

The Direct Synthesis of 2-*N*-Methyl-5,10,15,20-tetrakis-(4-sulfophenyl)-2-aza-21-carbaporphyrin J-Aggregates

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*Here we present the way of synthesis of very stable J-aggregates based on water-soluble 2-*N*-methyl-5,10,15,20-tetrakis-(4'-sulfophenyl)-2-aza-21-carbaporphyrin zwitter-ion, which are formed as the main product of 2-*N*-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin sulfonation by sulfuric acid. J-Aggregates and corresponding monomer were obtained for the first time and characterized using UV-Vis, ¹H NMR, MALDI-TOF, ESI-MS analysis.*

Keywords: Porphyrinoids, inverted (*N*-confused) porphyrins, 2-aza-21-carbaporphyrins, water-soluble porphyrins, J-aggregates.

Прямой синтез J-агрегатов на основе цвиттер-ионов 2-*N*-метил-5,10,15,20-тетракис(4-сульфофенил)-2-аза-21-карбапорфирина

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*В этом сообщении мы приводим способ получения очень устойчивых J-агрегатов цвиттер-иона водорастворимого 2-*N*-метил-5,10,15,20-тетракис(4'-сульфофенил)-2-аза-21-карбапорфирина, которые образуются в качестве основного продукта сульфирования 2-*N*-метил-5,10,15,20-тетрафенил-21-карбапорфирина серной кислотой. J-Агрегаты и мономер получены впервые и охарактеризованы методами электронной и ЯМР спектроскопии, MALDI-TOF и ESI спектрометрии.*

Ключевые слова: Порфириноиды, инвертированные порфирины, 2-аза-21-карбапорфирины, водорастворимые порфирины, J-агрегаты.

Introduction

Diprotonated porphyrinic platform H_4P^{2+} is a pH-dependent anion-molecular receptor, which exists only as homogeneous $[H_4P^{2+}](G)_2$ or mixed $[H_4P^{2+}](G)(G')$ complexes (Figure 1(a)) with molecules of solvents, co-solvents and anions.^[1-7] “Guest” molecules occupy two

opposite sites of H_4P^{2+} , which exists in 1,3-alternate conformation.

Zwitter-ions $H_4P^{2+}(PhSO_3^-)_2$ based on 5,15-bis(4'-sulfophenyl)porphine and its derivatives are self-complementary tectons for “head (H_4P^{2+})-to-tail ($-PhSO_3^-$)” staircase-type J-aggregates supramolecular self-assembly (Figure 1(b)).^[9-19] Here, aqua complex $[H_4P^{2+}(PhSO_3^-)_2]_n(H_2O)_2$

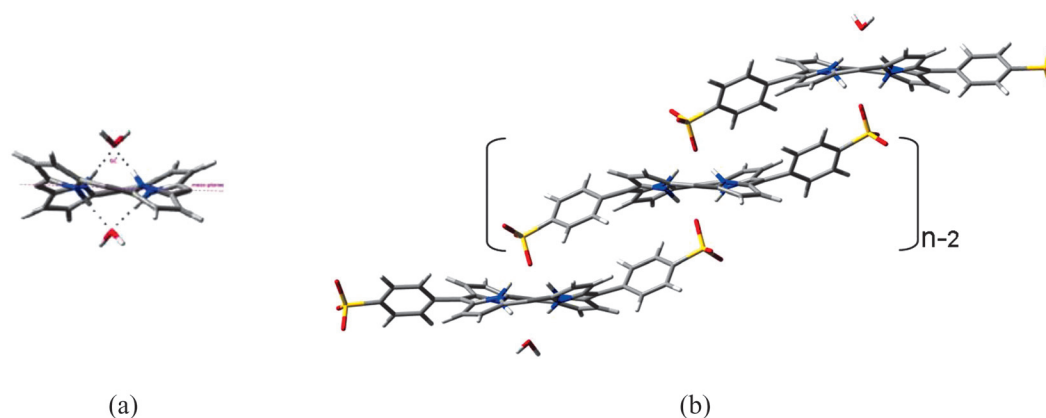


Figure 1. Optimized geometry of aqua complex $[\text{H}_4\text{P}^{2+}](\text{H}_2\text{O})_2$ (a) and J-aggregate $[\text{H}_4\text{P}^{2+}(\text{PhSO}_3^-)_2]_n(\text{H}_2\text{O})_2$ (b).^[6,8]

is a self-assembly monomer, and J-aggregates formation is a result of intermolecular substitution of water molecules for sulfonate groups. The unique characteristic of these structures is a strong red shift of absorption bands in UV-Vis spectra of J-aggregates as compared with monomers, caused by resonance absorption.^[20]

