

Proton-Coupled Electron Transfer with Photoexcited Metal Complexes

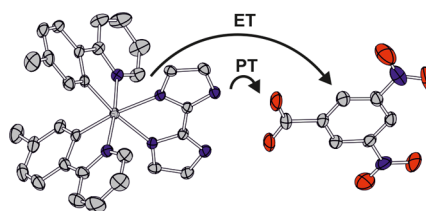
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RECEIVED ON OCTOBER 12, 2012

CONSPECTUS

Proton-coupled electron transfer (PCET) plays a crucial role in many enzymatic reactions and is relevant for a variety of processes including water oxidation, nitrogen fixation, and carbon dioxide reduction. Much of the research on PCET has focused on transfers between molecules in their electronic ground states, but increasingly researchers are investigating PCET between photoexcited reactants. This Account describes recent studies of excited-state PCET with d^6 metal complexes emphasizing work performed in my laboratory.



Upon photoexcitation, some complexes release an electron and a proton to benzoquinone reaction partners. Others act as combined electron-proton acceptors in the presence of phenols. As a result, we can investigate photoinduced PCET involving electron and proton transfer in a given direction, a process that resembles hydrogen-atom transfer (HAT). In other studies, the photoexcited metal complexes merely serve as electron donors or electron acceptors because the proton donating and accepting sites are located on other parts of the molecular PCET ensemble. We and others have used this multisite design to explore so-called bidirectional PCET which occurs in many enzymes. A central question in all of these studies is whether concerted proton-electron transfer (CPET) can compete kinetically with sequential electron and proton transfer steps.

Short laser pulses can trigger excited-state PCET, making it possible to investigate rapid reactions. Luminescence spectroscopy is a convenient tool for monitoring PCET, but unambiguous identification of reaction products can require a combination of luminescence spectroscopy and transient absorption spectroscopy. Nevertheless, in some cases, distinguishing between PCET photoproducts and reaction products formed by simple photoinduced electron transfer (ET) (reactions that don't include proton transfer) is tricky. Some of the studies presented here deal directly with this important problem.

In one case study we employed a cyclometalated iridium(III) complex. Our other studies with ruthenium(II) complexes and phenols focused on systematic variations of the reaction free energies for the CPET, ET, and proton transfer (PT) steps to explore their influence on the overall PCET reaction. Still other work with rhenium(I) complexes concentrated on the question of how the electronic structure of the metal-to-ligand charge transfer (MLCT) excited states affects PCET. We used covalent rhenium(I)–phenol dyads to explore the influence of the electron donor–electron acceptor distance on bidirectional PCET. In covalent triarylamine– $\text{Ru}(\text{bpy})_3^{2+}/\text{Os}(\text{bpy})_3^{2+}$ –anthraquinone triads (bpy = 2,2'-bipyridine), hydrogen-bond donating solvents significantly lengthened the lifetimes of photogenerated electron/hole pairs because of hydrogen-bonding to the quinone radical anion. Until now, comparatively few researchers have investigated this variation of PCET: the strengthening of H-bonds upon photoreduction.

1. Introduction

Proton-coupled electron transfer (PCET) is of pivotal importance for activation of small inert molecules to more energy-rich substances. For example, the conversion of CO_2 to formic acid is formally a two-electron/two-proton coupled reaction,¹ the oxidation of water requires the accumulated loss of four electrons and four protons,² while conversion of N_2 to NH_3 may even be regarded a coupled reaction of six electrons and six protons.³ When electrons and protons react in concerted fashion, charged high-energy intermediates

can be circumvented and the overall chemical conversion can occur with more shallow activation barriers.⁴ In this sense, concerted proton–electron transfer (CPET) can be a significantly more favorable reaction pathway than a sequence of individual electron and proton transfer steps. Currently, much fundamental research aims to elucidate under which circumstances CPET processes occur and how their rates and efficiencies can be optimized.^{5–10} Numerous mechanistic studies focused on phenols because their oxidation is accompanied by a large increase in acidity, leading

to the concerted release of an electron and a proton in many cases.^{5–7,11–18} Different experimental techniques have been used to trigger CPET with phenols, including the use of chemical oxidants,^{11,16} electrochemical methods,^{8,13,14} or photochemical methods.^{12,15,17–22} Ideally, the above-mentioned small molecule activation processes would be driven by solar energy; hence, it might be useful to understand how light can be used to perform CPET chemistry. Much research performed so far has focused on CPET between molecules in their electronic ground-states, even when using photochemical flash/quench methods to trigger the reaction.^{15,17,18} Mechanistic studies of true excited-state PCET involving electronically excited molecules are comparatively scarce, but this subdiscipline of PCET has received increasing attention over the past couple of years.^{20,22–25} The theoretical framework is essentially the same irrespective of whether ground- or excited-state PCET reactions are investigated. However, excited-state PCET can be triggered by short laser pulses, and this permits investigation of rapid reactions and in many cases opens the possibility to use luminescence spectroscopy for monitoring the reaction.

