Electronic Supplementary Material (ESI) for Soft Matter

Supplementary File

Assembly of Copolymer Functionalized Nanoparticles: A Monte Carlo simulation study

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Table S.1: Radius of gyration $\langle R_{g,chain}^2 \rangle^{1/2}$ (in nm) of the alternating (top) and diblock (bottom) chains grafted on particles of size D=2nm, 4nm and 12nm, and varying interaction parameters (also rows in Table 1 in the main text).

	D=2nm			D=4nm			D=12nm	
ALTERNATING	**Average**	**Error**		**Average**	**Error**		**Average**	**Error**
Interactions								
1	2.934	0.004		2.905	0.006		2.892	0.003
2	2.442	0.011		2.438	0.007		2.397	0.004
3	2.334	0.011		2.433	0.028		1.834	0.011
4	2.505	0.004		2.495	0.003		2.501	0.003
5	2.341	0.022		2.392	0.020		2.058	0.006
6	2.325	0.020		2.386	0.018		1.848	0.013
7	2.509	0.003		2.510	0.002		2.503	0.003
8	2.346	0.016		2.347	0.013		2.050	0.004
9	2.270	0.013		2.353	0.025		1.825	0.016
10	3.043	0.003		3.016	0.005		3.001	0.004
11	2.821	0.005		2.801	0.005		2.797	0.003
12	2.309	0.013		2.328	0.017		2.140	0.007
13	3.055	0.003		3.009	0.006		3.004	0.005
14	2.844	0.007		2.806	0.006		2.805	0.005
15	2.325	0.007		2.316	0.012		2.130	0.008
DIBLOCK								
Interactions	**Average**	**Error**		**Average**	**Error**		**Average**	**Error**
1	2.881	0.008		2.812	0.004		2.771	0.004
2	2.959	0.025		2.893	0.020		2.670	0.018
3	2.743	0.015		2.729	0.013		2.499	0.017
4	2.604	0.008		2.583	0.004		2.597	0.003
5	2.779	0.018		2.813	0.020		2.807	0.020
6	2.674	0.021		2.680	0.027		2.758	0.018
7	2.683	0.002		2.625	0.002		2.573	0.004
8	2.758	0.009		2.718	0.009		2.456	0.005
9	2.751	0.014		2.687	0.012		2.408	0.006
10	2.954	0.005		2.928	0.004		2.914	0.005
11	2.974	0.014		2.989	0.019		2.997	0.012
12	2.916	0.018		2.904	0.021		2.928	0.010
13	3.002	0.005		2.957	0.005		2.904	0.003
14	3.018	0.010		2.985	0.011		2.766	0.003
15	2.999	0.016		2.925	0.013		2.681	0.005

Figure S.1.

Simulation snapshots from five trials showing representative equilibrium clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=4nm** and six grafts of **24 monomers** arranged in diblock sequence. The rows in the figure, as labeled, correspond to the rows in Table 1.

