Supporting Information

Adjusting the inter-particle spacing of a nanoparticle array at sub-nanometre scale by thermal annealing

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^d College of Chemistry, State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China Materials and Instruments: Chloroauric acid (HAuCl₄ • 4H₂O), sodium borohydride (NaBH₄) and 1-dodecanethiol (DDT) were purchased from Alfa Aser. Teflon[™] tape was purchased from SPi SUPPLIES (USA). All of the chemicals were used without any further purification. Ultraviolet-Visible (UV-vis) spectroscopy was carried on a PERSEE TU-1810. Transmission electron microscope (TEM) images were obtained on a HITACHI H-7650. Grazing-incidence small-angle x-ray scattering (GISAXS) was carried on the Shanghai Synchrotron Radiation Facility.

Preparation of Au nanoparticles (Au NPs)¹: 95 μ L HAuCl₄/HCl aqueous solution (50 mM HAuCl₄ with the same molar amount of HCl) was added to 9.475 g water, followed by immediate injection of 425 μ L NaBH₄/NaOH aqueous solution (50 mM NaBH₄ with the same molar amount of NaOH). After shaken on a vortex mixer for 1 min and heated in a boiling water bath for 2.5 min, the aqueous solution of Au NPs was obtained. To transfer the Au NPs from water to hexane, 5.0 g acetone was added to the resulting solution, followed by mixing by hand for several seconds. And then a mixture of 0.1 μ L DDT and 5.0 g hexane was added. After shaken by hand for about 30 s, the Au NPs were transferred into the hexane solution, which was indicated by the phenomena that the water-acetone phase became colorless and the hexane phase turned dark red. The prepared hexane solution of Au NPs could be stored in the atmosphere for a couple of months without remarkable change and there was not any purification before the array fabrication. The Au NPs were characterized by UV-vis and TEM as shown in **Figure S1**.



Figure S1 TEM image (A) and UV-Vis spectrum (B) of Au nanoparticles.

Preparation of Au NPs array¹: 250 μ L toluene was dropped on the Teflon tape and 60 μ L Au NPs solution in hexane was spread out carefully on the toluene droplet. After evaporation in an organic glass box (40 × 30 × 30 cm) with air vent at room temperature for about 2 h, the Au NPs array was obtained.

Thermal annealing: The Au NPs array on the substrate was first put into a 50 ml screw-capped plastic tube with two holes punched by needle. And then the tube was heated at $80 \pm 1^{\circ}$ C and 70 \pm 5 Pa (vacuumed by a 2 L/S pump, measured by McLeod gauge) in a 3 L oven for certain time. After the oven was cooled to room temperature, the sample was taken out and stored in the atmosphere for characterization.

UV-vis spectroscopy substrate preparation: The substrate of the pursed Teflon tape is opaque and can't be used in UV-vis characterization directly. In order to obtain the UV-vis spectra, the Teflon tape was treated by immersion in ethyl acetate for 12 h, which separated the top Toflon layer from the underlying supporting substrate, resulting in a transparent Teflon sheet. It was used as the substrate for UV-vis spectroscopy.

TEM sample preparation: In TEM characterization, the Au NPs array was prepared on the carbon-membrane-covered Cu net. The preparation process is as same as that on the Teflon. The only difference is adding the Cu net on the Teflon in the middle of the droplet area. Because the Cu net is quite small and thin, the nanoparticles assembly should not be affected and the morphology on the Cu net is supposed to be identical to that on the Teflon.

GISAXS characterization: GISAXS experiments were carried out in beam line 14BL (λ =0.124 nm) at Shanghai Synchrotron Facility. The samples were first accurately aligned by using Huber diffractometer with scintillation counter. For one-dimensional GISAXS measurements, detector

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scan was carried out in in-plane direction with incidence angle of 0.2° and reflection angle of 0.4°. For two-dimensional GISAXS measurements, MarCCD area detector was used with incidence angle of 0.3°.

The inter-particles distance was calculated according to the formula as follows:

$$D = 2\pi / q \quad (1)$$

$$q = (q_X^2 + q_Z^2)^{1/2} \quad (2)$$

$$q_X = 4\pi \sin(\theta_x) / \lambda \quad (3)$$

$$q_Z = 4\pi \sin(\theta_Z) / \lambda \quad (4)$$

Where the D, q represented the distance between the adjacent nanoparticles and diffraction vector, respectively. θ_x was calculated from the peak position of curves as shown in Figure 1 and θ_z (0.2°) was calculated from the reflect angle. Here we use q instead of q_x to calculate the distance because in GISAXS the actual in-plane signals at q_z=0 is blocked by the sample with 0.2° incident angle.

Simulation model and method:

Model construction: In our simulations, we build up the nanoparticle (NP) model based on NP size of 29.5 Å in radius measured in our experiments and surface grafting density of 21.4 Å² per each alkyl sulhydrate molecule according to the literature^{2,3}. Lennard-Jones particles are packed to form a spherical structure for representing an NP. Specifically, for an NP with experimentally determined radius, we first use geodesic subdivision method⁴ to obtain all vertex positions on NP surface; then on the surface almost uniformly distributed anchoring points are constructed according to the grafting density reported in literature. From each anchoring point, one dodecane chain is generated with totally extended configuration.

Then this NP is duplicated several times in hexagonal packing mode to form a two-dimensional

film without any overlapping between the NPs. This film structure serves as the initial configuration for use in our molecular dynamics (MD) simulations to obtain the dependence of interaction energy between NPs on inter-NP distance. A schematic illustration of hexagonally NP packing is shown in **Figure S2**.



