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Complete List of Authors:	Richert, Sabine; Univeristy of OXford, Centre for Advanced Electron Spin Resonance, Department of Chemistry Peeks, Martin; Oxford University, Department of Chemistry Tait, Claudia E; University of Oxford, Department of Chemistry Anderson, Harry; University of Oxford, Department of Chemistry Timmel, Christiane; University of Oxford, Centre for Advanced Electron Spin Resonance, Department of Chemistry

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Photogenerated Triplet States in Supramolecular Porphyrin Ladder Assemblies: An EPR Study[†]

Sabine Richert,^a Martin D. Peeks,^b Claudia E. Tait,^{a‡} Harry L. Anderson,^{b*} and Christiane R. Timmel^{a*}

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Introducing bridging ligands such as DABCO to solutions of linear zinc porphyrin oligomers has previously been shown to lead to the formation of ladder-type assemblies in which the single porphyrin units in each strand adopt a predominantly co-planar conformation. Here, we employ transient Electron Paramagnetic Resonance (EPR) to study photogenerated triplet states of these complexes in frozen solution with a particular focus on the extent of spin delocalisation. We make use of two different techniques: (i) the zero-field splitting parameters D and E are determined using transient continuous wave (cw) EPR spectroscopy and (ii) the hyperfine coupling constants which directly reveal the extent of spin delocalisation are quantified by orientation-selective proton Electron Nuclear Double Resonance (ENDOR) spectroscopy. It is found that ladder formation does not encourage triplet state delocalisation either across the bridging ligand DABCO or along the individual porphyrin units despite their co-planar conformation, a structure previously shown to allow increased electronic delocalisation.

Conjugated linear porphyrin oligomers with different linkers and side groups have been synthesised in recent years^{1–3} and have gained particular interest due to their various potential applications including, for example, molecular wires^{4–6} and nonlinear optical materials.⁷ When bidentate nitrogen ligands such as

1,4-diazabicyclo[2.2.2]octane (DABCO) or 4,4'-bipyridine (bipy) are added to a solution of linear zinc porphyrin oligomers, porphyrin ladder complexes as shown in Fig. 1 can be formed by self-assembly.^{1,8,9} The ladder complexes were designed to limit rotation about the butadiyne linkers, thereby keeping the π -systems within a single porphyrin strand co-planar and maximising intra-oligomer π overlap.

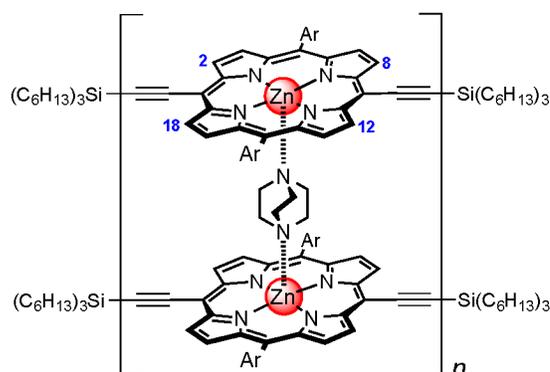


Fig. 1 Structure of the investigated DABCO ladder complexes $(Pn)_2 \cdot (DABCO)_n$ with the number of porphyrin units n ranging from two to four (Ar = 3,5-bis(*tert*-butyl)phenyl). The estimated distance between the two porphyrin strands amounts to 0.7 nm. Selected porphyrin atoms are labelled with their position numbers.

For similar porphyrin ladder complexes, using mainly bipy as the bridging ligand, it has been shown that the real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ are enhanced by an order of magnitude, as compared to the respective free linear porphyrin oligomers, which makes those complexes particularly interesting for nonlinear optical applications.^{10–12}

Charge transport was also found to be favoured in ladder type assemblies. A ten-fold increase in the charge carrier mobility was observed in ladder structures, presumably due to an enhanced conjugation as a consequence of the increased planarity of the individual porphyrin strands implying a reduced heterogeneity of

^a Centre for Advanced Electron Spin Resonance (CAESR), University of Oxford, South Parks Road, Oxford, OX1 3QR, United Kingdom.

^b Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, United Kingdom.

