

Spectral detection of J-aggregates of cationic porphyrin and investigation of conditions of their formation

Karolína Šišková^a, Blanka Vlčková^{a,*}, Peter Mojžeš^b

^aDepartment of Physical and Macromolecular Chemistry, Charles University, Hlavova 2030, Prague 2 12840, Czech Republic

^bInstitute of Physics, Charles University, Ke Karlovu 5, Prague 2 12116, Czech Republic

Received 6 September 2004; accepted 4 October 2004

Available online 13 December 2004

Abstract

Formation of J-aggregates of a cationic 5,10,15,20-tetrakis(1-methyl-4-pyridiniumyl)porphine ($[\text{H}_2\text{TMPyP}]^{4+}$) mediated by ion-pair interaction with four BH_4^- anions was determined by electronic absorption and resonance Raman spectroscopies. The participation of tosylate anions present as counterions in the original porphyrin sample, as well as of $[\text{HTMPyP}]^{3+}$ ion generated at strongly alkaline pH was excluded by a series of experiments employing the same spectroscopic methods. A partial desintegration of the aggregates on a time-scale of several days is attributed to hydrolysis of BH_4^- anions into borates. The specificity of BH_4^- anions in ion-pairing with $[\text{H}_2\text{TMPyP}]^{4+}$ and J-aggregate formation is tentatively ascribed to their small size and, consequently, minimal steric requirement within the aggregates.

© 2004 Elsevier B.V. All rights reserved.

Keywords: J-aggregates; $[\text{H}_2\text{TMPyP}]^{4+}$ ion; Resonance Raman spectroscopy; $[\text{HTMPyP}]^{3+}$ ion

1. Introduction

A cationic porphyrin 5,10,15,20-tetrakis(1-methyl-4-pyridiniumyl) porphine ($[\text{H}_2\text{TMPyP}]^{4+}$) is of a special interest as a potential sensitizer in the photodynamic therapy of cancer due to its interactions with nucleic acids, either through electrostatic binding or by intercalation [1–5]. This porphyrin is commercially available as a tetra-*p*-tosylate salt (H_2TMPyP) which dissociates in aqueous solution releasing a tetracation $[\text{H}_2\text{TMPyP}]^{4+}$. RR spectra of $[\text{H}_2\text{TMPyP}]^{4+}$ in the acidic and the neutral aqueous ambient were extensively studied and the assignment of the spectral bands of $[\text{H}_2\text{TMPyP}]^{4+}$ has been reported in [6]. Up to now, formation of aggregates of this porphyrin in aqueous solution has not been reported. While the charged porphyrin species are generally considered to be poor candidates for an efficient aggregate formation owing to the electrostatic repulsion, uncharged porphyrins are known to form two types of aggregates in water: H- and J-aggregates [7–14].

While H-aggregates result from the stacking arrangement of porphyrin macrocycles; in J-aggregates the macrocycles are most frequently arranged in a so called ‘card deck’ arrangement, i.e. the major (C_4) axes of the macrocycles are parallel but do not overlap one another.

In this contribution, we provide evidence that $[\text{H}_2\text{TMPyP}]^{4+}$, contrary to expectations, can form J-aggregates in aqueous solution under the conditions of an appropriate ion-pairing. Formation of the aggregates in the aqueous solution was followed by electronic absorption and RR spectroscopies. RR spectra of deposited aggregates are also reported.

2. Experimental

2.1. Materials

Deionized or redistilled deionized water and analytical grade chemicals were used for all sample preparations: NaBH_4 , sodium borohydride (Merck); H_2TMPyP , 5,10,15,20-tetrakis(1-methyl-4-pyridiniumyl)-21H,23H-porphine, tetra-*p*-tosylate salt (Aldrich); NaCl , sodium chloride (Lachema); NaOH , sodium hydroxide (Lachema); HNO_3 ,

* Corresponding author. Tel.: +4202 2195 2279; fax: +4202 2191 958.

E-mail addresses: siskova@natur.cuni.cz (K. Šišková), vlc@natur.cuni.cz (B. Vlčková).

nitric acid (Lachema); HCl, hydrochloric acid (Lachema); H₂SO₄, sulphuric acid (Lachema); H₂O₂, hydrogen peroxide (Peroxides, s.r.o.).

The glassware was cleaned by diluted nitric acid (1:1), extensively rinsed with distilled water and subsequently with redistilled deionized water. Alternatively, the mixture of sulphuric acid and hydrogen peroxide (1:1) was used, particularly when the glassware was polluted with the porphyrin.

For solid state resonance Raman measurements, glass slides (13×13 mm² cut from glass microscopic slides) were pre-cleaned, using 'piranha' solution (four parts of concentrated H₂SO₄ and one part of concentrated H₂O₂) for 20 min and aqua regia (three parts of concentrated HCl and one part of concentrated HNO₃) for 10 min.