Porphyrinoids with inverted porphyrin platform H_2IP (2-aza-21-carbaporphyrin derivatives)^[21,22] attract a great interest through its unique molecular structure.^[23-31] Water soluble *N*-confused porphyrin derivatives are very interesting objects for researchers due to their potential medical and biological application.^[32-36]

Previously it was established that porphyrinoids with inverted pyrrole ring possess an ability to form anion complexes $[\text{H}_4\text{IP}^{2+}(\text{Ph})_4](\text{CHCl}_2\text{COO}^-)$,^[37] $[\text{H}_4\text{MeIP}^{2+}(\text{Ph})_4](\text{CF}_3\text{COO}^-)$ and $[\text{H}_4\text{MeIP}^{2+}(\text{Ph})_4](\text{CF}_3\text{COO}^-)_2$ ^[38] and also J-aggregates $[\text{H}_4\text{IP}^{2+}(\text{PhSO}_3^-)_4]_n$ ^[39] in acidic media. Herein we present the new way of synthesis of J-aggregates, based on water soluble 2-*N*-methyl-5,10,15,20-tetrakis-(4'-sulfophenyl)-2-aza-21-carbaporphyrin zwitter-ion, which also was obtained for the first time.

Experimental

All commercially available solvents and reagents were used without further purification. 5,10,15,20-Tetraphenyl-(2-aza-21-carbaporphyrin, $(\text{H}_2\text{IP}(\text{Ph})_4)^{[40]}$ and 2-*N*-methyl-5,10,15,20-

tetraphenyl-21-carbaporphyrin ($\text{H}_2\text{MeIP}(\text{Ph})_4$)^[37] were synthesized according to the reported procedures (¹H NMR and MS spectra are presented in Supporting information, Figures S1-S6).

The following equipment was used for characterization: spectrofluorometer Avantes AvaSpec-2048-2, Bruker Avance III 500 spectrometer (Bruker Biospin AG, Germany, Rheinstetten) (500.17 MHz for ¹H) at 294 K. Mass-spectra (EI, MALDI-TOF) were recorded on Finnigan TSQ 70 MAT and Shimadzu Biotech AXIMA Confidence Linear/Reflectron MALDI-TOF Mass Spectrometer. All samples were run with α -cyano-4-hydroxycinnamic acid (CHCA) as the matrix.

Geometry optimization was performed at the B3LYP level of density functional theory using Gaussian software package.^[41]

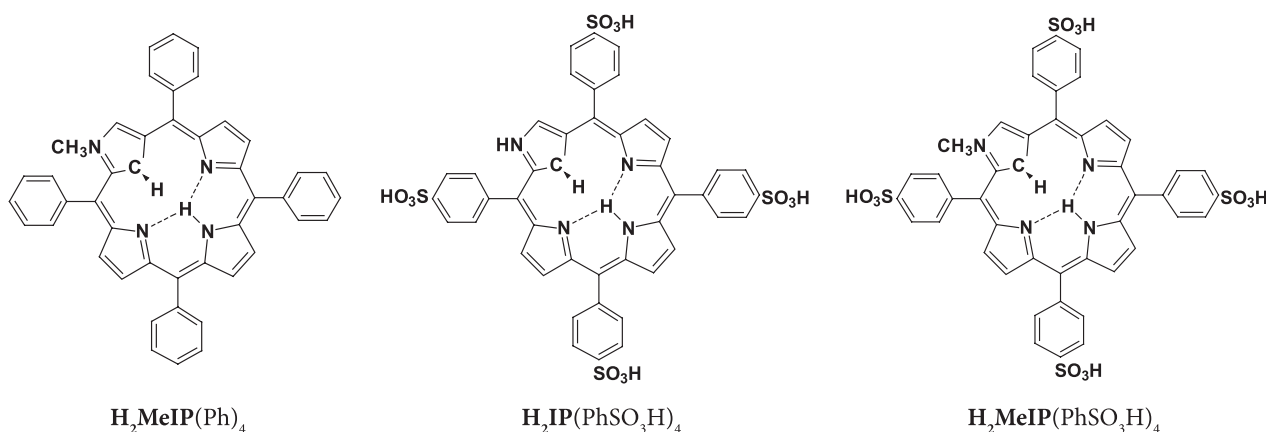
The Supporting Information is available free of charge on the www.macroheterocycles.isuct.ru website. UV-Vis, ¹H NMR, MALDI-TOF, ESI-MS data for all synthesized compounds are presented in Figures S1-S7.

