Supplementary Information

Excited-State Dynamics of the Medicinal Pigment Curcumin in a Hydrogel

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Additional details to 2.4 Femtosecond Transient Absorption Spectroscopic Studies.

Solutions of 100 μM curcumin in 1.5 wt% PAAC18 hydrogel were used in the transient absorption spectroscopic studies. Similarly, 100 μM curcumin in 1.5 wt% PAAC18 hydrogel solution of neat water and deuterated water were also used in the transient absorption spectroscopic studies to demonstrate a deuterium isotope effect. All the measurements were acquired using a quartz cuvette with a 2-mm path length. The solutions were stirred with a magnetic stirrer. The laser system used for the femtosecond transient absorption experiments consisted of a Ti:sapphire modelocked oscillator (Spectra-Physics, Tsunami), which seeded a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire Pro XP) pumped by a 20W Q-switched Nd:YLF laser (Spectra-Physics, Empower). The output of the amplifier was centered at 800 nm with a repetition rate of 1 kHz and pulse duration of 100 fs, which was then split into the pump and probe beam lines. The 400-nm pump pulse was generated using a 0.5-mm type-I BBO crystal, mechanically chopped at 500 Hz and then focused onto the sample with a spot size of 385 μm and pulse energy of 700 nJ. The spot size was determined using the Knife-Edge method. The probe beam line passed through a delay stage and was used to generate a white light continuum as the broadband probe in a 2-mm sapphire crystal. A 750-nm shortpass filter (optical density 4, 3 mm, Edmund Optics) was placed after the sapphire crystal to separate the probe from the 800-nm seed beam. The probe passed through a beam splitter to produce the sample and reference beams with a spot size of 80 μm (the Knife Edge measurement) at the sample position and pulse energy of < 10 nJ. The sample and reference beams were then directed into complementary CMOS detectors for detection in the visible region. The probe polarisation was oriented at the magic angle (54.7°) with respect to the pump polarisation. The same measurements were carried out with the solvent only, which was used for chirp correction of the obtained time-resolved spectra using SurfaceXplorer (Ultrafast Systems). In all the measurements, the full width at half maximum (FWHM) of 100 fs was used as the instrument response function (IRF) for data analysis. The error values were determined as standard deviations of three independent measurements (Table 1). Less than 10% of curcumin photo-degradation was observed after each set of data acquisition based on its absorption spectrum.

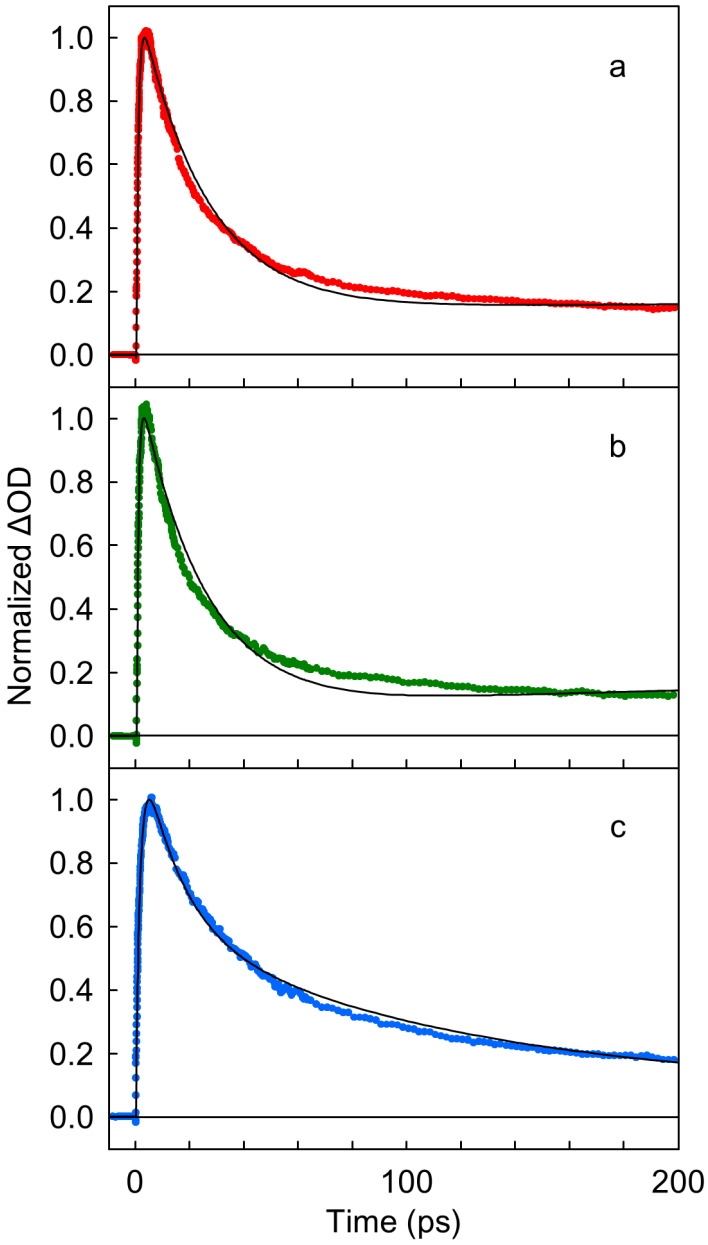

Figure S1. Decay kinetics of the integrated excited-state absorption signals of curcumin in the PAAC18 hydrogel of (a) 50mM phosphate buffer at pH 7.4, (b) those of H_2O and (c) those of D_2O, at 500 – 530 nm. The τ_1 time constants were determined when τ_2 was fixed to (a – b) 25 ps or (c) 14 ps while τ_3 and τ_4 were kept to 109 and 5000 ps, respectively, in order to justify the deuterium isotope effect on the τ_2 time constants. The resultant poor fitted curves (black) support the strong deuterium isotope effect on the τ_2 time constants. The resultant parameters were summarized in Table S1.