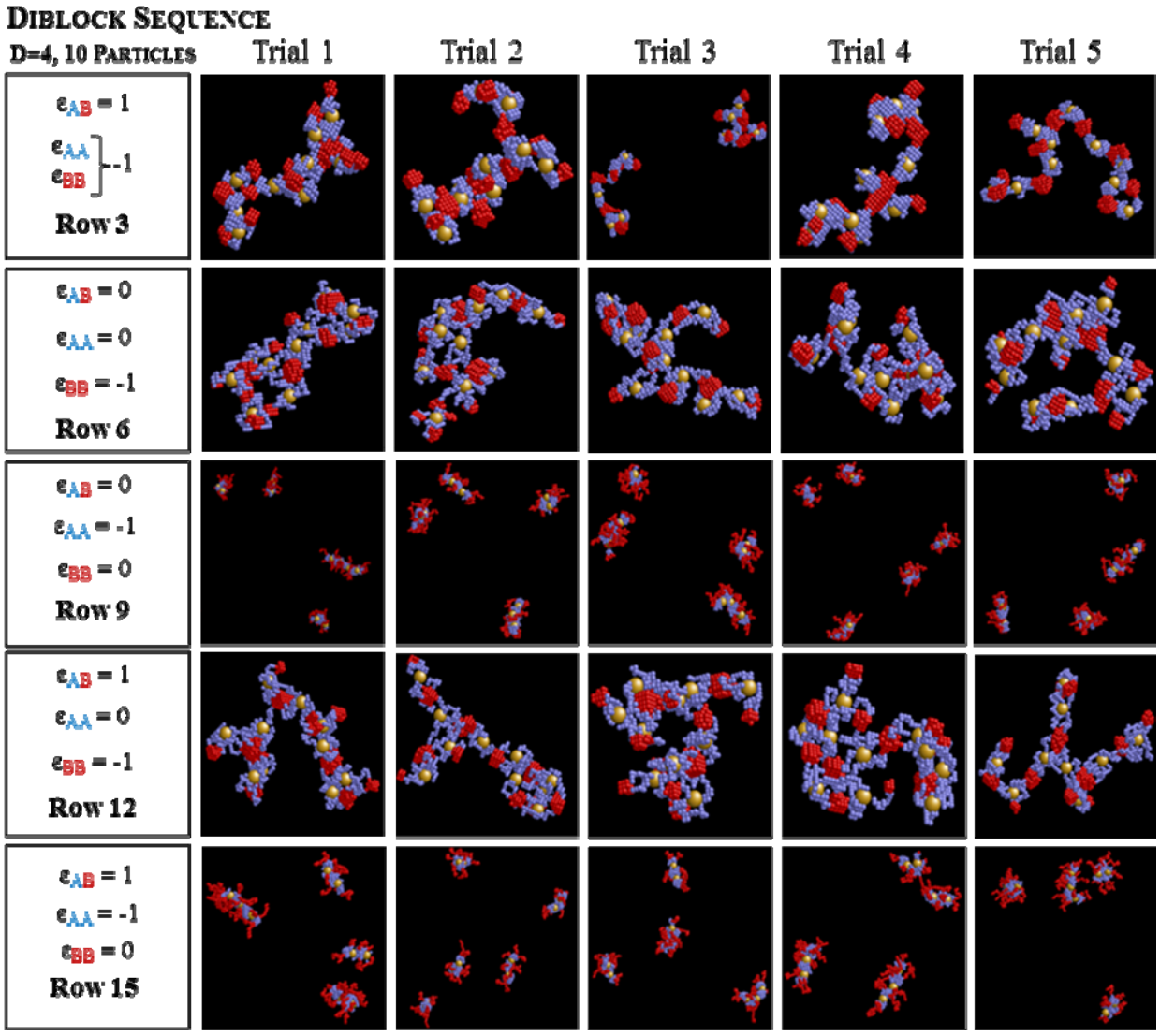


Figure S.2.

Simulation snapshots from one trial showing representative equilibrium clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=12nm** and six grafts of **24 monomers** arranged in alternating and diblock sequence. The rows in the figure, as labeled, correspond to the rows in Table 1.

