Supporting Information for a manuscript entitled

"Nanoarmoured" droplets of different shapes formed by interfacial self-assembly and crosslinking of metal nanoparticles

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Section 1. Materials and Methods.

All solvents and chemicals were purchased from VWR, except of 11-mercaptoundecanoic acid (MUA), N,N,N-trimethyl(11-mercaptoundecyl)ammonium chloride (TMA) and HS-$(CH_2)_{11}$-EG3 which were obtained from ProChimia Surfaces (www.prochimia.com), and hexanedithiol was obtained from Sigma-Aldrich. All chemicals were used as received.

Synthesis of nanoparticles. Nanoparticle precursors stabilized with weakly bound ligands (AuDDA) were synthesized according to a procedure from ***Ref. S1,S2***. The average sizes of the particles thus prepared were 5.5 ± 0.7 nm.

Synthesis of DFMP ligand. DFMP ligands were synthesized as described in ***Ref. S3***. In short, 2,6-difluorophenol and chlorosulfonic acid were refluxed in toluene for 2 hrs to obtain 2,6-difluoro-4-sulfonylchloride, which was then reduced with Zn dust in 40% boiling sulfuric acid in the course of 4 hrs.

Functionalization of nanoparticles. AuDFMP NPs were prepared by precipitation of precursor NPs from toluene with methanol, removal of solvents, and redispersion of the precipitate in a toluene solution of FMP (0.4 equivalents of ligands per gold atoms). After 2 hrs, the solution was precipitated with acetone (the precipitation may be facilitated/accelerated by alkalization with tetramethylammonium hydroxide, TMAOH, 25% solution in methanol). Precipitate was washed several times with dichloromethane and acetone, dried and finally redispersed in water (adjusting pH to 10-11 with aqueous solution of 0.2 M tetramethylammonium hydroxide) to give a stable (for several months) solution of AuFMP NPs.

Procedure for formation of NP films. The initial NP concentration was measured by UV-Vis from the absorbance in the wavelength corresponding to maximum of SPR peak (~520 nm). For all experiments AuDFMP NP solution of 36 mM (in terms of metal atoms). The calculation of concentration in terms of nanoparticles could be easily achieved knowing that each 5.5 nm nanoparticle contains ~5108 Au atoms.

Droplets of this silanized glass surface of the Petri dish filled with 3:1 v/v toluene-dichloromethane. To this Petri dish hexanedithiol crosslinker was added to reach the final dithiol concentration in organic phase C_{DT} ~10 μM.

Section 2. Estimation of film thickness. For a given volume of a droplet, its radius was calculated. Knowing the NP size and concentration in the solution and assuming that all NPs were crosslinked, the total volume the NP film was calculated (the size of single nanoparticle was 6.5 nm which accounts for 5.5 nm of metal core and additionally 1.0 nm for layer of DFMP ligands on the NP surface; we assumed the packing factor of NP to be 0.72, close to the hcp structures). The NP film volume was extracted from the total volume of the droplet and from that volume of the water inside the NP shell was calculated. From that volume r_{water} was obtained. Finally, thickness of the shell, d_{shell}, was derived from simple equation: $d_{shell} = r_{total} - r_{water}$ (FigS1). For V=10 μL of C=32 mM NP solution the film thickness was estimated to be ~400 nm.

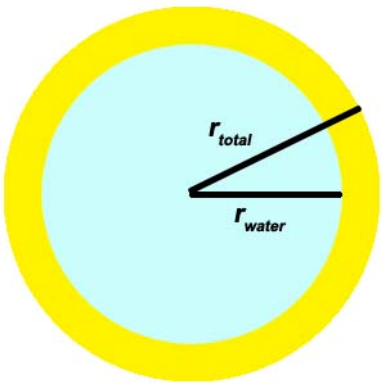

Fig. S1. The schematic picture showing how thickness of the NP shell (in yellow) around the droplet of water was estimated.

Section 3. SEM images of the NP shell.

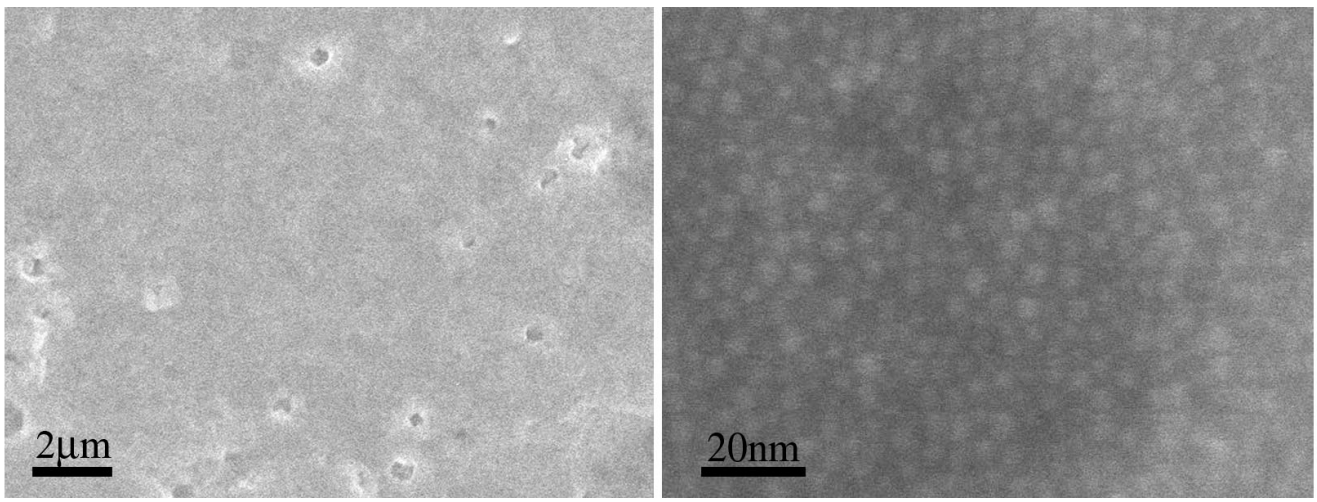

Fig. S2. The SEM images of film obtained by NP assembly on the interface.

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(S3) Sato, M.; Kawashima, Y.; Goto, J.; Yamane, Y.; Chiba, Y.; Jinno, S.; Satake, M.; Iwata, C. Synthesis and Evaluation of Novel Fluorinated Sulotroban-related Sulfonamide Derivatives as Thromboxane A2 Receptor Antagonists. *Eur. J. Med. Chem.* **1995**, *30*, 403↕414.