Femto- to Second Studies of a Water Soluble Porphyrin Derivative in Chemical and Biological Nanocavities

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Supporting Information

Experimental Setup

1. TCSPC

The emission signal was collected at the magic angle, and the instrument response function (IRF) was typically 70 ps. The emission decays were convoluted to the IRF and analyzed using the Fluofit package. The time-resolved anisotropy was constructed by the expression: $r(t) = (I_P - GI_\perp) / (I_P + 2GI_\perp)$, where G is a factor to compensate for the polarization bias of the detection system. The value of G was acquired by tail-matching of fluorescence intensity at parallel (I_P) and perpendicular ($I_\perp$) polarizations.

2. Femtosecond up-conversion

The system consists of a femtosecond Ti:sapphire oscillator Mai Tai HP (Spectra Physics) and coupled to second harmonic generation and up-conversion setups (CDP Systems). The oscillator pulses (90 fs, 2.5 W, 80 MHz) were centered at 830 or 840 nm and doubled in an optical setup through a 0.5 mm BBO crystal to generate a pumping beams at 415 or 420 nm (~ 0.1 nJ). The polarization of the latter was set to magic angle in respect to the fundamental beam. The sample has been placed in rotating cell with thickness of 1 mm. The fluorescence was focused with reflective optics into a 1-mm BBO crystal and gated with the fundamental fs-beam. The IRF of the apparatus (measured as a Raman signal of pure solvent) was 170 fs (FWHM).

3. Flash photolysis

The 355-nm pumped optical parametric oscillator (OPO) signal at 415 nm or 420 nm were used for the sample excitation. The probing light source was a 150 W xenon arc lamp. The light transmitted through a 1-cm sample quartz cuvette was dispersed by a monochromator and detected by a photomultiplier coupled to a digital oscilloscope (Agilent Infinium DS08064A, 600 MHz, 4 GSa/s). The pump pulse energy was attenuated to 2 mJ by a pair of a half-waveplate and a polarizer. For time windows shorter than 500 μs, the pulsed lamp was used, while for longer time windows the lamp worked in a continuous mode and the photomultiplier signal was connected with

additional resistance of 5 kΩ to the oscilloscope with a signal input impedance of 1 MΩ instead of 50 Ω.