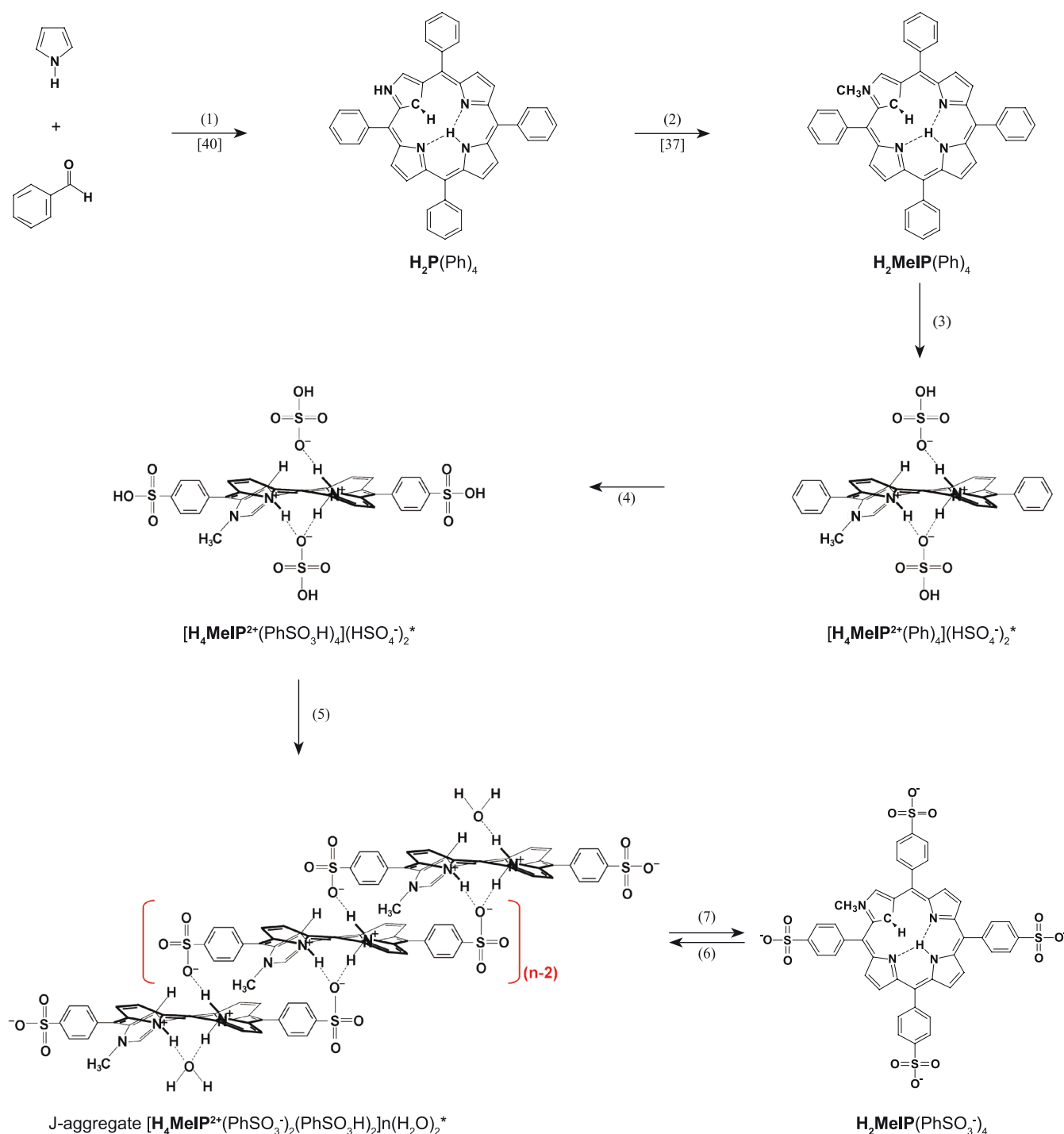
Results and Discussion

Synthesis

J-Aggregates $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_2(\text{PhSO}_3\text{H})_2]_n(\text{H}_2\text{O})_2$ based on 2-*N*-methyl-5,10,15,20-tetrakis-(4'-sulfophenyl)-21-carbaporphyrin ($\text{H}_2\text{MeIP}(\text{PhSO}_3\text{H})_4$) zwitter-ions were synthesized as shown in Scheme 1.

Sealed glass ampoule with $1.24 \cdot 10^{-4}$ mol $\text{H}_2\text{MeIP}(\text{Ph})_4$ and 2 ml of concentrated sulfuric acid were kept in the





Scheme 1. Synthesis of J-aggregates $[H_4MeIP^{2+}(PhSO_3^-)_2(PhSO_3H)_2]_n(H_2O)_2$ (two phenylsulfonate substituent groups $-PhSO_3H$ are not shown for better visualization).

