[Supporting Information]

Surface Engineering Superparamagnetic Nanoparticles for Aqueous Applications: Design and Characterization of Tailored Organic Bilayers

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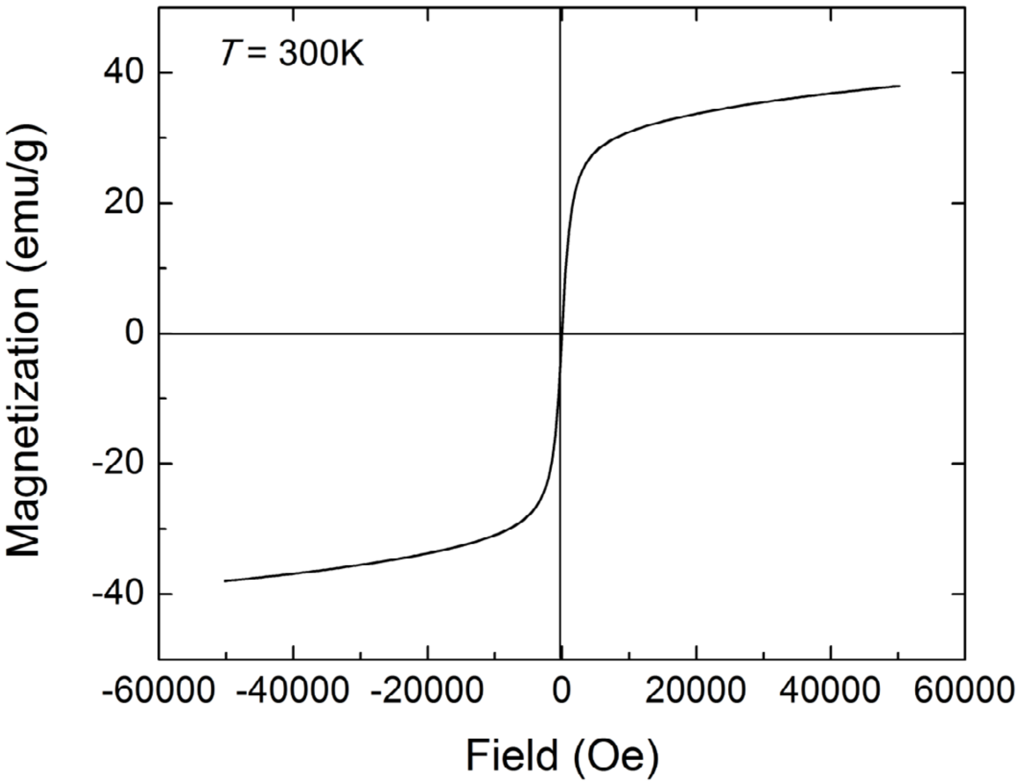

Figure S1. Hysteresis loops of 8 nm iron oxide NPs at 300 K.

