Supplementary Information for

# Probing the orientation of porphyrin oligomers in a liquid crystal solvent – a triplet state electron paramagnetic resonance study

Sabine Richert,\*<sup>1</sup> Harry L. Anderson,<sup>2</sup> Martin D. Peeks,<sup>2</sup> and Christiane R. Timmel\*<sup>1</sup>

<sup>1</sup> Centre for Advanced Electron Spin Resonance (CAESR), Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, United Kingdom.

<sup>2</sup> Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, United Kingdom.

\* E-mail: sabine.richert@pc.uni-freiburg.de, christiane.timmel@chem.ox.ac.uk

# **Table of Contents**

1	Experimental Details	<b>S</b> 2
	1.1 EPR Sample Preparation	S2
	1.2 TREPR	S2
2	Influence of the Excitation Wavelength on the EPR Spectra of P2	<b>S</b> 3
3	Simulations Assuming a Uniaxial Distribution	<b>S</b> 4
4	Validation of the Simulations assuming Biaxiality	S5

### List of Figures

Comparison of the transient cw EPR spectra of ${f P2}$ recorded at different excitation	
wavelengths	<b>S</b> 3
Angular distributions used in the simulations	S4
Effect of the width of the distribution on the simulated spectra of ${\sf P1}$ assuming a	
uniaxial distribution	S4
Effect of the width of the distribution on the simulated spectra of ${f P2}$ assuming a	
uniaxial distribution	S5
Effect of the variation of $\sigma_{arphi}$ on the simulated spectra of ${f P1}$	S6
Effect of the variation of $\sigma_{arphi}$ on the simulated spectra of ${f P2}$	S6
	Comparison of the transient cw EPR spectra of <b>P2</b> recorded at different excitation wavelengths

## **1** Experimental Details

#### 1.1 EPR Sample Preparation

The purity of the compounds, **P1** and **P2**, was verified by NMR, UV-vis and recycling GPC. All EPR samples were first prepared at concentrations of roughly 0.2 mM in 2-methyltetrahydrofuran. The solvent was subsequently removed and replaced by an equal amount of **5CB** (CAS 40817-08-1, TCI Ltd). The solutions were then transferred into EPR tubes, degassed by the freeze-pump-thaw method and sealed under vacuum.

#### 1.2 TREPR

All transient cw EPR measurements were carried out at X-band frequencies (9.75 GHz) on a Bruker ELEXSYS E680 spectrometer using a Bruker EN 4118X-MD4 resonator. The temperature was held constant at 90 K using a nitrogen gas-flow cryostat. Typically, the samples were photo-excited with 1-2 mJ pulses of 5 ns duration at wavelengths corresponding to the porphyrin Q-band region (cf. main text) using an OPO pumped by the third harmonics of a Nd:YAG laser (Opotek, Opolette) operated at a repetition rate of 20 Hz. Before reaching the sample, the excitation light was depolarised.

The transient cw EPR spectra were acquired in direct detection mode using the transient recorder and a microwave power of 0.2 mW (30 dB). Typically, for every field value, a time trace with 4096 points was recorded using a time base of 4 ns. Considering a background of about 800 ns before the laser pulse, these settings result in a time window of about 15  $\mu$ s. After data acquisition, the 2D spectra were baseline-corrected in both dimensions using a home-written MATLAB routine. The spectra shown in the main part were typically averaged over a time window from 0.2  $\mu$ s to 1  $\mu$ s after laser excitation and the spectral shape was generally found not to change significantly with time.

#### 2 Influence of the Excitation Wavelength on the EPR Spectra of P2

The influence of the excitation wavelength on the appearance of the aligned triplet spectra in **5CB** was tested for **P2** to explore the contribution of porphyrins with different conformations. Figure S1 shows a comparison of the spectra taken at || and  $\perp$  alignment for **P2** in **5CB** recorded after excitation at different wavelengths covering the *Q*-band region of the porphyrin UV-vis spectrum. All spectra were recorded at 90 K using an excitation energy of roughly 1 mJ (20 Hz).



