Features of Inverted Tetrasulfophenylporphyrin Protonation. Crucial Role of Hydrogen Bonds

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Diprotonation equilibria of inverted platform of tetraanionic 5,10,15,20-tetrakis(4′-sulfophenyl)-2-aza-21-carbaporphyrin, H2IP(PhSO3H)4, with perchloric acid in water was studied using DFT/B3LYP/6-31++G(d,p) and spectropotentiometric titration methods. In aqueous solution this porphyrinoid exists in the form of NH tautomer H2IP(PhSO3−)4 with an inverted pyrrolenine ring, which is stabilized by bifurcated intramolecular hydrogen bonds between two pyrrole hydrogens and one pyrrolenine nitrogen. Intramolecular hydrogen bonds protect intramolecular hydrogen-bonding sites from intermolecular interactions. For this reason, the external nitrogen atom is protonated first, and then the internal one is protonated. The second proton switches the intramolecular hydrogen bonds to intermolecular hydrogen bonds. Diprotonated platform H4IP2+(PhSO3−)4 has the geometry of elastic 1,3-alternate, which is a molecular and anionic receptor. The equilibrium of the second stage protonation in water is completely shifted to the aquaocomplex [H4IP2+(PhSO3−)](H2O)2, which is formed due to the hydrogen and electrostatic binding of the solvent molecules on both receptor sites. Aquacomplex [H4IP2+(PhSO3−)](H2O)2 is a monomer of linear J-aggregates self-assembly. The driving force of J-aggregates assembly is the formation of stronger anionic complexes as a result of water molecules intermolecular replacement by sulfonate groups of monomers.

Keywords: Tetrasulfophenyporphyrin, inverted (N-confused) porphyrins, protonation, hydrogen bond, J-aggregates.

Особенности протонирования инвертированного тетрасульфофенилпорфирин в воде. Критическая роль водородных связей

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Методами DFT/B3LYP/6-31++G(d,p) и спектропотенциометрического титрования исследованы равновесия дипротонирования инвертированной платформы тетрааниона 5,10,15,20-тетракис(4'-сульфофенил)-2-аза-21-карбапорфирин H2IP(PhSO3H)4 с хлорной кислотой в воде. В водном растворе этот порфириноид находится в виде NH-таутомера H2IP(PhSO3−)4 с инвертированным пирролениновым кольцом, который стабилизируется бифурканными ВМВС между двумя пиррольными водородами и одним пирролениновым атомом азота. ВМВС защищают внутримолекулярные центры водородного связывания от межмолекулярных взаимодействий. По этой причине первым протонируется внешний атом азота, а внутренний протонируется вторым. Второй протон переключает ВМВС на ММВС. Дипротонированная платформа H4IP2+(PhSO3−)4 имеет геометрию упругого 1,3-альтерната, который обладает свойствами молекулярного и анионного рецептора. Равновесие второй ступени протонирования в воде полностью сдвинуто в реакцию образования ауквакомплекса [H4IP2+(PhSO3−)](H2O)2, который образуется за счет водородных и электростатических связываний водородных атомов двух сайтов рецептора. Ауквакомплекс [H4IP2+(PhSO3−)](H2O)2 представляет собой мономер самосборки линейных J-агрегатов.
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является образование более прочных анионных комплексов в результате межмолекулярного замещения молекул воды сульфонатными группами мономеров.

Ключевые слова: Тетрасульфенилпорфирин, инвертированные порфирины, протонирование, водородная связь, J-агрегаты.

Introduction

The key part of supramolecular porphyrin assemblies in nature inspires researchers to developed biomimetic systems for a wide range of applications. The molecular structure of porphyrins is easily modified both on the core and periphery, providing a structural complementary of monomer units leads to supramolecular self-assembly.[1-12] Understanding such processes attracted great interest due to the apparent potential of the functional nanomaterials self-assembly strategy, which opens up the splendid perspectives for the directed design of chemosensors, molecular switches, luminescent sensors, photon wires and catalysts. To date, a wide range of regular discrete porphyrin nanostructures such as nanotubes, fibers, wheels, spheres, plates, etc. have been obtained.[13,14] Water-soluble derivatives of 5,10,15,20-tetrakis(4'-sulfophenyl)porphyrin H2P(PhSO3H)4 are widely used as building blocks for such structures, due to the successful combination of availability and good solubility of such compounds in water. Promising derivatives of H2P(PhSO3H)4 are water-soluble porphyrinoids with inverted pyrrole ring, such as 5,10,15,20-tetrakis(4'-sulfophenyl)-2-aza-21-carbaporphyrin H2IP(PhSO3H)4 and 2-N-methyl-5,10,15,20-tetrakis(4'-sulfophenyl)-2-aza-21-carbaporphyrin H2MeIP(PhSO3H)4. Investigations of inverted porphyrins properties, including aqueous media, have been carried out since their discovery due to the unique structure of these compounds.[15-25] Previously it was shown that diprotonated inverted platform possesses the properties of anionic receptor,[8,26] the zwitterions H4IP2+(PhSO3-)4 and H3MeIP2+(PhSO3-)4 are able to form supramolecular J-aggregates, stable in pH-neutral aqueous solutions.[21,27]

