Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Solvent Controlled 2D Structure of Bottom-up Fabricated Nanoparticle Superlattices

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1. TEM characterization

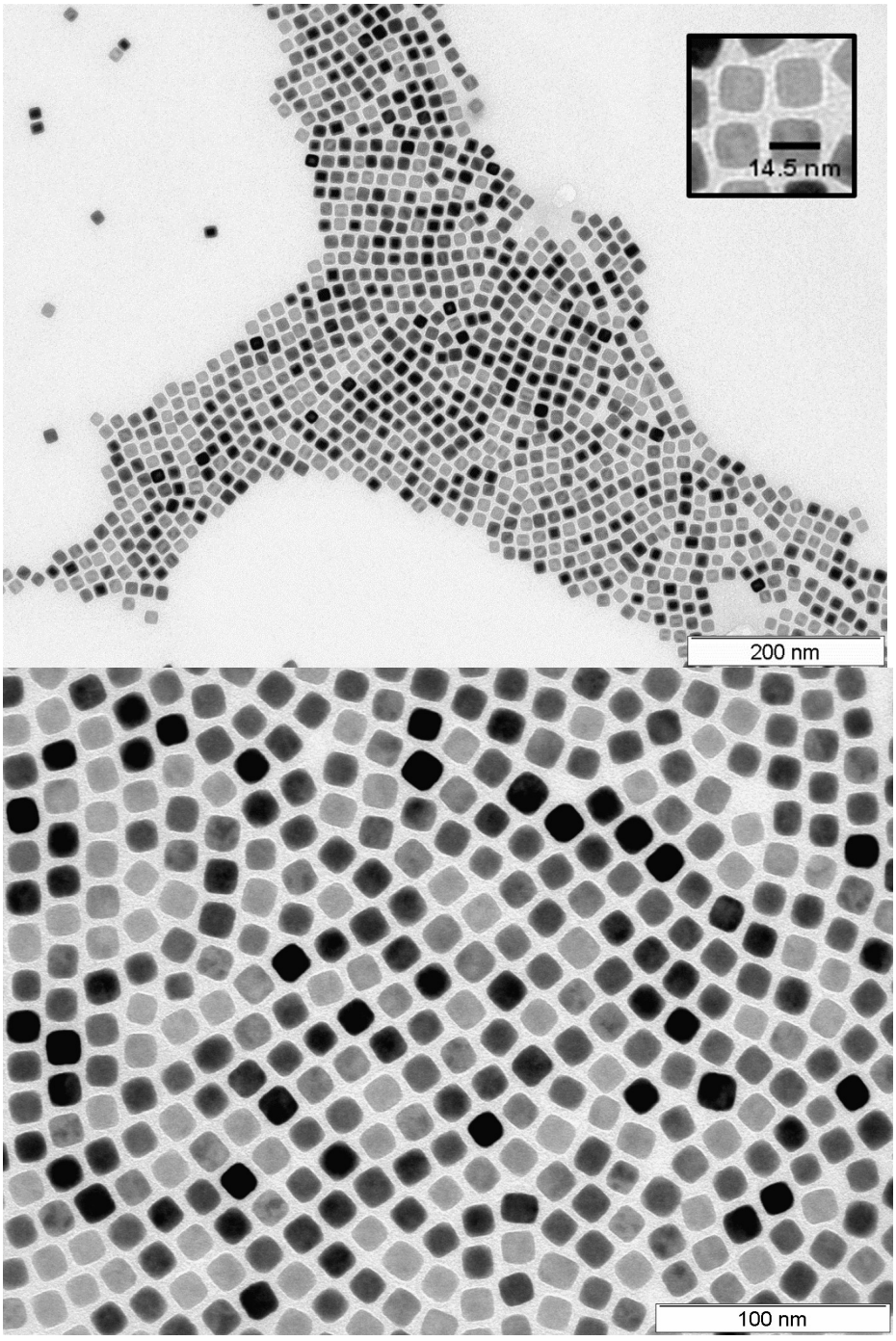

Figure S1: TEM images of the NPs showing their cubic, slightly truncated shape. Inset: Magnification of the TEM image showing the edge length of the particles.