ultrasonic bath for 1 hour at 50 °C, until complete dissolution of porphyrin (stage (3) in Scheme 1). Porphyrin dissolution is a result of inverted porphyrinic platform H_2MeIP internal nitrogen atoms diprotonation and following dihydrosulfate complex $[H_4MeIP^{2+}(Ph)_4](HSO_4^-)_2$ formation. Sulfonation of $[H_4MeIP^{2+}(Ph)_4](HSO_4^-)_2$ (4) was carried out for 6 hours using boiling water bath. For product isolation, cooled reaction mixture was poured into ice, then wine-color precipitate of J-aggregates $[H_4MeIP^{2+}(PhSO_3^-)_2(PhSO_3H)_2]_n(HSO_4^-)_2$ in sulfuric acid

was formed (5) (Figure 2,a,b). The excess of sulfuric acid was neutralized with aqueous ammonia until J-aggregates dissolution, the color has changed from dark-red to green as a result of tetraanion $H_2MeIP(PhSO_3^-)_4$ formation (6) (Figure 2,d). A part of tetraanions solution was evaporated in water bath until green color disappearance and J-aggregates reprecipitation (7). After the ammonium sulfate solution decantation the crude J-aggregates were isolated. The crude product was passed through a column containing aluminum oxide (90 standardized) using butanol

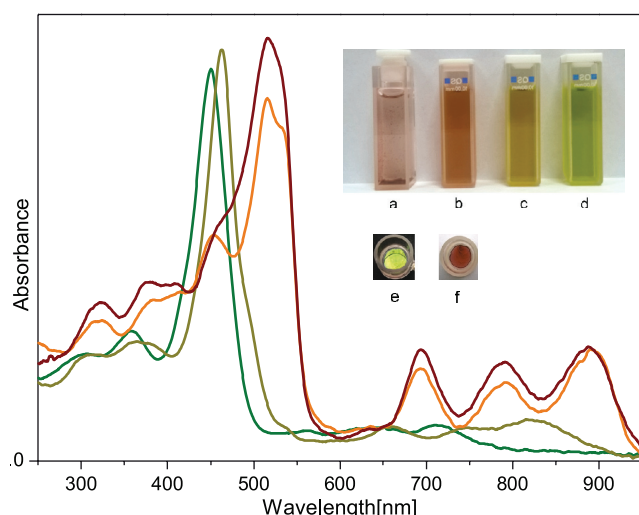
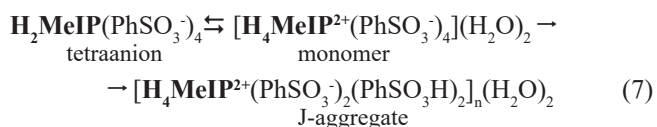


Figure 2. Thin solid layer of J-aggregates $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_2(\text{PhSO}_3\text{H})_2](\text{H}_2\text{O})_2$ (wine color line, a); suspension of J-aggregates in water at pH 1 (orange line, b); self-assembly monomer $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{H}_2\text{O})_2$ at pH 3 (dark yellow line, c); tetraanion $\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$ at pH 12 (olive line, d). Thin layer of J-aggregates is shown under reflected (e) and transmitted (f) light.

solution saturated with ammonia as an eluent. J-Aggregates were dissolved in small amount of ammonia solution and the bright green solution was mixed with alumina until the formation of homogeneous paste, which was carefully dried in water bath. This paste was mixed with eluent, put on the top of column and then chromatographed. The bright green fraction contained the desired tetraanion. Solvent was evaporated in water bath to yield sparkling green flakes of J-aggregates (Figure 2, e,f). Yield 80 % (calculation for 2-*N*-methyl-5,10,15,20-tetrakis-(4'-sulfophenyl)-2-aza-21-carbaporphyrin).

UV-Vis spectra of thin solid layer of J-aggregates, J-aggregates water suspension, tetraanion and self-assembly monomer water solutions are presented in Figure 2. J-Aggregates absorption bands are red shifted as compared with monomer by around 53 nm (Soret) and 70 nm (first Q-band) respectively.



UV-Vis spectra of J-aggregates are identical to the spectra of analogous unmethylated J-aggregates $[\text{H}_4\text{IP}^{2+}(\text{PhSO}_3^-)_4]n(\text{H}_2\text{O})_2$ (Figure S7). UV-Vis spectra of tetraanion and monomer water solution are similar to the spectra of H_2MeIP and $[\text{H}_4\text{MeIP}^{2+}](\text{Me}_2\text{SO})_2$ in DMSO (Figure 3).

