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DOI: 10.6060/mhc150871g

The Role of the Counterions in Self–Assembly of *J*–Aggregates from *meso*–Aryl Substituted Porphyrin Diacids in Aqueous Solutions

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This paper presents an attempt to separate the effect of the additive parameters of the reaction medium (the acidity and the ionic strength of the solution) and specific factors, such as the nature of the counterions and the presence of different binding agents and templating molecules, on self-assembly of meso-aryl-substituted porphyrin in acidic aqueous solutions. The studies reveal the importance of the specific intermolecular interactions that determine the structural, and hence, photophysical properties of the multiporphyrin arrays, as well as the kinetics of self-assembly. The particular attention in this paper is paid to the influence of the counterions on aggregation behaviour of a number of tetraphenylporphyrin derivatives, as well as to their role in J-aggregate structure stabilization. The results obtained can be applied for the development of the novel ways for design and synthesis of various supramolecular systems on the basis of diprotonated porphyrins with definite structure and desired properties for nonlinear optics and sensor applications.

Keywords: *J*-Aggregtaes, porphyrin self-assembly, aggregation kinetics, dynamic light scattering, CD spectroscopy.

О роли противоионов в процессе самосборки *J*–агрегатов на основе *мезо*–арилзамещенных порфиринов в водных растворах

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В данной работе продемонстрировано влияние природы противоиона на кинетику процесса агрегации ряда мезо-арилзамещенных порфиринов, а также на структуру и фотофизические свойства продуктов самосборки.

Ключевые слова: *J*-Агрегаты, самосборка порфиринов, кинетика агрегации, динамическое светорассеяние, КД-спектроскопия.

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Introduction

Self-assembly of supramolecular structures and highly-ordered macromolecular assemblies through non-covalent intermolecular interactions involved in the complex biological structure formation is also a promising strategy for the synthesis of the novel functional smart materials.[1,2] A characteristic feature of the above processes is a strong dependence of the resulting product structure and properties on the numerous external factors, including the main parameters of the reaction medium in the course of the self-assembly process. Hence, the detailed studies on the relationships between the above factors and the emergent properties of the soft matter assemblies allow to perform a medium-controlled self-assembly of the functionalized building blocks.

Among the numerous multifunctional building blocks suitable for designing supramolecular architectures porphyrins are probably the most promising ones due to their inherent tendency to form various highly-ordered aggregates with different photophysical properties governed by the molecular structure of the building blocks and the experimental conditions.[3,4] Due to their tendency to ionic and hydrogen bonding of a number of anions and neutral molecules with the nitrogen atoms in the diprotonated porphyrin core, *meso*-substituted porphyrin diacids are known to function as anionic and molecular receptors.[5-7]

The macrocycle affinity to various anions leads to the participation of the porphyrin-anion ionic pairs in the self-assembly process providing the basis for its counterion dependence. To date there is a number of papers considering the influence of the counterion nature on the aggregation behavior of *meso*-tetraphenylporphyrin derivatives. McHale's group was the first to report the dependence of the spectral features and morphological parameters of 5,10,15,20-tetrakis(4'-carboxyphenyl)-porphyrin (TPPC) *J*-aggregates on the nature of the acid residue.[8,9] They have proposed a structural explanation for their findings based on the influence of the intercalated anion charge and geometrical parameters on the interchromophore distance, and hence, the exciton coupling efficiency in the conjugated chromophore assembly. This hypothesis was later confirmed by Vas Serra *et al*. for bis-(4-carboxyphenyl)porphyrins.[10] In the case of 5,10,15,20-tetrakis(4'-sulfonatophenyl)porphyrin (TPPS) there is a clear experimental evidence for the participation of the bridging anions in both *J*- and *H*-aggregate structure formation in dichloromethane,[11] while in aqueous solutions such an effect was observed only at the high ionic strength values.[12]

Theoretical calculations by means of DFT and TDDFT, supported by the experimental studies performed by Rosa *et al*.[13] have provided a quantum chemical basis for the effect of the size and nature of the hydrogen-bonded acid residues on the structural and spectroscopic properties of *meso*-tetraphenylporphyrin (TPP) diacid derivatives in dichloromethane. These calculations suggested a significant impact of the halide lone pairs into the highest occupied molecular orbitals of the $[H_2TPP^{2+}](X^-)_2$ complex and proposed the charge-transfer covalent interactions to be an important component of the hydrogen bond energy between the pyrrole N-H groups and the halide anions. Similar calculations with the experimental studies on the non-radiative excited state deactivation kinetics reported by Avilov *et al*.[14] have confirmed the counterion dependence of the photophysical properties of the porphyrin diacids. However, the above studies carried out in dichloromethane did not consider the aggregated forms of H_2TPP^{2+} diacid, and hence, shed no light on the anion participation in the aggregate structure formation. Such an attempt was made for TPP *J*-aggregates deposited on a quartz substrate,[15] but the role of the anions in the aggregation behavior of H_2TPP^{2+} in homogeneous aqueous and aqueous-organic solutions to the best of our knowledge still remains poorly investigated.

This paper compares the aggregation behavior of *meso*-tetraphenylporphyrin and a number of its water soluble derivatives in homogeneous acidic aqueous solutions with different electrolytes.

