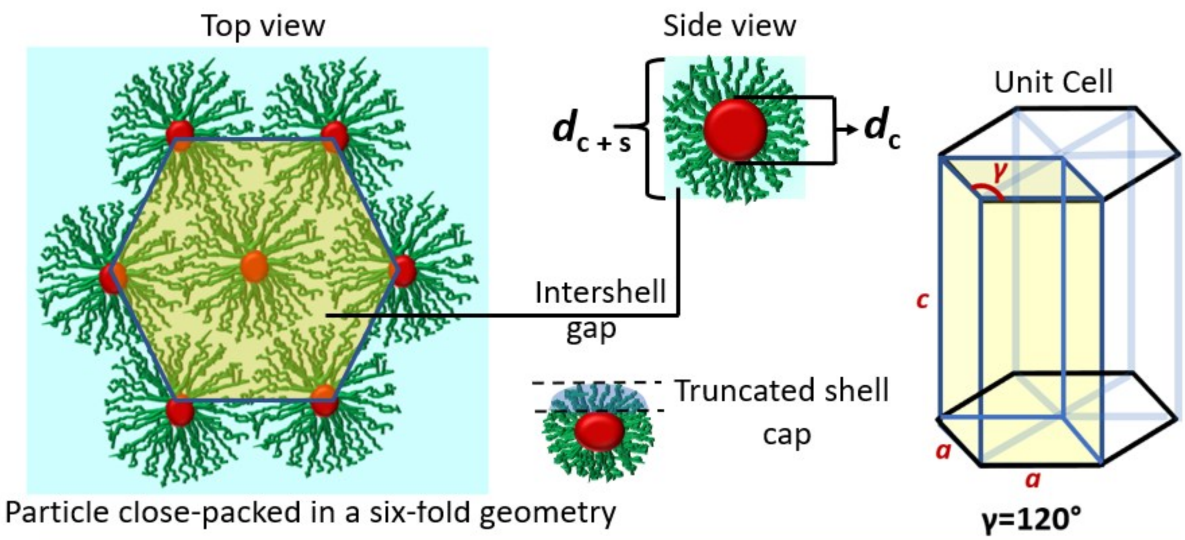
Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for Layering of magnetic nanoparticles in ferrofluids at amorphous magnetic templates with perpendicular anisotropy

Details of model calculations

The SLD of a dense layer of close-packed particles is calculated as single monolayer with six-fold symmetry, see Fig. S1. The figure illustrates the stack thickness, lattice parameter, vol. of hexagonal unit cell and the concentrations of the core and the shell materials.

Model Calculations



Layer thickness = $\boldsymbol{c}$

Unit cell lattice parameter = $\boldsymbol{a} : d_{c+s}$

Volume of hexagonal unit cell = $\frac{\sqrt{3}}{2} a^2 c$

Volume of core = $\frac{\pi}{6} d_c^3$

Volume of shell = $\frac{\pi}{6}\left(d_{c+s}^3 - d_c^3\right)$

Conc. core = $\frac{\pi}{3\sqrt{3}} \frac{(d_c)^3}{a^2 c}$

Conc. shell = $\frac{\pi}{3\sqrt{3}} \frac{\left(d_{c+s}^3 - d_c^3\right)}{a^2 c}$

Fig. S1. Core/shell particles forming a close-packed layer with hexagonal symmetry.

For the slabs having thickness > lattice parameter, the SLD values for an ideal close-packed monolayer of NPs are calculated by considering the difference in thickness being filled by the shell material arising from unbound ligands. Alternativerly, swelling of the shell material of the NP would also result in the increase in the slab thickness. The SLD for the slab just below the D_2O layer was calculated by assuming the extra volume filled by water. The reason for this is that after the washing procedure, the extra shell material is rinsed off. Model calculations for the three samples are summarised in Table S2 (i,ii, and iii).

Table S1. SLD values calculated for a layer of hexagonal close-packed particles. (i), (ii) and (iii) gives values for each sample and with the sample replaced by D_2O post surface cleaning; for FF5, FF15, and FF25, respectively. It was assumed that either water or shell material fills the interstitial gaps between the spherical shells. The SLD values in the column for the shell material only are calculated according to the volume fractions of core and shell material (column: Volume fraction) and the bulk values. The volume fractions were calculated from the dimensions extracted from the SANS measurements. The volume fractions are calculated assuming bulk values.