Table S1. Integrated Transient Absorption Kinetic Parameters of Curcumin in the PAAC18 Hydrogel Solutions of Different Solvents, Shown in Figure S1.

Solvent	a_1	τ_1	a_2	τ_2 [a]	a_3 [b]	a_4 [b]
Buffer [c]	-0.48±0.01	0.81±0.04	0.42±0.01	25.0	-0.03±0.01	0.07±0.01
H_2O	-0.43±0.01	0.69±0.04	0.43±0.01	25.0	-0.07±0.01	0.07±0.01
D_2O	-0.47±0.01	1.66±0.01	0.27±0.01	14.0	0.22±0.01	0.04±0.01

[a] τ_2 is fixed in order to justify the presence of deuterium isotope effect on this time constant.

[b] τ_3 and τ_4 are fixed to 109 and 5000 ps, respectively.

[c] 50 mM phosphate buffer at pH 7.4

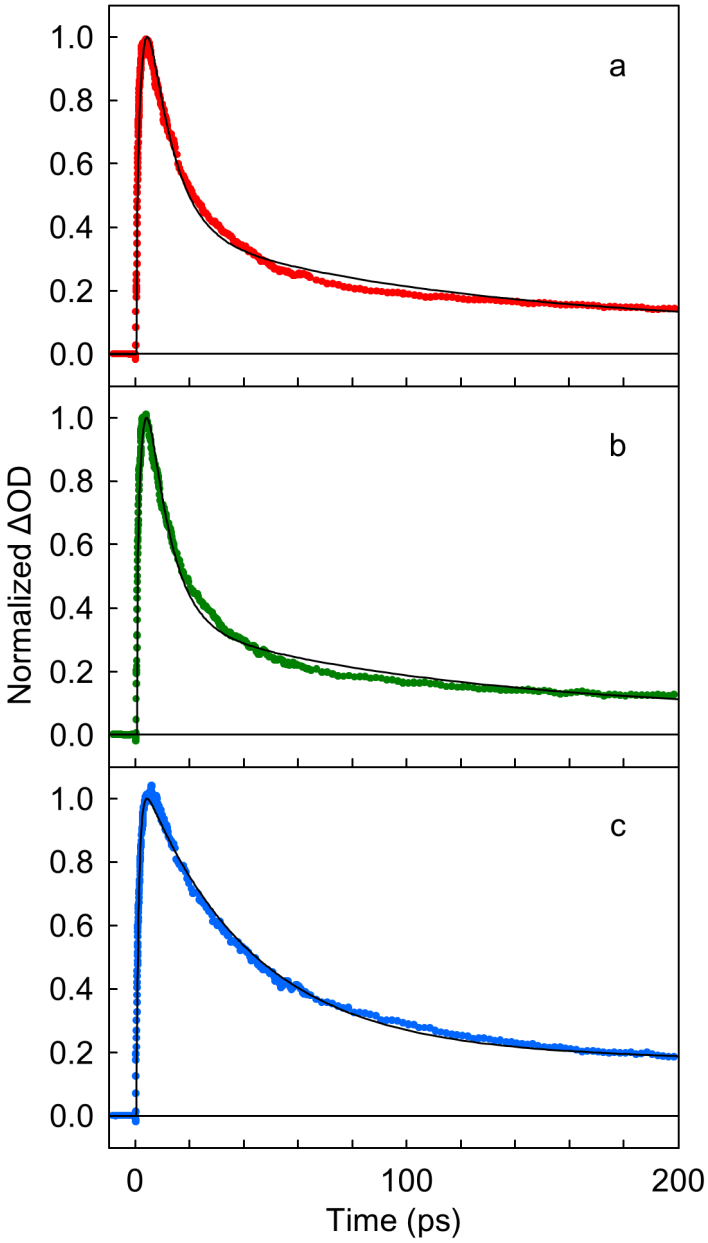

Figure S2. Decay kinetics of the integrated excited-state absorption signals of curcumin in the PAAC18 hydrogel of (a) 50mM phosphate buffer at pH 7.4, (b) those of H_2O and (c) those of D_2O, at 500 – 530 nm. The τ_2 time constants were determined when τ_1 was fixed to (a – b) 2 ps or (c) 1 ps while τ_3 and τ_4 were kept to 109 and 5000 ps, respectively, in order to examine the possible deuterium isotope effect on the τ_1 time constants. The resultant fitted curves (black) suggest a small or negligible level of the deuterium isotope effect on the τ_1 time constants. The results further support the presence of the deuterium isotope effect on the τ_2 time constants. The resultant parameters were summarized in Table S2.

Table S2. Integrated Transient Absorption Kinetic Parameters of Curcumin in the PAAC18 Hydrogel Solutions of Different Solvents, Shown in Figure S2.

Solvent	a_1	τ_1 [a]	a_2	τ_2 [a]	a_3 [b]	a_4 [b]
Buffer [c]	-0.43±0.02	2.00	0.43±0.01	10.0±1.2	-0.12±0.01	0.03±0.01
H_2O	-0.42±0.01	2.00	0.46±0.01	8.2±0.2	-0.10±0.01	0.02±0.01
D_2O	-0.50±0.01	1.00	0.39±0.01	39.3±0.4	0.03±0.01	0.08±0.01

[a] τ_1 is fixed in order to examine the presence of deuterium isotope effect on this time constant.

[b] τ_3 and τ_4 are fixed to 109 and 5000 ps, respectively.

[c] 50 mM phosphate buffer at pH 7.4