SUPPORTING INFORMATION

Insights into the phototautomerism in the excited states of free-base 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin

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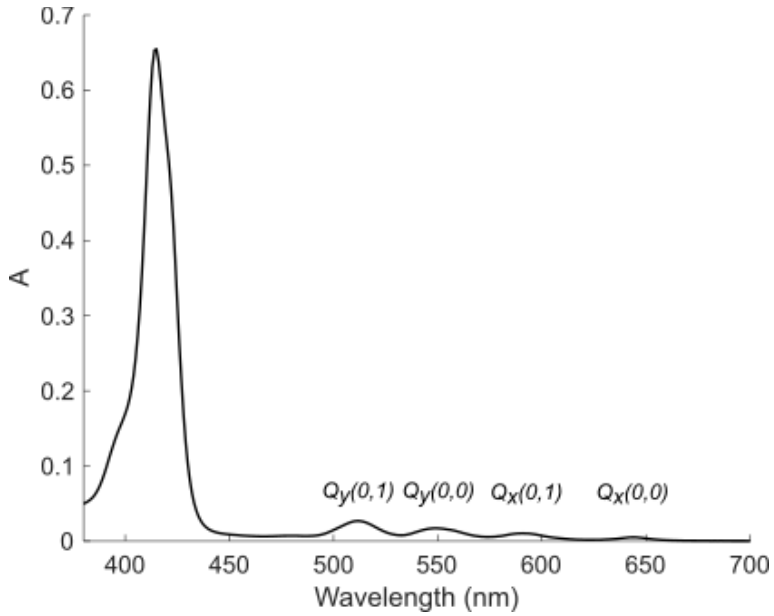

Figure S1. Absorption spectrum of **H_2TPPS^{4-}** in a 3:2 ethanol/methanol mixture at room temperature and assignation of the Q-bands.

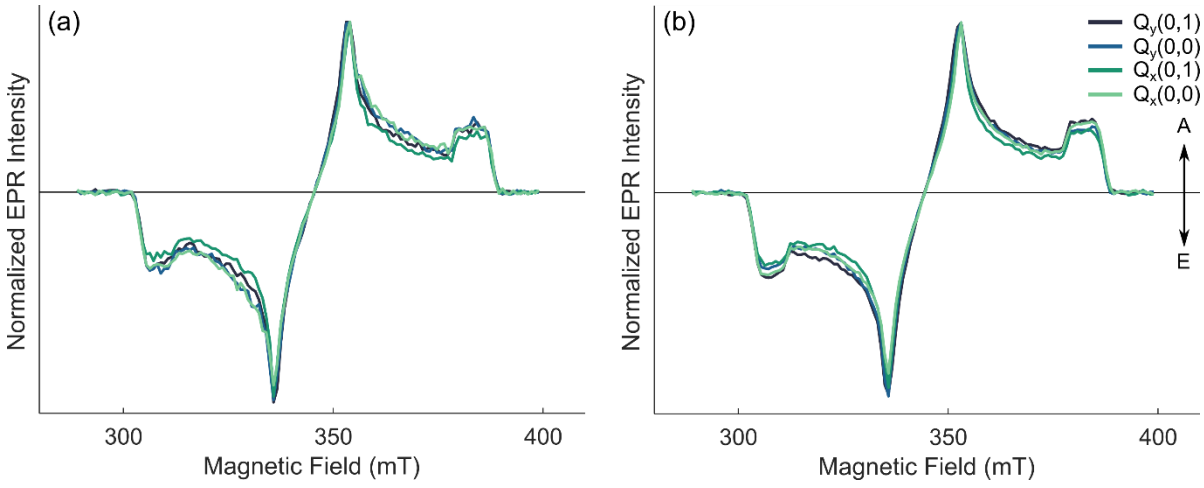

Figure S2. TR-EPR spectra obtained for (a) **H_2TPPS^{4-}** and (b) **D_2TPPS^{4-}** at 80K with light excitation at different wavelengths.

