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Original Citation:

Availability:

This version is available at: 11577/3325485 since: 2020-02-04T18:05:28Z

Publisher:

American Institute of Physics Inc.

Published version:

DOI: 10.1063/1.5131753

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(Article begins on next page)

Comprehensive investigation on the triplet state electronic structure of free-base 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin by a combined advanced EPR and theoretical approach

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Cite as: J. Chem. Phys. 152, 000000 (2020); doi: 10.1063/1.5131753

Submitted: 15 October 2019 • Accepted: 19 December 2019 •

Published Online: XX XX XXXX



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ABSTRACT

The nature of the photoexcited triplet state of free-base 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS^{4-}) has been investigated by advanced Electron Paramagnetic Resonance (EPR) techniques combined with quantum chemical calculations. The zero-field splitting (ZFS) parameters, D and E, the orientation of the transition dipole moment in the ZFS tensor frame, and the proton hyperfine couplings have been determined by magnetophotoselection-EPR and pulse electron-nuclear double resonance spectroscopy. Both time-resolved and pulse experiments exploit the electron spin polarization of the photoexcited triplet state. Comparison of the magnetic observables with computational results, including CASSCF calculations of the ZFS interaction tensor, provides an accurate picture of the triplet-state electronic structure. The theoretical investigation has been integrated with a systematic analysis on the parent free-base porphyrin molecule to assess the effect of the sulfonatophenyl substituents on the magnetic tensors. Additionally, the magnetophotoselection effects are discussed in terms of tautomerization in the excited singlet state of H_2TPPS^{4-} .

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I. INTRODUCTION

Porphyrins and their derivatives constitute an important class of biomolecules because of their involvement in several fundamental biochemical processes.^{1,2} To date, the main application of these compounds has been as model biosystems and, interestingly, also in the field of applied sciences. Porphyrin-based materials are good candidates for molecular electronic devices, new solar cells, and they have been shown to function as components of molecular and photonic wires and in nonlinear optical materials, to give only few significant examples.³⁻⁷

Among the properties that have received much attention in recent years, there is the ability of porphyrinoid molecules to participate in energy-transfer and electron-transfer reactions, playing a central role in these photoinitiated processes in a similar manner as chlorophyll and bacteriochlorophylls act in the primary events of photosynthesis.^{8,9} Inspired by natural photosynthetic antenna complexes and reaction centers, porphyrin-based systems are being designed and investigated for applications in artificial photochemical conversion and storage of solar energy.^{10,11} Water-soluble porphyrins are considered particularly suited for such applications. Among self-assembling chromophores, they are gaining a relevant

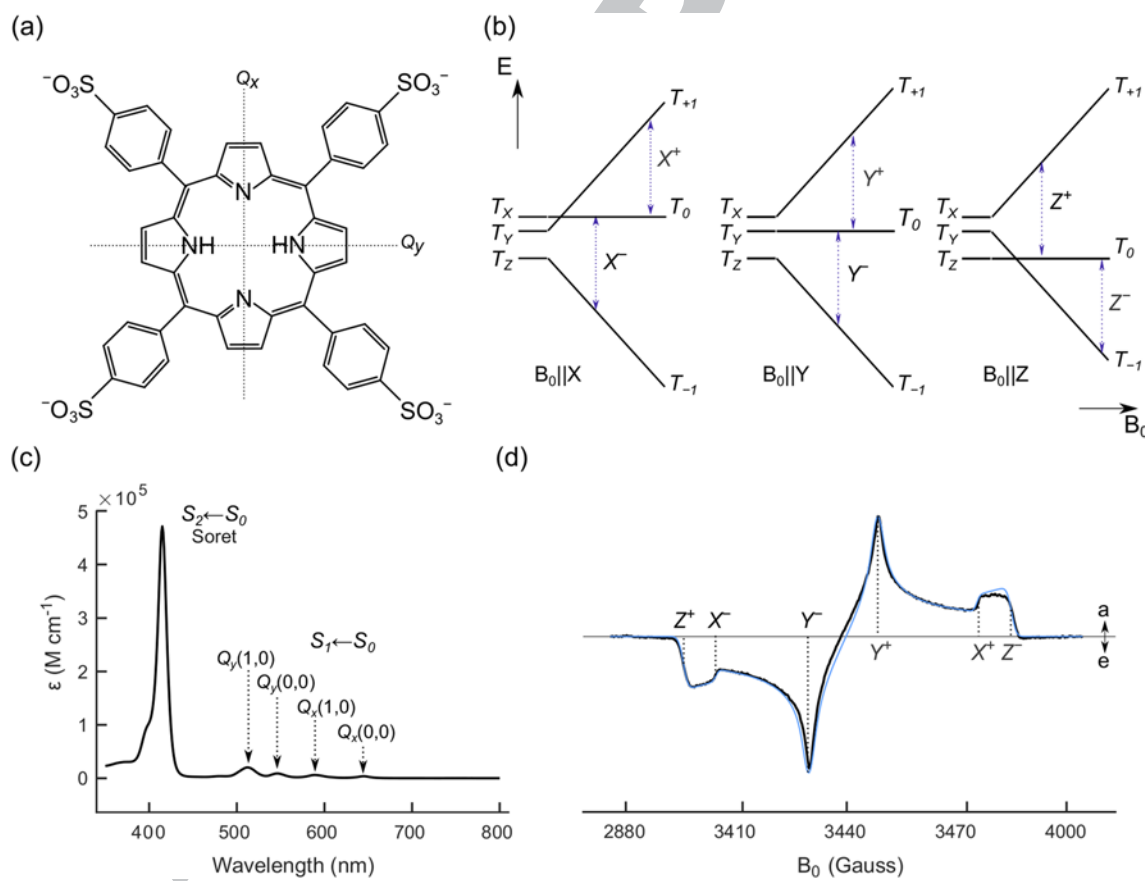
51 position as building blocks for the design of chlorosome-mimicking
52 antennas due to the possibility of fine-tuning of their spectro-
53 scopic and structural properties by conveniently modifying their
54 sidechains.^{12,13} A smart technique to control the aggregation pro-
55 cess of tetraphenylporphyrin derivatives involves functionalization
56 of the side chains with charged groups and the fine regulation
57 of the pH of the solvent,^{14,15} as in the case of the anionic free-
58 base 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2\text{TPPS}^{4-}$),
59 which forms J-aggregates in acidic aqueous solutions.¹⁶⁻¹⁸

60 Determining the extent to which the $\text{H}_2\text{TPPS}^{4-}$ moiety may
61 or may not be effective as a model compound in artificial photo-
62 synthesis requires a detailed understanding, and hence an extensive
63 characterization, of its photophysical properties in terms of excited
64 states. While the singlet excited states have been thoroughly investi-
65 gated also from the computational point of view, less is known about
66 the triplet state due to the *dark* nature of this state that precludes
67 the application of most of the optical spectroscopies. Photogener-
68 ated triplets are key reaction intermediates in many light-induced

73 processes and they show encouraging features that can be exploited
74 in the field of solar light harvesting.¹⁹

75 A time-resolved Electron Paramagnetic Resonance (TR-EPR)
76 investigation²⁰ on the triplet state of $\text{H}_2\text{TPPS}^{4-}$ in different
77 monomeric and aggregated forms has shown variations in the mag-
78 netic properties going from one species to the other, which have
79 prompted us to further investigate the free-base $\text{H}_2\text{TPPS}^{4-}$ (the
80 molecular structure is shown in Fig. 1) by advanced magnetic
81 resonance and theoretical methodologies.