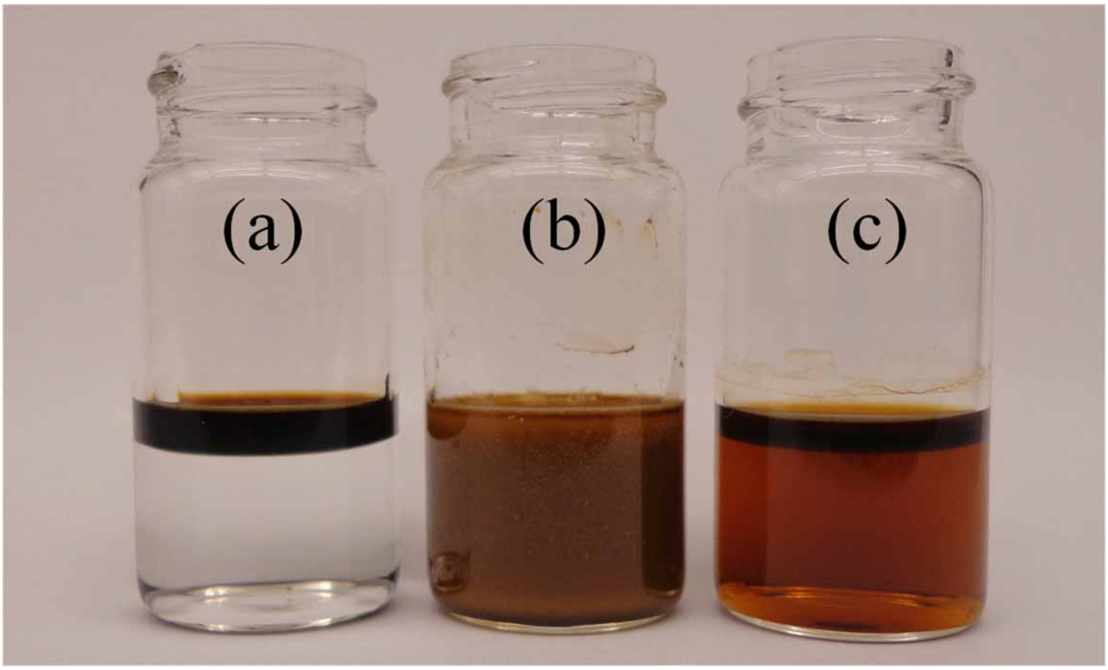

Figure S2. Bilayer phase transfer process at different stages: (a) at beginning, (b) just after sonication and (c) after 1 day settlement.

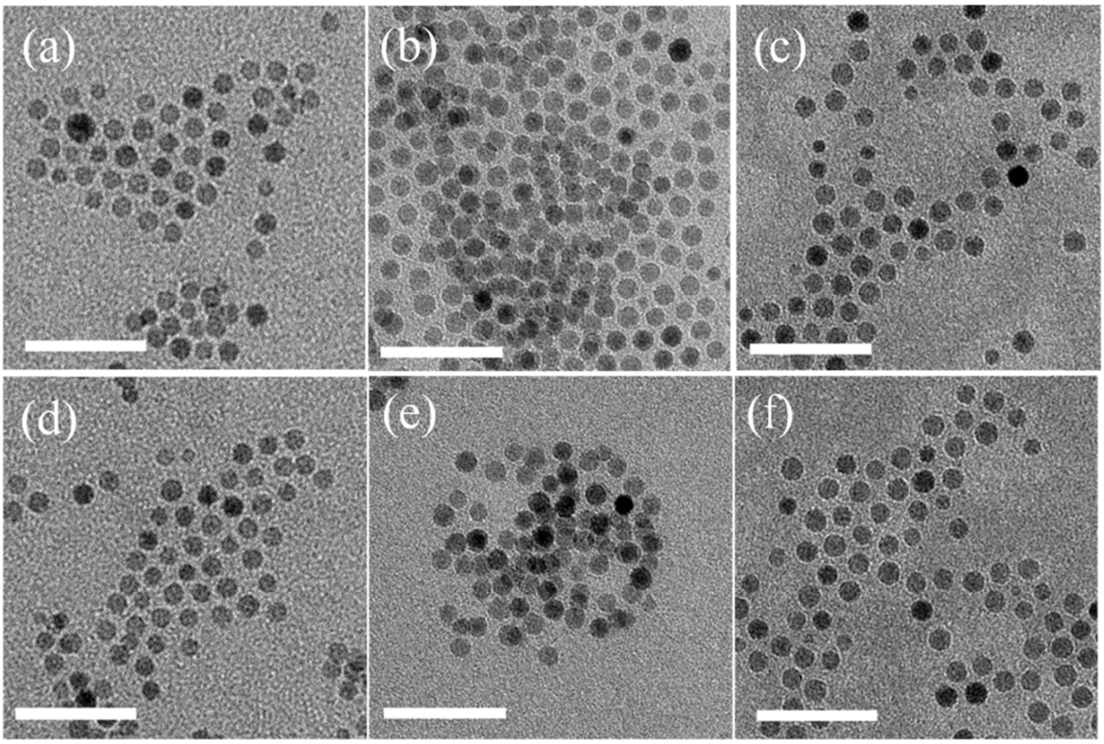

Figure S3. Representative TEM micrographs of (a) RA-NPs, (b) SA-NPs, (c) SDP-NPs, (d) SDS-NPs, (e) C_{12}TAB-NPs, and (f) EMPIGEN-NPs in water. All scale bars are 50 nm.