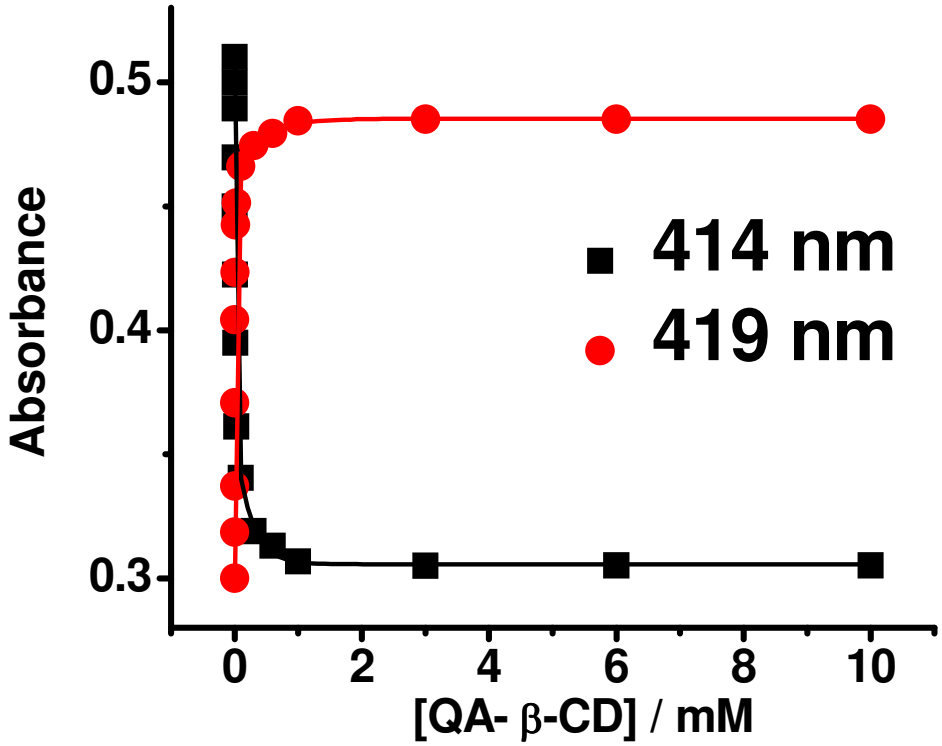

Figure S1. Absorbance variation of TSPP with QA-β-CD concentration observed at 414 and 419 nm. The solid lines are from the best fit using eq 1, assuming the formation of a 1:2 complex.

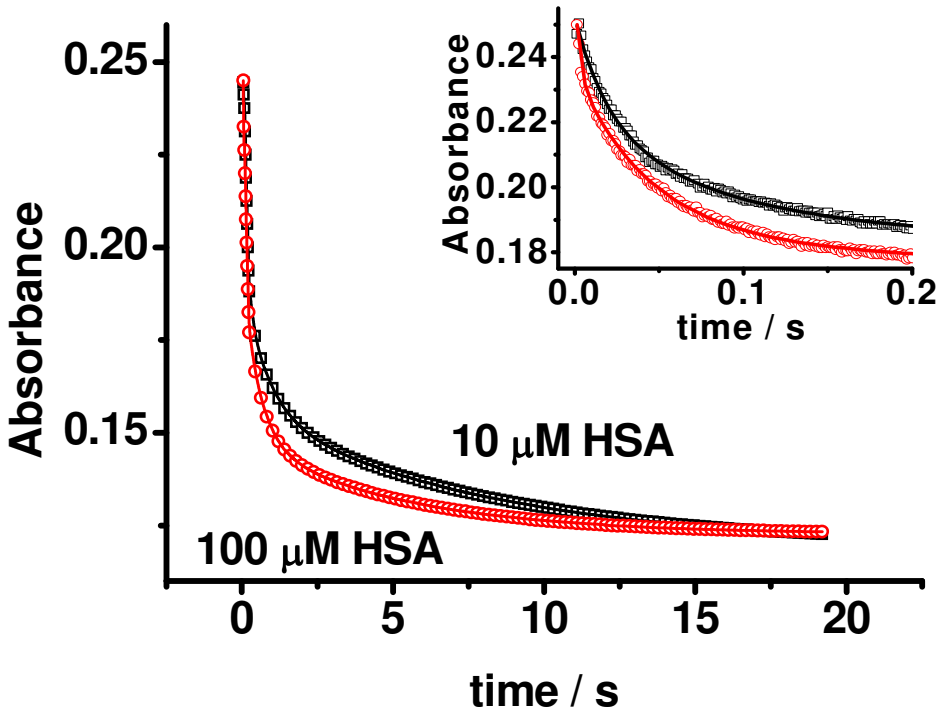

Figure S2. Kinetics of TSPP mixing with 10 μM HSA (□) and 100 μM HSA (O) collected at 414 nm. The inset shows the kinetics on a shorter time scale. The solid lines represent the best fits using a bi-exponential function model (see text for details)

