Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Ligand dynamics control structure, elasticity, and high-pressure behavior of nanoparticle superlattices

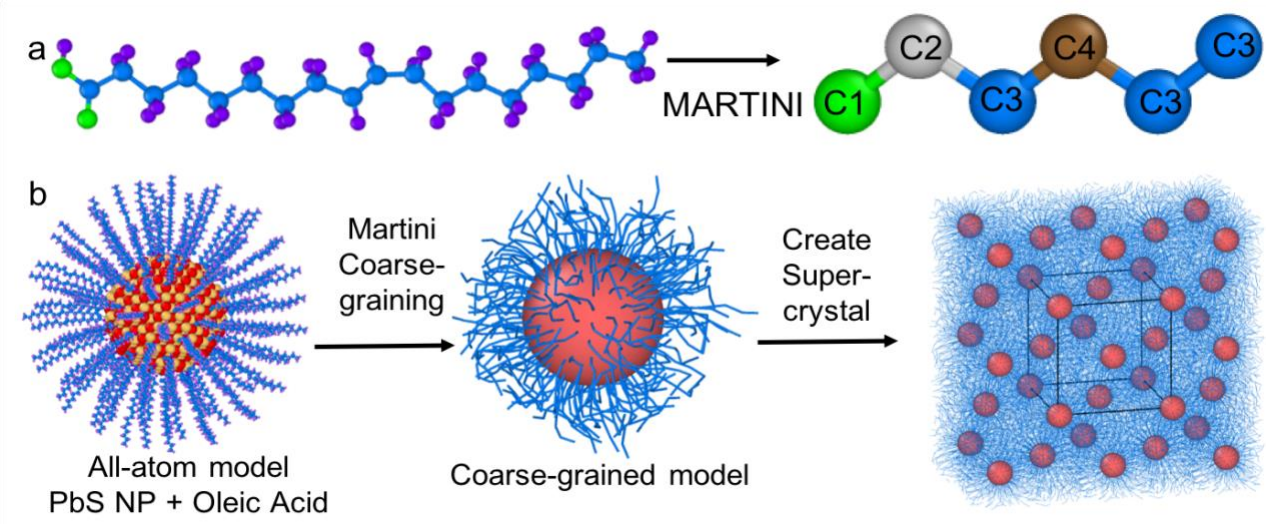
Tarak K. Patra,[1] Henry Chan,[1] Elena V. Shevchenko,[1*] Subramanian KRS Sankaranarayanan,[1*] and Badri Narayanan[2,3*]

[1]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

[2]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

[3]Department of Mechanical Engineering, University of Louisville, Louisville, KY 40292

Force Field



c

Type	ε(kcal/mol)	σ (Å)
NP	1.33	36.0
C1	1.19	5.27
C2	1.07	5.27
C3	0.8	5.27
C4	1.19	2.35

Type	k_0(kcal/mol)	r_0/θ_0 (Å)
NP-C1	3.0	20.63
C3-C4	8.96	3.2
All others bonds	1.49	4.7
C3-C4-C3	2.98	127
All other angles	2.98	180

Figure S1. Details of coarse-grained model employed to simulate nanoparticle superlattices. Each PbS nanoparticle is modelled as an indivisible bead called NP. (a) MARTINI mapping scheme is used to obtain coarse-grained model (composed of beads C1-C4) from all-atom configuration of oleic acid. (b) Illustration of the steps used to prepare a CG configuration of NPSL. (c) MARTINI force field parameters used in this study are tabulated.

We employed the well-established MARTINI scheme to coarse-grain the oleic acid ligand molecules; each nanoparticle is modeled as an indivisible bead (Figure S1). The MARTINI force-field parameters are used to model interactions between different ligand molecules, and the nanoparticles (the parameters are summarized in Figure S1c). For unlike interactions, we employed Lorentz-Berthelot mixing rule where the LJ parameters for interactions between beads *i* and *j* are given by: $\varepsilon_{ij} = \left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2}$, and

$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right)$,

where, (ε_{ii} , σ_{ii}) , and (ε_{jj} , σ_{jj}) are the LJ parameters for *i-i* and *j-j* interactions respectively.