Table S1. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for ricinoleic acid (RA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				20.4 ± 6.6	47.3 ± 1.3
60%				23.7 ± 2.1	72.0 ± 3.1
70%				22.4 ± 0.5	81.2 ± 2.2
80%				21.3 ± 0.6	84.1 ± 1.9
Time (min)	Dependent Variable	10	70%		
2				23.6 ± 0.9	53.7 ± 2.5
4				21.8 ± 1.8	81.2 ± 2.2
6				20.9 ± 1.7	75.9 ± 2.0
8				23.1 ± 3.3	77.3 ± 1.0
Conc. (mM)	5	Dependent Variable	70%		
2.5				24.3 ± 0.7	62.5 ± 1.5
5				24.2 ± 0.8	78.6 ± 2.2
10				21.8 ± 1.2	83.5 ± 1.6
15				21.3 ± 1.8	85.1 ± 3.5
20				22.2 ± 5.5	84.3 ± 1.5

Table S2. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for elaidic acid (EA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (uL)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	50	Dependent Variable		
50%				45.4 ± 2.9	13.4 ± 1.5
60%				41.2 ± 3.0	19.3 ± 2.3
70%				24.7 ± 5.7	26.2 ± 1.1
80%				22.7 ± 5.8	25.7 ± 3.2
Time (min)	Dependent Variable	50	75%		
2				31.4 ± 4.6	16.5 ± 1.7
4				18.5 ± 4.3	26.6 ± 2.2
6				20.5 ± 4.1	25.2 ± 1.4
8				19.8 ± 2.7	21.3 ± 0.5
Conc. (uL)	6	Dependent Variable	75%		
12.5				39.4 ± 10.5	17.7 ± 0.4
25				30.4 ± 5.2	21.1 ± 1.8
50				19.5 ± 5.5	25.8 ± 2.1
75				25.2 ± 4.2	24.1 ± 1.4
100				32.6 ± 2.7	16.0 ± 0.9

Table S3. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for stearic acid (SA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				14.9 ± 3.4	41.7 ± 3.2
60%				21.4 ± 2.5	65.1 ± 2.0
70%				18.6 ± 1.4	65.2 ± 1.7
80%				17.1 ± 2.1	71.5 ± 3.5
Time (min)	Dependent Variable	10	70%		
2				25.0 ± 10.4	47.4 ± 2.7
4				26.4 ± 8.0	63.3 ± 1.6
6				23.0 ± 3.5	75.4 ± 2.5
Conc. (mM)	5	Dependent Variable	70%		
2.5				17.7 ± 6.2	37.4 ± 0.3
5				33.5 ± 3.8	51.3 ± 2.4
10				20.8 ± 2.6	73.3 ± 4.0

Table S4. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for palmitic acid (PA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				24.7 ± 4.8	35.2 ± 1.3
60%				30.6 ± 2.6	61.0 ± 2.4
70%				26.2 ± 0.7	62.7 ± 5.1
80%				27.4 ± 3.3	71.4 ± 3.7
Time (min)	Dependent Variable	10	65%		
2				29.2 ± 3.5	57.3 ± 2.5
4				31.9 ± 3.9	63.3 ± 0.8
6				20.7 ± 7.4	67.4 ± 3.1
8				23.2 ± 2.8	67.2 ± 2.3
Conc. (mM)	6	Dependent Variable	65%		
2.5				31.2 ± 1.2	57.1 ± 3.3
5				33.5 ± 3.7	66.3 ± 3.4
10				33.2 ± 7.7	68.4 ± 1.7
15				30.8 ± 1.4	68.6 ± 3.2
20				23.7±11.1	70.7 ± 1.9

Table S5. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for myristic acid (MA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				24.3 ± 7.7	70.5 ± 2.3
60%				24.0 ± 2.7	81.0 ± 3.6
70%				24.3 ± 0.3	82.1 ± 3.9
80%				22.8 ± 0.6	80.0 ± 1.2
Time (min)	Dependent Variable	10	65%		
1				26.7 ± 1.1	73.3 ± 1.2
2				24.2 ± 1.8	82.5 ± 5.6
4				21.8 ± 1.0	83.9 ± 1.9
6				21.4 ± 0.3	80.4 ± 2.8
Conc. (mM)	4	Dependent Variable	65%		
2.5				25.4 ± 2.8	60.4 ± 2.1
5				24.2 ± 2.0	67.5 ± 1.8
10				21.5 ± 1.9	74.1 ± 2.3
15				20.9 ± 1.4	77.3 ± 2.7
20				21.1 ± 1.1	75.5 ± 4.4