82 TR-EPR is a powerful technique for the investigation of pho-
83 toexcited triplet states and extensive studies employing this spec-
84 troscopy have been performed on porphyrins.^{21,22} The key data are
85 the zero-field splitting (ZFS) parameters D and E , which are sen-
86 sitive indicators of the spatial extension and symmetry of the two
87 singly occupied molecular orbitals of the triplet state. In addition,
88 TR-EPR allows us to determine the orientation of this interaction
89 within the molecule, probing the geometrical relation between the
90 optical transition dipole moment (TDM) of the molecule and the



69 **FIG. 1.** (a) Molecular structure of $\text{H}_2\text{TPPS}^{4-}$ with the corresponding TDM directions for the Q_x and Q_y transitions. (b) Energy diagram of the triplet spin sublevels, for $D > 0$
70 and $E < 0$, as a function of the magnetic field B_0 , with the field vector parallel to the principal axes of ZFS. The arrows indicate the allowed EPR transitions according to the
71 selection rule $\Delta m_S = \pm 1$. (c) Room-temperature absorption spectrum of $\text{H}_2\text{TPPS}^{4-}$ in ethanol/methanol 3:2 solution, with the names of the absorption bands according to
72 the Gouterman model.⁶⁴ (d) Isotropically excited TR-EPR spectrum of $\text{H}_2\text{TPPS}^{4-}$ (black) and corresponding simulation (light blue). The simulation parameters are reported
in Table I.

91 resulting triplet state by using linearly polarized light for excita- 144
92 tion.^{21,23,24} In the past, such magnetophotoselection experiments 145
93 were performed on aromatic molecules and were crucial in reveal- 146
94 ing details of the electronic structure of the main chromophores 147
95 taking part in early events of photosynthesis.^{25,26} Magnetophoto- 148
96 selection has been recently repropoed to study porphyrin model 149
97 compounds.^{27,28}

98 The ZFS parameters are integral properties of the triplet wave- 150
99 function and depend on its overall spatial distribution. More spe- 151
100 cific information about the electron distribution in the HOMO and 152
101 LUMO orbitals is obtained from the electron-nuclear hyperfine cou- 153
102 pling (hfc) tensors, from which the distribution of the unpaired 154
103 electrons of the triplet state is obtained.^{22,29} In contrast to the large 155
104 body of EPR and Optically Detected Magnetic Resonance investi- 156
105 gations yielding *D* and *E* parameters and, in the case of TR-EPR, 157
106 also the electron spin-polarization pattern, there are only a few 158
107 studies on the hyperfine structure of the triplet state of porphyrins 159
108 resolved by Electron-Nuclear Double Resonance (ENDOR) spec- 160
109 troscopy.^{27,30–33} Pulse ENDOR, combined with repetitive laser exci- 161
110 tation, takes advantage of the large spin polarization of the triplet 162
111 state being present only in the first few microseconds after the laser 163

112 Detailed information on the structure of the porphyrin triplet 164
113 state may be derived by comparison of experimental ZFS parameters 165
114 and proton hfc values (hfcs) with the results of quantum mechanical 166
115 calculations. Nowadays, computational methods are well established 167
116 for most of the spin Hamiltonian parameters, such as hfc tensors and 168
117 *g* tensors.³⁴ The additional fine structure observed in triplet state 169
118 spectra due to the electron–electron spin coupling, in contrast to 170
119 the other spin Hamiltonian terms, has been addressed only for small 171
120 molecules and there is not a consolidated approach for its quantita- 172
121 tive analysis.^{35–37} A limited number of theoretical studies undertak- 173
122 ing the calculation of the ZFS tensor of porphyrins has been reported 174
123 so far and, to the best of our knowledge, no one based on multicon- 175
124 figuration post HF methods for this important class of heterocyclic 176
125 tetrapyrrolic compounds.^{27,38,39}

126 In this contribution, a comprehensive study of the triplet state 177
127 of $\text{H}_2\text{TPPS}^{4-}$ is provided by combining the advanced EPR techni- 178
128 ques, best-suited for the triplet state investigation, and state-of- 179
129 the-art computational methods, which permit accurate calculation 180
130 of the magnetic observables, i.e., ZFS parameters and proton hfcs. In 181
131 parallel, the free-base porphyrin (H_2P) molecule, which is the parent 182
132 compound, will be addressed to stress the similarities and differences 183
133 due to the substituents in $\text{H}_2\text{TPPS}^{4-}$. The nice agreement between 184
134 the experimental and computed hfcs and ZFS parameters, includ- 185
135 ing the ZFS tensor orientation with respect to the TDM, allows us to 186
136 propose a reliable and detailed picture of the triplet wavefunction of 187
137 a representative member of this important class of molecules. This 188
138 is essential for designing novel artificial systems and for develop- 189
139 ing further applications, which exploit the photophysics of the triplet 190
state. 191

140 II. MATERIALS AND METHODS

141 A. Sample preparation

142 $\text{H}_2\text{TPPS}^{4-}$ was purchased from Sigma Aldrich and used with- 192
143 out further purification. All the $\text{H}_2\text{TPPS}^{4-}$ solutions used for 193

144 spectroscopic characterization were freshly prepared by dissolving 145
146 the powder in a mixture of ethanol and methanol 3:2. The con- 147
148 centration of the solutions was determined by optical absorption 149
150 spectroscopy and has a final value of about 60 μM . The choice of 151
152 using a mixture of ethanol and methanol for the monomeric sam- 153
154 ples has the important advantage of generating a good glass when 155
156 frozen.

157 Samples for EPR were degassed by freeze and thaw cycles, 158
159 inserted into quartz EPR tubes (2.4 mm inner diameter, 4 mm 160
161 outer diameter), sealed under vacuum, and immediately frozen 162
163 in liquid nitrogen. Samples were stored in liquid nitrogen until 164
165 measurements. 166

167 B. EPR measurements

168 TR-EPR spectra were recorded at X-band on a Bruker Elexsys 169
170 E580 spectrometer equipped with a dielectric cavity thermostated 171
172 at 80 K with a cold nitrogen vapor flow inside a CF935 cryostat. 173
174 The microwave power used for the TR-EPR experiments was about 174
175 1.5 mW. TR-EPR spectra were recorded in direct detection mode 175
176 without applying any field modulation or phase-sensitive detection. 176
177 The EPR signals were collected from the microwave preamplifier 177
178 (bandwidth 20 Hz–6.5 MHz) and sampled with a LeCroy 9360 oscil- 178
179 loscope (10 ns per point). The time resolution of the spectrometer 179
180 has been estimated to be about 900 ns, mainly due to the cavity 180
181 response. Laser excitation of the samples was performed using an 181
182 optical parametric oscillator (OPO) pumped by the third harmonic 182
183 of a Nd:YAG laser (Quantel Rainbow), operating at a repetition rate 183
184 of 10 Hz. Laser pulses were 5 ns long, with energies of 3.5 mJ, and a 184
185 wavelength of 520 nm. Two different polarizations of the light were 185
186 employed for the magnetophotoselection experiments: one with the 186
187 electric field perpendicular and the other parallel to the static mag- 187
188 netic field of the spectrometer. The rotation of the polarization plane 188
189 of the light was obtained using a half waveplate; a linear polarizer 189
190 was added near the optical window of the cavity for a better con- 190
191 trol of the polarization. To record the isotropic TR-EPR spectrum, 191
192 a solution frozen to form a bad milky glass (therefore composed 192
193 of microcrystallites) was used in order to obtain depolarization by 193
194 multiple scattering events. 194

195 X-band pulse EPR experiments were conducted on a Bruker 195
196 Elexsys E580 equipped with a dielectric ENDOR cavity (EN4118X- 196
197 MD4) ~9.5 GHz. The temperature was maintained at 20 K with 197
198 a helium cryostat with optical access (Oxford CF935) driven by 198
199 a temperature controller (Oxford ITC503). The radio frequency 199
(RF) amplifier was ENI A-500W. Pulsed laser excitation at 532 nm 200
(5 mJ per pulse and repetition rate of 10 Hz) was provided by 200
201 the second harmonic of a Nd:YAG laser (Quantel Brilliant). Field- 201
202 swept electron spin echo spectra were recorded using a two-pulse 202
203 echo sequence according to the scheme: flash–DAF– $\pi/2$ – τ – π – τ – 203
204 echo (DAF = delay after flash). Mims ENDOR experiments were 204
205 recorded using the microwave pulse sequence, flash–DAF– $\pi/2$ – τ – 205
206 $\pi/2$ –T– $\pi/2$ –echo, with 16 ns pulse duration, in conjunction with an 206
207 RF pulse of 6 μs duration located during the delay T and starting 207
208 1.2 μs after the second microwave pulse. The delay τ was variable and 208
209 the time T was 8.8 μs , long enough to accommodate the RF pulse. 209
210 Mims ENDOR spectra were recorded at three different τ values (120, 210
211 180, and 240 ns) and added together to eliminate τ -dependent blind 211
212 spots. Pulse ENDOR spectra were accumulated for ~5 h. 212

C. Spectral analysis

TR-EPR data were processed by subtracting: (i) the average baseline before the trigger event and (ii) a time profile taken at an off-resonance position. Spectra were extracted as single time points at about 1.4 μs after pulsed laser excitation.