(i)

Model Slab	Slab thickness (nm)	dc+s (nm)	Volume fractions (water in intershell gaps)	SLD (water in gaps) *Nb* [10^{-2} nm^{-4}]	Volume fractions (shell matter in intershell gaps)	SLD (shell matter in gaps) *Nb* [10^{-2} nm^{-4}]	SLD from model fits [10^{-2} nm^{-4}]	Volume fractions (fitted layer)
#1a	16.04	16.01	C_{core} : 0.0050 C_{shell} : 0.5985 $C_{D2O/H2O}$: 0.3965	2.34	C_{core} : 0.0050 C_{shell} : 0.9950	0.19	2.87	C_{core} : 0.0050 C_{shell} : 0.5012 $C_{D2O/H2O}$: 0.4938
#2a	21.19	16.01	C_{core} : 0.0038 C_{shell} : 0.4530 $C_{D2O/H2O}$: 0.5432	3.12	C_{core} : 0.0038 C_{shell} : 0.9962	0.19	3.21	C_{core} : 0.0038 C_{shell} : 0.4381 $C_{D2O/H2O}$: 0.5581
#1b	17.20	16.01	C_{core} : 0.0046 C_{shell} : 0.5582 C_{D2O}: 0.4372	2.89	C_{core} : 0.0046 C_{shell} : 0.9954	0.19	3.29	C_{core} : 0.0046 C_{shell} : 0.4931 C_{D2O}: 0.5023
#2b	21.86	16.01	C_{core} : 0.0037 C_{shell} : 0.4391 C_{D2O}: 0.5572	3.62	C_{core} : 0.0037 C_{shell} : 0.9963	0.19	3.81	C_{core} : 0.0037 C_{shell} : 0.4087 C_{D2O}: 0.5876

(ii)

Model Slab	Slab thickness (nm)	dc+s (nm)	Volume fractions (water in intershell gaps)	SLD (water in gaps) *Nb* [10^{-2} nm^{-4}]	Volume fractions (shell matter in intershell gaps)	SLD (shell matter in gaps) *Nb* [10^{-2} nm^{-4}]	SLD from model fits [10^{-2} nm^{-4}]	Volume fractions (fitted layer)
#1c	31.87	25.26	C_{core} : 0.1082 C_{shell} : 0.3710 $C_{D2O/H2O}$: 0.5208	3.56	C_{core} : 0.1082 C_{shell} : 0.8918	0.89	2.42	C_{core} : 0.1082 C_{shell} : 0.5930 $C_{D2O/H2O}$: 0.2988
#2c	46.54	25.26	C_{core} : 0.0741 C_{shell} : 0.2541 $C_{D2O/H2O}$: 0.6719	4.09	C_{core} : 0.0741 C_{shell} : 0.9259	0.66	5.06	C_{core} : 0.0741 C_{shell} : 0.0666 $C_{D2O/H2O}$: 0.8594
#1d	24.02	25.26	C_{core} : 0.1435 C_{shell} : 0.4923 C_{D2O}: 0.3642	3.38	C_{core} : 0.1435 C_{shell} : 0.8565	1.13	2.61	C_{core} : 0.1435 C_{shell} : 0.6164 C_{D2O}: 0.2401
#2d	44.0	25.26	C_{core} : 0.0783 C_{shell} : 0.2687 C_{D2O}: 0.6529	4.72	C_{core} : 0.0783 C_{shell} : 0.9217	0.69	5.15	C_{core} : 0.0783 C_{shell} : 0.1986 C_{D2O}: 0.7230

(iii)

