Spectroscopic characterization of the water-soluble cationic porphyrins and their complexes with Cu(II) in various solvents

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Abstract

The spectroscopic properties of two cationic porphyrins with different residues in a periphery of the porphyrin plane (H\textsubscript{T}MePyP and H\textsubscript{T}TMePP) and their Cu(II) complexes were studied in water and organic solvents (MeOH, EtOH, DMSO and DMF). The wavelengths of the absorbance and fluorescence band maxima were correlated with the polarity of the solvents. The linear dependence of the spectral band blue shift from Reichardt’s polarity parameter is described. The relative quenching of the \( Q \) band in more polar solvents is shown. These effects are particularly strong for the porphyrins with spatial peripheral positively charged groups.

Keywords: Water-soluble porphyrins; Copper porphyrin complexes; UV–Vis spectroscopy; Fluorescence spectroscopy; Polarity parameter

1. Introduction

Porphyrins are known to play a significant role in several biological systems. For example, the presence of such complexes is essential for the activation and storage of oxygen (haemoglobin and myoglobin), electron transfer (cytochrome \( c \), cytochrome oxidase) and solar energy transfer (chlorophyll) [1,2]. Porphyrins are versatile molecules whose physicochemical properties can be easily adjusted by modifications of the electronic distribution on the aromatic ring via peripheral substitution. A series of water-soluble porphyrins are derived from porphyrin precursors insoluble in water (mainly phenyl- or pyridyl porphyrin) by introducing ionic groups such as \(-\text{COO}^-,\) \(-\text{SO}_3^-,\) \(=\text{N–CH}_3\), or \(-\text{N(CH}_3)_3^+\). These so-called peripheral charge groups influence chemical, spectral and redox properties of the compounds and their metal complexes [3–5]. Chemistry of water-soluble porphyrins has been intensively studied because of their importance in biological systems. In particular, cationic porphyrins became under a wide interest because of their ability to be bound with DNA and related compounds or even to preferential cleavage of DNA in particular sites [6–9]. Studies of such a DNA-porphyrin binding interaction have been mostly done by UV–Vis and fluorescence spectroscopy investigation in solutions [10–13], and from this point of view it is interesting to check how spectral bands vary with individual solvents.

The aim of the present study is a detailed analysis of the wavelength of band maxima of the UV–Vis and fluorescence spectra in different solvents. In addition, it is interesting to compare how different peripheral groups of cationic porphyrins affect the spectra in the same solvent. Solvent dependence of band position is a known phenomenon [14], and has not been described earlier for cationic porphyrins, while such studies were done in organic solvents for other porphyrins insoluble in water [15–17]. The changes in band energy depending on solvent have usually been associated with properties of solvents such as acceptor–donor or polarity parameter. The compounds studied in this work are soluble in a limited number of solvents (water and polar solvents). For this reason, we decided to check the dependence of band wavelength on Reichardt’s polarity parameter for the compounds considered here.

2. Experimental

The water-soluble porphyrins: H\textsubscript{T}MePyP [5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine] (Fig. 1) and H\textsubscript{T}TMePP \{tetrakis[4-(trimethylammonio)phenyl]-21H,23H-porphine\} (Fig. 2) were purchased in the form of the tetra-4-tosylate salts (Aldrich) and used without any modification.
using a 1-cm quartz cell. All the fluorescence spectra were excited at the wavelength of the Soret band and recorded at a temperature of 21±1°C in the range 200–900 nm. Absorption and emission spectra were recorded digitally and the SigmaPlot (Jandel Corp.) program was used in manipulation and plotting the data.

Porphyрин solutions were freshly prepared in the spectral purity solvents at the concentration range about 10–5 M. We tried to dissolve the examined porphyrins in less polar solvents, but they were insoluble or soluble in such small amounts that it was impossible to register a high quality spectrum. Solutions were kept in the dark to prevent photodegradation. All the fluorescence and absorption spectra were recorded for the same samples.

### 3. Results and discussion

The absorption spectra of porphyrins are extremely sensitive to such processes as metallation, protonation, ring oxidation or dimerization. The spectra shown in Fig. 3 illustrate the characteristic spectral changes that accompany porphyrin metallation. When one compares the spectra of free base porphyrins with those of their Cu(II) complexes, only a tiny shift of the Soret band can be observed, while dramatic changes in the Q band could be noticed. The Q band of the free base porphyrin consists of four components: $Q_{\nu}(0,0)$, $Q_{\nu}(1,0)$, $Q_{\nu}(0,0)$ and $Q_{\nu}(1,0)$, which are associated with $D_{2h}$ ($mmmm$) symmetry while in the spectra of Cu(II) porphyrins [symmetry $D_{4h}$ ($mmmym$)] only one component $Q_{\nu}(0,0)$ is observed. The appearance of additional Q bands when going from copper porphyrins to the free base porphyrins is associated with an increase in the vibrational accessible modes. The characteristics of the spectra of the porphyrins and their metal complexes are summarised in Table 1. It should be noticed that the wavelength of the Soret band maximum alters with various solvents. Additionally, the relative intensities of the Soret band to the Q bands differ in some solvents. The Soret band of H$_2$TMePyP and CuTMePyP is shifted by about 3 nm, whereas this shift is larger for H$_2$TTMePP and CuTTMePP (7 nm). It could be explained by the fact that the more spatial group –N(CH$_3$)$_3$ gives rise to stronger interactions of porphyrin with solvent dipoles. Relative intensities of the Soret band to the Q bands components confirm this conclusion. Ratios of the $B(0,0)$ intensity to $Q_{\nu}(1,0)$ vary from 14 for H$_2$TMePyP to 30 for H$_2$TTMePP in aqueous solution, and from 11 to 25 for CuTMePyP and CuTTMePP, respectively. It is obvious that the Q band is quenched by the polar solvents, but only in the case of H$_2$TTMePP by larger peripheral cationic groups.

