Supplementary Information

Effect of blockiness in grafted monomer sequences on assembly of copolymer grafted nanoparticles: A Monte Carlo simulation study

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I. Types of Monomer Contacts in Clusters/Dispersions of Copolymer Grafted Nanoparticles

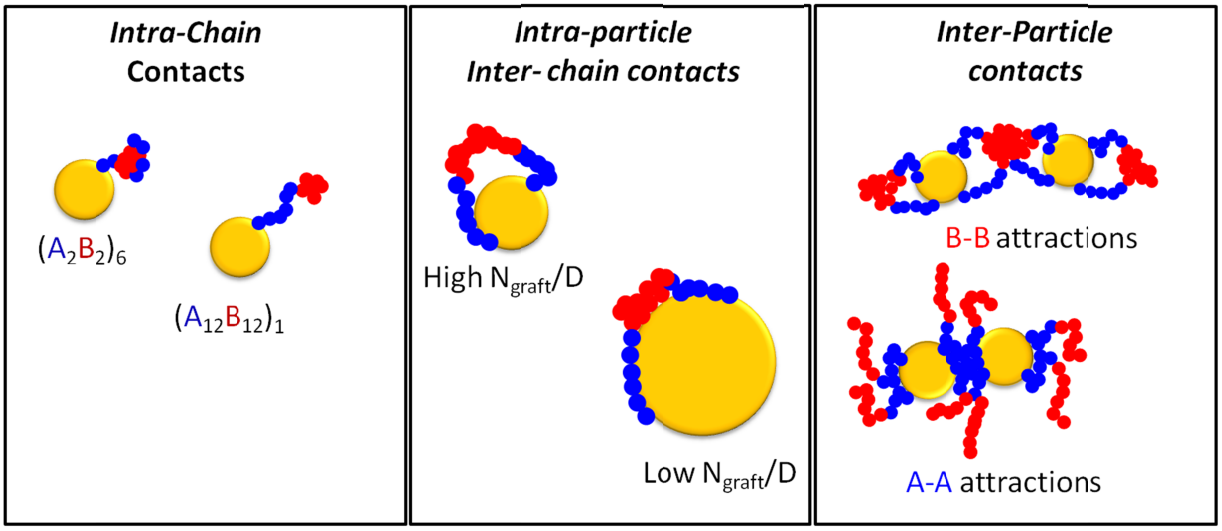

Figure S1: *Schematic showing the three types of monomer contacts that could be made in these systems of copolymer grafted nanoparticles.*

II. Effects of Monomer Sequence on Grafted Chain Conformations and Monomer Aggregation in the Cluster for D=4d and D=12d with and without Monomer-Particle Interactions

The figures in this section consist of parts a-i that connect to the interaction sets in a way different from the main manuscript. The table below should help with connecting the figure parts to interaction sets. We present the data in this order to show some symmetry in A-A and B-B interaction effects, in presence and absence of A-B repulsion, and monomer-particle attractions.

Table S1: Interaction sets and figure parts.

Interaction Set	Figure part	ε_{AB}/kT	ε_{AA}/kT	ε_{BB}/kT	χ_{AB}/kT
1	d	0.0	-0.5	0.0	1
2	b	0.0	-1.0	0.0	2
3	c	0.0	0.0	-0.5	1
4	a	0.0	0.0	-1.0	2
5	j	0.0	-0.5	-0.5	2
6	i	0.0	-1.0	-1.0	4
7	h	1.0	-0.5	0.0	5
8	f	1.0	-1.0	0.0	6
9	g	1.0	0.0	-0.5	5
10	e	1.0	0.0	-1.0	6
11	l	1.0	-0.5	-0.5	6
12	k	1.0	-1.0	-1.0	8

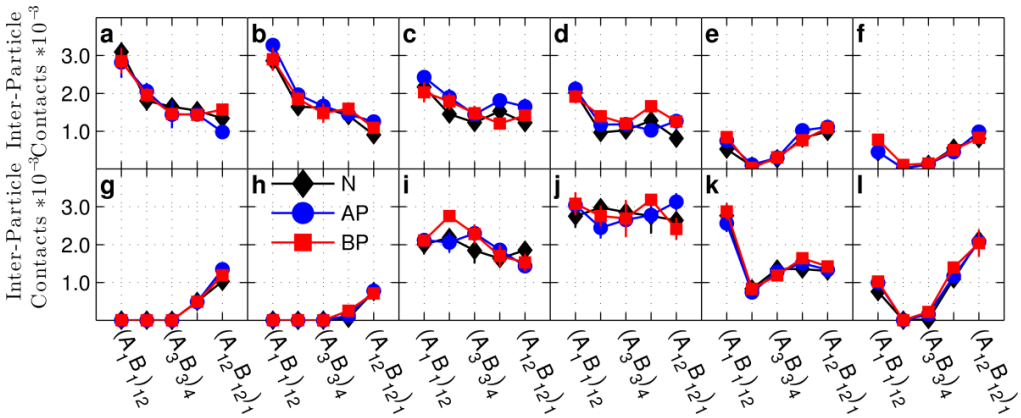

Figure S2: *Average number of interparticle contacts as a function of monomer sequence for copolymer grafted nanoparticles of D=4d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

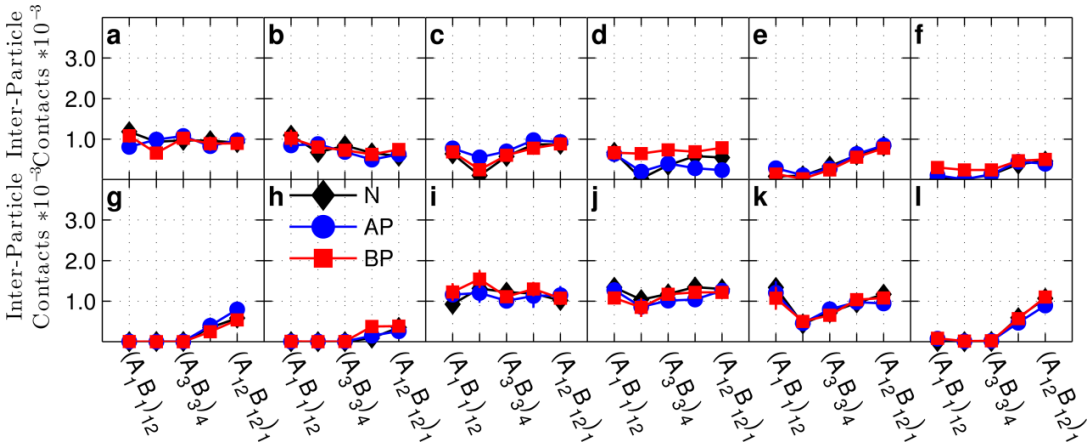

Figure S3: *Average number of interparticle contacts as a function of monomer sequence for copolymer grafted nanoparticles of D=12d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in Table S1 (with particle-monomer interactions indicated by line color)*