In this work we presented the results of theoretical and experimental studies of H2IP(PhSO3H)4 diprotonation equilibria, resulted in formation of aquacomplex [H2IP2+(PhSO3-)4](H2O)2, which is J-aggregates self-assembly monomer.

Experimental

All commercially available solvents and reagents were used without further purification: N,N-Dimethylformamide (0.01 % H2O, Panreac), dichloromethane (for HPLC, 99.8 %, Acros Organics), distilled water (ISC RAS), perchloric acid (70 %, ASC reagent, Aldrich). 5,10,15,20-Tetraphenyl(2-aza-21-carbaporphyrin, (H2IP(Ph))4, 5,10,15,20-tetrakis(4'sulfophenyl)-2-aza-21-carbaporphyrin[27] were synthesized according to reported procedures. Micropipette with scale division value 6.3·10-4 mL was used for titration experiment. The absorbance and fluorescence spectra were recorded synchronous at 25 °C in 1×1 cm optical quartz cells using a fluorescence spectrophotometer (Avantes AvaSpec 2048-2, Netherlands) equipped with a qpod© (Quantum). The basicity constants were calculated by the fitted parameters method using SigmaPlot® (Systat Software Inc. (SSI)) software. Quantum chemistry calculations were performed at the B3LYP level of density functional theory DFT/ B3LYP/6-31++G(d,p) using Gaussian software package.[29]
in presented article we consider the processes exclusively involving tetraanions $\text{H}_2\text{I}P(\text{PhSO}_3^-)_4$, $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$, and the products of the porphyrin platform protonation.

The porphyrin platform $\text{H}_2\text{P}$ is formed by different in structure pyrrole (A) and pyrrolenine (B) rings (Figures 1, 2(1)). As a result of the pyrrole or pyrrolenine ring inversion, two NH-tautomers $\text{H}_2\text{IP}$ with a different combination of three internal and one external centers of H-bonding (HB) are formed. Inversion of the pyrrole ring results in a $\text{H}_2\text{I}_{10}^0\text{P}$ tautomer formation with an external HB-donor NH-group and two bifurcated intramolecular hydrogen bonds (IMHB) of the NHN type. Porphyrine ring inversion results in a $\text{H}_2\text{I}_{10}^0\text{P}$ tautomer with an external HB-acceptor nitrogen atom and two bifurcated IMHB of the HNH type.

Enthalpy dissipations due to $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$ porphyrin platform inversion are 13.01 and 17.34 kcal/mol for $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ and $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$, respectively. Thus, in the absence of medium effects, the tautomer $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ is more stable than $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ by 4.33 kcal/mol, due to a more effective IMHB. Two opposite types of specific solvation external centers are the cause of the dependence of inverted porphyrins tautomeric equilibrium from solvents HB-donor ($\Sigma\beta$) and HB-acceptor ($\Sigma\alpha$) properties.

Conjugated tautomers of inverted porphyrins possessed the different UV-Vis spectra, which general view was used for identification of $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ and $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$, respectively. Thus, in the absence of media effects, the tautomer $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ is more stable than $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$ by 4.33 kcal/mol, due to a more effective IMHB. Two opposite types of specific solvation external centers are the cause of the dependence of inverted porphyrins tautomeric equilibrium from solvents HB-donor ($\Sigma\beta$) and HB-acceptor ($\Sigma\alpha$) properties.