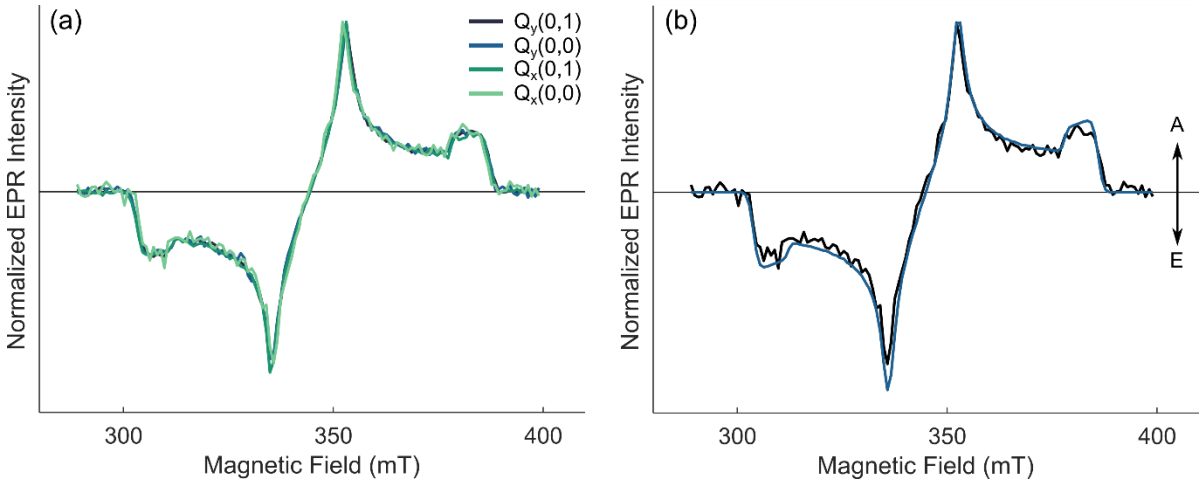

Figure S3. (a) TR-EPR spectra obtained for **H_2TPPS^{4-}** with the addition of KBr at 80K with light excitation at different wavelengths. (b) TR-EPR spectra (black) obtained with an excitation wavelength of 644 nm, on the *$Q_x(0,0)$*, and simulation (blue).

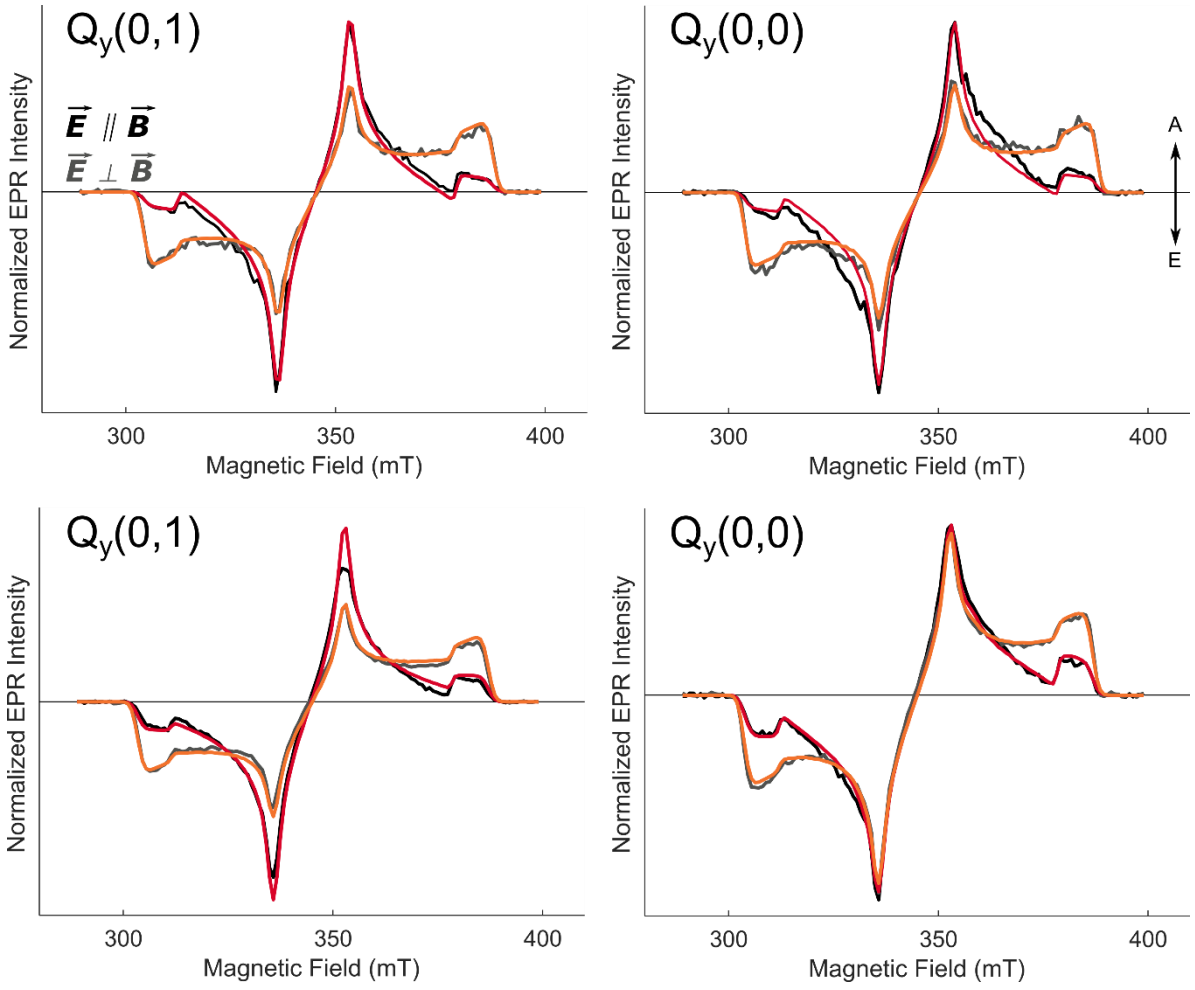

Figure S4. Triplet state TR-EPR spectra of **H_2TPPS^{4-}** in ethanol:methanol 3:2 mixture (top) and **D_2TPPS^{4-}** in deuterated methanol (bottom)), exciting with linearly polarized light within the *$Q_y(0,1)$* (left) and *$Q_y(0,0)$* absorption bands. Experiments were performed at X-band at 80 K. The experimental traces obtained with light polarized parallel and perpendicular to the magnetic field are reported, in black and grey respectively;

the corresponding simulations are shown in red and orange, in the same order. Simulation parameters are reported in Tables 1 and 2. A = enhanced absorption, E = emission.

