Effects of environment on the photophysical characteristics of mesotetrakis methylpyridiniumyl porphyrin (TMPyP)
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ABSTRACT

Porphyrins are an important class of organic molecules, with interesting linear and nonlinear optical properties given mainly by their extended π-conjugation structure. Their photophysical properties can be greatly affected by the surrounding environment, which can be used to tune its final properties. Here we report on an experimental study of the photophysical properties of meso-tetrakis (methylpyridiniumyl) porphyrin (TMPyP) in aqueous and in several organic solvents and its interaction with micelles formed from negatively charged sodium dodecyl sulphate (SDS), positively charged cetyl trimethyl ammonium bromide (CTAB) and neutral TRITON X-100. By using the Z-scan technique, flash-photolysis and time-resolved fluorescence techniques, we were able to evaluate the excited state dynamics of the TMPyP, and observed that the tetrapyrrole ring plays important role due to hydrogen bonds formation between nitrogen atom and water, while the side groups determine the porphyrin localization in non-aqueous micelle part.

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1. Introduction

The interest to the photophysical properties of porphyrin and porphyrin-like compounds has increased significantly during the last decades due to the wide variety of their applications. For instance, porphyrins are promising for the development of nonlinear photonic devices, such as optical limiters [1–3] and optical switches [4,5], because of the high optical nonlinearities arising from their structures presenting extended π-conjugated systems [6,7]. Moreover, owing to their specific photophysical properties, such as intense optical absorption in the visible spectral region and high triplet state quantum yield, porphyrins are applied in medicine and pharmacology as fluorescence probes in cancer fluorescence diagnostic (photodynamic diagnostics, PDD) and photosensitizers in photodynamic therapy (PDT) [8,9].

The interaction of porphyrin with environment and with natural or synthetic nano-organized structures, such as cell membranes, micelles and bio- and synthetic polymers greatly affects its electronic structure and, as a consequence, modifies its excited-state characteristics [10–17]. Although a large number of porphyrins with different side groups has been synthesized lately, further study of simple symmetric porphyrins continues to be of interest. Such porphyrins can be considered to be simple models of more complex molecules, which, nevertheless, permit to make adequate conclusions about general porphyrin characteristics, including the effect of porphyrin interaction with other structures, their aggregation, etc. Moreover, simple symmetric porphyrins are low-cost materials and depending on the application, demonstrate high efficiency, such as for optical devices [1–5]. Specifically, porphyrins/micelles interaction is of interest because micelles can be considered as a model of biological membrane [18–20], and, also because they as a matrix for active optical molecular systems [13,21].

Among simple porphyrins, the tetra-cationic water-soluble meso-tetrakis (methylpyridiniumyl) porphyrin (TMPyP) outstands by demonstrating high affinity with nucleic acids and preferential localization in tumor tissues, which is key role for PDT applications [17,22]. TMPyP has also demonstrated anti-HIV [21,23] and antibacterial activity [18], and it was used as active compound for singlet oxygen imaging of single cells [19] and for singlet oxygen photosensitization in skin fibroblasts [20]. Although TMPyP has already been demonstrated to present nonlinear optical response
[24], there is a lack of information how this molecule interacts with the distinct environments, such as organic solvents and micelles, and consequently, how its excited state dynamics is altered.

Here we report on the excited-state characteristics of TMPyP in aqueous, in organic solvents and also its interaction with micelles, formed from negative charged sodium dodecyl sulphate (SDS), positive charged cetyltrimethyl ammonium bromide (CTAB) and neutral TRITON X-100 surfactants. Besides, excited state dynamics in organic solvents were studied as a function of dielectric constants, viscosities, refraction indexes and ability to form hydrogen bounds. The effect of the TMPyP interaction with micelles was also characterized as a function of the micelle charges.

2. Experimental and methods

2.1. Materials

Meso-tetakis (methylpyridiniumyl) porphyrin (TMPyP) was purchased from Porphyrin Products Inc. Sodium dodecyl sulphate (SDS), cetyltrimethyl ammonium bromide (CTAB) and TRITON X-100 were purchased from Sigma–Aldrich Co, and were used without further purification. All the experiments involving micelles exceeded the critical micellar concentration (CMC). The samples were prepared in Milli-Q quality water at pH 6.8.