Due to their long-lived ³MLCT (metal-to-ligand charge transfer) excited states, d⁶ metal complexes with α -diimine ligands have long been used for investigations of photo-induced charge and energy transfer.²⁶ When equipped with protonatable or deprotonatable chemical functions, such complexes can become PCET reactants in their excited states.^{23,25} Sections 2 and 3 of this Account focus on recent mechanistic studies of PCET performed with such complexes in the author's group, put into the context of related work of other researchers. In section 4, multisite excited-state PCET between Re(I) complexes and phenol molecules is discussed, while section 5 concentrates on the influence of hydrogen-bonding on the lifetimes of charge-separated states formed after excitation of d⁶ metal complexes. Section 6 contains concluding remarks.

2. Photoexcited Complexes as Combined Electron/Proton Donors

Early studies of excited-state PCET made use of amidinium-carboxylate salt bridges between Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) complexes and electron donors/acceptors.^{27,28} While electron transfer (ET) can easily be monitored in these systems, proton transfer (PT) across the salt bridge interface is more difficult to detect because the acid/base chemistry occurs only on the periphery of the chromophoric unit. Inspired by Fe(II) biimidazole complexes which had been used

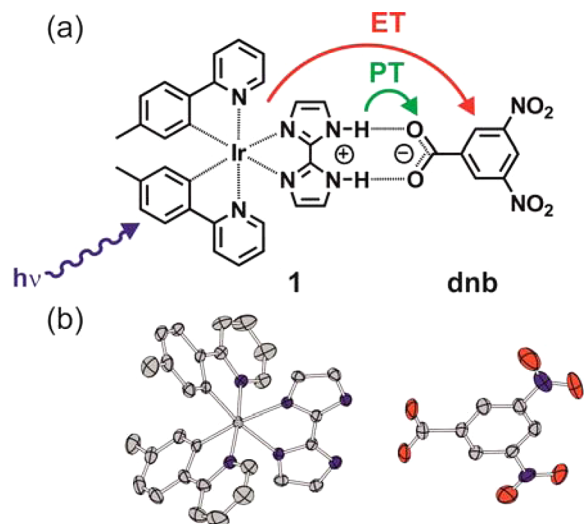


FIGURE 1. Salt-bridge adduct between complex **1** and 3,5-dinitrobenzoate (dnb). (a) Sketch of the photoinduced electron transfer (ET) and proton transfer (PT) processes. (b) Crystal structure of a cation–anion pair.³¹ Adapted with permission from ref 31. Copyright 2008 The Royal Society of Chemistry.

successfully for investigations of ground-state PCET,^{4,29,30} photoactive d⁶ metal complexes of 2,2'-biimidazole were therefore investigated in the context of excited-state PCET.^{31–33} Ir(III) complex **1** forms 1:1 adducts with dinitrobenzoate in CH₂Cl₂ (Figure 1); in the solid state there are two short N–O distances indicative of hydrogen bonding between the imidazole N–H functions and the carboxylate group.³¹

From early studies by Haga, it was known that biimidazole complexes of Ru(II) and Os(II) exhibit long-lived ³MLCT states from which electron and proton donation occurs more readily than from the ground state.³⁴ Given the proximity of the N–H functions to the metal center, it was hoped that deprotonation could be monitored by optical spectroscopy, and this was in fact one of the key motivations for this work. Luminescence spectroscopy was initially considered a particularly promising tool for this purpose. Indeed 3,5-dinitrobenzoate (dnb) quenches the emissive ³MLCT state of complex **1** oxidatively, and careful analysis of the luminescence spectra of **1** in presence of dnb reveals that ground and excited state potential energy surfaces are strongly displaced along a normal coordinate involving N–H motion.³¹ To be more specific, in the emissive excited state, substantial proton density is shifted from the biimidazole N atoms to the carboxylate O atoms, and hence, this excited state is preorganized to undergo PCET. However, it proved difficult to obtain much mechanistic insight from the biimidazole systems, and it seemed desirable to reduce the complexity of the excited-state PCET reagent by reverting to a Ru(II) complex

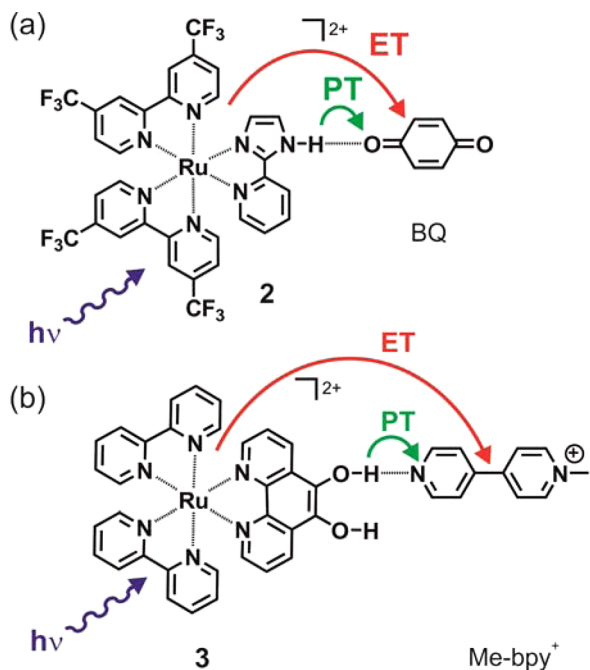


FIGURE 2. Combined photoacids/photoreductants with benzoquinone (BQ) and *N*-methylbipyridinium (Me-bpy⁺) reaction partners.^{23,35} Panel (a) adapted with permission from ref 35. Copyright 2013 The Royal Society of Chemistry. Panel (b) adapted from ref 23, copyright (2010), with permission from Elsevier; Reproduced with permission from ref 25. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