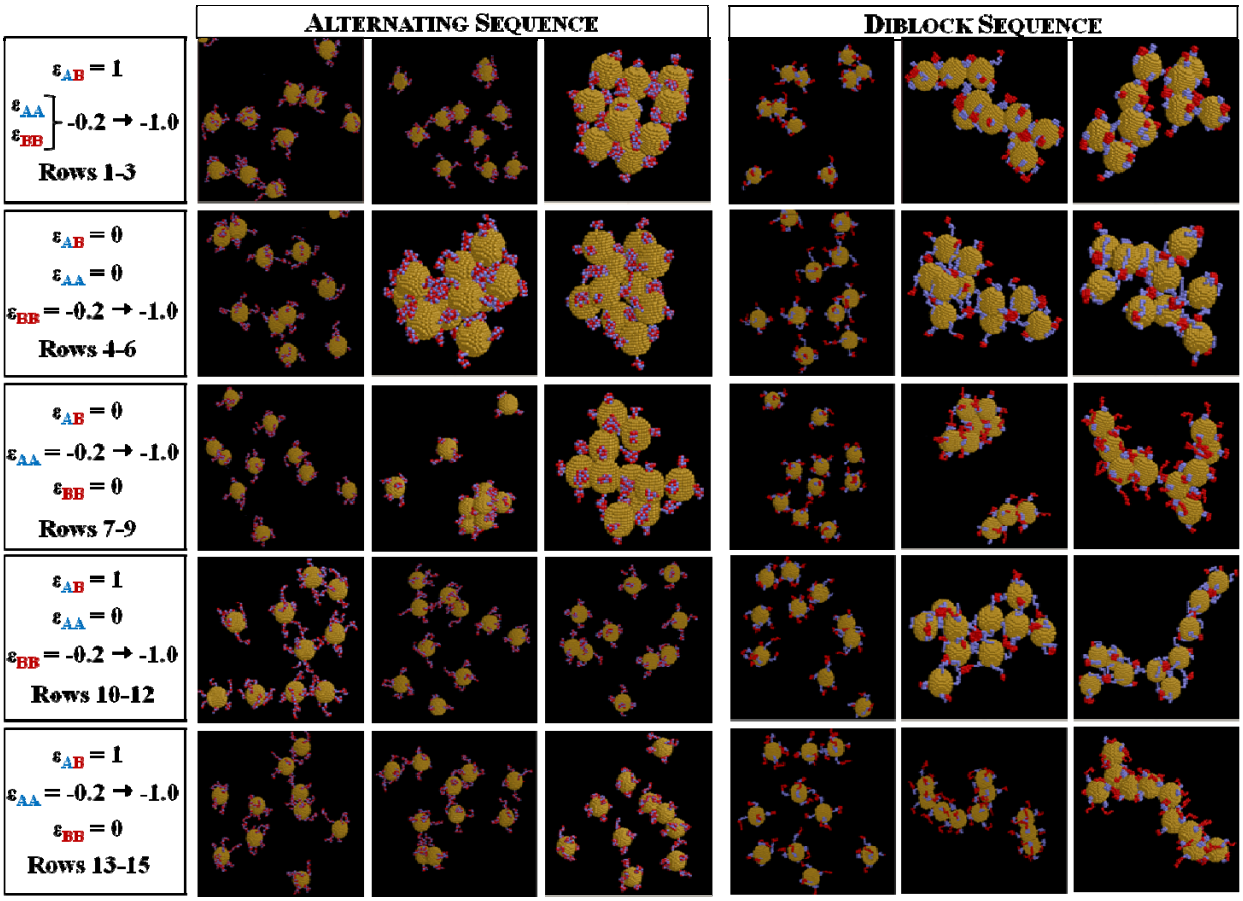


Figure S.3.

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=2nm** and six grafts of **24 monomers** arranged in either an alternating (solid lines) or diblock sequence (dashed lines) with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

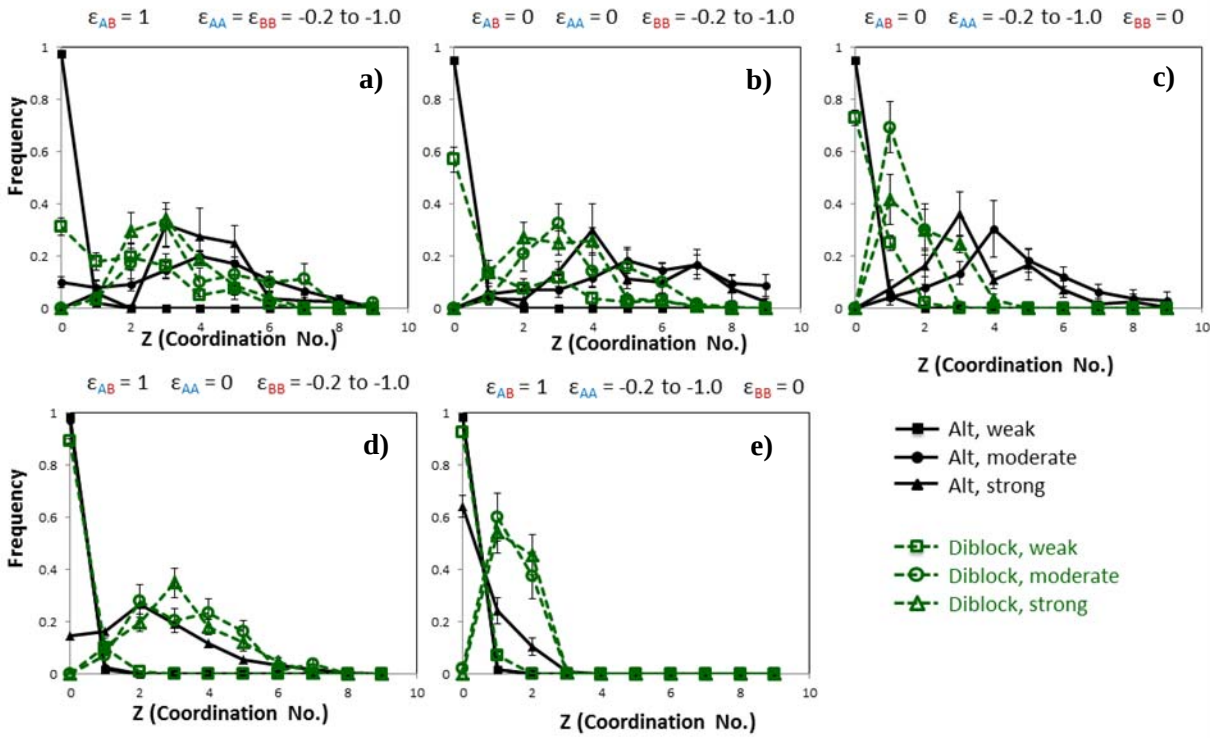


Figure S.4.