2.2. Sample preparation

Protonic methyl (MeOH), ethyl (EtOH) and propyl (PrOH) alcohols and aprotic acetonitrile were used to investigate the excited-state characteristics of porphyrin in organic media. The samples were prepared by adding aliquots of TMPyP aqueous stock solution to the organic solvents, resulting in final water concentration less than 5%. The TMPyP stock solution concentration was monitored by means of a Beckman DU 640 spectrophotometer.

2.3. Optical measurements

The linear absorption and fluorescence spectra were obtained with a Beckman DU 640 spectrophotometer and a Hitachi-F7000 spectrofluorimeter, respectively. Time–resolved fluorescence measurements were carried out with an apparatus based on the time-correlated single photon counting method, in which the excitation source was a titanium – sapphire laser (Tsunami 3950 – Spectra Physics), pumped by the second harmonic of a diode-pumped Nd:YVO4 laser (Millenia – Spectra Physics) and the frequency doubled to 465 nm in a LBO crystal (GWN-23PL – Spectra Physics).

TMPyP triplet state lifetime was determined by means of flash photolysis, using as excitation source a frequency doubled Q-switched Nd:YAG laser [25], which delivers 3 ns-pulses centered at 532 nm. The triplet state decay curve was monitored by measuring the triplet–triplet absorption at 470 nm. The measurements of absorbance, fluorescence and triplet state lifetimes were measured in 1 cm quartz cuvettes at concentration of \( \approx 33 \) \( \mu \)M.

Nonlinear optical properties were investigated with the open aperture Z-scan technique [26], which basically consists in monitoring the transmittance change as the sample is scanned through the focal plane of a Gaussian laser beam. In our Z-scan measurements we used a double frequency, Q-switched and mode–locked Nd:YAG laser, as the pumping source. It produced 70 ps pulses at 532 nm, in pulse trains containing 20 pulses separated by 13 ns intervals. Two regimes of Z-scan were applied: using the single pulse from the Q-switch envelope and using the technique called pulse train Z-scan (PTZ-scan), based on application of the complete set of pulses of the Q-switch envelope to the sample [27,28]. A Pockels cell was used to extract single pulses from the train for the single pulse Z-scan experiment. A low repetition rate (10 Hz) was employed in order to avoid cumulative thermal nonlinearities. The laser beam was focused into the sample with a 12 cm focal length lens, resulting in a 40 \( \mu \)m beam waist. The light transmitted through the sample is collected by a photodetector, connected to a digital oscilloscope and a computer. The amplitude of each individual pulse at a given Z-position was normalized to the one collected when the sample was far from the focus. This procedure gives a set of Z-scan signatures whether the pulse train is used, and only one curve for the single pulse regime. This method allows discriminating fast (sub-nanosecond) and cumulative contributions to the nonlinearity along the pulse envelope. The Z-scan experiments were carried out in a 0.2 cm path length quartz cuvette at concentration of \( \approx 100 \) \( \mu \)M. The maximum peak intensity used in our experiment was less than 5 GW/cm\(^2\).

3. Results and discussion

The photophysical properties of TMPyP can be explained by using the five-energy-level diagram displayed in Fig. 1, which includes the ground singlet state level \((S_0)\), two singlet excited-state levels \((S_1\) and \(S_n)\) and two triplet levels \((T_1\) and \(T_m)\). In the figure, \(\sigma_{ij}\) is the absorption cross-section for transitions from level \(i\) to \(j\) and \(\tau_j\) is the relaxation time level \(j\) to \(i\). \(\tau_{ij} = \tau_{ji}\) is the characteristic intersystem crossing time and \(\tau_f = \tau_{31}\) is the \(T_1\) state lifetime.

![Fig. 1. Five-energy-level diagram used to aid in the interpretation of the TMPyP excited state absorption.](image)

![Fig. 2. TMPyP absorbance spectra in aqueous, in organic solutions, and in the presence of SDS micelles.](image)
TMPyP absorption spectra, displayed in Fig. 2, present four characteristic peaks from 480 up to 700 nm (Q region). The positions and intensities of these peaks in organic solvents and micellar solutions are quite similar, being slightly changed in water. The ground-state absorption cross-sections at 532 nm are displayed in Table 1, which were calculated according to: 

\[
\sigma_{01} = \frac{2.3A}{1000L}
\]

where \(A\) is the absorbance, \(N\) is the sample concentration (molecules/cm\(^3\)), and \(L\) is the sample thickness. Although the absorption spectrum of compounds normally depends on the solvent nature, \(\sigma_{01}\) values obtained at 532 nm are virtually the same for all solutions studied.