Simulations of triplet spectra have been performed using a home-written MATLAB program. For the isotropically excited TR-EPR spectrum, the parameters of the simulations include the g and ZFS tensors and the relative triplet sublevel populations. For the magnetophotoselection TR-EPR spectra, in order to take into account the photoselection of specific orientations, a probability function is also included.

TR-EPR spectra recorded for light polarized parallel and perpendicular to the magnetic field direction were analyzed according to Ref. 23. Here, only a brief summary of the procedure is presented.

When a polarized light source is used to photoexcite the sample, the probability to excite each molecule depends on the angle between the TDM and the direction of the light polarization. Assuming that, after the light excitation, an efficient intersystem crossing (ISC) takes place, the orientational distribution of triplet states inside the sample is uneven and depends on the direction of the TDM in the ZFS reference frame. For the analysis of the TR-EPR spectra in the presence of magnetophotoselection, it is convenient to express the probability p of exciting a specific molecular orientation as a function of the three Euler angles, (α, β, γ) , between the laboratory frame and the ZFS axes. For a specific orientation of the TDM in the ZFS frame, defined by the angles ω, φ , the excitation probability is

$$p_{\omega, \varphi}^{\text{par/perp}}(\alpha, \beta, \gamma) = (\hat{\mathbf{u}}_{\text{TDM}} \cdot \hat{\mathbf{u}}_E)^2 / N, \quad (1)$$

where $\hat{\mathbf{u}}_{\text{TDM}}$ and $\hat{\mathbf{u}}_E$ are the unit vectors along the direction of the TDM and the electric field component of the light. This probability function takes into account that molecules with different orientations are excited when the polarization of the light is varied from a parallel to a perpendicular configuration with respect to the static magnetic field.

The spectrum is calculated as⁴⁰

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

where $G[B_{\text{res}}(\alpha, \beta) - B_0]$ is a Gaussian line shape function centered at the resonance field B_{res} , $P_{\pm}(\alpha, \beta, B_0)$ is the non-Boltzmann population difference between the two resonant states, and $p_{\omega, \varphi}^{\text{par/perp}}(\alpha, \beta, \gamma)$ is the excitation probability specific for the parallel and perpendicular configuration. The analytical expressions obtained for the integral within the square brackets for the two orientations of the light polarization with respect to the static magnetic field are reported in the [supplementary material](#).

In the simulation of the magnetophotoselection data, depolarization effects are taken into account by allowing a low-weight contribution from isotropic light excitation. These effects are mainly due to multiple reflections inside the cavity and scattering of the light.

For the Mims ENDOR experiments, the values of the proton hfcs along the principal axes of the ZFS tensor were determined by Gaussian deconvolution of the ENDOR spectra.

D. Computational details

All calculations were carried out with the Amsterdam Density Functional (ADF) suite of programs.^{41–43} The hybrid B3LYP functional was used^{44–46} combined with a triple- ζ quality basis set of Slater-type functions (TZ2P) augmented with two sets of polarization functions. The innermost orbitals of each element were kept constant during the SCF cycles (frozen core approximation): up to 1s for carbon, nitrogen, oxygen, and sulfur. Dispersion effects were included using the correction proposed by Grimme, i.e., D3 with a BJ damping function.⁴⁷ This level of theory is denoted B3LYP-D3(BJ)/TZ2P. First, geometry optimizations of the archetypal H_2P and of $\text{H}_2\text{TPPS}^{4-}$ were performed using D_{2h} symmetry constraint.

TD-DFT calculations were carried out on the optimized geometries using all-electron TZ2P basis sets for all the atoms. The approximate xc potential obtained with the statistical averaging of (model) orbital potentials (SAOP) was used to calculate the excitation energies, which is suitably designed with a correct asymptotic behavior^{48,49} and has been employed with success to investigate excited state properties.^{50–52}

For the calculation of the hyperfine tensor, zero field splitting tensor, and spin density, both B3LYP-D3(BJ) and BP86^{53–55} functionals were used combined with all-electron TZ2P basis set. The scalar zeroth order regular approximation (ZORA)^{56–58} was employed to account for relativistic effects. These levels of theory are denoted ZORA-B3LYP-D3(BJ)/TZ2Pae and ZORA-BP86/TZ2Pae, respectively. No appreciable differences were found and so only data computed at the former level of theory will be discussed in the text. In order to investigate the effect of different orientations of the phenyl rings, geometries were manually built starting from the D_{2h} optimized structures with the rings at 30° and 60° with respect to the tetrapyrrolic plane, without altering the porphyrin core. In addition, for these dihedral values (which are explained in detail in Fig. S9), different mutual orientations of the rings were considered. The magnetic observables were computed for these geometries at the ZORA-BP86/TZ2Pae level of theory.

Due to the unsatisfactory results for the D tensor, ascribed mainly to the limitations of the single-determinant DFT approach, CASSCF calculations were carried out to compute the zero field splitting tensor, as implemented in ORCA software package.⁵⁹ The structures obtained by D_{2h} constrained geometry optimizations at the B3LYP-D3(BJ)/TZ2P level were used. MP2 natural orbitals from the unrelaxed density matrix were generated and employed as starting guess. The def2-TZVP basis set was used for all the atoms and def2-TZVP/C was used for the RI approximation. In the CASSCF calculations, def2/J in conjunction with RIJCOSX was employed to approximate the Fock operator for $\text{H}_2\text{TPPS}^{4-}$. A CAS(4,4) active space was chosen including the two π and the two π^* frontier molecular orbitals of H_2P and $\text{H}_2\text{TPPS}^{4-}$. The sets of four MP2 natural orbitals are shown in Figs. S1 and S2. The spin orbit contribution to the D tensor was computed, but, as expected, it resulted to be negligible; thus, the values reported and discussed in the text correspond to the spin-spin contribution.

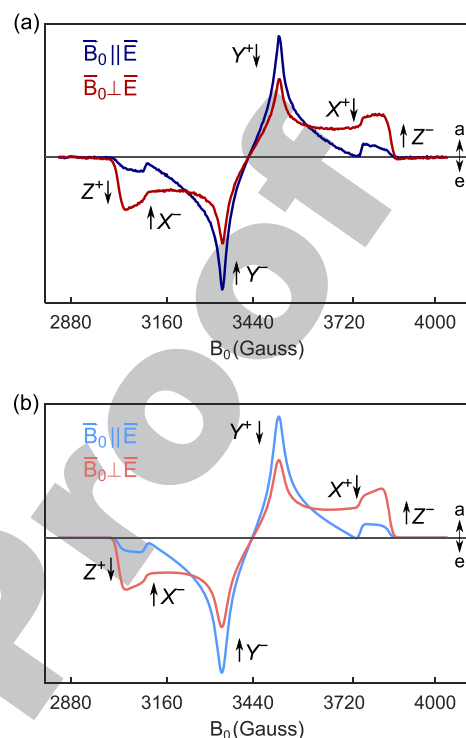
305 III. RESULTS

306 A. Time-resolved EPR and magnetophotoselection

307 Magnetophotoselection is a phenomenon observed for photo-
308 excited triplet states, generated by light polarized parallel or per-
309 pendicular to the magnetic field, making the relative intensities of
310 the EPR lines dependent on the light polarization. It is a consequence
311 of the fact that the EPR intensities depend not only on the population
312 difference between the triplet sublevels, but also on the nonuniform
313 spatial distribution of the molecules due to selective excitation. Mag-
314 netophotoselection has been used in a limited number of cases to
315 attain quantitative information on the relative orientation of the ZFS
316 tensor axes with respect to the optical transition moment, if one of
317 the two is known.^{23,60,61}