* E-mail: christiane.timmel@chem.ox.ac.uk; harry.anderson@chem.ox.ac.uk

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[‡] Present address: Department of Chemistry, University of Washington, Seattle, WA 98195, United States.

torsional angles and therefore more uniform site energies.^{13,14}

In earlier studies, including the investigation of photosynthetic reaction centres^{15–19} as well as systems designed for artificial photosynthesis^{20–23} or wire-like charge transport,^{24–26} it has been shown that transient EPR techniques are particularly suitable for the characterisation of photogenerated triplet excited states.

Triplet state delocalisation can be accessed either by determination of the zero-field splitting parameters D and E using transient cw EPR or by measurement of the hyperfine coupling constants using pulsed ENDOR spectroscopy. Assuming that the contribution of spin-orbit coupling to the zero-field splitting interaction can be neglected,²⁷ D can be related to the inter-spin distance, r , according to the following formula²⁸

$$D = \frac{3}{4} \frac{\mu_0}{4\pi} (g_e \beta_e)^2 \left\langle \frac{1 - 3 \cos^2 \theta}{r^3} \right\rangle \quad (1)$$

where θ is the angle between the spin-spin vector and the dipolar Z axis, g_e the electronic g -factor, β_e the Bohr magneton and μ_0 the vacuum permeability. The angled brackets indicate the expectation value. Care needs to be taken in the interpretation of the apparent $D \propto r^{-3}$ proportionality as the orientation of the zero-field splitting tensor within the molecular framework and hence the $\cos^2 \theta$ term may also change between oligomers of different length.²⁹

An attractive alternative in the investigation of triplet state delocalisation in such systems is therefore the application of pulsed ENDOR spectroscopy. The McConnell equation³⁰ states that the hyperfine coupling constant, A , of any magnetic nucleus in an aromatic, paramagnetic compound is directly proportional to the spin density, ρ . Consequently, in an oligomeric system consisting of N units, a reduction of the hyperfine coupling constants by a factor of $\frac{1}{N}$ is expected in the case of complete spin delocalisation. Here, we will employ both transient cw EPR and pulsed ENDOR spectroscopies to characterise triplet state delocalisation in porphyrin ladder assemblies.

In contrast to previous work, where porphyrin oligomers with 3,5-bis(trihexylsilyl)phenyl (THS) side groups were investigated in a 2-methyltetrahydrofuran:pyridine 10:1 (MTHF:py) solvent mixture,²⁶ the less bulky 3,5-bis(*tert*-butyl)phenyl (tBu) side groups are used in this work to minimise steric hindrance and thus facilitate ladder formation. The ladder complexes do not form in MTHF:py since coordinating solvents interfere with the binding of DABCO to zinc, therefore, toluene is chosen as the solvent.

UV-vis spectra of the the linear oligomers with one to four porphyrin units, referred to as P1 to P4, recorded at room temperature in the presence or absence of DABCO are shown in the ESI† (Fig. S1). No indications of a ladder-type complex formation are observed for P1, whereas the ladder complexes of the longer oligomers are found to be stable and become progressively more stable with increasing porphyrin oligomer length.⁸

Since the triplet EPR and ENDOR measurements need to be carried out in frozen solution, the stability of the ladder complexes was also tested at low temperatures. To this end, frozen solu-

tion UV-vis spectra of DABCO ladder samples of P2 to P4 were recorded and are shown in the ESI† (Fig. S2 and Fig. S3). The results indicate that the ladder complex is stable for P3 and P4 at 80 K, while it seems to break up (or form a complex with a different geometry) in the case of P2. The following discussion on the effect of ladder formation on triplet state spin delocalisation will therefore only focus on the longer oligomers P3 and P4.