(**2**) with a 2-pyridylimidazole ligand which has only a single deprotonatable N–H function.³⁵

Upon photoexcitation, complex **2** is able to reduce 1,4-benzoquinone (BQ) (Figure 2), and this makes the N–H group more acidic by roughly 3 orders of magnitude.³⁶ In the course of reduction, the basicity of BQ increases by several orders of magnitude; hence, one might expect photoinduced electron transfer between **2** and BQ to be coupled to proton transfer.⁵ Indeed, PCET photoproducts can be detected by transient absorption spectroscopy, but they form in low quantum yields because simple (= not proton-coupled) electron transfer is thermodynamically sufficiently favorable for rapid excited-state deactivation, and there is too little additional thermodynamic benefit from PCET.³⁵ More electron-rich quinones would decelerate simple ET and would increase the chances of observing excited-state PCET. An investigation of ground-state PCET between a Ru(II) pyridylimidazole complex and the TEMPO radical was far more successful in providing mechanistic insight.³⁷

Complex **3** has deprotonatable O–H groups and reacts with *N*-methylbipyridinium (Me-bpy⁺) via CPET after photoexcitation (Figure 2).²³ The Me-bpy⁺ reactant has the great advantage that PCET products can be detected unambiguously by transient absorption, and stepwise ET–PT or PT–ET reaction pathways can be ruled out on thermodynamic grounds.

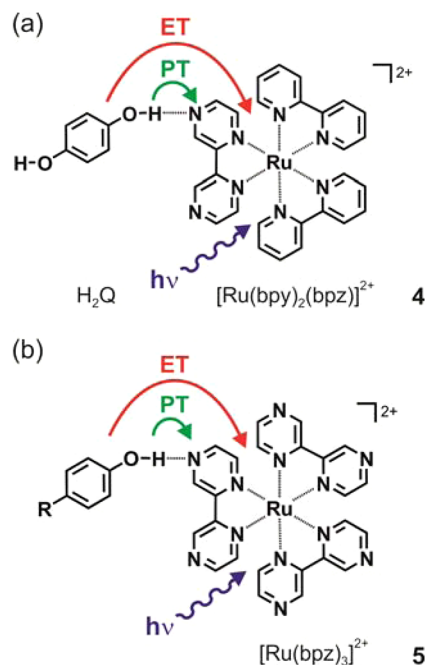


FIGURE 3. Ru(II) 2,2'-bipyrazine (bpz) complexes as combined electron/proton acceptors in photoreactions with 1,4-dihydroquinone (H₂Q) and simple phenols (R = OCH₃, CH₃, H, Cl, Br, CN).^{39,41} Panel (a) reproduced with permission from ref 25. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. (Panel (b) reprinted with permission from ref 41. Copyright 2012 American Chemical Society.)

An important fundamental question which the studies presented in this section aimed to address is whether electron and proton movement in the course of an overall PCET reaction can be followed by monitoring independent spectroscopic handles. Given sufficiently rapid excitation and detection techniques, a suitable system might provide very direct insight into the temporal evolution of a PCET process. Among the systems discussed in section 2, the combination of complex **3** and *N*-methylbipyridinium is the most promising in that regard.

3. Photoexcited Complexes as Combined Electron/Proton Acceptors

The redox and acid/base chemistry of Ru(II) complexes with 2,2'-bipyrazine (bpz) and 2,2'-bipyrimidine (bpm) ligands is well explored,³⁸ and the comparatively large amount of available thermodynamic data provides a solid basis for investigation of their excited-state PCET reactivity. Using transient absorption and EPR spectroscopy Meyer and co-workers found that 1,4-dihydroquinone reacts with photoexcited [Ru(bpy)₂(bpz)]²⁺ (**4**) via CPET, forming the reduced and protonated metal complex in addition to semiquinone (Figure 3a).^{39,40}

In related experiments, we explored the photochemistry of Ru(bpz)₃²⁺ (**5**) with five phenols bearing different *para*-substituents (Figure 3b).⁴¹ The rate constant for ³MLCT