318 For $\text{H}_2\text{TPPS}^{4-}$, having a D_{2h} symmetry, the two absorption
319 Q bands are not degenerate and this results in two resolved sets
320 of peaks exhibiting a vibronic structure,⁶² with both the 0–0 and
321 the 0–1 transitions visible in the absorption spectrum as shown in
322 Fig. 1(c). The Q_y and Q_x transitions are characterized by a TDM
323 aligned along and perpendicular to the NH bonds, respectively, as
324 reported in the literature⁶³ and confirmed by the present DFT cal-
325 culations (see Table S2 in the supplementary material). This config-
326 uration is opposite to the one reported for H_2P .⁶³ The overall set
327 of optical properties calculated for $\text{H}_2\text{TPPS}^{4-}$ is summarized in the
328 supplementary material as they are functional to the calculations of
329 the magnetic properties derived from EPR-magnetophotoselection.
330 The magnetophotoselection experiments were performed by excit-
331 ing the Q_y transition by irradiating at 520 nm, where both the Q_x
332 transition and the J-aggregates have negligible absorption.²⁰

333 At first, the isotropically excited TR-EPR spectrum was
334 obtained from the frozen solution of $\text{H}_2\text{TPPS}^{4-}$ (see the experi-
335 mental details in the Materials and Methods section and Fig. S7).
336 Then, the TR-EPR spectra recorded after excitation of $\text{H}_2\text{TPPS}^{4-}$,
337 in a transparent glass carefully prepared to avoid cracks, with light
338 polarized parallel and perpendicular to the magnetic field, were
339 obtained and they are shown in Fig. 2. Since the experimental
340 set-up assured the same excitation conditions, the spectra are dis-
341 played without renormalization and show an evident magnetopho-
342 toselection effect, with enhanced X and Y triplet transitions in the
343 parallel spectrum and enhanced Z transitions in the perpendicular
344 spectrum. The spectra are also different from that obtained
345 by isotropic irradiation. To further confirm isotropic excitation of



359 **FIG. 2.** (a) TR-EPR spectra of $\text{H}_2\text{TPPS}^{4-}$, recorded at 80 K, using an excita-
360 tion light polarized parallel (blue) and perpendicular (red) to the magnetic field. (b)
361 Simulations of the TR-EPR spectra of $\text{H}_2\text{TPPS}^{4-}$ with polarization of the light par-
362 allel (light blue) and perpendicular (light red) to the magnetic field. The simulation
363 parameters are reported in Table I. The black arrows represent the enhancement
364 or the reduction of the signal when going from parallel to perpendicular excitation
365 at the canonical positions.

366 the molecules, we have compared the spectrum lineshape obtained
367 with isotropic irradiation with the one calculated as the sum of the
368 experimental spectrum recorded after excitation with polarization
369 of the light parallel to the external magnetic field and twice the spec-
370 trum obtained with perpendicular polarization, in analogy to optical
371 polarization measurements.⁶⁵ A nice matching of the lineshape of

346 **TABLE I.** ZFS parameters, relative triplet sublevel populations, and TDM orientation in the ZFS axes system determined
347 through simulation of the TR-EPR spectra.

	$D(10^{-4} \text{ cm}^{-1})$	$E(10^{-4} \text{ cm}^{-1})$	p_x	p_y	p_z	ω (deg)	φ (deg)	Weight (%)
Simulation ^a	391	-76	0.3	0.6	0.1	90	0	50
						90	90	50
Computation ^b	208	5

353 ^aThe D and E parameters and p_x, p_y, p_z were obtained from simulation of the isotropically excited TR-EPR spectrum. ω, φ , and
354 weight were extracted from simulation of the TR-EPR spectra recorded in the magnetophotoselection experiments. ω is the angle
355 between the Z axis of the ZFS axes system and the TDM, and φ is the angle between the X axis of the ZFS axes system and the
356 TDM projection into the XY plane (see Fig. 2). Weight is the contribution of each set of angles to the simulation.

357 ^bLevel of theory: CASSCF(4,4)/def2-TZVP//B3LYP-D3(BJ)/TZ2P.

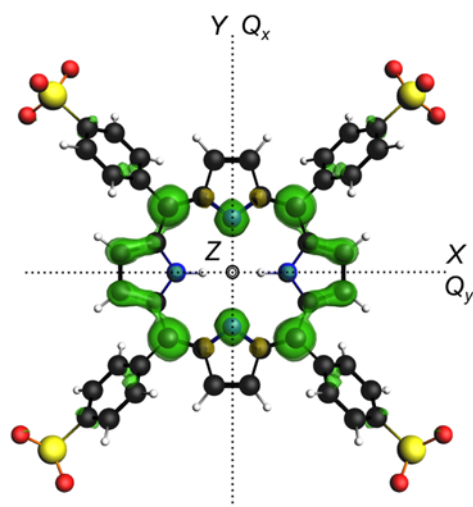


FIG. 3. Optimized geometry of $\text{H}_2\text{TPPS}^{4-}$ [level of theory: B3LYP-D3(BJ)/TZ2P] and triplet state spin density [level of theory: BP86/TX2Pae//B3LYP-D3(BJ)/TZ2P] with the calculated orientations of the optical TDM and the ZFS principal axes [level of theory: CASSCF(4,4)/def2-TZVP//B3LYP-D3LYP(BJ)/TZ2P].

the experimental and the calculated spectra was obtained, as shown in Fig. S7.

Spectral simulations were performed in order to define quantitatively the geometrical relation between the TDM and the ZFS tensor axes in the magnetophotoselection experiments. The key parameter of the simulation is the orientational distribution function reported in Eq. (1), while D , E , and the relative triplet population rates are fixed parameters and are derived from the isotropically excited spectrum. The simulations exhibit not only the correct line-shape, but also the experimental trend in terms of relative intensities. Unexpectedly, the outcome of the global fitting is that the distribution function is the sum of two contributions, with either the principal axes X and Y of the ZFS system aligned along the TDM with an equal weight and an estimated error of 5° at most (for details see Fig. S8 in the supplementary material). A single contribution is unable to reproduce all the features of the spectra and the intensity variations from the parallel to the perpendicular configuration. No optical TDM is associated with the triplet Z axis, confirming the assignment of this axis to the out-of-plane direction and the positive value of D for $\text{H}_2\text{TPPS}^{4-}$ as found for other free-base analogs.⁶⁶ Table I summarizes the outcome of the spectral analysis, comparing the results on the ZFS tensor with those calculated using the CASSCF method. The orientation of the ZFS tensor in the molecular frame, as derived from computations, is displayed on top of the optimized geometry of $\text{H}_2\text{TPPS}^{4-}$ in Fig. 3.

