Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

SUPPORTING INFORMATION

Unexpected solvent isotope effect on the triplet lifetime of Methylene Blue associated to Cucurbit[7]uril

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Experimental details

Materials

Methylene blue (MB) as chloride salt (>99%), curcubituril[7] (CB7) and deuterium oxide (D_2O>99.99%) were purchased from Sigma-Aldrich. Aqueous solutions were freshly prepared by using 0.22μm filtered Milli-Q water (18.2 MΩ·cm) previously treated for 24 hours with Chelex-100 in order to remove any metal traces.

Absorption and fluorescence measurements

Absorption spectra were recorded using a Cary-100 UV-Visible spectrophotometer. Steady-state fluorescence spectra were measured on a Photon Technology International (PTI) spectrofluorometer. Fluorescence quantum yields were calculated as we previously reported (E. Alarcón, A. M. Edwards, A. Aspée, D. Gonzalez-Nilo, F. E. Moran, C. D. Borsarelli, E. A. Lissi, H. Poblete and J. C. Scaiano, *Photochem. Photobiol. Sci.*, 2010, 9, 93-102). In all cases the absorbance of the samples at the excitation wavelength was maintained lower than 0.2.

Laser flash photolysis measurements

Methylene blue triplet transient absorption measurements were carried out in a LFP 111 laser-flash photolysis system (Luzchem Research Inc., Ottawa, Canada) by using a Surlite OPO Plus (pump with a Nd-YAG 355 nm) at 650 nm and 3.0 mJ/pulse in 1.0 cm path-length fussed silica cuvettes. Methylene blue triplet quantum yields in different media were calculated as follows:

$$\Phi_{T,sample} = \Phi_{MB\_Water} \frac{\left(\frac{\Delta OD_{sample}}{A_{Laser,sample}}\right)}{\left(\frac{\Delta OD_{MB\_Water}}{A_{MB\_Water}}\right)} \qquad \textbf{(1)}$$

In this equation, $\Phi_{T,Sample}$ corresponds to the triplet quantum yield of the sample, $\Phi_{T\ MB\_water}$ is the triplet quantum yield of MB in water equal to 0.55 (S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Mercel Decker Inc, New York, 1993). ΔOD_{Sample} and

ΔOD_{MB_water} are the initial optical density at time zero for the sample and the standard MB. Finally, the $A_{Laser,\ Sample}$ and $A_{\ MB\_water}$ are the corresponding absorbances at the excitation wavelength (650 nm). Laser flash photolysis measurements at different temperatures were carried out in a home made adapted temperature control system with an accuracy of ± 0.5°C in degassed aqueous solutions. Sample degassing was carried out by using 99.99% pure N_2 where 2 mL of each solution was purged for 40 min. In control experiments no further changes in MB triplet lifetime were observed after 25 min nitrogen bubbling, using a 10 cm 18G steel needle coupled to a teflon tubing 0.5 mm (*Note; only the teflon tubing was in contact with the solution*), however in order to remove any remaining O_2 traces 40 min as purging time was chosen. For all the samples measured here exactly the same setup was employed.

Computational simulation

Molecular simulations were carried out by using Hyperchem 7, this software provides four force fields (MM+, AMBER, BIO+ and OPLS) and allows to perform molecular mechanics calculations that use three components: equations that define the potential energy of a molecular system as a function of the atomic coordinates, atom types and parameter sets that fit the equations to experimental data. Between them, MM+ is considered the most general force field method developed principally for organic molecules as an extension of MM2 due to Hyperchem 7 assigns atom types and parameters not normally available to MM2 users, extending the range of chemical compounds that this force field can accommodate. MM+ also provides cutoffs for non-bounded interactions, solvation, constraints and molecular dynamics not normally associated with MM2 calculations. Calculations were carried out assuming a geometrical optimization of a supramolecular complex with a methylene blue molecule inside CB7 cavity surrounded by a periodic box, a rectangular box surrounding a molecular system, full of solvent molecules (water or deuterium oxide). Hyperchem 7 can add standard water molecules equilibrated at 300 K one atmosphere to the box, providing a constant-density solvent that simulates a constant density of molecules. All solvent molecules experience the same forces due to all of their atoms exhibit the same motions. Periodic boundary conditions are effective only