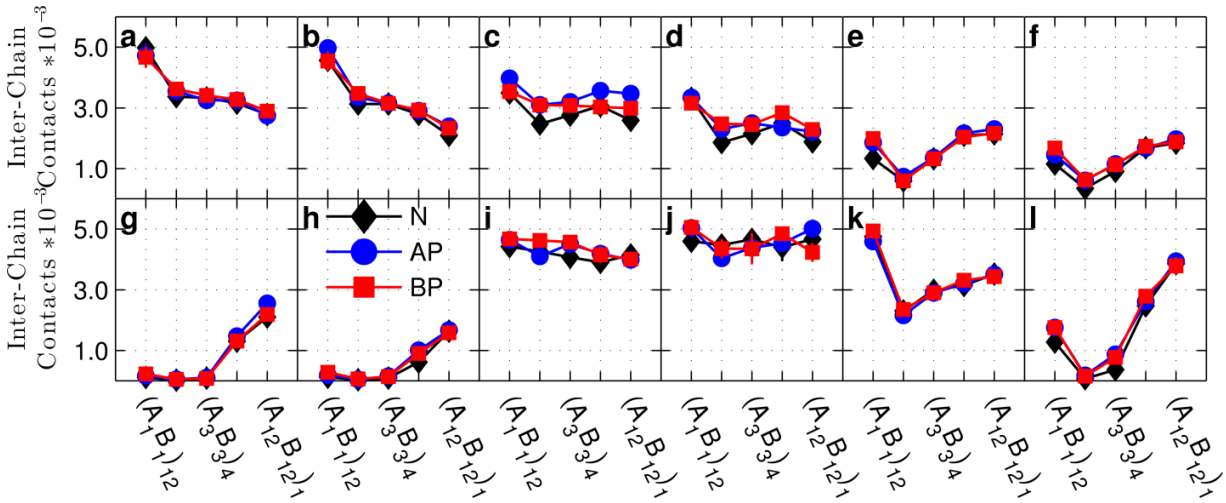

Figure S4: *Average number of inter-chain contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=4d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color).*

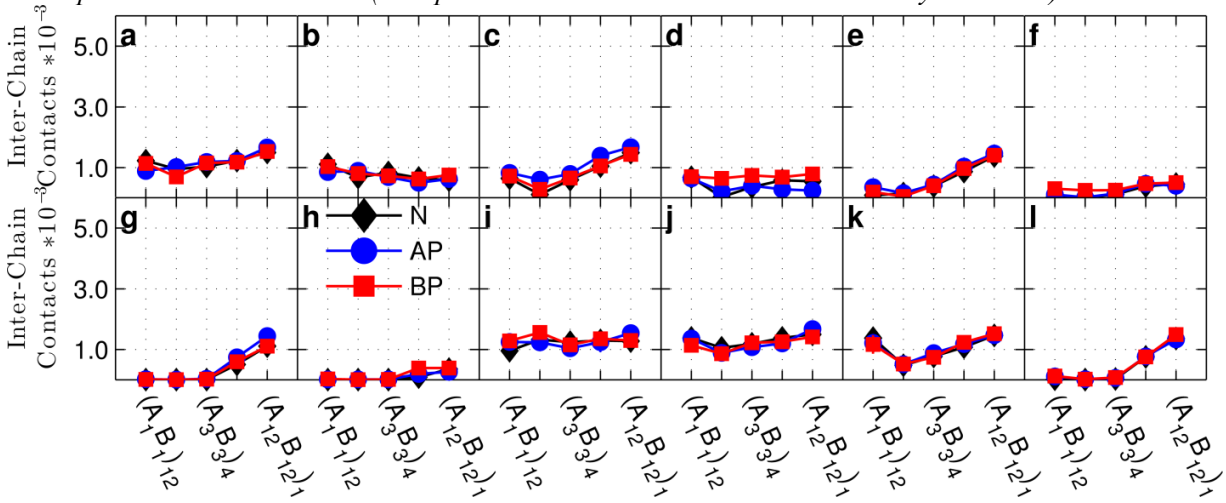

Figure S5: *Average number of inter-chain contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=12d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

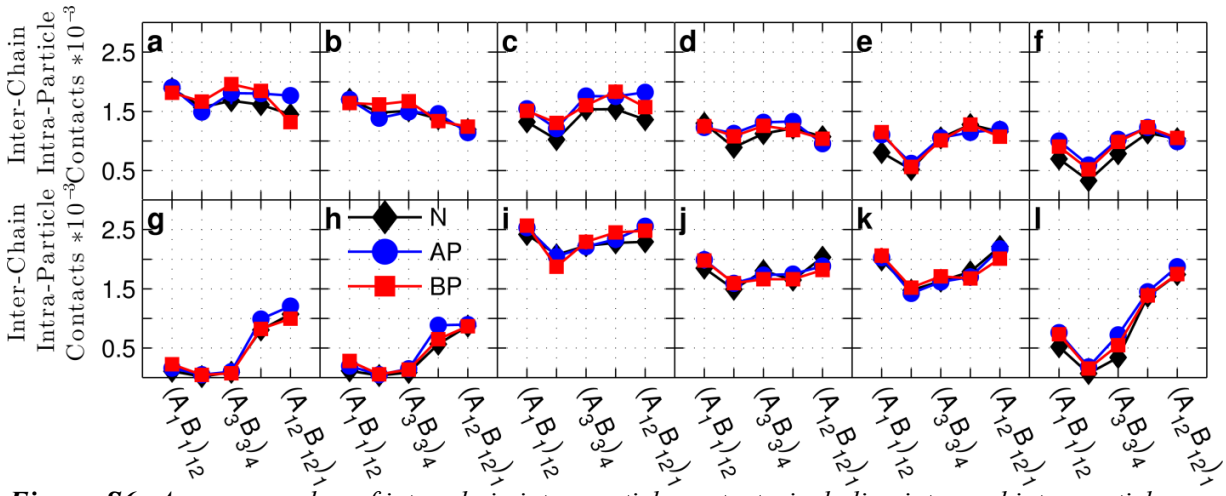

Figure S6: *Average number of inter-chain intra-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=4d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