B. Triplet state ^1H ENDOR

Triplet state ^1H ENDOR permits measurement of the hfc tensor component in the reference frame of the ZFS tensor, since it is characterized by a strong orientation selection. For each EPR canonical transition, there are two ENDOR resonance frequencies at

$$\nu_{\text{ENDOR}}(0) = \nu_H, \quad (3)$$

$$\nu_{\text{ENDOR}}(\pm 1) = \nu_H \pm A_i, \quad \text{with } i = X, Y, Z, \quad (4)$$

where ν_H is the free-proton nuclear Larmor frequency, A_i is the sum of the Fermi-contact interaction, A_{iso} , and the dipolar contribution.^{21,67}

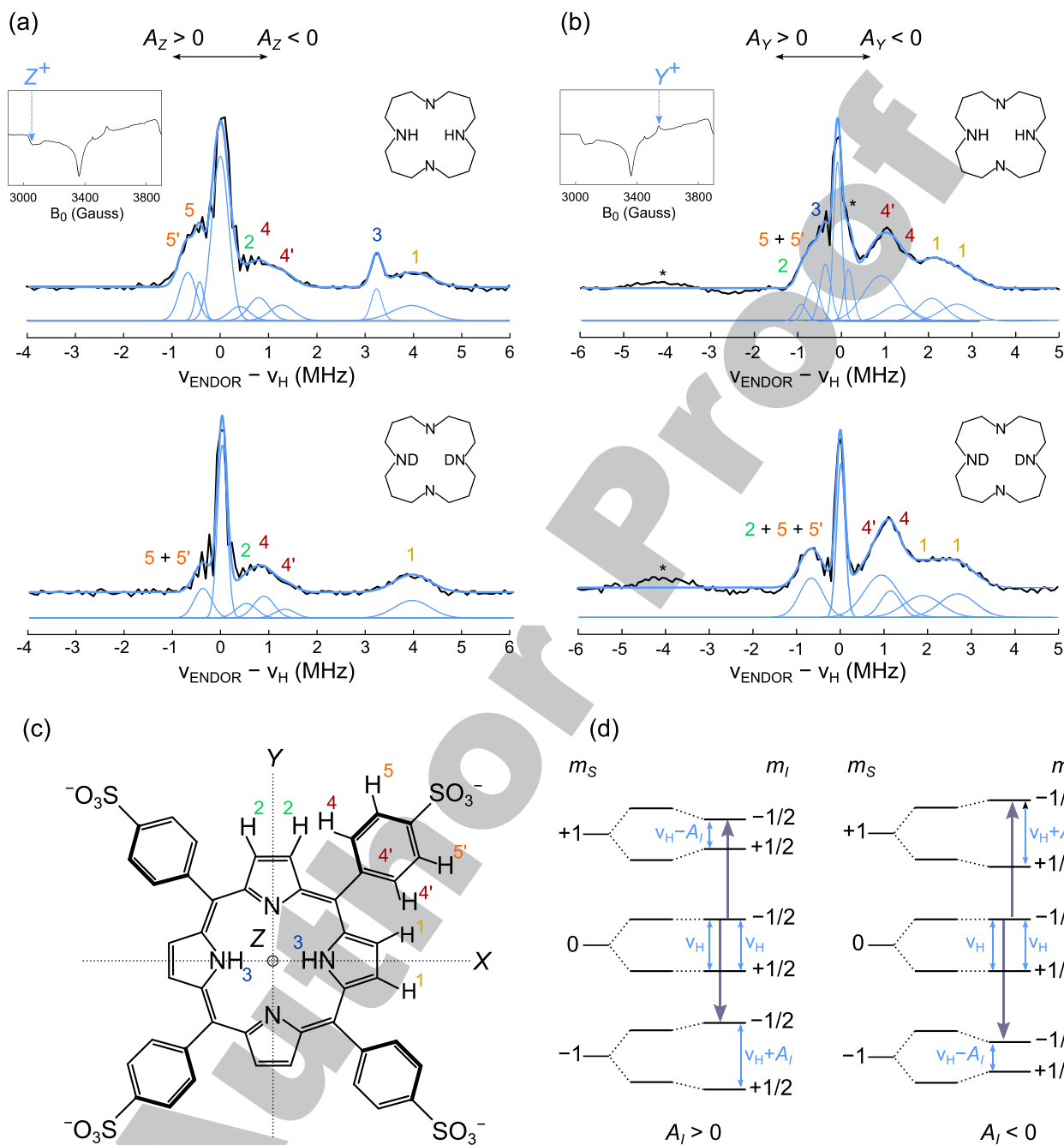
It can be seen from these equations that the resulting triplet-state ENDOR spectrum is asymmetric, providing the further advantage of allowing us to determine the sign of the hfcs relative to the sign of the D value. The line at resonance frequency ν_H is common for all protons and, consequently, attains a high intensity.

The ^1H Mims ENDOR spectra recorded for $\text{H}_2\text{TPPS}^{4-}$ at two of the canonical field positions, Y^+ and Z^+ , in protonated and deuterated solvent, are shown in Figs. 4(a) and 4(b). In the corresponding insets, the echo-detected spectrum is reported in order to highlight the working field positions. Since the D value for $\text{H}_2\text{TPPS}^{4-}$ is known to be positive from CASSCF calculations, the sign of the proton hfcs is assigned as indicated on top of the ENDOR spectra. The hfcs along the Y and Z axes of the ZFS tensor were determined through Gaussian deconvolution, and the results are shown in Table II. The spectral features, which disappear in the spectra of $\text{D}_2\text{TPPS}^{4-}$ in the deuterated solvent, are unambiguously assigned to the NH protons (3) since deuterium exchange takes place for those central protons.

A comparison with the results of the DFT calculations at the ZORA-BP86/YZ2Pae//B3LYP-D3(BJ)/TZ2P level on the excited triplet state of $\text{H}_2\text{TPPS}^{4-}$ has allowed assignment of all the hfcs to specific protons. The calculations were performed in the ZFS tensor frame, as the principal hfc tensor components are, in most cases, not collinear with the ZFS tensor. The hfcs have been calculated for several different conformers with imposed rotations of the phenyl rings, as shown in Fig. S9. The calculated hfc tensors, reported in Table II, refer to the conformer, in which the phenyl rings have been rotated, counterclockwise-clockwise-clockwise-counterclockwise, by 60° with respect to the tetrapyrrolic plane. The choice of a specific conformer has been guided by the matching between the calculated and experimental hfcs. However, it has emerged from the analysis that, while the angle between the tetrapyrrolic macrocycle and the phenyl substituents is affecting the hfcs significantly, the mutual orientation of the rings is not relevant. The conformation with the phenyl rings at 90° with respect to the tetrapyrrolic plane shows a number of ENDOR peaks smaller than that experimentally observed. Finally, the conformers with the rings at 30° , beyond being unstable from an energetic point of view, present strong deviations from the experimental hfcs in the Z components of H (4).⁶⁸ The results for all the conformations are summarized in Table S5 and the comparison between the experimental and calculated hfcs is reported in Fig. S10.

DFT calculations predict a single hfc for the H (1) and H (2) protons, while experimentally two hfcs can be attributed to the H (1) protons. This can be clearly seen in the ENDOR spectra corresponding to the Z transition and for this reason the deconvolution of the corresponding peaks requires a large Gaussian component or even two components. In the literature, the symmetry lowering from D_{2h} to C_{2h} was ascribed to interactions with the solvent or to the admixture of a second triplet state.^{32,69}

The trend of the computed A_Z components is in excellent agreement with those determined experimentally: the α -protons H (2) have small negative hfcs, while the H (1) and the NH (3) have



464 **FIG. 4.** X-band pulsed Mims ENDOR spectra of $\text{H}_2\text{TPPS}^{4-}$ (top) and $\text{D}_2\text{TPPS}^{4-}$ (bottom) recorded at 20 K along the Z^+ (a) and the Y^+ (b) ZFS canonical transitions, as
 465 indicated by the red arrows in the field-swept electron spin echo spectra shown in the insets. The ENDOR spectra are displayed together with the best fit (light blue) given
 466 by Gaussian functions below the spectra. The signs of the hfc's are shown above the spectra. The attribution of the peaks in the ENDOR spectra is represented according
 467 to the numbering scheme shown in (c). The asterisks denote the ENDOR peak arising from residual contributions of other orientations or free-proton lines disappearing after
 468 deuteration. (c) Molecular structure of $\text{H}_2\text{TPPS}^{4-}$ and corresponding orientation of the ZFS principal axes and numbering scheme of the protons adopted in this work. (d)
 469 Energy of the spin sublevels of a triplet state coupled to a nucleus $I = 1/2$ with positive and negative hyperfine splitting, for the magnetic field parallel to a generic ZFS axis.
 470 The gray arrows indicate the EPR transitions for $m_I = -1/2$ (those for $m_I = +1/2$ are omitted), the light blue arrows indicate the ENDOR transitions.

