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Spectroscopic study of associated systems formed between water-soluble cationic porphyrins or their copper (II) complexes and nucleic building blocks

Research Article

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Abstract: The association process between two water soluble cationic porphyrins, 5,10,15,20-tetrakis[4-(trimethyl-ammonio)phenyl]-21*H*,23*H*-porphine tetra-*p*-tosylate (H_2TTMePP) and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine tetra-*p*-tosylate (H_2TMePyP), as well as their Cu (II) complexes, with five series of nucleic agents has been studied using UV-VIS spectroscopy in aqueous solutions. During the titration with nucleic compounds the bathochromic effect of porphyrins absorption spectra can be observed as well as the hypochromicity of the Soret maximum. The association constants were calculated using a curve-fitting procedure (K_{AC} of the order of magnitude of 10^3-10^5 mol^{-1}). It has been shown that the interactions of H_2TTMePP with nucleic agents are much stronger than interactions of H_2TMePyP, which is most likely related to the kind and the size of the porphyrin substituent groups partaking in the process of stacking. The strength of the observed associated systems increases generally in a series: nucleic base < nucleoside < nucleotide.

Keywords: *Water-soluble cationic porphyrins • Copper complexes • Nucleosides • Nucleotides • Binding constants*

1. Introduction

The subject regarding specific interactions of porphyrins and their complexes with nucleic acids building blocks has been extensively studied [1-7]. The main reason for such popularity is the application of the interactions mentioned above in gene technology and photodynamic therapy of cancer (PDT) [8-11] and in such medical diagnosis methods as magnetic resonance imaging (MRI) [12].

In the consequence of the specific interactions between porphyrins and nucleic acids in aqueous solution the different processes can occur, depending on the conditions of a particular reaction - either the formation of new biological systems, or the cleavage or destruction of a polynucleotide structure. Metal complexes of porphyrins usually play the role of the cleavage agents, in particular during the experiments related to the studies of nucleic acids tertiary structures [4]. The metalloporphyrins may also be a very useful tool in studies of porphyrin – DNA interactions under *in vivo* conditions. Such compounds as ZnTMePyP or H_2TMePyP have demonstrated promising *in vivo* anti-cancer and anti-inflammatory activities [13-15]. The porphyrin molecule influences the DNA chain by its particular elements [16], therefore the study of porphyrin interactions with nucleic bases and their derivatives represents the simplification of the real model of porphyrin – DNA interactions.

One of the main characteristics of the described systems is a great affinity of cationic porphyrins to react with nucleic building blocks. Based on this principle, it was decided to compare the results presented previously in literature [6,7] with the several preliminary spectrophotometric titration experiments [17]. The first objective of the research presented in this paper was to analyse the interactions, occurring in basic aqueous

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solutions, between free-base porphyrins, H_2TTMePP (*meso*-tetrakis[4-(trimethylamino)phenyl]porphyrin) and H_2TMePyP (*meso*-tetrakis(1-methyl-4-pirydyl) porphyrin), and their copper complexes, CuTTMePP and CuTMePyP, with 5 series of compounds: nucleic base – nucleoside – nucleotide, where the starting compound was adenine, guanine, cytosine, thymine, and uracil, respectively. As opposed to H_2TMePyP and its metal complexes, H_2TTMePP porphyrin is not so prevalent in the studies of porphyrin – DNA interactions. Therefore the primary aim of this study was to compare the behaviour of these two water-soluble cationic porphyrins or their copper (II) complexes to find a suitable porphyrin compound being the strongest binding agent for nucleic building blocks.

There are many research papers discussing the analysis of interactions between porphyrins and nucleic agents, but these articles describe mainly H_2TMePyP and primarily its interactions with a DNA chain [18] or merely with chosen nucleic building blocks [19]. To the best of my knowledge this paper presents for the first time the analysis of complex interactions of the two water-soluble cationic porphyrins and their copper (II) complexes with all the nucleic bases and their derivatives as well as the association constants values of all the systems mentioned above.