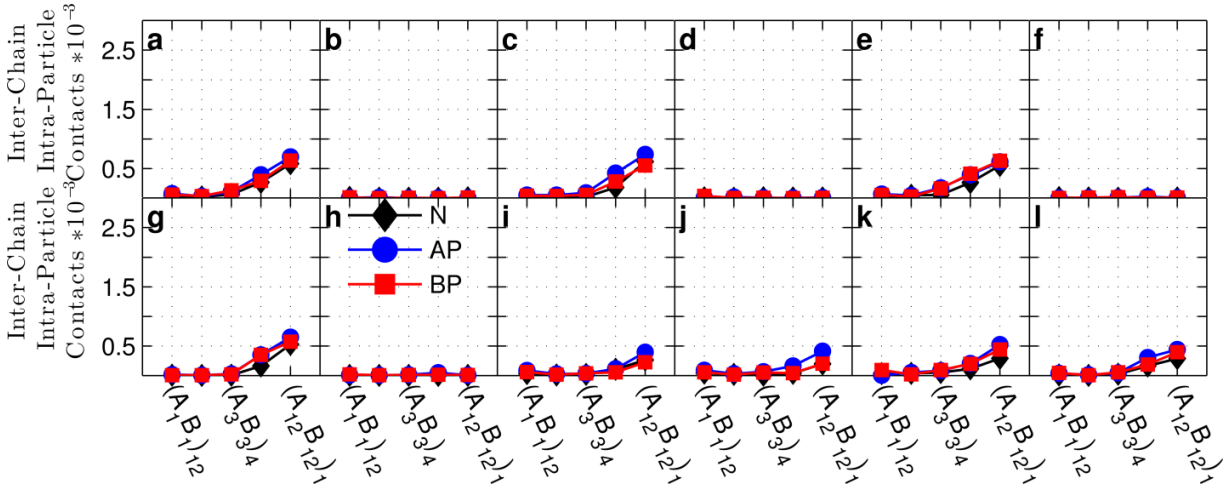

Figure S7: *Average number of inter-chain intra-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=12d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

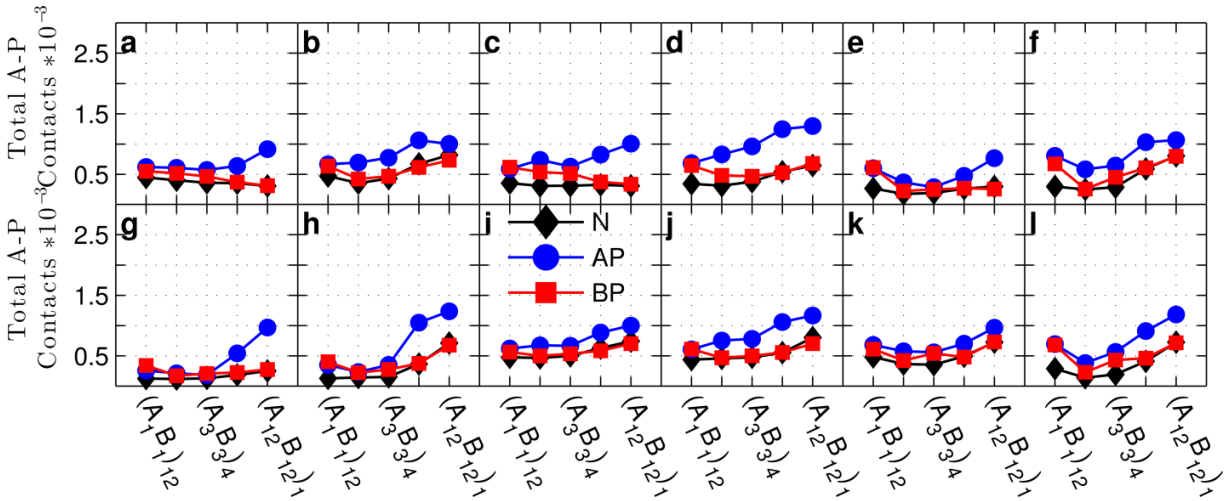

Figure S8: *Average number of A-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=4d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

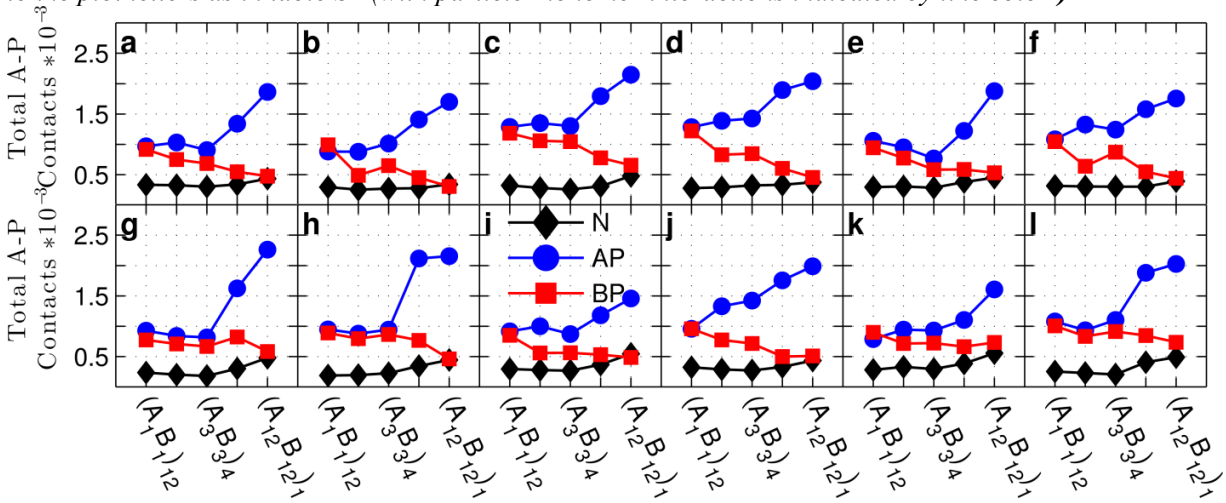

Figure S9: *Average number of A-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=12d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

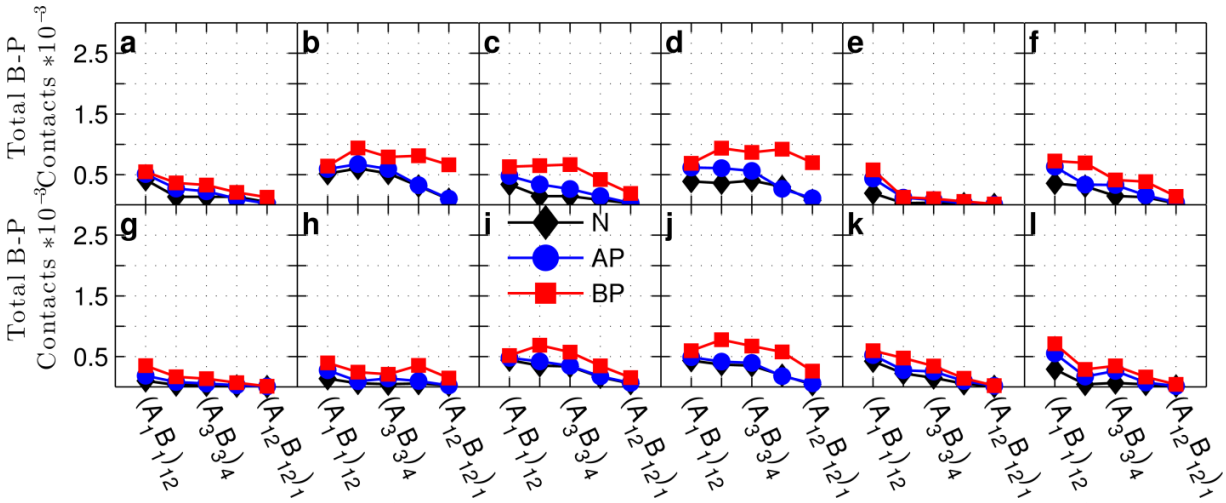

Figure S10: *Average number of B-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=4d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