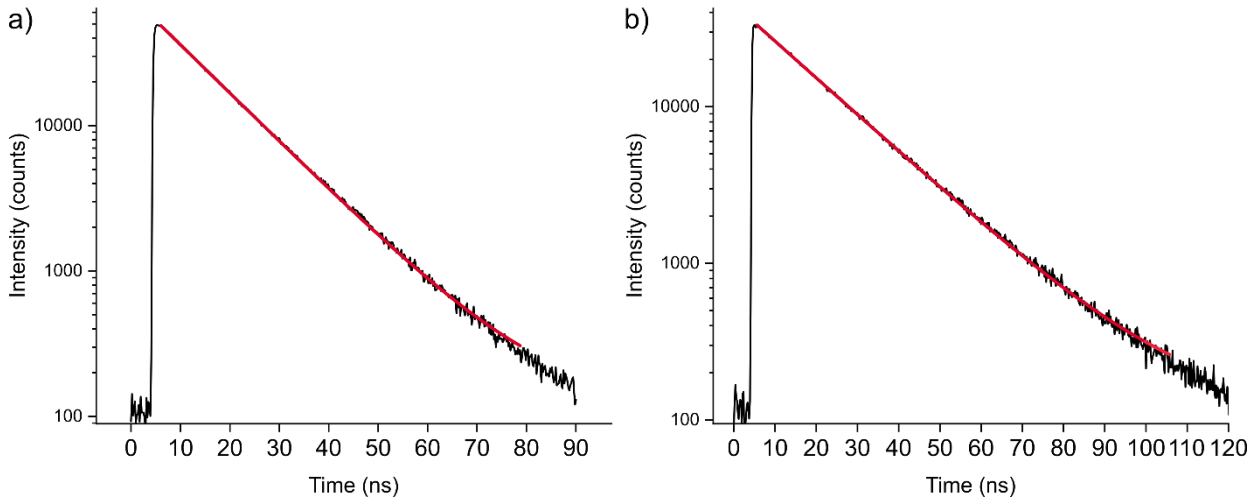

Figure S5. Fluorescence decay in MeOD for a solution of **D_2TPPS^{4-}** measured at 660 nm with excitation at 403 nm at a) room temperature and b) 77 K, each accompanied by the corresponding monoexponential decay fit in red, with decay times of 13.01 ± 0.02 ns and 18.40 ± 0.03 ns respectively.

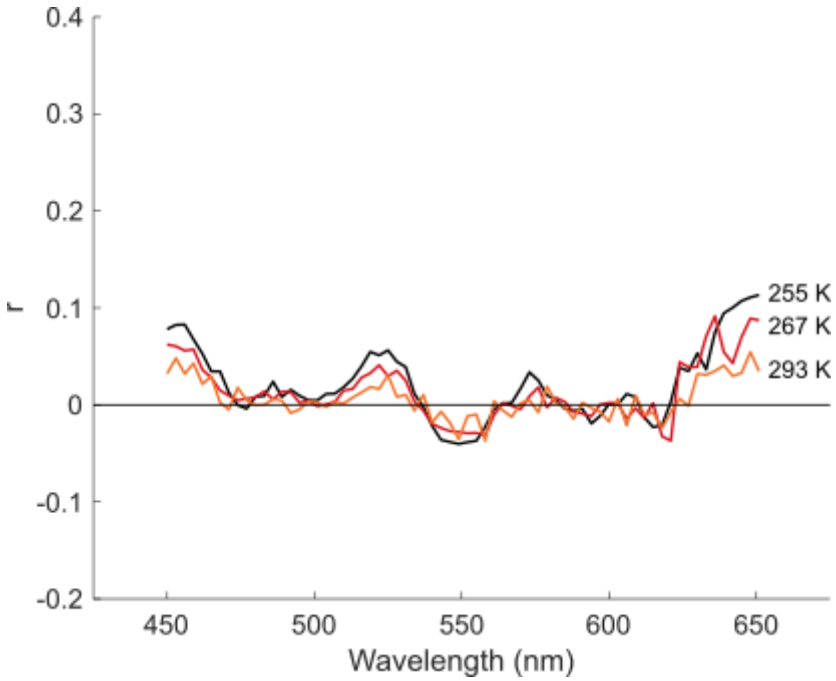

Figure S6. Fluorescence anisotropy as function of the excitation light at different temperatures for a solution of **H_2TPPS^{4-}** in glycerol/H_2O (9:1) in a 1 cm cell measured at the 650 nm emission band.

