

***In-situ* Formation of Electronically Coupled Superlattice of Cu_{1.1}S Nanodiscs at the Liquid/Air Interface**

Sonam Maiti^{1,2}, Santanu Maiti^{*,1}, Andre Maier², Rupak Banerjee³, Chen Shen⁴, Bridget M. Murphy^{5,6}, Marcus Scheele^{2,7}, Frank Schreiber^{1,7}

¹Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany.

²Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany.

³Department of Physics, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar 382355, India.

⁴Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany

⁵Institute for Experimental and Applied Physics, Kiel University, D-24098 Kiel, Germany

⁶Ruprect Heansel Laboratory, Kiel University, D-24098 Kiel, Germany

⁷Center for Light-Matter Interaction, Sensors & Analytics LISA+, University of Tübingen, Auf der Morgenstelle 15, 72076 Tübingen, Germany

Contents

- Experimental Details.
- Supplementary Figures
- Supplementary Table

- **Experimental Methods**

Synthesis of Cu_{1.1}S Nanocrystals: Cu_{1.1}S NDs were prepared by adapting the heat-up synthesis procedure from Xie et al.¹

Synthesis of Ligands: Co-4,4',4'',4'''-tetraaminophthalocyanine (Co4APc) was purchased from Abcr and used without further purification.

***In-situ* formation of NC film at the liquid/air interface and ligand exchange.**

At first, the nitrogen flushed chamber is filled up to 5 mm below the window edge with dry, oxygen free DMSO (99,7+%, extra dry, Acros organics). Then 200µL of the 5µM ND solution in Toluene (97%, extra dry, nitrogen flushed, Acros Organics) is dispersed on top of the acetonitrile at a rate of 1 mL/min. The time resolved GISAXS patterns are collected afterwards from the ND film.

After the investigations on the oleylamine capped NC film are finished, the ligand solution (1mg/mL solution of CoTAPc in DMSO) is injected in the bulk DMSO. The start of the injection process marks the time zero of our experiment. The subphase height was adjusted about every 15 minutes for perfect alignment. For better control on the experiment, all the injection or dispersion processes are performed with the help of a syringe pump.

***In-situ* Grazing Incidence Small Angle X-ray Scattering (GISAXS).**

In-situ GISAXS measurements were performed at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany at the Liquid Interface Scattering Apparatus (LISA), P08 beamline. The x-ray beam energy was set at 18 keV by using a Si(111) double crystal monochromator and Ge(311) Large-Offset-Monochromator, focused with CRL lens.^{2, 3} A beam of size 100 µm x 400µm (V x H) was illuminated on the liquid surface at a grazing angle of 0.065 degree, set by the double crystal deflector of LISA.⁴ The GISAXS signals were collected with a Lambda detector, having a pixel size of 55 x 55 µm². The detector was placed at a distance of 1103 mm and each GISAXS images were collected over 5 seconds of exposure time.

Instrumentation

Scanning transmission electron microscopy (STEM, Hitachi SU 8030 microscope operating at 30 kV) was employed to determine the particle size and shape. The surface morphology was measured by AFM using a JPK Nanowizard II instrument in tapping mode under ambient conditions. Image analysis was performed with Gwyddion. We perform Raman spectroscopy to ratify the ligand exchange in the nanodisc superlattices over depositing them onto Si-substrates. Raman spectra were acquired using a Horiba Jobin Yvon Labram HR 800 spectrometer with a CCD-1024 × 256-OPEN-3S9 detector. Excitation for Raman was performed using a He:Ne laser (wavelength 633 nm). The superlattice films were illuminated at room temperature with the excitation in the range of 350-1800 cm⁻¹. Electrical measurements were performed in a glovebox at room temperature with a homemade probe station using a Keithley 2634B dual source-meter

unit, controlled by the included test script builder program. The NC films after ligand exchange were deposited on a commercially available bottom-gate, bottom-contact transistor substrates (Fraunhofer Institute for Photonic Microsystems, Dresden, Germany) with interdigitated Au electrodes of 10 nm width and 2.5 μm channel length followed by annealing at 250°C for 2 h under nitrogen atmosphere.