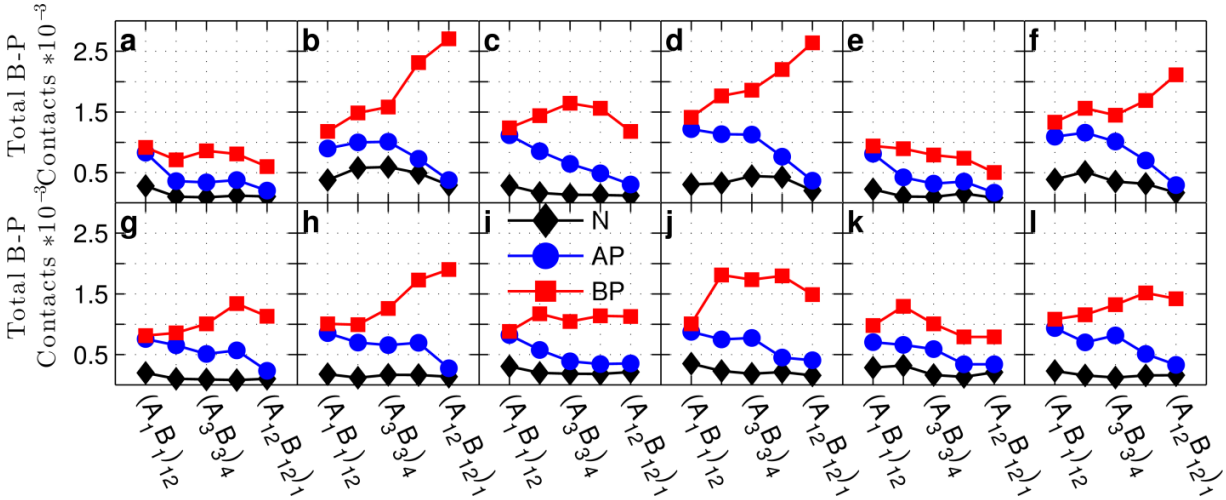

Figure S11: *Average number of B-particle contacts, including inter and intra particle, as a function of monomer sequence for copolymer grafted nanoparticles of D=12d each with six grafts of length Ngraft=24 with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

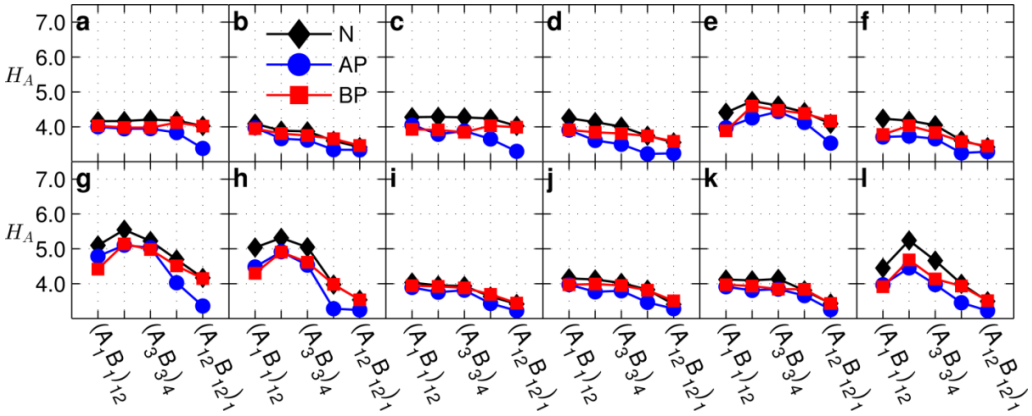

Figure S12: *Average height of an A-monomer as a function of monomer sequences for copolymer grafted nanoparticles of D=4d each with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

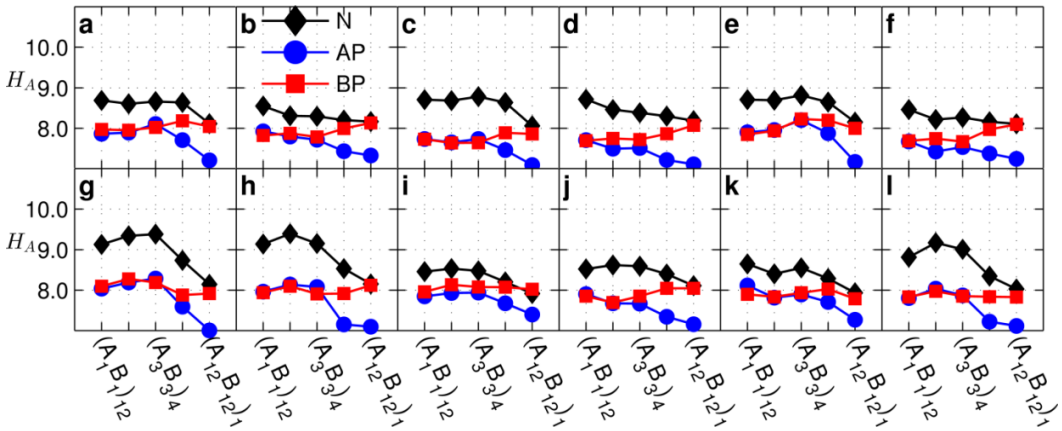

Figure S13: *Average height of an A-monomers as a function of monomer sequences for copolymer grafted nanoparticles of D=12d each with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