Triplet state and EPR spectroscopy

A triplet state of an organic molecule like a porphyrin is normally obtained by inter-system crossing (ISC) from the excited singlet state. It is characterized by the presence of two unpaired electrons located in two different π-orbitals that interact through exchange and dipolar interactions [1]. In porphyrins the exchange interaction is much higher than the dipolar interaction and determines the energy difference between the singlet and the triplet state.

The magnetic dipolar interaction between the unpaired electrons is present into the spin Hamiltonian as a second rank traceless tensor **D**, called zero-field splitting (ZFS) tensor, whose principal values are D_i= -X, -Y and -Z (by convention, |Z| > |X|,|Y|)[2]. They are average values of quantities that depend on r^{-3}, where r is the electron-electron distance, and they also depend on the triplet electron distribution. For prolate electronic distributions (as in the case of the toroid-like π-orbital wavefunctions) Z < 0 and the relative principal direction ($\hat{z}$) is perpendicular to the π-plane. If there is a C_n symmetry axis with n>2 along $\hat{z}$, the tensor is necessarily axial, therefore X=Y.

In the principal reference frame of the dipolar tensor the principal values D_i (*i*=X, Y, Z) are given as:

$$D_i = \langle \frac{r^2 - 3x_i^2}{r^5} \rangle \qquad \text{(S1)}$$

where $\vec{r}$ is the electron-electron distance vector in the ZFS frame and x_i the *i*th-component. As **D** is a traceless tensor, the principal values can be expressed through two independent parameters, D and E, defined as $D = -\frac{3}{2}Z$ and $E = \frac{(Y-X)}{2}$.

The spin Hamiltonian of a general triplet state, assuming for simplicity an isotropic g-value, is the following:

$$H = \mu_B g \cdot \boldsymbol{B} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S} \qquad \text{(S2)}$$

where μ_B is the Bohr magneton, **B** is the magnetic field and **S** the spin operator.

At zero field, the three triplet sublevels (T_X, T_Y and T_Z, or zero-field splitting ZFS states - eigenstates of the second term - whose energies are X, Y and Z) are non-degenerate states because of the dipolar interaction (also called ZFS interaction).

When a magnetic field is applied, the high-field eigenstates (T_{+1}, T_0 and T_{-1}) are mixing of the ZFS states [3] and the energies of the new eigenstates changes as a function of B.

Triplet state EPR spectra are typically governed by the electronic Zeeman and ZFS interactions, while hyperfine couplings are not resolved. The ZFS interaction is responsible for the presence of three pairs of features in the powder-type EPR spectra of the photoexcited triplet states (see Fig. S1, bottom). To a good approximation in the case of porphyrin triplet the distance between the pairs of lines, almost symmetrically distributed with respect to the center of the spectrum (ΔB_i, see Fig. S7 for ΔB_y) is related to the principal ZFS values D_i as:

$$\mu_B g \Delta B_i = 3|D_i| \qquad \text{(S3)}$$

To complete the description of the system, the mechanism of population of the triplet state is considered. The ISC process leads to the selective population of the ZFS states (blue thick arrows), producing electron spin polarization. Each high-field eigenstate is populated on the base of the mixing of the three ZFS states [3]

and the two allowed transitions can be either in enhanced absorption (a) or in emission (e); for simplicity, in Fig. S7 the three situations in which the magnetic field is oriented along the three principal directions are shown.