TABLE II. Experimental and computed proton hfc tensors of $\text{H}_2\text{TPPS}^{4-}$ in the ZFS frame.

	Hyperfine coupling (MHz)	H (1) ^a	H (2)	H (4)	H (4)'	H (5)	H (5)'	NH (3) ^b
ENDOR ^c	A_X
	A_Y	-2.17/-2.75	+0.84	-1.40	-1.00	+0.57	+0.57	+0.28
		-1.86/-2.69	+0.67	-1.15	-0.94	+0.67	+0.67	
	A_Z	-3.96	-0.40	-0.80	-1.28	+0.43	+0.67	-3.24
		-3.93	-0.50	-0.86	-1.30	+0.40	+0.40	
	A_{iso}
DFT	A_X	-1.81	+0.25	-0.69	-1.15	+0.81	+0.58	-0.08
	A_Y	-3.73	+1.03	-0.84	-0.60	+0.74	+0.80	-0.09
	A_Z	-3.79	-0.50	-0.75	-0.97	+0.66	+0.68	-3.08
	A_{iso}	-3.11	+0.26	-0.76	-0.91	+0.73	+0.69	-1.09

^aTwo values are reported for the A_Y component of H (1), because its ENDOR signal has been deconvoluted employing two Gaussian functions.

^bThe only hyperfine coupling available for the NH proton is that of the protonated porphyrin $\text{H}_2\text{TPPS}^{4-}$.

^cFor each proton, two experimental hfc values are reported: one for the fully protonated porphyrin, $\text{H}_2\text{TPPS}^{4-}$ (top value), and the other for $\text{D}_2\text{TPPS}^{4-}$ (bottom value).

larger negative hfcs. A similar behavior has been observed previously for both the H_2P and the free-base tetraphenylporphyrin molecules, indicating that the presence of the $(\text{SO}_3)^-$ substituent does not significantly affect the spin density distribution in the triplet state.³² The small hfcs, in the vicinity of the strong Larmor peak, have been assigned to the different types of phenyl protons. Close to ν_{H} , there is also a contribution from protons with weak dipolar interactions with the unpaired electrons, such as protons in the solvent, which give rise to the “matrix” ENDOR line. These peaks disappear, as expected, in deuterated solvent.

The assignment of the experimental values obtained for A_Y , which has been reported in the literature only in the case of H_2P and for an incomplete set of protons,⁷⁰ is not as straightforward as for the A_Z components. Although the hfc calculated in the Y direction of the ZFS tensor is slightly overestimated for protons (1), even considering different possible conformers, the overall picture of the hfcs is perfectly in line with the experimental results. Small positive values are computed for the both the α -protons H (2) and the NH (3), while a larger negative contribution is found for the α -protons H (1).

Experimentally, the directions of the in-plane principal axes could not be distinguished by magnetophotoselection, as already pointed out in Sec. III A. Furthermore, although CASSCF calculations were performed to improve the accuracy of the ZFS parameters, E remains a critical parameter to be computed as it derives from the difference between two large components of the dipole-dipole coupling tensor. A significant inaccuracy in the estimation of E is accompanied by a potential mismatch of the directions of the associated in-plane principal axes. Indeed, a satisfactory agreement can also be obtained when comparing the ENDOR experimental values with the calculated A_X components, improving the accordance for protons (1) but at the expense of protons (2). This uncertainty is exacerbated by the impossibility to use the ENDOR data recorded along the X field position for an unequivocal assignment, due to the contamination of residual lines from other orientations. In addition, the orientation selection at the Y field positions is not as good as for the Z position, and therefore, hfcs are not as reliable.

From the assigned hfcs, a map of the spin-density distribution of the triplet electrons over the molecule can be obtained. The calculated spin-density plot is depicted in Fig. 3.

IV. DISCUSSION AND CONCLUSIONS

In this work, we elucidate the electronic structure of the lowest excited triplet state of $\text{H}_2\text{TPPS}^{4-}$. The interpretation requires a combination of magnetic resonance and accurate quantum chemistry methods in order to yield precious information on the triplet wavefunction. This is essential if a deeper understanding of the nature of this excited state has to be attained.

The approach here adopted is the combination of multiple EPR spectroscopic observables and computational results. The experiments allowed both ZFS and hfc tensors to be determined, the former with respect to the TDM in the magnetophotoselection experiment and the latter in the ZFS frame using pulsed ENDOR spectroscopy, as presented in the Results section. The existing literature on the EPR of the triplet state of porphyrins is complete in terms of ZFS parameters and spin polarization pattern but few EPR-magnetophotoselection experiments are available and no simulations are reported, allowing only a qualitative interpretation of the spectra, which contain important structural information.^{27,71,72} For triplet states, in general, due to technical difficulties of performing ENDOR on transient species, only sparse experimental data have been reported on molecules of biological interest, including porphyrinoids.^{21,22,32,73} In most cases, including the H_2P triplet state, only the A_Z component of the hfc tensor has been measured.^{30,32} This prompted us to perform this comprehensive investigation. The interest for $\text{H}_2\text{TPPS}^{4-}$ derives from the relevant applications of water-soluble porphyrins due to their ability to form J-aggregates. The accuracy in the study of porphyrin monomers appears as an important prerequisite for their use in aggregates.

The computational investigation on the electronic and magnetic features of the lowest excited triplet state of $\text{H}_2\text{TPPS}^{4-}$ was preceded by a systematic analysis on the parent H_2P , which is the basic building block of the porphyrins, to assess the role of the

substituents on the magnetic tensors, while the electronic absorptions have been more extensively discussed in the literature, as commented in the following.

For ${}^1\text{H}_2\text{P}$, the four-level Gouterman model works well, since the frontier orbitals consist of two almost degenerate filled levels well separated from two almost degenerate empty levels. Based on different DFT methods, these orbitals span the irreducible representation a_u (HOMO-1), b_{1u} (HOMO), b_{3g} (LUMO), b_{2g} (LUMO+1),^{32,74,75} with some changes in the relative order of the filled and the empty levels depending on the potential. CASSCF calculations provided this order: b_{1u} (HOMO-1), a_u (HOMO), b_{3g} (LUMO), b_{2g} (LUMO+1).⁷⁶ The lowest computed dipole allowed absorptions have been reported to have ${}^1\text{B}_{3u}$, ${}^1\text{B}_{2u}$, and ${}^1\text{B}_{1u}$ irreducible representations both with TDDFT methods^{77,78} as well as with CASPT2 calculations.^{76,79} This assignment is also consistent with the Gouterman four-orbital model,⁶⁴ according to which the Q (and higher energy B) bands derive primarily from transitions from the two highest π occupied molecular orbitals into the two π^* lowest unoccupied orbitals. The spectrum, computed by us in gas phase using the SAOP potential, shows the Q-bands at 2.188 eV (B_{3u}) and 2.312 eV (B_{2u}) with oscillator strengths of 0.17×10^{-4} and 0.12×10^{-3} , polarized along the NH (3) pyrrole rings and the N pyrrole rings. The energy values are in rather good agreement with the experimental data, which fall in the range of 1.98–2.02 and 2.33–2.42,^{80–82} but the splitting is too low if compared to the gas-phase measured value (0.44 eV). The same issue was reported by Baerends and co-workers⁷⁷ and was ascribed to the geometry sensitivity. Also, the values of the computed oscillator strengths are geometry-dependent and similar very small values have been reported in the literature.⁷⁸ Finally, although Q_y is commonly considered the most intense transition,⁸⁰ different computational studies identify Q_x as stronger,^{78,81} in agreement with our findings. Q_x and Q_y absorptions are ascribed to HOMO-LUMO (54%) and HOMO-1-LUMO+1 (45%) and to HOMO-LUMO+1 (58%) and HOMO-1-LUMO (42%), clearly denoting the mixed character of the lowest singlet excitons, which involve the four Gouterman orbitals. This is in agreement with the analysis by Rubio and co-workers⁷⁵ and Barone *et al.*⁶³ We point out that no mixing of states with different orientation of transition dipole moment is present. In contrast, the lowest triplet excitons have almost mono-electronic character: for H_2P , they are computed at 1.804 eV and 2.017 eV (B_{2u}) and at 1.906 eV and 2.024 eV (B_{3u}) and are due to HOMO-LUMO+1 (96%) and HOMO-1-LUMO (96%) and to HOMO-LUMO (99%) and HOMO-1-LUMO+1 (99%).