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=12nm** and six grafts of **24 monomers** arranged in either an alternating (solid lines) or diblock sequence (dashed lines) with varying monomer chemistries corresponding to a) rows 1-3 b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

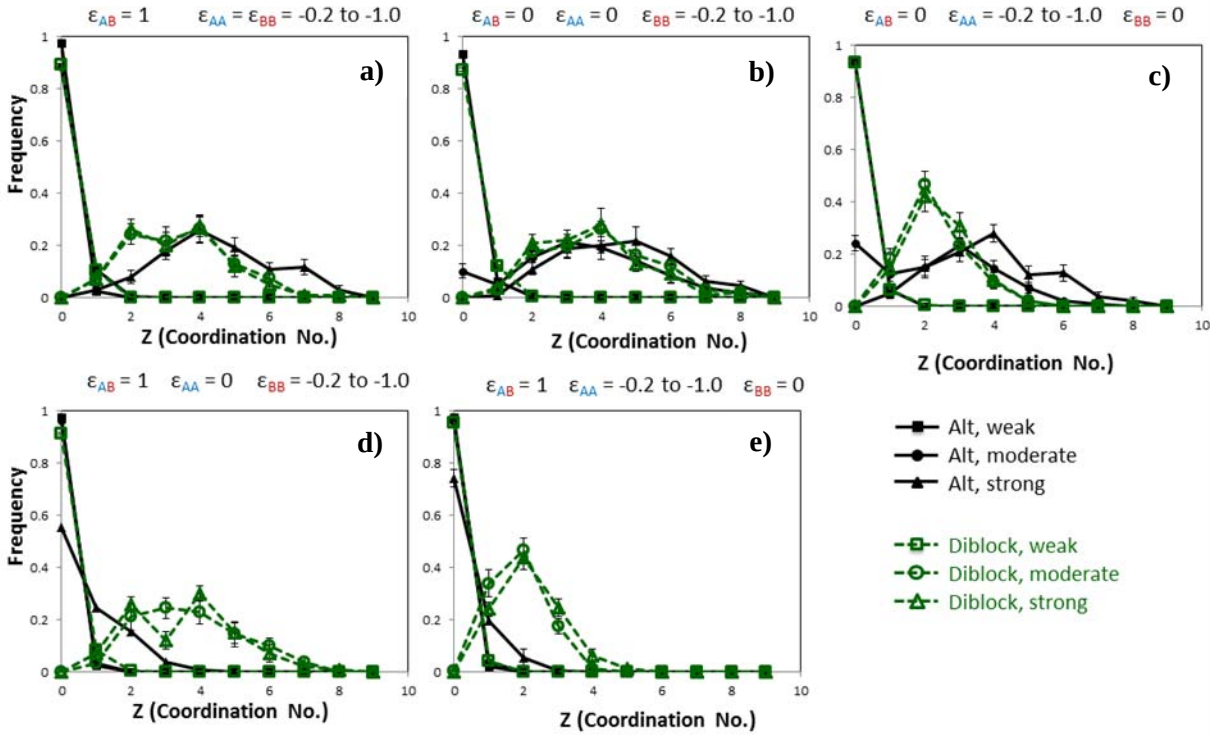


Figure S.5.

Simulation snapshots from one trial showing representative equilibrium clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=4nm** and six grafts of **24 monomers or 48 monomers** arranged in **diblock sequence**.