2.1.1. Preparation of samples of H₂TMPyP–NaBH₄ systems

- For electronic absorption spectra and pH-dependence measurements in aqueous solution: 12 mL of 1×10⁻⁴ and/or 1×10⁻⁶ M aqueous solution of H₂TMPyP were titrated upon constant stirring by incremental addition of 100 μL of 1 and/or 1×10⁻² M solution of NaBH₄ in doubly distilled, deionized water, cooled to 2 °C in an ice-bath. The progress was monitored from 0 addition of NaBH₄ up to the NaBH₄:porphyrin ratio of 1700.
- For RR spectral measurements in aqueous solution: 2.4 mL of 1×10⁻⁴ and/or 1×10⁻⁵ M aqueous solution of H₂TMPyP was titrated upon constant stirring by incremental addition of 20 μL of 1 M, 1×10⁻¹ and/or 1×10⁻³ M solution of NaBH₄ in doubly distilled, deionized water, cooled to 2 °C in an ice-bath. The progress was monitored from 0 addition of NaBH₄ up to the NaBH₄:porphyrin ratio about 1700.
- For RR spectral measurements of deposited aggregates on glass slides: to 2.4 mL of 1×10⁻⁴ M aqueous solution of H₂TMPyP, 40 μL and/or 300 μL of 1 M solution of NaBH₄ in doubly distilled, deionized water, precooled to 2 °C, were added upon constant stirring. The resulting macroscopic aggregates were transferred to a glass microscopic slide by a micro-pipette.
- For electronic absorption spectral measurements testing obedience of the Lambert-Beer law: to 5 mL of 1 M, 1×10⁻² and/or 1×10⁻³ M NaBH₄ solution in doubly distilled, deionized water, cooled to 2 °C in an ice-bath, 5, 25, 50, 250 and/or 560 μL of 1×10⁻³ M H₂TMPyP aqueous solution from the micro-pipette were added upon constant stirring. Absorption spectra were measured in 0.2 and 1 cm cuvettes. The spectral bands at 422 and 444 nm were separated in two Lorentzian bands and their integral intensities were determined.
- For measurement of time-evolution of electronic absorption spectra: 0.0429 g NaBH₄ in 9 mL of doubly distilled, deionized water were cooled to 2 °C in an ice-bath. To the solution, 1 mL of 1×10⁻³ M H₂TMPyP

aqueous solution from the micro-pipette were added upon constant stirring.

2.1.2. Preparation of samples for assessment of the alkaline pH effect on the aggregation state of H₂TMPyP by electronic absorption and resonance Raman spectral measurements

- Electronic absorption spectra and pH-dependence measurements in the aqueous solution: 12 mL of 1×10⁻⁴ and/or 1×10⁻⁶ M aqueous solution of H₂TMPyP were titrated upon constant stirring by incremental addition of 100 μL of 1 and/or 1×10⁻² M solution of NaOH in doubly distilled, deionized water. The progress was monitored from 0 addition of NaOH up to the NaOH:porphyrin ratio approx. 1300.
- Effect of the 15 M NaOH solution on electronic absorption spectra, pH and RR spectra: to 8 mL of the 8.6×10⁻⁵ M H₂TMPyP aqueous solution: 0.3, 0.5, 1.0, 1.5 and 2.0 mL of 15 M NaOH aqueous solution were added upon constant stirring. After each step of the addition of NaOH solution, the absorption spectrum and the value of pH were measured. From the final system containing the 3 M concentration of NaOH and the 6.9×10⁻⁵ M concentration of H₂TMPyP a RR spectrum was observed.

2.1.3. Preparation of samples for assessment of increasing of ionic strength effect on aggregation state of H₂TMPyP by electronic absorption spectral measurements

Twelve-milliliters of 1×10⁻⁴ and/or 1×10⁻⁶ M aqueous solution of H₂TMPyP were titrated upon constant stirring by incremental addition of 100 μL of 1 and/or 1×10⁻² M solution of NaCl in doubly distilled, deionized water. The progress was measured from 0 addition of NaCl up to the NaCl:porphyrin ratio about 1300.

2.2. Instrumentation

RR spectra were recorded at room temperature using a multichannel Raman spectrometer equipped with a Monospec-600 monochromator and a liquid N₂-cooled CCD detector system (Princeton Instruments). A holographic notch-plus filter (Kaiser) was placed in front of the entrance slit of the monochromator to remove the Rayleigh line from scattered light. The Raman scattering was collected in a right-angle scattering geometry. Excitation was provided with 441.6 nm line of a He–Cd laser (Liconix 4230N). The average laser power at the sample in a 10 mm quartz glass five-window cuvette was about 13 mW. The spectra were accumulated five times to six frames with 2 s exposure time. Basic data spectral treatment [15–17] included removing of spikes (program CSA3) and background correction (in the selected cases). Smoothing of the spectra was avoided.

A Hewlett-Packard diode array UV–vis absorption spectrometer (HP 8547) with spectral range 190–820 nm and 0.2 or 1 cm quartz glass cuvette were employed.

For pH measurements PHM 210 standard pH meter (Meter Lab) was used.