2. Experimental procedure

2.1. Reagents and measurements

The porphyrins: 5,10,15,20-tetrakis[4-(trimethylammonio)phenyl]-21*H*,23*H*-porphine tetra-*p*-tosylate (H_2TTMePP, ε = 390000 L mol^{-1} cm^{-1}) and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine tetra-*p*-tosylate (H_2TMePyP, ε = 210000 L mol^{-1} cm^{-1}) were purchased from ALDRICH and used without any additional purification (Fig. 1). α,α,α-Tris(hydroxymethyl)methylamine (TRIS) as well as nucleic compounds (adenine, adenosine, adenosine 5'-triphosphate disodium salt hydrate, guanine, guanosine hydrate, guanosine 5'-triphosphate trisodium salt hydrate, thymine, thymidine, uracil, uridine, uridine 5'-triphosphate trisodium salt hydrate, cytosine, cytidine, cytidine 5'-triphosphate disodium salt hydrate) were also supplied by ALDRICH. The copper (II) complexes of H_2TTMePP and H_2TMePyP (CuTTMePP and CuTMePyP) were synthesized by modification of the method described earlier in literature [5,20,21].

The titration experiments were carried out using a 10^{-3} mol dm^{-3} stock solution of each ligand. All the solutions of nucleic agents were prepared using sodium hydroxide to improve their solubility in water. The measurements were carried out in a 0.025 mol dm^{-3} TRIS buffer, at pH value adequate for each series of compounds. TRIS buffer was chosen previously for the preliminary experiments with cytosine and adenine solutions within the pH range 9.1 - 9.3 [17], thus the same buffer was used in these measurements in order to make a proper comparison.

All the initial porphyrin solutions (at the concentration range approximately 10^{-6} mol dm^{-3}) were freshly prepared in a 0.025 mol dm^{-3} TRIS buffer. Both, the initial porphyrin solution and the reference TRIS solution, as well as the ligand (nucleic agent) solution, had the same pH value for the particular systems. The initial volume of the porphyrin solution was 2 cm^3. The volumes of the stock solution of nucleic compounds, added at each step during titration of a porphyrin with the ligands from each group, were as follows: 0, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 cm^{-3} (the final volume of a stock ligand solution was 1.585 cm^{-3}). The final concentration of a nucleic compound in the mixture was 4.42×10^{-4} mol dm^{-3}.

Absorption spectra were taken using an UV-VIS M42 spectrophotometer (Carl Zeiss Jena) and 1 cm Hellma quartz cells to record spectra between 200 and 900 nm at the temperature of 21°C. Photometric accuracy of the spectrophotometer used was equal ± 0.003 AU. The database program Sigma Plot (version 9.0) (Jandel Corp.) was used in the manipulation and plotting of the data.

2.2. Calculation of association constants for porphyrin - nucleic agent systems

To calculate the association (binding) constants the absorbance values in the Soret band maximum of porphyrin compounds were used. The calculations were done using the Beck equation [22], which could be applied only on condition that the concentration of the titrant is at least 100 times greater than the concentration of the compound examined.

For the determination of binding constants of porphyrin – ligand (nucleic compounds) complexes, according to reaction:

$$P + L \longleftrightarrow PL \xleftrightarrow{L} P(L)_2 + \ldots \xleftrightarrow{L} P(L)_n \qquad (1)$$

the equilibrium constant K_n was written as:

$$K_n = \frac{[P(L)_n]}{[P(L)_{n-1}][L]} \qquad (2)$$

To calculate the final results the following equation, based on the Bjerrum function modified by Beck [22], was applied:

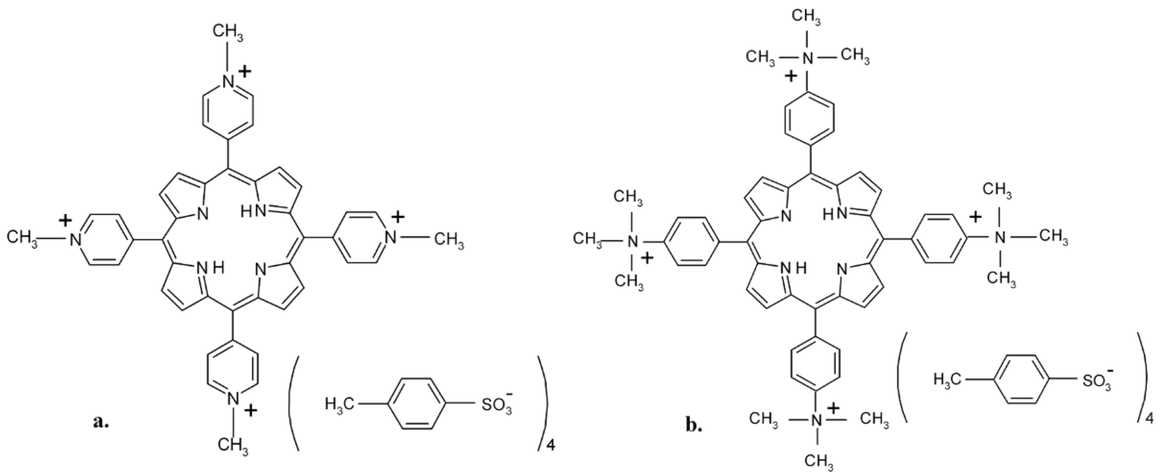

Figure 1. Molecular structures of 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine (H_2TMePyP) and 5,10,15,20-tetrakis[4-(trimethylammonio)phenyl]-21*H*,23*H*-porphine (H_2TTMePP).

$$A=\frac{\varepsilon_0+\varepsilon_1K_1[L]+\varepsilon_2K_1K_2[L]^2+\ldots}{1+K_1[L]+K_1K_2[L]^2+\ldots+} \qquad (3)$$
$$\frac{+\ldots+\varepsilon_nK_1K_2\ldots K_n[L]^n}{\ldots+K_1K_2\ldots K_n[L]^n}[P]$$

where A is the absorbance; ε_0, the molar absorbance index for the starting porphyrin; ε_1 and K_1, ε_2 and K_2, ..., etc. are the molar absorbance indexes and the gradual binding constants for complexes with the stoichiometry 1:1, 1:2, ..., *etc*., respectively; [L] and [P] stand for the analytical concentration of the ligand (nucleic agent) and the porphyrin.

Taking into consideration the 1:1 model of complex formation, the values of K_1 for all the porphyrin compounds examined were determined by fitting the experimental data to Eq. 4, using the non-linear fitting procedure based on the Marquardt–Levenberg algorithm (program Sigma Plot, version 9.0).

$$A=\frac{\varepsilon_0+\varepsilon_1K_1[L]}{1+K_1[L]}[P] \qquad (4)$$

The fitting procedure performed for the 1:2 model did not make any physical sense.

3. Results and discussion

The dilution experiments carried out with 0.025 mol dm^{-3} TRIS buffer obeyed the Beer-Lambert law. The slight deviations from the linearity, observed in the event of free-base porphyrins examined at pH > 12, are related to the beginning of the protonation process leading to the change of the porphyrin form, from free-base (H_2P) to monoanion (HP^-), according to the equation:

$$H_2P+OH^-=HP^-+H_2O \qquad (5)$$

Such changes do not occur in CuTTMePP and CuTMePyP, which confirms the stability of these metalloporphyrins (Fig. 2). At the porphyrin concentrations of approximately 10^{-6} mol dm^{-3}, like in described experiments, the porphyrin compounds in aqueous solution exist in the monomeric form, which confirms the data presented previously in literature [23-25].