Figure S1: Comparison of the transient cw EPR spectra of P2 recorded at different excitation wavelengths (as indicated) for || (*left*) and  $\perp$  (*right*) alignment in 5CB at 90 K. The excitation energy was around 1 mJ at 20 Hz.

The changes in the triplet spectra observed after excitation at different wavelengths are small for **P2**, which points towards a uniform alignment. Ideally, if all molecules were perfectly aligned and only one particular conformation (i.e. dihedral angle between the porphyrin planes) was contributing to the triplet spectrum, no changes in the shape of the EPR spectrum should be observed when scanning the excitation wavelength. Molecules with different conformations, however, could in principle have different EPR triplet spectra and different UV-vis spectra, so their relative contribution to the recorded triplet spectrum is expected to depend on the excitation wavelength, leading to small changes in intensity in certain parts of the EPR triplet spectrum when scanning the excitation wavelength. Since the excitation light was depolarised, any contribution of magneto-photoselection effects can be excluded.

The changes observed in the spectra corresponding to  $\perp$  alignment are hardly noticeable for **P2**. In the case of || alignment, a shoulder in the spectrum is observed for certain excitation wavelengths, in a spectral region corresponding to neither one of the three canonical orientations of **P2**. A comparison with the triplet spectrum of **P1** reveals, however, that the onset of this shoulder is in very good agreement with the spectral position of the X transition of **P1**. Furthermore, the shoulder is only observed when exciting at wavelengths were **P1** absorbs and absent when exciting at lower or higher wavelengths. It is thus speculated that these spectral changes arise from a small contribution of the twisted conformation of **P2** (i.e. a conformation where the porphyrin planes are at a dihedral angle of 90°) which should have a spectrum similar to that of **P1**.

#### 3 Simulations Assuming a Uniaxial Distribution

At first, a uniaxial distribution was assumed. In this case, the only two variable parameters are  $\theta_c$  and  $\sigma_{\theta}$ , where  $\theta$  is the angle between the magnetic field direction (i.e. liquid crystal director axis) and the Z axis of the molecule. For **P1**, || alignment should correspond to an angle  $\theta$  of 90° since the Z axis of the zero-field splitting tensor corresponds to the out-of-plane axis of the molecule, whereas in **P2** an angle  $\theta$  of 0° should be expected for || alignment. In general, it is reasonable to assume that the centre of the distribution will be located at either 0° or 90°, which additionally reduces the degrees of freedom of the fit.

The influence of the width of the distribution,  $\sigma_{\theta}$ , on the simulated spectra was studied for  $\theta_{c} = 0^{\circ}$ and  $\theta_{c} = 90^{\circ}$  for **P1** and **P2**. To this end, spectra were simulated for different values of  $\sigma_{\theta}$  spanning the range between 10° and 180°, where 180° corresponds to the isotropic case and 10° represents a very well aligned sample. The distribution functions used in these simulations are shown in Figure S2 and the simulated spectra together with the corresponding experimental spectra are depicted in Figures S3 and S4. The colour-code used is the same in all three figures.



**Figure S2:** Angular distributions centred at  $\theta_c = 0^\circ$  (*left*) and  $\theta_c = 90^\circ$  (*right*) used in the simulations of the spectra of the aligned samples of **P1** and **P2**. The colour-code is the same as in the figures below.



**Figure S3:** Simulated spectra using the parameters for **P1** in combination with the angular distribution functions  $P(\theta)$  shown above for  $\theta_c = 0^\circ$  (*left*) and  $\theta_c = 90^\circ$  (*right*). The corresponding experimental spectrum is superimposed in black (dashed line).



Figure S4: Simulated spectra using the parameters for P2 in combination with the angular distribution functions  $P(\theta)$  shown above for  $\theta_c = 0^\circ$  (*left*) and  $\theta_c = 90^\circ$  (*right*). The corresponding experimental spectrum is superimposed in black (dashed line).