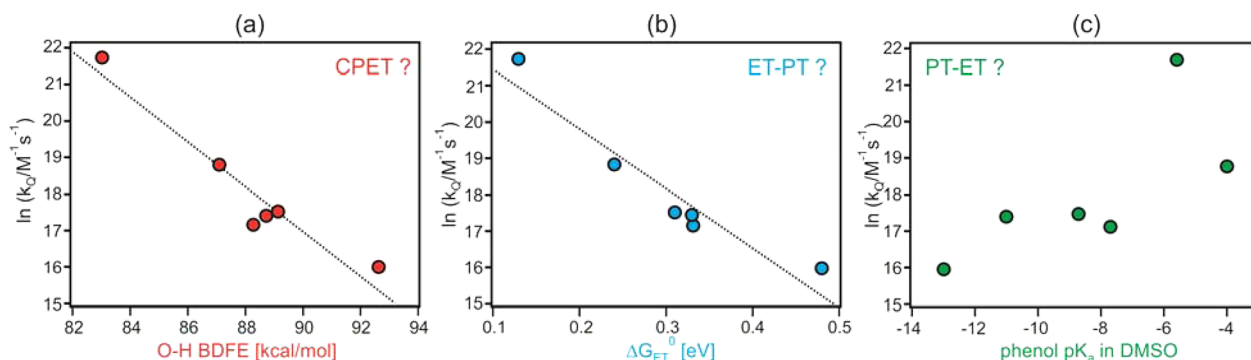


FIGURE 4. (a) Correlation of the rate constant for excited-state quenching (k_Q) of $\text{Ru}(\text{bpz})_3^{2+}$ (**5**) with the O–H bond dissociation free energy (BDFE in DMSO) of five different *para*-substituted phenols; (b) correlation of k_Q and the free energy associated with photoinduced ET from the phenols to photoexcited complex **5**;⁴¹ (c) correlation of k_Q and the $\text{p}K_a$ values of the five phenols in DMSO. The thermodynamic parameters were taken from ref 5.

deactivation (k_Q) by the phenols correlates with the O–H bond dissociation free energy (BDFE) (Figure 4a), suggesting that all five phenols react with photoexcited $\text{Ru}(\text{bpz})_3^{2+}$ via CPET. There is a similarly good correlation between k_Q and the phenol oxidation potentials (Figure 4b) which would be in line with ET as a rate-determining reaction step, but the observation of significant H/D KIEs for four out of five phenols seems incompatible with an ET–PT reaction sequence. There is no correlation of phenol $\text{p}K_a$ values with k_Q (Figure 4c), making a PT–ET sequence unlikely as well.⁴² Interestingly, the H/D KIE increases with increasing electron-withdrawing character of the phenol *para*-substituent (R), ranging from 1.0 for R = OCH_3 to 10.2 for R = CN. The correlation between KIE and the nature of R is not understood. The fact that 4-methoxyphenol fits the correlation between k_Q and the O–H BDFE might suggest that a CPET mechanism is operative despite the absence of any significant H/D KIE in this particular instance.⁴²

Conceptually, there is much analogy between this investigation of excited-state PCET⁴¹ and previous studies of ground-state PCET with phenols.^{11–19} Here, the use of a ruthenium(II) complex permits application of luminescence spectroscopy as a convenient detection tool. The following study addresses a fundamental question which is more specific to excited-state PCET chemistry.

Using rhenium(I) tricarbonyl complexes the influence of the directionality of MLCT excitation on the photoinduced PCET chemistry with 4-cyanophenol was explored.⁴³ Complexes **6** and **7** have protonatable bpz and 1,4-pyrazine (pz) ligands, respectively, and it appears reasonable to assume that in CH_3CN solution 4-cyanophenol forms hydrogen-bonded encounter adducts with the peripheral N atoms of the bpz and pz ligands (upper half of Figure 5). In complex **6** the MLCT-excited electron is located on the bpz ligand,

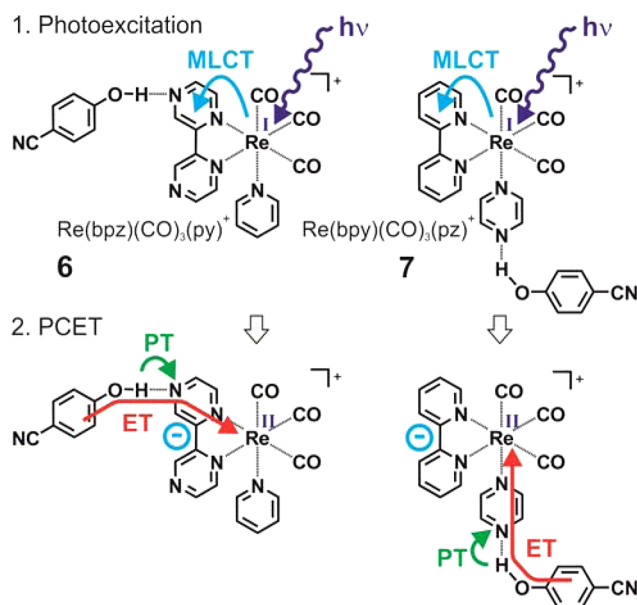


FIGURE 5. MLCT excitation and photo-PCET reactions in two rhenium(I) complexes with different protonatable sites. Reprinted with permission from ref 43. Copyright 2012 American Chemical Society.

making its peripheral N atoms more basic than in the ground state. This is favorable for proton donation from the phenol but at the same time the MLCT-excited electron is in the middle of the ET pathway from phenol to the metal center (Figure 5, bottom left). In complex **7** the MLCT-excited electron is located on the bpy ligand which is beneficial for ET because there is now a direct ET pathway without Coulomb barrier (Figure 5, bottom right). However, in complex **7** the basicity of the pz ligand is decreased upon MLCT-excitation, making PT a less favorable process. Transient absorption spectroscopy provides direct evidence for the 4-cyanophenoxy radical and it is clear that excited-state PCET takes place with both complexes.⁴³ H/D KIEs and thermodynamic considerations are in line with a concerted