Experimental

The absorption spectra were measured using spectrophotometer HACH DR-4000V (USA) in a 10 mm quartz cell at room temperature either in a scanning mode within 350-850 nm region, or in a single wavelength mode for the aggregation kinetics monitoring. The emission spectra were recorded using spectrofluorometer Shimadzu RF-5000 (Japan) at the same conditions with the excitation wavelength corresponding to the Soret absorption maximum of the sample. CD measurements were performed using Chirascan-Plus CD spectrometer (UK) in a 10 mm quartz cell at 20 ºC. DLS measurements were carried out using Photocor Complex (Russia) instrument at a scattering angle 90º with a 15 mW HeNe laser source ($\lambda = 632$ nm) linearly polarized perpendicular to the scattering plane.

5,10,15,20-Tetrakis(4'-sulfonatophenyl)porphyrin was synthesized in G.A. Krestov Institute of Solution Chemistry RAS (Ivanovo, Russia) as an ammonium salt and was used as a 100 μM aqueous stock solution with p*H*=11. Both *meso-tetraphenylporphyrin* and *5,10,15,20-tetrakis(4'-carboxyphenyl)porphyrin* were synthesized in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia) and used as 100 μM stock solutions in acetone and water, respectively. All aqueous solutions were prepared using bidistilled water and the appropriate p*H* value was obtained by the addition of the necessary amount of either 0.1M H_2SO_4, or 0.1M NaOH, unless otherwise stated.

J-Aggregates of TPP and TPPC were obtained in 2M aqueous salt solutions with $pH < 1$ according to the method described before.[16] Equal amounts of the dye stock solutions were added to the pre-acidified up to $pH=0.6\div0.8$ isotonic aqueous solutions of different salts in order to reveal the dependence of *J*-aggregate self-assembly from the diprotonated H_2TPP^{2+} or H_2TPPC^{2+} species on the nature of the counterion.

Origin 8.0 was applied for spectral data representation and Dynals 2.0 (Photocor) software was used for processing the results of DLS measurements.

Results and Discussion

In strongly acidic medium at $pH < 1$ both TPP and TPPC readily undergo diprotonation of the imine nitrogen atoms in the macrocycle core to form dicationic species (H_2TPP^{2+} and H_2TPPC^{2+}, respectively, with the peripheral carboxylic residues in TPPC in this case being uncharged). The above transformation leads to the distortion of the planar macrocycle conformation to a saddled one accompanied by the decrease of the interplanar angle between the phenyl residues and the porphyrin core, resulting in the enhancement of the resonance interactions between the aromatic π-electron systems and the upshift of the HOMO in the porphyrin molecule, leading to the bathochromic shift of the Soret band.[13] The increasing symmetry of the porphyrin diacid (D_{2d}) compared to the free base porphyrin (D_{2h}) provides the reduced number of the *Q*-bands because of the excited state degeneracy.[17,18] Besides the significant spectral changes, diprotonation of the chromophore promotes self-assembly of the porphyrin diacid building blocks into the highly-ordered ladder-type supramolecular assemblies known as *J*-aggregates.[19]

However, positive charges of the tectons prevent the porphyrin diacid monomers from direct aggregation, so the formation of the chromophore system capable of coherent excitation requires additional counterions for charge neutralization. For this reason a number of counteranions available in the reaction medium readily participate in self-assembly of the aggregated species, providing the bridged binding between the adjacent chromophores. Therefore, the counterion charge, geometry, ionic radius and electron density distribution significantly affect the aggregate structure, and particularly, the interchromophore distance and the transition dipole moment orientation of the individual monomers, and hence, the exciton coupling between the neighboring macrocycles and the coherence length, *i.e.* the number of electronically coupled chromophores in the framework of the molecular exciton model.[20] Variation of the above parameters in the aggregated porphyrin species results primarily in the spectral changes, and therefore they can be easily detected using spectroscopic methods allowing a comparison of the photophysical properties and aggregation kinetics of the same porphyrins in different experimental conditions.

The comparison of the absorption spectra given in Figure 1 suggests the difference in the counterion dependence of the structural and spectral features of *J*-aggregates assembled from H_2TPP^{2+} and H_2TPPC^{2+} species in acidic aqueous medium. The above effect can be probably attributed to the participation of the carboxylic residues of the neighbouring H_2TPPC^{2+} macrocycles in the aggregate structure stabilization *via* the additional hydrogen bonding. It is noteworthy that the data obtained for TPPC are in a good agreement with the data reported earlier in[8,9] for aqueous HCl and HNO_3 solutions with p*H*=0.9, which confirms the feasibility of the explanation proposed.

Despite the structural similarity with the only difference in pK_a of the peripheral ionic groups, the aggregation behaviour of TPPC and TPPS in acidic aqueous medium appears to be fundamentally different. Since the diprotonated form of TPPS is a self-complementary zwitter-ion capable of self-assembly into *J*-aggregated species by means of ionic and hydrogen bonding between the sulfonate groups of one macrocycle and the N-H groups of the other one, the self-assembly process in aqueous medium occurs independently of the external anions which slightly (if any) affect the structure of the resulting aggregates.[11] The excess negative charge neutralization on the peripheral substituents is provided by the protons abundant in acidic medium, but the presence of the external cations in the solution can significantly change the aggregation kinetics and the final product structure according to the recent observations.[12]