3. Results and discussion

3.1. Electronic absorption and RR spectral titrations of $[H_2TMPyP]^{4+}$ by BH_4^-

Electronic absorption spectra of the initial 1×10^{-4} M stock solution of $[H_2TMPyP]^{4+}$ (the $NaBH_4$:porphyrin ratio equal to 0) and of systems with the increasing BH_4^- : $[H_2TMPyP]^{4+}$ ratio are compared in Fig. 1. The position of the Soret band (maximum at 422 nm) of the initial system (after 100 times dilution) is shown as insert in Fig. 1. The measurements were performed at a rather high concentration of $[H_2TMPyP]^{4+}$, in order to study simultaneously spectral changes both in the Soret and in the Q-band region. With the increasing BH_4^- : $[H_2TMPyP]^{4+}$ ratio, a new peak at 444 nm has appeared, while the initial Soret band has decreased in intensity, and distinct changes in the Q-band region have occurred (Fig. 1). The solution pH values at $NaBH_4$ concentrations corresponding to the spectral points during the titration of 1×10^{-4} M H_2TMPyP by the 1 M $NaBH_4$ solution are presented in Table 1.

Furthermore, for determination of the amount of $NaBH_4$ necessary for the appearance of the spectral changes,

the 1×10^{-3} M $NaBH_4$ aqueous solution was used for a RR spectral titration. From the set of the RRS spectra depicted in Fig. 2, it has been determined that the appropriate value of the $NaBH_4$: H_2TMPyP ratio is close to 4. The following pronounced shifts and relative intensity changes in the RR spectrum have been observed: (a) the 333 band shifts to 327 cm^{-1} and becomes the most intense peak of the spectrum, (b) the 951, 1665 cm^{-1} bands and three bands about 1350 cm^{-1} appear, (c) the 1191, 1219 and 1251 cm^{-1} bands change their relative intensities and the middle one shifts to lower wavenumbers and (d) the 1298, 1555 and 1643 cm^{-1} bands shift to lower wavenumbers. Moreover, fluorescence of the sample disappears, since it is no longer observed in the RR spectrum as the deformation of its spectral background (Fig. 2).

It is possible to conclude that at the BH_4^- : $[H_2TMPyP]^{4+}$ ratios higher than 3.4, RR spectral bands of a new porphyrin species are detected. This new porphyrin species shows the following distinct differences from the monomeric H_2TMPyP : the Soret band is red-shifted and decreases in its intensity (Fig. 1) and fluorescence is quenched (Fig. 2); these three characteristics indicate aggregate formation [7–14,18]. Formation of aggregates is usually encountered for uncharged porphyrins, since an electrostatic repulsion among positively (or negatively) charged porphyrin species is expected. On the other hand, compensation of charges by formation of molecular complexes and/or ion-pair associates with species of the opposite charge can lead to aggregate formation [19,20]. The results of the investigations described above thus

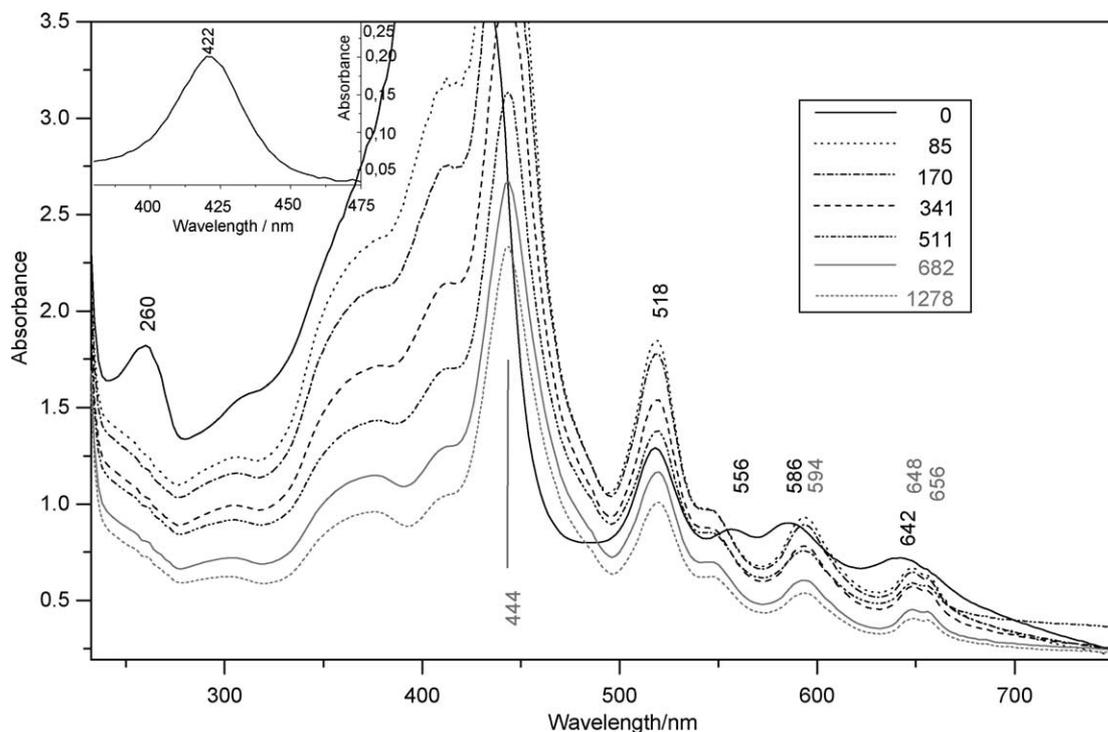


Fig. 1. Electronic absorption spectra of H_2TMPyP (1×10^{-4} M)– $NaBH_4$ system as a function of $NaBH_4$ concentration. Numerical notation of the spectra signifies the BH_4^- : $[H_2TMPyP]^{4+}$ molar ratio. The insert depicts the electronic absorption spectrum of 1×10^{-6} M $[H_2TMPyP]^{4+}$.

