

Electronic Supplementary Information for

Photo-Triggered J-Aggregation and Chiral Symmetry Breaking of an Anionic Porphyrin (TPPS) in Mixed Organic Solvent

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Experimental

Meso-tetrakis-(4-sulfonatophenyl) porphyrin (TPPS) was purchased from Dojindo Laboratories. D-, L-lysine was obtained from Aldrich and used without purification. Ethanol was purchased from Beijing chemical plant and redistilled before used. Certified A. C. S. grade DMSO was purchased from Fisher Scientific and used without further purification. TPPS solution was prepared by dissolving the tetrasodium salt into DMSO or ethanol. UV-Vis spectra were recorded on a JASCO V-530, CD spectra on a JASCO J-810. RLS measurements were carried out on a Hitachi F-4500 fluorescence spectrometer. An Ultraviolet (UV) lamp (254nm 20w) was used for irradiation. The distance between the center of the cell and the lamp was 25 cm. In investigating the effect of L-lysine and D-lysine, a 0.1 mM lysine was added onto the solution and all the experiments were performed as in the case of lysine-free solution. A Gas chromatography equipped with a mass spectrometry (QP2010, SHIMADZU) was used for the analysis of the mixed solvents of DMSO and EtOH before and after the

irradiation. The GC-MS conditions were as follows: a HP-5ms capillary column of 30m×0.32mm with helium carrier gas at 0.9 mL min⁻¹(constant flow) was used for all analyses. Injection (1μL) was at split ratio 4:1 at 250 °C. Oven temperature program, 50°C for 2min, then a 15 °C/min ramp to 250 °C (held for 20 min); MS ion trap temperature 250 °C; data acquisition in full scan mode (*m/z* 20-650).

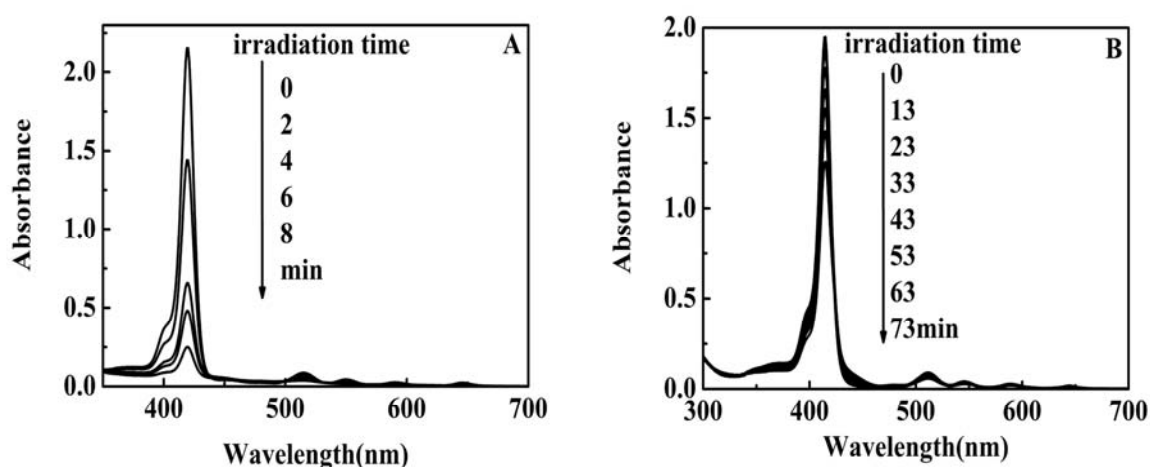


Figure S1. The photobleach process of TPPS in (A) DMSO and (B) ethanol solution under UV irradiation (20 W, 25 cm from the solution).

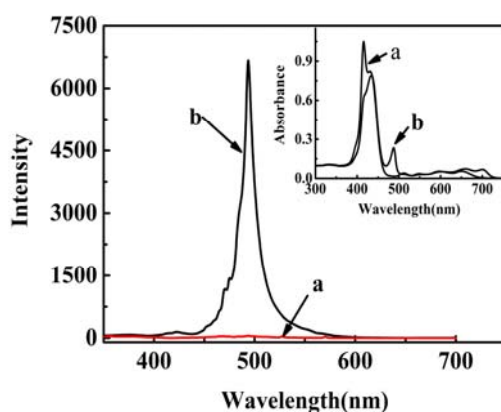


Figure S2. RLS spectra of TPPS in the mixed solution of ethanol and DMSO under ultraviolet irradiation. (a) before and (b) after the formation of J-aggregate. Inset: the corresponding UV-Vis spectra.

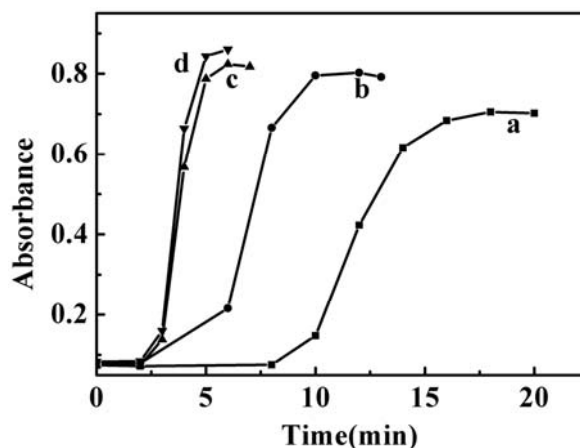


Figure S3 The absorbance at 431 nm as a function of irradiation time with the solution containing various amount of DMSO. 15 μ l (a); 30 μ L (b); 45 μ L (c); 60 μ L (d) in 3ml 4.2×10^{-6} M TPPS ethanol solution.