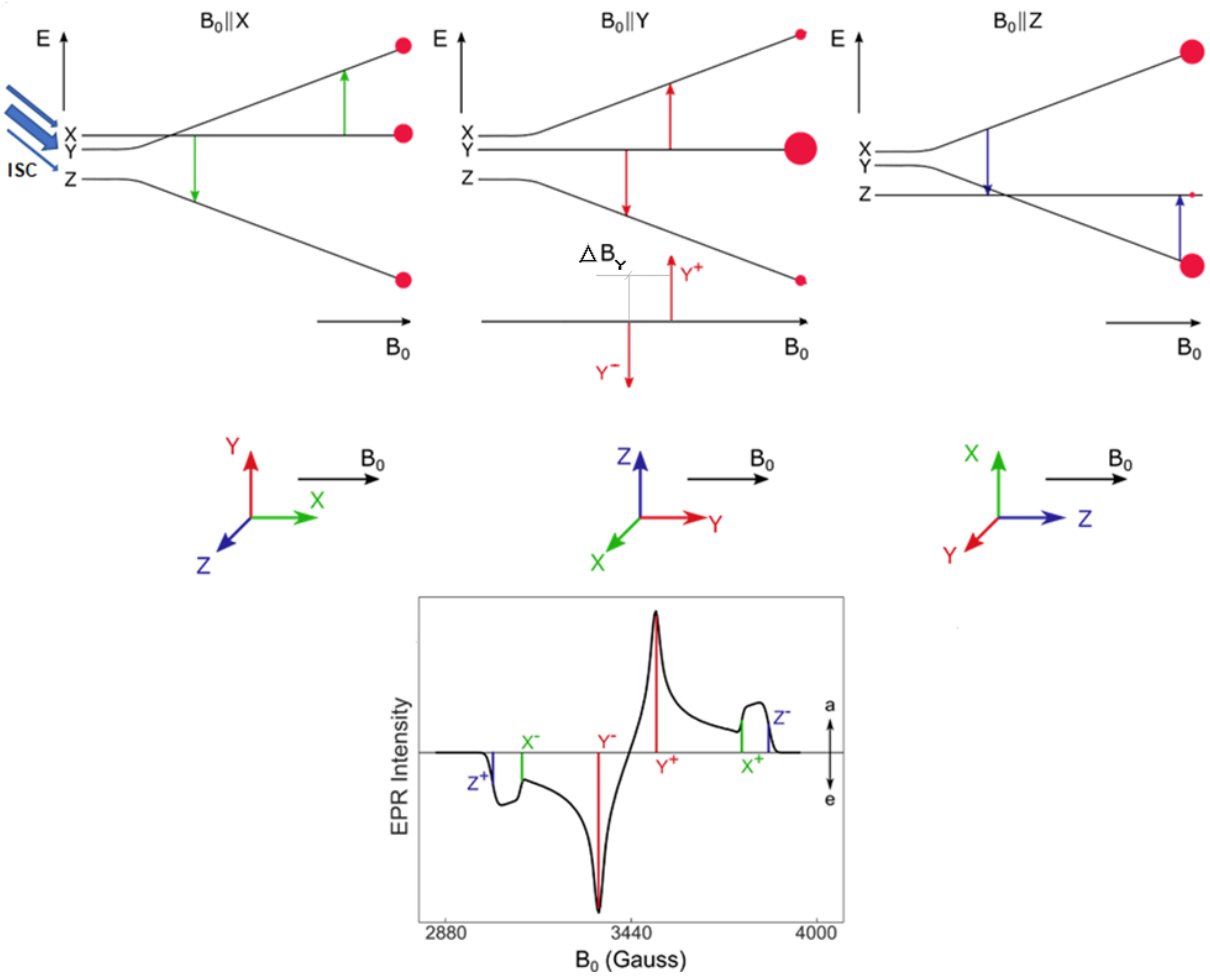

Figure S7: Electron spin polarized TR-EPR spectra. The figures represent, for the system oriented along the three principal directions of the ZFS tensor (D>0 and E<0), a scheme of the energy levels as function of the magnetic field for the studied porphyrin. The population of the high-field states (red balls) is a linear combination of the population of the zero-field states. The vertical arrows indicate the resonance conditions with a fixed-frequency microwave radiation. For $B_0||Y$ we represent the two spectral transitions, one in emission (Y^-) and one in absorption (Y^+), that can be retrieved in the powder spectrum shown in the bottom. The resonance magnetic field difference for the main features ΔB_i is directly related to the dipolar components (eq. S3).