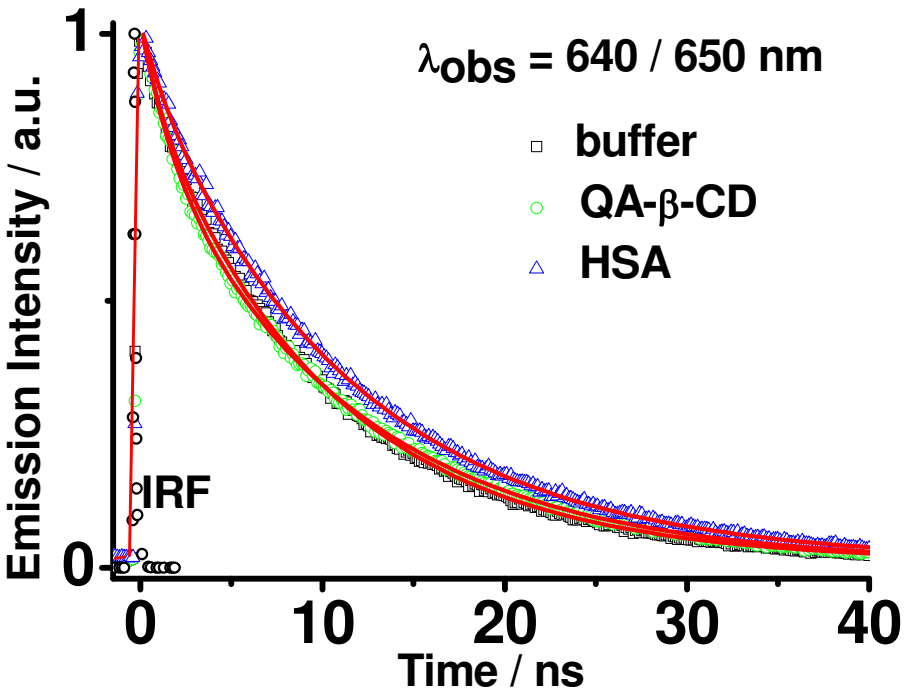

Figure S3. Decays of of TSPP emission (□) in buffer at pH=7, (O) in presence of 10 mM QA-β-CD, and (Δ) in 20 μM HSA, collected at 640 nm for TSPP in buffer and at 650 nm for others. The solid lines represent the best fits using two-exponential functions. Excitation wavelength was 433 nm.

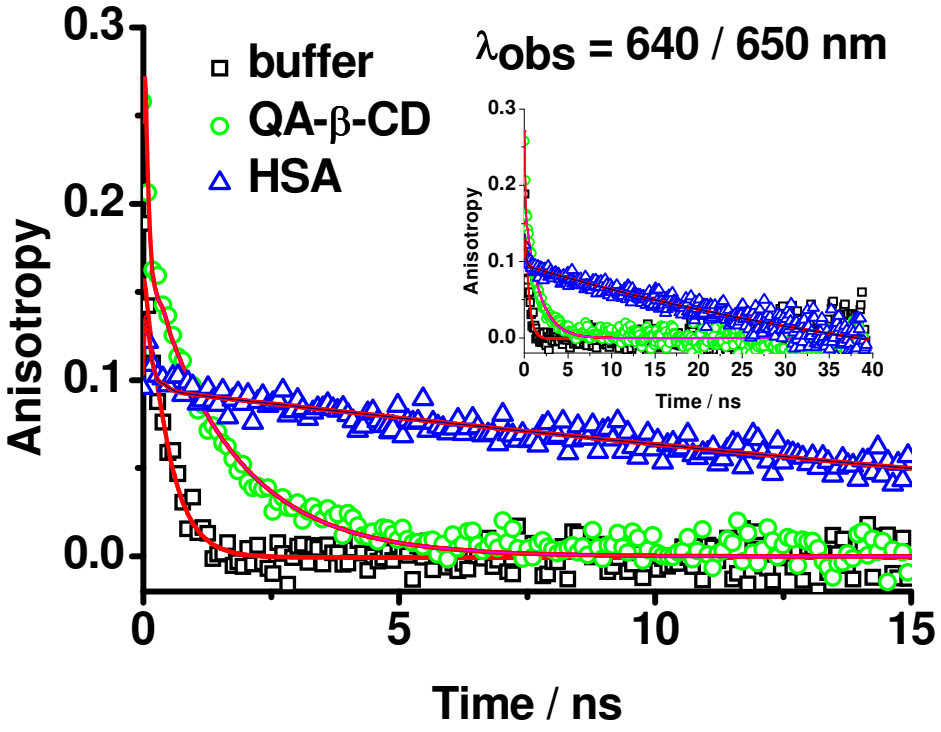

Figure S4. Emission anisotropy decays of TSPP (□) in buffer (pH=7), (O) in presence of 10 mM QA-β-CD, and (Δ) in 20 μM HSA, collected at 640 nm for TSPP in buffer and at 650 nm for others. The inset shows the decays of emission anisotropy on a longer time scale. The solid lines represent the best fits using single- or two-exponential functions. Excitation wavelength was 433 nm.

