Photoinduced Electron and Proton Transfer with Metal Complexes and Organic Molecules

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Abstract: This article provides an overview of some of the research performed in the author's group over the past few years. This includes work on organic mixed-valence species with photoisomerizable components, as well as studies of proton-coupled electron transfer between photoexcited metal complexes and organic reaction partners. This research relies on a combination of synthetic work with optical spectroscopic and electrochemical studies, and the results are relevant in the greater context of light-to-chemical energy conversion.

Keywords: Electron transfer · Mixed valence · Photochemistry · Photoisomerization · Proton transfer

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1. Introduction

Electron transfer can occur between reaction partners that are spatially well separated from each other and so-called long-range electron transfer reactions play an important role in many enzymes.[1,2]

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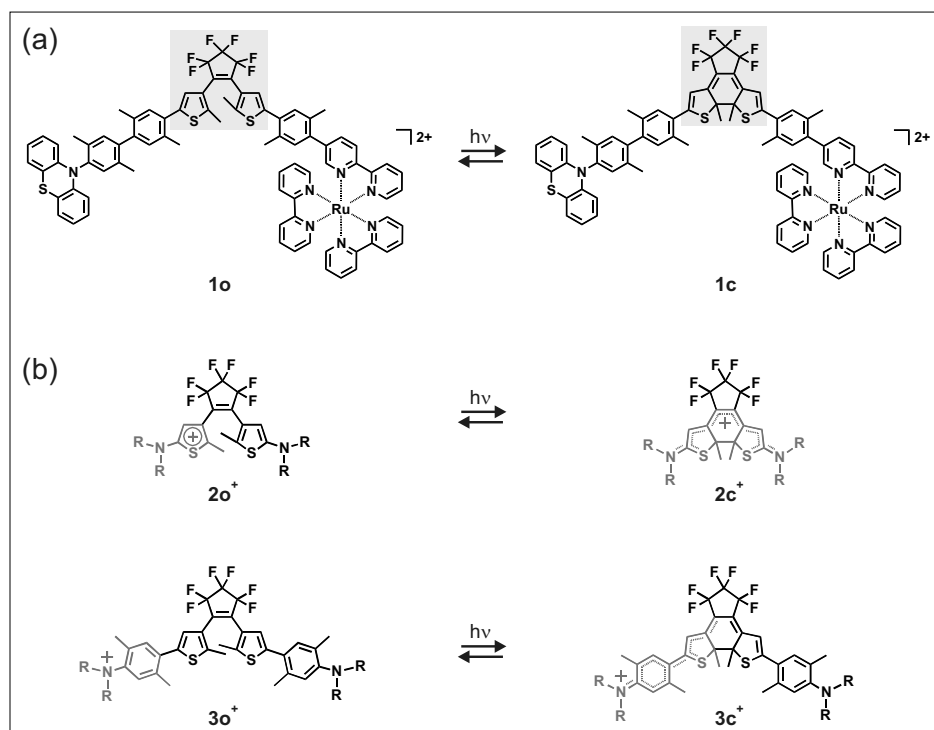Tel. +41 61 267 11 46
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Photoinduced electron transfer is an elementary reaction step in natural photosynthesis, and if we are to emulate biological light-to-chemical energy conversion with artificial systems a thorough understanding of photoinduced electron transfer seems desirable. However, many of the most interesting fuel-forming reactions are not 'simple' electron transfers in the sense that they require multiple redox equivalents and proton-coupled electron transfer (PCET) chemistry. To name just one specific example, the oxidation of water to dioxygen requires the accumulated loss of four electrons and four protons. Against this background the author's group performs mechanistic studies of 'simple' photoinduced electron transfer and phototriggered PCET using suitable model compounds which are either transition metal complexes or purely organic molecules. Recently, the focus has been on understanding elementary aspects of charge delocalization (section 2) and proton-electron coupling (section 3).

2. Charge-delocalization in Organic Mixed-valence Compounds

Initial studies of 'simple' electron transfer in the author's group concentrated on photoinduced electron tunneling in covalent donor-bridge-acceptor molecules,[3,4] but for investigation of certain aspects the study of organic mixed-valence compounds turned out to be more favorable. The donor-bridge-acceptor molecule (**1o**) shown in Fig. 1a contains a phenothiazine electron donor, a photoisomerizable dithienylethene bridge, and a Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) acceptor.[5] The dithienylethene spacer can reversibly photoisomerize between a relatively weakly π-conjugated open form (**1o**) and a more strongly π-conjugated closed form (**1c**). The question how much better the more π-conjugated closed isomer (**1c**) mediates electron transfer than the open form (**1o**) is of long-standing interest.[7] Unlike in prior studies of comparable systems a so-called flash/quench technique was used to generate a strongly oxidizing Ru(III) species out of the initially present Ru(II) complex, but nevertheless the photochemistry of the overall system remains complicated:[5] The basic problem is that photoexcitation of the Ru(bpy)$_3^{2+}$ complex triggers electron transfer and photoisomerization at the same time, and it is difficult to disentangle the two competing photoreactions.

