Supplementary information to

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

Janneke Ravensbergen[A], Chelsea L. Brown[B], Gary F. Moore[B], Raoul N. Frese[A], Rienk van Grondelle[A], Devens Gust[B], Thomas A. Moore[B], Ana L. Moore[B] and John T. M. Kennis[A]

[A] Department of Physics and Astronomy, Faculty of Sciences, VU University, De Boelelaan 1081, 1081 HV, Amsterdam, The Netherlands.
[B] Center for Bioenergy and Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA 85287-1604

Materials and methods

The synthesis of compound **1**, **2** and **3** was described previously.[1] 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.[2] 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.[3] 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.[4] In global analysis all wavelengths are analyzed simultaneously with a set of common time constants and spectra.[5, 6] 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.[7-9] For a more detailed description of global analysis we refer to Van Stokkum et al. 2004.[5, 6]

Transient absorption spectroscopy of compound 3

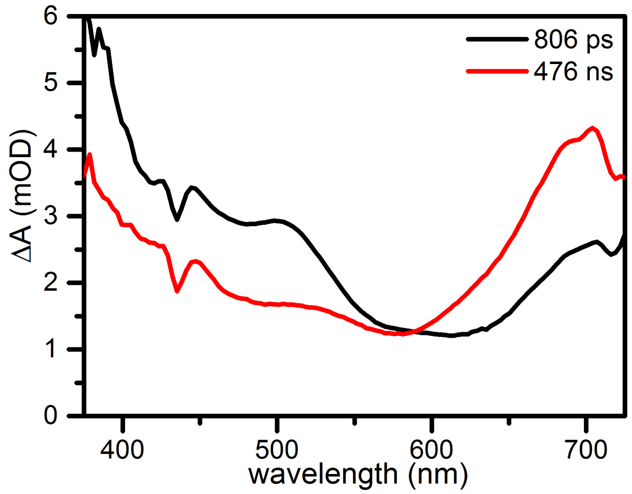

*Figure S 1. EADS of **3** in benzonitrile upon 705 nm excitation.*

Raw transient absorption data

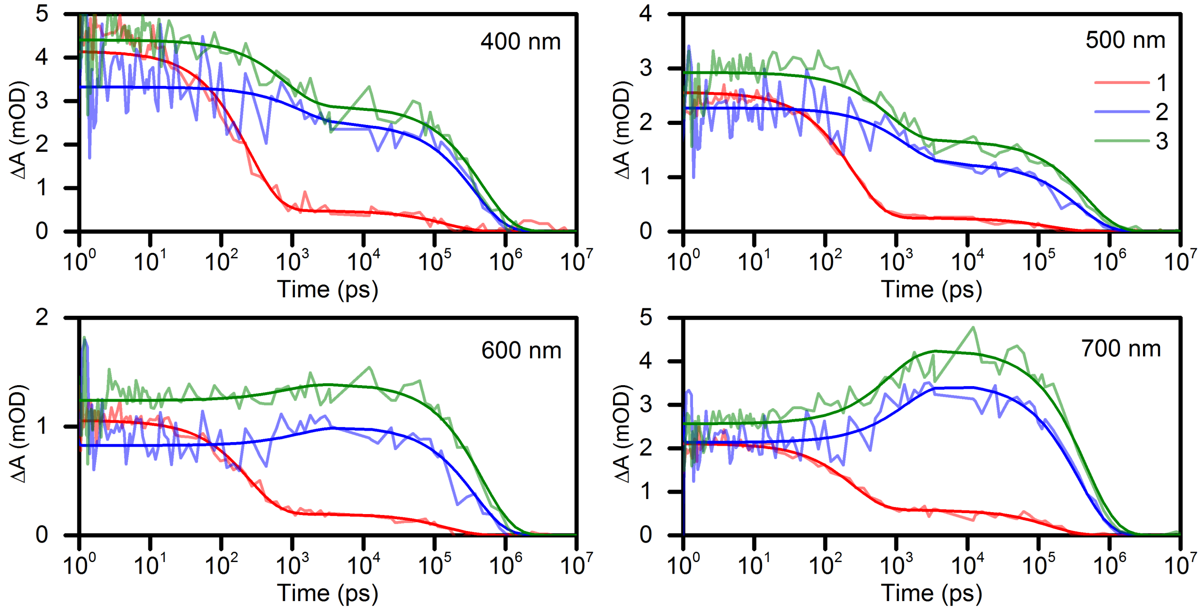

Figure S 2. Raw transient absorption data presented as time traces at 400, 500, 600 and 700 nm. The semi-transparent lines are raw data, the solid lines the fits of compound 1 (red), 2 (blue) and 3 (green).