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Figure 1. Scheme of $\text{H}_2\text{P}(\text{PhSO}_3^-)_4$ porphyrin platform inversion. meso-Substituents are omitted for clarity. UV-Vis spectra of inverted NH-tautomers in different solvents are presented on the right side. Bold line shows the aromatic 18π-electron conjugated cycle. DFT-enthalpies of inversion and tautomerization values in kcal/mol, calculated in gaseous phase, are above the arrows. UV-Vis spectrum in DCM corresponds to $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$. Additionally, there is information on the molecular structure of $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$, coordination cage of $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$, and the coordination cage of $\text{H}_2\text{I}_{10}^0\text{P}(\text{PhSO}_3^-)_4$. The singularity of aromatic tetrapyrrole platforms is the presence of the conventional meso-plane C5C10C15C20, which is only slightly deformed even with a strong distortion of the macrocycle. As a result of intramolecular hydrogen repulsion (IMHR) internal CH-proton escapes from the meso-plane at 0.59 nm, and the inverted
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Figure 2. (1) – Indexing of tetrapyrrole platform. (2) – Tetraanion $\text{H}_4\text{IP}((\text{PhSO}_3^-)_4$ DFT-optimized geometry. Gray dashed lines – bifurcated IMHB, red dashed lines – H-π interactions between $\beta$-protons and phenyl rings (distance to phenyl plane center is 3.32 Å). Sulfonate groups, located perpendicular to the figure plane, are omitted for clarity.

Table 1. Deviations of intramolecular interatomic distances (Å) from the sum of Van der Waals radii ($R_v$) (H(1.16), N(1.50) O(1.29)).

| Compound                        | IMHR | IMHB |
|---------------------------------|------|------|
|                                | AB   | BC   | CD   | AD   | AC   | BD   | AB   | BC   | CD   | DA   |
| $\text{H}_2\text{P}((\text{PhSO}_3^-)_4$ | -0.12 |      | +0.05 |      |      |      | -0.33 | -0.33 | -0.33 | -0.33 |
| $\text{H}_3\text{P}^+(\text{PhSO}_3^-)_4$ | +0.25 | +0.25 | +0.25 | +0.25 | +0.57 | +0.57 |       |      |      |      |
| $\text{H}_4\text{P}^{2+}((\text{PhSO}_3^-)_4$ | +0.23 | +0.23 | +0.23 | +0.23 | +0.5 | +0.51 |       |      |      |      |
| $\text{H}_4\text{IP}((\text{PhSO}_3^-)_4$ | -0.32 | -0.31 | +0.09 |      |      |      | -0.37 | -0.36 |      |      |
| $\text{H}_4\text{IP}^{2+}((\text{PhSO}_3^-)_4$ | +0.14 | +0.18 | +0.13 | +0.12 | +0.32 | +0.5 |      |      |      |      |

Table 2. Deviation of pyrrole and pyrrolenine rings (dihedral angle) and intramolecular hydrogen atoms (distance) from different platforms meso-plane: (+) if nitrogen atom is above the plane, (-) if nitrogen atom is below the plane.

| Compound                        | ms-plane | A(+) | B(-) | C(+) | D(-) |
|---------------------------------|----------|------|------|------|------|
| $\text{H}_2\text{P}((\text{PhSO}_3^-)_4$ | 0.18     | 5.87 (0.05) | 6.74 | 5.87 (+0.05) | 6.74 |
| $\text{H}_3\text{P}^+(\text{PhSO}_3^-)_4$ | 0.20     | 19.13 (0.37) | 23.55 (0.79) | 9.14 (+0.38) | 17.22 |
| $\text{H}_4\text{P}^{2+}((\text{PhSO}_3^-)_4$ | 0.20     | 33.56 (0.78) | 33.56 (0.78) | 33.56 (+0.78) | 33.56 (0.78) |
| $\text{H}_4\text{IP}((\text{PhSO}_3^-)_4$ | 0.20     | 32.10 (0.79) | 32.10 (0.79) | 32.10 (+0.79) | 32.10 (0.79) |
| $\text{H}_4\text{IP}^{2+}((\text{PhSO}_3^-)_4$ | 0.58     | 33.04 (0.93) | 27.93 (0.79) | 30.03 (+0.87) | 26.58 (0.70) |
ring unfolds at 21.53 degrees (Table 2). In addition, the IMHR and H-π interactions between β-protons and phenyl rings (dihedral angles with meso-plane are close to 40°), appreciably alternating the H3IP(PhSO3)-4 platform (Figure 2(2)).

**Molecular Structure of H3IP(PhSO3)-4**

NH-tautomer H3I(e)P(PhSO3)-4 stabilized by IMHB is more stable, so external nitrogen atom of inverted ring is protonated first (Figure 3).

**Molecular Structure of H4IP2+(PhSO3)-4**

Further H3I(e)P(PhSO3)-4 protonation leads to substitution of a IMHB for the IMHR. Perimeter of the aromatic conjugation circuit is expanding, and, as a result, the flexibility of H4IP2+ molecular core increased (Figure 3).

