A new protonated form of porphyrins in solutions

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The H-associate as a new protonated form of metalloporphyrins in strong acid media has been obtained and a qualitative reaction for its determination has been found; the properties and structure of a protonated form have been analyzed by spectral methods and quantum-chemical calculations.

Water-soluble porphyrins are of great interest in biological chemistry, photodynamic therapy,[1,2] or the catalytic synthesis of biologically important compounds,[3] and porphyrins soluble in aggressive media are of interest in the development of catalytic systems,[4–8] such as catalysts for obtaining fuel hydrogen in the sulfuric acid cycle.[6–8] The synthesis of super-stable metalloporphyrins (MPs) and the determination of their forms in different mixtures are necessary for the development of the theoretical fundamentals of catalysis. Organic liquids are more or less good solvents for MP without active functional substituents[9,10] while concentrated sulfuric acid is the same for porphyrin aza analogues (particularly, phthalocyanines MPcs).[11] Previously, it was believed that porphyrins in very strong sulfuric acid undergo irreversible destruction resulting in a final brown solution. We found[12] that it is not true: we extracted unmodified MPs from their solutions in sulfuric acid and quantitatively reprecipitated other MPs in the form of double-protonated porphyrins without macrocycle destruction. The UV-VIS spectra of MPs in both sulfuric acid and organic solvents were similar. At the same time, the absence of an intense green colour near a precipitate during dissolution indicates that already dissociated on a central atom metalloporphyrin transfers into solution. Thus, a brown solution with a very specific UV-VIS spectrum belongs to either MP or doubly protonated porphyrin of an unknown form. However, up to now it was impossible to study other properties of this form of MP or H_4P^{2+} by classic titration, potentiometry and conductometry because concentrated sulfuric acid is highly corrosive.

In this study, the presence of an additional proton in a new form of MPs was directly confirmed for the first time by ^{1}H NMR spectroscopy[†] and its most probable location was determined by quantum-chemical calculations.[‡]

Complexes of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin with some *p* metals and *d* metals were synthesized[§,¶] for this investi-
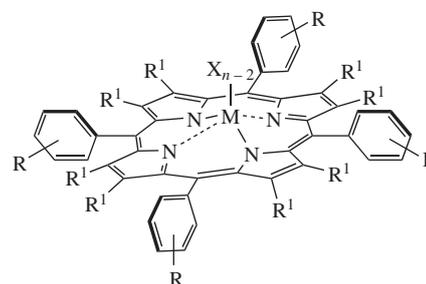
R = *p*-Br, *o*-NH$_2$, *p*-F, *p*-OMe, *p*-adamantanoylamino
R^1 = β-Br, β-Alk
X = Cl$^-$, Br$^-$, AcO$^-$, HSO$_4^-$, SCN$^-$, AcacO$^-$, OH$^-$, O^{2-}, OPh$^-$, N^{3-}
n = 2, 3, 4, 5

gation. The stability of MP complexes [(Cl)MnT(R)$_m$PP(R$_1$)$_p$] and [(X)MnTPP] in AcOH, AcOH–H$_2$SO$_4$, concentrated H$_2$SO$_4$ (up to 100%) and other acids were studied by UV-VIS spectroscopy. It was established that the MP new form has a unique two-band UV-VIS spectrum (Figure 1) with maxima near 540 and 700 nm. The first band position (700 nm) is practically independent of metal nature and noticeably changes under functional substitution (Table 1). A second band (540 nm) is shifted to shorter wavelengths compared to corresponding spectrum in CHCl$_3$. A band at 700 nm undergoes a slight shift when the concentration of a strong acid changes. Thus, in the spectrum of (AcO)TlTPP visible bands are at 700, 545, 452 nm in 100% H$_2$SO$_4$ and at 692, 545, 445 nm
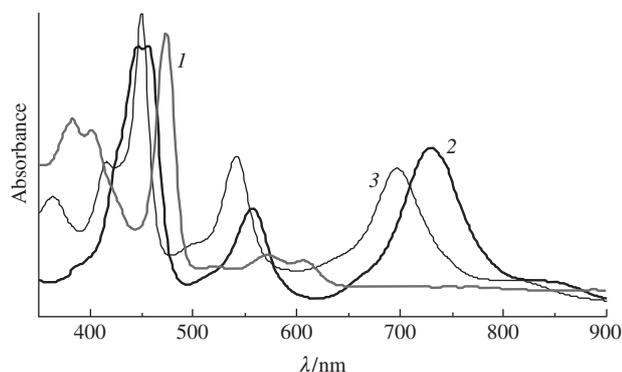

