ESRF	Experiment title: **Identification and structural study of new unique nanostructures – magnesium porphine supermolecules at the air-water interface**	**Experiment number**: SC4673
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Report:

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). 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 [1]. 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.

To understand the MgPor layers structure 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. We have studied the structure of the layers formed on water at different surface pressures, ranging from 0 to 30 mN/m, and under three different initial coverage of water surface by MgPor molecules: c=17%, 36% and 48%. The floating layers were prepared by spreading at the water surface of the MgPor monomers dissolved in organic solutions and compressing such a layer to the surface pressures, ranging from 0.1 to 30 mN/m. The multilayer films prepared at the same concentrations and pressures were tranfered at home on solid support (silicon wafers or quartz plates) with LS technique and were also measured at ID10 to confirm the structure conservation upon the MgPor film transfer.

Studied layers and films were irradiated with a monochromatic synchrotron beam with energy of 22 keV (wavelength λ = 0.5636 Å). Figure 1 shows the X-ray reflectivity (b,c) and Grazing incidence XRD (d) from MgPor floating layer (b) and LS film on Si-substrate (c,d). The floating layer was made by spreading of MgPor monomers in DCM solution ($C=1.2\times10^{-4}$ M) onto the water surface (initial coverage degree 48%) and its compression to the surface pressure π= 20 mN/m. The multilayer film on silicon wafer was prepared at π= 23 mN/m with 10 tactions (10 layers).

It was found that the layer thickness on water is equal to 42 Å (Figure 1b) that corresponds to the tetralayer with edge-on molecular arrangement ("L_1" dimension of the monomer is equal to 11 Å, Figure 1a). The result completely confirms estimation of the number of the layers derived from pressure-area per molecule isotherm, made according to our model of nanostructured layers of macrocyclic compounds at air-water interface [2].

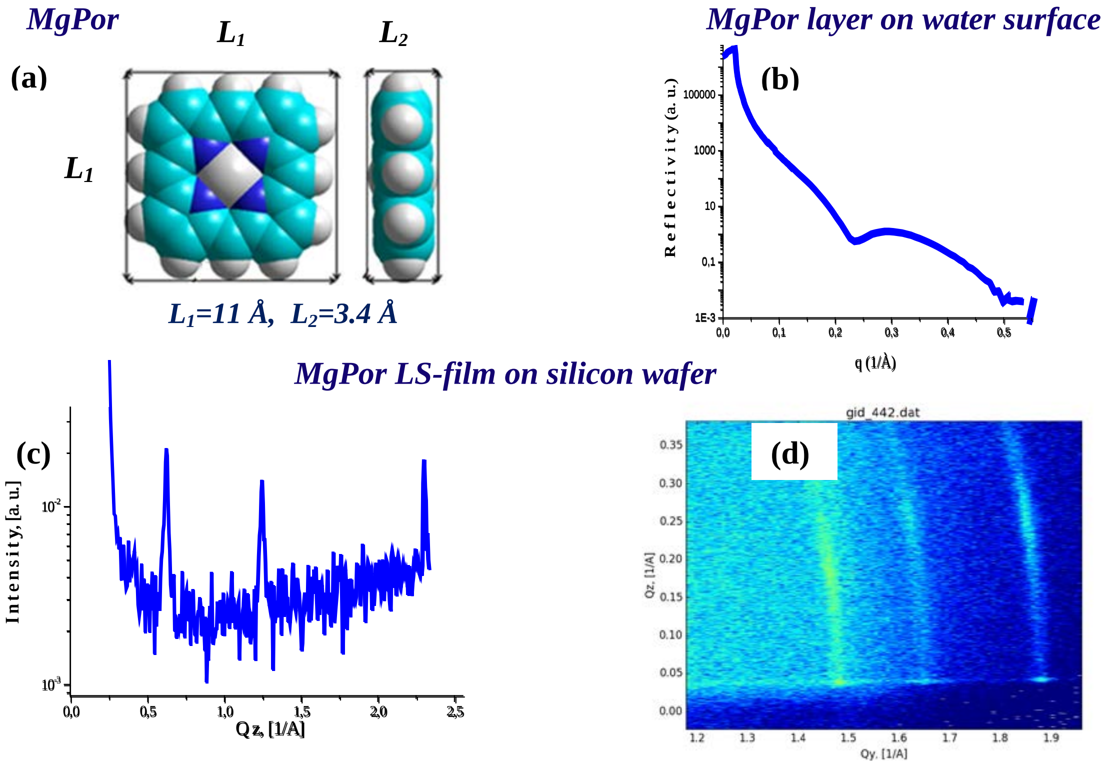

Figure 1. Molecular dimensions of MgPor (a), X-ray reflectivity (b,c) and Grazing incidence XRD (d) from MgPor layer on water surface (b) and Langmuir-Schaefer film (c, d).

Intermolecular distances in the film on silicon wafer, determined from the diffraction pattern (Figure 1c) are: a=10.1 Å (two orders: Qz= 0.62 1/Å and Qz= 1.24 1/Å) that corresponds to slightly tilted molecules and b=2.7 Å (Qz= 2.3 1/Å). The molecular tilt is corroborated by the GID mearurements (Figure 1d) where the scattering intensity maxuma are at Qz ≠0. Observed in-plane d-Spacings (Figures 1d) are: 4.2 Å, 3.8 Å, 3.3 Å. Note, that a distance between the molecules in usual molecular system should be not less than 3.3 Å (“L_2” dimension of the monomer is equal to 3.4 ± 0.1 Å, Figure 1a). So the actual distance b=2.7 Å is substantially shorter and we might claim that some specific force draws and keeps the molecules together. Thus we can conclude that neighbor molecules in formed MgPor supramolecular assemblies exhibit unusually strong, not van der Waals interactions, they are “pressed” into each other. In fact, no solvent was found that could separate molecules in such assemblies.

Thus, on the basis of the experiments that were carried out at beamline ID10 of the ESRF we report two key results. (1) Confirmation of the formation of unique porphyrin nanostructures – magnesium porphine supermolecules using Langmuir-Schaefer technology. (2) Data on the internal structure the supermolecules that have been missing so far. Determined intermolecular distance unusually short for organics proves our suggestion on “covalent-like” intermolecular interactions in LS-films and explanes their unique properties. The nature of these interactions is still an open question.

Further studies are required to determine whether formation of the porphyrin supermolecules starts directly on water surface or during transferring the layers onto solid support. The answer to this question may be elucidated by the X-ray studies (XRR and GID) of the layers on water surface formed at another conditions, including very big and small initial surface coverage. Another point of further research is measuring the length of the supermolecules. We estimate their size is in the range of 50-70 Å or even more. GISAXS can be very instrumental for this purpose.

References

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