¹H NMR in DMSO-*d*₆. J-Aggregates, dissolved in high-basic *d*-DMSO, were exposed to solvolysis. Solvolysis process leads to complex formation with solvent molecules $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{DMSO})_2$ in analyzed concentrated solutions. In highly diluted solutions the formation of tetraanions is observed, what indicates the self-acidification

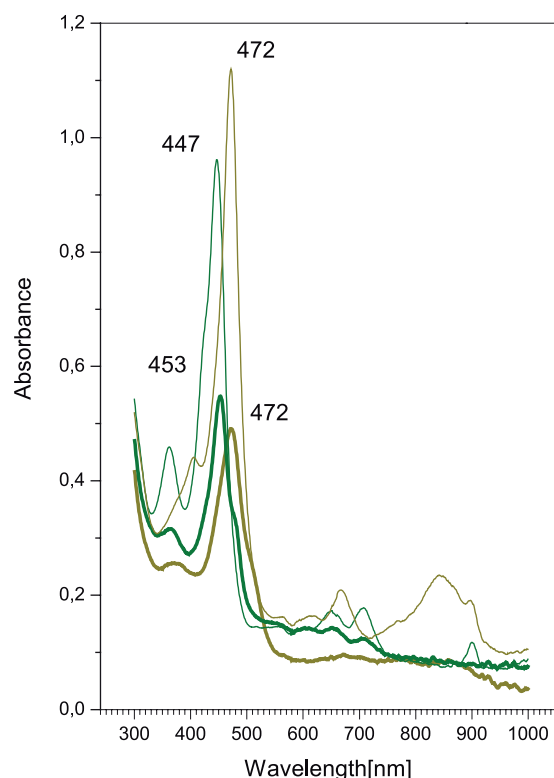


Figure 3. UV-Vis spectra of complex $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4]$ (DMSO)₂ (thick dark-yellow line) and tetraanion (thick olive line) solution thin film in DMSO-*d*₆ on inner surface of NMR tube. UV-Vis spectra of H_2MeIP (thin dark-yellow line) and $[\text{H}_4\text{MeIP}^{2+}]$ (DMSO)₂ (thin olive line) in solution are shown for comparison.

of a solvent, when concentration of porphyrin's tetrasulfonic acid increases.

The ¹H NMR spectrum of complex with solvent molecules $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{DMSO})_2$ is not clear, probably because of strong influence of two coordinated DMSO-*d*₆ molecules (Figure 4,a). Therefore, for NMR analysis we used $\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$ tetraanion solution in DMSO-*d*₆, which was obtained by treatment of initial $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{DMSO})_2$ acidic solution with ammonia vapor (Figure 4,b).

$\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$ (Figure 5). ¹H NMR (500 MHz, DMSO-*d*₆) δ_H ppm: 8.05 (1H, s, "confused pyrrole", H3); 7.94 (6H, m, β-pyrrole: H17, H8; *ortho*-Ph: H26, H30, H44, H48); 7.90 (4H, m, β-pyrrole: H13, H12; *meta*-Ph: H45, H47); 7.88 (6H, m, *meta*-Ph: H41, H39, H33, H35, H27, H29); 7.80 (4H, m, *ortho*-Ph: H32, H36, H38, H30); 7.52 (1H, d, *J*=4.27 Hz, β-pyrrole H18); 7.50 (1H, d, *J*=4.3 Hz, β-pyrrole H7); 3.56 (3H, s, -CH₃); 1.2 (1H, s, inner NH); 0.6 (1H, s, inner CH, H21).

Mass-spectra. Under spectrum registration conditions J-aggregates decayed on individual molecules $\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$ (Figures 6, 7).

DFT modeling. J-aggregate were analyzed using B3LYP level of density functional theory with the 3-21G(d,p) basis set for calculations. Initially, geometry optimization and molecular parameters calculation of all $\text{H}_2\text{MeIP}(\text{Ph})_4$ sulfonation scheme objects, from dihydrosulfate complex $[\text{H}_4\text{MeIP}^{2+}(\text{Ph})_4](\text{HSO}_4^-)_2$ to $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{HSO}_4^-)_2$, were performed.