[†] ^{1}H NMR spectra were measured on a Bruker Avance-500 spectrometer.
5,10,15,20-Tetraphenyl-21H,23H-porphyrin, H$_2$TPP. ^{1}H NMR (CDCl$_3$) δ: 8.77 (s, 8 H, C$_4$H$_2$N), 8.33 (d, 8 H, *o*-C$_{Ph}$, *J* 6.1 Hz), 7.78 (m, 12 H, *m*-C$_{Ph}$, *p*-C$_{Ph}$), –2.76 (s, 2 H, NH). ^{1}H NMR (CF$_3$COOH) δ: 8.85 (s, 8 H, C$_4$H$_2$N), 8.6 (d, 8H, *o*-C$_{Ph}$, *J* 6.1 Hz), 8.05 (m, 12H, *m*-C$_{Ph}$, *p*-C$_{Ph}$), –1.98 (s, 4H, NH).
(5,10,15,20-Tetraphenylporphinato)silver(II), AgTPP. ^{1}H NMR (CDCl$_3$) δ: 7.77 (s, 8 H, C$_4$H$_2$N), 7.65 (s, 8 H, *o*-C$_{Ph}$), 7.1 (m, 8 H, *m*-C$_{Ph}$), 6.55 (m, 4 H, *p*-C$_{Ph}$). ^{1}H NMR (CF$_3$COOH) δ: molecular form (AgTPP): 7.84 (s, 8 H, C$_4$H$_2$N), 7.66 (m, 8 H, *o*-C$_{Ph}$), 7.23 (m, 4 H, *p*-C$_{Ph}$), 7.15 (m, 8 H, *m*-C$_{Ph}$); H$^+$-associated form (AgTPP···H$^+$): 8.67 (s, 8 H, C$_4$H$_2$N), 8.14 (d, 8 H, *o*-C$_{Ph}$, *J* 7.3 Hz), 7.55 (m, 4 H, *p*-C$_{Ph}$), 7.48 (m, 8 H, *m*-C$_{Ph}$), 4.25 (m, 1H, H$^+_{meso}$), 4.46 (m, 1H, H$^+_β$).

[‡] Computer modeling of hydrogen bonds between MP and proton stepwise formation was carried out for (Cl)InTPP, AgTPP and H$_4$TPP^{2+}. Molecule structure of complexes, H$_4$TPP^{2+} and H$^+$-associates H$_4$TPP^{2+}···*n*H$^+$, AgTPP···*n*H$^+$, (Cl)InTPP···*n*H$^+$ (*n* = 1, 2, 3) were optimized by PM3 and ZINDO quantum-chemical techniques,[13–16] and the geometry and energy parameters of these structures were also obtained. The isolated H$^+$, H$_3$O$^+$ and a neutral molecule of H$_2$SO$_4$ were used as proton active forms.

[§] Metalloporphyrins were obtained by the reaction of a porphyrin with a metal salt, or, in the case of Ru, Re, Os, Ir and Pt porphyrins, with potassium salt of corresponding acid in an organic solvent according to published procedures,[17–24] as exemplified below. Low-boiling solvents (DMF, Py, DMF–Py, AcOH, AcOH–Py, CHCl$_3$–THF and CHCl$_3$–AcOH) were used for the synthesis of complexes with Al, Tl, Si, Sn, Pb, Ti, metals from Mn to Zn, Pd, Ag, Pt (Pt^{IV} complex) and Au. High-boiling solvents (benzene, benzonitrile and quinoline) were used for the synthesis of complexes with Ga, In, Ge, V, Cr, Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, Os, Ir, Pt (Pt^{II} complex). (N)Mn^{V}TPP was obtained by the oxidation of (Cl)Mn^{III}TPP according to technique[25,26] for the synthesis of nitride complexes of MPc and Mn tetraazaporphyrins.

Figure 1 UV-VIS spectra of (Cl)MnT(4-Br)PP in (*1*) AcOH and (*2*) conc. H_2SO_4, (*3*) (N)MnTPP in conc. H_2SO_4.

in 14.5 M H_2SO_4. We divided all studied MPs into three groups: MPs unstable in strong acids media,[††] the complexes forming a new H⁺-associated form $MP\cdots H^+_{Solv}$, and MPs existing in a molecular form in an acid solution.[‡‡] (N)MnTPP, $MnCl_3\cdot H_2MPOMP$ and PdTPOEP are reprecipitated in an unchanged form when their acid solutions are poured onto ice. The other MPs transform to corresponding porphyrins under reprecipitation.

