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Kinetic isotope effect of proton-coupled electron transfer in a hydrogen bonded phenol–pyrrolidino[60]fullerene

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4.1 ABSTRACT

Proton-coupled electron transfer (PCET) plays a central role in photosynthesis and other biological processes. Studies of PCET models increase our understanding of biology and can provide design principles for solar-to-fuel systems, where intermediates involving PCET can bridge the fast timescale of photoinduced electron transfer and the slow timescale of catalysis. Compound **1**, a phenol–pyrrolidino[60]fullerene has an internal hydrogen bond between the phenol and pyrrolidine. Compounds **2** and **3** lack this hydrogen bond and act as reference. We report a singlet lifetime of 250 ps for the fullerene moiety in **1**, compared to lifetimes around 1 ns for the reference compounds. The quenching of the singlet excited state of the fullerene in **1** is assigned to PCET. A H/D exchange study reveals a kinetic isotope effect (KIE) of 3.0, consistent with a concerted PCET mechanism. Compound **1** can act as a model for the Tyr_Z – HIS 190 system in photosynthesis and can be used to further develop the theoretical background of the KIE in these systems.

4.2 INTRODUCTION

Proton-coupled electron transfer (PCET) is of key importance in photosynthesis and various other biological processes.[16] In photosystem II, after the initial charge separation the oxidized chlorophyll is reduced in a PCET step by a tyrosine (Tyr_Z). The tyrosine phenolic proton is donated to a nearby histidine residue (His 190).[114,115] When the tyrosine is reduced by the water oxidation complex it regains a proton. By the coupling of proton movement to these redox reactions photosynthesis avoids high energy intermediates and stabilizes the charge separated state.[15,17,18]

In artificial photosynthesis one aim is to use design principles from nature to develop a solar fuel producing system. PCET is one of these principles that can play a crucial role in bridging the timescale of short-lived, reactive intermediates formed by photoinduced charge separation to that of the relative slow process of multi-electron catalysis. Various studies have been performed on artificial PCET systems with various degrees of molecular complexity.[16,18,116-125] In search of a minimal biomimetic construct for photoinduced PCET, Moore et al., have previously reported a fullerene-based dyad in which the fullerene fluorescence

lifetime in benzonitrile is reduced from 1.3 ns to 260 ps.[126] This reduction of the fluorescence lifetime was not found in acidified solvent, strongly suggesting a PCET mechanism for the quenching of excited fullerene. This could be either a 'proton first', 'electron first' or concerted transfer process. We will refer to both the step-wise and concerted mechanisms as PCET.

Here we report a transient absorption spectroscopy study of this putative PCET in the phenol-pyrrolidino[60]fullerene **1** depicted in Figure 4.1. In this isomer the phenol hydroxyl group is *ortho* to the pyrrolidine moiety and designed to hydrogen bond to the lone pair electrons of the nitrogen on the pyrrolidine. This internal hydrogen bond provides a well-defined structural framework for the PCET process. Reference compound **2** has a hydroxyl group at the *para* position where the internal hydrogen bond cannot be formed. Reference compound **3** lacks the hydroxyl group.

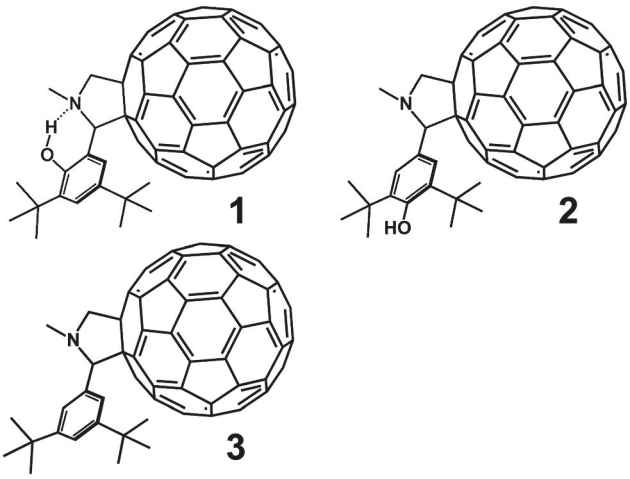


Figure 4.1 Phenol–pyrrolidino[60]fullerene compounds investigated in the present work.