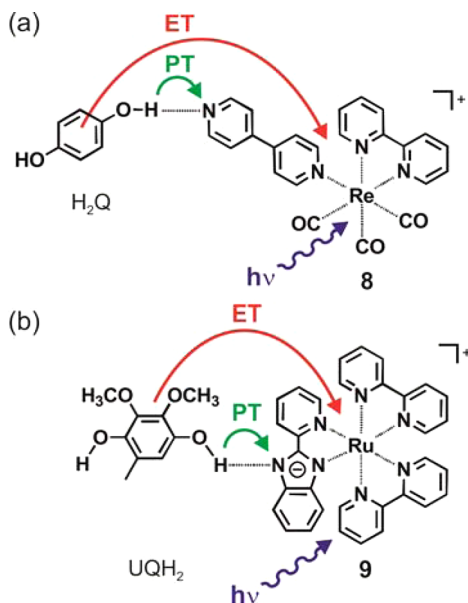


FIGURE 6. Excited-state PCET systems with protonatable 4,4'-bipyridine (a) or pyridylbenzimidazole (b) ligands.^{44,45} Panel (b) reproduced with permission from ref 25. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

reaction in both cases. The rate constant for excited-state deactivation via CPET is nearly identical for the two complexes, and thus the directionality of the MLCT excitation has little influence on the overall reaction kinetics in this case. This might be due to the fact that each of the two reaction couples has one favorable and one unfavorable contribution to the overall PCET reaction when thinking in thermodynamic cycles ("square schemes").⁴ With complex **6**, PT is favorable while ET is comparatively unfavorable; with complex **7**, the opposite is the case.

Complex **8** differs from **7** by the presence of a 4,4'-bpy instead of a pz ligand, and this makes protonation of the metal complex more easily detectable by transient absorption. This favorable property formed the basis for investigation of PCET reaction pathways between photoexcited **8** and 1,4-hydroquinone (H₂Q) (Figure 6).⁴⁴ Depending on conditions two different reaction mechanisms were found to be active. The first mechanism operates at low H₂Q concentrations (in 1:1 CH₃CN/H₂O mixtures) and is comprised of an ET–PT reaction sequence resulting from the photoexcitation of isolated (i. e., non-hydrogen-bonded) complexes; the rate-determining ET step leads to an H/D KIE of 1.1. At high H₂Q concentrations (>0.1 M) in the same solvent a substantial percentage of rhenium complexes are hydrogen-bonded to H₂Q at the moment when they are excited by the laser pulse, and these encounter adducts react via CPET with an H/D KIE of 1.7. The overall PCET reaction

mechanism thus crucially depends on the presence of hydrogen-bonded encounter adducts, and this is attributable to the short-range nature of proton transfer.

An investigation of PCET between an ubiquinol analogue (UQH₂) and a photoexcited Ru(II) complex bearing a deprotonated 2-pyridylbenzimidazole ligand (**9**) (Figure 6) provided insight into the oxidation of ubiquinol by the mitochondrial cytochrome bc₁ complex.⁴⁵ Complex **9** is chemically closely related to complex **2**; the main conceptual difference is that **9** is used in its deprotonated form to act as a combined proton/electron acceptor whereas complex **2** is a combined photoacid/photoreductant. Excited-state deactivation of **9** by UQH₂ occurs via CPET, manifesting an H/D KIE of 1.87. Stepwise ET–PT and PT–ET pathways were ruled out on thermodynamic grounds, and the semiquinone CPET product (UQH·) was detected by EPR. Indeed, EPR can a powerful technique for distinguishing simple redox products from PCET products.⁴⁰

4. Bidirectional PCET with Photoexcited Complexes

PCET plays an important role in many enzymes,^{46–48} and the P₆₈₀⁺/Tyr_Z/His-190 reaction triple of photosystem II is an example which has received particular attention.⁴⁹ This reaction triple exhibits bidirectional ground-state PCET; that is, from the phenolic function of Tyr_Z, the electron is transferred to P₆₈₀⁺ while the proton is released to His-190. Numerous artificial model systems mimicking the PCET chemistry of the above-mentioned triple have been explored,^{15,17–20,50} and d⁶ metal complexes were frequently used to phototrig the overall reaction. However, in many cases a flash/quench technique was employed in order to generate highly oxidizing species which would then initiate a ground-state PCET reaction.^{15,17,18,21,51} A notable early exception is the study of phenol oxidation by photoexcited C₆₀ in presence of pyridine, which revealed that electron transfer from phenol to the excited fullerene occurs in concert with release of the phenolic proton to the pyridine base.¹⁹