Although the main structural features of the resulting *J*-aggregates seem to be counterion-independent, the kinetic parameters of TPPS self-assembly have appeared to be remarkably influenced both by the medium acidity, the ionic strength and the nature of the counterions. From the kinetic curves presented in Figure 2 one can conclude that the maximum reaction rate and the highest degree of aggregation are observed for the equimolar mixture of 1M H_2SO_4 with 1M Na_2SO_4, while in the more acidic 1M H_2SO_4 with the same ionic strength the reaction rate is twice lower. These data can be easily explained in the framework of the concept postulating the zwitter-ionic nature of the tectons for TPPS self-assembly, which requires a slightly acidic p*H* sufficient for the inner nitrogen atom diprotonation without preventing the peripheral sulfonic group dissociation and a relatively high ionic strength, promoting the aggregation process. However, in 2M HCl, as well as in the mixtures of HCl and NaCl with the same p*H* and ionic strength values (the data are not shown here) the aggregation rate is substantially reduced.

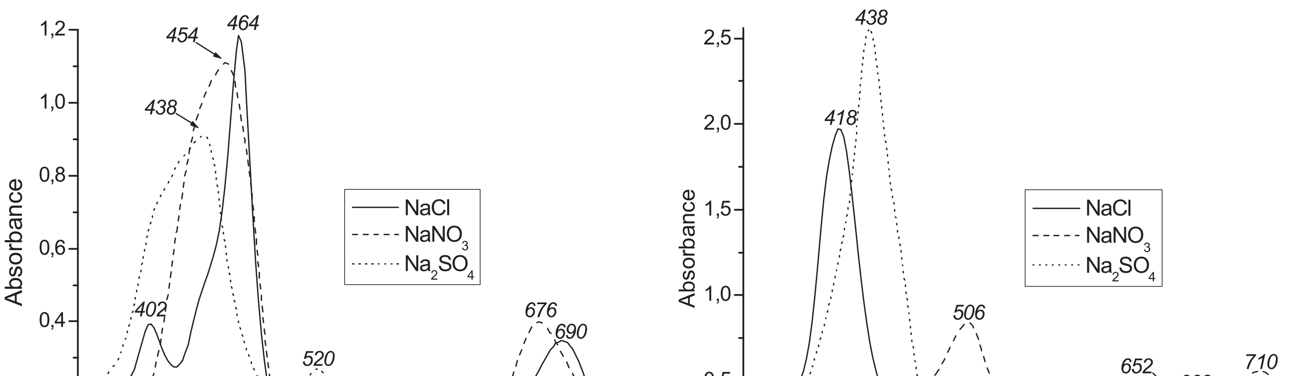

Figure 1. Absorption spectra of TPP (left) and TPPC (right) in acidified aqueous salt solutions (p*H* < 1, ionic strength 2M).