In the absence of bridging ligands, triplet state delocalisation has been shown to be restricted to just two porphyrin units in both P3 and P4.²⁶ Here we explore whether introduction of a bridging ligand further enhances delocalisation either (i) along the porphyrin chain which is forced into a more co-planar conformation which could encourage further delocalisation, or (ii) between the two porphyrin strands. In the latter case, DABCO itself might act as a mediator or, more likely, the near co-planar arrangement of the two porphyrin strands held at a separation distance of only 0.7 nm might encourage inter-oligomer delocalisation, in analogy to the situation found in the special pair of the bacterial photosynthetic reaction centre.¹⁶

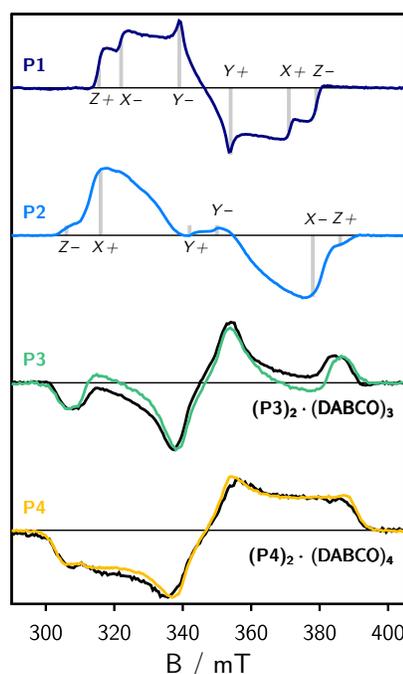


Fig. 2 Transient cw EPR spectra of the triplet states of the linear oligomers P1 to P4, excited at 532 nm, averaged from 0.2–1 μ s after laser excitation, recorded at 20 K. The gray lines indicate the field positions of the canonical orientations for P1 and P2. The ordering of the triplet sublevels was chosen such that $|Z\rangle > |X\rangle > |Y\rangle$ and + and – refer to the $m_S = 0 \rightarrow m_S = +1$ and the $m_S = 0 \rightarrow m_S = -1$ transitions, respectively. The spectra of the ladder complexes of P3 and P4 are shown in black.

The influence of the DABCO bridging ligand on triplet state delocalisation can only be quantified reliably if the properties of the single porphyrin strands are known. Since previously published results were obtained in different solvents and with different porphyrin side groups and can therefore not be used for reference, the linear oligomers first needed to be characterised in the absence of DABCO in toluene. All samples (50 μ M) were excited at 532 nm with a pulsed Nd:YAG laser (10 Hz, 5 mJ, 5 ns pulse

length) and the spectra were acquired at 20 K. Further experimental details can be found in the ESI†. Fig. 2 shows the transient cw EPR spectra of **P1** to **P4** averaged over a time window from 0.2 to 1 μ s after the laser pulse. The spectral shape did not change significantly over the course of the triplet state lifetime and the obtained triplet state spectra are in good agreement with earlier results although small differences in the triplet state polarisations are observed.²⁶

Numerical simulations of the spectra were carried out to determine the zero-field splitting parameters D and E as well as the relative populations of the triplet sublevels, see ESI†(Fig. S5). The D value was assumed to be positive for **P1** as it is usually the case for an oblate spin system and the ordering of the triplet sublevels was chosen such that $|Z\rangle > |X\rangle > |Y\rangle$ as indicated in Fig. 2 (cf. also ESI†, Fig. S9). The validity of the assumption of a positive D value for **P1** has been confirmed experimentally for a similar porphyrin monomer by magnetophotoselection experiments.²⁹ The zero-field splitting parameter D increases from **P1** to **P2**, whereas no further significant changes are observed between **P2** and the longer oligomers. Interpretation of these data in terms of Eq. 1 would suggest that the triplet state localises on just a single porphyrin unit. It has, however, been shown before that a reorientation of the zero-field-splitting tensor occurs from **P1** to **P2** and is consistent with a slight increase of D and complete delocalisation over two porphyrin units.^{26,29} Consequently, in the longer oligomers, the axis of maximum dipolar coupling (Z) is now oriented along the inter-porphyrin axis.