The H4IP2+(PhSO3)-4 platform is a elastic 1,3-alternate in which IMHR is balanced by the natural tendency of the aromatic system to planarity. The contribution of H-π interactions between β-protons and phenyl rings leads to an additional increase in intramolecular HH-distances, which in H4IP2+(PhSO3)-4 transcends the sum of hydrogen atoms van der Waals radii Rw(H).

The H4IP2+(PhSO3)-4 platform, as well as H4P2+(PhSO3)-4, possesses molecular and anion receptor properties. Receptor H4IP2+(PhSO3)-4 has accessible HB-donor NH-groups, which along with delocalized ring charge form two sites of H-bonding “guests” in complexes “double roost” type. The internal weakly polar CH-group generates the inequality of these two binding sites. A porphyrin-type site with a pair of converging NH-groups is pre-arranged for synergistic hydrogen and electrostatic binding of the contact oxygen atom with the geometric configuration AX2E2, while the inverted site with one NH-group is a monodentate. Inversion of pyrrole ring improves the complementarity of the porphyrin-type site of the receptor H4IP2+(PhSO3)-4 to the water molecule as compared to H4P2+(PhSO3)-4. This is indicated by the higher value of the charge transferred from the bound water molecule to the receptor, -0.160 and -0.139 (Mulliken charges), respectively, while for the inverted site this value is only -0.106. As a result, the total charge transferred from water molecules to the inverted receptor is slightly less (-0.266 and -0.279, respectively) and hardly influence on relative stability of the [H4IP2+(PhSO3)-4]2(H2O)2 complex as compared with [H4P2+(PhSO3)-4]2(H2O)2. This fact implied a total shift in the equilibrium of the H4IP2+(PhSO3)-4 second protonation stage in water to the double aquocomplex, as well as for [H4P2+(PhSO3)-4]2(H2O)2.34,38

**Equilibria of H4IP2+(PhSO3)-4 Protonation with Perchloric Acid in Water**

For protonation of H4IP2+(PhSO3)-4 in water perchloric acid have been used, in which indifferent anion is not able to extrude water from aquacomplex [H4P2+(PhSO3)-4]2(H2O)2. Acidification of the H2IP(PhSO3)-4 aqueous solution is accompanied by a synchronous two-step response in the absorption and fluorescence (weak intensity) spectra (Figure 4(1)).

Analysis of the results showed the presence of two individual protolytic equilibria (1) and (2), with the own families of isosbestic points and linear parts on AA dependencies (Figure 4(2)), which strictly obey the equation (6) in the pH ranges 2.00–6.18 and 6.80–10.00, but are violated in the transition pH region 6.18–6.80, where three light-absorbing centers are simultaneously presented.
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Figure 4. (1) – UV-Vis spectra of aqueous solutions $H_2I(i)P(\text{PhSO}_3^-)_4$ (red: 443; 552; 603 and 746 nm), 87% $H_3I(e)P^+(\text{PhSO}_3^-)_4$ in mixture with conjugated forms: (blue: 453; 567; 647 and 811 nm), $[H_4IP^2+(\text{PhSO}_3^-)_4(H_2O)_2$ (green: 458; 599; 654 and 807 nm), (2) – correlation between absorbance at 443 nm and 458 nm (AA), (3) – titration curve at 458 nm.

\[
\begin{align*}
H_2I_{10}P(\text{PhSO}_3^-)_4 + H^+ & \rightleftharpoons H_3I_{10}P^+(\text{PhSO}_3^-)_4 \\
H_3I_{10}P^+(\text{PhSO}_3^-)_4 + H^+ & \rightleftharpoons [H_4IP^2+(\text{PhSO}_3^-)_4(H_2O)_2 \\
H_3I_{10}P^+(\text{PhSO}_3^-)_4 + H^+ & \rightleftharpoons H_4IP^2+(\text{PhSO}_3^-)_4 \\
H_4IP^2+(\text{PhSO}_3^-)_4 + 2H_2O & \rightleftharpoons [H_4IP^2+(\text{PhSO}_3^-)_4(H_2O)_2
\end{align*}
\]

(1 - 4)

The protonation constants of the inverted platform $H_2I_{10}P(\text{PhSO}_3^-)_4$ $K_{b1}$ and $K_{b2}$ (in literature $K_{b2}$ is taken as $K_{b2}$) in water (Table 3) were calculated by fitting the parameters in equation (7) of the two-step titration curve (Figure 4(3)), as described for $H_2P(\text{PhSO}_3^-)_4$,[38] as a constant $C_{H_2O} = 1.74$ mol/L for pure water at 25 °C approxima-
tion. For $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ and $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ a good agreement between the constants of reactions (1)-(4), measured in water, and the corresponding DFT enthalpies, calculated in the absence of the medium (Table 3), was found.