Model Slab	Slab thickness (nm)	dc+s (nm)	Volume fractions (water in intershell gaps)	SLD (water in gaps) *Nb* [10^{-2} nm^{-4}]	Volume fractions (shell matter in intershell gaps)	SLD (shell matter in gaps) *Nb* [10^{-2} nm^{-4}]	SLD from model fits [10^{-2} nm^{-4}]	Volume fractions (fitted layer)
#1e	38.17	35.05	C_{core} : 0.1248 C_{shell} : 0.4304 $C_{D2O/H2O}$: 0.4448	3.06	C_{core} : 0.1248 C_{shell} : 0.8752	1.0	1.10	C_{core} : 0.1248 C_{shell} : 0.8602 $C_{D2O/H2O}$: 0.015
#2e	42.77	35.05	C_{core} : 0.1114 C_{shell} : 0.3841 $C_{D2O/H2O}$: 0.5045	3.24	C_{core} : 0.1114 C_{shell} : 0.8886	0.91	3.24	C_{core} : 0.1114 C_{shell} : 0.3846 $C_{D2O/H2O}$: 0.5040
#1f	34.67	35.05	C_{core} : 0.1374 C_{shell} : 0.4738 C_{D2O}: 0.3888	3.49	C_{core} : 0.1374 C_{shell} : 0.8626	1.09	1.45	C_{core} : 0.1374 C_{shell} : 0.8038 C_{D2O}: 0.0588
#2f	43.57	35.05	C_{core} : 0.1093 C_{shell} : 0.3771 C_{D2O}: 0.5136	4.07	C_{core} : 0.1093 C_{shell} : 0.8907	0.90	4.07	C_{core} : 0.1093 C_{shell} : 0.3766 C_{D2O}: 0.5141

In order to check the efficacy of the cleaning procedure sample FF25 (identical to the one used in our previous study [1]) was first spin-coated onto an APTES coated Si wafer (also described in [1]). Thereafter, the cleaning was performed as detailed in the main text. SEM images were taken for comparison of the surface before and after the cleaning procedure, see Fig. S2. Clearly cleaning the wafer is adequate to remove the NPs deposited on the Si substrate coated with an APTES layer. The NPs were chemically linked to the APTES layer through amide (-CONH) linkages, known to be potent [2]. After the washing procedure, more than 95% of particles were rinsed off from the Si surface.

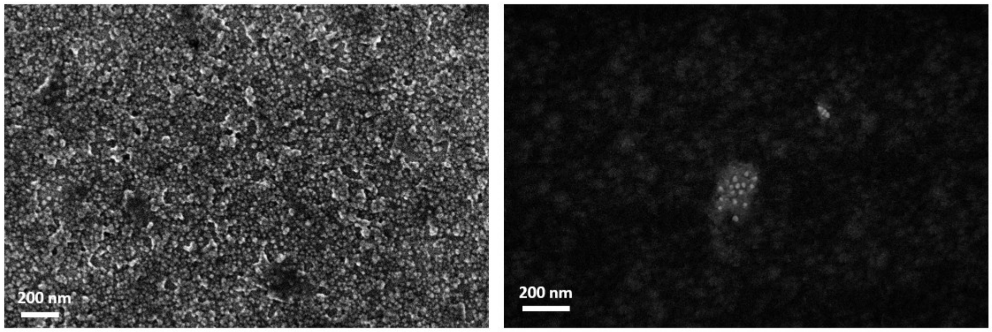


Fig. S2. SEM images of NPs from FF25 spin coated on an APTES coated Si surface before (left) and after (right) cleaning and rinsing of the substrate.

References

[1] Self-Assembled Layering of Magnetic Nanoparticles in a Ferrofluid on Silicon Surfaces, K. Theis-Bröhl, E. C. Vreeland, A. Gomez, D. L. Huber, A. Saini, M. Wolff, B. B. Maranville, E. Brok, K. L. Krycka, J. A. Dura, J. A. Borchers, ACS Appl. Mater. Interfaces 2018, 10, 5, 5050-5060.

[2] Labeling Primary Amine Groups in Peptides and Proteins with N-Hydroxysuccinimidyl Ester Modified Fe3O4@SiO2 Nanoparticles Containing Cleavable Disulfide-bond Linkers Ujwal S. Patil, Haiou Qu, Daniela Caruntu, Charles J. O'Connor, Arjun Sharma, Yang Cai, and Matthew A. Tarr, Bioconjug Chem. 2013 Sep 18; 24(9): 10.1021/bc400165r.