The organic systems shown in Fig. 1b are monocations of bis(biarylamines) with a central dithienylethene spacer. Radical monocations of bis(triarylamines) may be regarded as mixed-valence compounds in which the odd electron is delocalized to different extents depending on the molecular bridge connecting the two redox-active amino-groups. Compared to many mixed-valence species based on coordination compounds the intervalence absorption bands of bis(triarylamine) monocations are relatively easy to detect, and triarylamines bearing *para*-substituents show nicely reversible electrochemistry.[8,9] The results obtained from cyclic voltammetry and optical absorption are compatible with the scenario illustrated in Fig. 1b. In the one-electron oxidized forms of molecules **2o** and **3o** the unpaired electron is essentially localized on one of the two triarylamine branches. Upon photoisomerization to the closed isomers (**2c⁺**, **3c⁺**), partial charge delocalization is occurring in the case of the molecule with *p*-xylene spacers between the N atoms and the dithienylethene unit (**3c⁺**) while in the other mixed

Fig. 1. (a) Donor-bridge-acceptor molecule with a photoisomerizable spacer;[5] (b) monocations of bis(triarylamine) compounds for organic mixed-valence studies.[6]

valence species (**2c⁺**) there is complete charge delocalization. In other words, the extent of charge delocalization can be controlled using UV and visible light, and out of class I mixed-valence compounds (**2o⁺**, **3o⁺**) one obtains class II (**3c⁺**) or class III (**2c⁺**) mixed-valence species. Because the extent of charge delocalization can be probed with infrared light by monitoring intervalence absorption bands, the experimental difficulties mentioned above for the donor-bridge-acceptor molecule **1o** do not occur for **2o⁺** and **3o⁺**.[10] Similar studies can be performed by monitoring optical electron transfer between electron-rich triarylamine units and electron-deficient triarylboryl groups.[11] The ability to control the extent of charge delocalization in functional molecules is of key interest in view of a possible future molecular electronics technology.

Related work on biarylamine end-capped oligothiophene monocations provided additional insight into charge-delocalization across heteroaromatic systems (Fig. 2). Comparison to analogous phenylene-bridged systems is particularly insightful. Based on a combination of electrochemical, optical spectroscopic and EPR investigations **4⁺** was found to be a class III mixed-valence species while the longer congeners **5⁺** and **6⁺** seem to be at the borderline of class III and class II.[12] The analogous phenylene-bridged systems **7⁺**, **8⁺**, and **9⁺** show a much steeper distance dependence of charge delocalization: Only **7⁺** is a class III mixed valence compound (at the borderline to class II),

8⁺ is a class II species, and **9⁺** is already a fully charge-localized class I species.[8,9] Such investigations of charge delocalization phenomena in oligothiophenes and related heteroaromatics are relevant in the context of organic light-emitting diodes.

3. Phototriggered PCET

The $Ru(bpz)_3^{2+}$ (bpz = 2,2'-bipyrazine) complex (**10**) differs from the more commonly used $Ru(bpy)_3^{2+}$ complex mainly by the presence of peripheral N atoms that can be protonated under favorable circumstances. This permits investigation of phototriggered PCET with phenols as reaction partners (Fig. 3a).[13] In the course of the

overall PCET reaction an electron is transferred from the phenolic unit to the photoexcited $Ru(bpz)_3^{2+}$ complex, and this is coupled to the transfer of the phenolic proton to a peripheral N atom of a bpz ligand. The overall reaction can be monitored by transient absorption and luminescence spectroscopy. Depending on what phenol is used, sizeable hydrogen/deuterium kinetic isotope effects are detected (up to ~10), and this contains information about the reaction mechanism.[14,15] With most of the investigated phenols (R = OCH_3, CH_3, H, Cl, Br, CN), electron and proton transfer seems to occur in a concerted fashion. To be able to predictably perform photoinduced concerted proton/electron transfers is of key interest for artificial light-to-chemical energy conversion.

