SUPRAMOLECULAR SELF-ASSEMBLY OF POLYELECTROLYTE-BASED COMPLEXES CONTAINING PORPHYRIN DERIVATIVES

Gradov O.V.[1], Gradova M.A.[1], Bychkova A.V.[2], Lobanov A.V.[1]

[1]N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygin Street 4, Moscow, 119991, Russia, e-mail: m.a.gradova@gmail.com
[2]N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin Street 4, Moscow, 119991, Russia

Polyelectrolyte complexes are considered as promising supramolecular systems for biomedical applications, especially for targeted drug delivery[1]. Polyelectrolyte-porphyrin nanoassemblies are known to be photocatalytically and biologically active systems[2-4]. Combination of the photosensitizing properties and catalytic activity of porphyrin molecules with the cooperative stimuli-responsive behavior of polyelectrolyte complexes (PECs) allows to obtain hybrid photoactive supramolecular systems with emergent properties.

Here we report the aggregation behavior and photophysical properties of catonic (TMPyP), anionic (TSPP, TCPP) and neutral (TPP, THPP) porphyrin derivatives within soluble non-stoichiometric polyelectrolyte and polymer-surfactant complexes obtained from biological and synthetic polymers.

Electrostatic binding to the oppositely charged polyelectrolytes results in the porphyrin fluorescence quenching due to the dipole-dipole interactions between the macrocycles bound to the neighboring units of the polymer chain. In non-stoichiometric polyelectrolyte complexes the spectral properties of the porphyrin molecules are similar to those in an aqueous solution of the excess polyelectrolyte / surfactant. Phase-separated coacervate droplets were shown to accumulate fluorescent porphyrin derivatives in a monomolecular form from the bulk solution with the partition coefficient determined both by the microparticle surface charge and the HLB value of the porphyrin molecule.

The above photochemically-active porphyrin-loaded coacervate droplets can be considered as the primitive protocell models[5-6], and hence, the data obtained contributes to the origin of life studies.

References
1. Buriuli M., Verma D. Advances in Biomaterials for Biomedical Applications. Springer, 2017.
2. Fruhbeisser, S.; Grohn, F. Macromolecular Chemistry and Physics 2017, 218, 1600526.
3. Zhao, L.; Qu, R.; Li, A.; Ma, R.; Shi, L. Chemical Communications 2016, 52, 13534.
4. Fruhbeisser, S.; Mariani, G.; Grohn, F. Polymers 2016, 8, 180.
5. Koga, S.; Williams, D.; Perriman A.W.; Mann S. Nature Chemistry 2011, 3, 720
6. Kumar B.P.; Fothergill J.; Bretherton J.; Tian L.; Patil A.J.; Davis S.A.; Mann S. Chemical Communications 2018, 54, 3594.

This work was financially supported by the Russian Foundation for Basic Research (Project No 18-03-00539).