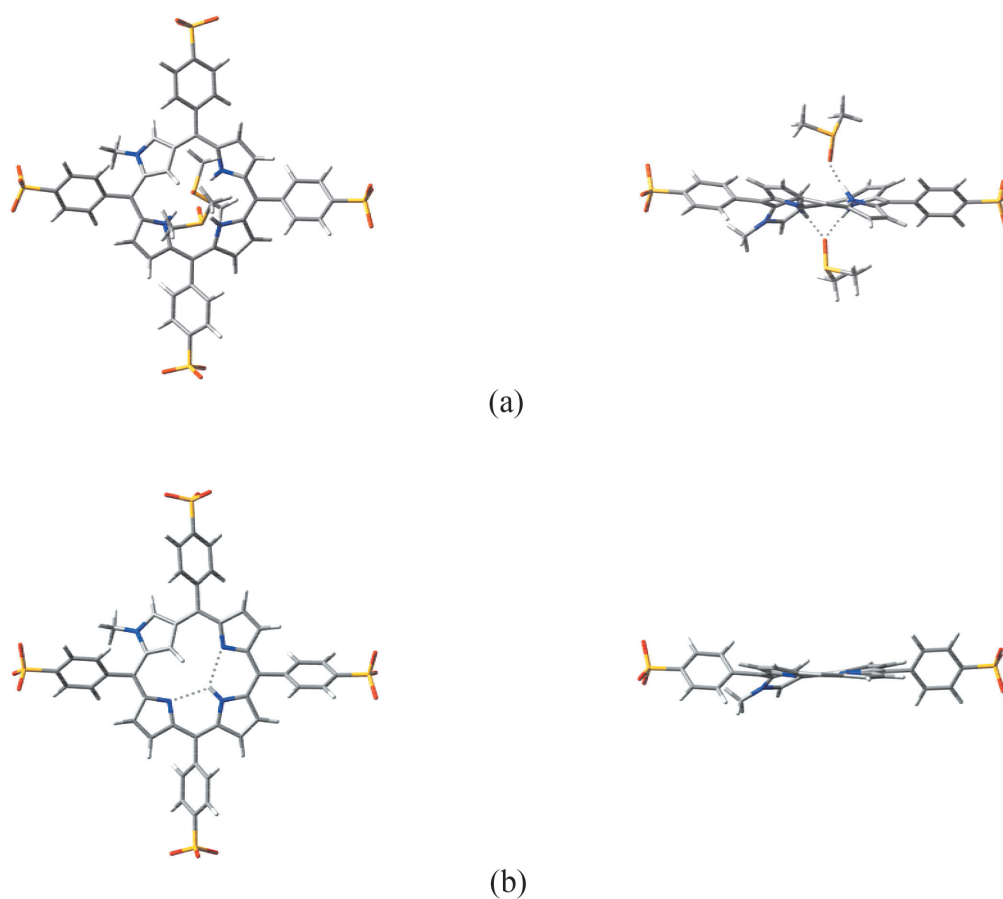


Figure 4. Optimized structures of: (a) complex $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4](\text{DMSO})_7$, two phenylsulfonate substituent groups are not shown for better visualization; (b) tetraanion $\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$. Calculated at the DFT/B3LYP/6-31G⁺⁺(d,p).

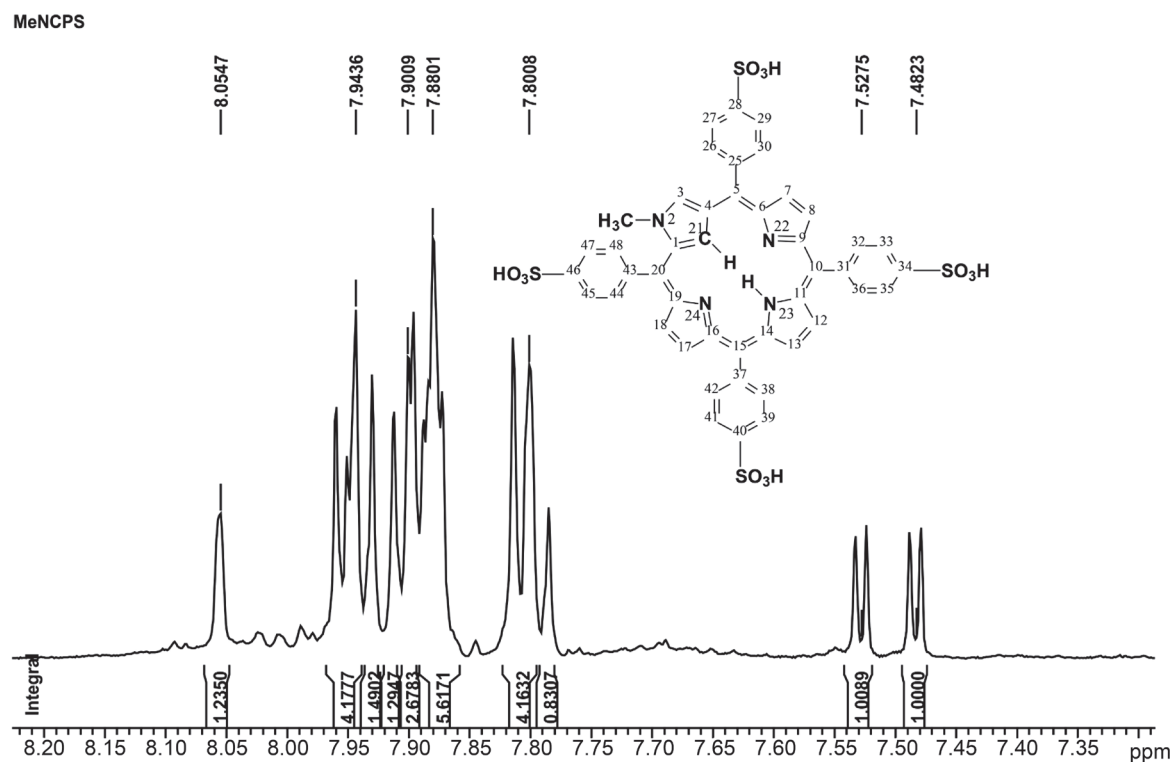


Figure 5. ^1H NMR spectrum of $\text{H}_2\text{MeIP}(\text{PhSO}_3^-)_4$ tetraanion in $\text{DMSO}-d_6$.