More recently, efforts to observe bidirectional excited-state PCET focused on covalent rhenium(I)–phenol dyads. The rhenium(I) tricarbonyl complex in molecule **10** is a strong photooxidant capable of triggering intramolecular phenol-to-rhenium ET in the excited state, and this is coupled to release of the phenolic proton to aqueous solution (Figure 7).^{22,52} The driving-force for photoinduced intramolecular ET is sufficiently strong in this system to make an ET–PT reaction sequence the preferred pathway, and a

concerted reaction is comparatively inefficient for this particular dyad. In this context, numerous studies (involving mostly species in their electronic ground states) concentrated on the question how PCET rates and mechanisms depend on pH and buffer concentration in aqueous solution.^{13–15,22,53} A recent study with dyad **11** explored excited-state PCET in CH₂Cl₂ in presence of pyridine and imidazole, and it was found that the overall reaction rate depends strongly on the strength of the base in this aprotic solvent,⁵⁴ in agreement with prior studies of ground-state PCET.⁵⁵

An important fundamental question in the field of PCET is how the overall reaction depends on the electron and proton transfer distance.^{56–58} Using dyads **12** and **13** the dependence of excited-state PCET on the distance between the electron donor (phenol) and the electron acceptor (rhenium) was explored, a 1:1 mixture of H₂O/CH₃CN served

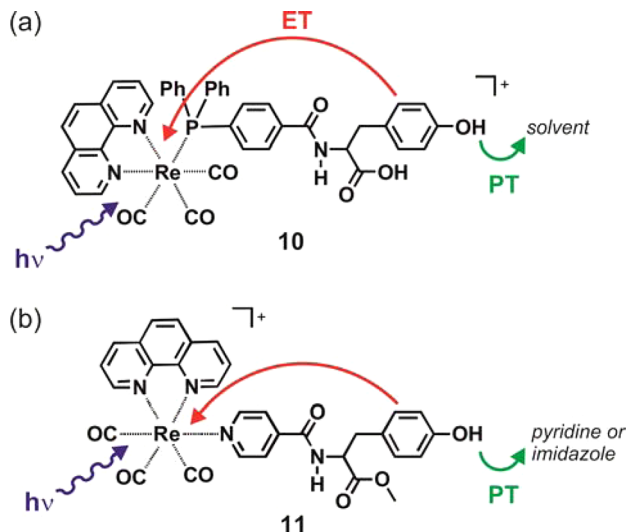


FIGURE 7. Artificial models mimicking the function of the P₆₈₀⁺/TyrZ/His-190 reaction triple of photosystem II.^{22,54} Reproduced with permission from ref 25. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

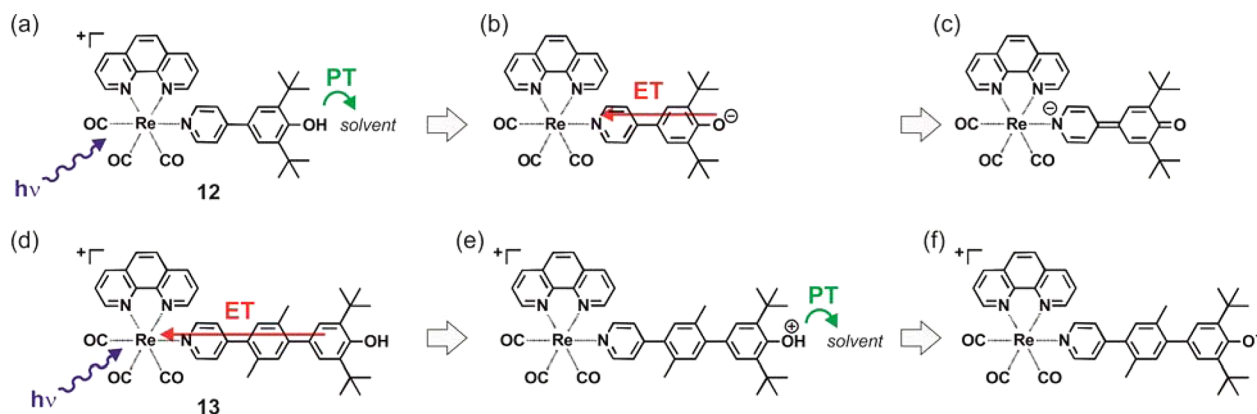


FIGURE 8. Influence of electron donor–electron acceptor distance on the photochemistry of rhenium(I)–phenol dyads in 1:1 CH₃CN/H₂O.⁵⁹

as proton accepting medium (Figure 8).⁵⁹ Dyad **12** is an electronically strongly coupled donor–acceptor compound, whereas **13** is an electronically more weakly coupled donor–bridge–acceptor molecule. Transient absorption spectroscopy reveals that **12** acts principally as a photoacid. Photoinduced proton release to the solvent is accompanied by charge-reorganization on the phenol-substituted pyridine ligand to afford a tautomeric quinonoid form (Figure 8c) with negative charge transferred toward the metal center. This pyridone-like form seems to be more stable than a pyridine-phenolate tautomer. When a *p*-xylene unit is incorporated between the phenol and the pyridine the photochemistry changes, and dyad **13** exhibits excited-state PCET occurring through an ET–PT sequence. The ET step is rate-determining hence no significant H/D KIE is associated with the formation of photoproducts, but thermal back reaction to reform the initial starting material occurs with KIE = 3.7 ± 0.5, compatible with CPET or a PT–ET sequence.