Table 1
pH study of 1×10^{-4} M H_2TMPyP with aliquot additions of 1 M $NaBH_4$ or $NaOH$ solution

Ratio agent: H_2TMPyP	pH of the systems H_2TMPyP with	
	$NaBH_4$	$NaOH$
0	4.44	4.48
85	9.30	11.81
170	9.38	12.05
256	9.46	12.19
341	9.52	12.28
426	9.58	12.34
511	9.61	12.41
597	9.65	12.44
682	9.68	12.47
767	9.73	12.49
852	9.76	12.51
937	9.79	12.53
1023	9.80	12.54
1108	9.82	12.56
1193	9.84	12.57
1278	9.85	12.58
1364	9.86	–
1449	9.87	–
1534	9.88	–
1619	9.89	–
1705	9.90	–

provide us with strong indicies that for the $[H_2TMPyP]^{4+}$ charge compensation has been achieved at the $BH_4^-:[H_2TMPyP]^{4+}$ ratio close to 4. This value is in a good agreement with the requirements for compensation of the entire $[H_2TMPyP]^{4+}$ charge, which would enable formation of aggregates. In particular, the red-shift of the Soret band in the electronic absorption spectra of the aggregates with respect to that of monomeric porphyrin indicates formation of J-type aggregates or dimers.

3.2. Electronic absorption spectra of J-aggregates as a function of porphyrin concentration

Another characteristic property of porphyrin aggregates is that the intensities of the Soret band do not fulfill the Lambert–Beer law during the concentration-dependence measurements of the electronic absorption spectra [21]. Therefore, electronic absorption spectra of systems prepared by addition of aliquots of the 1×10^{-3} M H_2TMPyP solution to the 1×10^{-3} M $NaBH_4$ solution upon constant stirring were measured, and are shown in Fig. 3.

While the integral intensities of the band at the 422 nm wavelength were determined at all concentration points, those of the 444 nm band were not detectable for the lower concentration of H_2TMPyP in the system (Table 2). The integral intensity values of the 422 nm band (Table 2) increase with the increasing H_2TMPyP concentration, however, this increase does not fulfill the Lambert–Beer law, as follows from the comparison of the measured integral intensities and those calculated for a linear dependence of spectral intensity on the porphyrin concentration. Simultaneously, the values of integral intensities of the 444 nm band (assigned to the J-aggregates) increase for higher concentrations of H_2TMPyP , which is in good agreement with the increasing trend in the differences between the calculated and the measured integral intensities of the 422 nm band. This experiment demonstrates that the concentration dependence of electronic absorption spectra of H_2TMPyP in the H_2TMPyP – $NaBH_4$ system is typical for formation of porphyrin aggregates.

3.3. Solid state RR spectra of J-aggregates

Investigations of the J-aggregates of H_2TMPyP generation have revealed formation of macroscopic aggregates in

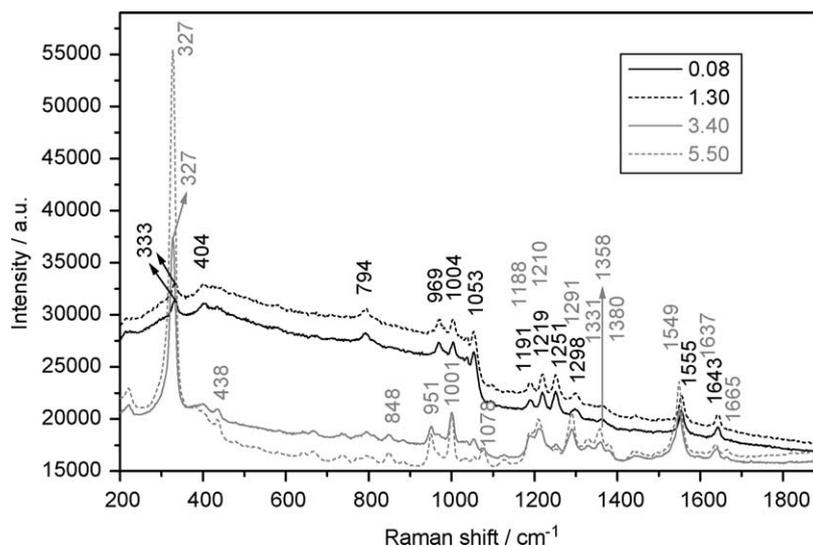


Fig. 2. RR spectra of H_2TMPyP (1×10^{-5} M)– $NaBH_4$ system as a function of $NaBH_4$ concentration. Numerical notation of the spectra signifies the $BH_4^-:[H_2TMPyP]^{4+}$ molar ratio.