^{1}H-NMR of compounds 1 and 2

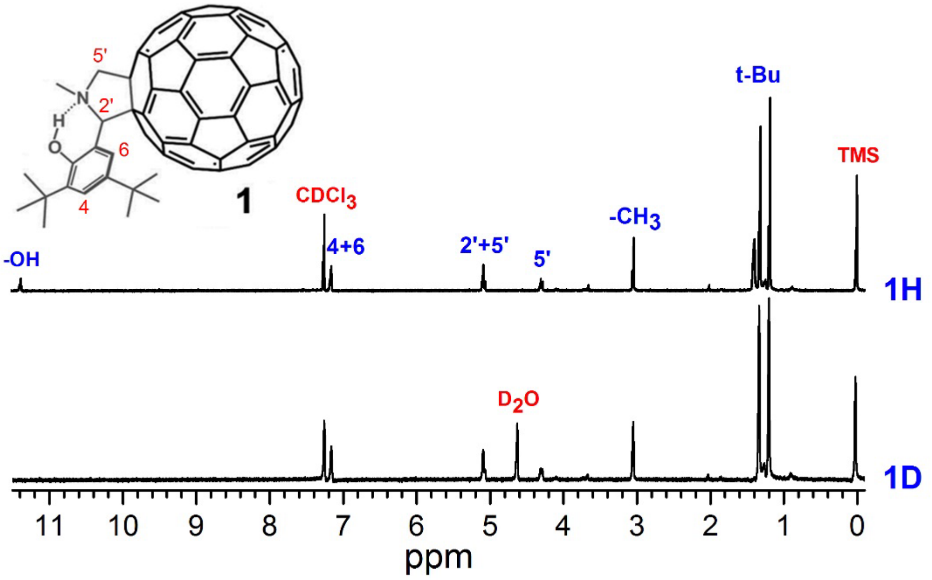

*Figure S 3. ^{1}H-NMR of compound **1** in equal parts $CDCl_3/CS_2$ with 2% H_2O (**1-H**) or 2% D_2O (**1-D**).*

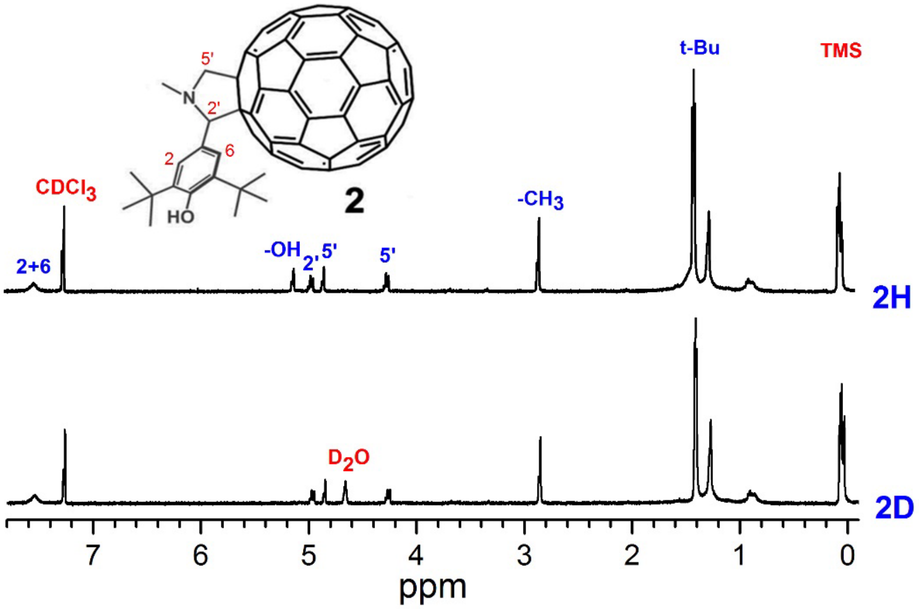

Figure S 4. ^{1}H-NMR of compound ***2*** *in equal parts $CDCl_3/CS_2$ with 2% H_2O (****2-H****) or 2% D_2O (****2-D****).*

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