
Supporting Information

Femto- to Micro-second Photobehavior of Photosensitizer

Drug Trapped within a Cyclodextrin Dimer

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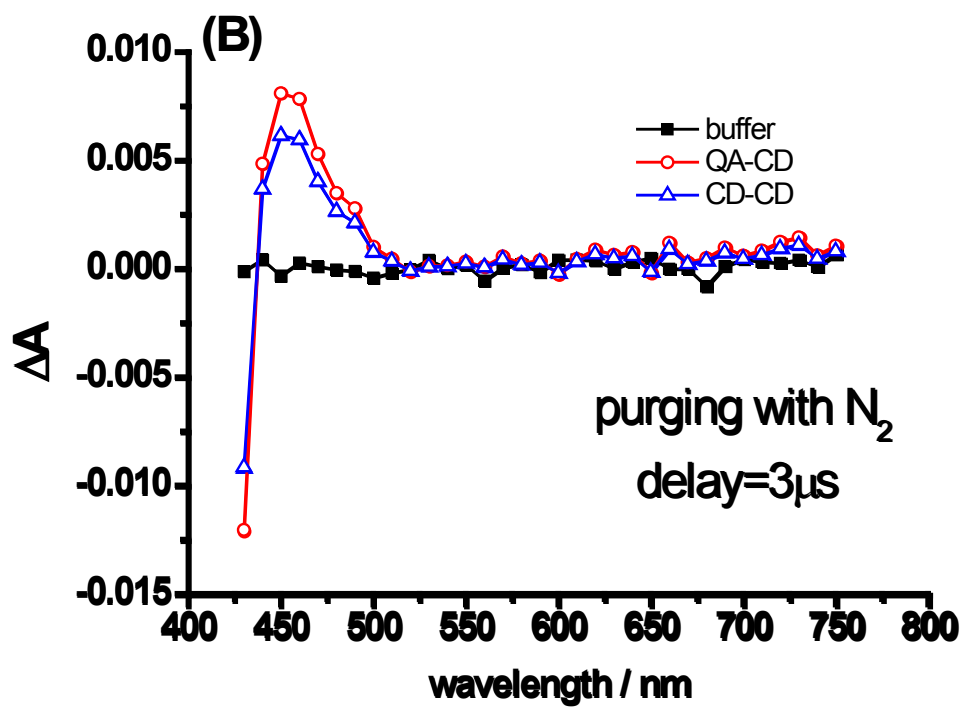
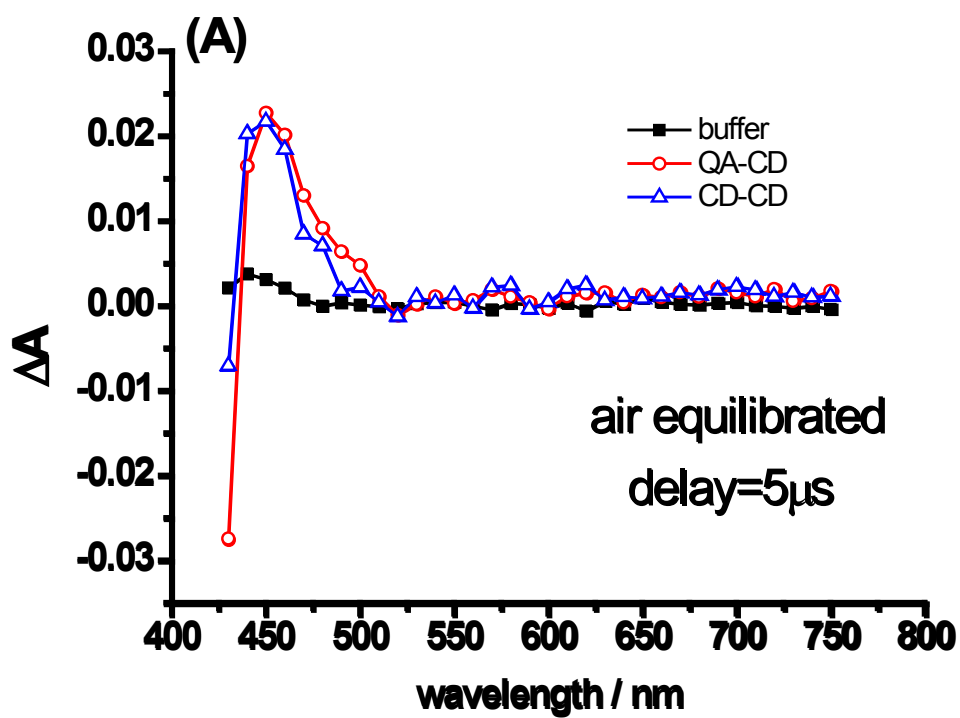
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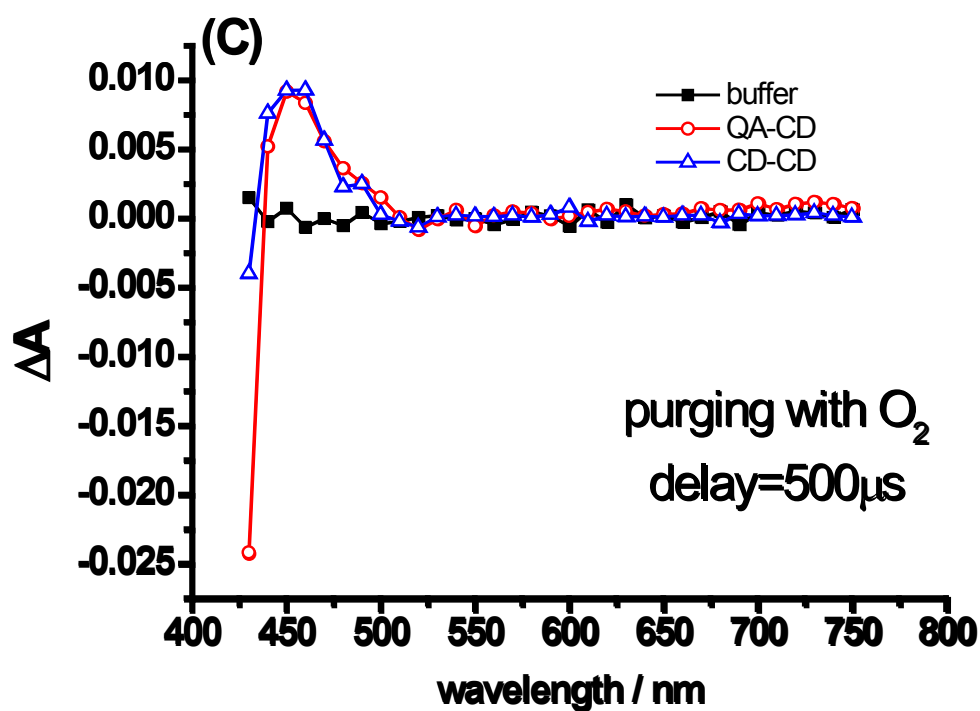


