Electronic Supplementary Information (17 pages)

Supramolecular photocatalysis: insights into cucurbit[8]uril catalyzed photodimerization of 6-methylcoumarin

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1. General methods

6-Methylcoumarin 1 was purchased from Alfa Aesar[®] and was used as received without further purification. Cucurbit[8]uril (CB8) was synthesized using previously reported procedures.¹⁻⁵ Nanopure water ($\geq 17.8 \text{ M}\Omega \cdot \text{cm}$) was used as the solvent for carrying out photoreactions and photophysical measurements. All organic solvents were used as is without further purification. Stock solution $(1 \times 10^{-4} \text{ M})$ of CB8 was prepared in a 1000 mL volumetric flask. Stock solution $(1 \times 10^{-3} \text{ M})$ of 1 was prepared in a separate 500 mL volumetric flask. Solutions for MS and LC-MS studies were prepared by using 100 μ M 1@CB8 complexes with 0.1% HBr. Irradiation of MS and LC-MS samples was done with a home-made xenon lamp and were irradiated for 4 h (> 90% conversion) and the emission was cutoff below 300 nm and in NIR region by using a glass/water filter. Absorbance measurements were performed using Shimadzu UV-2501PC UV-Vis spectrophotometer. Fluorescence measurements were performed using a Horbia Jobin-Yvon Fluorolog-3. The stopped flow experiments were performed using an Applied Photophysics SX-18MV stopped-flow system. The stopped-flow system (dead time = 1.3 ms) was operated in the fluorescence mode with an emission path length of 2 mm. The time-dependent changes in 1 fluorescence was monitored by exciting the reaction at 325 nm, and the emission intensity was detected after passing the light through a 395 nm high-pass cut-off filter. All stopped flow kinetic experiments were performed at least five times and the resultant kinetic traces were analyzed by the data analysis package provided by Applied Photophysics. ESI-MS measurements were performed with a Bruker Daltonics HCT ultra mass spectrometer (ion trap), equipped with a ESI source (Agilent) that utilized a nickel-coated glass capillary with an inner diameter of 0.6 mm. Ions were continuously generated by infusing the aqueous solution samples into the source with a syringe pump (KdScientific, model 781100, USA). LC-MS separations The LC-MS system is an Agilent Technologies 1200 Series LC, equipped with a photodiode array detector, coupled to a Bruker Daltonics HCT *ultra* (ion trap). Laser flash photolysis experiments employed the pulses from a Lambda Physik Excimer laser (CompEX 100) 308 nm pulse length 15 ns) and a computer-controlled system that has been described elsewhere.⁶ To determine oxygen quenching rate constants, aqueous solutions were saturated with gas mixtures with different O_2/N_2 ratios.

2. Single crystal X-ray

2a. Structure determination

Single crystal X-ray diffraction data of the compound was collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at T = 100 K. Cu radiation was used. The structure was processed with Apex 2 v2010.9-1 software package (SAINT v. 7.68A, XSHELL v. 6.3.1). Direct method was used to solve the structures after multiscan absorption corrections. Details of data collection and refinement are given Table S1. All non-hydrogen atoms of the main molecules, which are subject of interest of this paper, are refined anisotropically. All H-atoms are generated by HFIX. In addition to the host and the two guests, we observed 54 molecules of water per cell. H-atoms of all water molecules are not located or generated.

2b. Host-guest crystal formation

Crystals of the host-guest complex of 1@CB8 was grown by taking a concentrated aqueous solution of 1 (1.0 x 10^{-3} M) and layering with a concentrated solution of CB8 (1.0 x 10^{-4} M) in equal volumes.

	12@CB8
Formula	$C_{48}H_{48}O_{16}N_{32} \cdot 2xC_{10}H_8O_2 \cdot 13.5H_2O$
FW	1892.78
cryst. size [mm]	.15 x .18 x .20
cryst. system	Orthorhombic
Space Group, Z	Pbca, 4
a [Å]	16.4918(3)
b [Å]	22.0793(4)
c [Å]	22.2875(4)
α[Å]	90
β [Å]	90
γ [Å]	90
V [Å ³]	8115.5(3)
$\rho_{calc} [g/cm^3]$	$1.527 (1.549)^{a}$
$\mu [cm^{-1}]$	1.078
F(000)	3856
no of measured refl.	44959
no of indep. refl.	6974
no of refl. (I $\ge 2\sigma$)	6587
R _{int} [%]	2.46
Resolution [Å]	.84
$R1/wR2 (I \ge 2\sigma)^{b} [\%]$	7.05/19.66
R1/wR2 (all data) [%]	7.70/20.84

 Table S1: Single crystal collection and refinement parameters.