Magnetophotoselection

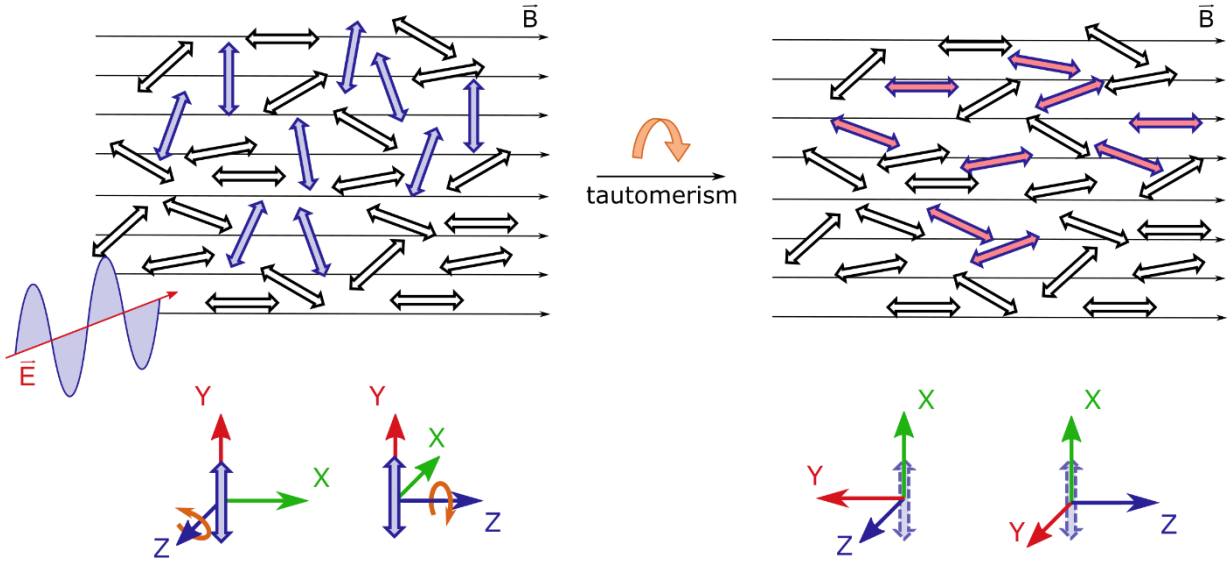

Fig. S8 Representation of the effect of tautomerism on the ZFS orientation in a magnetophotoselection-EPR experiment. On the left, some molecules whose TDM (blue) is parallel to the linearly polarized light are excited and the corresponding relative main orientations of the ZFS axes in the triplet state with respect to the field direction are shown. For the specific orientation of the light polarization with respect to the magnetic field (perpendicular) in the TREPR we expect to observe only X and Z features (see fig. S3). On the right, the orientation of the axes for the same molecules that have undergone tautomerism in the excited singlet state is depicted. If 100% of molecules would undergo tautomerism, only Y and Z features should be observed (see fig. S7).

The orientation of the TDM with respect to the ZFS principal reference frame can be obtained from magnetophotoselection experiments [4,5]. The use of linearly polarized light for photoexcitation in the TR-EPR experiments generates a non-uniform orientational distribution of photoexcited molecules, which is a function of the tilt angle of TDM with respect to the light polarization direction.
The analysis, which allows obtaining the direction of the TDM in the ZFS frame, requires to fit the spectrum with the following expression:

$$I(B_0)^{\mathrm{par/perp}} = const \sum_{+/-} \int_0^{2\pi} \int_0^{\pi} G[B_{\mathrm{res}}(\alpha,\beta) - B_0] \cdot P_{\pm}(\alpha,\beta,B_0) \cdot \left[\int_0^{2\pi} p_{\omega,\varphi}^{\mathrm{par/perp}}(\alpha,\beta,\gamma)\, d\gamma\right] \sin\beta \, d\alpha \, d\beta \qquad \text{(S4)}$$

where $G[B_{\mathrm{res}}(\alpha,\beta) - B_0]$ is a Gaussian line shape function centered at the resonance field B_{res}, $P_{\pm}(\alpha,\beta,\gamma)$ is the non-Boltzmann population difference between the two resonant states and $p_{\omega,\varphi}^{par/perp}(\alpha,\beta,\gamma)$ is the excitation probability specific for the parallel and perpendicular configuration. The $p_{\omega,\varphi}^{\mathrm{par/perp}}$ term contains the orientation (ω,φ) of the TDM in the ZFS system in terms of the two polar angles (ω,φ).
For the analytical expressions of the different terms that have been used to simulate the TR-EPR spectra we refer the reader to Ref.s [6,7].