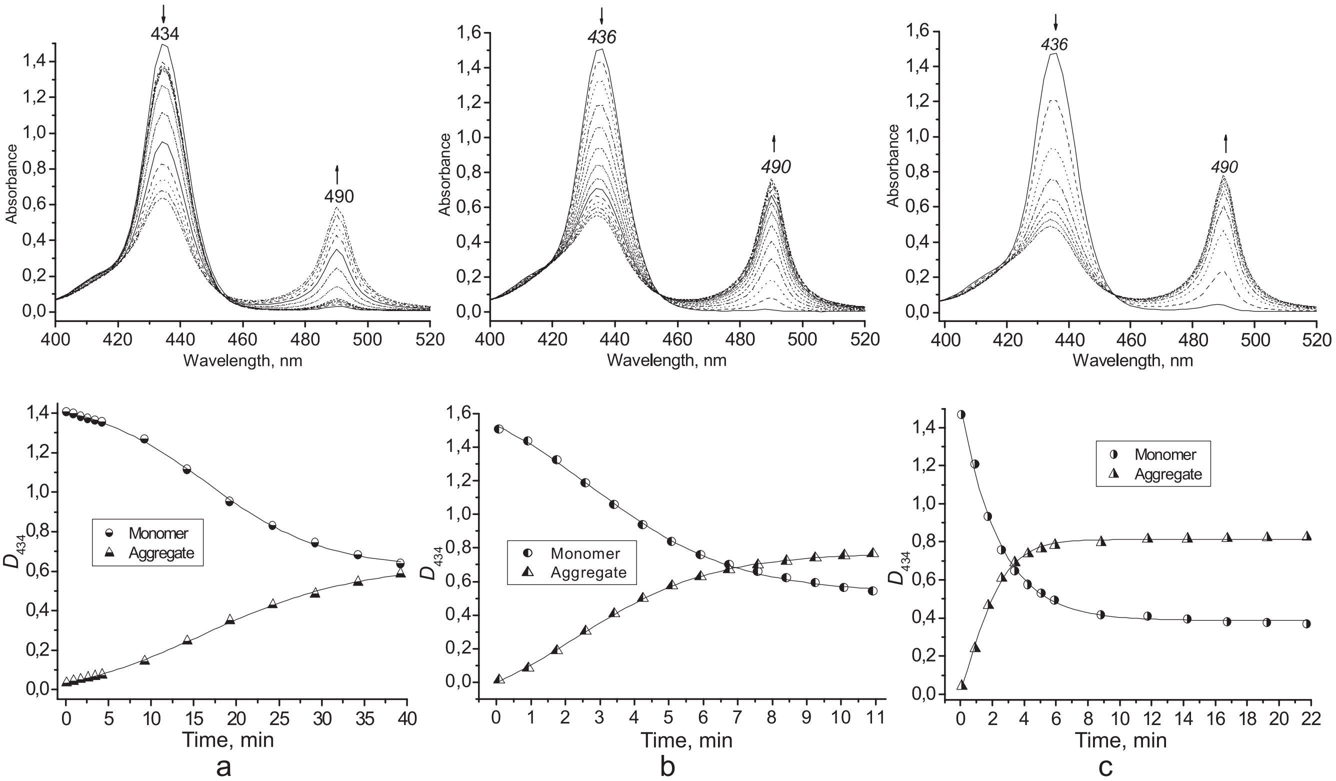

Figure 2. Aggregation kinetics of TPPS in aqueous sulfuric acid at different p*H* and ionic strength values: a – 0.5M H_2SO_4; b – 1M H_2SO_4; c – 1M H_2SO_4 / 1M Na_2SO_4.

The above kinetic profiles represent the initial stage of TPPS *J*-aggregate formation and can be successfully fitted with a sigmoidal curve demonstrating a typical induction period characteristic for an autocatalytic process with the rate-determining stage corresponding to the critical nucleus formation.[21-23] In the case of a rapid nucleation process promoted by the increased ionic strength (Figure 2c) an exponential aggregation kinetics are usually observed.

Despite the absence of any significant spectral changes in the equilibrated reaction system, it undergoes further structural evolution by means of the secondary association of the primary *J*-aggregates into the micrometer-size particles. The particle growth mechanism can include either a subsequent addition of the free monomers to the growing nucleus (a so-called particle-cluster aggregation), or a secondary association of several small clusters into a bigger one (a so-called cluster-cluster aggregation). The experimental support for one of the prevailing mechanisms of the particle growth can be obtained from the monitoring of the aggregation process by means of the dynamic light scattering (DLS) technique. The evolution of the hydrodynamic radius illustrates the aggregate particle growth*, while the simultaneous decrease in the scattered light intensity occurring due to the fluorescence quenching in the course of the aggregation process provides the information on the monomer consumption rate, since the fluorescence of the residual TPPS monomers makes a significant contribution to the analytical signal intensity when the light source of the appropriate wavelength is used.[24] The comparison of the plots given in Figure 3 provides the evidence for the correspondence between the exponential kinetics of the fluorescence quenching in the course of the aggregation process obtained from the fluorescence spectroscopic data and the similar exponential scattered light intensity plot obtained from DLS measurements at the same time interval.

A detailed analysis of the DLS monitoring data given in Figure 4 confirms a two-step aggregation mechanism suggested earlier by Micali and co-authors.[25] An instant decrease of the scattered light intensity observed at the first minutes after acidification due to the rapid consumption of the fluorescent TPPS monomer corresponds to the initial ultrafast aggregation stage which involves a small cluster formation from the monomer building blocks through reaction-limited aggregation mechanism. Due to the statistical nature of the analytical signal in DLS requiring several time for the relevant signal acquisition this rapid process is hardly observable using this technique. Further monitoring reveals the constant value of the scattered light intensity for each suspension upon the particle size growth, suggesting the predominant cluster-cluster interactions at the second stage of the large micrometer-scale aggregate formation. This step proceeds slowly but its longitude DLS monitoring is limited by the increase in the polydispersity of the aggregate suspension.

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* Since the colloidal suspensions of TPPS *J*-aggregates under investigation do not completely satisfy the approximation of monodisperse spherical particles adopted in DLS data processing, we applied the above method for monitoring of the dynamics of the aggregate growth rather than for an accurate estimation of the particle size in the suspension.