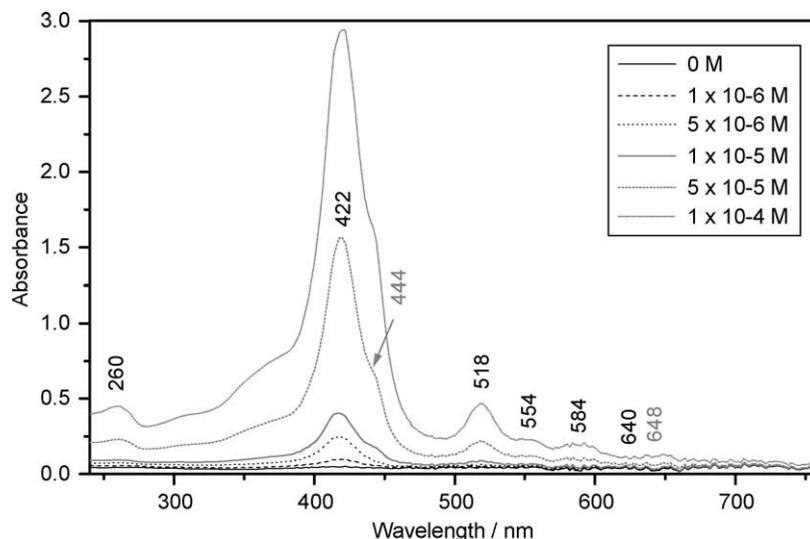


Fig. 3. Electronic absorption spectra of NaBH_4 (1×10^{-3} M)– H_2TMPyP system as a function of H_2TMPyP concentration.

the H_2TMPyP – NaBH_4 system, prepared by addition of 1 M NaBH_4 aqueous solution to 1×10^{-4} M H_2TMPyP solution. The macroscopic aggregates were transferred onto glass slides and their RR spectra were measured. The main goal of the study was to identify the anion which compensates the charge of the $[\text{H}_2\text{TMPyP}]^{4+}$ in the J-aggregates. Both the BH_4^- anion and the tosylate anion, which is present in a commercially available micro-crystalline sample of the porphyrin, could possibly act as counterions of $[\text{H}_2\text{TMPyP}]^{4+}$ in the resulting J-aggregates.

Two systems with different $\text{BH}_4^- : [\text{H}_2\text{TMPyP}]^{4+}$ ratios were prepared: the first with the ratio equal to 160, the second with the ratio approx. 1100 (while concentration of the tosylate ions was the same in both systems ca. 4×10^{-4} M). Their RR spectra are shown in Fig. 4A and B, respectively.

In addition to those, the RR spectrum of solid (micro-crystalline) H_2TMPyP (the tetratosylate salt) (Fig. 5) was measured using the rotational cuvette technique. The RR spectrum in Fig. 5 shows an abrupt change in the spectral background due to fluorescence of the sample. Both the wavenumbers and relative intensities of spectral bands of H_2TMPyP in the solid state RR spectrum are well comparable to the solution Raman spectra in the neutral ambient [6].

Comparing the spectra in Fig. 4A to that in Fig. 5, the following changes are observed: (a) the 330, 952, 1214, 1291, 1494, 1551 and 1636 cm^{-1} bands in the spectrum in Fig. 4A are shifted to lower wavenumbers with respect to their counterparts in the spectrum in Fig. 5, (b) the relative intensities of the bands at 1000, 1252 and 1350 cm^{-1} change, (c) new bands at 284, 1271, 1430 and 1452 cm^{-1} appear, and finally, (d) the 903, 968, 1043 and 1059 cm^{-1} bands disappear.

Comparison of Fig. 4A and B enables to pinpoint the effect of an increase $\text{NaBH}_4 : \text{H}_2\text{TMPyP}$ ratio on the spectra of the aggregates: the 330, 1090, 1214, 1382 and 1452 cm^{-1}

RRS bands (Fig. 4A) shift further to lower wavenumbers, being positioned at 325, 1080, 1211, 1377 and 1447 cm^{-1} , respectively (Fig. 4B).

Solid state RR spectra of J-aggregates were thus found to show pronounced differences from the solid state RR spectra of H_2TMPyP (the tosylate salt). Therefore, we propose that the counterion to $[\text{H}_2\text{TMPyP}]^{4+}$ cation in the aggregates is borohydride anion BH_4^- .

3.4. Effect of alkaline pH and of increased ionic strength on aggregation state of $[\text{H}_2\text{TMPyP}]^{4+}$ in aqueous solution

The J-aggregates formation was found to be induced by addition of the NaBH_4 aqueous solution to H_2TMPyP aqueous solution, in which tosylate anions are present. Addition of sodium borohydride solution leads to an increase of the ionic strength as well as of the pH value of the resulting system. The goal of the following experiments was to establish, whether BH_4^- anions are specifically required as the counterions in the $[\text{H}_2\text{TMPyP}]^{4+} \cdot 4\text{BH}_4^-$ ion-pair aggregate formation, or, alternatively, the increase of the ionic strengths and pH of the system could induce formation of aggregates with tosylates as counterions of

Table 2
Integral intensities of electronic absorption spectral bands as a function of porphyrin concentration in the NaBH_4 – H_2TMPyP system