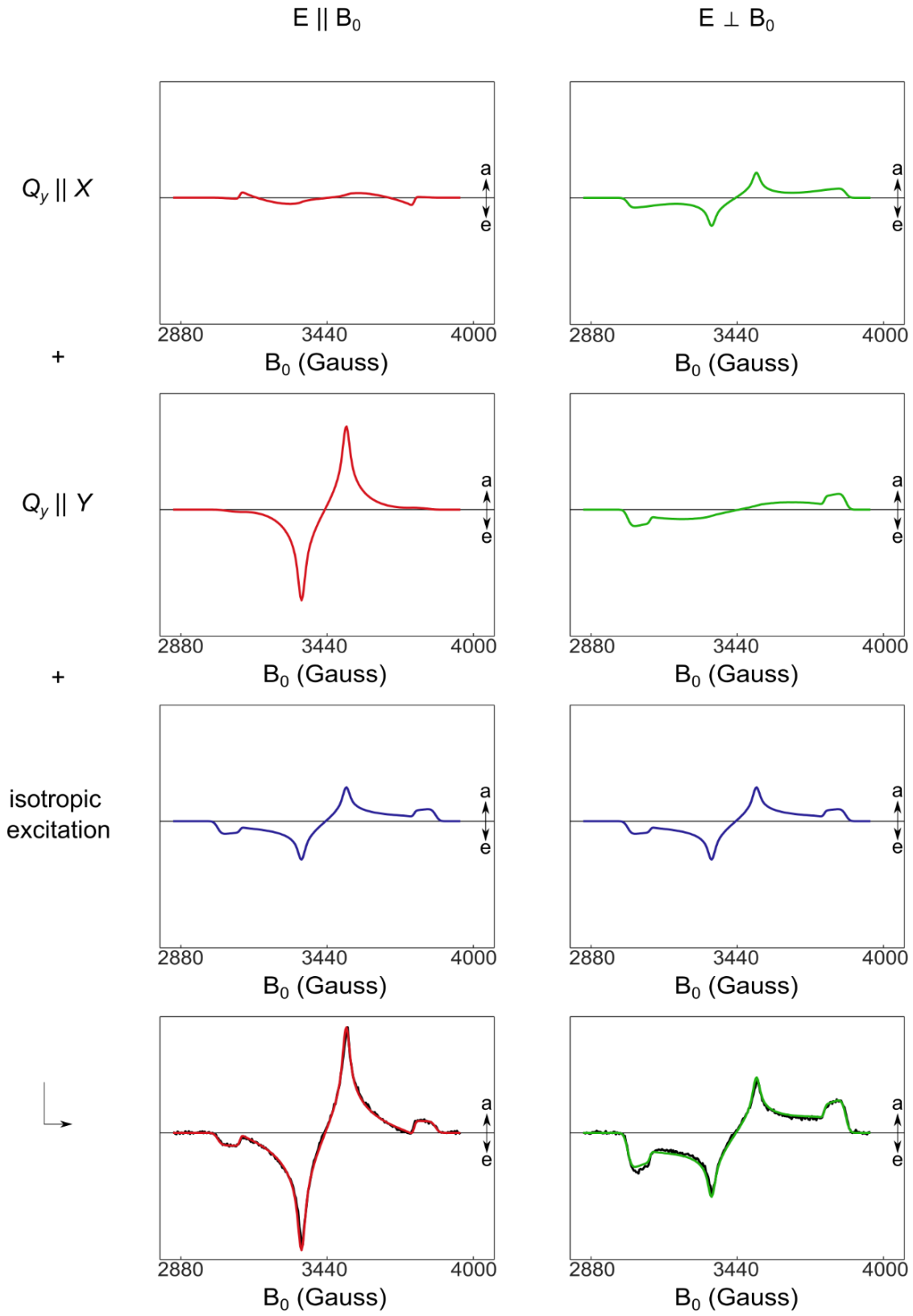

Fig. S9 Simulations of triplet state TR-EPR spectra of **D_2TPPS^{4-}** in deuterated methanol at 80 K for the light polarized parallel (blue) and perpendicular (red) to the magnetic field. First row: simulations for the transition dipole moment parallel to the X axis of the ZFS axes frame. Second row: simulations for the transition dipole moment parallel to the Y axis of the ZFS axes frame. Third row: isotropic contribution to the final simulations. Fourth row: comparison between experimental magnetophotoselection TR-EPR spectra (black) and simulations obtained as a sum with 0.37:0.63 contributions of the components with Q_y || X and Q_y || Y and 20 % of the isotropically-excited powder spectrum.

Estimate of the tautomerism upper-limit exchange rates in the triplet state

An estimate of the upper limit for the exchange rate for the molecule in the triplet state can be obtained from the coalescence conditions and/or from linewidth effects. Quantum mechanical calculations have shown that the directions of the ZFS axes in the molecular frame of the **H_2TPPS^{4-}** triplet state are along the N-H bonds (X), and parallel to the two non-protonated nitrogen distance vector (Y), while the Z axis is perpendicular to the plane (see Fig. 1 in the main text). When hypothetically coalescence conditions are satisfied, instead of two pairs of EPR lines relative to the X and Y components we expect to observe just one pair of lines and an axial ZFS tensor. At coalescence we should have:

$$\tau_L^{-1} = \frac{\Delta\omega}{2\sqrt{2}} = \frac{3}{2\sqrt{2}}\pi|X - Y| \qquad \text{(S5)}$$

where τ_L is the lifetime of the tautomers for the triplet state ($\tau_L^{-1} = k_T$, the forward reaction constant for tautomerism) and $\Delta\omega$ is the difference in the resonance frequency of the X and Y components (in Hz).

Based on the ZFS parameters reported in Table 1, we obtain $\tau_L^{-1} = 8 \cdot 10^8 s^{-1}$; we must conclude that in our case, where coalescence is not occurring, the tautomerization in the triplet state is a process much slower, both for **H_2TPPS^{4-}** and **D_2TPPS^{4-}** .

Another estimate of the upper limit can be obtained by considering the effects on the linewidth. The largest contribution to the linewidth in the presence of an exchange process (slow interconversion) is [23]:

$$\tau_L{}^{-1} = \frac{1}{T_2^{exch}} \qquad \text{(S6)}$$

Assuming that the minimum observable T_2 contribution to linewidth broadening is 0.3 μs ca (1 G), we obtain that the tautomerization in the triplet state is a process much slower than $\tau_L^{-1} = 3 \cdot 10^6 s^{-1}$ for **H_2TPPS^{4-}**, therefore we can assert that, within the slow exchange *régime*, $k_T$is lower than $10^6 s^{-1}$, as expected from line broadening. Another unobserved evidence is the averaging of the population of the X and Y states: we can, in fact, predict how the triplet-state spectrum would evolve in time with a spin polarization modification produced by a fast tautomerization in the triplet state. This is due to the appearance of a porphyrin species having the X, Y principal direction exchanged due to the proton transfer, and, at the same time, the population of the zero-field states determined by the original intersystem crossing (ISC) process are conserved. In Fig. S10 we report the initial spectrum, as derived from simulation of the experimental spectrum at initial times, together with that obtained by an exchange of the principal direction of the X and Y components while the triplet relative populations remain unmodified. The observable spectrum, in the presence of an effective tautomerization effect, should be a combination (1:1) of the initial and inverted spectrum for **H_2TPPS^{4-}**and for **D_2TPPS^{4-}** at temperatures starting from 110 K. In the time-evolution of the experimental spectrum (see Fig. S11a) we never observe the appearance of the emission signal at low field and an enhanced absorption at high field in correspondence of the X transition, as depicted in Figure 3. *Au contraire*, the transitions in emission tend to convert into absorption because of T_1 processes. Therefore, estimating a T_1 of the order of 30 μs (see time trace in Fig. S11b), we can definitively estimate that the $k_T < 3 \cdot 10^4 s^{-1}$.