[a] The density value of 1.549 was calculated by taking into account all the non-localized hydrogen atoms in the water molecules. For density value of 1.527, non-localized hydrogen atoms in the water molecules were not taken into account.

$$[\mathbf{b}] R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, wR2 = \{ [\Sigma[(F_0)^2 - (F_c)^2]^2] / [\Sigma w(F_0^2)^2] \}^{1/2} \text{ for } F_0^2 > 2\sigma(F_0^2), w = [\sigma^2(F_0^2)^2 + (AP)^2 + BP]^{-1} \text{ where } P = [(F_0)^2 + 2(F_c)^2] / 3; A (B) = 0.1168 (18.2196) \}$$

3. Stopped flow kinetics

The initial concentration and final concentration of CB8 for all experiments are 2.0 μ M and 1.0 μ M respectively. The excitation wavelength 325 nm and emission was monitored >395 nm. The initial and final concentration of **1** for all experiments was 1.0 mM and 0.5 mM respectively.

3a. Stopped flow experiment for the formation of CB8 and 1 HG complex from free CB8 in aqueous solution.

Stock solutions of CB8 and **1** were mixed and monitored at both short time scales (Fig. S1; A) and at long time scales (Fig. S1; B).



Figure S1. Stopped flow experiment to ascertain the rate constant for the formation of 1:1 CB8:1 complex (A) and 1:2 CB8:1 complex (B) from free CB8 in aqueous solution.

3b. Stopped flow experiment for the formation of CB8 and 1 HG complex from CB8-*syn*photodimer HG complex in aqueous solution.

The CB8-*syn*photodimer HG complex was prepared by irradiating CB8 [20 μ M] in the presence of **1** [40 μ M] at a 1:2 HG ratio using a Pyrex cutoff (>295 nm) for 3 h. The formation of the photoproduct was ascertained by UV-Vis spectroscopy (monitoring the absorbance decrease at 340 nm; *cf.* Fig. S4). This solution was employed with appropriate concentration of CB8 for the stopped flow kinetic experiments at both short (Fig. S3; A) and long (Fig. S3; B) time scales.



Figure S2. Stopped flow experiment to ascertain the rate constant for the formation of 1:1 CB8:1 complex (A) and 1:2 CB8:1 complex (B) from CB8-*syn*photodimer HG complex in aqueous solution.

4. LC-MS procedure

The LC–MS system is an Agilent Technologies 1200 Series LC, equipped with a photodiode array detector, coupled to a Bruker Daltonics HCT *ultra* (ion trap). The ESI-MS parameters were the following: ionization in the positive polarity; capillary voltage -4.0 kV; nebulizer gas pressure 60 psi; drying gas flow 12 L/min; drying gas temperature 300 °C; capillary exit voltage = 210 V; skimmer voltage: 57.5 V. A Purospher STAR (Merck) LiChroCART 125-2 (12.5cm length, 2 mm internal diameter, RP-18, 5 µm) column stabilized at 30 °C was used. The flow was 0.4 mL/min. The mobile phase consisted in water and acetonitrile, both with 0.1% of formic acid. The eluent composition started with 20%-80% acetonitrile-water for 2 minutes, then changed to 80%-20% acetonitrile-water until 10 minutes, then kept constant for 4 minutes and finally changed to 100% of acetonitrile to clean the column. Non-irradiated and irradiated aqueous solutions containing ~ 100 μ M 1@CB8 complexes and 0.01 % of HBr. The irradiation was done using a home-made xenon lamp. The solutions were place in quartz cells at 10 cm from the lamp surface. The emission below 300 nm and in the NIR region was filtered by placing in between a glass / water filter 4 h irradiation lead to conversions higher than 90%



Figure S3. A) LC-MS trace of an irradiated aqueous solution of 1@CB8 with 0.01 % of HBr (> 90% conversion). Assignments: m/z 321: [Syn-PD + H]⁺; 161: $[1 + H]^+$; 665: $[CB8 + 2•H]^{2+}$.



Figure S4. UV absorption spectra of 1 and the syn-photodimers from LC.

5. Ion-trap ESI-MS studies mass spectrometry studies.

The mass spectrometric experiments were performed with a Bruker Daltonics HCT *ultra* mass spectrometer (ion trap), equipped with a ESI source (Agilent) that utilized a nickelcoated glass capillary with an inner diameter of 0.6 mm. Ions were continuously generated by infusing the aqueous solution samples into the source with a syringe pump (KdScientific, model 781100, USA) at flow rates of 4 μ L/min. The parameters were adjusted and are typically as follows: polarity: positive; capillary voltage: - 4.0 kV; capillary exit voltage: CE = 70 V; skimmer voltage: 25 V; temperature of drying gas: 300 °C. The experiments were carried out with a nebulizer gas pressure of 20 psi and a drying gas flow of 6 L/min. Non-irradiated and irradiated aqueous solutions containing ~ 100 μ M 1@CB8 complexes and 0.01 % of HBr. The irradiation was done using a home-made xenon lamp. The solutions were place in quartz cells at 10 cm from the lamp surface. The emission below 300 nm and in the NIR region was filtered by placing in between a glass / water filter respectively. Irradiation for 4 h led to conversions higher than 90% (based on UV-Vis).



