## Supporting Information Pressure-controlled formation of crystalline, Janus, and core-shell supraparticles

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## Calculation of packing fraction

The volume fraction  $\theta_{AB13}$  of AuNP cores in the AB<sub>13</sub> supraparticles was estimated as

$$\theta_{\rm AB13} = \frac{V_{\rm NP}}{V_{\rm UC}} = \frac{\frac{4}{3}\pi (104R_1^3 + 8R_2^3)}{a_{\rm AB13}^3} \tag{1}$$

with the total volume  $V_{\rm NP}$  of AuNP cores (without the ligand) in the unit cell and the volume  $V_{\rm UC}$  of the AB<sub>13</sub> unit cell.  $R_1$  and  $R_2$  are the core radii of the different AuNP and  $a_{\rm AB13}$  is the edge length of the AB<sub>13</sub> unit cell.

We measured the NP core radii  $R_1$  and  $R_2$  in TEM micrographs by counting more than 2500 nanoparticles of each type with ImageJ 1.45s. The calculated radii and standard deviations were 2.00(16) nm and 4.00(18) nm for  $R_1$  and  $R_2$ , respectively.

The unit cell edge length  $a_{AB13}$  of the AB<sub>13</sub> unit cell was calculated from SAXS data as

$$a_{\rm AB13} = \frac{2\pi\sqrt{h^2 + k^2 + l^2}}{q_{(hkl)}} \tag{2}$$

were h, k, and l are Miller's indices and q is the scattering vector. The resulting value of  $a_{AB13} = 27.1 \text{ nm}$  leads to an overall packing fraction of  $\theta_{AB13} = 0.283$ .

The core volume fraction of the Janus-type and the core-shell supraparticles was calculated by assuming crystalline face-centered cubic (fcc) packings of both nanoparticle types. The theoretical fcc packing fraction for hard spheres is  $\theta_{\rm fcc} = 0.74$ . To estimate the packing fraction of the cores, the ratio between the core volume and the volume of the cores with the soft ligand shell was multiplied by the theoretical packing fraction of fcc:

$$\theta = 0.74 \frac{V_{core}}{V_{core+shell}} = 0.74 \frac{\frac{4}{3}\pi (13R_1^3 + R_2^3)}{\frac{4}{3}\pi [13(R_1 + L_1)^3 + (R_2 + L_2)^3]}$$
(3)

with the thicknesses of the ligand shells in the packing  $L_1$  and  $L_2$ . Note that the ligand shells are considerably compressed during assembly. We estimated the compressed ligand shell thickness from SAXS data and found  $L_1 \approx 0.4$  nm and  $L_2 \approx 0.3$  nm for Janus particles, which corresponds to a core volume fraction of  $\theta_{\text{Janus}} = 0.48$ . Core-Shell-particles had  $L_1 = 0.45 \text{ nm}$ and  $L_2 = 0.5 \text{ nm}$ , which corresponds to a core volume fraction of  $\theta_{\text{Core-shell}} = 0.44$ .

## Molecular dynamics simulations

We performed molecular dynamics simulations<sup>1</sup> of a binary mixture of nanoparticles confined to a spherical container. To mimic varying solubility, we blended between an attractive Lennard-Jones potential and a purely repulsive but finite WCA (Weeks-Chandler-Andersen) potential<sup>2</sup>

$$V_{ij}(r,\lambda_{ij}) = (1-\lambda_{ij})WCA_{ij}(r) + \lambda_{ij}LJ_{ij}(r)$$
(4)

The properties of the mixture were specified by choosing the mixing parameters  $\lambda_{AA}$ ,  $\lambda_{BB}$  and  $\lambda_{AB}$ . The Lennard-Jones parameter  $\sigma$ , which corresponds to the particle "diameter", is additive for the inter-species interaction,  $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ . We set the diameter ratio to  $\sigma_{BB}/\sigma_{AA} = 0.55 - 0.58$ . For this ratio the icosahedral AB<sub>13</sub> lattice has been shown to form entropically.<sup>3,4</sup> The length and energy scales were set by  $\sigma_{AA} = 1$  and  $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = 1 k_B T$ , where k<sub>B</sub> is the Boltzmann constant, T is the temperature and  $\epsilon$  is the interaction strength. We used identical parameters in the WCA and the Lennard-Jones potential. The interactions of the nanoparticles with the walls of the spherical container were modeled using the WCA potential with parameters  $\epsilon_{WA} = \epsilon_{WB} = \sigma_{AW} = 1$  and  $\sigma_{WB} = 0.775 - 0.79$ . The number ratio between big and small particles was 1/13.