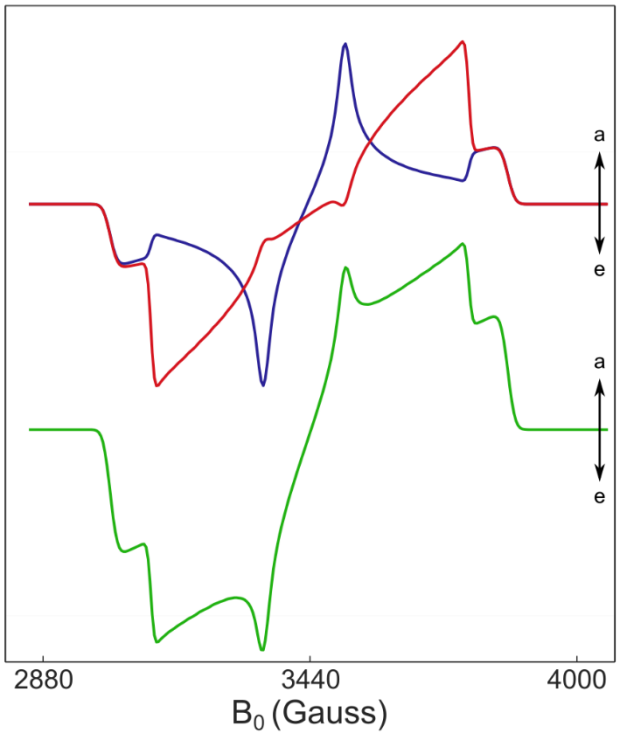

Figure S10. Theoretical effects that would be produced by an efficient tautomerization in the triplet state on the EPR spectrum of **H_2TPPS^{4-}**: the initial spectrum (in red), the inverted spectrum (in blue) and the combination (1:1) of the initial and inverted spectrum (in green), the latter representing how the spectrum should evolve in time in the presence of fast tautomerization in the excited triplet state.

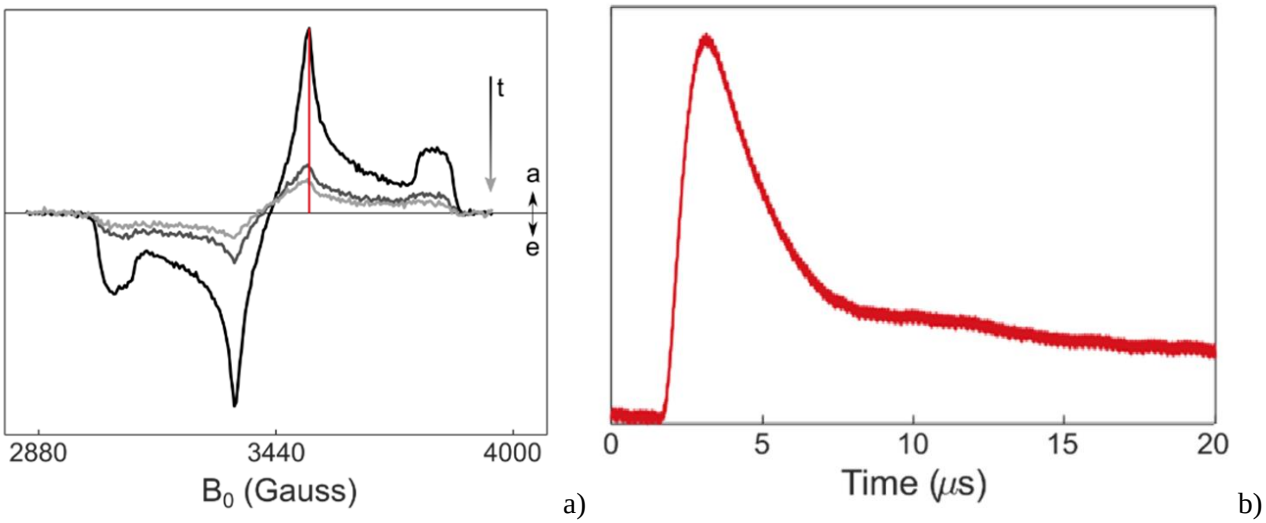

Figure S11. a) Triplet state TR-EPR spectra of **D_2TPPS^{4-}** in deuterated methanol at 80 K extracted 3 (black), 10 (dark gray) and 20 μs (light gray) after the laser flash. b) EPR decay trace at the Y canonical ZFS transition, (indicated with a red bar on the TR-EPR spectra).