Concentration of H_2TMPyP in system ($\mu\text{mol}/\text{dm}^3$)	Integral intensities		Calculated intensities at λ_{422}
	λ_{422}	λ_{444}	
1	2.64	–	2.64
5	9.35	–	13.21
10	16.13	0.28	26.41
50	67.67	3.02	132.07
100	140.99	11.02	264.14

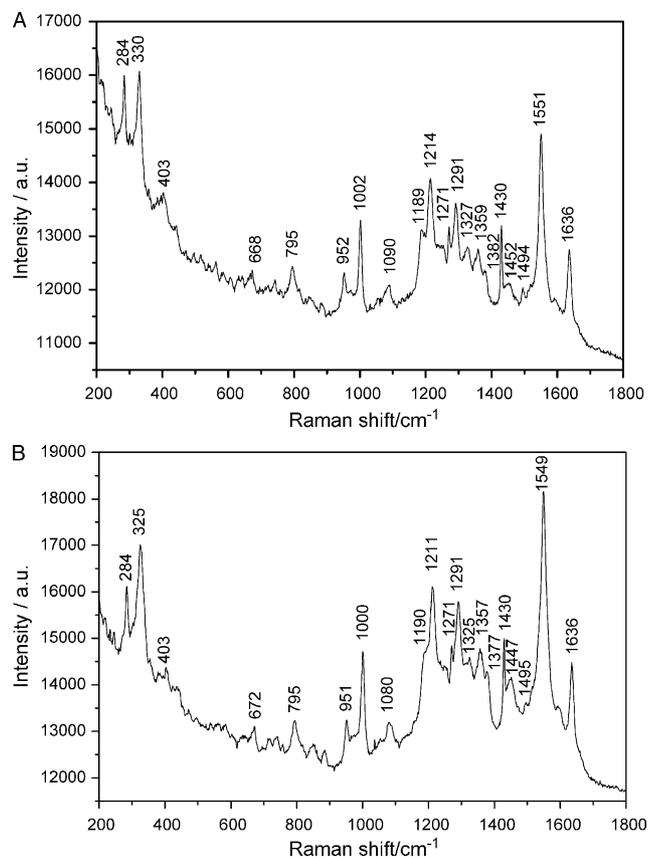


Fig. 4. (A) RR spectrum of the deposited J-aggregates isolated from H_2TMPyP (1×10^{-4} M)– NaBH_4 (1.6×10^{-2} M). (B) RR spectrum of the deposited J-aggregates isolated from H_2TMPyP (1×10^{-4} M)– NaBH_4 (1.1×10^{-1} M).

$[\text{H}_2\text{TMPyP}]^{4+}$. Towards this goal, electronic absorption spectra of H_2TMPyP were measured as a function of pH (adjusted by addition NaOH aqueous solution), and of the ionic strength of the solution (adjusted by addition of NaCl aqueous solution). No significant spectral changes were observed even at the pH=10 (caused by addition of NaOH) which is the highest pH value achieved by addition

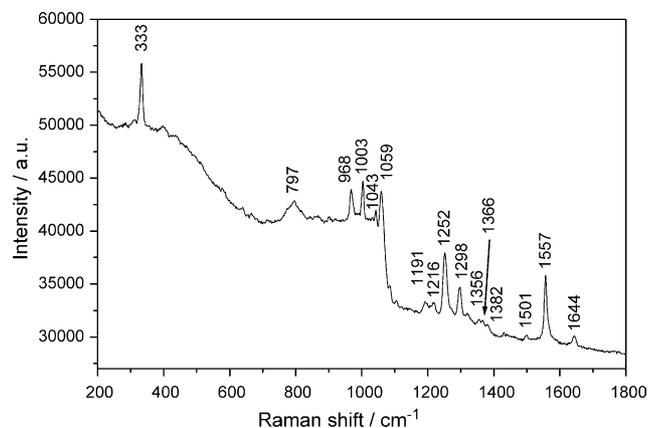


Fig. 5. RR spectrum of H_2TMPyP in micro-crystalline state (without a baseline correction).

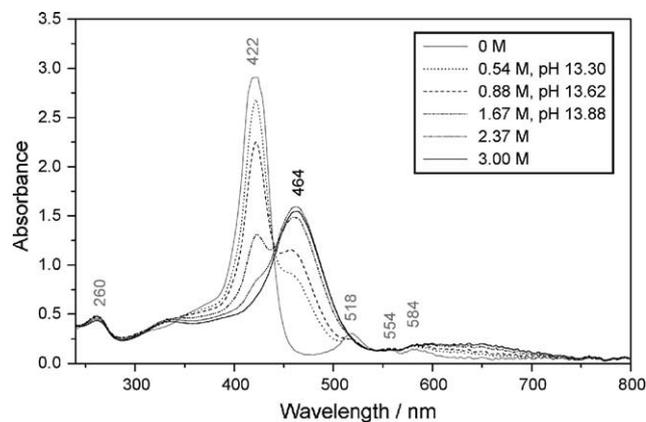


Fig. 6. Electronic absorption spectra of H_2TMPyP (8.6×10^{-5} M)–NaOH system as a function of NaOH concentration: generation of $[\text{HTMPyP}]^{3+}$ ion.

of the NaBH_4 solution to H_2TMPyP solution (Table 1). No effect of the increasing NaCl concentration (and, consequently, of the increasing ionic strength of the solution) on the electronic absorption spectra was observed (spectra not shown here). These results provide evidence that formation of J-aggregates of the $[\text{H}_2\text{TMPyP}]^{4+}$ is conditioned by ion-pairing of the cationic porphyrin with BH_4^- anions.