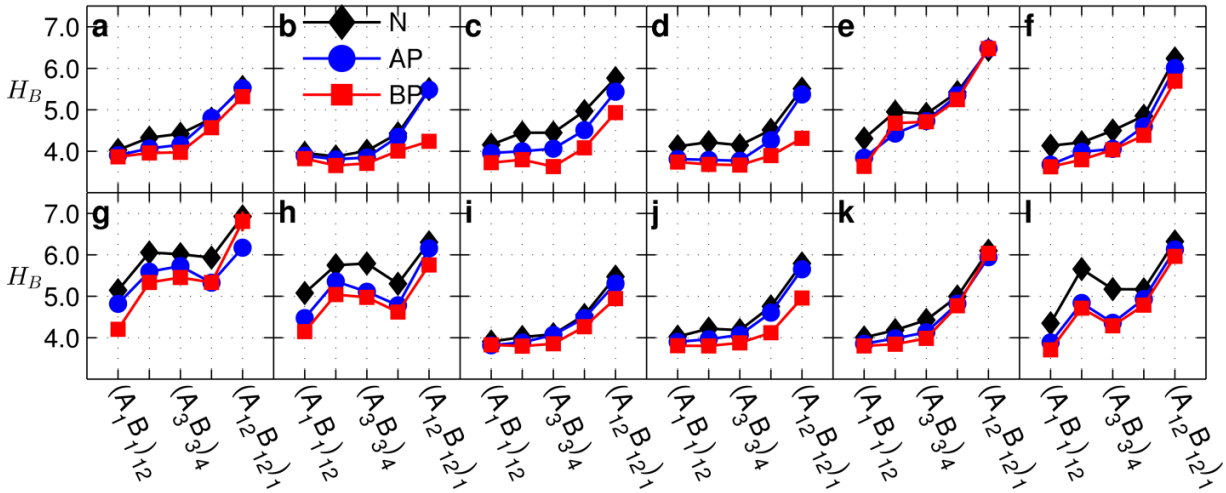

Figure S14: *Average height B-monomer as a function of monomer sequences for copolymer grafted nanoparticles of D=4d each with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

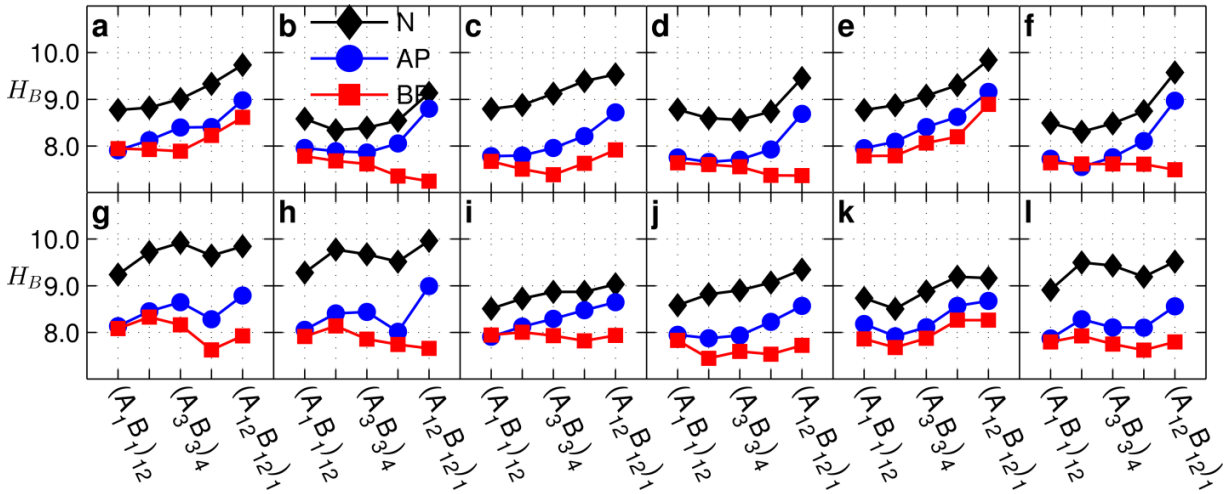

Figure S15: *Average height B-monomer as a function of monomer sequences for copolymer grafted nanoparticles of D=12d each with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). The system interactions correspond to the plot letters as in table S1 (with particle-monomer interactions indicated by line color)*

III. Discussion of Lattice Effects and the Alternating Sequence

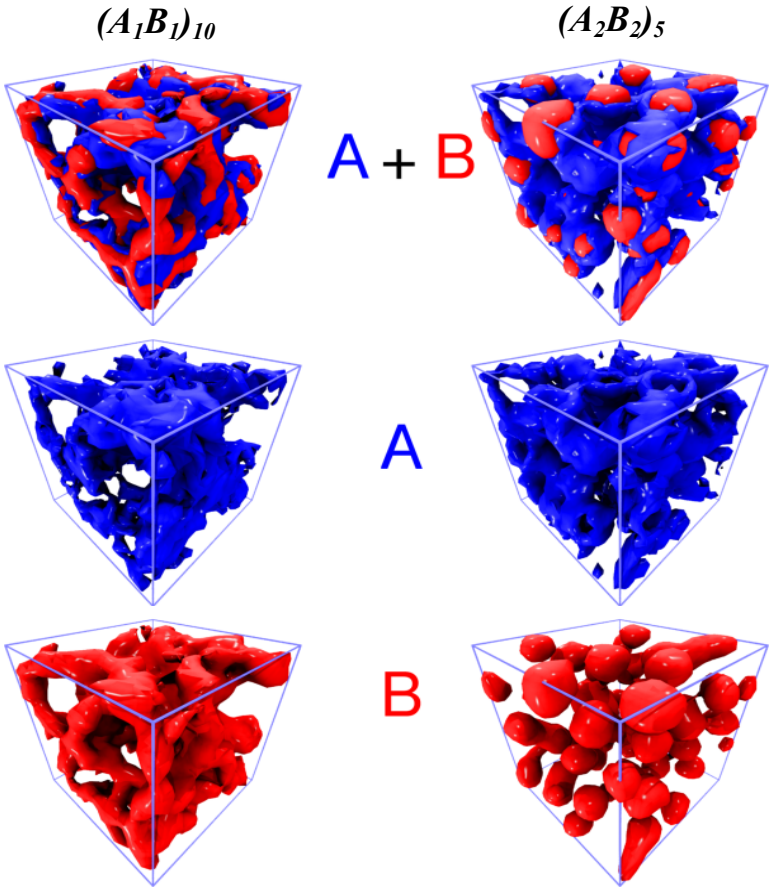

Figure S16: *Simulation snapshots from Brownian dynamics of ungrafted copolymers of sequence $(A_1B_1)_{10}$ (left) and $(A_2B_2)_6$ (right) represented as iso-surfaces of density equal to 0.3 monomers/d^3. The top row shows both A and B iso-surfaces together while the middle and bottom show iso-surfaces calculated from only A and only B monomers respectively. In both of these simulations, only the BB interactions are attractive and all others interactions are purely repulsive. The figures show that the $(A_2B_2)_5$ sequence produces distinct, homogeneous domains of attractive B monomers (right column bottom figure), the $(A_1B_1)_{10}$ sequence produces networked domains that span the simulation box (left column bottom figure).*

In order to alleviate concerns that the cubic lattice in our Monte Carlo (MC) simulations was biasing our results of monomer aggregation and domain shapes, specifically the unique behavior of $(A_1B_1)_{12}$, we have conducted short off-lattice Brownian Dynamics (BD) simulations of ungrafted copolymers. We have only done ungrafted copolymers here to focus the discussion on monomer-aggregation as a function of sequence, and not to mimic any nanoparticle assembly. We chose to run off-lattice BD simulations, as opposed to MC simulations, due to the availability of the open source HOOMD-blue platform[1,2], which allowed us to quickly build our simulations and then rapidly simulate using GPU accelerated computing.