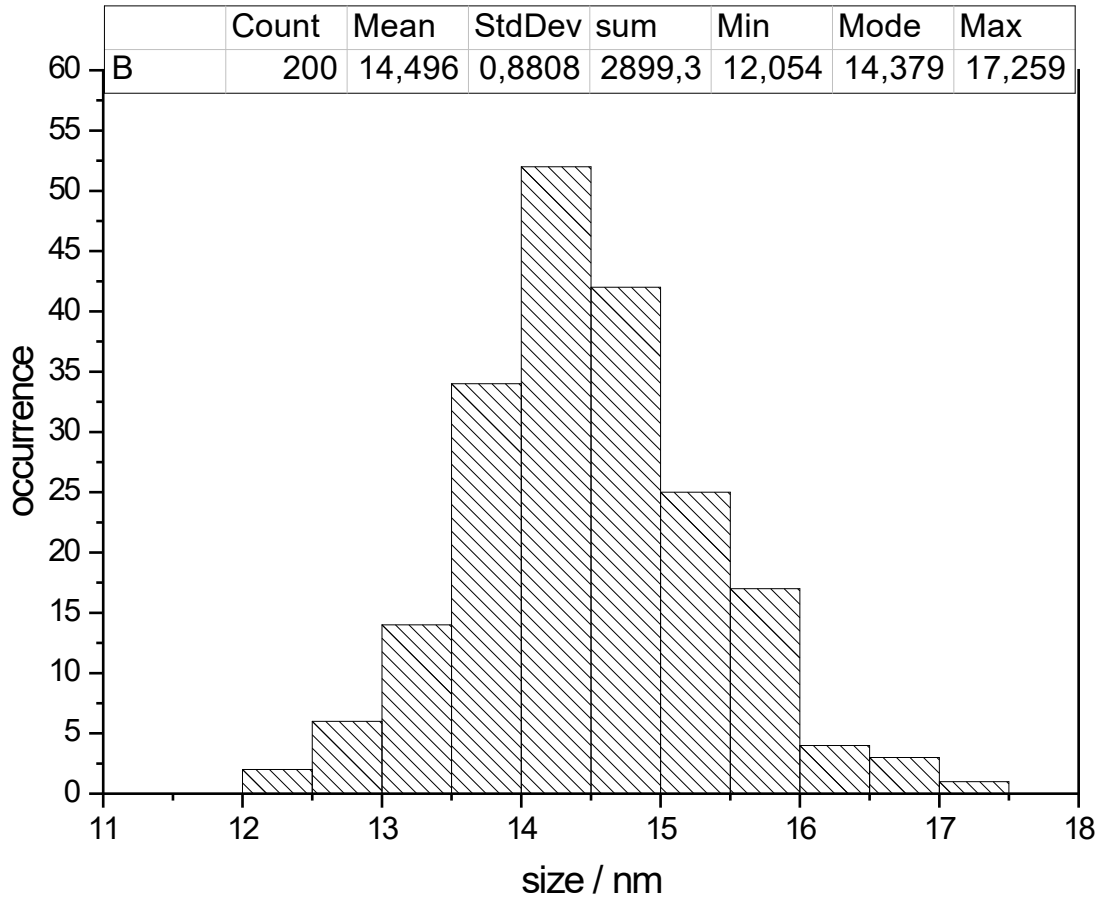

Figure S2: Occurrence distribution of the diameter.