- **Supplementary Figures**

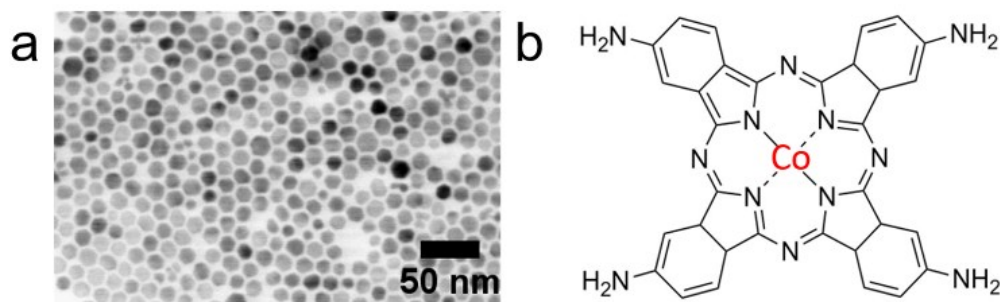


Figure S1. a) TEM image of Olm-passivated Cu_{1.1}S NDs. b) Structural formula of CoTAPc.

Figure S1a shows a typical transmission electron microscopy (TEM) image of as-synthesized Cu_{1.1}S NCs. The NCs are disc in shape (i.e. NDs) and have two hexagonal and six rectangular side facets. The NCs have an average in-plane diameter (d) and thickness of 12.7 ± 0.5 nm and 5.6 ± 0.5 nm, respectively. The NC surfaces are encapsulated with native oleylamine (Olm) and dispersed in toluene. Here, we use rectangular-shaped CoTAPc OSC molecules (size: 1.3 ± 0.6 nm) for the ligand exchange reaction. The CoTAPc molecule has four amines (-NH₂) groups on their backbone as shown the structural formula in Figure S1b.