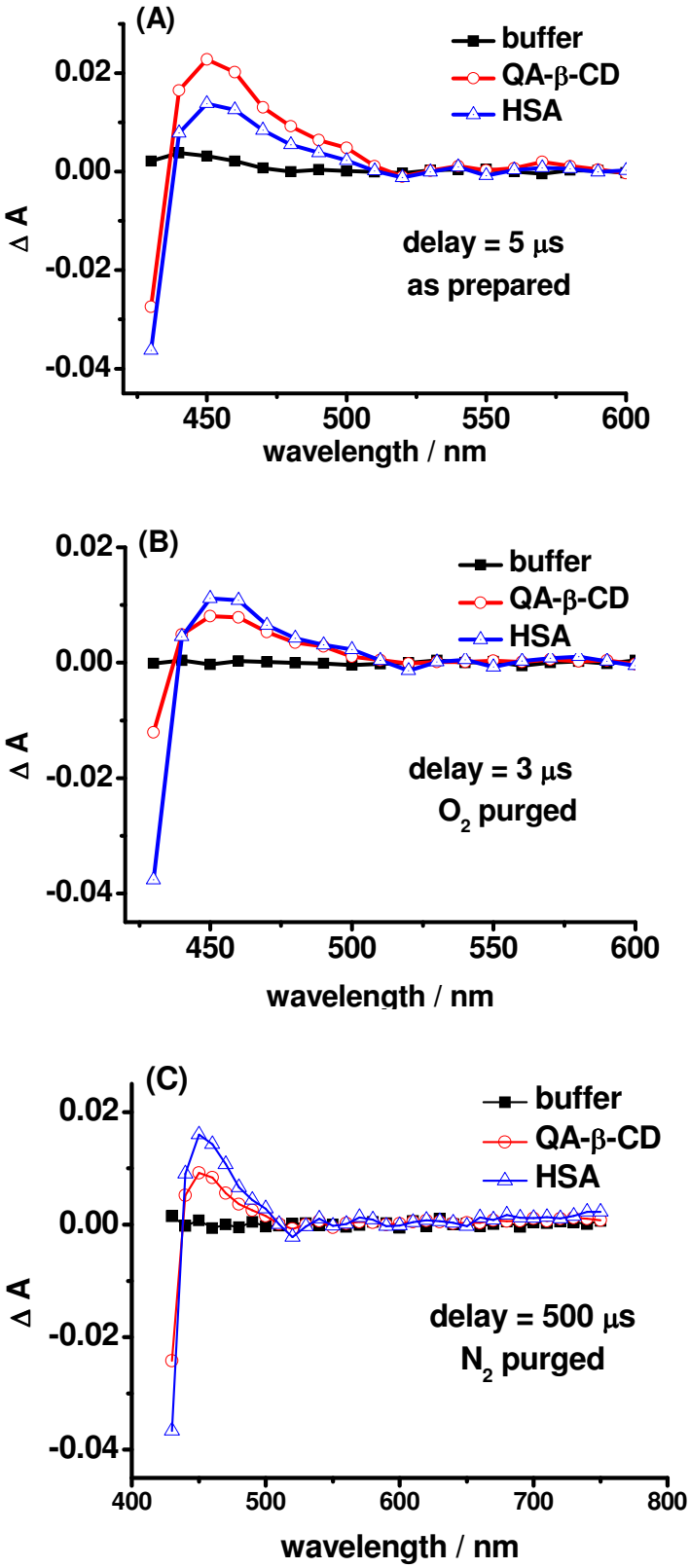

Figure S5. Transient uv-visible absorption spectra of TSPP in (□) buffer (pH=7), (O) in presence of 10 mM QA-β-CD, and (Δ) in 20 μM HSA under different concentrations of molecular oxygen: (A) as prepared (without purging N_2 or O_2) and recorded at 5 μs delay, (B) deoxygenated (purging with N_2) and recorded at

3 μs delay, and (C) saturated with molecular oxygen (purging with O_2) and recorded at 500 μs delay. The excitation wavelength was 415 nm.