In addition to the pH range up to pH=10 (Table 1) electronic absorption spectra of H_2TMPyP were studied at higher pH values as well. The goal of this study was generation of $[\text{HTMPyP}]^{3+}$ species reported in [22], acquisition of its RR spectrum and its comparison to that of the J-aggregates. The $[\text{HTMPyP}]^{3+}$ species is also abbreviated as $[\text{HTMPyP}]^-$ which stresses the presence of a negative charge on the N-atom one of the pyrrole rings after its deprotonation.

Electronic absorption spectra of the 8.6×10^{-5} M H_2TMPyP measured as a function of pH > 13.3 are shown in Fig. 6. The red-shift of the Soret band achieves the 464 nm value and the Q-bands decrease in their intensities. The absorption spectrum is distinctly different from that of

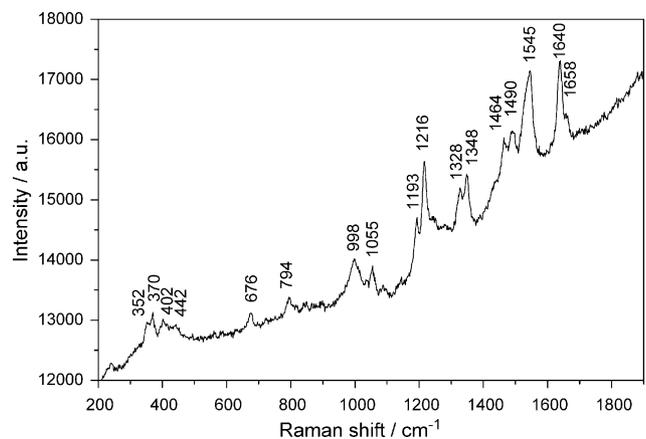


Fig. 7. RR spectrum of $[\text{HTMPyP}]^{3+}$ ion (7×10^{-5} M aqueous solution).

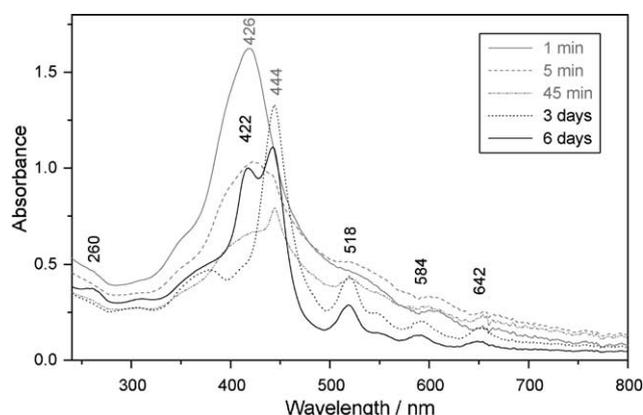


Fig. 8. Time-evolution of electronic absorption spectra: depicting of formation and desintegration of J-aggregates in NaBH_4 (1.13×10^{-1} M)– H_2TMPyP (1×10^{-4} M).

monomeric $[\text{H}_2\text{TMPyP}]^{4+}$ as well as of the J-aggregates (Fig. 1).

Furthermore, $[\text{HTMPyP}]^{3+}$ species was generated in the $\text{H}_2\text{TMPyP}/3$ M NaOH system and its RR spectrum (Fig. 7) was measured. The newly reported RR spectrum of the $[\text{HTMPyP}]^{3+}$ species (Fig. 7) differs significantly throughout the overall spectral region from that of the J-aggregates (Fig. 2), which indicates, that the partially zwitterionic species $[\text{HTMPyP}]^{3+}$ does not participate in J-aggregate formation.

3.5. Time evolution electronic absorption spectra: formation and desintegration of J-aggregates

Reversibility of the J-aggregates formation was tested by measuring of the electronic absorption spectra of the NaBH_4 – H_2TMPyP system during a long-time evolution (several days) (Fig. 8). The 444 nm peak decreases in the course of days and the original Soret band (422 nm for monomeric $[\text{H}_2\text{TMPyP}]^{4+}$ species) appears, which indicates the J-aggregates formation under the conditions of this experiment is reversible. The partial desintegration of the aggregates is attributed to a partial hydrolysis of BH_4^- anions into borates in aqueous ambient and under aerobic conditions [23]. These results point to the specificity of BH_4^- anions in ion-pairing with $[\text{H}_2\text{TMPyP}]^{4+}$ and the consequent J-aggregate formation. This specificity probably stems from the small size of BH_4^- anions, and consequently from their minimal steric demands within the aggregate structure. BH_4^- anions thus provide not only an efficient porphyrin charge compensation, but also allow for unhindered porphyrin–porphyrin interactions stabilizing the aggregate structure.