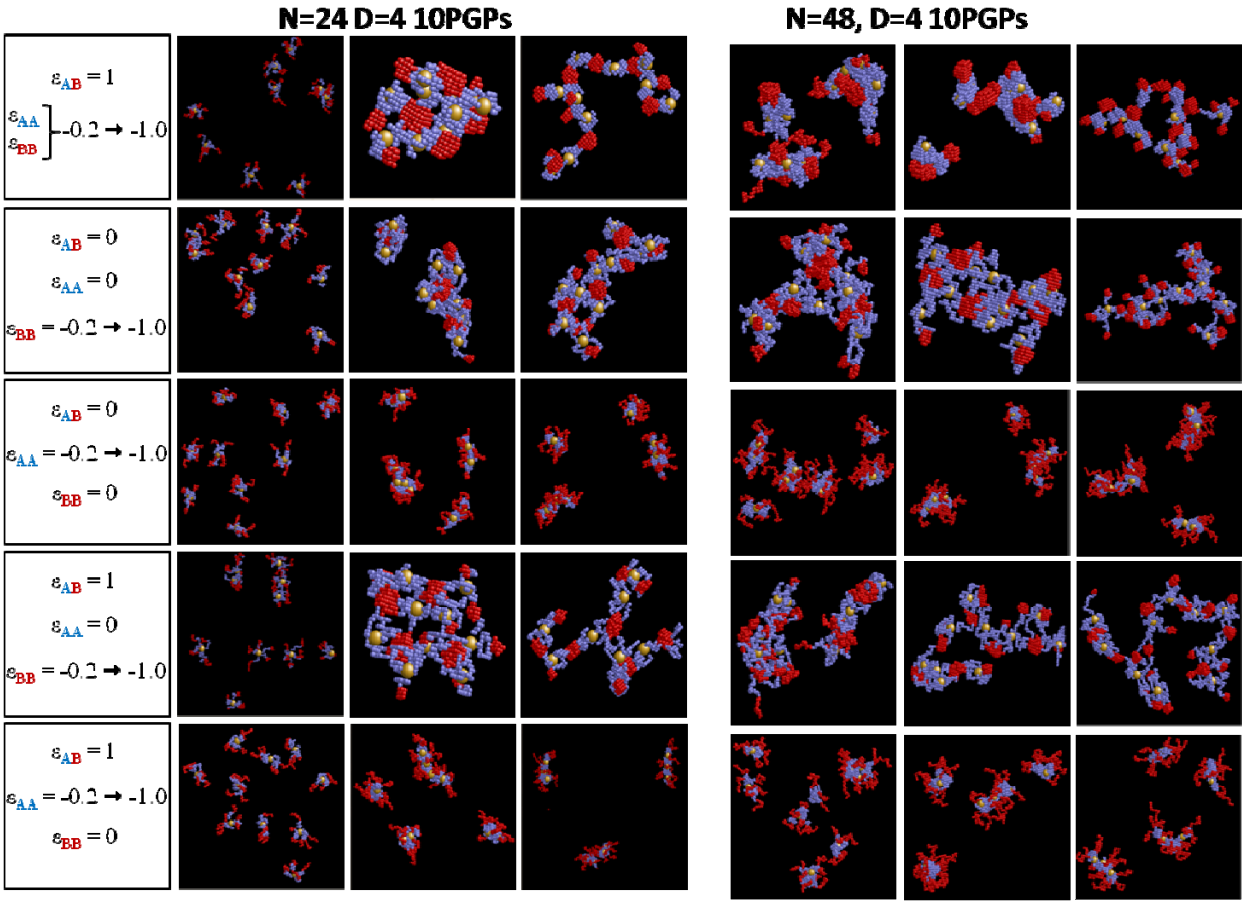


Figure S.6.

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with varying particle diameter (top panel) and six grafts of varying length (bottom panel) arranged in **alternating** sequence with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