The simulations consisted of 350 *ungrafted* copolymer chains of length $N = 20$ of either $(A_1B_1)_{10}$ or $(A_2B_2)_5$ sequence. The simulations progressed as follows. Initially, we modeled all interactions as purely repulsive Weeks-Chandler-Andersen (WCA) potentials. First, the system was integrated for 1e6 steps at T=5 and a volume fraction of $\phi = 0.029$ to remove any bias in the growth algorithm and "randomize" the system. The system was then compressed at T=5 to a volume fraction of $\phi = 0.23$ over a period of 2e6 time steps. At this point, the B-B interactions were switched to Lennard-Jones potentials with an attractive well depth of 3 while A-A and A-B interactions were maintained as WCA. After annealing the system using a linear gradient from T=5 to T=1 over 5e6 steps, we sampled our system and generated snapshots for 1e5 steps at T=1. We note that the energy profiles of the simulations were relatively constant during the sampling period.

Figure S16 shows snapshots from simulations of $(A_1B_1)_{10}$ (left) and $(A_2B_2)_5$ (right) copolymers with the B and A monomers hidden for the second and third rows respectively. The isosurfaces represent a density value of 0.3 monomers/d^3**. Similar to our results from MC simulations, we observe that while the $(A_2B_2)_5$ sequence produces distinct, homogeneous domains of attractive monomers, the $(A_1B_1)_{10}$ sequence produces networked domains that span the simulation box. These simulations support our conjecture that the alternating sequence is forced to assume networked morphologies due to the frustrating—ABAB—sequence both on and off lattice.**

[1] *HOOMD-blue web page: http://codeblue.umich.edu/hoomd-blue*

[2] *J. A. Anderson, C. D. Lorenz, and A. Travesset. General purpose molecular dynamics simulations fully implemented on graphics processing units Journal of Computational Physics 227(10): 5342-5359, May 2008. 10.1016/j.jcp.2008.01.047*

IV. Tabulated Data for the number of A and B Domains for D=4d and D=12d

Table S2: Number of A Domains for copolymer grafted nanoparticle of varying sequences and monomer interactions as specified in Table 1 and D=4d, Ngraft=24, and Ng=6. Note that all of these interaction sets are in the absence of particle monomer interactions.

	Interaction Set 1		Interaction Set 2		Interaction Set 3		Interaction Set 4		Interaction Set 5		Interaction Set 6	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	4.60	0.93	6.40	0.75	6.40	1.29	8.40	0.24	8.80	1.66	6.20	0.66
(A2B2)6	22.80	1.53	49.80	3.72	40.80	4.47	64.20	4.07	31.40	1.08	28.80	3.85
(A3B3)4	19.00	1.05	28.80	2.25	27.60	1.91	39.20	1.91	28.80	3.12	20.00	0.77
(A6B6)2	14.40	1.36	18.20	1.20	38.20	3.99	36.40	4.68	18.00	2.05	16.40	3.09
(A12B12)1	12.40	1.29	13.40	0.81	28.80	2.46	29.20	1.24	12.60	0.68	6.00	0.95
	Interaction Set 7		Interaction Set 8		Interaction Set 9		Interaction Set 10		Interaction Set 11		Interaction Set 12	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	18.40	1.96	94.40	2.62	28.00	2.30	118.60	4.06	7.80	0.97	20.00	2.00
(A2B2)6	94.60	3.14	279.40	3.84	234.40	3.27	326.80	2.18	73.40	4.08	263.80	3.62
(A3B3)4	66.20	2.08	194.60	2.09	144.20	3.15	218.80	1.24	52.20	2.35	157.60	4.51
(A6B6)2	23.00	0.95	57.80	2.46	75.80	2.13	98.40	1.69	32.20	1.80	43.00	2.47
(A12B12)1	13.00	0.45	13.00	0.32	35.00	1.92	38.00	1.14	16.60	0.40	11.40	0.75

Table S3: Number of B Domains for copolymer grafted nanoparticle of varying sequences and monomer interactions as specified in Table 1 and D=4d, Ngraft=24, and Ng=6. Note that all of these interaction sets are in the absence of particle monomer interactions.

	Interaction Set 1		Interaction Set 2		Interaction Set 3		Interaction Set 4		Interaction Set 5		Interaction Set 6	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	5.40	1.03	7.20	0.20	5.80	0.86	5.80	0.66	7.80	0.80	5.20	0.73
(A2B2)6	29.80	2.40	78.00	8.42	16.20	1.50	36.60	3.66	18.20	2.37	20.00	2.68
(A3B3)4	19.40	2.36	44.80	3.87	13.80	1.39	22.00	1.82	14.20	1.16	8.80	0.73
(A6B6)2	31.40	2.80	35.80	4.93	11.60	1.40	12.40	1.33	15.40	1.94	12.00	3.54
(A12B12)1	34.40	2.32	37.20	1.93	11.00	0.55	10.60	0.51	10.60	0.81	4.40	0.68
	Interaction Set 7		Interaction Set 8		Interaction Set 9		Interaction Set 10		Interaction Set 11		Interaction Set 12	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	27.00	1.48	119.20	3.57	17.00	1.30	98.20	1.83	6.60	1.17	23.20	2.89
(A2B2)6	235.20	4.16	315.60	2.01	81.20	4.04	289.80	3.34	55.00	3.99	258.60	4.38
(A3B3)4	154.00	1.82	215.40	1.25	44.20	0.58	189.80	2.65	34.80	0.97	159.20	2.91
(A6B6)2	73.40	2.27	102.60	1.86	19.20	1.32	33.40	1.29	21.20	1.59	25.20	1.32
(A12B12)1	42.80	0.80	47.00	1.05	14.80	1.16	13.60	0.87	13.40	1.03	9.20	0.37

Table S4: Number of A Domains for copolymer grafted nanoparticle of varying sequences and monomer interactions as specified in Table 1 and D=12d, Ngraft=24, and Ng=6. Note that all of these interaction sets are in the absence of particle monomer interactions.

