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Nanostructures formed by noncovalent self-organization of porphyrins at air-water interface under conditions of confined space at the nanolevel

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Porphyrin nanostructures can present an energy transfer between adjacent molecules, which is strongly affected by the structure of the ensemble. This makes them promising for the conversion of solar energy into chemical or electrical energy in, for example, photocatalytic applications, sensors, organic light emitting diodes and organic photovoltaics. Recently, we have formed particular type of porphyrin systems – supramolecular assemblies of magnesium porphine (MgPor), structural basis of chlorophyll, with strong noncovalent intermolecular interactions and with functional properties extrinsic to the constituent molecules. These assemblies were formed using Langmuir-Schaefer (LS) technology (horizontal lifting) within nanoaggregates at air-water interface under conditions of confined space at the nanolevel [1-3]. It was shown that solution of the LS-films in such organic solvents as DCM or DMSO is transparent for visible light in contrast to pink colour of the solution of monomers. It was therefore hypothesised that structural units of the film are not individual molecules but rather supermolecular assemblies. Each of these assemblies functions like one supermolecule [4]. To understand the layers structure of MgPor and some other porphyrins directly on water surface, from which they are transferred to the solid substrate via LS technique, in-situ measurements were carried out at ID10 beamline, European Synchrotron Radiation Facility, Grenoble, France. Studied layers and films were irradiated with a monochromatic synchrotron beam with energy of 22 keV (wavelength $\lambda = 0.5636 \text{ \AA}$). We have studied the structure of the layers formed on water at different surface pressures, ranging from 0 to 30 mN/m, and under different initial coverage of water surface by molecules. The floating layers were prepared by spreading at the water surface of the monomers dissolved in organic solutions. The multilayer films prepared at the same concentrations and pressures were transferred on solid supports (silicon wafers or quartz plates) with LS technique and were also measured at ID10 to confirm the structure conservation upon the films transfer. In the talk we will present our data on the aggregation process of some porphyrins at different stages ranging from formation of M-aggregates on water surface to nanocrystallization in thin films and data on the internal structure the porphyrin nanostructures that have been missing so far.

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