during molecular mechanics calculations, not during quantum-mechanics calculations. Using these conditions, we have optimized the geometry of the system using Polak-Ribiere algorithm in which termination conditions are when RMS gradient is of 0.1 kcal/Å mol in a periodic box of 27 Å3 with 651 solvent molecules with a minimum distance between solvent and solute atoms of 1.5 Å.

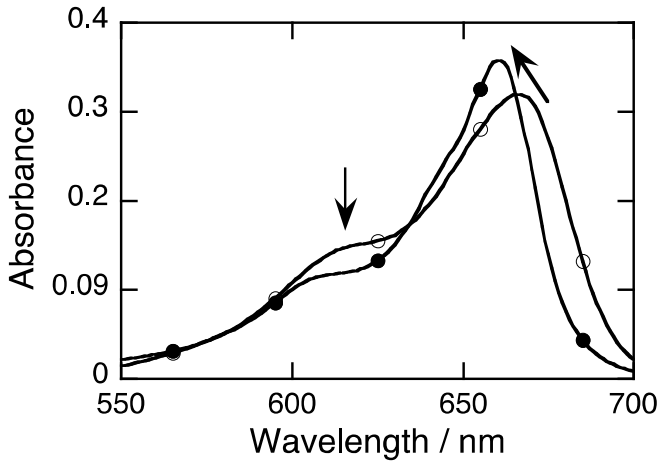

Figure S1. Absorption spectra of methylene blue 5 μM in the presence (●) or absence (○) of CB7 0.1 mM. All measurements were carried out in D_2O/N_2 saturated solutions.

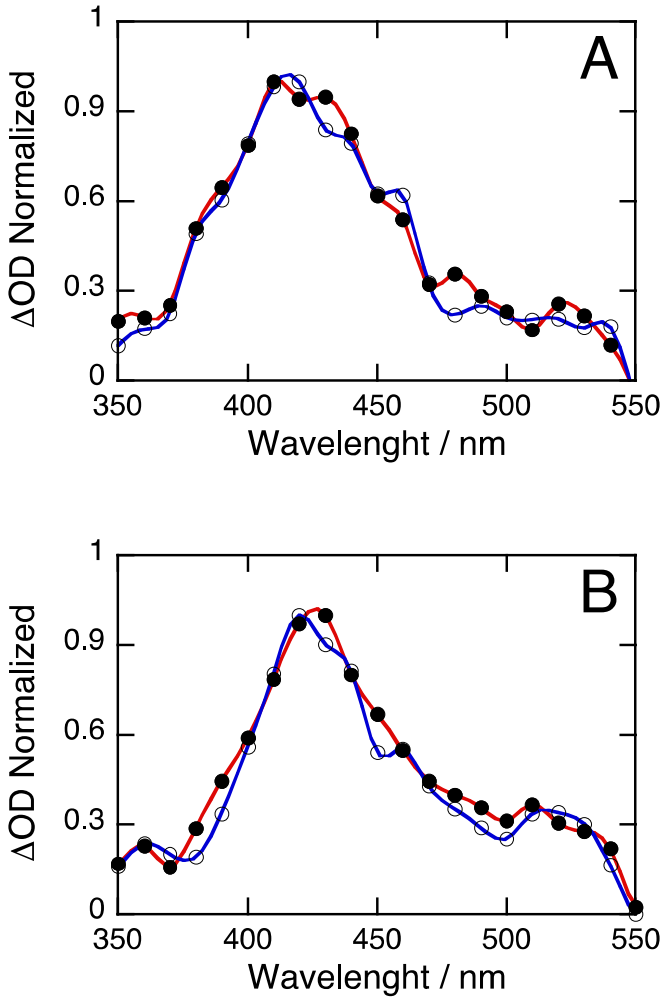

Figure S2. Methylene blue triplet transient absorption spectra 10 μs after 650 nm laser excitation obtained in the absence (A) or in the presence of 0.1 mM CB7 (B) measured in D_2O (○) or water (●). All the measurements were carried out in N_2 saturated solutions at 22°C.