	Interaction Set 1		Interaction Set 2		Interaction Set 3		Interaction Set 4		Interaction Set 5		Interaction Set 6	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	42.60	1.03	56.00	3.70	42.40	3.20	57.60	4.18	47.60	2.87	40.60	2.84
(A2B2)6	54.00	2.63	117.20	5.17	141.60	7.17	185.40	3.60	69.00	5.05	76.60	4.86
(A3B3)4	46.60	1.03	78.80	3.97	101.20	2.78	127.00	9.45	58.40	1.63	65.40	4.30
(A6B6)2	47.20	0.86	53.00	2.57	88.60	1.50	84.60	1.03	50.00	1.18	53.00	2.49
(A12B12)1	46.00	1.92	46.80	1.77	54.80	1.16	54.80	1.20	50.40	1.89	46.20	1.71
	Interaction Set 7		Interaction Set 8		Interaction Set 9		Interaction Set 10		Interaction Set 11		Interaction Set 12	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	69.60	1.57	112.40	3.22	95.40	2.06	139.00	2.28	40.00	1.41	94.00	2.55
(A2B2)6	103.20	4.43	292.80	2.82	274.20	3.71	316.00	2.59	119.20	3.29	279.00	3.96
(A3B3)4	80.00	1.14	203.80	2.06	194.20	3.32	225.80	1.28	106.80	4.57	196.00	1.92
(A6B6)2	51.20	0.80	88.40	3.63	107.00	1.18	111.60	1.21	61.00	1.10	78.40	1.86
(A12B12)1	47.60	1.29	48.60	0.75	57.00	0.84	57.40	0.81	49.20	1.69	49.80	2.22

Table S5: Number of B Domains for copolymer grafted nanoparticle of varying sequences and monomer interactions as specified in Table 1 and D=12d, Ngraft=24, and Ng=6. Note that all of these interaction sets are in the absence of particle monomer interactions.

	Interaction Set 1		Interaction Set 2		Interaction Set 3		Interaction Set 4		Interaction Set 5		Interaction Set 6	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	44.00	1.38	60.60	3.25	40.60	2.48	51.20	2.63	47.40	2.54	40.40	3.30
(A2B2)6	152.00	4.52	178.80	5.11	47.80	2.48	117.40	4.30	60.80	1.77	77.00	4.83
(A3B3)4	111.20	5.21	129.20	7.61	44.60	1.96	70.40	4.80	49.40	2.04	55.20	2.56
(A6B6)2	91.20	1.80	91.40	2.20	36.80	1.59	41.00	1.34	42.40	1.72	42.00	2.88
(A12B12)1	55.60	1.25	54.80	0.97	26.20	1.77	24.20	1.83	35.80	2.76	33.20	1.83
	Interaction Set 7		Interaction Set 8		Interaction Set 9		Interaction Set 10		Interaction Set 11		Interaction Set 12	
Sequence	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
(A1B1)12	91.80	3.26	138.00	2.28	66.60	2.36	110.60	3.47	39.40	1.63	91.80	4.07
(A2B2)6	271.40	5.19	320.40	1.50	96.20	4.93	284.20	2.58	108.60	2.32	273.40	1.12
(A3B3)4	204.20	1.53	224.40	1.60	64.60	0.60	201.40	1.54	78.40	2.54	188.40	2.62
(A6B6)2	110.20	1.77	115.00	1.26	40.80	1.28	64.80	1.24	45.80	1.59	59.40	1.96
(A12B12)1	57.40	0.81	57.60	0.68	26.00	2.21	27.00	0.89	32.00	1.87	29.80	2.58

V. Additional Results Showing Effect of Graft Length to Particle Size Ratio on Nanoparticle Assembly and Chain Conformations

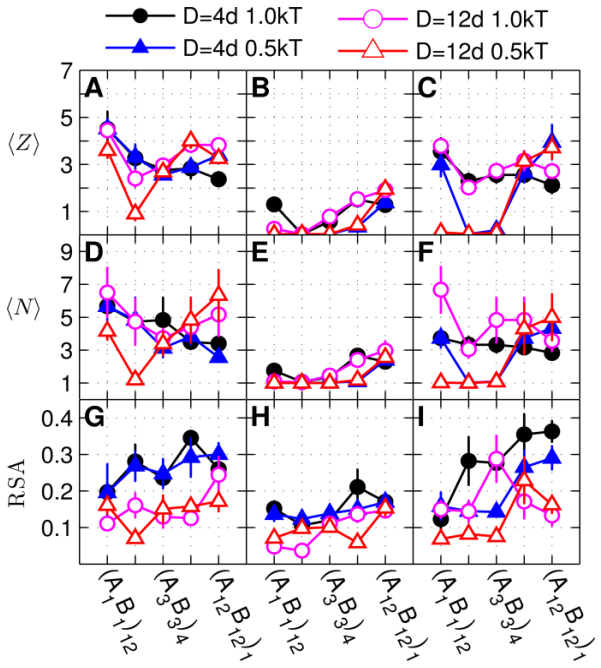

Figure S17: *Average coordination number* ⟨Z⟩ *, average number of particles per cluster* ⟨N⟩*, and relative shape anisotropy (RSA) as a function of monomer sequences for copolymer grafted nanoparticles of D=4d and D=12d each with six grafts of length N=24. The lines on plot a, d, and g correspond to interaction sets 3 (blue and red triangles) and 4 (black and magenta circles), lines on plot b, e, and h correspond to interaction sets 7 (blue and red triangles) and 8 (black and magenta circles), lines on plot c, f, and i correspond to interaction sets 11 (blue and red triangles) and 12 (black and magenta circles). The circles represent attractive monomer-monomer interactions at a strength of 1kT while the triangles represent 0.5kT. The filled symbols represent nanoparticles of size D=4d while open symbols represent interaction sets with nanoparticles of size d=12d.*

Figure 7 in the main manuscript presented the data ⟨Z⟩, ⟨N⟩, and RSA for three selected sets of system interactions and both D=4d and 12d. In Figure S16 we show the remaining interaction sets. For systems with B-B interactions in the absence of A-B repulsion (Figures S16 a,d,g), we observe very similar trends to the data for the systems with only A-A attractions (Figure 7a,d,g). The largest difference between the two interaction sets is that the dip at $(A_2B_2)_6$ for weak monomer-monomer attraction (solid red line) seems to be much more pronounced in the case of B-B attraction. The data for A-A attraction in the presence of A-B repulsion (Figure S16 b,e,h) shows that there is little effect from particle size on any of the assembly data. This is because the system is completely dispersed at low blockiness, where particle size has the greatest effect on assembly characteristics, and clusters only form at $(A_6B_6)_2$ and $(A_{12}B_{12})_1$ where we have already shown that particle size has the least effect. The final column in Figure S16 represents the data for systems with both A-A and B-B attraction along with A-B repulsion. Here we observe that particle size seems to only strongly affect ⟨Z⟩ and ⟨N⟩ at $(A_1B_1)_{12}$ where the trend in the data for weak monomer-monomer attraction and D=4d (solid blue line) deviates from the trend for weak monomer-monomer attraction and D=12d. This is mostly likely an artifact of the way that $(A_1B_1)_{12}$

aggregates attractive monomers (distributed networks) and it only affects D=4d because D=12d cannot form enough *intra-particle* contacts to form these networks of like monomers.