Equation of State (EOS)

We have computed the equation state of the NPSL from our coarse-grained simulation and compare with experiment. At each pressure, the system is equilibrated for 10ns in an isothermal isobaric ensemble at temperature T = 300K. The equilibrium volume is computed by averaging over 10000 frames collected over a period of 1 ns. The MARTINI force-field describes the equation of state of NPSLs in good qualitative accordance with experiments (Figure S2). This suggests that the coarse-grained model qualitatively capture the thermophysical properties of the experimental system.

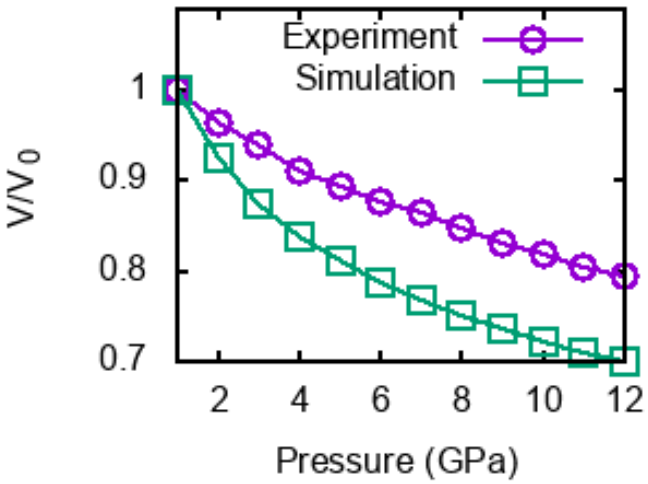


Figure S2. Equation of state of a ligand-rich nanoparticle superlattice (ρ=4.9/nm^2) from coarse-grained molecular dynamics and experiments at 300 K. The unit cell volume (V) at a given pressure is normalized by its value at pressure P = 1GPa (V_0).

Radial Distribution Function (RDF)

Figures S3 shows the NP-NP radial distribution in NPSL (for various ligand coverage densities) at selected pressures during a compression-release cycles. It clearly suggests the NPSL sustain high applied pressure without losing their crystallinity at high ligand coverage densities (ρ =1.8 - 5.5 nm^{-2}).

