

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Delocalized triplet state in porphyrin J-aggregates revealed by EPR spectroscopy

Luca Bolzonello, Marco Albertini, Elisabetta Collini, and Marilena Di Valentin\*

Department of Chemical Sciences, University of Padova, Via Marzolo 1, 31531 Padova, Italy

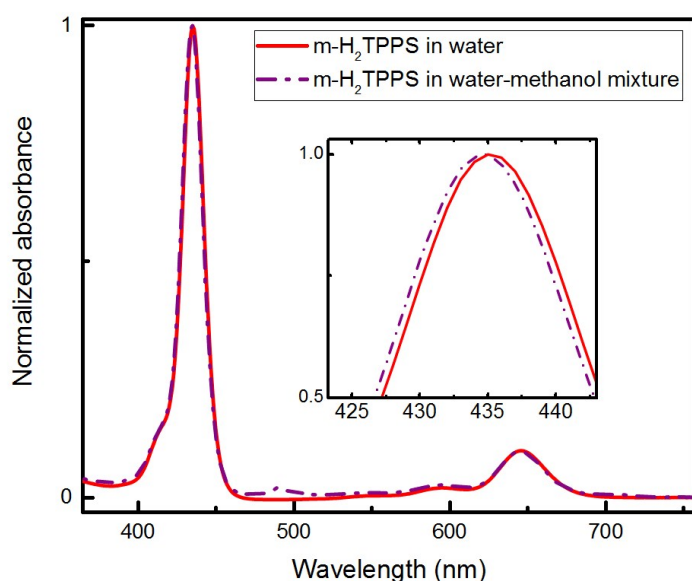
#### Experimental procedures

##### *Sample preparation*

5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) was purchased from Sigma Aldrich and used without further purification. All the TPPS solutions used for spectroscopic characterization were freshly prepared dissolving the TPPS powder in the solvent before the characterization. The concentration of the solutions has been determined by optical absorption spectroscopy and has a final value of about 60  $\mu\text{M}$ .

Solutions of free-base monomeric TPPS (m-TPPS) have been obtained by dissolving TPPS powder in a mixture of water and methanol 1:1. Acidified monomeric TPPS (m-H<sub>2</sub>TPPS) solutions have been prepared starting from the neutral TPPS solution in water:methanol 1:1 previously prepared by adding concentrated H<sub>2</sub>SO<sub>4</sub> to a final concentration of ca. 0.1 M (pH=1). J-aggregates of the acidified form of TPPS (a-H<sub>2</sub>TPPS) have been prepared by dissolving TPPS powder in water and again by adding concentrated H<sub>2</sub>SO<sub>4</sub> to a final concentration of ca. 0.1 M (pH=1). The optical properties of a-H<sub>2</sub>TPPS aggregates are typically described using an ideal model of a linear homogeneous aggregate of N monomers with nearest-neighbour coupling only. The macroscopic geometry is thus not significant for this study.

The choice of using a mixture of water and methanol for the monomeric samples has two important advantages: the formation of the aggregate is strongly inhibited and this mixture is known to generate better glass when frozen. This allowed obtaining solutions of the m-H<sub>2</sub>TPPS species concentrated enough to generate an EPR signal with a significant signal-to-noise ratio. On the other hand, a-H<sub>2</sub>TPPS solutions have been prepared in water at higher acid concentration as this experimental condition is known to strongly drive fast and complete aggregation [1]. Absorption spectra of m-TPPS and m-H<sub>2</sub>TPPS do not show any relevant difference when dissolved in water and in the water/methanol mixture meaning that the different solvents do not induce any relevant change in the electronic properties of the molecules. Finally, a water solution containing a mixture of monomeric and aggregated H<sub>2</sub>TPPS was prepared at higher pH value (ca 4) and freezing the solution before complete aggregation took place.



