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Electronic supplementary information

## Water Concentration Dependent Photochemistry of Ketoprofen in Aqueous Solutions

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Description of the method used to obtain the kinetics of the intermediates investigated in the paper.

Generally, the strong Raman band of the intermediate was chosen as the characteristic Raman band of the intermediate species and then this band was fit to Lorentzian functions to obtain an integrated area of the characteristic Raman band. Then a plot of the integrated area against the time delay of the spectra the data was obtained from was made. The points in this plot were then fit by a single-exponential or a two-exponential function as needed to obtain a satisfactory fit to the data so as to determine the growth time constant and the decay time constants for the plotted data.

**Fig. 1S.** The time dependence of the 1538 cm<sup>-1</sup> Raman band areas of  ${}^{3}$ [KP] obtained in a 1:9 H<sub>2</sub>O:MeCN solution (closed squares) which were fit by a single-exponential function with a decay time constant of ca. 119 ns is shown.



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**Fig. 2S.** The extracted ns-TR<sup>3</sup> spectra of 1 mM KP obtained from those spectra acquired after photolysis of KP in a 7:3 H<sub>2</sub>O:MeCN solution by removing the contribution of the <sup>3</sup>[KP] and triplet protonated biradical carbanion species is shown. All of the spectra were obtained with a 266 nm pump excitation wavelength and a 319.9nm probe wavelength. The asterisk (\*) marks regions affected by solvent subtraction artifacts and/or stray light.



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**Fig. 3S.** The ns-TR<sup>3</sup> spectra of 1 mM KP in a 9:1 PBS:MeCN solution obtained using a 266 nm pump excitation wavelength and a 319.9 nm probe wavelength at various time delays indicated next to the spectra are shown. The asterisk (\*) marks regions affected by solvent subtraction artifacts and/or stray light.



**Fig. 4S.** In a 9:1 PBS:MeCN solution, the time dependence of the 1579 cm<sup>-1</sup> Raman band areas of the triplet protonated biradical carbanion species (closed squares) were fit by a two-exponential function with a ca. 91 ns growth time constant and a ca. 1770 ns decay time constant. The data displayed here were derived from the ns- $TR^3$  spectra shown in Fig. 3S.

