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From highly-correlated molecular systems to supermolecules

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Porphyrins are functional elements of important biomolecules, whose assemblies play a central role in fundamental processes such as electron transfer, oxygen transport, enzymatic catalysis and light-harvesting. The design of porphyrin nanostructures, including self-assembled architectures, has been mainly focused on the artificial reproduction of organization and functions of natural assemblies. It was shown that the properties of the nanostructures, in particular the energy transfer rate between adjacent molecules, are strongly affected by the structure of the ensemble. This makes them promising for the use of these materials to convert solar energy into chemical or electrical energy in, e.g., photocatalytic applications, sensors and organic photovoltaics.

Earlier we demonstrated that supramolecular design at the air-water interface with controlled self-assembly of organic compounds in 2D and 3D nanostructures becomes possible if one has quantitative information on the structure of the floating layer [1,2]. Studies of floating layers of azaporphyrins and their analogs showed that the size, morphology and stability of nanoaggregates are defined not only by the molecular structure of the macroheterocycle (the presence of side substituents, their nature, length and position, the size of the macrocycle), but also by the layer formation conditions.

In this talk we will present an approach to formation of porphyrin supermolecules, particular type of nanoparticles with unusually strong noncovalent intermolecular interactions. Key differences of the supermolecules from noncovalent nanostructures described earlier are (1) supermolecules consist of molecules of the same type without side groups promoting the self-assembly and without any spacers; no surfactant or catalyst to assist the process is needed (2) they exhibit unusual photophysical properties and remain stable even in organic solvents. Their formation occurs under specially selected conditions in highly-correlated molecular systems formed at the air-water interface at room temperature.

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