium.[19]

Time-resolved electronic spectroscopy yields only little structural information on reaction intermediates. In collaboration with the group of E. Nibbering in Berlin, we have studied these bimolecular CS processes using ultrafast IR spectroscopy.[16,18] We could, for the first time, distinguish two types of ion pairs by their spectroscopic signatures. The predominant one corresponds to the above-mentioned TIPs, whereas the other, which is favoured at low quencher concentrations, can be ascribed to a loose ion pair (LIP, Fig. 1) structure. Polarisation sensitive measurements revealed that, in a TIP, the two ions have a sandwich-like geometry. Although many more D/A pairs with different ΔG_{CS} should be investigated with these techniques, one can already conclude that the prevailing belief that highly exergonic CS only results in LIPs is not correct. This is in strong disfavour of hypothesis 2.

Proving or refuting hypothesis 1 is much more problematic than it can be thought *a priori*, because excited radical ions are extremely elusive species. Before we started our investigations, almost nothing was known about their excited-state dynamics. All the radical ions that we have studied so far are characterised by very short excited-state lifetimes, ranging from ~100 fs to a few ps, and by weak excited-state absorption features.[20–23] Therefore, if excited radical ions are formed in a bimolecular CS, their detection is extremely difficult. Substantial efforts in this direction are being invested.

The CR of ion pairs is known to exhibit the inverted regime. We have shown that this behaviour is totally suppressed if an electronic excited state of the neutral CR product is located below the ion pair. Indeed, in such cases, CR was found to be ultrafast and to populate the excited state of the neutral product.[24,25] Whether this also happens with bimolecular CS still remains to be proved.

ET in More Complex Systems

Although all the details of photoinduced ET are far from being totally understood, our current knowledge in this field can be used to design molecular systems for specific applications, such as artificial photosynthesis or photovoltaics. For most of these applications, it is desirable to have ultrafast CS and very slow CR, so that the charge-separated state lives long enough to undergo further transformation instead

of decaying back to the initial ground state while releasing its energy as heat. Fig. 2 illustrates different examples of molecules investigated in our group to better understand the factors influencing intramolecular charge transfer dynamics. The multichromophoric systems **1–5** are studied within a fruitful collaboration with the group of S. Matile at the University of Geneva. Molecules **3–5** have been shown to self-organise in lipid bilayers in a supramolecular architecture, allowing photoinduced transmembrane electron transport and the creation of a pH gradient, a crucial step in natural photosynthesis.[26,27] Beside this, **1–5** can be organised in zipper-type assemblies on a gold surface to generate a photocurrent.[28–30] These functions are associated with rather unusual photoinduced CS pathways taking place in these systems as indicated by the arrows in Fig. 1.[31] Molecules **6–9** allowed us to inspect the effect of the torsion angle between the D and A moieties on the charge transfer dynamics,[32] whereas ET between strongly coupled D and A was explored with **10** and **11**.[33] Other molecules such as **12–15** have been designed to probe the interplay between structural changes and ET.[34,35] Although our knowledge has considerably increased, much effort is still needed before a full understanding of intramolecular charge transfer is reached.

ET at Liquid Interfaces

Liquid interfaces (air–liquid, liquid–liquid) play a crucial role in many areas of science and technology, from the origin of life to chemical extraction.[36] Furthermore, solar energy conversion relying on photoinduced ET at liquid–liquid interfaces seems to be very promising.[37] The properties of liquid solutions, where

molecules are randomly oriented, can be characterised by isotropic values such as viscosity and dielectric constant. The situation is not the same at liquid interfaces, where the asymmetry of forces leads to an anisotropy of molecular orientation and hence to totally different properties. Therefore, the photochemistry at interfaces can be expected to substantially differ from that in bulk phases. However, the measurement of the dynamics of photoinduced processes at interfaces is a problematic task, because the spectroscopic response originating from this very thin region, typically 1–2 nm, is totally buried in that arising from the bulk phases.

Among the various approaches developed to limit or circumvent this problem,[38,39] the most powerful are probably those probing the second order nonlinear optical susceptibility, which is only non-zero in anisotropic media, such as the interface between two isotropic liquid phases. This is the case of the surface-second harmonic (SSHG) and surface-sum frequency generation (SSFG) techniques, which have become the most widely used optical methods for investigating all kinds of interfaces.[40,41] However, their time-resolved (TR) implementation is much less widespread.[40] We are applying TRSSHG to explore the dynamics of photoinduced processes at interfaces, including ET. The photoinduced process is first triggered by a pump pulse, which excites the solute molecules dissolved in one of the phases (Fig. 3). Interfacial information is obtained by SSHG probing. If the probe pulse and/or the SSHG signal are resonant with an optical transition of the solute molecules, the SSHG signal is strongly enhanced and the interfacial response from the solvent is negligibly small.