In the organic solvents and in the presence of SDS micelles, TMPyP fluorescence spectra, displayed in Fig. 3, show pronounced similarities, displaying two separated peaks around 654 and 715 nm. In water, however, TMPyP fluorescence spectrum is broadened, presenting a maximum at 656 nm and a shoulder around 705 nm. The fluorescence quantum yields, \(\psi_F\), given in Table 2, were calculated according to:

\[
\psi_F = \frac{\int I_e \ d\lambda}{\int I_{F0} \ d\lambda} \times \frac{A_{H_2O}}{A_{H_2O}} \frac{\psi_{F0}}{\psi_F},
\]

where \(I_e\) and \(I_{F0}\) are the integrated fluorescence intensities for the TMPyP in solution and in water (reference), respectively. \(A\) and \(A_{H_2O}\) are the sample absorbances in solution and water, respectively, at the excitation wavelength (586 nm) and \(\psi_{F0} = 0.05\) is the quantum yield for the TMPyP fluorescence in aqueous solution [17]. For all organic solutions and in the presence of SDS micelles, \(\psi_F\) values obtained are similar and nearly 2.5 times higher than in water.

Relaxation time from \(S_1\) to \(S_0, T_1\), also presented in Table 2, were determined from single-exponential fittings of the fluorescence decay curves displayed in Fig. 4. In organic and micellar solutions, \(\tau_F\) is approximately twice longer than in water. In contrast, the radiative \(S_1\) state lifetime, \(\tau_r\), calculated as \(\tau_r = T_1 / \psi_F\), is longer in water than in organic and micellar solutions. The \(T_1\) state lifetimes, \(\tau_T\), obtained by flash-photolysis technique [25], were obtained by fitting the time evolution of the \(T_1 \rightarrow T_m\) absorption at 470 nm, after the laser pulse, which induces changes in the optical absorption due to the difference between the cross-sections of \(S_0 \rightarrow S_1\) and \(T_1 \rightarrow T_m\) transitions. The absorption change is given by:

\[
\Delta \alpha = n_T \sigma_{34} - n_S \sigma_{01}
\]

where \(\sigma_{34}\) is the \(T_1\) state cross-section. We monitored \(\Delta \alpha\) at 470 nm, where \(\sigma_{01}\) is negligible. In this case, \(\Delta \alpha\) is proportional to the \(\sigma_{34}\) at 470 nm. \(T_1\) state lifetimes in liquid solutions are generally determined by the quenching due to the energy transfer to molecular oxygen dissolved in the sample. To exclude this process, we have deaerated the solutions by bubbling nitrogen through the sample. In all cases, the \(T_1 \rightarrow T_m\) absorption/time curves were single-exponentials, as displayed in Fig. 5, with characteristic lifetimes, \(\tau_T\), shown in Table 2. The single-exponential decay behavior demonstrates that the contribution of bimolecular triplet quenching processes, such as T–T annihilation, was negligible under the current conditions. Similar to the \(S_1\) state lifetime, \(\tau_T\) is longer in organic solvents and in micellar solutions than in pure water.

In order to analyze the nonlinear absorption of porphyrins we employed the five-energy-level diagram shown in Fig. 1. Under resonant conditions, one-photon absorption prevails over any simultaneous two-photon absorption (2PA) process, which can be thus neglected [13,28]. The nonlinear absorption effects are associated solely with the absorption changes due to the redistribution of molecular population between ground and excited states, caused by laser excitation. In our model, we consider that the lifetimes of highest electronic excited-states are of the order of hundred of