4.3 RESULTS AND DISCUSSION

Electrochemical measurements revealed that the phenol moiety in compound **2** and the phenyl group in **3** are both thermodynamically incapable of reducing singlet excited C_{60}. This also holds for compound **1** in acidified solvent, where the internal hydrogen bond is disrupted.[126]

The steady-state absorption spectra in Figure 4.2 are dominated by features from fullerene.[78] The extinction coefficient of the compounds is largest in the UV. A small amplitude tail spans the visible part of the spectrum, where maxima are found at 433 nm and 705 nm.

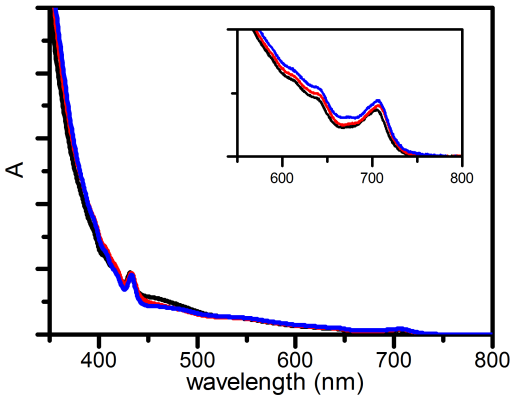


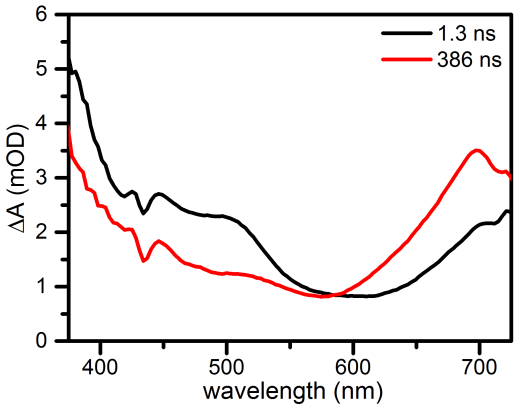
Figure 4.2 Normalized absorption spectra of 1 (black), 2 (red) and 3 (blue) in benzonitrile, normalized at 433 nm.

For transient absorption spectroscopy the compounds were excited at 705 nm in the lowest-energy absorption band of fullerene; the instrument response time was 100 fs. Global analysis yields the Evolution Associated Difference Spectra (EADS) in Figure 4.3. These are the interconverting spectra that follow from analysis with a sequential model. Further details of the measurements and analysis are given in the Materials and Methods section in the supporting information.

For compound **2** (Figure 4.3A) in aerated benzonitrile two lifetime components are needed for a sufficient fit of the data: 1.3 ns and 386 ns. The spectra are assigned to the singlet and triplet excited state of fullerene and are very similar to those reported for methylfulleropyrrolidine.[78] The first EADS (black) assigned to the singlet state shows excited state absorption in the full probed window. Overlapping, but with smaller amplitude we find ground state bleach. This has a negative contribution to the ΔA signal that can be recognized by the minima at 433 nm and 705 nm. The singlet excited state has a lifetime of 1.3 ns. The second EADS, assigned to the fullerene triplet, has lower amplitude at wavelengths

shorter than 585 nm and higher amplitude at longer wavelengths. A maximum is found around 700 nm. The triplet decays to the ground state in 386 ns. Very similar results are found for **3** (Figure SI 4.1).

A



B

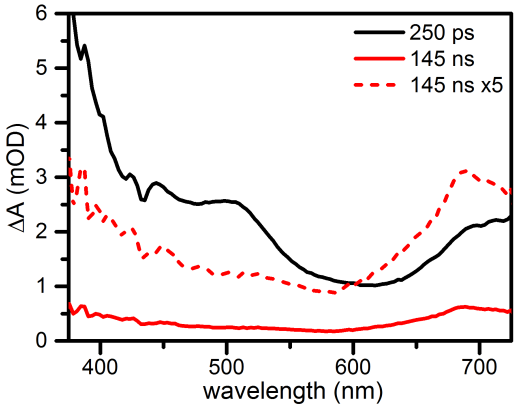


Figure 4.3 Evolution Associated Difference Spectra (EADS) of compounds 2 (A) and 1 (B) in aerated benzonitrile upon 705 nm excitation. The lifetimes of the interconverting spectra are given in the legend.