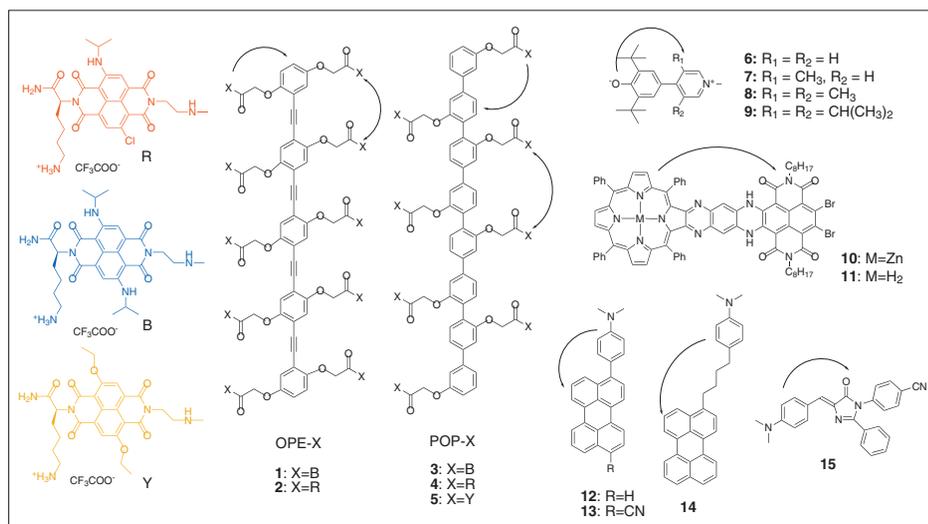For example, we have investigated interfacial friction using Brilliant Green (BG)

Fig. 2. Examples of donor/acceptor systems undergoing photoinduced intramolecular charge transfer (the direction of the ET is depicted by arrows).
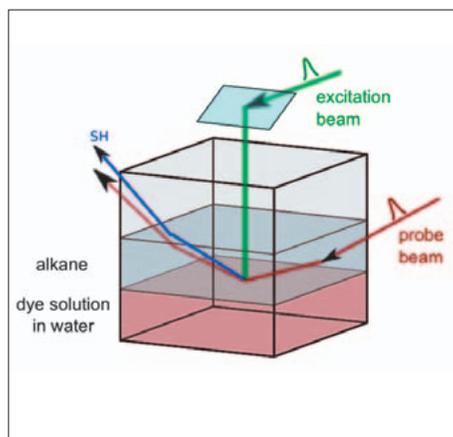
Fig. 3. TRSSHG setup.

Fig. 4. Hemicyanine at a liquid–liquid interface.

and Malachite Green (MG).[42,43] The first singlet excited state (S$_1$) of these dyes decays mainly through a non-radiative channel involving a torsional motion of the phenyl rings. The S$_1$ lifetime depends strongly on the viscosity of the environment. For instance, the S$_1$ lifetime of MG amounts to 550 fs in bulk water and to 1.1 ps at the air–water interface.[42] This shows that the friction exerted by interfacial water is substantially larger than that experienced in bulk water. Similar experiments have also been performed at alkane–(water-glycerol) interfaces.[43,44]

Information on other interfacial properties can be obtained by performing TRSSHG measurements with appropriate probe molecules. For example, the excited-state lifetime of Eosin B has been found to strongly depend on its ability to form hydrogen bonds with surrounding solvent molecules.[45] We have used this property to probe hydrogen bonding at liquid–liquid interfaces.[46]

Measurements at liquid–liquid interfaces can also be used to obtain mechanistic information on the deactivation pathway of an excited molecule. This has been done with an hemicyanine, whose S$_1$ state decays non-radiatively through large amplitude motion (Fig. 4). In order to find out which coordinate is responsible for this decay, the viscosity dependence of the S$_1$ state lifetime of this dye at liquid–liquid interfaces has been studied. Whereas the lifetime is independent of the viscosity of the polar phase, a substantial viscosity dependence of the nonpolar phase has been measured, indicating the involvement of a mode localised in the apolar part of the molecule.[47]

We have recently started to investigate the dynamics of photoinduced ET at liquid–liquid interfaces. Preliminary measurements point to substantial differences between bulk and interfacial dynamics. However, further experiments and new instrumental developments are needed before more definitive conclusions can be drawn.
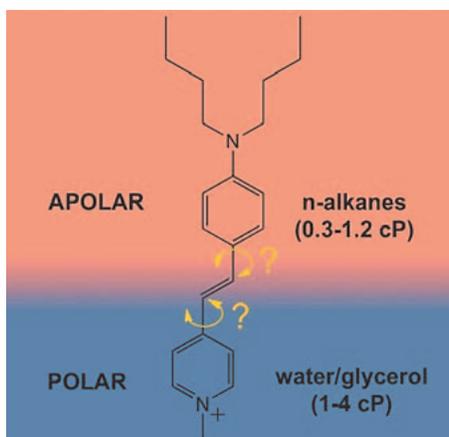
Conclusion and Outlook

We hope that with this brief overview, we could show that photoinduced ET reactions in solution are still far from being entirely understood. We are convinced that the combination of new experimental and theoretical tools being developed within the NCCR MUST will allow the elucidation of several old problems and that novel and original insights into these ubiquitons processes will be obtained.

Acknowledgements

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