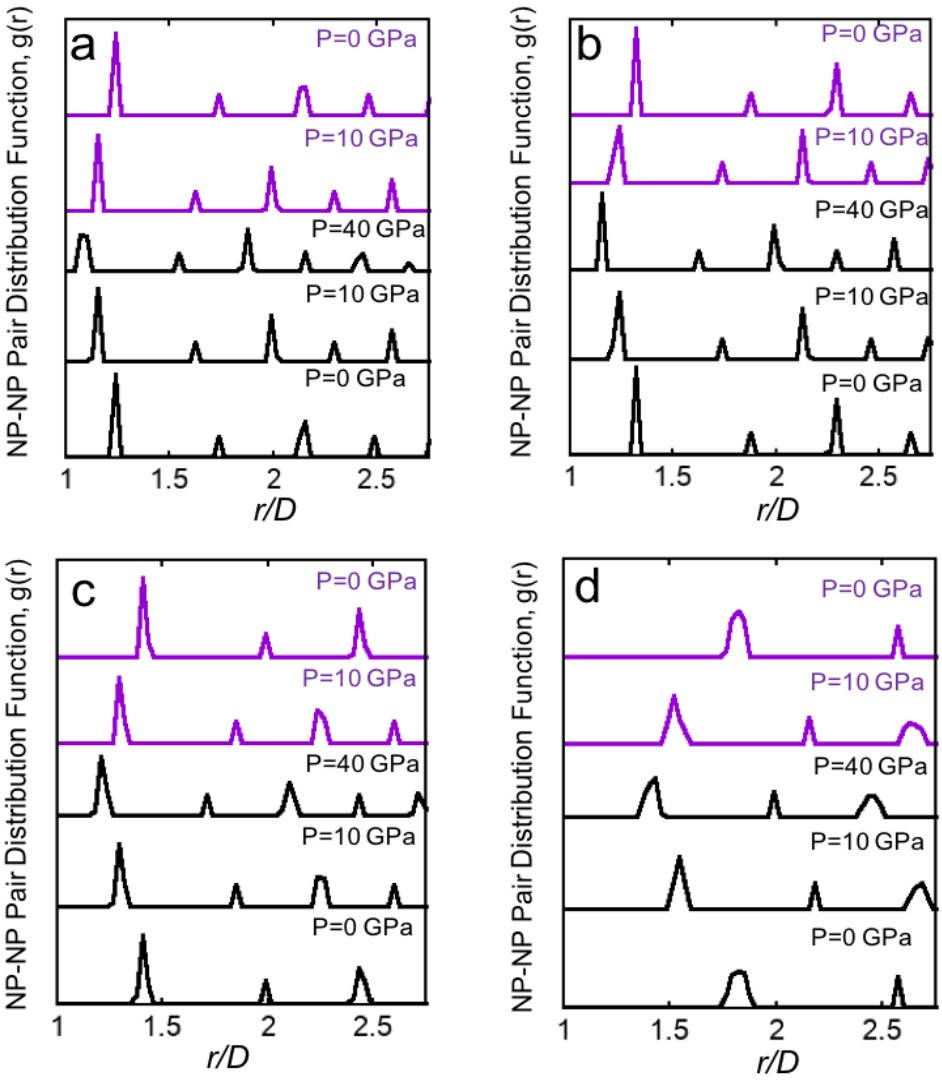


Figure S3. Radial distribution functions: a, b, c and d correspond to ligand density ρ =1.8 nm^{-2}, 2.4nm^{-2}, 3.6nm^{-2} and 5.5nm^{-2}, respectively.

Thermogravimetric Analysis

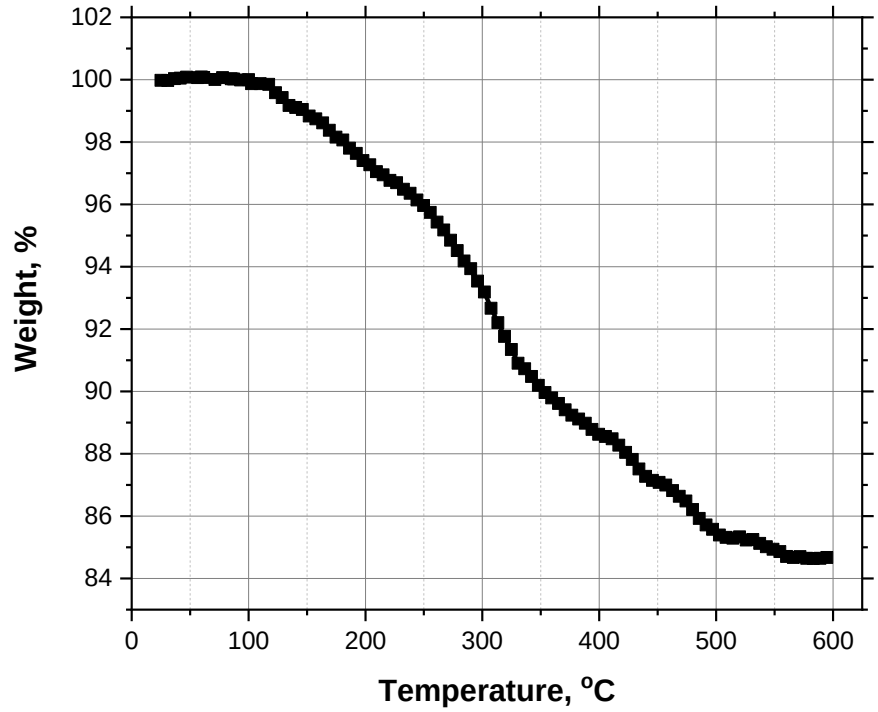


Figure S4. The thermogravimetric analysis (TGA) data obtained for the PbS NPSLs obtained by destabilization of the toluene solution of 7 nm PbS by isopropanol.