Initial particle configurations were prepared as disordered fluid mixtures. Most simulations were performed under shrinking confinement to emulate the evaporating emulsion droplets. The exception were simulations in which all particles interacted with strongly attractive potentials (modeling low pressure) and those in which all interactions were purely repulsive (modeling high pressure). We kept the volume of the container, and thus the particle density, constant for these extreme cases in which nucleation of the crystalline phase is a rare event. All simulations were run in parallel on the 12 cores of two Intel Xeon L5640 2,26 GHz CPUs. A simulation leading to an AB<sub>13</sub> crystals of 1750 particles at a fixed container volume required approximately 3 days to finish. The AB<sub>13</sub> crystal formed at a temperature  $T_{\rm LJ} = 0.6 \,\rm k_B/\epsilon_{AA}$  and a packing fraction  $\rho = 0.8$ , which we estimated using the effective radius of the particles,  $r_{\rm eff} = 2^{1/6}\sigma/2$ . All simulations were carried out at the same temperature and the same final packing fraction as those leading to AB<sub>13</sub> crystals.

We used a time step of  $0.004(\epsilon_{AA}/m/\sigma_{AA}^2)^{1/2}$ , where *m* is the mass of particle. For constant volume simulations we allowed up to  $10^9$  steps to equilibrate the system, for the shrinking container  $10^7$ . Most simulations converged to a crystalline structure in that time. The crystallization event was accompanied by a drop in the potential energy and a decrease in the slope of the average mean square displacement of particles as shown in figure S4 for a system with periodic boundary conditions and a fixed volume.

As a consequence of the curved boundary conditions imposed by the walls of the spherical container the central core with the  $AB_{13}$  crystal structure is surrounded by a disordered shell made of both types of particles as shown in figure S5.

Table S1:	Minimum	free energy	structures	obtained	by	simula	tion f	or o	different	combin	ations
of $\lambda i j$ .											

$\lambda_{AA}$	$\lambda_{ m BB}$	$\lambda_{ m AB}$	structure
0	0	0	$AB_{13}^{1}$
1	0	0.1	core-shell
1	0.01	0.1	core-shell
$\geq 0.8$	0	0	Janus
1	$\geq 0.1$	0.1	Janus
1	1	1	$AB_{13}$

Table S1 summarizes the structures of supraparticles that form for different interactions. The structures are affected by entropy, the interactions between the different particle types, and the interactions with the wall. Crystalline  $AB_{13}$ , core-shell and Janus supraparticles were the only ordered final states that we found for our set of interactions and the mixing ration of 1/13. Most parameter combinations led to disordered structures with a fluid-like mixture of the different particles.

## References

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Figure S1: TEM micrograph of 4 nm Au nanoparticles



Figure S2: TEM micrograph of 8 nm Au nanoparticles



Figure S3: Histogram of the size distribution of 4 nm and 8 nm nanoparticles.



Figure S4: Crystallization of  $AB_{13}$  binary lattice for 1750 particles in bulk.



Figure S5: Supraparticle with the  $AB_{13}$  crystal structure which resulted from the simulation of a binary mixture of 14000 nanoparticles with a size ratio of 0.55 in a fixed spherical container at T = 0.6 and  $\rho = 0.8$ . (a) Complete supraparticle including the disordered shell. (b) The crystalline core of supraparticle without the disordered shell. (c) The size of small particles is decreased for clarity. (d) Model of a supraparticle with  $AB_{13}$  crystal structure without defects.