The rhenium-phenol dyads in Fig. 3b (**11**, **12**) were synthesized to mimic the function of the P680/Tyr-Z/His-190 reaction triple of photosystem II.[16] Transient absorption studies reveal that the photochemistry of these dyads is strongly dependent on the distance between the Re complex and the *p*-hydroxy group of the benzene ring. Molecule **11** essentially acts like a photoacid; Re(ɪ) excitation leads to the release of the phenolic proton. By contrast, molecule **12** exhibits PCET chemistry; phenol-to-Re electron transfer is followed by release of the phenolic proton to the CH_3CN/H_2O solution. In molecule **12**, the photoinduced PCET process leading to the phenoxyl radical seems to occur *via* a sequence of electron and proton transfer steps (one after the other), whereas the thermal backward reaction (re-establishing the initial Re complex in its ground state and neutral phenol) appears to involve either concerted proton-electron transfer, or a rate-limiting proton transfer step. Understanding the fundamentals of such bidirectional PCET reactions could be important for example for building up charge and proton gradients across an interface.
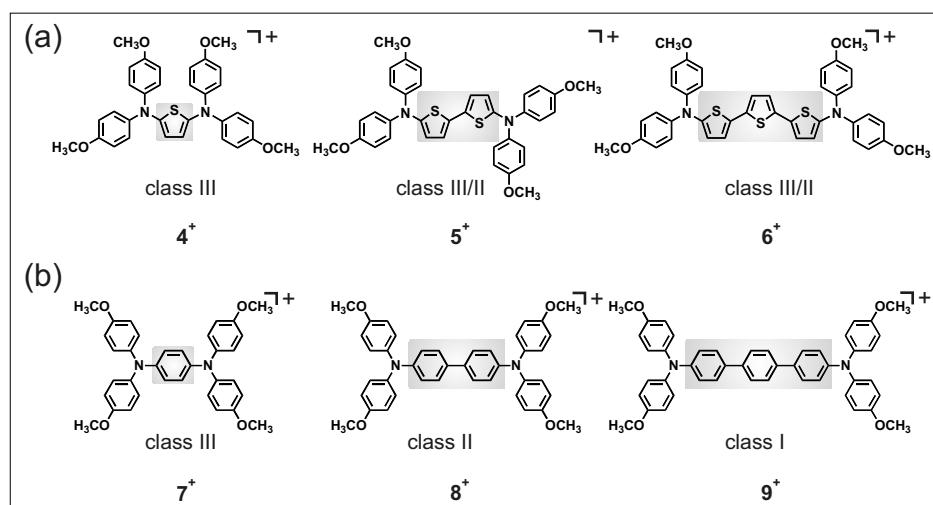

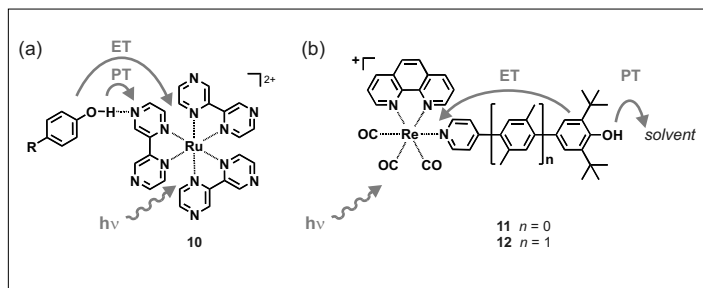Fig. 2. Comparison of thiophene- and phenylene-bridged mixed-valence systems.[8,9,12]

Fig. 3. (a) Phenol/ Ru(2,2'-bipyrazine)$_3$$^{2+}$ reaction couples for phototriggered PCET (R = OCH$_3$, CH$_3$, H, Cl, Br, CN);[13–15] (b) rhenium-phenol dyads for bi-directional PCET;[16] (ET = electron transfer; PT = proton transfer).

In molecular dyads and triads photoexcitation often creates a short-lived electron-hole pair, or a so-called charge-separated state. This is the case also in the triads shown in Fig. 4 (**13**, **14**) which are comprised of a triarylamine donor, a Ru(bpy)$_3$$^{2+}$ (**13**) or Os(bpy)$_3$$^{2+}$ (**14**) photosensitizer, and an anthraquinone acceptor.[17,18] Excitation of the metal complexes with visible light leads to the formation of such a charge-separated state with the electron localized on the anthraquinone and the hole localized on the triarylamine unit. The lifetime (τ_{CR}) of this charge-separated state turns out to be strongly solvent dependent. Interestingly, this lifetime correlates with the hydrogen-bond donor strength of the solvent rather than with the solvent dielectric constant.[19,21] For example, in molecule **14** τ_{CR} increases from 50 ns in CH$_2$Cl$_2$ to 2 µs in hexafluoroisopropanol.[20] This suggests that the anthraquinone radical anion is stabilized by hydrogen-bond formation, and this may be considered a variant of PCET.
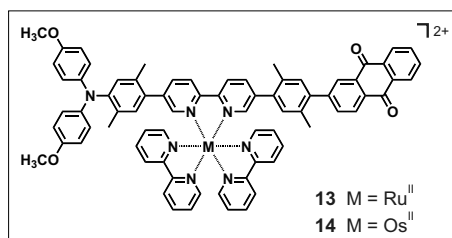

Fig. 4. Molecular triads exhibiting hydrogen-bond stabilized charge-separated states.[17-20]

4. Summary and Outlook

Research in the author's group combines synthetic work with optical spectroscopic and electrochemical studies. The key experimental technique is transient absorption spectroscopy, spectro-electrochemistry is an important complementary technique. Aside from the mixed valence phenomena and PCET processes outlined herein, photoinduced multi-electron transfer is an important line of research currently pursued in the author's group.

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