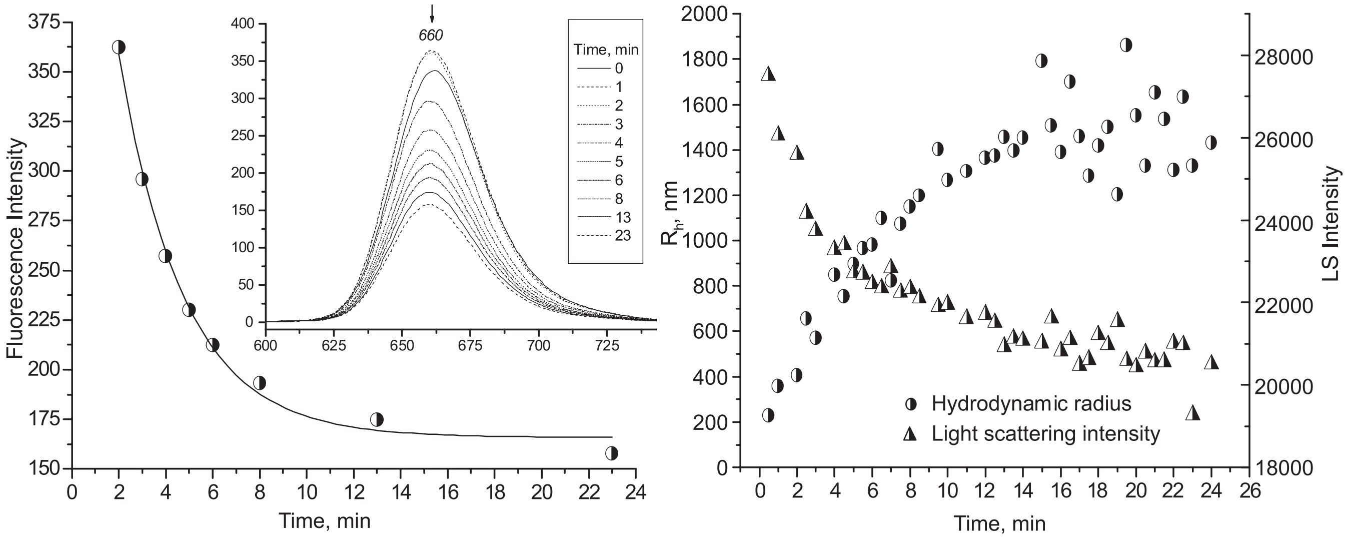

Figure 3. Fluorescence quenching kinetics (left) and the evolution of the particle size and light scattering intensity (right) in the course of TPPS aggregation in 1M aqueous sulfuric acid.

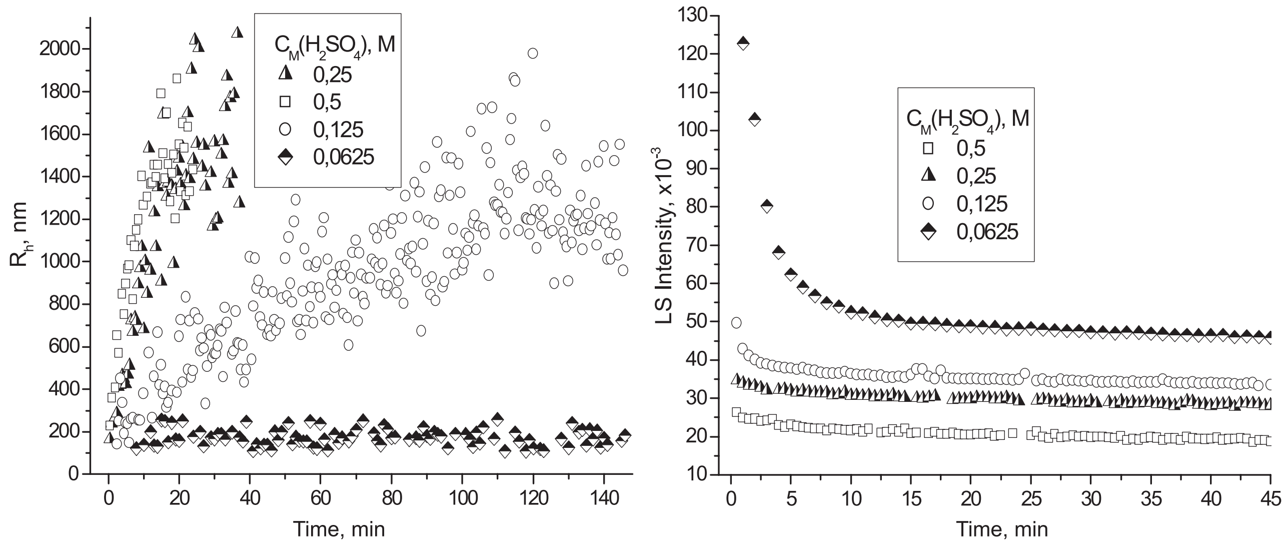

Figure 4. DLS monitoring of the particle hydrodynamic radius (left) and the light scattering intensity (right) during TPPS aggregation in aqueous sulfuric acid solutions of different concentrations.

It is also noteworthy, that the absolute value of the light scattering intensity observed in acidic TPPS solutions with different H_2SO_4 concentrations corresponds to the equilibrium concentration of the residual TPPS monomers in the reaction medium, while the rate of the secondary particle growth predictably depends on p*H* and ionic strength of the reaction medium with the latter parameter being a crucial one. In the most diluted H_2SO_4 solution with p*H* ~ 1 and ionic strength ~ 0.2 M one can observe the most slow monomer concentration decay at the initial stage and further stabilization of the small aggregate suspension without a subsequent particle growth due to the insufficient ionic strength, and hence, the low effective dielectric constant of the reaction medium, which fails to prevent electrostatic repulsion between the small clusters formed.

Besides the well known experimental protocols for TPPS-based *J*-aggregate synthesis in acidic aqueous solutions in presence of different low molecular electrolytes or promoting agents such as cationic surfactants and polyelectrolytes, we have proposed to carry out the aggregation process in aqueous solutions of several metal salts which produce a slightly acidic medium with the presence of polycationic species resulting from hydrolytic polycondensation of their aquacomplexes. The above approach allows to reduce significantly the acidity and ionic strength thresholds for *J*-aggregate formation due to the templating role of the polycationic species and their coagulating properties, i.e. the ability to reduce zeta potential of the fine dispersed colloidal particles leading to the effective precipitation.[26] For this purpose we have tested a number of water soluble ferric and aluminium salt solutions with the latter being more suitable due to their transparency in the visible spectral region and a relatively high value of the hydrolysis constant.

Further studies on the dependence of the degree of TPPS aggregation on the salt concentration (Table 1) have revealed the maximum aggregate-to-monomer ratio in the case of $Al(NO_3)_3$ at p*H*=3.76 and ionic strength 0.03 M. The linear dependence of the *J*-type aggregate concentration on the hydrogen ion activity is observed within 4.25–3.25 p*H* range, while its increasing above 500 μM results in a rapid increase of the aggregate-to-monomer ratio. In both cases the increasing acidity leads to the bathochromic shift of the aggregate *Q*-band from 700 to 710 nm indicating a more close packing of the monomer units in the aggregate structure.