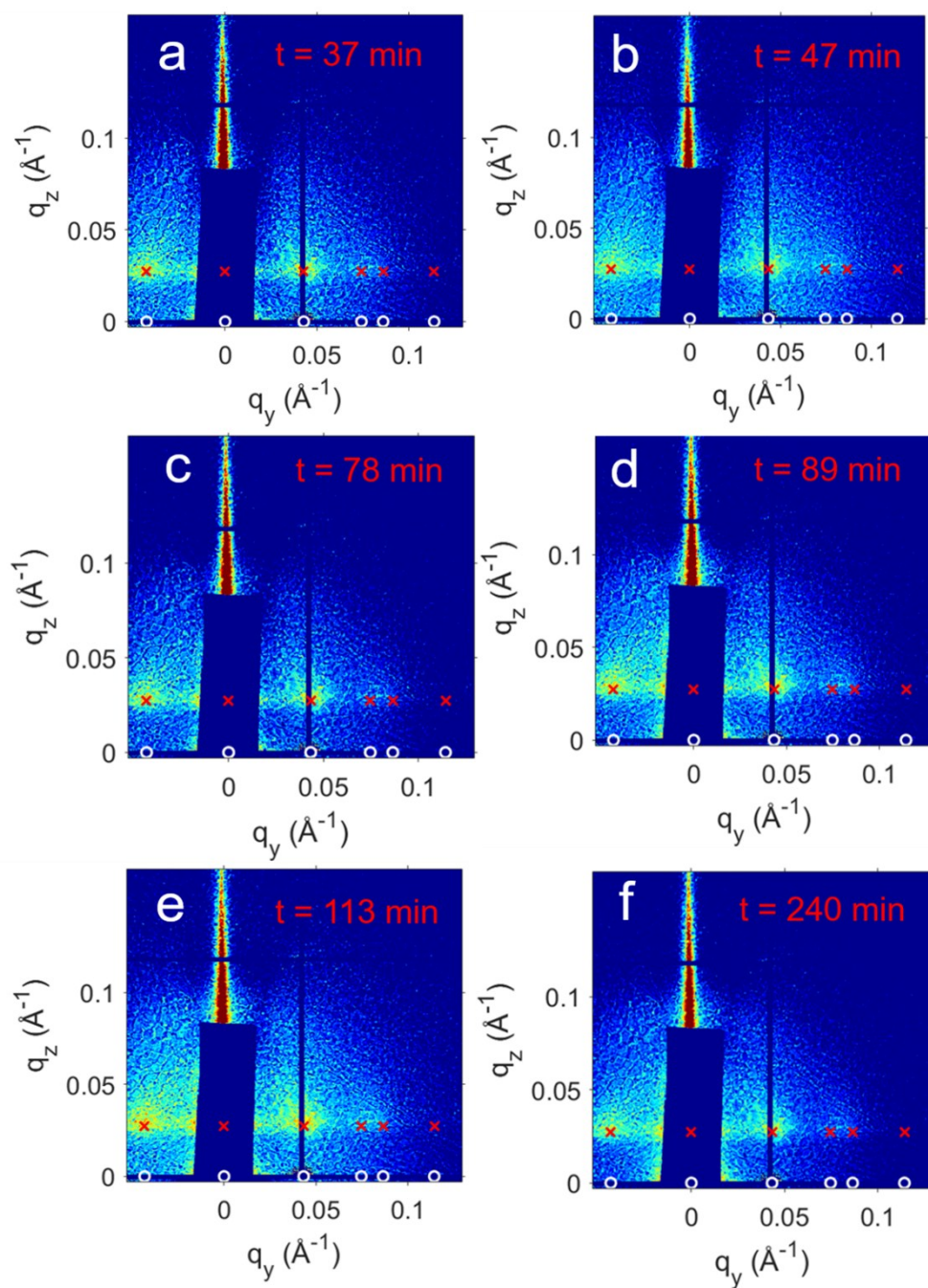


Figure S2. a-f) GISAXS patterns from the self-assembly without ligand exchange at different intermediate times marked at the right corner of each images. The pink and red spots are the simulated diffraction peak position of bcc superlattice considering DWBA method.