Table S6. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for lauric acid (LA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	3	5	Dependent Variable		
50%				23.2 ± 10.4	58.4 ± 0.8
60%				25.7 ± 8.6	61.5 ± 3.6
70%				26.5 ± 2.1	77.4 ± 5.4
80%				25.6 ± 2.7	84.5 ± 3.6
90%				24.3 ± 0.5	87.3 ± 4.1
Time (min)	Dependent Variable	5	75%		
1				37.6 ± 4.8	80.3 ± 4.1
2				31.6 ± 2.6	86.5 ± 2.6
3				20.8 ± 4.0	88.2 ± 3.3
4				28.0 ± 1.7	84.2 ± 3.9
5				22.4 ± 9.0	88.5 ± 2.6
Conc. (mM)	3	Dependent Variable	75%		
1.25				34.5 ± 0.7	70.1 ± 2.8
2.5				31.6 ± 2.5	74.5 ± 1.7
5				26.9 ± 1.7	85.1 ± 4.4
7.5				25.2 ± 1.7	88.8 ± 2.6
10				19.2 ± 0.4	87.6 ± 1.9

Table S7. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for decanoic acid (DA) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				24.4 ± 2.5	26.7 ± 3.1
60%				27.5 ± 1.5	30.8 ± 5.0
70%				26.1 ± 2.3	40.6 ± 2.4
80%				28.4 ± 0.6	59.3 ± 4.2
Time (min)	Dependent Variable	10	75%		
2				28.4 ± 0.4	55.4 ± 2.0
4				26.5 ± 0.6	54.3 ± 2.4
6				25.1 ± 0.7	55.0 ± 1.8
8				25.4 ± 0.8	59.3 ± 3.6
Conc. (mM)	4	Dependent Variable	75%		
2.5				30.4 ± 8.9	38.4 ± 0.7
5				28.9 ± 0.7	40.4 ± 2.1
10				28.5 ± 0.6	46.4 ± 1.1
15				27.4 ± 1.9	45.6 ± 1.6
20				28.9 ± 0.3	53.4 ± 3.0

Table S8. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for sodium monododecyl phosphate (SDP) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	3	5	Dependent Variable		
50%				44.5 ± 0.5	51.2 ± 3.4
60%				41.6 ± 2.4	67.4 ± 3.9
70%				39.1 ± 2.9	85.6 ± 4.6
80%				36.2 ± 0.6	93.1 ± 4.9
90%				39.0 ± 1.0	91.4 ± 5.5
Time (min)	Dependent Variable	5	70%		
1				53.2 ± 3.2	67.4 ± 1.3
2				43.7 ± 1.6	79.3 ± 5.7
3				38.7 ± 0.8	90.9 ± 4.7
4				39.0 ± 1.0	92.7 ± 3.2
5				38.4 ± 2.5	95.2 ± 1.9
Conc. (mM)	3	Dependent Variable	70%		
1.25				54.9 ± 3.3	66.9 ± 1.1
2.5				43.1 ± 2.3	77.3 ± 2.2
5				40.6 ± 1.2	87.6 ± 3.9
7.5				34.3 ± 0.2	85.2 ± 6.7
10				23.4 ± 3.5	90.1 ± 2.3

Table S9. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for sodium monododecyl sulfate (SDS) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	5	5	Dependent Variable		
50%				20.9 ± 3.0	40.8 ± 0.6
60%				20.4 ± 1.1	50.4 ± 1.2
70%				19.0 ± 1.0	64.3 ± 3.6
80%				20.2 ± 1.6	72.3 ± 7.4
90%				20.3 ± 0.1	70.7 ± 0.9
Time (min)	Dependent Variable	5	70%		
1				22.6 ± 10.4	55.2 ± 2.0
2				20.9 ± 2.6	59.7 ± 1.0
3				21.9 ± 0.2	73.6 ± 4.0
4				22.1 ± 1.3	79.1 ± 0.7
5				22.2 ± 1.5	74.1 ± 1.8
Conc. (mM)	3	Dependent Variable	70%		
1.0				28.1 ± 1.0	57.5 ± 2.7
2.5				25.0 ± 0.5	76.2 ± 2.1
5				20.6 ± 0.7	75.9 ± 3.2
7.5				19.7 ± 0.3	78.2 ± 3.1
10				16.6 ± 0.7	76.0 ± 1.8