Mechanism of the protonation of TPPS in DMSO/EtOH mixture

The mixed solvents of DMSO/EtOH after photo-irradiation were measured by gas chromatograph, as shown in Figure S4. Two new peaks appeared in GC/MS spectra, besides the peak of DMSO (3.119 min.). The first peak is at 3.860min, while the second peak is at 3.960min. Coupled with the mass spectra, the first peak corresponds to acetaldehyde diethylacetal and the second peak corresponds to methanesulfonic acid ethyl ester.

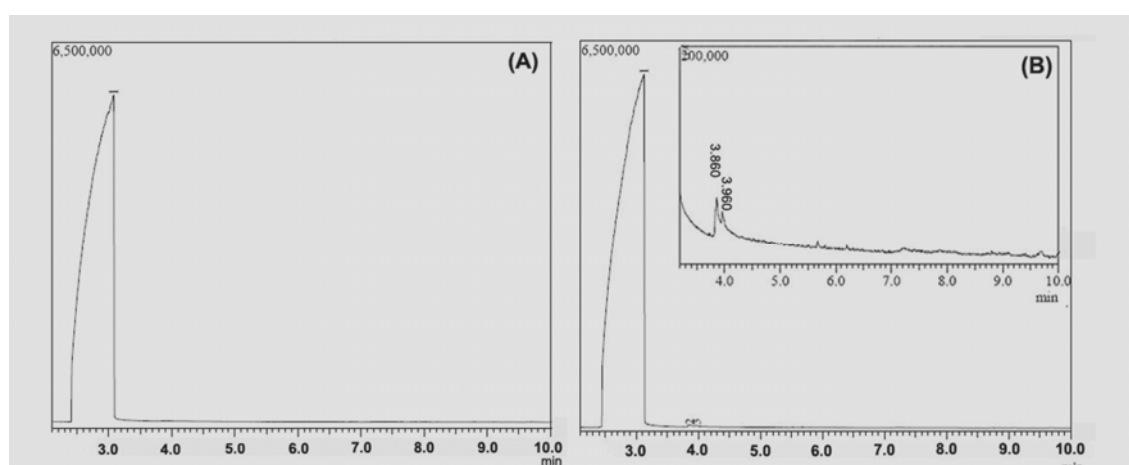
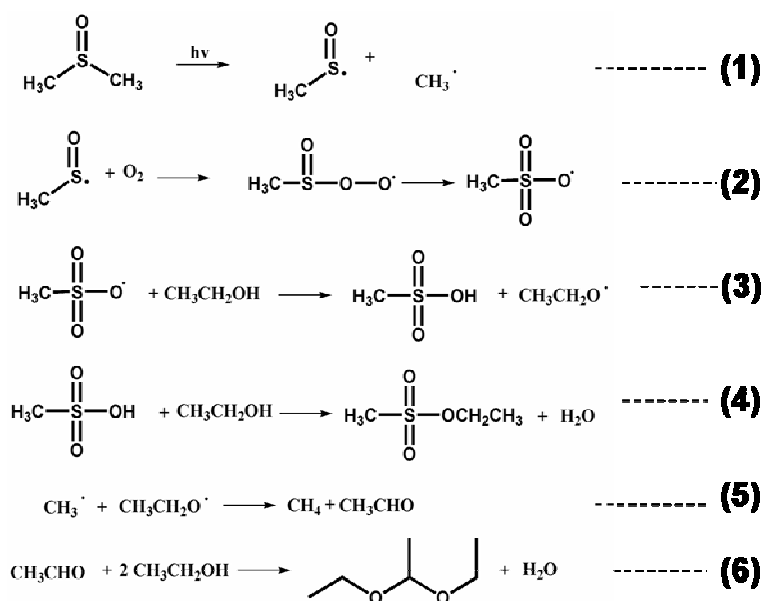


Figure S4. The gas chromatogram of mixture of DMSO and ethanol before (A) and after UV irradiation (B). The inset shows GC spectra from 3.3min to 10min.

As shown in figure S4, methanesulfonic acid ethyl ester was directly detected after irradiation. We suggest that the methanesulfonic acid ethyl ester came from the methanesulfonic acid and ethanol. It has been reported that DMSO experienced the photolysis through the homolytic cleavage of C-S bond with the formation of a CH_3SO and a CH_3 radical.¹ The CH_3SO radical can form methanesulfonic acid through a radical reaction in the presence of ethanol and oxygen, as noted below.



Scheme S1. Possible formation process of methanesulfonic acid ethyl ester through a radical reaction in the DMSO/EtOH mixture after photoirradiation.

In this process, ethanol acted as a donor of hydrogen and oxygen acted as capture agent of electron. Such mechanism was supported by the fact that protonation of TPPS could not happen if O_2 was removed by bubbling Ar gas.

Second, we did the parallel experiments with mixed $\text{DMSO-D}_6/\text{CD}_3\text{OD}$ and $\text{DMSO-D}_6/\text{CD}_3\text{OH}$ mixture in the same condition. It was found that while similar J-aggregation of TPPS could proceed in $\text{DMSO-D}_6/\text{CD}_3\text{OH}$, no J-aggregation could occur in $\text{DMSO-D}_6/\text{CD}_3\text{OD}$ mixture. This indicated that the proton in the system was abstracted from the OH of the alcohol.

1. a) Y. S. Guo and W. S. Jenks, *J. Org. Chem.* 1995, **60**, 5480. (b) M. H. Chen, R. J. Yang, R. H. Ma and M. F. Zhou *J. Phys. Chem. A*, 2008, **112**, 7157.