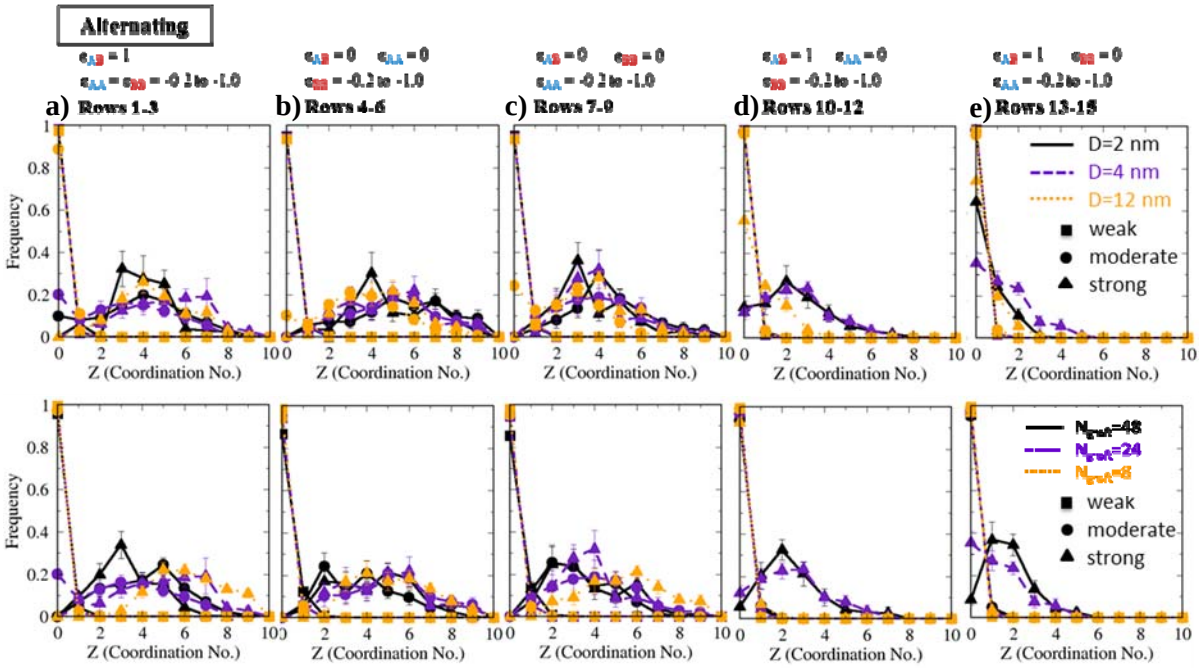
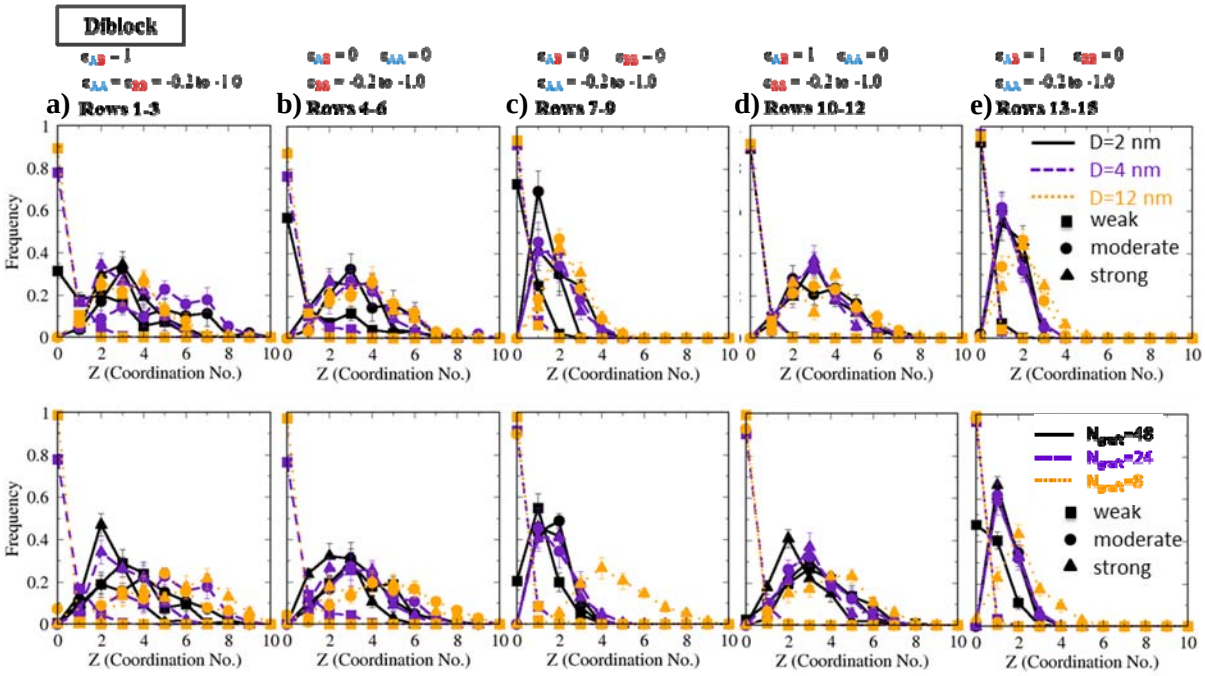


Figure S.7

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **10 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with varying particle diameter (top panel) and six grafts of varying length (bottom panel) arranged in **diblock** sequence with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.



Figue S.8

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **20 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particle diameter **D=2nm** and six grafts of **24 monomers** arranged in either an alternating (solid lines) or diblock sequence (dashed lines) with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