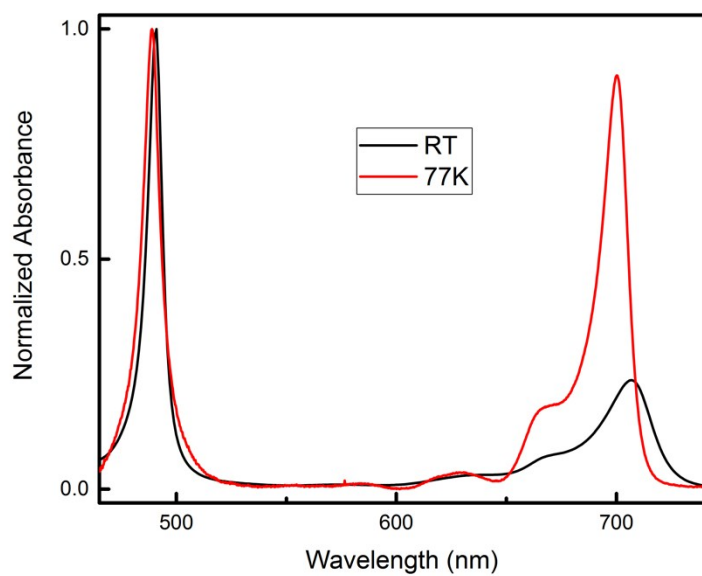
**Figure S1.** Normalized absorption spectra of m-H<sub>2</sub>TPPS (30 μM) in water (red solid line) and water/methanol 1:1 mixture (dashed purple line). The maxima are shifted less than 1 nm (inset). In the water solution a weak peak at 490 nm is recorded, due to the initial aggregate formation.

Since EPR measurements had to be performed at liquid nitrogen temperature, we collected absorption spectra at 77 K. The results are shown in figure S2. It is possible to notice that the 490 nm peak does not shift at low temperatures allowing us to selectively excite aggregates in mixture sample.

Samples for EPR were degassed by freeze and thaw cycles, inserted into 2.4x4 mm quartz EPR tubes, sealed under vacuum and immediately frozen in liquid nitrogen. Samples were stored in liquid nitrogen until measurements.