In linear porphyrin oligomers with 3,5-bis(octyloxy)phenyl side groups aggregation was observed in non-coordinating solvents.^{31,32} The relatively low concentration employed in this EPR study and the similarity of the obtained triplet state parameters to those obtained for porphyrins with **THS** side groups in a **MTHF:py** solvent mixture,²⁶ suggests, however, that aggregation is not a confounding variable in the present case. To further support this statement, a spectrum of **P3** with the bigger and bulkier **THS** side groups, which are less prone to aggregation, was also recorded in toluene. The result is shown in the ESI†(Fig. S7) and numerical simulation of the data resulted in triplet state parameters almost identical to those obtained for **P3** with **tBu** side groups in toluene, suggesting that the different side chains do not significantly influence the triplet state spectra and that the small differences in the triplet state polarisations with respect to earlier work are caused by the use of a different solvent.

Since hyperfine couplings provide a more accurate estimate of the extent of triplet state delocalisation, ^1H ENDOR experiments were carried out on the linear porphyrin oligomers in toluene at 20 K. The largest (and best resolved) hyperfine coupling constants of the systems are found along the Y axis of the zero-field splitting tensor which corresponds to the axis along the phenyl groups in the porphyrin oligomers. Consequently, only the ENDOR spectra recorded at magnetic fields corresponding to the respective Y -transitions are compared in Fig. 3.

Based on DFT calculations, the largest coupling can be assigned to the protons in positions 2, 8, 12, and 18 of the porphyrin core of **P1**, labelled in Fig. 1, and the corresponding positions for the longer oligomers. A visualisation of the ^1H hyperfine cou-

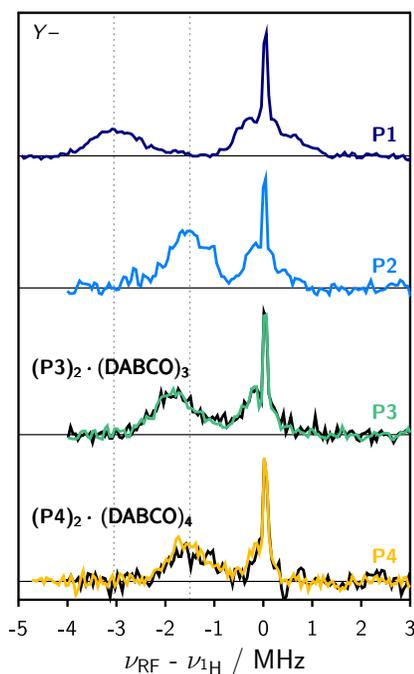


Fig. 3 Triplet state proton ENDOR spectra at 20 K of the linear oligomers **P1** to **P4** recorded at the Y – orientation corresponding to magnetic fields of 339, 350, 352 and 353 mT for **P1**, **P2**, **P3**, and **P4**, respectively. Details of the measurement and a description of the applied experimental parameters can be found in the ESI†. The spectra of the ladder complexes of **P3** and **P4** are shown in black. The grey dotted lines indicate the maximum of the hyperfine coupling peak for **P1** and half of that value, respectively.

pling tensors obtained from DFT is shown in the ESI†(Fig. S8) for **P1** and **P2**. In frozen solution Experimentally, it is found that the largest hyperfine coupling of -3 MHz in **P1** is halved in **P2**, indicating complete delocalisation over two porphyrin units (cf. Fig. 3). The small changes observed for the longer oligomers **P3** and **P4** (as compared to **P2**) are consistent with uneven delocalisation as shown before for similar systems.²⁶

The influence of the bridging ligand **DABCO** on the extent of triplet state delocalisation in the linear oligomers was tested by comparing the transient cw EPR and ENDOR results for **P3** and **P4** to those of the corresponding ladder complexes. At first glance, the transient cw triplet EPR spectra acquired for the ladder structures are very similar to the spectra acquired in the absence of **DABCO** in Fig. 2. However, on closer inspection (and simulation, cf. ESI†Fig. S6), it is noted that the relative populations of the individual triplet state sublevels and therefore the spin polarisation of the spectrum of **P3** are slightly altered upon addition of the bridging ligand resulting in the small differences in spectral shape seen in the figure. This result is in keeping with previous studies which demonstrated that the spin polarisation of the triplet state spectrum is very sensitive to the conformation of the porphyrin oligomer.³³ A numerical simulation of the spectra reveals a slight decrease in the out-of-plane (X) triplet sublevel population upon ladder formation in **P3** which would be consistent with an increased planarisation of the porphyrin π -system.³³

For **P4** the addition of **DABCO** has an even smaller effect on

the appearance of the triplet spectrum. Importantly, formation of the ladder structure does not seem to affect the width of the spectrum (corresponding to $2|D|$) of either oligomer providing a first piece of evidence that the bridging ligand does not promote further delocalisation.