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### Table 1

<table>
<thead>
<tr>
<th>Solution</th>
<th>(\sigma_{01} \times 10^{-17} \text{ cm}^2)</th>
<th>(\sigma_{12} \times 10^{-17} \text{ cm}^2)</th>
<th>(\sigma_{34} \times 10^{-17} \text{ cm}^2)</th>
<th>(\sigma_{12} / \sigma_{01})</th>
<th>(\sigma_{34} / \sigma_{01})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>3.0 (±0.2)</td>
<td>3.8 (±0.5)</td>
<td>5.7 (±0.3)</td>
<td>1.3 (±0.3)</td>
<td>1.3 (±0.3)</td>
</tr>
<tr>
<td>SDS, 15 mM</td>
<td>2.8 (±0.2)</td>
<td>3.7 (±0.5)</td>
<td>3.6 (±0.3)</td>
<td>1.3 (±0.3)</td>
<td>1.3 (±0.3)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.5 (±0.2)</td>
<td>3.7 (±0.5)</td>
<td>3.3 (±0.3)</td>
<td>1.5 (±0.3)</td>
<td>1.3 (±0.3)</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.5 (±0.2)</td>
<td>3.6 (±0.5)</td>
<td>3.8 (±0.4)</td>
<td>1.4 (±0.3)</td>
<td>1.5 (±0.3)</td>
</tr>
<tr>
<td>EtOH</td>
<td>2.5 (±0.2)</td>
<td>3.5 (±0.5)</td>
<td>3.2 (±0.3)</td>
<td>1.4 (±0.3)</td>
<td>1.3 (±0.3)</td>
</tr>
<tr>
<td>PrOH</td>
<td>2.8 (±0.2)</td>
<td>3.6 (±0.5)</td>
<td>3.5 (±0.3)</td>
<td>1.3 (±0.3)</td>
<td>1.3 (±0.3)</td>
</tr>
</tbody>
</table>

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Fig. 3. Normalized fluorescence spectra of TMPyP in aqueous, in organic solutions, and in the presence of SDS micelles, by using as excitation 586 nm.

Fig. 4. Normalized fluorescence decay curves of TMPyP in water, in EtOH and in the presence of SDS micelles. The excitation and emission wavelengths are 586 nm and 655 nm, respectively.
femtoseconds, and therefore, the populations of these states are negligibly small.

Fig. 6 displays normalized transmittance as a function of the pulse fluence. Once pulse duration is much shorter than the intersystem crossing time, we can neglect the triplet state population, and the energy diagram presented in Fig. 1 can be simplified by considering only a three-energy level diagram, corresponding to the left part of Fig. 1. Moreover, we also neglect relaxation from $S_1$ to $S_0$ state, because its lifetime is on the order of nanoseconds (see Table 2), much longer than the pulse duration (70 ps). Therefore, the simplified equation that describes the evolution of $S_0$ population as a function of time is:

$$\frac{dn_{S_0}}{dt} = -W_{01}n_{S_0}.$$  \hfill (3)

where $W_{01} = \sigma_0 \Omega(t) / h\nu$ is the one-photon transition rate and $\Omega(t)$ is the time-dependent irradiance of the laser pulse. The population condition is $n_{S_0} + n_{S_1} = 1$, where $n_{S_0}$ and $n_{S_1}$ are the population fractions of the $S_0$ and $S_1$ states, respectively.

![Fig. 5. Normalized decay curves of TMPyP triplet absorption in water, in EtOH and in the presence of SDS micelles. The excitation and absorption wavelengths are 532 nm and 470 nm, respectively.](image)

![Fig. 6. Normalized transmittance (single pulse) as a function of the laser fluence of TMPyP in aqueous, in organic solutions and in the presence of SDS micelles. The solid line represents the theoretical fitting obtained using the five-energy-level diagram depicted in Fig. 1.](image)
One can integrate Eq. (3) to obtain the time-evolution of the ground-state population:

\[ n_{S_0}(t) = \exp \left\{ -\frac{\sigma_0 F(t)}{h} t \right\} \]  

(4)

where \( F(t) = \int l(t) \, dt \) is the fluence incident onto the sample. For media exhibiting population effects involving just the three singlet levels, the time-dependent absorption coefficient is given by:

\[ \alpha(t) = N(n_{S_0}(t)\sigma_{01} + n_{S_1}(t)\sigma_{12}) = \alpha_0 \left\{ 1 + n_{S_1}(t) \left( \frac{\sigma_{12}}{\sigma_{01}} - 1 \right) \right\} \]  

(5)

where \( \alpha_0 = N\sigma_{01} \) is the linear absorption for the \( S_0 \rightarrow S_1 \) transition. The Beer’s law equation, which associates the variation of irradiance \( I \) with the penetration depth \( z \), can be written as:

\[ \frac{dI}{dz} = -\alpha_{0} \left( 1 + n_{S_1} \left( \frac{\sigma_{12}}{\sigma_{01}} - 1 \right) \right) I(t) \]  