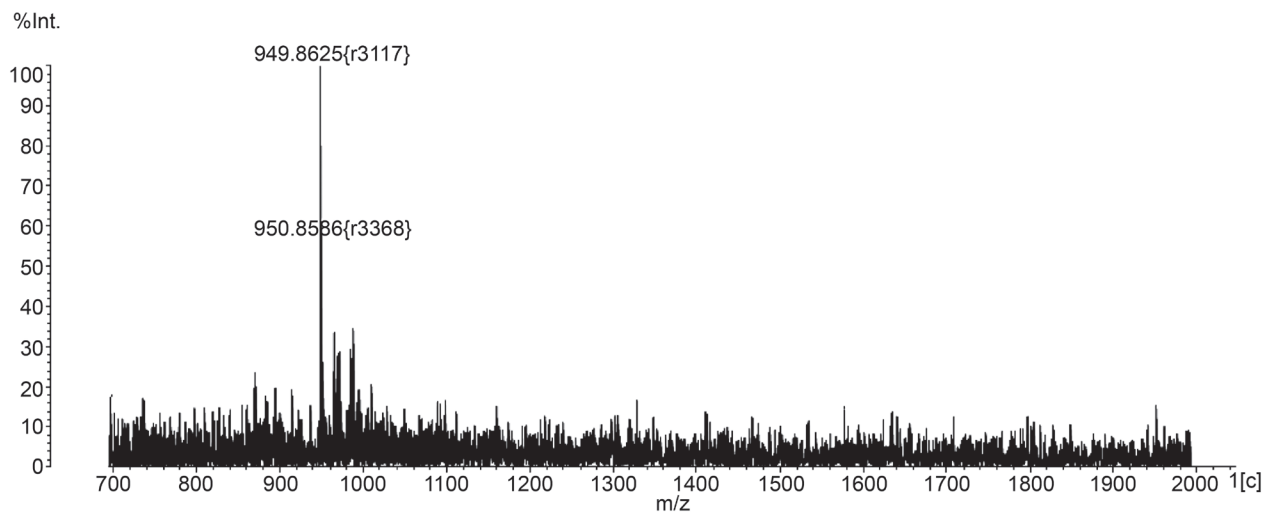


Figure 6. MALDI-TOF spectrum of $\text{H}_3\text{MeIP}^+(\text{PhSO}_3\text{H})_4$: m/z 949.86 ($\text{C}_{45}\text{H}_{33}\text{N}_4\text{O}_{12}\text{S}_4$) $^+$, α -cyano-4-hydroxycinnamic acid (CHCA) was used as matrix.