Table 1 shows that the following conditions for the existence of H-associates of MPs are necessary: (1) the coordination centre should be stable in acid medium; (2) the macrocycle should not include electron-acceptor substituents; (3) it should contain σ- or σπ-donor acido ligands in the first coordination sphere, or alternatively, the *d*-orbitals of central metal cation should not contain less than six electrons. Thus, the common request is a possibility to realize the electron-excess state of aromatic macrocycle together with coordination centre stability.

The spectrophotometric titration of MP with sulfuric acid by original technique, detection of additional proton signals in the NMR spectrum and a theoretical optimization of a molecule structure of MP and $MP\cdots H^+_{Solv}$ were carried out to determine the nature and number of H^+_{Solv} particles in H⁺-associate, the localization place and energy of stable hydrogen bond. A classical technique for the preparation of a solutions series for spectrophotometric titration of (Cl)InTPP with H_2SO_4 was not used because of heating upon mixing H_2SO_4 and water. Initially, we determined the values of ε at each H_2SO_4 concentration in the range of 12.02–17.60 mol dm⁻³ based on known MP concentration and optical density at the working wavelengths (447, 535 or 682 nm). Then, optical densities were calculated for a constant MP to produce the titration curve. In the concentration range

Table 1 UV-VIS spectral characteristics for MP forming H⁺-associate in strong acids medium.[a]

MP	λ^I_{max}/nm {$\log\varepsilon$}	λ^{II}_{max}/nm {$\log\varepsilon$}	λ^{III}_{max}/nm {$\log\varepsilon$}	I and II bands intensities correlation
H_4TPP^{2+}	700	550	448.2	I ≈ II
(Cl)AlTPP	695	600	459	I < II
(OH)AlTPP	695	600	459	I < II
(AcO)GaTPP	716	541	not studied	I ≈ II
(Cl)InTPP	682 {4.81}	535 {4.87} (559)	447 {5.19}	I ≈ II
	682 {4.30}	535 {4.86}	447 {5.17}	
	681 {4.80}	536 {4.86}	447 {5.16}	
	681 {4.65}	536 {4.83}	447 {5.14}	
	680 {4.65}	536 {4.73}	446 {5.12}	
(AcO)TlTPP	700	545 (565)	455	I ≈ II
$(OH)_2SiTPP$	698	540 (557.5)	not studied	I ≈ II
$(AcO)_2PbTPP$	660	520 (584)	440, 470	I ≈ II
O=TiTPP	694	540 (550)	not studied	I ≈ II
(Cl)MnTPP	697	540 (582)	448	I ≈ II
(AcO)MnTPP	697	540 (584)	448	I ≈ II
(HSO_4)MnTPP	697	540 (581)	448	I ≈ II
(Cl)MnT(4-Br)PP	732	557	446, 456	I > II
(Cl)MnTPP(β-Br)	715	555	not studied	I ≈ II
(Cl)MnTPP(β-Br)₄	742	578 (600)	476	I < II
$(N)Mn^VTPP$	695	540 (534.5)	449	I ≈ II
$MnCl_3\cdot H_2MPOMP$ (SAT complex)	694	542 (514.5, 550)	not studied	I ≈ II
(Cl)FeTPP	691	540	450	I ≈ II
PdTPP	691	538 (552)	437	I ⩽ II
PdTPOEP	710	562	not studied	I < II
PdOEP[b]	720–725	not studied (545)	not studied	not studied
PdMPOEP[c]	715	548 (550)	not studied	I ≪ II
AgTPP	694	541 (541)	not studied	I ≈ II
OsTPP	≈730	≈525 (551.5)	not studied	I ⩽ II
$(Cl)_2PtTPP$	694	539 (548)	455, 420	I ≈ II
(O)Re(OH)TPP	690	538	448	I < II

[a]In concentrated sulfuric acid. For (Cl)InTPP $C_{H_2SO_4}$ is (top-down) 16.09, 15.04, 14.04, 13.00, 12.02 mol dm⁻³; (Cl)AlTPP, $C_{H_2SO_4}$ > 17.5 mol dm⁻³; (OH)AlTPP, $C_{H_2SO_4}$ > 16.5 mol dm⁻³; OsTPP, $C_{H_2SO_4}$ = 18.22 mol dm⁻³. Maxima λ_{max} in chloroform are given in parentheses. [b]In AcOH, 0.9–1.4 M H_2SO_4. [c]In AcOH, 2.8–4.5 M H_2SO_4.