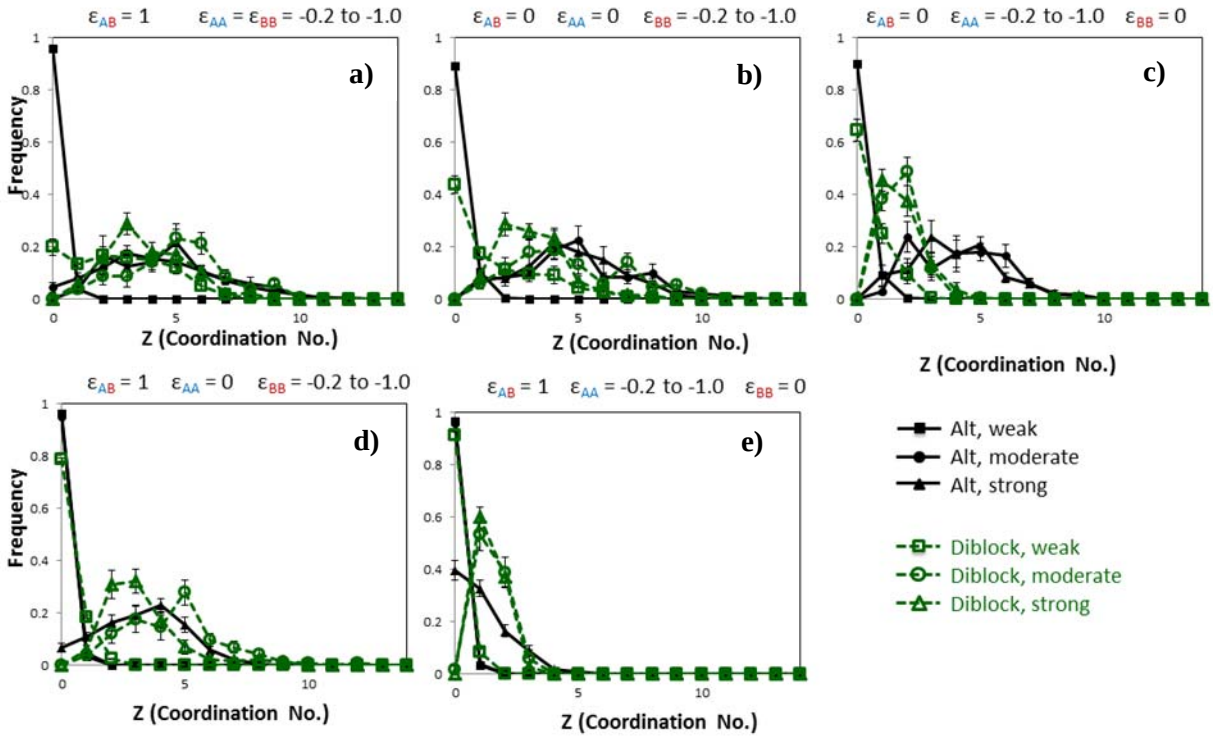


Figure S.9.

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **20 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particles diameter **D=4nm** and six grafts of **24 monomers** arranged in either an alternating (solid lines) or diblock sequence (dashed lines) with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

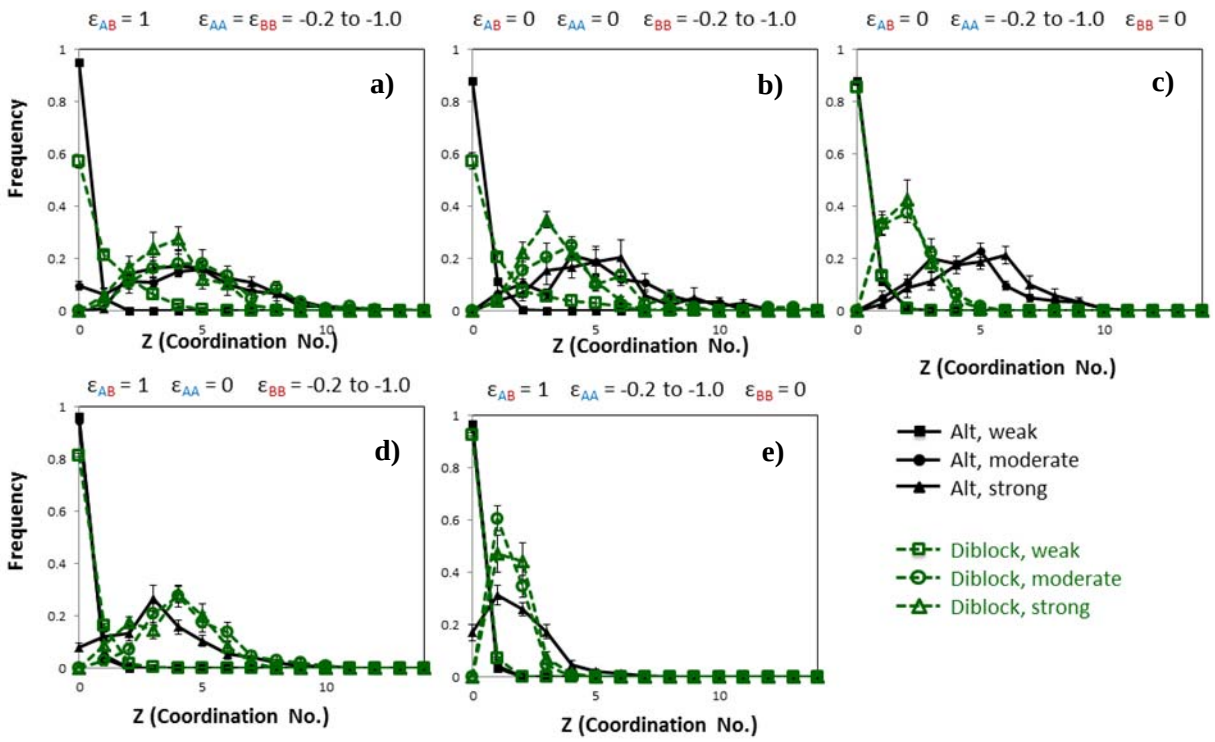


Figure S.10.