The fluorescence spectra of H$_2$TMePyP and H$_2$TTMePP in various solvents are shown in Figs. 4 and 5, respectively. Their copper complexes do not exhibit any emission, in agreement with Gouterman’s theory [20] and, additionally,
Fig. 3. Absorption spectra of the 10^{-5} M solutions of H$_2$TMePyP, H$_2$TTMePP, CuTMePyP and CuTTMePP in methanol.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Soret band</th>
<th>$Q_x$(1,0)</th>
<th>$Q_y$(0,0)</th>
<th>$Q_y$(1,0)</th>
<th>$Q_y$(0,0)</th>
<th>Relative intensities</th>
<th>$B(0,0)/Q_x$(1,0)</th>
<th>$B(0,0)/Q_y$(0,0)</th>
<th>$B(0,0)/Q_y$(1,0)</th>
<th>$B(0,0)/Q_y$(0,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$TMePyP</td>
<td></td>
<td>423.1</td>
<td>518.9</td>
<td>555.5</td>
<td>586.2</td>
<td>642.0</td>
<td>14.4</td>
<td>34.6</td>
<td>28.8</td>
<td>86.5</td>
<td></td>
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<tr>
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<td></td>
<td>425.3</td>
<td>516.7</td>
<td>552.6</td>
<td>588.9</td>
<td>644.9</td>
<td>13.6</td>
<td>32.8</td>
<td>32.8</td>
<td>82.0</td>
<td></td>
</tr>
<tr>
<td>CuTMePyP</td>
<td></td>
<td>426.3</td>
<td>–</td>
<td>549.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>11.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuTTMePP</td>
<td></td>
<td>413.2</td>
<td>–</td>
<td>540.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>24.6</td>
<td>–</td>
<td>–</td>
</tr>
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Table 1
Parameters of the absorption spectra of H$_2$TMePyP, H$_2$TTMePP, CuTMePyP and CuTTMePP in various solvents.
confirms the purity of the copper complexes synthesized in this work. The fluorescence spectra are seemingly similar but one can notice that emission of $Q(0,0)$ for $\text{H}_2\text{TTMePP}$ is about one order of magnitude more intensive than emission of the same band for $\text{H}_2\text{TMePyP}$. For both porphyrins, we observed $Q(0,0)$ and $Q(0,1)$ bands which were shifted in various solvents. The $Q(0,0)$ fluorescence band of $\text{H}_2\text{TMePyP}$ is unusually shifted to a longer wavelength in water resulting in an overlap with the $Q(0,1)$ band, as was firstly described by Kano and co-workers [21,22]. In the emission spectra of $\text{H}_2\text{TTMePP}$ the third component of the $Q$ band was found. It can be assigned as the $Q(1,0)$ band, which has been observed for all the solvents with the exception of ethanol. In the case of $\text{H}_2\text{TTMePP}$ aqueous solution, disappearance of the $Q(0,1)$ band was observed.
Trying to find a correlation between the change in the porphyrin wavelength of the spectral band maxima and solvent properties we considered the following parameters: Jørgensen optical basicity [23], Gutman donor or acceptor numbers [24]. However, no relationship was found. In a series of solvents there are sometimes separate correlations for a given spectroscopic data set, for example that for –OH solvents and another one for non-hydroxyl solvents, but cationic porphyrins, free base as well as their copper complexes are soluble only in a very limited set of solvents. The change in Soret band energy could be associated with solvent polarity [25]. A plot of $\lambda_{\text{max}}$ against Reichardt’s solvent polarity parameter is shown in Fig. 6. The blue shift of bands with increasing polarity parameter should be noticed for both porphyrin and their Cu(II) complexes, and this shift can also be observed in

Fig. 6. The wavelengths of the maxima of the spectral bands of the analysed compounds versus empirical Reichardt’s solvent polarity parameter.
fluorescence spectra, with the exception of unusual red shift of the $Q(0,0)$ band in water, as was described above. An analogous situation takes place for the spectra of CuTMePyP and CuTTMePP, however, in DMSO an extra red shift of the Soret band was observed. This is due to the very strong electron donor properties of DMSO. Most probably, additional complexation of copper should be considered and, certainly, metal is involved in this process, as such a shift is not observed for the free base porphyrins. It must also be emphasised that the polarity of the solvent has a more important influence on H$_2$TTMePP Soret band energy than is the case for H$_2$TMePyP. The H$_2$TTMePP porphyrin bears more spatial groups with additional positive charge and therefore its interactions with the dipoles of more polar solvents are stronger.

4. Conclusions

In the absorption and emission spectra of cationic porphyrin in various solvents, the blue shift of the spectral bands was observed with increasing solvent polarity. Much of the Soret band wavelength is almost linear against Reichardt’s polarity parameter. There is only one exception in the fluorescence spectra where unusual red shift in water was observed.

The $Q$ bands in the absorption spectra are quenched in more polar solvents. This is more evident for H$_2$TTMePP with larger peripheral cationic groups than for H$_2$TMePyP porphyrin.

One can conclude that for the spectroscopic studies of (usually weak) cationic porphyrin interactions with molecules of biological interest, less polar solvents are more suitable.

References