To confirm this hypothesis, the triplet state proton ENDOR spectra of **P3** and **P4** were compared with those recorded for the corresponding ladder complexes (see Fig. 3). From the spectra it can be seen that the hyperfine coupling constants of the linear oligomers **P3** and **P4** appear not to be affected by ladder formation, which suggests that the extent of triplet state delocalisation remains unchanged.

In summary, our experimental results allow us to draw the following firm conclusions: (1) Low temperature UV-vis spectroscopy confirmed the stability of the ladder complexes for **P3** and **P4**. (2) Formation of the ladder complexes does not promote further triplet state delocalisation either between or along the porphyrin chains.

The bridging ligand forces the porphyrin strands into a near co-planar arrangement with a centre-to-centre distance between the porphyrins of 0.7 nm ³⁴ similar to that found in the special pairs of photosynthetic reaction centres some of which exhibit (asymmetric) delocalisation¹⁶ and others do so only at certain temperatures.^{35,36} The degree of triplet state delocalisation between two non-covalently linked porphyrins is known to be affected by as diverse factors as inter-porphyrin distance, geometry, symmetry, local environment (solvent/protein matrix) and temperature. Any in-depth investigation of the factors preventing delocalisation of the triplet state between the porphyrin strands in the **DABCO** bridged systems investigated here would necessarily have to commence with (or at least include) an investigation of (**P1**)₂·**DABCO** which unfortunately is not stable at low concentrations in toluene.

Our results also show that formation of a predominantly co-planar structure of the porphyrin units does not promote further delocalisation within the individual strands although it was previously shown for the dimer that complete triplet delocalisation across both porphyrins occurs when the porphyrins are in a planar but not in a perpendicular conformation.³³ It is possible that in our frozen solution, the majority of the free porphyrin oligomers is indeed already in a predominantly co-planar arrangement in the absence of **DABCO**,³⁷ but low temperature UV-vis spectra indicate that the ladder complexes of **P3** and **P4** have significantly more planar conformations than the unbound oligomers (cf. ESI†Fig. S2 and S3). The latter were of course taken at 80 K rather than the EPR temperature of 20 K and moreover, UV-vis might be more sensitive to the presence of different conformations than EPR. More likely is the explanation that delocalisation across the porphyrin chains is possible for a large range of dihedral angles between the porphyrin units. DFT calculations on a porphyrin dimer have shown that the transition between dimeric and monomer-like behaviour occurs only for dihedral angles between 50 and 60°. ³³ It seems therefore plausible that small dihedral angles of up to 50° do not disrupt delocalisation.

Communication between the two porphyrin strands forming the ladder complex would still be possible, for example, via fast

triplet-triplet (T-T) energy transfer at a rate of less than 10^7 Hz . During T-T energy transfer in the presence of an external magnetic field, the spin polarisation is conserved.^{38–40} The relative sublevel populations influencing the appearance of the triplet EPR spectrum of the acceptor porphyrin depend on the triplet state sublevel populations of the donor triplet and the relative orientation of the zero-field splitting tensors of donor and acceptor.⁴⁰ In the present case, the porphyrin units are likely to be co-planar and are chemically equivalent so that they cannot be distinguished spectroscopically, which complicates any type of further analysis based on triplet state populations. A potential way of investigating the possibility of T-T energy transfer in the studied ladder complexes could be via a careful examination of the relaxation rates since T-T energy transfer was found to considerably increase spin-lattice relaxation.⁴¹ No pronounced differences in the relaxation rates were observed between the linear oligomers and the corresponding ladder complexes in this work, making T-T energy transfer between the single porphyrin strands unlikely. However, further investigations would be necessary to draw any definite conclusions regarding the presence and mode of communication between the single porphyrin strands forming the ladder complex.

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