Table 1. The aggregate-to-monomer ratio for TPPS in $Al(NO_3)_3$ aqueous solutions with different salt concentrations.

C, mol/l	$5 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
p*H*	3.08	3.56	3.76	4.23
$D_{432(mon.)}$	0.342	0.244	0.189	0.209
$D_{492(aggr.)}$	0.318	0.254	0.286	0.255
$D_{Q(aggr.)}$	0.169	0.145	0.113	0.079
$D_{aggr.}/D_{mon}$	0.93	1.04	1.51	1.22

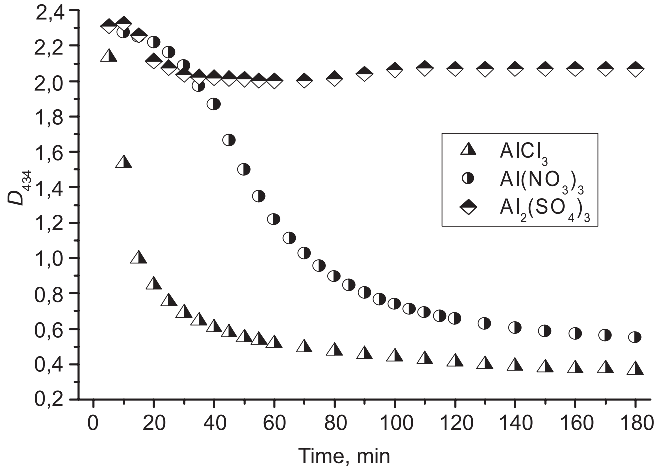

Figure 5. TPPS aggregation kinetics in different Al^{3+} salts.

Surprisingly, the aggregation kinetics of TPPS in various aluminium salt solutions were found to depend on the nature of the counteranion. Figure 5 presents the kinetic curves of the monomer consumption in the course of TPPS *J*-aggregate self-assembly with the maximum reaction rate in $AlCl_3$ medium and the almost complete inhibition of the aggregation process in $Al_2(SO_4)_3$ solution with the same Al^{3+} concentration. Interestingly, the order of the anions in the series $Cl^{-} > NO_3^{-} > SO_4^{2-}$ is similar to that observed for TPP *J*-aggregate formation in strongly acidic solutions with a high ionic strength (see Figure 1a), suggesting the similarity in the mechanism of their participation in the aggregate structure stabilization, probably resulting from the peripheral substituent charge neutralization by the metal-containing cationic species leading to the self-assembly of dicationic building blocks mediated by the counteranions as observed in the case of TPP and TCPP.

Since the geometric parameters of the monomer unit arrangement in supramolecular assemblies determine their stereochemical properties, and particularly, the possibility of manifestation of the so-called exciton supramolecular chirality,[27] The latter can also be expected to depend on the nature of the counterions involved in the aggregate structure formation. Thus, one of the recent papers speculates on the counterion dependence of the CD signal intensity in *J*-aggregate thin films obtained from the diprotonated form of 3,5-dimethoxy-TPP derivative at the chloroform / aqueous acidic solution interface.[28] The superposition of the electron transition dipole moment vectors of the adjacent porphyrin monomers arranged in a spiral aggregate structure is responsible for the Cotton effect observed in the CD spectra with the most intense exciton couplets corresponding to the absorption bands of *J*-aggregates, therefore the CD spectra can provide indirect information on the structural features and the strength of the exciton coupling within the chromophore assembly. In our experiments TPPS-based *J*-aggregates obtained in acidic media also demonstrated intense CD signals at 490 nm with the two smaller bisignate signals at 422 and 698 nm (Figure 6). The signal amplitude has varied with the porphyrin concentration and the storage time of the suspension, while the chirality sign in