Histogram of Z coordination numbers characterizing the structure within clusters formed from the assembly of **20 copolymer grafted particles** (in a 100x100x100 nm^3 simulation box) with particles diameter **D=12nm** and six grafts of **24 monomers** arranged in either an alternating (solid lines) or diblock sequence (dashed lines) with varying monomer chemistries corresponding to a) rows 1-3, b) rows 4-6, c) rows 7-9, d) rows 10-12 and e) rows 13-15 in Table 1. The symbols for weak, moderate and strong attraction strength are square, circle and triangle, respectively.

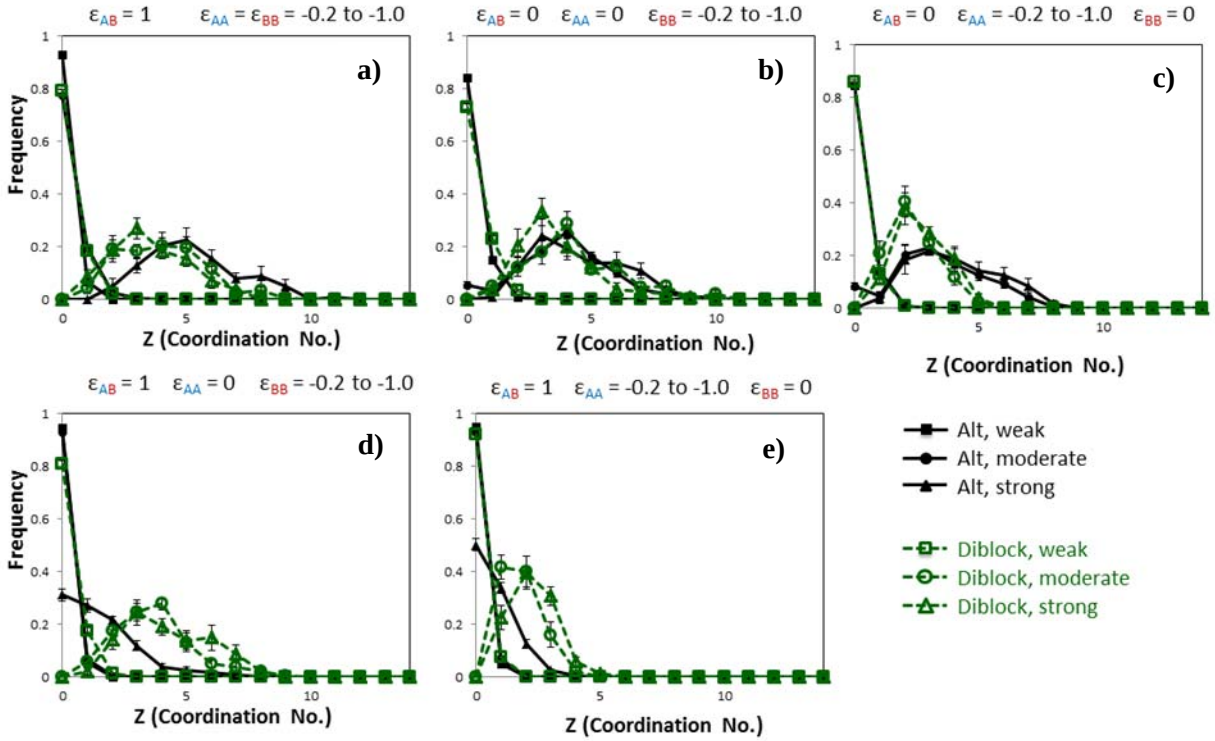


Table S.2 Average values of inter-particle distances for particles in a cluster (at equilibrium) for alternating grafted particles and selected chemistries.

Chemistry (ε_{AA}, ε_{BB}, ε_{AB}) in kT	**Average inter-particle distance for particles within a cluster**
-0.5, -0.5, 1.0 (row 2 in Table 1 of main manuscript)	10.72 +/- 0.50
-1.0, -1.0, 1.0 (row 3 in Table 1 of main manuscript)	12.89 +/- 0.30
0.0, -0.5, 0.0 (row 5 in Table 1 of main manuscript)	11.40 +/- 0.37
0.0, -1.0, 0.0 (row 5 in Table 1 of main manuscript)	12.73 +/- 0.49

The metal fill fraction in Figure 2c does not increase monotonically for x-axis values 1-3 (black solid); the fill fraction is the highest for moderate strength (0.5kT). This is because at larger like-monomer attractions (1kT), monomers along the alternating copolymer grafts on different particles are strongly pulled together and aggregate within the cluster leading to increased spacing between nanoparticles at 1kT than at 0.5kT thus leading to lower metal fill fraction for 1kT than 0.5kT. This Table presents average inter-particle distances within a cluster.