Table S10. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for sodium dodecylbenzenesulfonate (SDBS) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				16.4 ± 3.1	36.3 ± 0.7
60%				15.0 ± 0.6	58.4 ± 2.2
70%				17.1 ± 1.5	63.3 ± 0.4
80%				16.2 ± 1.9	66.6 ± 1.7
Time (min)	Dependent Variable	10	70%		
2				21.0 ± 2.7	53.0 ± 1.7
4				16.6 ± 1.9	67.5 ± 1.6
6				15.1 ± 3.0	68.4 ± 1.6
Conc. (mM)	5	Dependent Variable	70%		
5				18.9 ± 0.3	45.5 ± 1.4
10				17.2 ± 0.8	62.8 ± 1.0
20				15.2 ± 4.1	66.1 ± 1.4
30				18.2 ± 3.4	64.9 ± 5.5
40				17.9 ± 0.3	64.5 ± 2.3

Table S11. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for dodecyltrimethylammonium bromide ($C_{12}TAB$) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	4	10	Dependent Variable		
50%				22.3 ± 4.1	28.7 ± 3.4
60%				19.7 ± 1.7	33.8 ± 2.2
70%				21.3 ± 1.3	35.5 ± 5.2
80%				21.5 ± 0.8	42.8 ± 2.3
Time (min)	Dependent Variable	10	75%		
2				19.6 ± 1.0	38.5 ± 0.7
4				20.7 ± 1.0	45.1 ± 1.9
6				20.3 ± 2.3	47.4 ± 1.4
Conc. (mM)	4	Dependent Variable	75%		
5				34.5 ± 0.4	30.2 ± 2.9
10				20.7 ± 1.0	44.6 ± 1.6
20				36.1 ± 0.6	41.1 ± 3.5
30				43.8 ± 11.5	42.6 ± 2.2
40				59.2 ± 3.4	40.4 ± 4.5

Table S12. Detailed hydrodynamic diameter and transfer yield as functions of sonication amplitude, sonication time and surfactant concentration tested for N,N-Dimethyl-N-dodecylglycine betaine (EMPIGEN) coated NPs.

Dependent Variable	Time Tested (min)	Conc. Tested (mM)	Amplitude Tested	Hydrodynamic Diameter (nm)	Transfer Yield (%)
Amplitude	5	20	Dependent Variable		
50%				29.0 ± 9.8	30.2 ± 2.7
60%				36.9 ± 8.1	38.4 ± 1.2
70%				36.0 ± 6.9	42.3 ± 3.3
80%				33.1 ± 13.7	46.3 ± 4.5
90%				38.3 ± 1.9	46.1 ± 2.3
Time (min)	Dependent Variable	20	70%		
2				36.1 ± 0.9	46.4 ± 3.5
4				33.8 ± 9.9	42.4 ± 1.2
5				30.8 ± 7.4	50.5 ± 2.3
6				30.0 ± 0.9	55.8 ± 3.6
8				32.1 ± 0.7	52.8 ± 2.8
Conc. (mM)	6	Dependent Variable	70%		
10				56.8 ± 6.6	37.1 ± 1.3
20				31.5 ± 2.9	46.4 ± 2.6
30				27.9 ± 3.5	54.9 ± 1.9
40				17.3 ± 1.5	65.4 ± 4.3
50				21.6 ± 1.0	67.9 ± 3.1

Table S13. Total organic carbon (TOC) concentrations of bilayer coated iron oxide NPs (50 ppm Fe).

Outer layer	**TOC (ppm)**	**Outer layer density (mol/mol Fe_3O_4)[α]**	**Outer layer density (mol/mol # NPs)[α]**	**Out layer density (10^{-5} mol/m^2)[α]**
Oleic acid (OA)	102.8 ± 0.3	1.32	4953	3.99
Ricinoleic acid (RA)	100.1 ± 0.9	1.28	4792	3.86
Elaidic acid (EA)	85.0 ± 0.2	1.04	3917	3.16
Stearic acid (SA)	99.8 ± 0.9	1.27	4777	3.85
Palmitic acid (PA)	99.4 ± 0.2	1.43	5350	4.31
Myristic acid (MA)	94.3 ± 0.5	1.53	5730	4.62
Lauric acid (LA)	87.2 ± 0.5	1.62	6063	4.89
Decanoic acid (DA)	81.3 ± 0.3	1.77	6655	5.36
SDP	86.7 ± 0.5	1.60	6016	4.85
SDS	88.8 ± 0.4	1.65	6207	5.00
SDBS	100.5 ± 1.9	1.28	4814	3.88
C_{12}TAB	95.0 ± 0.1	1.44	5395	4.35
EMPIGEN	98.3 ± 1.6	1.41	5276	4.25