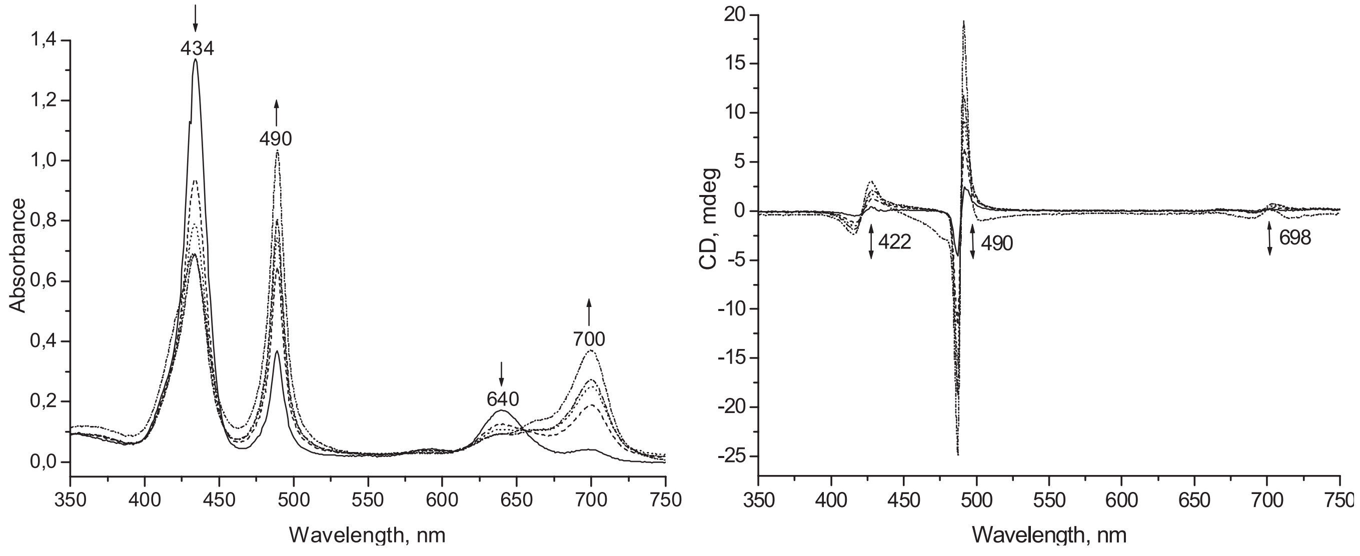

Figure 6. Evolution of the absorption (left) and CD (right) spectra of 10 μM TPPS in 0.5M H_2SO_4 (10 min interval).

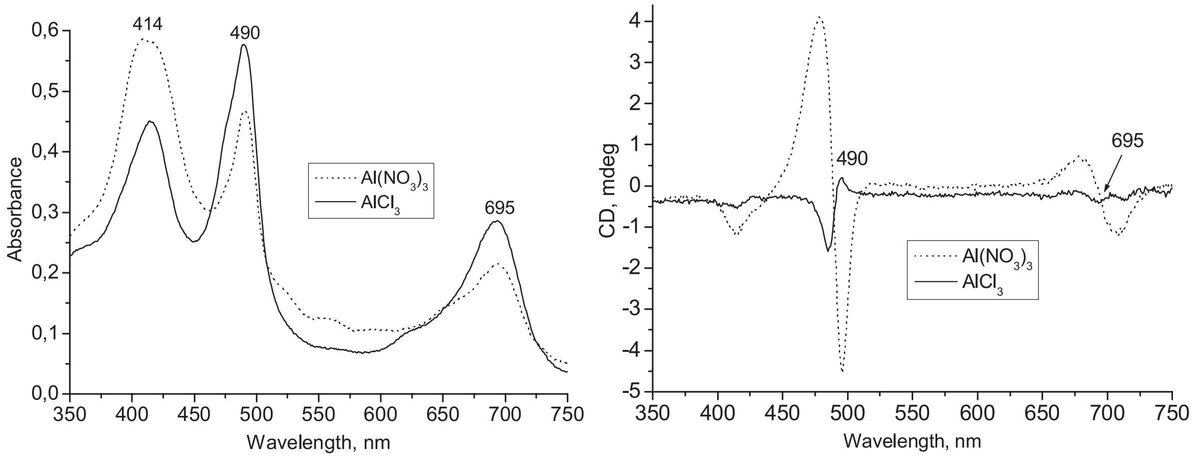

Figure 7. The absorption (left) and CD (right) spectra of TPPS *J*-aggregates in 5 mM aqueous Al^{3+} salt solutions.

all the cases has remained unchanged indicating a similar supramolecular arrangement of the chromophore molecules within the aggregate structure and the independence of the signal emergence on the presence of the incidental chiral contaminants.

In the case of the aluminium salt solutions a counterion-dependence of the CD spectra was also observed. The comparison of the absorption and CD spectra of TPPS *J*-aggregates obtained in AlCl$_3$ and Al(NO$_3$)$_3$ media (Figure 7) reveals the substantial difference in the chirality sign and the signal intensity for the solutions with the similar absorption spectra. The above difference correlates with the counterion-dependent aggregation kinetics (Figure 5), suggesting the rapid self-assembly process in the case of AlCl$_3$ less suitable for highly-ordered asymmetrical structure formation.

Moreover, the most intense bisignate curve appeared to be of the opposite chirality sign compared to the CD spectra of TPPS *J*-aggregates obtained in aqueous sulfuric acid (see Figure 6). This effect is certainly associated with the structural differences resulting from the anion geometry and requires a comparison with the CD spectra of TPPS *J*-aggregates obtained in aqueous nitric acid medium. The above results can be also attributed to the possible contribution of the asymmetric light scattering to the emergence of the CD signal in the suspensions of the aggregated chromophores arising from the anisotropy of the scattering particles which are mostly described in the literature as tubular structures.[29-30] Anyway, this issue requires more detailed studies which are expected to be reported in our further papers.

Conclusions

Thus, it was shown that the nature of the counterions significantly effects the structure and photophysical properties of TPP-based *J*-aggregates obtained in strongly acidic aqueous-organic solutions with the high ionic strength. DLS monitoring of TPPS self-assembly in acidic aqueous solutions confirmed that the aggregation process occurs through a two-step mechanism with the predominance of the electrostatic interactions at the first rapid stage of the gradual addition of the monomer units to the initially formed critical nuclei, and the primary role of the hydrophobic interactions at the second slow stage of the individual nanoscale cluster association into the large micrometer-size particles. Further studies on the aggregation behaviour of TPPS in aluminium salt solutions revealed counterion dependence of both the aggregation kinetics and the CD spectra of the resulting aggregated species.