(6)

Since the detector response (\( \approx 1 \) ns) in our Z-scan setup is much longer than the pulse duration, the measurement provides the pulse fluence, which must be numerically integrated over the full pulse width, according to Eq. (6):

\[ \frac{d\phi}{dz} = -\alpha_{0} \left\{ 1 + \frac{\sigma_{12}}{\sigma_{01}} \left( \frac{e^{h\nu t} - 1}{\sigma_{01}} \right) \right\} \phi(t) \]  

(7)

where \( \phi \) is the total pulse fluence. In order to find the energy reaching the detector after a single laser pulse, we numerically integrate this equation over the sample thickness and the beam cross-section (assuming a Gaussian laser beam). The result is then normalized to the linearly transmitted energy, \( E = \frac{\alpha_0 L}{\sigma_{01}} \), and is used to fit the data of Fig. 6, as shown by the solid lines. This procedure provides the \( \sigma_{12} \) values given in Table 1, which are very close for all samples studied.

In order to determine the \( T_1 \) state cross-sections, \( \sigma_{34} \), and the \( S_1 \rightarrow T_1 \) intersystem crossing lifetimes, \( \tau_{isc} \), we used the pulse train Z-scan technique. Fig. 7 shows normalized transmittance as a function of pulse number for TMPyP in several solvents. Only for convenience, in this figure the strongest pulse in the train is arbitrarily labeled “0”, and the pulses before and after this one are labeled with negative and positive numbers respectively. In these experiments, the time interval between adjacent pulses of the pulse train is longer than \( \tau_{S_1} \). As a consequence, there is enough time between sequential pulses for populating \( T_1 \) state. On the other hand, the Q-switch envelope is about 200 ns long, which is approximately 10 times shorter than \( T_1 \) state lifetimes (\( \approx 2 \mu s \) in the air saturated water solutions). Therefore, \( T_1 \) state population increases progressively during the pulse train action, while depopulation can be neglected. In this case, the five-energy-level diagram displayed in Fig. 1 is necessary for analyzing the transmittance curves. The experimental data were fitted by the following set of equation set:

\[ \frac{dn_{S_2}}{dt} = -W_{01}n_{S_0} + \left( \frac{1}{\tau_{isc}} + \frac{1}{\tau_r} \right) n_{S_1} \]  

(8a)

\[ \frac{dn_{S_1}}{dt} = W_{01}n_{S_0} - \left( \frac{1}{\tau_{isc}} + \frac{1}{\tau_r} + \frac{1}{\tau_{isc}} \right) n_{S_1} \]  

(8b)

\[ \frac{dn_{T_1}}{dt} = \frac{n_{S_1}}{\tau_{isc}} \]  

(8c)

where:

\[ \frac{1}{\tau_{isc}} = \frac{1}{\tau_{S_1}} + \frac{1}{\tau_r} + \frac{1}{\tau_{isc}} \]  

(9)

is the rate constant for all transitions depopulating level \( S_1 \),

\[ \frac{1}{\tau_{10}} = \frac{1}{\tau_{isc}} + \frac{1}{\tau_r} \]  

(10)

is the rate constant for all transitions that populate the ground-state level \( S_0 \) from \( S_1 \), \( (\tau_{isc})^{-1} \) is the rate constant for \( S_1 \rightarrow S_0 \) intern conversion, and \( (\tau_{isc})^{-1} \) is the intersystem crossing rate constant. The condition \( n_{S_0} + n_{S_1} + n_{T_1} = 1 \) was also applied.

This set of equations was numerically solved using the temporal intensity pattern of the Q-switched mode-locked pulse train employed in our Z-scan experiments, along with initial conditions \( n_{S_0}(\infty) = 1 \), \( n_{S_1}(\infty) = 0 \), and \( n_{T_1}(\infty) = 0 \). The absorption time-evolution was calculated according to:

\[ \frac{d\alpha}{dt} = -N[n_{S_0}\sigma_{01} + n_{S_1}\sigma_{12} + n_{T_1}\sigma_{34}] \]  