Analysing the changes in the absorption spectra of the two water-soluble porphyrins and their copper (II) complexes during the titration with nucleic ligands, in each case the hypochromicity of the peak in a Soret band and its bathochromic shift is observed. According to literature, addition of various nucleic agents to the porphyrin solutions results generally in a red shift and hypochromism of the absorption bands, characteristic of a π-stacked complex formation [19,26-29]. Such differences observed in the absorption spectra reflect the approach of the nucleic compound to the porphyrin moiety [27] and the appearance of a new absorbing component in the examined system. As it was found by Jasuja [26], the porphyrin interactions with nucleic building blocks lead to electronic perturbations arising from the solvent effects and dipole moment changes in the porphyrin macrocycle. The distortion of the porphyrin plane owning to the process mentioned above has a significant effect on the electronic absorption [30]. The representative examples of such changes in the spectra of H_2TTMePP and CuTTMePP during the titration with ATP at pH = 9.1 are presented in Fig. 3.

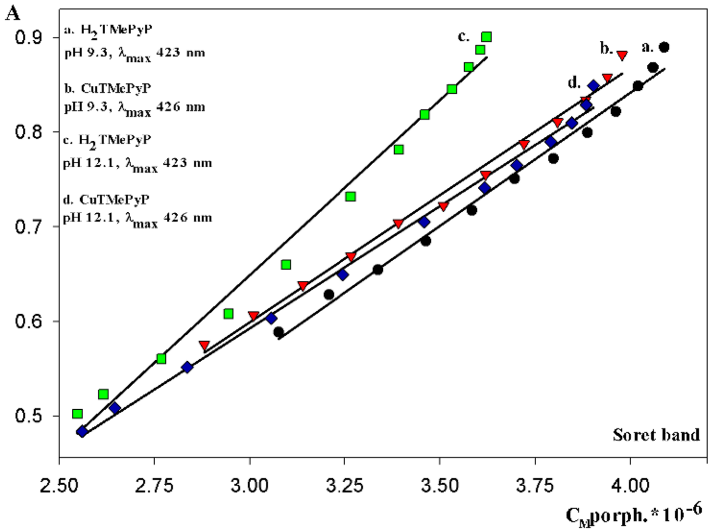

Figure 2. The linearity of Beer-Lambert law in the dilution experiment.

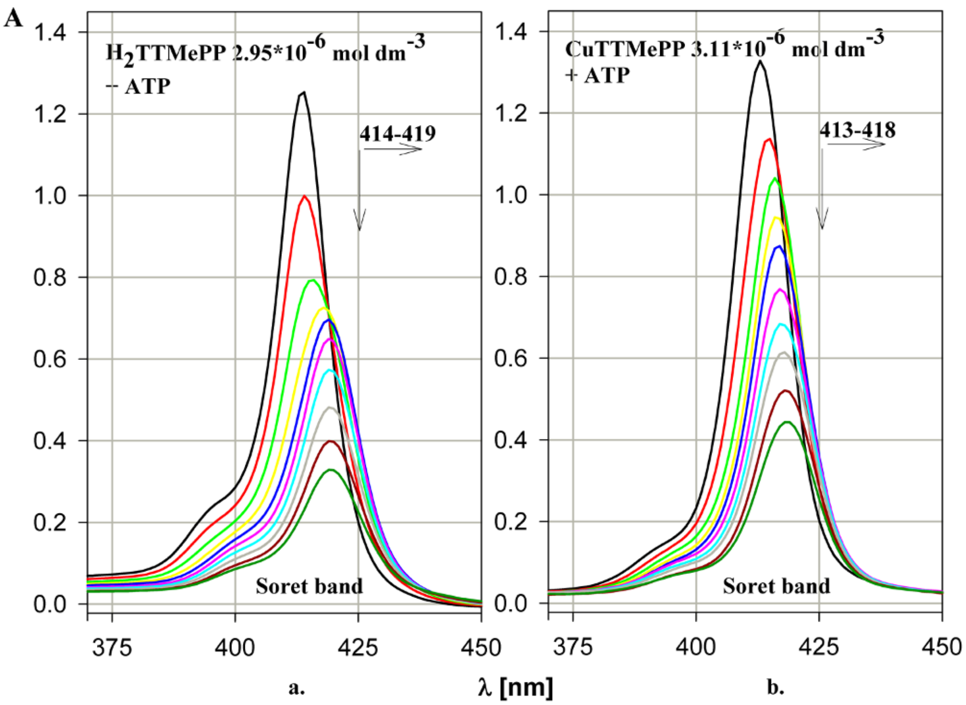

Figure 3. Evolution of H_2TTMePP (a) and CuTTMePP (b) spectra during titration with ATP in 0.025 mol dm^{-3} TRIS buffer, at pH = 9.1.