$\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ is a stronger base and possesses a higher proton affinity, so protonation begins already in the alkaline pH region. A different diprotonation scheme for the inverted platform and the weaker aqua-complex $[\text{H}_4\text{IP}^+\text{Na}_2(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$ are the reasons for the increase in the difference between step enthalpies $\Delta H_{b1} - \Delta H_{b2}$, calculated without medium consideration and the corresponding protonation constants $\lg K_{b1} - \lg(K_{b2} K_{w1,2})$ in water. As a result, the anomalous proximity of the $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ stepwise diprotonation constants in water, due to the aqua-complex formation, is withdrawing for inverted derivative $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ and leads to appearing two clear steps on corresponding titration curves.

Aquacomplex $[\text{H}_4\text{IP}^+\text{Na}_2(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$, resulting from the diprotonation of the inverted platform, is the monomer of supramolecular $J$-aggregates self-assembly. The driving force of the $J$-aggregates self-assembly is the more stable anion complexes formation as a result of intermolecular substitution of the bound water molecules by the phenylsulfonate groups (Figure 5).

![Figure 5](image-url)

**Figure 5.** Scheme of $J$-aggregates $[\text{H}_4\text{IP}^+\text{Na}_2(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$ self-assembly by intermolecular substitution of the bound water molecules by the phenylsulfonate groups.

### Table 3. The reactions (1)-(4) constants in water and corresponding enthalpies, calculated in gaseous phase.

| Compound                                      | $\lg K_{b1}$ | $\lg K_{b2}$ | $\lg(K_{b1} K_{b2})$ | $\Delta H_{b1}$ | $\Delta H_{b2}$ | $\Delta H_{w1,2}$ | $\lg K_{b1} - \lg(K_{b2} K_{w1,2})$ | $\Delta H_{b1} - \Delta H_{b2}$ | $\Delta H_{w1,2}$ |
|-----------------------------------------------|--------------|--------------|-----------------------|-----------------|-----------------|------------------|-------------------------------------|-------------------------------|------------------|
| $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ | 4.85±0.03    | 4.71±0.03    | 1.22                  | −387.40         | −330.51         | −351.10          | 3.63                  | −36.30                        | −36.30           |
| $\text{H}_2\text{I}(i)\text{P}^+(\text{PhSO}_3^-)_4$ | 7.84±0.04; (7.7)[21] | 5.57±0.06; (5.8)[21] | 2.08                  | −399.34         | −333.44         | −349.55          | 5.76                  | −49.79                        | −49.79           |

* - volume titration of $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ with methanesulfonic acid

### Conclusions

1. In aqueous solution $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ exists as NH-tautomer $\text{H}_2\text{I}(i)\text{P}^+(\text{PhSO}_3^-)_4$ with inverted pyrrolenine ring, stabilized by bifurcated IMHB between two pyrrole hydrogens and one pyrrolenine nitrogen. IMHB protects intramolecular centers of hydrogen bonding from intermolecular interactions.

2. Inversion of pyrrolenine ring leads to increasing of proton affinity, and, as a result, basicity of $\text{H}_2\text{I}(i)\text{P}^+(\text{PhSO}_3^-)_4$.

3. Sequence of protonation of main centers in the inverted platform $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ is determined by intramolecular hydrogen bonds at the first protonation stage and intermolecular hydrogen bonds at the second protonation stage.

4. The $\text{H}_2\text{IP}^+(\text{PhSO}_3^-)_4$ diprotonated platform is elastic 1,3-alternate, which possesses anion and molecular receptor properties. Equilibrium of the $\text{H}_2\text{I}(i)\text{P}^+(\text{PhSO}_3^-)_4$ second protonation stage in water is total shifted to the aqua-complex $[\text{H}_4\text{IP}^+(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$ formation due to hydrogen and electrostatic binding of solvent molecules at two receptor sites.

5. Aquacomplex $[\text{H}_4\text{IP}^+(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$ is the monomer of supramolecular $J$-aggregates self-assembly. The driv-
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Substitution of the bound water molecules by the phenylsulfonate groups.

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