2. Additional SEM images

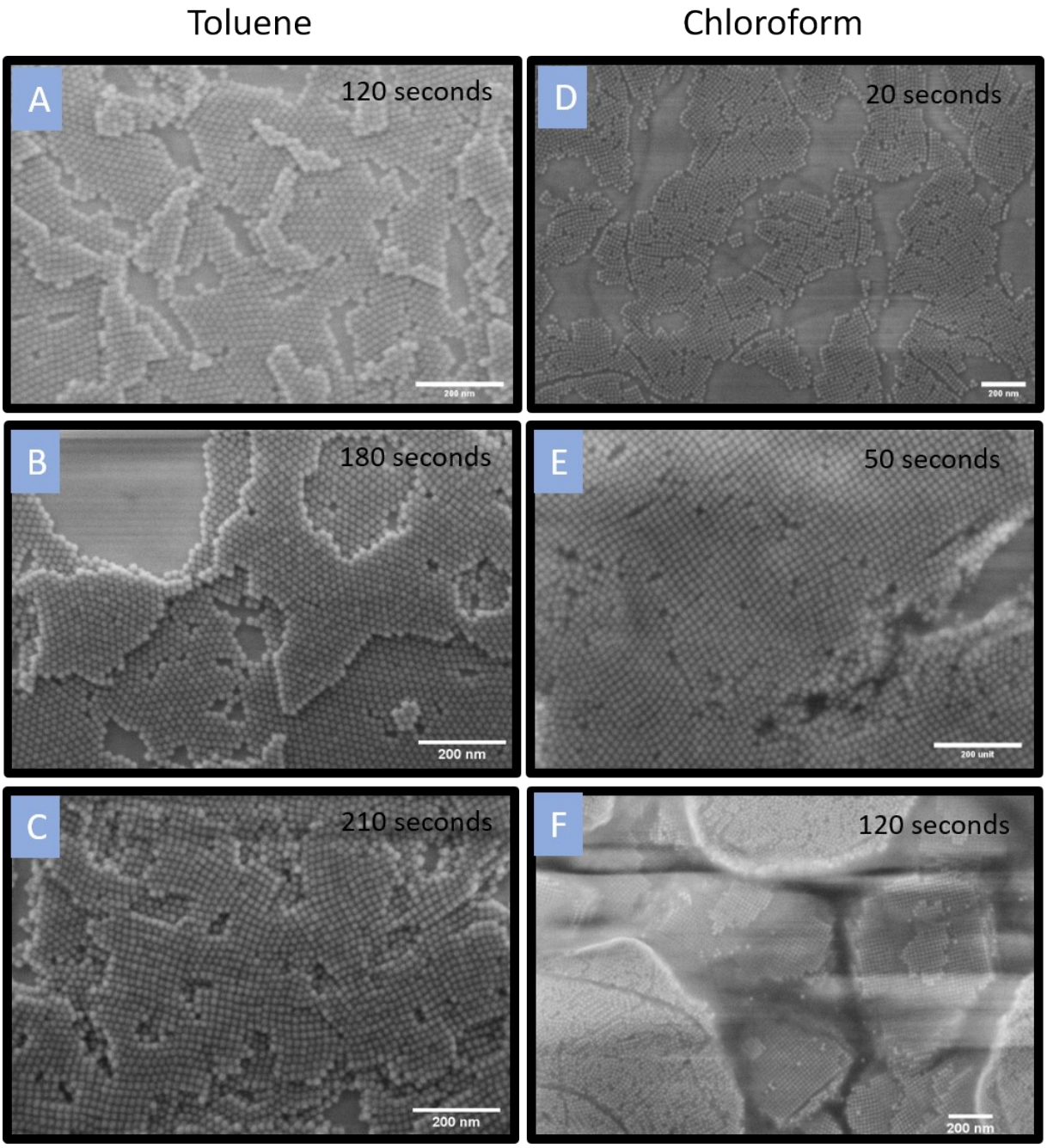

Figure S3: A-C) Toluene samples with increasing spin-coating duration from 120 seconds (A) to 210 seconds (C). Increase in number of deposited monolayers from 1.3 monolayers (A) to close to 3 monolayers (C). A-B) both samples show only hexagonal ordering of the particles. C) First nanoparticle layer (left edge, upper half of the image) shows hexagonal ordering, consecutive layers show square ordering. D-F) Chloroform samples with increasing spin-coating duration from 20 seconds (A) to 120 seconds (F). All chloroform samples show mostly square ordering. Defects and holes in the first monolayer are "stable" even when large amounts of additional nanoparticles are deposited onto the first layer.