Figure S5. Fragmentation of m/z 825 (1:2 complex). Assignments: m/z 825: $[CB8 + 2\cdot 1 + 2\cdot H]^{2+}$; 745: $[CB8 + 1 + 2\cdot H]^{2+}$ (1:1 complex); 665: $[CB8 + 2\cdot H]^{2+}$ (empty host). The fragmentation of the 1:2 (m/z 825) complex leads mainly to the loss of one guest and consequent formation of the 1:1 complex (m/z 745).



Figure S6. Fragmentation of m/z 745 (1:1 complex). Assignments: m/z 745: $[CB8 + 1 + 2 \cdot H]^{2+}$; 665: $[CB8 + 2 \cdot H]^{2+}$. The fragmentation of the 1:1 complex (m/z 745) leads to the loss of the guest and consequent formation of the empty host (m/z 665).



Figure S7. Fragmentation spectrum of the *syn*-photodimer (m/z 321). The arrow indicates the fragmented peak.



Figure S8. ESI-MS spectrum (full scan) of an irradiated aqueous solution of 1@CB8 with HBr 0.01% (> 90% conversion). Assignments: m/z 161 $[1 + H]^+$; 665 $[CB8 + 2 \cdot H]^{2+}$; 834 $[CB8 (H_2O) + syn$ -photodimer + $2 \cdot H]^{2+}$.



Figure S9. Consecutive fragmentations of m/z 834 (*syn*-photodimer@CB8, 1:1) A) MS^2 834; B) MS^3 , 834 \rightarrow 674. The fragmented peak at 834 (A) leads to the mass peaks in (B). Assignments: m/z 665 [CB8 + 2•H]²⁺; 674 [CB8 (H₂O) + 2•H]²⁺; 834 [CB8 (H₂O) + *syn*-photodimer + 2•H]²⁺. The loss of the *syn*-photodimer and the loss of a water molecule by m/z 674 confirms the assignment.

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6. Triplet-triplet absorbance



Figure S10. Transient absorption spectrum of 1@CB8 (50% CB8) recorded $0.4 - 4 \mu s$ after the laser pulse (308 nm, pulse width 15 ns). Deoxygenated aqueous solutions; [1] = 50 μ M; [CB8] = 25 μ M. The transient absorption was assigned to the triplet state of 1 based on similarities with previously published spectra of ³(1)*.⁷



Figure S11. Transient absorption decay traces recorded at 420 nm of ${}^{3}(1)$ * in the absence and presence of different amounts of CB8. The decay traces in the absence and 190% CB8 fitted to a monoexponential function with lifetimes of 4.6 µs and 0.74 µs, respectively. The decay trace at 40% CB8 fitted best to a biexponential function with lifetimes of 10 µs and 0.74 µs.



Figure S12. First order decay rate constants of triplet-triplet absorption generated by pulsed laser excitation (308 nm) of deoxygenated aqueous solutions of 1 monitored at 420 nm of 1 vs. the concentration of 1. The slope of this plot gives the bimolecular self-quenching rate constant of ${}^{3}(1)$ * by 1.



Figure S13. First order decay rate constants of triplet-triplet absorption generated by pulsed laser excitation (308 nm) of aqueous solutions of **1** in the absence (red) and presence (blue) of CB8 (190 mol%) monitored at 420 nm of **1** vs. the concentration of dissolved oxygen. The slopes of this plots give the bimolecular quenching rate constant of ${}^{3}(1)^{*}$ by oxygen. While ${}^{3}(1)^{*}$ is quenched in pure aqueous solutions with a rate constant close to the diffusion limit, only minor quenching of ${}^{3}(1)^{*}$ is observed in 1:1 guest host complexes of **1**@CB8 due to shielding by the host.

References:

- A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, 66, 8094.
- 2. A. I. Day, A. P. Arnold and R. J. Blanch, *Molecules*, 2003, **8**, 74.
- 3. J. Lagona, J. C. Fettinger and L. Isaacs, J. Org. Chem., 2005, 70, 10381.
- 4. J. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem., Int. Ed.*, 2005, **44**, 4844.
- 5. W. Ong, M. G.-. Kaifer and A. E. Kaifer, Org. Lett., 2002, 4, 1791.
- 6. Y. Yagci, S. Jockusch, N.J. Turro, *Macromolecules*, 2007, 40, 4481.
- 7. T. Wolff and H. Gorner, *Phys. Chem. Chem. Phys.*, 2004, 6, 368.