The same analysis of the singlet and triplet lowest absorptions was carried out for $\text{H}_2\text{TPPS}^{4-}$, and some analogies with H_2P have emerged. The Q_y and Q_x bands are computed at 1.969 eV (B_{2u}) and at 2.502 eV (B_{3u}) with oscillator strengths of 0.0012 and 0.070, respectively. Their composition is HOMO-4-LUMO (98%) and HOMO-LUMO+1 (60%) and HOMO-5-LUMO+1 (28%). These values nicely compare to the experiment⁸³ and to those reported by Barone *et al.* in water.⁶³ Particularly, the polarization of the lowest absorptions is inverted (see Fig. 1), as amply discussed by the latter authors. The lowest triplet absorption of $\text{H}_2\text{TPPS}^{4-}$ is computed at 1.6739 eV (B_{2u}) and corresponds to HOMO-LUMO+1 (97%) at the employed level of theory.

It is important to stress that in this work we have not put effort in optimizing the absorption wavelengths, since our primary goal

is the investigation of the magnetic properties and their relation to the triplet wavefunction. As an efficient approach, we imposed D_{2h} symmetry to our systems, which very well describes H_2P , but represents only one conformer of $\text{H}_2\text{TPPS}^{4-}$ due to the orientation of the phenyl rings, which are forced to be at 90° with respect to the porphyrin plane. Calculations of the optical properties, and in particular the polarization of the Q-bands, are relevant for the magnetophotoselection experiment, because they are employed to assign the relative orientation of the ZFS tensor axes within the molecule.

We extended the calculations to derive the ZFS parameters and the spin density distribution of the lowest triplet state of $\text{H}_2\text{TPPS}^{4-}$, evaluating in parallel the corresponding magnetic observables for H_2P , for which experimental and theoretical data are already available.^{30,32,38} While in the main text the focus is on $\text{H}_2\text{TPPS}^{4-}$, the outcome of the calculations for H_2P is reported in the [supplementary material](#).

The analysis of the frontier molecular orbitals and of the lowest excited states of H_2P and $\text{H}_2\text{TPPS}^{4-}$ pointed out that, in both cases, a single Slater determinant description of the triplets might be nonadequate and this evidence must be taken into account when calculating the magnetic properties. Particularly, if the DFT approach gives spin density values and hyperfine tensors in nice agreement with the ENDOR experiment,^{84,85} the ZFS tensor is more sensitive to the wavefunction. We started our analysis employing a DFT approach. The geometries of H_2P and $\text{H}_2\text{TPPS}^{4-}$ were both optimized at the B3LYP-D3(BJ)/TZ2P level of theory in the triplet state. The hyperfine and ZFS tensors were also computed at the ZORA-B3LYP-D3(BJ)/TZ2Pae level as well as at the ZORA-BP86/TZ2Pae level, but no significant differences were found when comparing the results of the two approaches for H_2P .

The magnetic results were first obtained for D_{2h} constrained geometries. In order to investigate the effect of different orientations of the phenyl rings, two structures were obtained manually by imposing orientations of 30° and 60° with respect to the tetrapyrrolic plane while maintaining the geometry of the porphyrin core frozen. Importantly, the rings can be displaced in different manners and thus more conformations can be explored. We considered selected cases generated by rotating the rings clockwise (conformers A30 and A60), alternated clockwise and counterclockwise (conformers B30 and B60), and counterclockwise-clockwise-clockwise-counterclockwise (C30 and C60). Based on the energetics, the conformers with the phenyl rings rotated by 30° were discarded. The conformers with the phenyl rings rotated by 60° are the lowest energy structures, although the D_{2h} constrained geometry with the rings at 90° lies only 1 kcal mol⁻¹ above. Among the 60° structures, C60 is the most stable, although by less than 0.5 kcal mol⁻¹ at the employed level of theory. The hfcs of all the three conformers with the phenyl rings at 60° are found to be in excellent agreement with the experimental ENDOR data, especially for the Z component, which is also the most reliable direction due to the strong orientation selection that can be achieved. On the other hand, comparison with the ENDOR data provided further evidence that all the 30° conformations are unlikely to be present.

The combination of DFT calculations and ENDOR experiments allowed us to draw an accurate picture of the spin density distribution of the $\text{H}_2\text{TPPS}^{4-}$ triplet state. Compared to the H_2P parent compound (Fig. S4), even if a small amount of spin

668 density is moved to the phenyl rings, the overall distribution on the
669 tetrapyrrole macrocycle is conserved.

670 While the values of the A tensors are in good agreement with
671 the experiment, in the case of H_2P even slightly improving the
672 results reported in the literature,³² the computed ZFS tensor ele-
673 ments were unsatisfactory. Thus, we considered CASSCF as the
674 method of choice to improve the wavefunction. For the CASSCF
675 multiconfigurational approach, the inclusion of the whole π system
676 of the parent H_2P is already computationally demanding (24 orbitals
677 and 26 electrons), as extensively commented by Werner.⁸⁶ As the
678 Gouterman four orbitals model has proved to be robust, we decided
679 to define an active space formed by the four frontier orbitals, ranging
680 from HOMO-1 to LUMO+1, which in H_2P as well as in $\text{H}_2\text{TPPS}^{4-}$
681 have strong contribution from the π porphyrin core. MP2 natural
682 orbitals were generated as guess for the CASSCF calculation. For
683 H_2P , we computed two triplet states, i.e., ${}^3\text{B}_{2u}$ and ${}^3\text{B}_{3u}$, and the
684 former was found to be more stable, in agreement with the liter-
685 ature. For $\text{H}_2\text{TPPS}^{4-}$, we computed ${}^3\text{B}_{1u}$ and ${}^3\text{B}_{2u}$ and the latter
686 turned out to be more stable. The ZFS tensor was calculated using
687 the CASSCF wavefunction, showing that the spin-orbit component
688 is negligible, as already pointed out.

689 To the best of our knowledge, this is the first example of
690 calculation of the ZFS tensor based on a CASSCF calculation for
691 porphyrins. Further improvement might be obtained including
692 dynamic correlation, but the multiconfigurational approach itself
693 using the small Gouterman active space has provided good semi-
694 quantitative results.

695 A number of relevant aspects about the electronic structure of
696 the triplet state were revealed based on the comparison between
697 $\text{H}_2\text{TPPS}^{4-}$ and its parent compound H_2P . As a main result, while
698 the ZFS parameters vary significantly, the ZFS tensor orientation is
699 conserved and the triplet electron spin density distribution is found
700 to be similar. The D parameter is about 10% smaller in $\text{H}_2\text{TPPS}^{4-}$
701 than in H_2P . In contrast, the A_Z hfcs show differences of about
702 3%, as already pointed out in analogous comparison between the
703 free-base tetraphenyl porphyrin and H_2P .³² The excellent agreement
704 between the experimental and calculated hfcs provides a valida-
705 tion of the triplet wavefunction. Calculations and experiments also
706 agree in indicating that the presence of the sulfonate groups does
707 not significantly alter the electronic features, as already highlighted
708 when introducing phenyl substituents to H_2P .³² This outcome is
709 important, since the polar groups are introduced to provide solu-
710 bility and should not cause unwanted variations of the electronic
711 structure.