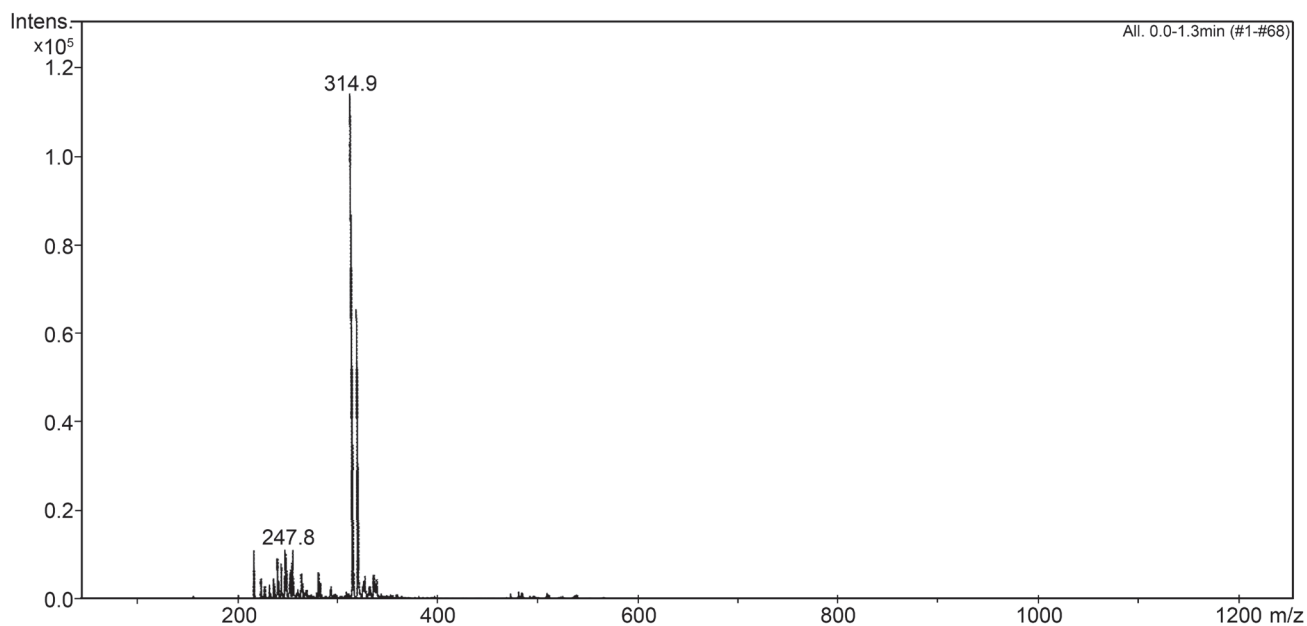


Figure 7. ESI-MS spectrum of $\text{H}_2\text{MeIP}(\text{PhSO}_3\text{H})(\text{PhSO}_3^-)_3$: m/z 314.9 (calcd. for $\text{C}_{45}\text{H}_{29}\text{N}_4\text{O}_{12}\text{S}_4$) $^{3-}$.



Figure 8. Molecular structure of dihydrosulfate complex $[\text{H}_4\text{MeIP}^{2+}(\text{Ph})_4](\text{HSO}_4^-)_2$. Two phenyl rings are not shown for better visualization; calculated at the DFT/B3LYP/3-21G(d,p) level.

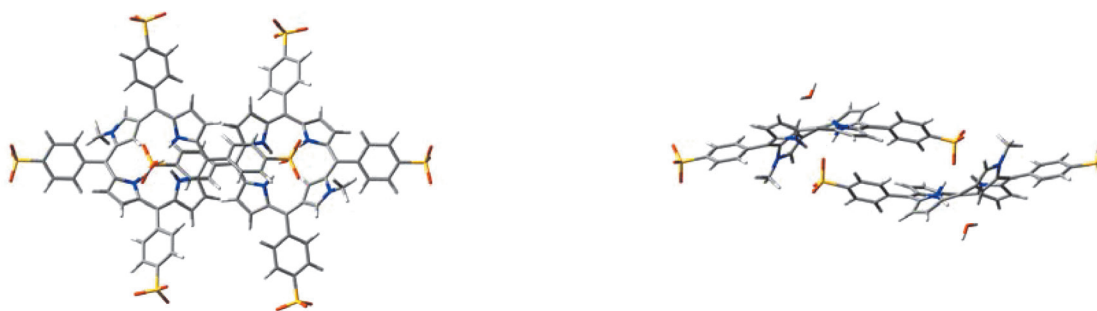


Figure 9. Inferred molecular geometry of dimer $[\text{H}_4\text{MeIP}^{2+}(\text{PhSO}_3^-)_4]_2(\text{H}_2\text{O})_2$. Two phenyl rings are not shown for better visualization; calculated at the DFT/B3LYP/3-21G(d,p) level.

Dihydrosulfate complex formation activates dication $\text{H}_4\text{MeIP}^{2+}(\text{Ph})_4$ for electrophilic substitution due to partial charge transfer from HSO_4^- anion. The reason of asymmetric charge distribution on carbon atoms of inverted porphyrin platform and phenyl groups is the presence of unsymmetrical “guests” HSO_4^- . The most reactive sulfonation centers are 7 and 8 β -positions of $\text{H}_4\text{MeIP}^{2+}$, as well as 4'-position of phenyl rings, at all stages of sulfonation. However, β -isomers are thermodynamically unstable (the difference is about 6 kcal/mol in terms of total energy E_1) as compared with 4'-phenyl isomers, which should lead to $\beta \rightarrow 4'$ rearrangement. Besides, rotation of phenyl rings creates the steric hindrance to sulfonation in β -position.^[42–44] Thus, combination of these two factors determines the existence of 4'-tetrasulfoderivative as the single product of sulfonation. Inferred molecular geometry of J-dimer is shown in Figure 9.

Conclusions

In summary, a new zwitter-ion J-aggregates, stable in neutral aqueous solutions, were obtained as a result of 2-*N*-methyl-(5,10,15,20-tetrakis)-2-aza-21-carbaporphyrin sulfonation. The strong red shift of absorption bands in UV-Vis spectra of J-aggregates as compared with monomers was observed. Further investigations concerning 2-*N*-methyl-5,10,15,20-tetrakis-(4'-sulfophenyl)-2-aza-21-carbaporphyrin properties, pH-dependent J-aggregates self-assembly and J-aggregates morphology are in progress.

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