These two dyads illustrate nicely the close relationship between the fields of excited-state PCET and excited-state proton transfer.⁶⁰ Dyad **12** represents an electronically strongly coupled donor–acceptor system that might be better described by the term “photoacid”. Dyad **13**, by contrast, is a weakly coupled donor–bridge–acceptor molecule for which it is more appropriate to speak of individual reaction partners (rhenium acceptor vs phenol donor) participating in separate electron and proton transfer reactions.

5. Hydrogen-Bond Strengthening in the Course of Photoinduced ET

The presence of hydrogen bonds to (pendant or free) bases enables a CPET mechanism for phenol oxidation in many cases.^{6,8,11,12,14–16,21,51,57,61} Similarly, reduction of quinones is

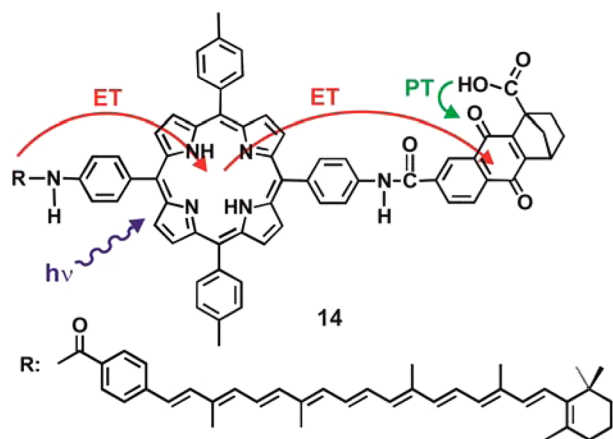


FIGURE 9. Carotenoid–porphyrin–quinone triad exhibiting intramolecular excited-state PCET.⁶⁶

facilitated when hydrogen-bond donors are present.^{5,35,62,63} Given the importance of quinones as primary and secondary electron acceptors in bacterial photosynthesis there has been much work on artificial porphyrin-quinone dyads,^{26,64} but the aspect of hydrogen-bonding or proton-coupling has received surprisingly little attention in such studies.⁶⁵ A famous exception is triad **14** in which photoexcitation of the porphyrin leads to a charge-separated state containing oxidized carotenoid and reduced quinone, with the latter being protonated by the pendant carboxylic acid function (Figure 9).^{66,67} Another early study of excited-state PCET with quinone acceptors made use of triplet-excited C₆₀ which was oxidized by chloranil, coupled to proton donation from trifluoroacetic acid to reduced chloranil.⁶⁸

Photoinduced electron transfer in molecular dyads and triads often leads to long-lived charge-separated states in which light energy is transiently stored in the form of chemical energy (an electron–hole pair).⁶⁴ One of the challenges is to obtain charge-separated states which are as long-lived as possible, and this provided the motivation for a series of studies presented below.

In dyad **15** photoinduced ET from Ru(bpy)₃²⁺ to anthraquinone (AQ) is endergonic in CH₂Cl₂ and consequently does not occur at appreciable rates.^{69,70} However, addition of 3 mM hexafluoroisopropanol (HFIP) makes ET a competitive excited-state deactivation process (Figure 10a). Electrochemical investigations lead to the conclusion that reduction of AQ to AQ^{•−} increases the average number of HFIP molecules which are hydrogen-bonded to the anthraquinone moiety of dyad **15** from 1 to 2.5, and at the same time the (mean) binding constant per HFIP molecule increases from ~1 to ~66 M^{−1}.⁶⁹ In other words, not only more HFIP molecules bind to AQ^{•−} than to charge-neutral AQ,

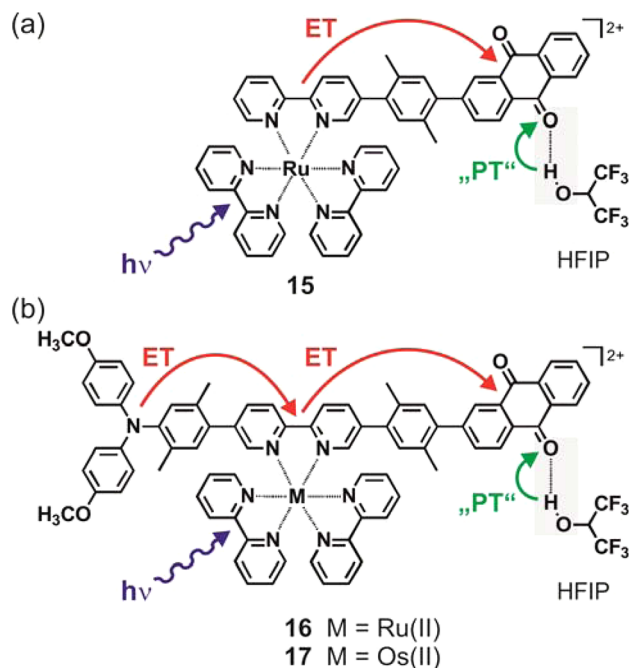


FIGURE 10. Dyad (a) and triads (b) in which photoproduced anthraquinone radical anions are stabilized by hydrogen-bonds donated by hexafluoroisopropanol (HFIP).^{69–74} H-bonds are strengthened in the course of photoinduced ET; hence, “PT” denotes the transfer of some finite proton density rather than the transfer of a full proton.

but individual HFIP species also bind more tightly. Photo-reduction of AQ in dyad **15** may therefore be regarded as a variant of excited-state PCET: Hydrogen bonds are strengthened in the course of photoinduced ET, implying that some finite proton density (rather than a full proton) is transferred from HFIP toward AQ. Whether hydrogen-bond strengthening takes place in concert with AQ (photo)reduction is not clear; at any rate no significant H/D KIEs were detected.