The singlet excited state spectrum of **1** (Figure 4.3B, black) closely resembles the singlet spectra of **2** and **3**. The lifetime of the singlet state is found to be 250 ps, in agreement with the reported fluorescence lifetime.[126] As a result of the shorter singlet lifetime, less triplet is formed, and the triplet spectrum (which is similar to that of **2** and **3)**, is smaller in amplitude (Figure 4.3B, red and red dash). The

reduced singlet lifetime has been assigned to a proton-coupled electron transfer process forming a neutral phenoxyl radical and a zwitterionic pyrrolidino[60]fullerene group ($PhO^{\cdot}$–$PyrH^{+}$-$C60^{\cdot -}$). The zwitterionic state could not be detected. Most probably, the rate constant for recombination is larger than that for formation of the zwitterionic state. In such 'inverted kinetics', the zwitterionic state signal would rise with the time constant of its lifetime, and its transient concentration would be low. The detection of such recombination time constants on fast timescales is further complicated by a large coherent and cross-phase modulation artifact around zero time delay.

To confirm the involvement of proton migration in the photophysical pathway we performed transient absorption spectroscopy of compound **1** in aerated benzonitrile with 2% v/v H2O or D2O. The protons or deuterium from H2O or D2O will exchange with the phenolic proton, the only exchangeable proton of compound **1**. The H/D exchange was confirmed by ^{1}H-NMR. The ^{1}H-NMR spectrum of the compound in equal parts CDCl3/CS2 with 2% H2O was compared to the ^{1}H-NMR spectrum in equal parts CDCl3/CS2 with 2% D2O. The disappearance of the peak for the phenolic proton was observed after addition of D2O (Figure SI 4.2 and Figure SI 4.3). We refer to the deuterated compound as **1-D (1-H** for H_2O**)**. Figure 4.4 shows the time trace for the absorption of both compounds at 538 nm. For **1-H** we find a singlet lifetime of 250 ps, similar to the measurement in benzonitrile. In contrast, the singlet lifetime of **1-D** is 546 ps. Based on the lifetime for decay of **2** of 1.3 ns, we estimate the rate of PCET at 3.2×10^{9} s^{-1} and 1.1×10^{9} s^{-1} for **1-H** and **1-D** respectively. Thus, excited state quenching by PCET is associated with a H/D kinetic isotope effect (KIE) of 3.0. For compounds **2** and **3** in benzonitrile with 2% v/v H2O or D2O no kinetic isotope effect was found.

This significant kinetic isotope effect for **1** confirms the involvement of proton migration in the quenching of the singlet state. We propose that this PCET process occurs by a concerted mechanism. The size of the KIE shows that the proton is involved in the rate determining step and excludes the 'electron first' mechanism for this non-equilibrium PCET process.[116-120,127,128] The 'proton first' mechanism is excluded by the large difference in acidity. The ΔpKa of phenol and pyrrolidine is ~10 based on values in acetonitrile.[129,130] Prato et al. have shown that pyrrolidine is several orders of magnitude more acidic when attached to fullerene.[131] The pKa

of pyrrolidine is not expected to change much upon excitation of fullerene, because the HOMO and LUMO do not include the atoms around the H-bond.[132] Due to the large ΔpKa, proton transfer from phenol to pyrrolidine prior to electron migration would be energetically steeply uphill. Concerted PCET avoids this high energy intermediate.

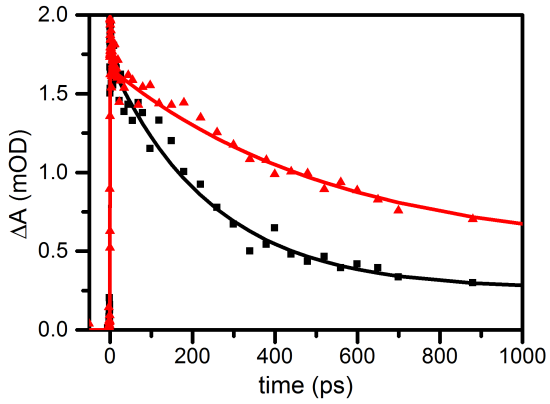


Figure 4.4 Time trace of 1 at 538 nm in aerated benzonitrile with 2% H2O (1-H, black) and 2% D2O (1-D, red). The sharp peak at 0 ps is due to a coherent and cross-phase modulation artifact.