12.02–16.09 mol dm⁻³, a linear correlation $\lg[(A_p - A_0)/(A_\infty - A_p)]$ *vs.* $-H_0$ was obtained, where A_0, A_p and A_∞ is the absorbance (at the working wavelengths) of (Cl)InTPP solutions, equilibrium mixture at a certain concentration of H_2SO_4 and H⁺-associate, respectively. Mathematical processing of the correlation by the method of least squares gives the slope closed to 1 ($\tan\alpha$ is 0.67, 0.66 or 0.80 at 447, 535 or 682 nm, respectively), which corresponds to one proton involved in the reaction and the equilibrium constant $K = 10^7$ dm³ mol⁻¹. The test range of H_2SO_4 concentrations does not cover the investigated equilibrium between (Cl)InTPP molecules and H⁺-associates in the leftmost position due to low solubility of the (Cl)InTPP molecular form. Therefore, the constant K should be considered as an approximate value.

Since the experimental possibility of obtaining precise ¹H NMR spectra of H⁺-associated form in strong acid is limited, we performed NMR measurements for anhydrous $CF_3COOH^†$ solutions of AgTPP and H_2TPP that according to EAS exist in this medium as the H⁺-associated form and dication H_4TPP^{2+}, respectively. Low complex solubility, H_2SO_4 impurity and MP instability, in particular (Cl)InTPP, in 100% acid did not allow us to record spectra in D_2SO_4. Higher stability of the Ag complex is known from a comparative study[12,24] of (Cl)InTPP and AgTPP complexes dissociation kinetics in concentrated H_2SO_4. Corresponding parameters: rate constants k^{298}, activation energies E and activation entropies $\Delta S^{\neq}$ are 0.36×10^{-6}, (75±11), (−125±32) and

[¶] *(5,10,15,20-Tetraphenylporphinato)palladium(II), PdTPP.*[27] H_2TPP and $PdCl_2$ in a molar ratio of 1:10 were boiled in DMF until H_2TPP bands (λ_{max}/nm: 648.0, 592.0, 551.0, 516.0, 485.0, 420.0) disappeared from the UV-VIS spectrum of the reaction mixture. Then, the solvent was distilled off *in vacuo*, the residue was dissolved in minimum $CHCl_3$ and purified twice by column chromatography (Al_2O_3 L 40/250, Chemapol) with chloroform as an eluent. UV-VIS [$CHCl_3$, λ_{max}/nm ($\log\varepsilon$)]: 541 (3.92), 511 (4.11), 402 (4.84). IR (KBr, ν/cm⁻¹): benzene ring vibrations, 696, 744 (γ_{C-H}), 1071, 1075 (δ_{C-H}), 1485, 1562, 1598 ($\nu_{C=C}$), 3040, 3054 (ν_{C-H}); pyrrole ring vibrations, 791 (γ_{C-H}), 1016 (C^3–C^4, ν_{C-N}, δ_{C-H}), 1312 (ν_{C-N}), 1438 ($\nu_{C=N}$), 1540 (skeletal vibrations in pyrrole ring), 2853, 2973 (ν_{C-H}); 440, 470 (Pd–N). ¹H NMR (CDCl₃) δ: 8.81 (t, 8H, C_4H_2N, J_{HH} 3 Hz), 8.16 (t, 8H, *o*-C_{Ph}, J_{HH} 3 Hz), 7.75 (m, 12H, *m*-C_{Ph}, *p*-C_{Ph}). MS (MALDI-TOF), *m/z*: 719.05 [M⁺]. Found (%): C, 73.31; H, 3.76; N, 7.80. Calc. for $C_{44}H_{28}N_4Pd$ (%): C, 73.49; H, 3.92; N, 7.79.

For synthesis and characteristics of complexes $(AcO)_2PbTPP\cdot Py$ and O=W(OH)TPP, see Online Supplementary Materials.

[††] For a number of unstable metal pophyrins (A number 1), see Online Supplementary Materials.

[‡‡] For a number of stable metal pophyrins dissolved as a molecular form (Table 1S), see Online Supplementary Materials.