Triads **16** and **17** represent an extension of dyad **15** in that they contain an additional triarylamine (TAA) donor (Figure 10b).⁷² Photoexcitation of their Ru(bpy)₃²⁺ and Os(bpy)₃²⁺ moieties leads to the rapid formation (<10 ns) of a charge-separated state containing oxidized TAA and reduced AQ.^{71,73} The decay time (*k*_{CR}) of this charge-separated state correlates with the Gutmann acceptor number of the solvent in which it is measured (Figure 11a), while the correlation of *k*_{CR} with the solvent dielectric constant is poor (Figure 11b).⁷¹ These observations suggest that the electron/hole pair is stabilized by H-bond donation from the solvent. The most acidic solvent used in this study was HFIP, and it seems that photoreduction of AQ is coupled to H-bond strengthening rather than to the transfer of a full proton; transient absorption data are consistent with this interpretation. In the case of the osmium triad (**17**) the change in

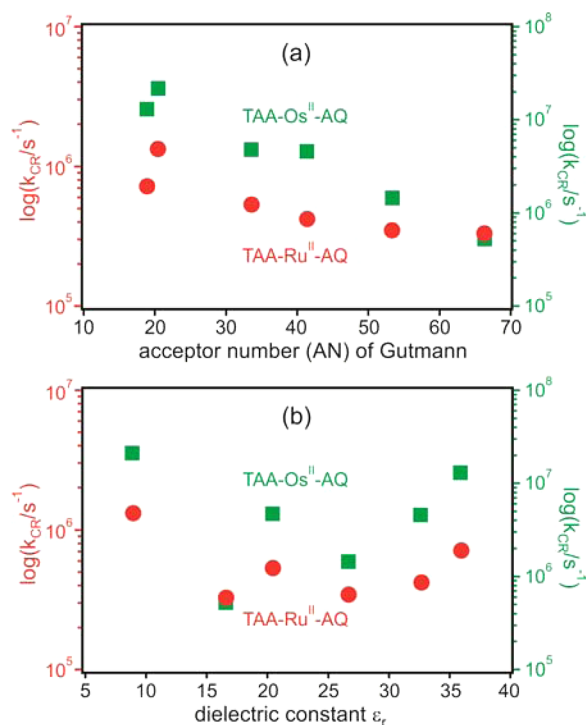


FIGURE 11. Rate constant for electron–hole recombination (k_{CR}) after photoexcitation of triads **16** (red) and **17** (green) as a function of (a) Gutmann acceptor number of the solvent, (b) dielectric constant of the solvent. Adapted with permission from ref 71. Copyright 2012 American Chemical Society.

solvent from CH_2Cl_2 to HFIP increased the lifetime of the charge-separated state from ~ 50 to ~ 2000 ns.^{71,74} Interestingly, the rates for photoinduced forward processes, specifically AQ reduction, were much less affected by the change in solvent. Furthermore, HFIP seems to have little influence on the redox chemistry of TAA. The main conclusion from these recent works and related prior studies is that photoproduced charge-separated states can be stabilized thermodynamically and kinetically by hydrogen-bonding, and this might be of interest for light-to-chemical energy conversion.

6. Concluding Remarks

Light pulses have been used quite frequently to trigger PCET reactions, but the number of true excited-state PCET systems with photoexcited reactants is small compared to studies of PCET between molecules which are in their electronic ground states. In principle, excited-state PCET offers the possibility for direct conversion of light energy into chemical energy, but appropriate catalytic energy conversion cycles are yet to be successfully implemented. Investigations of excited-state PCET need not be limited to metal complexes with long-lived triplet excited states. Given sufficiently high reaction rates and fast detection techniques, purely organic

reagents are amenable to studies of excited-state PCET as well.²⁴

Laser-triggering is clearly an interesting tool for investigation of rapid PCETs, and the results obtained from studies of excited-state PCET can be understood in the same theoretical framework as ground-state PCET reactions. However, the subdiscipline of excited-state PCET often suffers from the fact that thermodynamic quantities such as redox potentials and pK_a values for the relevant photoexcited species can only be estimated.

Solar energy conversion will not necessarily have to rely on excited-state PCET. For example, the PCET reactions of photosystem II involve species in their electronic ground states. Indeed, ground-state PCET might be an equally feasible way to convert solar energy as excited-state PCET. On the other hand, electronically excited species are usually more reactive than molecules in their ground states, and this might pave the way to more unusual PCET reactions than those which have been explored to date.

The author thanks his collaborators and colleagues for their work cited in this Account. Funding from the Swiss NSF through Grant Number PP002-110611, by the DFG through Grant Number WE4815/1-1, and through IRTG-1422 is gratefully acknowledged.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

The authors declare no competing financial interest.

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