Figure S2 Top view of the NPs densely grafted with dodecane chains. The yellow spheres represent the gold NPs. The grey lines represent the grafted dodecane chains. The blue boundary represents the simulation box viewing from top. The particles outside of the box are all periodic images.

The force field: In this film system, the interactions between dodecane chains dominate the inter-NP distance. We use TraPPE (transferable potentials for phase equilibria) united atom force field to describe the interactions between dodecane chains. The TraPPE force field, developed by Siepmann and co-workers⁵⁻⁸, can reasonably reproduce thermophysical properties over a wide range of physical conditions for hydrocarbons, thus is widely used in MD simulations⁹.

The TraPPE force field uses pseudo-atoms located at the sites of heavy atoms, and applies the pairwise-additive Lennard-Jones (LJ) potentials to describe the nonbonded interactions:

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$
(4)

where r_{ij} is the particle-particle separation, ϵ_{ij} the LJ well depth and σ_{ij} the LJ diameter parameter for the particles *i* and *j*. These LJ potentials are used for describing nonbonded interactions of pseudo-atoms belonging to different molecules or belonging to the same molecule. Besides, fixed bond lengths for neighboring pseudo-atoms, harmonic bond bending potentials for pseudo-atoms separated by two bonds, and torsion potentials for pseudo-atoms separated by three bonds are adopted in our simulations.

(pseudo)atom	σ[Å]	ϵ/k_{B} [K]
CH ₃ (sp3)	3.750	98.0
CH ₂ (sp3)	3.950	46.0

Table S1 Nonbonded LJ parameters for the pseudo-atoms of dodecane in TraPPE force field.

For the dodecane chain used in our model, the LJ parameters for CH3 and CH2 groups with sp3 carbon hybridization can be found in TraPPE force field parameter file, as shown in **Table S1**. The LJ parameters for the interactions between unlike pseudo-atoms can be reasonably defined via Lorentz-Berthelot combining rules^{10,11}.

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

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}}$$
(5)

All bond lengths in dodecane chain are fixed at 1.54 Å in our simulations. A harmonic potential is used to control bond angle bending in dodecane with

$$U_{bend} = \frac{1}{2} k_{\theta} (\theta - \theta_0)^2 \tag{6}$$

where θ , θ_0 and k_{θ} are the measured bond angle, the equilibrium bond angle, and the force constant, respectively. The equilibrium bond angle and force constant used for dodecane are

listed in Table S2.

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Bond angle type	θ_0 [degree]	$k_{ heta} / k_B$ [K]			
CH _x CH ₂ (sp3)CH _y	114	62500			

Table S2 Equilibrium bond angle and force constant in TraPPE force field.

We also use torsion potentials to describe the energy variation for rotations about a bond in dodecane chains:

$$U_{tors} = C_0 + C_1 [1 + \cos(\phi)] + C_2 [1 - \cos(2\phi)] + C_3 [1 + \cos(3\phi)]$$
(7)

where ϕ is the equilibrium torsion angle and $c_0 \sim c_3$ are the constants. The parameters are listed in

Table S3.

Table S3. Constants used for describing torsion potentials in TraPPE force field.

torsion type	$c_0 / k_B $ [K]	$c_1 / k_B $ [K]	$c_2 / k_B $ [K]	$c_3 / k_B $ [K]
CH _x -CH ₂ -CH ₂ -CH _y	0.0	355.03	-68.19	791.32

Simulation details: The main target of our simulations is to explain why the inter-NP distance can be lowered to ~ 0.5 nm in our experiments and to rationalize whether at this inter-NP distance the packing of the NPs is thermodynamically stable. Therefore, a series of MD simulations is carried out in constant-volume and constant-temperature (NVT) conditions. The Nosé-Hoover thermostat¹²⁻¹³ is used to control the temperature at 348 K. All the simulations are carried out using GPU accelerated large-scale molecular simulation toolkit (GALAMOST)¹⁴. As illustrated in Fig. S1, the periodic boundary conditions are applied in X, Y, and Z directions in our simulations, but in Z direction a vacuum layer is adopted to control the film single-layer.

Starting from the initial NP packing configuration, we first resort to using ultra-soft harmonic repulsion potential (in practice, the dissipative particle dynamics¹⁵ potential) to describe interactions between dodecane particles; in this way, energetically unfavorable initial

configuration can be efficiently relaxed since the particles can sometimes overlap one another and the bonds can cross without large energy penalty. After that, we switch back to use TraPPE force field to describe the true interactions between dodecane chains. A period of 10⁵ time steps NVT MD simulation is then conducted to further relax the configuration based on the prerelaxed configuration using soft potential. Following up is the 2×10^6 time steps MD production run with NPs being frozen at their positions, so only dodecane chains are allowed to move. In equilibrium, we calculate the potential energy for NPs packing at this inter-NP distance. Then we slightly decrease inter-NP distance while keeping the hexagonal packing mode (accordingly, the simulation box side lengths in X and Y directions are decreased), and repeat the MD simulations described above to calculate potential energy at another inter-NP distance. This simulation protocol is continued until the inter-NP distance is small enough. Finally we obtain the dependence of potential energy per CH_2 on the distance between NPs, as shown in **Figure S3**. Apparently, the potential energy non-monotonically changes with varying distance between NPs. The lowest potential energy, signaling thermodynamically stable packing between NPs, corresponds to a center of mass distance between NPs at about 6.3 nm, which is very close to the experimental measurement of 6.4 nm for the distance between NPs. This simulation result proves that by suitably annealing, the distance between NPs can be tuned to a value corresponding to a thermodynamically equilibrium structure.



Figure S3 The dependence of potential energy per CH₂ on the distance between neighboring nanoparticles.

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