712 When comparing ZFS parameters, although they differ quite
713 significantly in absolute values from the calculated ones, the 10%
714 decrease in the case of $\text{H}_2\text{TPPS}^{4-}$ with respect to the parent com-
715 pound is also fulfilled, proving that CASSCF calculations, describing
716 correctly the multiconfigurational nature of porphyrins, are more
717 suitable than DFT to predict the ZFS interaction tensors. The dis-
718 crepancies in the absolute values are likely due to the limited active
719 space and to the lack of dynamic correlation. The difference in the
720 sensitivity of the ZFS parameters and the hfcs to mesophenyl sub-
721 stitution finds confirmation in this work. The ZFS tensor is very
722 sensitive, because the frontier orbitals are mainly contributing to this
723 interaction and upon substitution part of the electron density gets
724 slightly delocalized on the phenyl rings. Conversely, the mechanism
725 of spin polarization governing the isotropic contribution to the hfcs

726 derives from spin density on the core orbitals, which are unaffected
727 by substitution effects.

728 In the magnetophotoselection experiments, an important
729 aspect regarding the structural properties of $\text{H}_2\text{TPPS}^{4-}$ has also
730 emerged. As already pointed out in the Results section, the analy-
731 sis of the corresponding EPR spectra has shown that the principal
732 axes X and Y of the ZFS system are aligned along the TDM but
733 unexpectedly the best fit has been obtained with an equal contri-
734 bution of both ZFS axes, although optical excitation was performed
735 on the main vibronic band of the Q_y transition. The apparent exci-
736 tation of both Q_x and Q_y transitions with an equal contribution
737 definitely does not match to the relative absorption of the two tran-
738 sitions at the excitation wavelength, and therefore, the result cannot
739 be associated with a direct absorption process. In the quest for the
740 mechanism that accounts for this effect, we first considered and
741 later excluded energy transfer processes in fixed-geometry assem-
742 blies, like in the typical π -stacking aggregation. The energy transfer
743 from one molecule to another, within the stack, and with a 90°
744 relative rotation of the ZFS X , Y axes of two adjacent molecules, would
745 result in the transfer of the excitation to form a distribution func-
746 tion that is equivalent to that generated by a pseudo Q_x -excitation.
747 This occurrence was excluded, first because there is no excitation of
748 any absorption band of J-aggregates at the excitation wavelength,²⁰
749 which was carefully selected to avoid any contribution; then, because
750 both the polarization and the lineshape of the spectra did not
751 change with concentration in diluted solutions; finally, because a
752 population equilibration of the X and Y states is not observed
753 experimentally.

754 Alternatively, a pseudorotation of the molecule may be
755 obtained by a N-H tautomerism between two equivalent *trans* struc-
756 tures involving donation of the two N-H protons to the unproto-
757 nated nitrogen atoms, with the *cis* tautomer only present as a tran-
758 sitory intermediate.⁸⁷ We have interpreted our experimental obser-
759 vations invoking a fast phototautomerization process occurring in
760 the excited singlet state, which is slowed down in the triplet state
761 precluding its observation in the EPR time-scale. The model we
762 have introduced to explain the magnetophotoselection experiments
763 is represented in Fig. 5. Photoexcitation in correspondence of the Q_y
764 band generates a distribution of the excited $\text{H}_2\text{TPPS}^{4-}$ molecules
765 with respect to the polarization of the light (see the correspond-
766 ing orientational distribution function in Fig. 5) with a maximum
767 when the molecules are oriented with the Q_y TDM parallel to the
768 light polarization. The phototautomerization exchanges the TDM
769 directions and also the distribution function because of the molecu-
770 lar pseudorotation; this is equivalent to the excitation of part of the
771 molecules through the Q_x TDM. When singlet excitation is followed
772 by ISC to the corresponding triplet state, the two tautomers are
773 equivalent from the microscopic point of view, namely, the relative
774 population rates of the three triplet sublevels are the same but their
775 orientational distribution function is different. This is the reason
776 why simulation of the spectra obtained by magnetophotoselection
777 requires that both the in-plane ZFS canonical orientations are ori-
778 ented along the optical polarization direction. This model accounts
779 for the presence of two overlapping orientational distribution func-
780 tions taking into account the fictitious excitation of both Q_x and Q_y
781 bands produced by the phototautomerization in the excited singlet
782 state. The process should be fast enough to explain the 1:1 popula-
783 tion of the singlet excited states polarized along X and Y . At the same

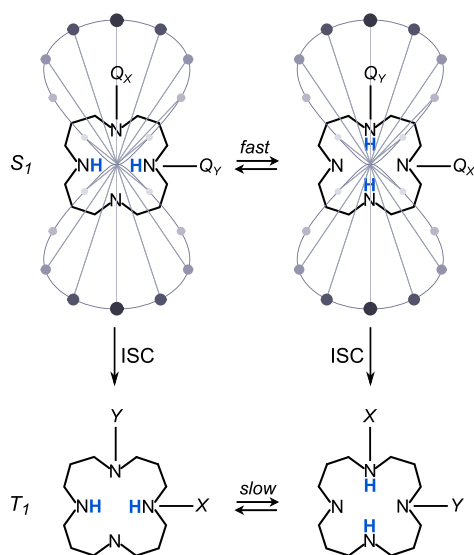


FIG. 5. Schematic representation of the photophysics and of the tautomerization process for $\text{H}_2\text{TPPS}^{4-}$ in the excited states based on the magnetophotoselection experiments. Top: exchange of protons in the excited singlet state. The probability to excite one of the TDM directions is represented by the circles in a gray scale (with the darkest circles representing the highest probability of excitation). Bottom: ISC to the corresponding triplet state. In-plane ZFS axes are indicated.

time, a slow rate of interconversion in the triplet state accounts for the inequivalence of the X and Y transitions ($|E| \neq 0$).

Literature data support the hypothesis of a fast tautomerism in the excited singlet state for porphyrinoid molecules.^{87,88} Phototautomerization of H_2P occurs even at cryogenic temperatures, demonstrating that it is a nonthermally activated process.⁸⁹ From the point of view of the triplet state, the process was extensively discussed for porphycenes.^{90,91} EPR data are reported showing that single proton tautomerism is frozen out at low temperatures and increases as the temperature is raised and becomes visible in the EPR time-scale. Axial symmetry of the ZFS tensor has been reported for few free-base porphyrinoid model compounds, indicating fast-tautomerism also in the triplet state in these specific cases.^{92,93} Free-base porphyrins show mainly rhombic symmetry ($|E| \neq 0$),⁶⁶ indicating that if tautomerization is occurring in the triplet state it is on a time scale slower than that given by the splitting of the X and Y canonical transitions. Most EPR studies of free-base porphyrins have been performed at relatively high temperatures, where thermal activation might be envisaged. Magnetophotoselection experiments, including wavelength, temperature dependence, and deuteration effects, are underway in order to clarify the complex phototautomerization behavior of this important class of molecules, which must be much slower in the triplet state as compared to the excited singlet state as highlighted in the present paper.

In conclusion, for the first time, the full characterization of the magnetic properties of $\text{H}_2\text{TPPS}^{4-}$ was performed with an approach based on quantitative interpretation of the magnetophotoselection experiments and direct comparison of the triplet-state EPR and ENDOR data with accurate theoretical methods including CSSCF calculations of the ZFS interaction tensor. This systematic study,

providing the overall picture of the triplet state and including the structural issue of tautomerization, paves the route to further triplet EPR studies on acidified and aggregated water-soluble porphyrin molecules.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for computational details, spectral analysis of the magnetophotoselection experiments, and ^1H -ENDOR spectra analysis.

ACKNOWLEDGMENTS

This work was supported by the University of Padova (Grant No. PRAT 2014-CPDA145097/14). CINECA (Casalecchio di Reno, Italy) is gratefully acknowledged for providing the supercomputing facilities used for the quantum chemistry calculations through the ISCRA Grant REBEL2 (REdox state role in Bio-inspired ELEMentary reactions 2); P.I.: L.O. The authors thank E. Collini and C.W.M. Kay for helpful discussions and M. Dalla Tiezza and M. Bortoli for software support.

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