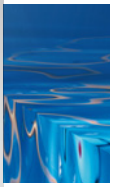

3D arrays on quantum dots embedded within a bio-inspired template studied by SAXS

SWING beamline
Crystallization of fluorescent quantum dots within a 3D bio-organic template of actin filaments and lipid membranes

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Generating new physical properties using the crystallization of nanoparticles is highly challenging. The design of such new materials with unexpected physical properties is thus the major motivation in the investigation of new strategies for controlling the crystallization of nanoparticles [1]. In this context, biological molecules and molecular self-assemblies are promising templates to organize well-defined inorganic nanostructures [2]. This approach allows the spontaneous formation of structures of well-defined shapes and monodisperse characteristic sizes [3]. The SWING Beamline have been designed and is powerful to study these bottom-up nanomaterials by Small Angle X-ray Scattering, SAXS. SWING is a highly versatile setup whose the investigated distances can vary from 0.5 to 500 nanometers. For example, we recently studied by SAXS on SWING a library of 17 peptides forming nanotubes of monodisperse diameter ranging from 9 to 36 nm [4].

Here we report on the ability of a self-assembled three-dimensional crystal template of helical actin protein filaments and lipids bilayers to generate a hierarchical self-assembly of quantum dots (Figure 1). With this goal, functionnalized tricystein peptidic quantum dots (QDs) are incorporated during the dynamical self-assembly of this actin/lipid template through electrostatic interaction. This slow mixing results in the formation of crystalline fibers (Figure 2). This process ensures the high quality of the crystal. We demonstrate the formation of a very well-defined 3D crystal of QDs by SAXS performed with Florian Meneau on SWING (Figure 3). The crystal parameters, 26.5 x 18.9 x 35.5 nm^3, are imposed by the membrane thickness, the diameter, and the pitch of the actin self-assembly. In a first simple approach, we used only lipid multilayers to insert water soluble functionalized QDs [5] and the 3D order was lost. The inclusion of extraneous objects providing additional well-defined length scales such as actin is necessary to create 3D order. The fluorescence properties of the 3D crystals of quantum dots demonstrate a direct effect of the nanostructuration of the quantum dots within the crystal.

Such a formation of 3D arrays of nanoparticles opens new route toward optical materials that are easily prepared by using self-assembling of vesicles, proteins, and hydrophilic nanoparticles in aqueous environment. This strategy could be extended to any kind of hydrophilic nanoparticles with various morphologies. Furthermore, the range of characteristic lengths can be extended by using other biological materials.

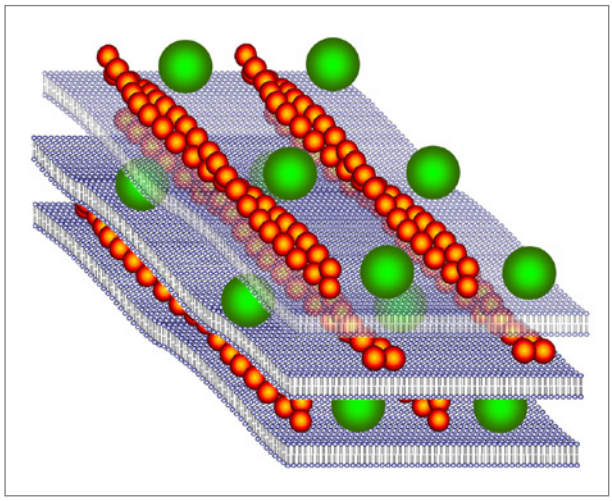

Figure 1: Schematic view of the structure. Strong electrostatic interactions between anionic microfilaments (red) and cationic lipids results in large undulations of the lipid bilayers (blue).
Quantum Dots (Green) are embedded between actin filaments as well as lipid membranes.

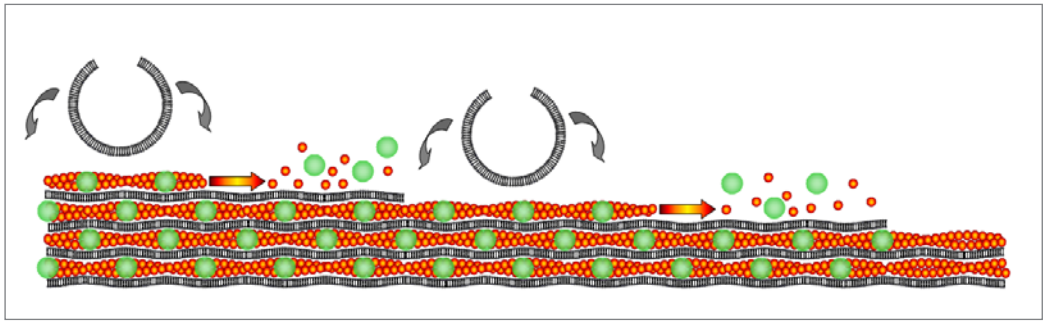

Figure 2: Self-assembly mechanism: (i) the electrostatic adsorption of anionic quantum dots QD and actin proteins onto the cationic membranes; (ii) the actin polymerisation and (iii) the rupture of cationic vesicles by adhesion onto the anionic filaments.

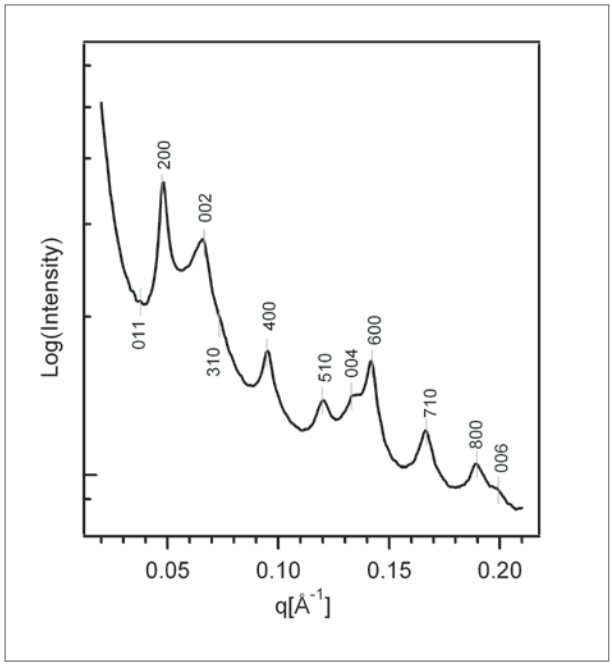

Figure 3: Powder diffraction observed by SAXS experiments performed with a 3m sample-detector distance at SWING@SOLEIL and the corresponding peak indexations in a 3D centered orthorhombic lattice. The HWHM of the Bragg peaks (<0.004Å^{-1}) shows a positional order larger than 3000Å.

References:

[1] Z. H. Nie et al. Nat. Nanotechnol. 2010 5, 15
[2] Nykypanchuk et al. Nature 2008 451, 549
[3] E. Pouget et al. Nature Materials 2007, 6, 434
[4] C. Tarabout et al. Proc. Natl. Acad. Sci. USA 2011, 108 (19) 7679
[5] A. Dif et al. J. Am. Chem. Soc. 2008, 130(26), 8289