Technical Report:

X-ray reflectivity (XRR), grazing incidence small and wide angle x-ray scattering (GISAXS and GIWAXS) and grazing incidence x-ray diffraction (GIXD) measurements from the monolayer of electronically coupled organic-inorganic nanostructure (COIN), prepared on Si-substrates have been performed under ambient conditions at ID03 beamline at ESRF, Grenoble, France. All the techniques are used also for characterizing the bi(multi-)layer of nanoparticles (NPs), grown on top of the COIN templates. The GISAXS patterns were collected using a two-dimensional (2D) ADSC Quantum 315 detector (pixel size 102 x 102 μm^2) and the XRR, GIXD and GIWAXS profiles/images were obtained using single 2x2 Maxipix detector. A monochromatic and focused beam of energy 12.8 KeV (λ = 0.0968 nm) and of 50 x 28 (V x H) μm^2 size was set for all measurements. The Maxipix detector was kept at 550 mm away for sample center. Specular XRR was collected with a pre-defined ROI (region of interest) across the direct beam. GIXD and GIWAXS spectra were obtained with the same Maxipix detector scanning over high in-plane azimuthal angle (γ) and wide out-of -plane angle (δ), respectively with a fixed grazing incidence beam. A 37.75M ADSC detector was placed at a distance of 1568 mm away from the goniometer center along the direct beam in order to access small q-range for resolving nanoscopic features in the samples. Most of the GISAXS/GIWAXS/GIXD spectra form the samples were obtained by choosing the incident angle near the critical angle of the NP assembly (0.19 degree).

We have synthesized monolayers of native oleic acid (OA) capped PbS nanoparticle (NC-OA) self-assembled film as well as COIN monolayer of PbS-Cu-tetraaminophthalocyanine(NC-CuTAPc) and PbS-tetrathia-fulvalenedicarboxylate (NC-TTFDA) films after inter-exchange of native insulating OA ligands with corresponding organic semiconductor molecules (CuTAPc/TTFDA) through ligand exchange process at air-liquid interface. We have prepared adlayers of NPs (NC-OA or COIN in form of bi/multi-layers) on top of the COIN templates by the drop-cast method. We have grown the adlayer of NCs with similar as well as different sizes with respect to NPs, used for preparing COIN templates. Our aim was to examine the soft-epitaxy between layers and determine the evolved strain on NPs in the superstructures. All the ex-situ samples were prepared at University of Tuebingen, Germany.

We have collected the various scattering data from both types (monolayer and bi/multi-layers) of samples. We have observed nice in-plane and out-of-plane scattering patterns in GISAXS images and pronounced Kiessig oscillations for monolayer and multilayer samples in XRR (**Fig 1**). We are in the process of determining the nanoscopic information of the superstructure assembly from the obtained GISAXS and XRR data for all the measured samples. From the obtained GIXD/GIWAXS data, taken from the corresponding samples, we will quantify the atomic orientation of the NPs within the superlattices. With help of all these measurements, we will determine the structural changes in the samples in nano and atomic level. The analysis of the complex GISAXS pattern from the bilayer samples will determine the soft epitaxy between the layers and strain in the superstructure. In brief, we have already observed/analyzed the following

(1) a significant relative shift in q-space after ligand exchange; (2) highly long-range positional and orientational ordering of NCs for template layer as well as adlayers. Based on the initial observations we could say that the experiment is successful and very likely going towards publication. Finally, we would like to thank the professional support provided by the local contact Dr. Maciej Jankowski.

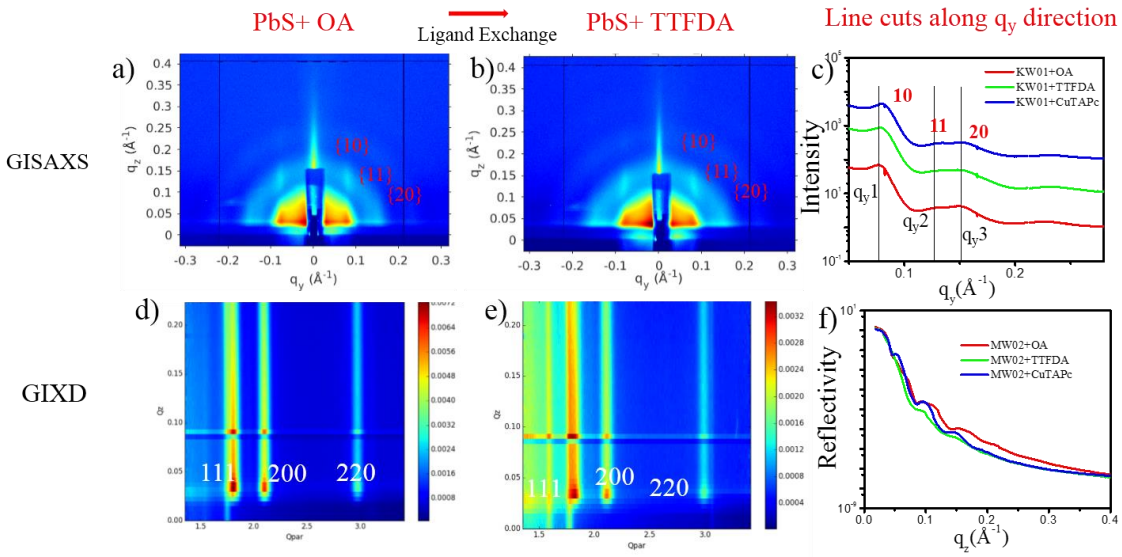

Fig. GISAXS pattern of a) PbS-OA (uCOIN) and b) PbS-TTFDA (COIN) monolayer. c) Extracted scattering intensity profile along q_y at q_z = 0.035 Å^{-1}. GIXD pattern of corresponding d) PbS-OA and e) PbS-TTFDA samples f) XRR data at different samples.