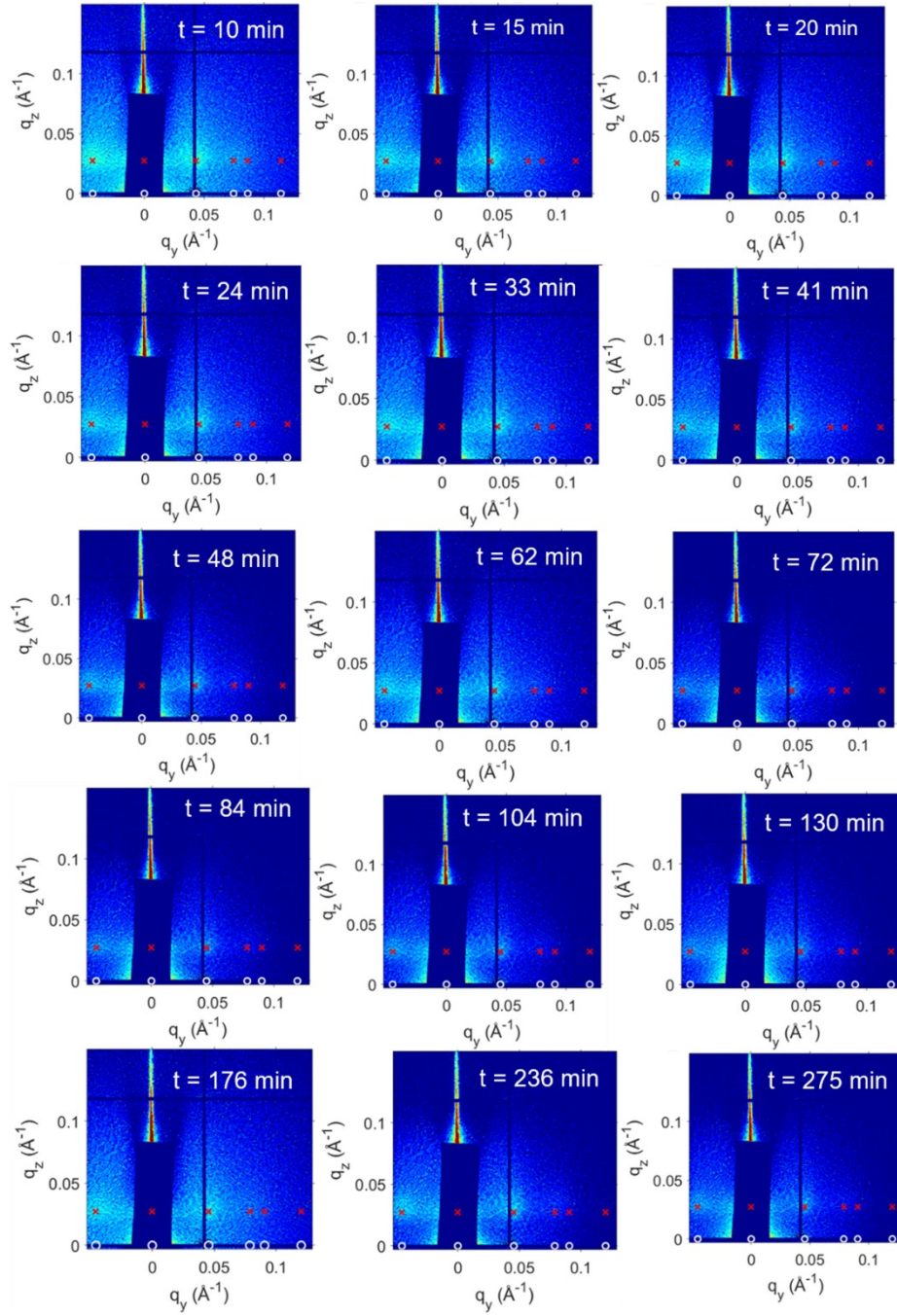


Figure S3. GISAXS patterns from the self-assembly during ligand exchange process at different intermediate times marked at the right corner of each images. The pink and red spots are the simulated diffraction peak position of bcc superlattice considering DWBA method.