4. Conclusions

Summarizing the results of the study of the $[\text{H}_2\text{TMPyP}]^{4+}$ porphyrin J-aggregates structure and of the

conditions of their formation, we conclude: (i) interaction of $[\text{H}_2\text{TMPyP}]^{4+}$ with BH_4^- anions results into formation of the J-aggregates; (ii) alkaline pH or high ionic strength of the system are insufficient for inducing J-aggregate formation despite the fact that tosylate anions are present in the system; (iii) the newly reported RR spectrum of $[\text{HTMPyP}]^{3+}$ species which markedly differs from those of the J-aggregates provides evidence that the partially zwitterionic $[\text{HTMPyP}]^{3+}$ units do not participate in the aggregate formation; (iv) the J-aggregates (or dimers) are most probably constituted by ion-pair associates of $[\text{H}_2\text{TMPyP}]^{4+}$ cation with four BH_4^- anions; (v) desintegration of the aggregates can be achieved by oxidation of BH_4^- anions into borates; (vi) the specificity of BH_4^- is attributed to their minimal steric demands within the aggregates stemming from a small size of the anion. In summation, ion-pairing of a cationic porphyrin with BH_4^- anions outlines a prospective pathway towards porphyrin aggregate formation. Desintegration of the aggregates by oxidation of BH_4^- anions into borates indicates, that the process of aggregate formation—desintegration could possibly be controlled by controlling redox potential of the system. Information about the conditions of cationic aggregate formation—desintegration processes can be further exploited in designing efficient transport pathways for porphyrin photosensitisers towards their target as well as nanoscale sensors and devices based on porphyrin molecules.

Acknowledgements

Financial support by the 203/04/0688 grant awarded by the Grant Agency of Czech Republic and by the MSMT 113100001 long term research project are gratefully acknowledged.

References

- [1] R.R. Monaco, M. Zhao, *Int. J. Quantum. Chem.* 6 (1993) 701.
- [2] R.T. Wheelhouse, D.K. Sun, H.Y. Han, F.X.G. Han, L.H. Hurley, *J. Am. Chem. Soc.* 13 (1998) 3261.
- [3] G. Valduga, B. Breda, G.M. Giacometti, G. Jori, E. Reddi, *Biochem. Biophys. Res. Com.* 1 (1999) 84.
- [4] L.A. Lipscomb, F.X. Zhou, S.R. Presnell, R.J. Woo, M.E. Peek, R.R. Plaskon, L.D. Williams, *Biochemistry* 9 (1996) 2818.
- [5] T. Uno, K. Hamasaki, M. Tanigawa, S. Shimabayashi, *Inorg. Chem.* 8 (1997) 1676.
- [6] N. Blom, J. Odo, K. Nakamoto, *J. Phys. Chem.* 90 (1986) 2847.
- [7] R.F. Pasternack, P.R. Huber, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G.C. Ventura, L.de C. Hinds, *J. Am. Chem. Soc.* 94 (1972) 4511.
- [8] R.F. Pasternack, L. Francesconi, D. Raff, E. Spiro, *Inorg. Chem.* 12 (1973) 2606.
- [9] J.A. Shelnut, M.M. Dobry, J.D. Satterlee, *J. Phys. Chem.* 88 (1984) 4980.
- [10] G.A. Schick, I.C. Schreiman, R.W. Wagner, J.S. Lindsey, D.F. Bocian, *J. Am. Chem. Soc.* 146 (1989) 165.

- [11] D.C. Barber, R.A. Freitag-Beeston, D.G. Whitten, *J. Phys. Chem.* 95 (1991) 4074.
- [12] O. Ohno, Y. Kaizu, H. Kobayashi, *J. Chem. Phys.* 99 (1993) 4128.
- [13] G.A. Schick, M.R. O'Grady, R.K. Tawari, *J. Phys. Chem.* 97 (1993) 1339.
- [14] J.H. Van Esch, M.C. Feiters, A.M. Peters, R.J.M. Nolte, *J. Phys. Chem.* 98 (1994) 5541.
- [15] M. Procházka, Master Thesis, Charles University, Prague, 1994.
- [16] N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, London, 1975.
- [17] B. Schrader, *Infrared and Raman Spectroscopy (Methods and Applications)*, WCH, Weinheim, 1995. p. 115.
- [18] D.L. Akins, H.-R. Zhu, Ch. Guo, *J. Phys. Chem.* 100 (1996) 5420.
- [19] N. Foster, *J. Magnet. Reson.* 56 (1984) 140.
- [20] J.R. Ferraro, K. Nakamoto, C.W. Brown, *Introductory Raman Spectroscopy*, Academic Press, San Diego, 2003. p. 233.
- [21] J.E. Maskasky, M.E. Kenney, *J. Am. Chem. Soc.* 95 (1973) 1443.
- [22] S. Mosseri, G.S. Nahor, P. Neta, P. Hambright, *J. Chem. Soc. Faraday Trans.* 87 (1991) 2567.
- [23] J. Hanzlík, *Chemical Papers* 67 (1973) 1239.