Figure S1. Transient uv-visible absorption spectra of TSPP in (■) buffer (pH=7), (○) in presence of 10 mM QA- β -CD^a, and (Δ) in 10 μ M CD-CD under different concentrations of molecular oxygen: (A) air equilibrated and recorded at 5 μ s delay, (B) deoxygenated (purging with N₂) and recorded at 3 μ s delay, and (C) saturated with molecular oxygen (purging with O₂) and recorded at 500 μ s delay. The excitation wavelength was 415 nm for TSPP in buffer and 420 nm for others. ^a From ref. 1

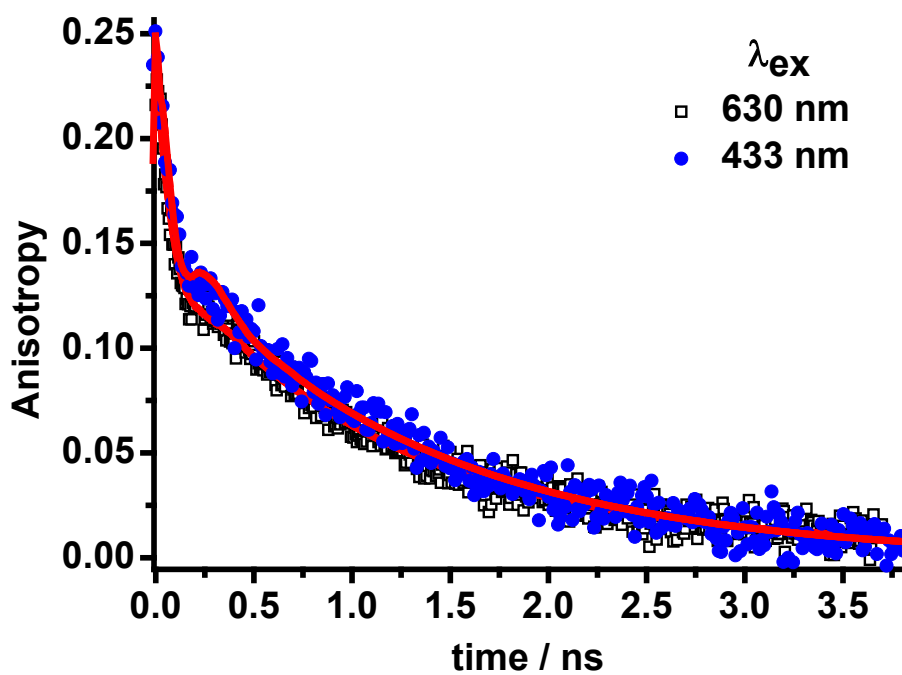


Figure S2. Emission anisotropy decays of TSPP in presence of 10 μM of CD-CD, excited at (\square) 433 and (\bullet) 630 nm, and collected at 650 nm. The solid lines represent the best fits using two-exponential function.

Binding constant determination

To determine the binding constant between TSPP, CD-CD, and the complexes, we used equations 1-7, which assume a 1:1 stoichiometry of the complexes. We took into consideration the fact that the host (CD-CD) is not in very large excess compared to the guest (TSPP). The equilibrium constant is expressed by the following equation:

$$K_e = \frac{[TSPP : CD - CD]}{[TSPP][CD - CD]} \quad (1)$$

The concentrations of free HPTS and HSA can be described by

$$[TSPP] = [TSPP]_T - [TSPP : CD - CD] \quad (2)$$

$$[CD - CD] = [CD - CD]_T - [TSPP : CD - CD] \quad (3)$$

where $[TSPP]_T$ and $[CD-CD]_T$ are the total concentrations of TSPP and CD-CD, respectively.

The concentration of the complex is given by

$$[TSPP : CD - CD] = \frac{1}{2} [([TSPP]_T + [CD - CD]_T + K_e^{-1}) \pm \sqrt{([TSPP]_T + [CD - CD]_T + K_e^{-1})^2 - 4[TSPP]_T[CD - CD]_T}] \quad (4)$$

The following equations relate the absorbance measurements of the bimolecular equilibrium:

$$\frac{\Delta A}{A_1 - A_0} = \frac{[TSPP : CD - CD]_i}{[TSPP : CD - CD]_s} = \frac{[TSPP : CD - CD]}{[TSPP]} \quad (5)$$

$$\Delta A = \frac{(A_1 - A_0) \times [TSPP : CD - CD]}{[TSPP]} \quad (6)$$

where ΔA is the absorbance change of HPTS produced by the binding of increasing quantities of CD-CD, A_0 is the absorbance of TSPP without CD-CD, A_1 is the absorbance of TSPP forming 1:1 complex with CD-CD. $[TSPP:CD-CD]_i$ is the concentration of the complex as varying quantities (i) of CD-CD are added to a constant amount of TSPP, and $[TSPP:CD-CD]_s$ is the concentration of the complex at saturation of HSA. Substituting eq 4 into eq 6 yields the final equation:

$$\Delta A = \frac{A_1 - A_0}{2 \times [TSPP]} \times \left[(K_e^{-1} + [TSPP] + [CD - CD]) - \sqrt{(K_e^{-1} + [TSPP] + [CD - CD])^2 - 4 \times [TSPP] \times [CD - CD]} \right] \quad (7)$$