(11)

where \( \sigma_{34} \) is \( T_1 \rightarrow T_0 \) absorption cross-section at 532 nm. Eqs. (8a)–(8c) and (11) were numerically solved using \( \sigma_{01} \), \( \tau_{S_1} \) and \( \sigma_{12} \) obtained in the previous experiments. The values of \( \tau_{isc} \) and \( \sigma_{34} \) were obtained from fitting the Z-scan data, displayed as solid lines in Fig. 7, while \( \tau_{10} \) values were calculated from Eq. (10). The intersystem crossing and internal conversion quantum yields were calculated as \( \psi_{isc} = \tau_{isc} / \tau_{10} \) and \( \psi_{10} = 1 - (\psi_{isc} + \psi_r) \), respectively. We have observed a reduction of the \( \sigma_{34} \) value and an increase of \( \tau_{isc} \) and \( \tau_r \) in organic and micellar solutions, as compared with aqueous ones, while both \( \psi_{isc} \) and \( \psi_r \) remained practically unchanged.

The spectra and excited-state dynamics of a molecule depend on a high number of parameters of the interaction between that molecule and surrounding environment [29]. By our experimental results, we attempted to arrive at some general conclusions about the TMPyP interaction with solvents and micelles. The analysis of TMPyP absorption spectra demonstrates that the positions of TMPyP absorption maxima in the organic solvents analyzed differ by less than 2.5 nm. The same result is observed for the position of the TMPyP fluorescence maximum. The Stokes shift, calculated according to \( \Delta \nu_{St} = \nu_{abs} - \nu_{em} \), where \( \nu_{abs} \) is the absorption peak position with lowest frequency and \( \nu_{em} \) is the position of the fluorescence peak with highest frequency, does not exceed 200 cm\(^{-1}\) (\( \approx 8 \) nm) and differs in different organic solvents by less than 10 cm\(^{-1}\), as shown in Table 3. According to Lipert–Mataga’s theory [30,31], the Stokes shift associated to the solvent is:

\[ \Delta \nu_{St} = \frac{2\Delta}{hc_k} (\mu^* - \mu)^2 \]  

(12)

where \( \Delta \) is the reorientation polarizability, \( h \) is the Planck’s constant, \( c \) is the speed of light, \( a_0 \) is the radius of the molecule.
Table 3
TMPyP photophysical parameters in several solvents: solvent dielectric constant (ε), refraction index (n), viscosity (× 10^5 n), TMPyP band position of maximum of absorption (νabs) and maximum of fluorescence (νem). Stock shift (Δν = νabs – νem) and orientation polarizability (Δf).

<table>
<thead>
<tr>
<th>Solution</th>
<th>ε*</th>
<th>n*</th>
<th>Viscosity, × 10^5 n</th>
<th>νabs, cm⁻¹</th>
<th>νem, cm⁻¹</th>
<th>Δν, cm⁻¹</th>
<th>Δf</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>80.4</td>
<td>1.3328</td>
<td>10.1</td>
<td>15,610</td>
<td>15,260</td>
<td>350</td>
<td>0.320</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>36.2</td>
<td>1.34</td>
<td>3.45</td>
<td>15,510</td>
<td>15,310</td>
<td>200</td>
<td>0.306</td>
</tr>
<tr>
<td>MetOH</td>
<td>33.1</td>
<td>1.329</td>
<td>5.45</td>
<td>15,460</td>
<td>15,270</td>
<td>190</td>
<td>0.309</td>
</tr>
<tr>
<td>EtOH</td>
<td>24.3</td>
<td>1.36</td>
<td>10.8</td>
<td>15,460</td>
<td>15,270</td>
<td>190</td>
<td>0.289</td>
</tr>
<tr>
<td>PrOH</td>
<td>21.8</td>
<td>1.39</td>
<td>20.0</td>
<td>15,450</td>
<td>15,250</td>
<td>200</td>
<td>0.275</td>
</tr>
</tbody>
</table>

* Data obtained from Ref. [36].

residence cavity, and μ* and μ are excited- and ground-state dipole moments, respectively. The shift Δνabs results from the reorganization of solvent molecules around those of the solute and it should increase as the interaction between solute and solvent molecules increases. Typically, a correlation is observed between the Δνabs and the reorientation polarizability, given by:

\[ Δf = \frac{ε - 1}{2ε + 1} - \frac{n^2 - 1}{2n^2 + 1} \]  

(13)

where ε and n are the solvent dielectric constant and refraction index, respectively [29]. However, in our experimental results, we did not observe any significant dependence of Δνabs on Δf.