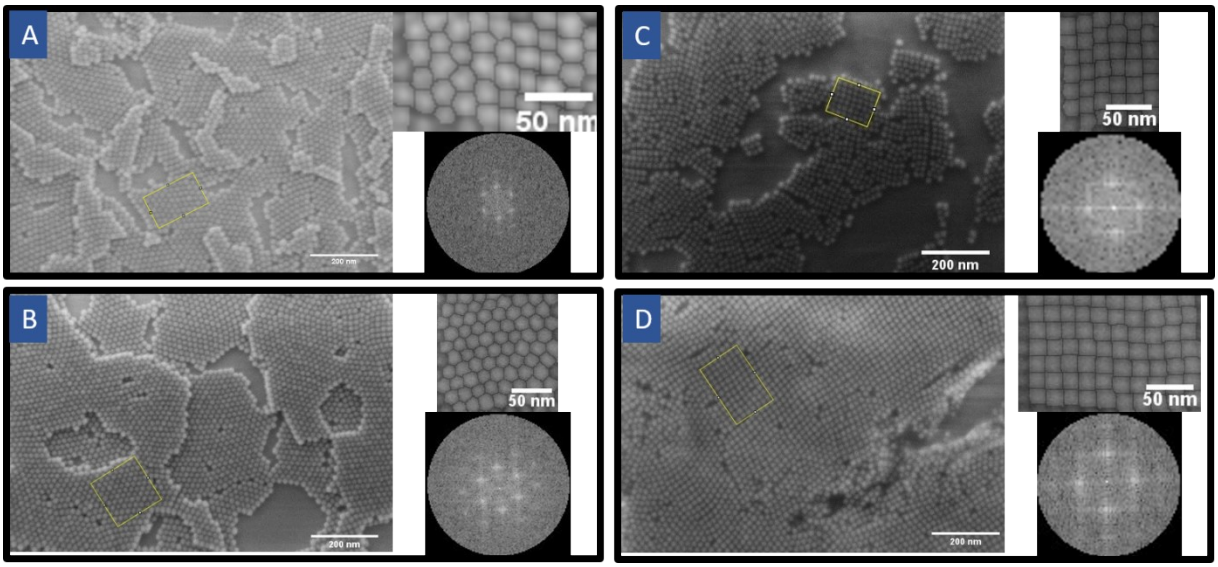

Figure S4: SEM images taken for the analysis of the particle sizes and nearest neighbor distance. The yellow rectangles show the analyzed area, which is seen as a close up to the right of the images with the corresponding FFT result. A-B) Toluene sample with self-assembly duration of 120 seconds (A) and 180 seconds (B). C-D) Chloroform samples with self-assembly duration of 20 seconds (C) and 120 seconds (D).

Sample	*SC1*	*SC2*	*Average*	*SC5*	*SC8*	*Average*
Lattice type	hexagonal	hexagonal	hexagonal	square	square	square
	Particle analysis					
Measured avg. area [nm^2]	223.0	223.3	223.2 +- 0.2	280.1	257.2	268.7 +- 11.5
Edge length [nm]	14.9	14.9	14.9 +- 0	16.7	16.1	16.4 +-0.3
	FFT analysis					
Avg. nearest neighbor distance [nm]	15.2	15.1	15.2 +- 0.1	17.8	17.2	17.5 +- 0.3
Resulting ligand length [nm]	0.3	0.2	0.3 +-0.1	1.1	1.1	1.1 +- 0

Table S1: results of the particle analysis from SEM images seen in SI Figure 2.

3. AFM height analysis

AFM image number	1	2	3
Height of substrate [Å]	-5.10	1.50	6.66
Height of first layer [Å]	122.67	124.90	129.98
Height of second layer [Å]	263.06	265.89	270.22
Thickness of first layer [Å]	127.77	123.40	123.32
Thickness of second layer [Å]	140.40	140.99	140.25
Average: Thickness first layer: (124.83 +- 1.96) [Å] Thickness of second layer: (140.54 +- 0.30 [Å]			

Table S2: Results of AFM height analysis for three different AFM images taken from Sample-hexa.

4. X-ray reflectivity results and calculations

Density of Fe_3O_4 with 100% coverage = 0.013505 Formel units (FU)/ Å^3		
Value	Sample-hexa	Sample-cube
Density of first layer [FU/ Å^3]	0.0124	0.0129
Density of second layer [FU/ Å^3]	0.00499	0.00753
Coverage first layer [%]	91.8	95.3
Coverage second layer [%]	36.9	55.7

Table S3: X-ray scattering length densities

The oscillations in the XRR curve are caused by interference between X-rays reflected at different interfaces of the sample and are also referred to as Kiessig fringes. The position of these Kiessig fringes can be calculated using the following equation:

$$m\lambda = 2\Delta\sqrt{\theta_m^2 - 2\delta}$$

With the wavelength λ, the order of the fringe m, the layer thickness Δ and the δ value from the refractive index.

5. Evaporation rates of solvents

According to the respective chemical safety sheets by LabChem, the relative evaporation rates with respects to butyl acetate are:
Toluene: Relative evaporation rate (butyl acetate=1): 2.24
Chloroform: Relative evaporation rate (butyl acetate=1): 11.6