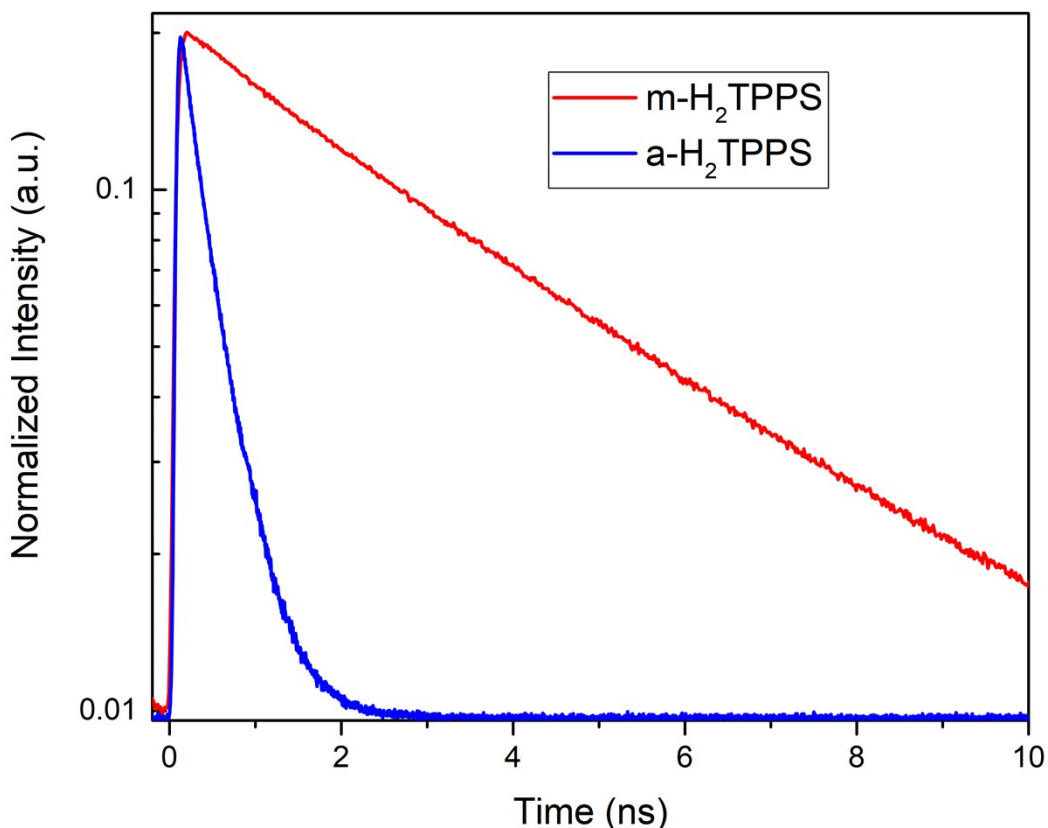
### ***Optical spectroscopy.***

Absorption UV-Vis spectra have been acquired on a Varian Cary 5 spectrophotometer. The sample was held in 1 mm thick quartz cuvettes. The concentration of m-TPPS solutions has been calculated from the maximum of the absorption bands at 413 nm (molar absorptivity,  $\epsilon=4.3 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ ). The concentration of m-H<sub>2</sub>TPPS and a-H<sub>2</sub>TPPS solutions has been estimated taking into account the initial m-TPPS solution and the subsequent dilutions. Because EPR measurements are performed at liquid nitrogen temperature, we collect absorption spectra at low temperature thanks to an oxford instruments cryostat (fig S2). The B band is actually not shifted in wavelength and this allows us using the OPO for the EPR experiment in the mixed sample.



**Figure S2.** Normalized absorption spectra of a-H<sub>2</sub>TPPS (30  $\mu$ M) in water at room temperature (black line) and 77 K (red line). In the 77 K measurements the peaks become generally narrower but the B band at 490 nm remains almost unaffected by the low temperature and the shift in wavelength is negligible.

Lifetimes of the first excited state were recorded with the setup described in [2].



**Figure S3.** Fluorescence lifetime traces of m-H<sub>2</sub>TPPS (red) and a-H<sub>2</sub>TPPS (blue) at room temperature. Time constants are about 3.6 and 0.3 ns, respectively.

### EPR spectroscopy.

TR-EPR experiments were performed using a modified Bruker ER200D spectrometer with an extended detection bandwidth (6 MHz), disabling magnetic field modulation and using pulsed photo-excitation from the second harmonic of a Nd:YAG pulsed laser (Quantel Brilliant,  $\lambda = 532$  nm pulse length = 5 ns, pulse energy = 5 mJ, repetition rate = 50 Hz). The spectrometer was equipped with a nitrogen flow cryostat for sample temperature control. Experiments were performed at 120 K. The signal was recorded with a LeCroy LT344 digital oscilloscope, triggered by the laser pulse. Transient signal rise time was about 150 ns. The experiments were carried out with a microwave power in the cavity of 2 mW. Selection of different laser excitation wavelengths when needed was obtained by an optical parametric oscillator (OPO) module. Simulations of the powder spin-polarized triplet spectra were performed using the Easypin [3] routine in Matlab. The program is based on the full diagonalization of the triplet state spin Hamiltonian, comprehensive of the Zeeman and magnetic dipole-dipole interactions. The line shape of the EPR spectrum is calculated

assuming a powder distribution of molecular orientations with respect to the magnetic field direction. Triplet state input parameters are the relative population probabilities at zero field and the ZFS parameters D and E. The population probabilities in the applied field are linear combinations of the zero-field population rates with coefficients derived from the unitary transformation diagonalizing the spin Hamiltonian.

[1] Micali *et al.* *J. Phys. Chem. B*, **2006**, *110* (16), pp 8289–8295

[2] Minotto *et al.* *J. Phys. Chem. C*, **2014**, *118* (41), pp 24117–24126

[3] Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 45.