The changes in the TMPyP absorption and fluorescence spectra due to variations of the solvent polarity could be associated with charge transfer (CT) between the porphyrin core and lateral groups, which contributes to the formation of their lowest absorption maximum [32–34]. However, when CT transitions do occur at the change of the environment polarity, the absorption and fluorescence spectra appear significantly shifted [35] while in our experiments we have observed just a weak effect of solvent polarity on the TMPyP spectra. Therefore, we can affirm low contribution of the CT mechanism in the TMPyP spectra formation.

The profiles and peak positions of the TMPyP absorption and fluorescence spectra and characteristics of its excited-states dynamics (Tables 1–3) does not show any significant difference between aprotic acetonitrile and protonic alcohols. This fact demonstrates that the formation of hydrogen bonds between the TMPyP and organic solvent molecules is insignificant. This is in agreement with the fact that TMPyP spectra in organic solvents essentially differ from those in water, where the formation of hydrogen bonds between TMPyP nitrogen atoms and water hydrogen was confirmed [37]. Moreover, the excited-state cross-sections (σ₁₂ and σ₃₄) and dynamic characteristics, such as excited state lifetimes and quantum yields, were close in all used organic solvents, demonstrating the independence from solvent polarity, polarizability and capacity to form hydrogen bonds. Significant increase was observed only for triplet state lifetime in the sequence: acetonitrile < EtOH < PrOH (Table 2). However, we associate this effect to the increase of the solvent viscosity in the same sequence (see Table 3), which increases the rigidity of the environment around the molecule, thus reducing the probability of radiationless T₁ state energy dissipation. Other possible viscosity effect on T can be by the reduction of the rate of diffusion controlled quenching of TMPyP triplet by residual oxygen in the solution, which also should increase T value as the viscosity increases.

On contrary to organic solvents, TMPyP demonstrated relatively large Stokes shift Δνabs (Table 3) in aqueous solutions, accompanied by the broadening of the fluorescence spectrum (Fig. 2). The larger Stokes shift in water, compared to that of organic solvents, can be associated to a higher Δε in water. It can also be associated to the solvent polarity effect on the CT transition, as proposed in the literature [32–34]. However, the increase of environment polarity generally induces a red shift of the CT absorption band [35]. The same trend also happens in π → π⁺ transitions [38,39]. If the absorption band, located at the 630–670 nm region, is really a result of the superposition of CT and π → π⁺ transitions, one should expected this red shift in water, while conversely, experiences a blue shift (Fig. 2). Moreover, we have not observed any changes of the band profile, which could be expected for the superposition mentioned. Therefore, we believe that the blue shift observed and the increase of Δν are due to the formation of hydrogen bonds between the nitrogen atom of TMPyP core and water hydrogen atoms. Besides, it was observed in [37] a contraction of the porphyrin molecule following the triplet and, probably, singlet excitations. According to Eq. (12), this can also produce a Δνabs increase caused by the reduction of the radius of the molecule residence cavity, a₀.

Concerning water environment, we also observed (see Table 2) a decrease of the TMPyP S₁ excited state lifetime, τ₁, and fluorescence quantum yield, ϕₐ, follow by increase of nonradiative processes rate equations kₑ and kᵦₑ, and a strong reduction of the T₁ excited state lifetime, τ₁. Such behavior should not be associated to changes of the solvent viscosity, once water has the same viscosity of EtOH and nearly a threefold higher viscosity than acetonitrile, while τ₁ in EtOH and acetonitrile are, respectively, 8.5 and 5 times longer than in water. One should not associate τ₁ reduction to the quenching by residual oxygen, as far as the oxygen solubility in water (1.27 mM) is lower than in EtOH (7.87 mM) and in acetonitrile (9.1 mM) [40]. Our results are in agreement with the theory presented in [41–44], where an increase of nonradiative transition probability (increase of kₑ and kᵦₑ) is observed when the density of vibration energy levels of ground and/or excited states of a molecule increases. Gensch and co-authors [37] also suggested that the contraction of the porphyrin molecule following the excitation is due to the fact that the four nitrogen atoms in the porphyrin macrocycle are more strongly hydrogen-bonded with the surrounding water molecules in the excited-state compared with the ground-state. The interaction of the TMPyP ring with surrounding water molecules can be responsible for the appearance of new vibrational levels and the subsequent increase of rates of the radiationless excited-state relaxation. According to [33,34], the broadening of the TMPyP fluorescence spectrum in water, as well as the reduction of S₁ state lifetime, result from intramolecular charge-transfer. However, we believe that this broadening can be employed as an indirect argument in favor of the increase of numbers of vibrational levels in TMPyP excited–state. The simultaneous decrease of τ₁ and increase of kₑ and kᵦₑ makes ϕₐ = τ₁/₇ and ϕₐₑ = τ₁/ₗₑ be practically identical in water and in organic solutions (Table 2). We can see that triplet state or intersystem crossing quantum yield is higher than that of internal conversion or radiative (fluorescence) one in all cases. This means that the probability of intersystem crossing is higher than that of internal conversion and fluorescence.