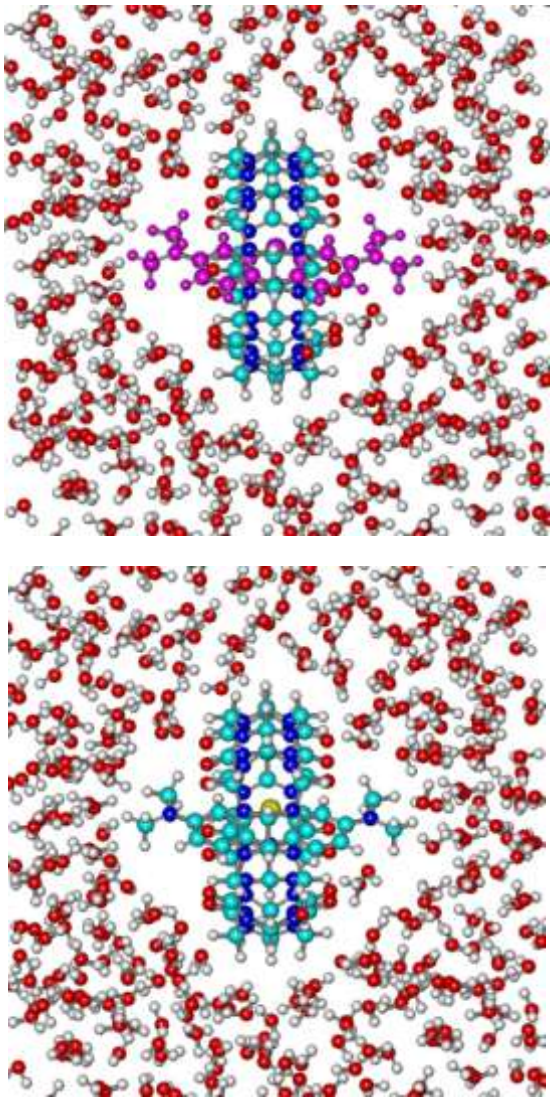

Figure S3. Selected images for MB@CB7 complex computational simulation solvent disposition around the complex for water (top) or D_2O (bottom).

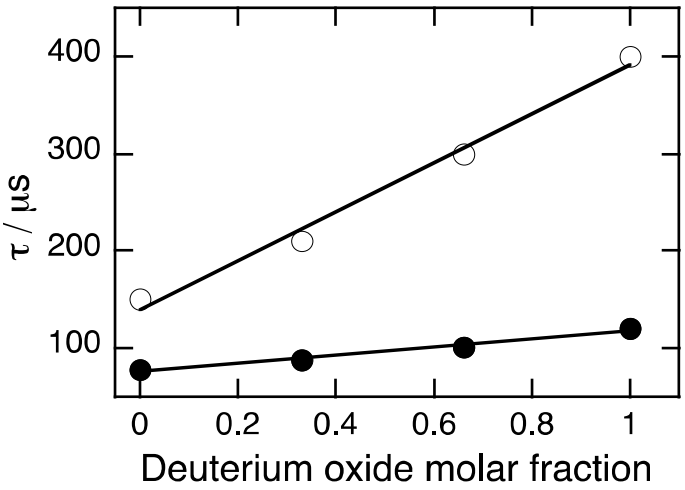

Figure S4. Methylene blue triplet lifetime measured at 420 nm as a function of deuterium oxide concentration in the absence (●) or in presence of 0.1 mM CB7 (○). All measurements were carried out in N_2 saturated solutions at 22°C of a 5.0 μM solution, experimental error was < 10%.