When having a closer look at the spectra for different  $\sigma_{\theta}$  in comparison with the experimental spectra, one realises, especially in the case of **P1**, that the experimental spectra cannot satisfactorily be reproduced if only a distribution in  $\theta$  is considered. The discrepancy between experiment and simulation is particularly large for **P1** and || alignment where  $\theta_c = 90^\circ$ : In the experimental spectrum, the X transition strongly dominates, whereas the two other transitions are almost absent. In the simulated spectra, however, the Y transition is always strongly present no matter the width of the distribution,  $\sigma_{\theta}$ , and consequently no distribution can be found which allows the shape of the simulated spectrum to closely approach the experimental one. This is maybe not surprising given that for  $\theta_c = 90^\circ$  the porphyrin molecule might have a strong preference to align either along the X or along the Y axis which should lead to marked differences in the respective triplet spectra. In such cases, the influence of the azimuthal angle  $\varphi$  can become significant.

#### 4 Validation of the Simulations assuming Biaxiality

It was shown in Figures S3 and S4 that simulations which rely on angular distributions depending only on  $\theta$  are not able to satisfactorily reproduce all experimental spectra. The large discrepancies between such simulations and the experimental spectra, particularly for **P1**, where  $\theta_c = 90^\circ$ , justify the use of a biaxial angular distribution  $P(\theta, \varphi)$ .

To validate the simulations, the effect of the width of the distribution in  $\varphi$  on the spectral shape was verified. If  $\sigma_{\varphi}$  is chosen to be sufficiently large, the obtained spectrum should be identical to that for a uniaxial distribution  $P(\theta)$ . Generally, the influence of  $\sigma_{\varphi}$  should be large for  $\theta_{c} = 90^{\circ}$ and relatively small for  $\theta_{c} = 0^{\circ}$ , except if  $\sigma_{\theta}$  is also large. For a fixed distribution in  $\theta$  and a fixed  $\varphi_{c}$ , the width of the distribution in  $\varphi$  was varied and the simulated spectra were compared to the corresponding experimental ones. The results are shown in Figure S5 for **P1** and in Figure S6 for **P2**. From these figures, in comparison with Figures S3 and S4, the following observations can be made:

• The spectra for  $\sigma_{\varphi} = 180^{\circ}$  are identical to the corresponding uniaxial ones where only a distribution in  $\theta$  is considered.



**Figure S5:** Simulated spectra for different values of  $\sigma_{\varphi}$  using the parameters for **P1** in combination with a biaxial angular distribution  $P(\theta, \varphi)$  with  $\theta_c = 90^\circ$  (*left*) and  $\theta_c = 0^\circ$  (*right*). The corresponding experimental spectra are superimposed in black (dashed line) and  $\sigma_{\theta}$  and  $\varphi_c$  were fixed to the indicated values.



**Figure S6:** Simulated spectra for different values of  $\sigma_{\varphi}$  using the parameters for **P2** in combination with a biaxial angular distribution  $P(\theta, \varphi)$  with  $\theta_c = 0^\circ$  (*left*) and  $\theta_c = 90^\circ$  (*right*). The corresponding experimental spectra are superimposed in black (dashed line) and  $\sigma_{\theta}$  and  $\varphi_c$  were fixed to the indicated values.

- The influence of  $\sigma_{\varphi}$  is large for  $\theta_{c} = 90^{\circ}$  and smaller for  $\theta_{c} = 0^{\circ}$ . The reason why the influence of  $\sigma_{\varphi}$  is still not negligible for  $\theta_{c} = 0^{\circ}$  is most likely the relatively wide distribution in  $\theta$  observed in all cases.
- The influence of σ<sub>φ</sub> on the experimental spectrum of P1 for θ<sub>c</sub> = 90° is striking (cf. Figure S5, *left*). For a proper description of the experimental observations, a biaxial distribution is clearly required.
- In the case of P2 (Figure S6), since the value of σ<sub>φ</sub> which was found to best reproduce the experimental data is relatively large, the experimental spectra can nearly be simulated taking only a distribution in θ into account. However, the improvement of the simulations obtained when using a biaxial distribution is significant.