Transmission Electron Microscopy (TEM)

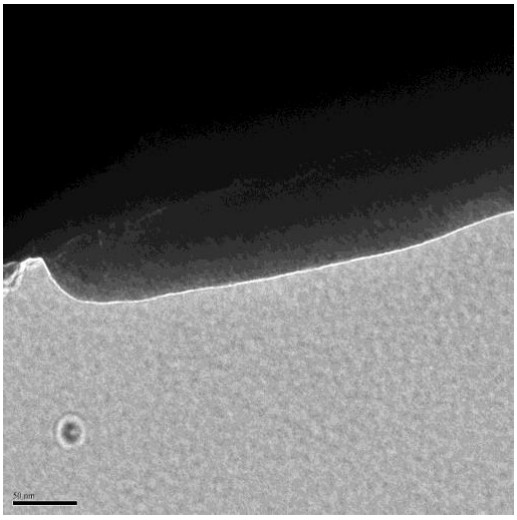


Figure S5. The TEM image of a fragment of PbS NPSL after compression.

Small-Angle X-ray Scattering (SAXS) experiments

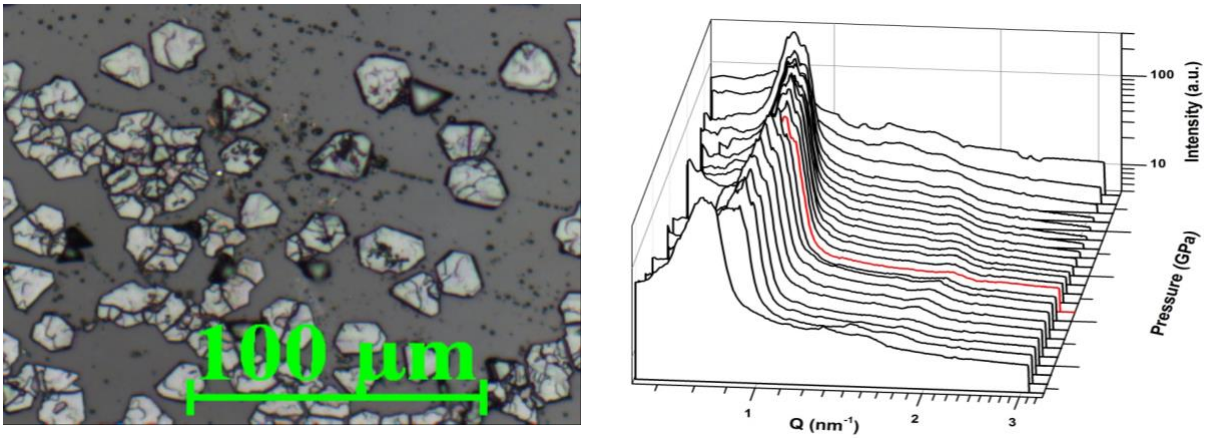


Figure S6. (Left) Optical micrograph and (Right) SAXS data on face-centered cubic NPSLs grown on Si substrate from 9.5 nm PbS NPs compressed up to 55.86 GPa and after pressure release**.**

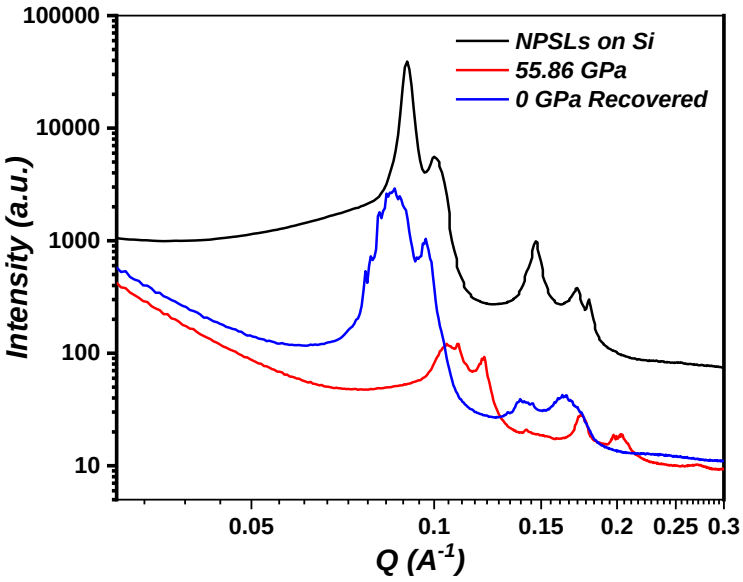


Figure S7. SAXS of face-centered cubic NPSLs (assembled from 9.5 nm PbS NPs) grown on Si substrate (black), and of individual NPSL at 55.86 GPa (red) and after pressure release (blue).