In these cases a decrease of the Soret maximum and a red shift of the λ_{max} from 414 to 419 nm and from 413 to 418 nm, respectively, are observed. The absorbance changes during titration of these porphyrin solutions with ATP are shown as the function of the H_2TTMePP and CuTTMePP concentration (Fig. 4) and as the function of adenine, adenosine and ATP concentration (the same for these three ligands) (Fig. 5) for the studied processes.

The association (binding) constants calculated for all the studied systems are presented in Table 1. It can be clearly noticed that the binding constants for the associated systems of H_2TTMePP with nucleic agents are much larger than for the associated systems of H_2TMePyP. According to literature the interactions between porphyrins and aromatic ligands occur through the attractive non-covalent process of π-π stacking [26,31]. It is also known that the interactions of a

Table 1. The binding (association) constants of associated systems [mol^{-1}] formed between porphyrins or their copper complexes and nucleic bases, nucleosides and nucleotides (error limits: ± 5 %).

	H_2TMePyP	CuTMePyP	H_2TTMePP	CuTTMePP
		pH=9.1		
adenine	7 189 1.85%[a] 0.9954[b]	1 226 0.78%[a] 0.9994[b]	19 022 3.09%[a] 0.9941[b]	6 719 1.42%[a] 0.9981[b]
adenosine	5 270 0.85%[a] 0.9983[b]	1 281 1.09%[a] 0.9984[b]	39 589 4.83%[a] 0.9851[b]	2 690 2.11%[a] 0.9966[b]
di-Na-ATP	37 995 4.46%[a] 0.9801[b]	9 472 4.48%[a] 0.9721[b]	179 945 1.21%[a] 0.9990[b]	32 681 3.40%[a] 0.9883[b]
		pH=12.4		
guanine	58 279[c] 0.56%[a] 0.9945[b]	26 307 1.13%[a] 0.9948[b]	177 455[c] 1.55%[a] 0.9986[b]	18 047 1.23%[a] 0.9957[b]
guanosine	2 581[c] 2.73%[a] 0.9879[b]	4 714 0.63%[a] 0.9982[b]	14 681[c] 4.75%[a] 0.9856[b]	28 143 2.02%[a] 0.9892[b]
tri-Na-GTP	1 746[c] 3.67%[a] 0.9778[b]	25 152 0.68%[a] 0.9980[b]	22 195[c] 4.60%[a] 0.9850[b]	41 811 1.22%[a] 0.9974[b]
		pH=12.4		
uracil	1 890[c] 2.36%[a] 0.9937[b]	5 322 1.13%[a] 0.9961[b]	95 211[c] 4.22%[a] 0.9813[b]	9 375 2.16%[a] 0.9875[b]
uridine	3 762[c] 1.09%[a] 0.9969[b]	23 646 1.23%[a] 0.9936[b]	9 996[c] 5.06%[a] 0.9760[b]	30 172 1.09%[a] 0.9960[b]
tri-Na-UTP	5 173[c] 1.53%[a] 0.9906[b]	60 034 0.62%[a] 0.9977[b]	71 470[c] 3.86%[a] 0.9901[b]	57 106 1.93%[a] 0.9934[b]
		pH=12.1		
thymine	1 289[c] 0.87%[a] 0.9977[b]	10 270 0.99%[a] 0.9953[b]	32 494[c] 2.47%[a] 0.9868[b]	5 997 1.60%[a] 0.9942[b]
thymidine	3 391[c] 1.00%[a] 0.9973[b]	19 844 1.19%[a] 0.9941[b]	9 031[c] 1.28%[a] 0.9923[b]	10 216 2.42%[a] 0.9900[b]
		pH=9.3		
cytosine	15 101 1.06%[a] 0.9933[b]	1 708 0.54%[a] 0.9986[b]	32 340 0.60%[a] 0.9982[b]	59 700 1.50%[a] 0.9896[b]
cytidine	4 274 0.99%[a] 0.9948[b]	4 652 0.58%[a] 0.9976[b]	21 278 0.90%[a] 0.9966[b]	22 312 1.18%[a] 0.9920[b]
di-Na-CTP	8 309 0.87%[a] 0.9963[b]	5 455 0.70%[a] 0.9977[b]	60 662 1.19%[a] 0.9949[b]	13 081 1.40%[a] 0.9935[b]