Constentin et al. reported a phenol-pyrrolidine system with an electrochemically observed KIE of 1.8.[133] A possible explanation for the larger KIE in our experiments is the lower pKa of pyrrolidinofullerene, as compared to pyrrolidine, which leads to a weaker hydrogen bond. Hammes-Schiffer and co-workers discussed the KIE dependence on hydrogen bond strength in PCET processes.[134] The trend of increasing KIE with weaker hydrogen bond is explained by the more localized wavefunction in case of deuterium, leading to a faster decay of overlap with increasing donor-acceptor distance. However the opposite trend has been observed in some systems and explained by the role of vibronic states.[134]

To summarize, our transient absorption spectroscopy results for compound **1** show a quenching of the singlet excited fullerene, assigned to a proton coupled electron transfer process. We observe a H/D kinetic isotope effect of 3.0 consistent with a concerted PCET mechanism.

SUPPORTING INFORMATION TO CHAPTER 4

SI 4.1 MATERIALS AND METHODS

The synthesis of compound **1**, **2** and **3** was described previously.[126] The ^{1}H-NMR spectra were taken on a Varian spectrometer at 400 MHz. Samples were prepared using equal parts of $CDCl_3$ and CS_2 with 2% H_2O or D_2O and with 0.03% tetramethylsilane as an internal standard. For the spectroscopic investigations the compounds were dissolved in benzonitrile, benzonitrile with 2% v/v D_2O, and benzonitrile with 2% v/v H_2O. Benzonitrile and D_2O were purchased from Sigma Aldrich and used without further purification or deoxygenation.

Room-temperature steady-state absorption spectra were recorded on a Perkin Elmer Lambda 40 UV/VIS spectrometer. Both steady-state and transient absorption spectra were recorded using a 1 mm quartz cuvette.

Transient absorption spectroscopy was performed on a setup using two electronically synchronized amplified Ti:sapphire laser systems (Legend and Libra, Coherent, Santa Clara, CA) as described previously.[135] The amplifiers were seeded by a single 80 MHz oscillator (Vitesse, Coherent) and pumped with separate pump lasers (Evolution, Coherent). Both lasers have an 800 nm output at a repetition rate of 1 kHz. The output power is 3.0 W for the Legend and 4.5 W for the Libra.

For the measurements in benzonitrile, the output of the Legend was used to drive an optical parametric amplifier (OperA SOLO, TOPAS, Coherent) with which the excitation wavelength was set to 705 nm. Excitation energies of 1 µJ were used at a spot size of ~300 µm. A broadband probe beam was generated by focusing part of the output of the Libra on a CaF_2 or sapphire plate. The transient absorption signal was acquired in a multichannel fashion by spectrally dispersing the probe through a spectrograph projecting it on a 256-element diode array detector.[76] The instrument response function had a width of 100 fs (full width at half maximum).

The time difference between pump and probe was controlled in two ways. An optical delay line was used for delays of the pump beam in the fs to 3.5 ns regime. Delay steps of 12.5 ns were generated by selection and amplification of consecutive seed pulses of the oscillator. The timing of the amplification process

of the Libra was controlled by a signal delay generator (SDG Elite, Coherent). A second signal delay generator – one that synchronizes with the first – governed the timing of the Legend (SDG, Coherent). By varying the triggering of the second SDG with respect to the first, delays of the probe were achieved up to 10 μs. Both delay methods were applied simultaneously, addressing the fs to μs range in a single experiment.

For the measurements in benzonitrile with 2% v/v D_2O or H_2O the pump and probe beam were both generated from the Libra. The time difference between pump and probe was set with an optical delay line, addressing the fs to 3.5 ns regime.

Global analysis of the transient absorption data was performed using the Glotaran program.[8] The spectral chirp was fitted with a third order polynomial. In global analysis all wavelengths are analyzed simultaneously with a set of common time constants and spectra.[7,77] Here, we present the results using a sequentially interconverting model. In a sequential analysis (1 → 2 → 3 →….) the numbers indicate evolution-associated difference spectra (EADS) that interconvert with successive mono-exponential decay times, each of which can be regarded as the lifetime of each EADS. The first EADS corresponds to the time-zero difference spectrum. The first EADS evolves into the second EADS with time constant τ_1, which in turn evolves in the third EADS with time constant τ_2, etc. This procedure clearly visualizes the evolution of the excited and intermediate states of the system. In general, the EADS may well reflect mixtures of difference spectra of pure electronic states, which may arise from heterogeneous ground states or branching at any point in the photo-induced evolution.[33,85,136] For a more detailed description of global analysis we refer to Van Stokkum et al. 2004.[7,77]