α Assumes the surface area per oleic acid molecule (*A*) to be 0.2 nm^2,[1] the radius of IONPs (r) to be 8.1/2=4.05 nm, the density of iron oxide (ρ) is 5.17 g/cm^3. The base oleic acid layer is calculated to be 23.2 mg per 50 mg Fe, which is equal to 0.28 mmol oleic acid/mmol Fe_3O_4.

$$Base\ OA\ layer = \frac{(base\ OA\ layer\ weight\ on\ each\ NP)*Fe\ concentration}{each\ NP\ weight\ (as\ Fe)} =$$

$$\frac{(\#\ of\ OA\ molecule\ on\ each\ NP)*(molecular\ weight\ of\ OA)/N_A}{(volume\ of\ each\ NP)*(density\ of\ iron\ oxide)*(percentage\ of\ Fe\ in\ each\ NP)} Fe\ concentration =$$

$$\frac{(4\pi r^2/A)*(M_w\ of\ OA)/N_A}{\left(4\pi r^3/3\right)*\rho_{Fe_3O_4}*\left(3*M_w\ of\ Fe/M_w\ of\ Fe_3O_4\right)} Fe\ concentration \qquad (1)$$

$$The\ C\ content\ in\ the\ base\ OA\ layer = \frac{18*(M_w\ of\ C)}{M_w\ of\ OA} base\ OA\ layer\ content \qquad (2)$$

The C concentration in the base OA layer was calculated to be 17.74 mg per 50 mg Fe. By subtracting the C concentration from the total carbon concentration, we can derive the C concentration in the second layer and thus the mol concentration of second layer.

$$The\ mol\ concentration\ of\ Fe_3O_4 = \frac{Fe\ concentration}{3*(M_w\ of\ Fe)} = 0.298 \text{ mmol as in 50 ppm Fe} \qquad (3)$$

$$Outer\ layer\ density\ \left(mol/_{mol}Fe_3O_4\right) = \frac{mol\ concentration\ of\ second\ layer}{mol\ concentration\ of\ Fe_3O_4} \qquad (4)$$

$$Outer\ layer\ density\ \left(mol/_{mol\ \#\ NPs}\right) = \frac{mol\ concentration\ of\ second\ layer}{mol\ \#\ NPs} =$$

$$\frac{mol\ concentration\ of\ second\ layer}{\left(total\ weight\ as\ Fe_3O_4 / each\ NP\ weight*N_A\right)} \qquad (5)$$

$$Outer\ layer\ density\ \left(mol/_{m^2}\right) = \frac{mol\ concentration\ of\ second\ layer}{mol\ \#\ NPs} =$$

$$\frac{mol\ concentration\ of\ second\ layer}{(surface\ area\ of\ each\ NP)*(total\ weight\ as\ Fe_3O_4) / (each\ NP\ weight)} \qquad (6)$$

Table S14. Summary of CCC values for bilayer coated iron oxide NPs.

Outer layer	Critical Coagulation Concentration	
	NaCl (mM)	**$CaCl_2$ (mM)**
Oleic acid (OA)	710	10.6
Ricinoleic acid (RA)	746	10.8
Elaidic acid (EA)	260	7.4
Stearic acid (SA)	452	9.3
Palmitic acid (PA)	257	5.3
Myristic acid (MA)	94	3.9
Lauric acid (LA)	16	0.5
Decanoic acid (DA)	27	1.6
SDP	250	3.6
SDS	45	1.4
SDBS	46	6.0
C_{12}TAB	555	11.1
EMPIGEN	766	11.3

References

1. A. G. Roca, M. P. Morales, K. O'Grady and C. J. Serna, *Nanotechnology*, 2006, **17**, 2783.