Acknowledgements. The authors gratefully acknowledge the contribution of Sheinin V.B. (G.A. Krestov Institute of Solution Chemistry RAS) for providing TPPS. Special thanks are also due to Shubin V.V., the CCU research fellow at the A. N. Bach Institute of Biochemistry of the Russian Academy of Sciences, for his kind assistance in the CD-spectral measurements under the Project RFMEFI 62114X0002.

The work was supported by the Russian Foundation for Basic Research (Project No 15-03-03591).

References

1. *Supramolecular Soft Matter: Applications in Materials and Organic Electronics* (Nakanishi T., Ed.), New Jersey: John Wiley & Sons, **2011**. 508 p.
2. Busseron E., Ruff Y., Moulin E., Giuseppone N. *Nanoscale* **2013**, *5*, 7098–7140.
3. Goldberg I. *Cryst. Eng. Comm*. **2002**, *4*, 109–116.
4. D’Urso A., Fragalà M.E., Purrello R. *Chem. Commun*. **2013**, *49*, 4441–4443.
5. Sheinin V.B., Ratkova E.L., Mamardashvili N.Zh. *J. Porphyrins Phthalocyanines* **2008**, *12*, 1211–1219.
6. Sheinin V.B., Shabunin S.A., Bobritskaya E.V., Koifman O.I. *Macroheterocycles* **2011**, *4*, 80–84.
7. Zhang Z., Kim D.S., Lin C.-Y., Zhang H., Lammer A.D., Lynch V.M., Popov I., Miljanic O.S., Anslyn E.V., Sessler J.L. *J. Am. Chem. Soc*. **2015**, *137*, 7769–7774.
8. Choi M.Y., Pollard J.A., Webb M.A., McHale J.L. *J. Am. Chem. Soc*. **2003**, *125*, 810–820.
9. Doan S.C., Shanmugham S., Aston D.E., McHale J.L. *J. Am. Chem. Soc*. **2005**, *127*, 5885–5892.
10. Vaz Serra V., Andrade S.M., Neves M.G.P.M.S., Cavaleiro J.A.S., Costa S.M.B. *New J. Chem*. **2010**, *34*, 2757–2765.

11. De Luca G., Romeo A., Scolaro L.M. *J. Phys. Chem. B* **2006**, *110*, 7309–7315.
12. Ma H.-L., Jin W.-J. *Spectrochim. Acta Part A* **2008**, *71*, 153–160.
13. Rosa A., Ricciardi G., Baerends E.J., Romeo A., Scolaro L.M. *J. Phys. Chem. A* **2003**, *107*, 11468–11482.
14. Avilov I.V., Panarin A.Yu., Chirvony V.S. *Chem. Phys. Lett*. **2004**, *389*, 352–358.
15. Zhou M., Ouyang S., Liu Z., Lu G., Gao S., Li Z. *Vibr. Spectrosc*. **2009**, *49*, 7–13.
16. Gradova M.A., Zaytsev E.V., Lobanov A.V. In: *VIIIth All Russian Conference of Young Scientists* "*Theoretical and Experimental Chemistry of Liquid-Phase Systems*", Ivanovo, **2013**. p. 112–113 (in Russ.).
17. Kruk M.M., Starukhin A.S., Maes W. *Macroheterocycles* **2011**, *4*, 69–79.
18. Sheinin V.B., Shabunin S.A. Bobritskaya E.V., Koifman O.I. *Macroheterocycles* **2011**, *4*, 80–84.
19. *J-Aggregates, Vol. 2* (Kobayashi T., Ed.), Singapore: World Scientific, **2012**. 520 p.
20. Kasha M., Rawls H.R., El-Bayoumi A. *Pure Appl. Chem*. **1965**, *11*, 371–392.
21. Pasternack R.F., Fleming C., Herring S., Collings P.J., DePaula J., DeCastro G., Gibbs E.J. *Biophys. J*. **2000**, *79*, 550–560.
22. Chibisov A.K., Görner H., Slavnova T.D. *Chem. Phys. Lett.* **2004**, *390*, 240–245.
23. Slavnova T.D., Chibisov A.K., Görner H. *J. Phys. Chem. A.* **2005**, *109*, 4758–4765.
24. Gradova M.A., Kuryakov V.N. In: *Vth International Conference on Crown Compounds, Porphyrins and Phthalocyanines*, Tuapse, **2014**. p. 97 (in Russ.).
25. Micali N., Villari V., Romeo A., Castriciano M.A., Scolaro L.M. *Phys. Rev. E. Stat. Nonlin. Soft Matter Phys*. **2007**, *76*, 011404.
26. Duan J., Gregory J. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 475–502.
27. Simonyi M., Bikádi Z., Zsila F., Deli J. *Chirality* **2003**, *15*, 680–698.
28. Zhang Y., Chen P., Ma Y., He S., Liu M. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2036–2043.
29. Short J.M., Berriman J.A., Kübel C., El-Hachemi Z., Naubron J.-V., Balaban T.S. *Chem. Phys. Chem*. **2013**, *14*, 3209–3214.
30. Sheinin V.B., Bobritskaya E.V., Shabunin S.A., Koifman O.I. *Macroheterocycles* **2014**, *7*, 209–217.

Received 28.08.2015
Accepted 10.10.2015