[a] *standard error*

[b] *correlation coefficient (R^2)*

[c] *partial deprotonation of a free-base porphyrin molecule ($H_2P \rightarrow HP^-$)*

porphyrin molecule with DNA are determined by the space size of the porphyrin peripheral groups [3] so this phenomenon may be explained by the considerably stronger stacking process occurring between the nucleic ligands and the molecule of H_2TTMePP porphyrin, owning the bigger, in comparison with H_2TMePyP, substituent groups. Moreover, in case of H_2TTMePP the larger values of association constants can be observed for the free-base porphyrin comparing with the values characterizing its copper complex. This effect can be explained by the greater screening of Cu (II) ion by the spacial groups of the H_2TTMePP substituents. The porphyrin molecule, which plays the role of a ligand in the copper complex, presumably causes the decrease in the interactions

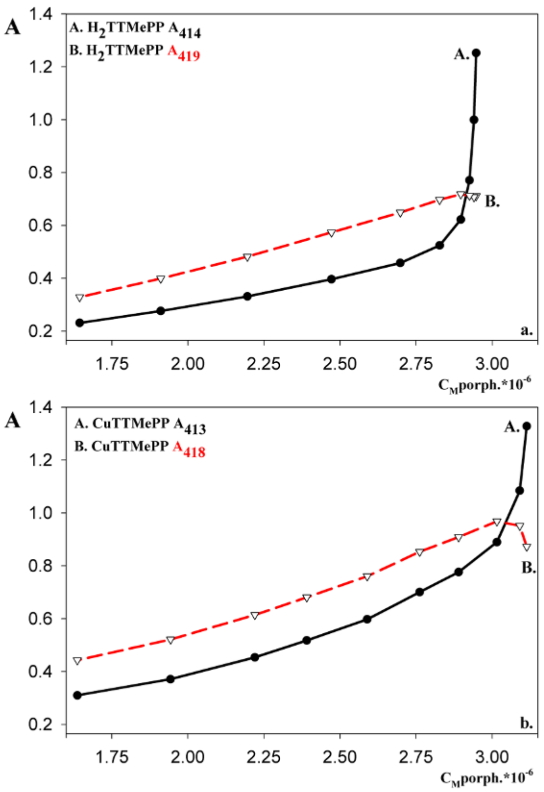

Figure 4. Dependence of absorbance on porphyrin compound concentration for the processes presented in Fig. 3. The concentrations of H_2TTMePP (a) and CuTTMePP (b) in solution changed as follows: 2.95, 2.94, 2.93, 2.90, 2.83, 2.70, 2.47, 2.20, 1.91, 1.64 ($\times 10^{-6}$ mol dm^{-3}) and 3.11, 3.09, 3.02, 2.89, 2.76, 2.59, 2.39, 2.22, 1.94, 1.64 ($\times 10^{-6}$ mol dm^{-3}), respectively.