0.24×10^{-8} s^{-1} mol^{-1} dm^3, 116 kJ mol^{-1}, –28 J mol^{-1} K^{-1}. Two additional signals at 4.25 and 4.46 ppm were detected in the AgTPP spectrum compared to the H$_4$TPP^{2+} spectrum in CF$_3$COOH and the NH-proton signal observed in the H$_4$TPP^{2+} spectrum in CF$_3$COOH at –1.98 ppm was not detected.[†,§§] On the basis of quantum-chemical calculations, two additional signals were attributed to two additional protons in H$^+$-associate presumably at the *meso*- and β-positions of macrocycle. Addition of two protons to AgTPP is probably connected with increasing medium acidity.

Bounding of additional protons to the aromatic atoms C$_{meso}$ and C$_\beta$ differs from a similar case of protonated benzene because the interaction is finished upon incomplete proton transition and formation of a hydrogen bond only. Really, specified C atoms in H$_2$TPP according to calculation[28] and X-ray electron spectroscopy[29] have a negative effective charge.

Thus, the use of the isolated proton H$^+$ in calculations[‡] provides the best prediction of the structure of H$^+$-associated forms.[§§] The energies of accession of one proton which are equal or higher than the energy of protonation of a water molecule (170–166.5 kcal mol^{-1}) or an ammonia molecule (207 kcal mol^{-1})[30,31] were used as a criterion of possibility of stepwise proton accession. As follows from calculations, formation of H$_4$TPP$^{2+}\cdots$H$^+_{meso}$ with localization of one proton at the *meso*-carbon of macrocycle is unlikely (protonation energy E_{prot} = –86.93 kcal mol^{-1}, bond length C$_{meso}\cdots$H$^+$ is 1.127 Å). Formation of mono- and diprotonated forms is energetically favourable for cases of (Cl)InTPP and AgTPP. Three isomers (Cl)InTPP$\cdots$H$^+_{meso}$, (Cl)InTPP$\cdots$H$^+_\beta$ and (Cl)InTPP$\cdots$H$^+_\alpha$ are possible as mono-associate of (Cl)InTPP with E_{prot} = –208.45, –208.80 and –199.57 kcal mol^{-1} and bond length C$\cdots$H$^+$ of 1.128, 1.111 and 1.130 Å, respectively. Accession of the second proton is accompanied by formation of three isomers with localization of the protons at the C$_{meso}$ and C$_\beta$ of the neighbouring pyrrole fragment (E_{prot} = –140.02 kcal mol^{-1}, bond lengths C$_{meso}\cdots$H$^+$ = 1.129 Å, C$_\beta\cdots$H$^+$ = 1.115 Å), at the C$_{meso}$ and C$_\beta$ of the pyrrole fragment not connected with 'protonated' C$_{meso}$ (E_{prot} = –141.71 kcal mol^{-1}, bond lengths C$_{meso}\cdots$H$^+$ = 1.129 Å, C$_\beta\cdots$H$^+$ = 1.112 Å) and at the C$_{meso}$, C$_\beta$ of the pyrrole fragment which is not neighbouring one (E_{prot} = –129.45 kcal mol^{-1}, bond lengths C$_{meso}\cdots$H$^+$ = 1.129 Å, C$_\beta\cdots$H$^+$ = 1.128 Å).

Mono-protonation of AgTPP is more probable at the *meso*-position of macrocycle with AgTPP$\cdots$H$^+_{meso}$ formation (E_{prot} = = –320.22 kcal mol^{-1}, bond length C$_{meso}\cdots$H$^+$ = 1.10 Å). The di-associated form is represented by three isomers with hydrogen bond at two C$_{meso}$ in *trans*- and *cis*-positions (E_{prot} = –237.80 and –195.0380 kcal mol^{-1}, bond lengths $C_{meso}\cdots$H$^+$ = 1.102, 1.102 Å and 1.111, 1.111 Å) and at C$_{meso}$ which is not neighbouring to C$_\beta$ (E_{prot} = –286.08 kcal mol^{-1}, bond lengths C$_{meso}\cdots$H$^+$ = 1.10 Å, C$_\beta\cdots$H$^+$ = 1.102 Å).

The formation of H$^+$-associate with three hydrogen bonds for both studied complexes is characterized by significantly lower energy of interaction [for (Cl)InTPP with localization of the protons at the C$_{meso}$ and two C$_\beta$ E_{prot} = –50.77 kcal mol^{-1}]. The molecular structure of such an associate is very strained and distorted. Thus, the analysis of calculated data allows us to draw a conclusion to the absence of interaction both at the third and forth steps in the model system.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.09.019.

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§§ For ^{1}H NMR spectrum of AgTPP and H$_2$TPP (Figure 1S), as well as data for neutral and H$^+$-associated forms (Table 1S), see Online Supplementary Materials.

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