We also observed that TMPyP molecules possess higher affinity with water than with organic environment. However, in the presence of SDS micelles, the TMPyP characteristics are similar to those in organic solvents (Tables 1 and 2; Figs. 2 and 3), demonstrating that TMPyP molecules tend to be located rather in micellar phase than in aqueous one. We consider that this effect arises from electrostatic attraction between positive charges of TMPyP molecules...
and negative charges of SDS micelles. To confirm this observation, we analyzed TMPyP characteristics in the presence of positively charged CTAB and neutral TRITON X-100 micelles. In both cases, we obtained the TMPyP characteristics similar to those observed in water (Table 4). Our results indicate electrostatic attraction plays a key role on porphyrin localization in non-aqueous micelle part, although displaying a low affinity to non-aqueous media. This conclusion is in agreement with the experimental data reported in literature [16, 17, 45]. We can see that in the SDS micelles presence the porphyrin binding with micelles reduces the internal conversion probability in favor to fluorescence and intersystem crossing ones.

Analysis of the cross-sections (Table 1) showed that $\sigma_0$ and $\sigma_{12}$ at 532 nm are nearly independent on the environment nature, while $\sigma_{32}$ is higher for water environment compared to organic one. In all cases, $\sigma_{12}$ and $\sigma_{34}$ values are higher than $\sigma_{01}$. The ratio $\sigma_{12}/\sigma_{01}$ in all solvents and $\sigma_{34}/\sigma_{01}$ in organic solvents are $\approx$ 1.3. The ratio $\sigma_{34}/\sigma_{01}$ in water reaches 1.9. This increase can be associated to contraction of the porphyrin molecule in the triplet state, as observed in [37].

The effects of interaction of the positively charged TMPyP with negatively charged SDS micelles on the porphyrin spectral characteristics and excited state dynamics are similar to those for negatively charged meso-tetrakis(sulphonato phenyl) porphyrin (TPPS4) in its bi-protonated state with interaction with positively charged cetyl trimethyl ammonium bromide micelles (CTAB) [13, 19]. Indeed, in both cases in aqueous solutions the absorption spectrum was blue shifted and the fluorescence bands were broadened as compared with the micellar media. In addition, for both porphyrins, the $S_1$ and $T_1$ excited state lifetimes are shorter in water than in organic and micellar environment. Our results point out that photophysical properties of TMPyP are strongly dependent on the interaction with environment, where tetrapyrrole ring plays important role due to hydrogen bonds formation between nitrogen atom and water, while the side groups determine the porphyrin localization in non-aqueous part of micelles.

4. Conclusion

In summary, by measuring the excited-state dynamics of meso-tetrakis (methylpyridiniumyl) porphyrin (TMPyP) in water, in organic solvents and in the presence of micelles, we observed that the environment has a great influence on its excited state properties. In the presence of water, formation of hydrogen bonds between water molecules and the porphyrin core are observed, which increases the probability of energy dissipation through radiationless decay, reducing fluorescence quantum yield, and singlet and triplet excited-state lifetimes. TMPyP in organic solvents, however, demonstrates low sensitivity to polarity and low ability to form hydrogen bonds. In the presence of SDS micelles, formation of hydrogen bonds between TMPyP and water is weakened due to negatively charged SDS micelles, and as a consequence, its photophysical properties tend to be similar to those in organic solutions. The study of the TMPyP photophysical characteristics in water, in the presence of negatively charged SDS, positively charged CTAB and neutral TRITON X-100 micelles demonstrated a strong interaction between the porphyrin ring and the surrounding molecules, while the porphyrin’s lateral side group is responsible for interaction with the non-aqueous part of micelles.

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