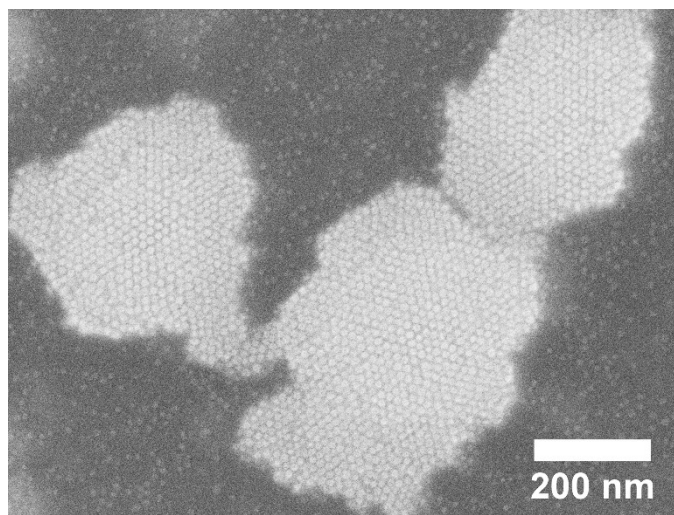


Figure S4. STEM image of $\text{Cu}_{1.1}\text{S}$ NC superlattice

Further material characterization

Atomic force micrograph of the ligand-exchange nanocrystal superlattice

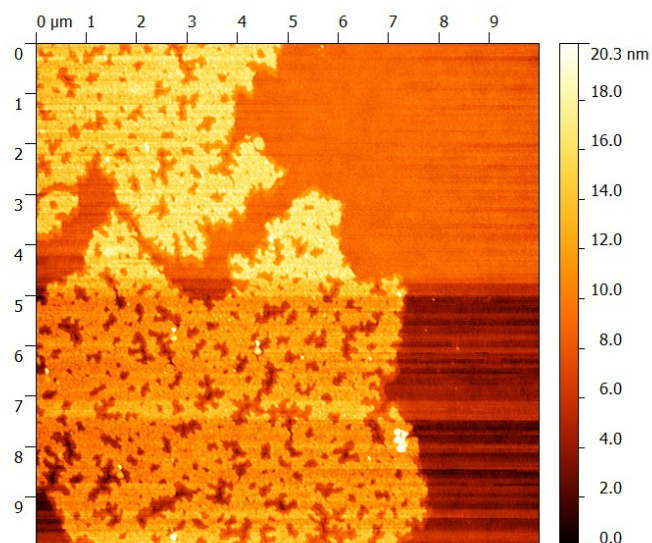


Figure S5. Atomic force micrograph of the nanocrystal superlattice after complete ligand-exchange and drying on a silicon substrate. The average height of the superlattice is ~ 11 nm.

- **Supplementary Table**

Table S1: Superlattice parameters

Waiting time (min)	a = b = c (Å)	$\alpha = \beta$ (deg)	γ (deg)	SG Symmetry
-42	171	90	120	P6mm
0	169	90	120	P6mm
6	168	90	120	P6mm
10	166	90	120	P6mm
15	165	90	120	P6mm
20	164	90	120	P6mm
24	163	90	120	P6mm
29	162,5	90	120	P6mm
33	162	90	120	P6mm
36	161,5	90	120	P6mm
41	161	90	120	P6mm
48	160,5	90	120	P6mm
62	160	90	120	P6mm
72	160	90	120	P6mm
78	160	90	120	P6mm
84	160	90	120	P6mm
93	160	90	120	P6mm
104	160	90	120	P6mm
114	160	90	120	P6mm
130	160	90	120	P6mm
176	160	90	120	P6mm
236	160	90	120	P6mm
276	160	90	120	P6mm

1. Xie, Y.; Riedinger, A.; Prato, M.; Casu, A.; Genovese, A.; Guardia, P.; Sottini, S.; Sangregorio, C.; Miszta, K.; Ghosh, S.; Pellegrino, T.; Manna, L., Copper sulfide nanocrystals with tunable composition by reduction of covellite nanocrystals with Cu⁺ ions. *J Am Chem Soc* **2013**, *135* (46), 17630-7.
2. Seeck, O. H.; Deiter, C.; Pflaum, K.; Bertam, F.; Beerlink, A.; Franz, H.; Horbach, J.; Schulte-Schrepping, H.; Murphy, B. M.; Greve, M.; Magnussen, O., The high-resolution diffraction beamline P08 at PETRA III. *J Synchrotron Radiat* **2012**, *19*, 30-38.
3. Murphy, B. M.; Greve, M.; Runge, B.; Koops, C. T.; Elsen, A.; Stettner, J.; Seeck, O. H.; Magnussen, O. M., A novel X-ray diffractometer for studies of liquid-liquid interfaces. *J Synchrotron Radiat* **2014**, *21*, 45-56.
4. Murphy, B. M.; Greve, M.; Runge, B.; Koops, C. T.; Elsen, A.; Stettner, J.; Seeck, O. H.; Magnussen, O. M., A new Diffractometer for Studies of Liquid - Liquid Interfaces. *Aip Conf Proc* **2010**, 1234.