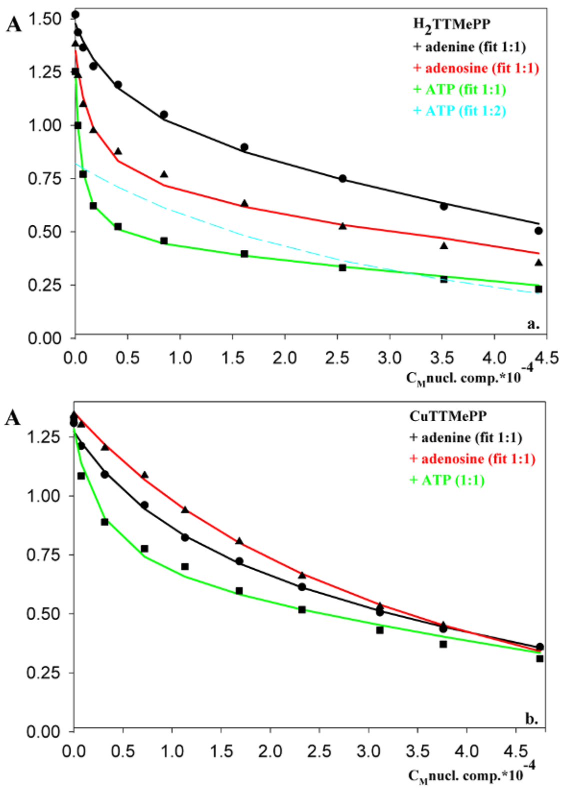

Figure 5. Dependence of absorbance on nucleic compound concentration for titration series of H_2TTMePP (a) and CuTTMePP (b) with adenine, adenosine and ATP in 0.025 mol dm^{-3} TRIS buffer, at pH = 9.1. The concentrations of nucleic compounds in solution changed as follows: (a) 0.00, 0.03, 0.07, 0.17, 0.41, 0.85, 1.61, 2.55, 3.52, 4.42 ($\times 10^{-4}$ mol dm^{-3}) and (b) 0.00, 0.07, 0.31, 0.72, 1.13, 1.68, 2.32, 3.12, 3.76, 4.74 ($\times 10^{-4}$ mol dm^{-3}), respectively. The points pertain to experimental data obtained during the titration and the solid lines are the fitted curves for experimental points (1:1 model fit). The dashed line (a) reflects the example of the fitted curve obtained according to the 1:2 (P:L) fitting procedure.

between the central ion and the nucleic compounds. Nevertheless, the relatively large values of the binding constants in case of Cu (II) complexes, in particular with nucleic agents from the guanine series, could testify to the interactions between the donor oxygen or nitrogen atoms from the nucleic base (via a water molecule, which is immobilized through the hydrogen bonding with either O or N of the nucleic compound) and the central Cu (II), which influence the strength of the generated associated molecules [32]. Since the hydrogen bond is often described as a strong electrostatic dipole–dipole interaction, the interactions between copper complexes of examined porphyrins and nucleic compounds can be partly considered to be electrostatic.

Analysing the values of binding constants it becomes obvious that the largest values were usually obtained for the nucleic bases containing two aromatic rings. The process of stacking is stronger for the bicyclic purine system in comparison with the single pyrimidine ring, because of the larger surface of interactions [5] with a porphyrin molecule. Furthermore, the values of association constants increase generally in a series: nucleic base < nucleoside < nucleotide (especially in the case of the systems with Cu (II) complexes) as it was presented earlier in literature [3]. The largest values of the association constants for nucleotide - cationic porphyrin systems can be explained by the simultaneous existence of both stacking and electrostatic interactions; the second one occurs between the negatively charged phosphate groups of the nucleotides and the positively charged substituent groups of the porphyrin compounds. According to Tabata [3] the contribution of such interactions involves up to 25% of the binding interactions in the examined systems. The similar processes were also observed for other metalloporphyrins, for instance for complexes with gadolinium [33]. The inverse relationship was observed in case of the systems containing guanine, guanosine and GTP (probably because of the strong ability to aggregation of GTP [34]).