SI 4.2 TRANSIENT ABSORPTION SPECTROSCOPY OF COMPOUND 3

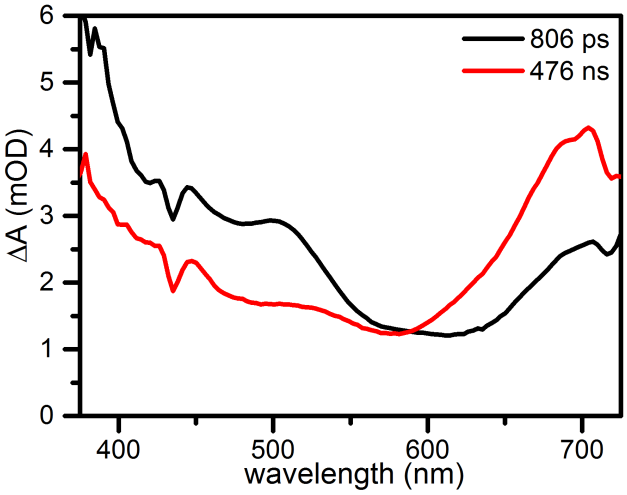


Figure SI 4.1 EADS of 3 in benzonitrile upon 705 nm excitation.

SI 4.3 1H-NMR OF COMPOUNDS 1 AND 2

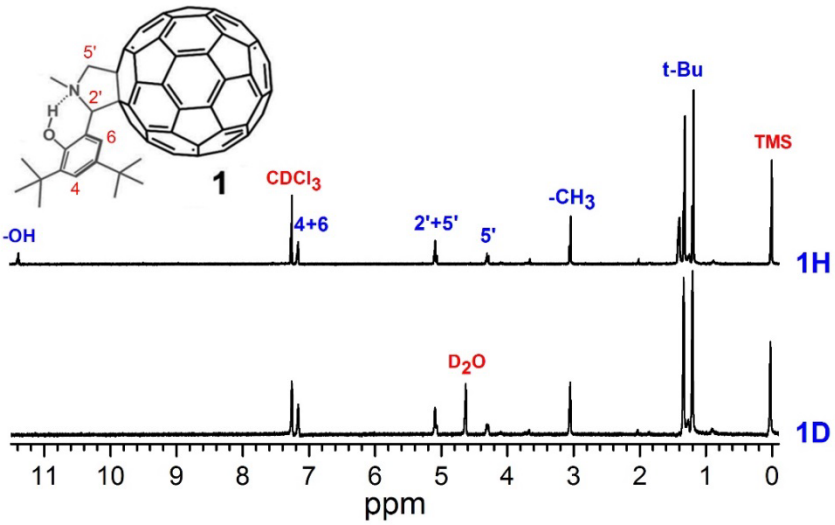


*Figure SI 4.2 ^{1}H-NMR of compound 1 in equal parts $CDCl_3/CS_2$ with 2% H_2O (**1-H**) or 2% D_2O (**1-D**).*

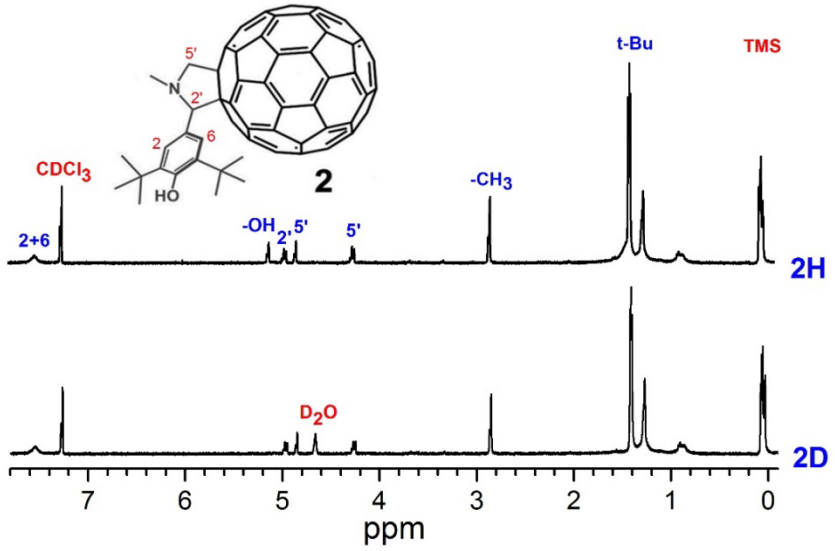


*Figure SI 4.3 ^{1}H-NMR of compound 2 in equal parts $CDCl_3/CS_2$ with 2% H_2O (**2-H**) or 2% D_2O (**2-D**).*