The adsorption spectra of aqueous solutions of H_2TTMePP and H_2TMePyP at pH 7.0 show a λ_{max} of 414 nm and 423 nm, respectively, which correspond to the monomeric forms of these free-base porphyrins. At the pH value of approximately 12.0 the evolution of the porphyrin Soret band spectrum begins, due to the partial deprotonation of a free-base porphyrin and the formation of a monoanionic form HP^- (Eq. 5). As a consequence the red shift of a porphyrin spectrum is observed. At the pH > 12 the porphyrins interact simultaneously with the nucleic bases and the sodium base, which influences to a certain degree the process of association with the nucleic agents and therefore the values of the binding constants. However, the porphyrin spectra obtained during titration with nucleic agents at higher values of pH cannot be compared with the spectra recorded during the process of porphyrin deprotonation by NaOH, because the results obtained in both of these cases are different. In the case of copper complexes obtained by a method of classic synthesis, where Cu(II) ions are stably bound to a porphyrin cave, the formation of an anionic form is not observed (Fig. 2) Therefore it can be presumed that depending on the structure of a particular porphyrin system different pH values of nucleic compounds solutions create possibly the opportunity to form more than one type of an associated molecule in each studied system [35].

Increasing the pH value of the reaction environment can simultaneously imply the oxidation of the nucleic bases. Among the all nucleobases, guanine is the easiest target in oxidation process because of its high electronic density and consequently its lowest oxidation potential [36]. As a result of this process the products of guanine oxidation can be formed [37,38] increasing the number of types of associated molecules, and therefore increasing the values of the association constants (Table 1). Thus it is worth considering that at the pH > 12 the process of porphyrin monoanions formation does not exclude the concurrent formation of the associated systems between both H2P and HP- forms of porphyrins with nucleic agents (both non-oxidised and oxidised).

During the described experiments a several competitive interactions can potentially occur – not only the association phenomena and, in case of the free-base porphyrins, the protonation effects mentioned above, but also the process of dilution [2]. The changes in porphyrins concentration during titration process are not particularly large, but nevertheless the porphyrin concentration is not constant, which can slightly influence the clear separation of the dilution effects from the association phenomena [1]. Although dilution is an extremely significant factor affecting the porphyrin form present in a solution and therefore the types of porphyrin interactions, at the concentrations about 10^{-6} mol dm^{-3} used in the experiments the porphyrins exist presumably in a monomeric form [23,25,39]. So if we exclude, or at least limit, the influence of the protonation processes, the observed changes in the absorption spectra may be attributed to the association between the porphyrins and the nucleic agents. It is very likely that both, electrostatic interactions (attraction between the phosphate groups of the nucleotides and the substituent groups of cationic porphyrins) and, primarily, stacking interactions (involving an extensive overlap of the π-systems of porphyrin and purine or pyrimidine bases) contribute to the binding of porphyrins to the nucleic agents [1,5,19].

4. Conclusions

The experimental data obtained during the measurements and the association constants calculated from these data indicate the existence of specific interactions between porphyrins H_2TMePyP and H_2TTMePP, and their copper (II) complexes, and nucleic bases and their derivatives.

Interactions of H_2TTMePP with nucleic agents are much stronger than interactions of H_2TMePyP, due to the distinct degree of a non-covalent π-π stacking process influenced by different substituent groups of these porphyrins. The strength of the obtained associates increases in a series: nucleic base < nucleoside < nucleotide (especially in case of Cu complexes), although certain deviations from this rule are observed. The largest values of the association constants are found for H_2TTMePP, which points to the great tendency of this porphyrin for stacking interactions occurring in aqueous environment.

The studies described in this paper can be, to some extent, helpful in analysis of the reactions occurring in living organisms (for the sake of high pH value of examined solutions), but first of all they are indispensable for investigating of the processes related to porphyrin chemistry. The obtained results could be utilized in searching for substances strongly influencing the porphyrins to be useful “quenchers”, in the development of new classes of modified porphyrins of special properties [18,40] or artificial receptors [41-46] (particularly with the capability for a strong discrimination between the nucleic bases [47]), as well as in monitoring of the porphyrin-toxic substances interactions [48] or environmental and sanitary parameters, where there is a great demand for different kinds of chemical sensors [41,43,49].

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