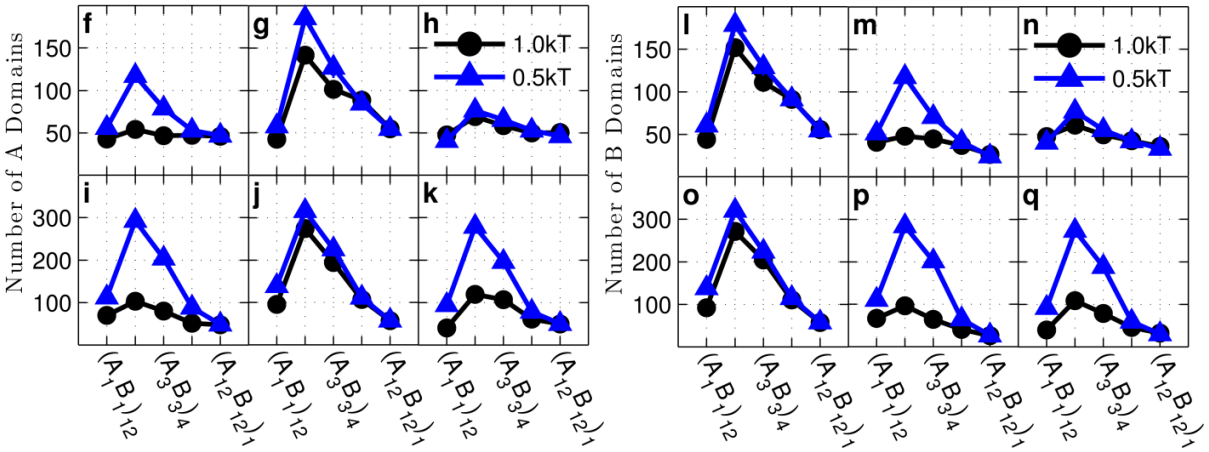

Figure S18: *(f-k) Plots showing the average number of A domains in a system for D=12d. (l-q) Plots showing the average number of B domains in a system. The system interactions correspond to the plot letters as follows: The system interactions correspond to the plot letters as follows: lines on plot f and l correspond to interaction sets 1 (blue triangles) and 2 (black circles), lines on plot g and m correspond to interaction sets 3 (blue triangles) and 4 (black circles), lines on plot h and n correspond to interaction sets 5 (blue triangles) and 6 (black circles), lines on plot i and o correspond to interaction sets 7 (blue triangles) and 8 (black circles), lines on plot j and p correspond to interaction sets 9 (blue triangles) and 10 (black circle), and lines on plot k and q correspond to interaction sets 11 (blue triangles) and 12 (black circles). The black circles represent attractive monomer-monomer interactions at a strength of 1kT while the blue triangles represent ttractive monomer-monomer interactions at a strength of 0.5kT*

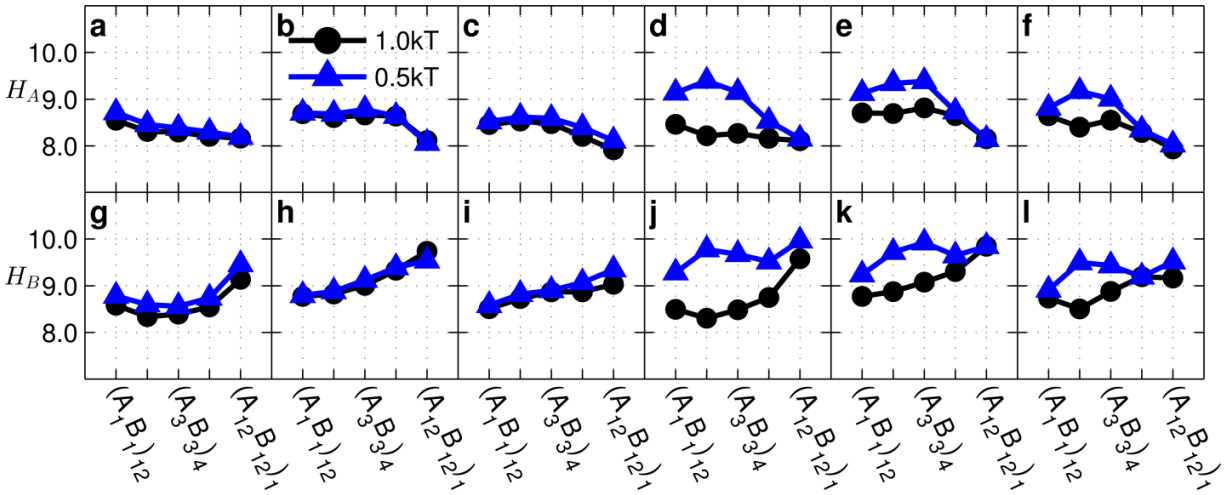

Figure S19: *Plots showing the average height of an A-monomer (top row) and B-monomer (bottom row) as functions of monomer sequences for copolymer grafted nanoparticles of D=12d each with six grafts of length N=24. The system interactions correspond to the plot letters as follows: lines on plot a and g correspond to interaction sets 1 (blue triangles) and 2 (black circles), lines on plot b and h correspond to interaction sets 3 (blue triangles) and 4 (black circles), lines on plot c and i correspond to interaction sets 5 (blue triangles) and 6 (black circles), lines on plot d and j correspond to interaction sets 7 (blue triangles) and 8 (black circles), lines on plot e and k correspond to interaction sets 9 (blue triangles) and 10 (black circles), and lines on plot f and l correspond to interaction sets 11 (blue triangles) and 12 (black circles). The black circles represent attractive monomer-monomer interactions*

at a strength of 1kT while the blue triangles represent attractive monomer-monomer interactions at a strength of 0.5kT.

VI. Effect of Monomer Sequence on Nanoparticle Arrangement in the Cluster for D=4d and D=12d with and without Monomer-Particle Interactions

In the main manuscript in Section III C, we presented a detailed analysis of the effect of particle-monomer interactions on the assembly of copolymer grafted nanoparticles. We found that particle monomer interactions had limited effect on the assembly characteristics of the system due to limitations on available nanoparticle surface area, conformational restrictions of making particle-monomer contacts, and an overall inferiority of monomer-particle contacts to monomer-monomer contacts (Supplementary Section VII). In order to keep the analysis concise and avoid redundant analysis, we focused on three particular systems for D=12d and discussed how these systems were affected by particle-monomer interactions. For posterity, on the following pages we present here in our complete data set of data on $\langle Z \rangle$, $\langle N \rangle$, $\langle R^2_{g,cluster} \rangle^{0.5}$, RSA for D=4d and D=12d. These data support the conclusions discussed in the main article, therefore we will not provide any further analysis on them.

In the following figures the system interactions correspond to the plot letters as listed in Table S1 (with particle-monomer interactions indicated by line color).

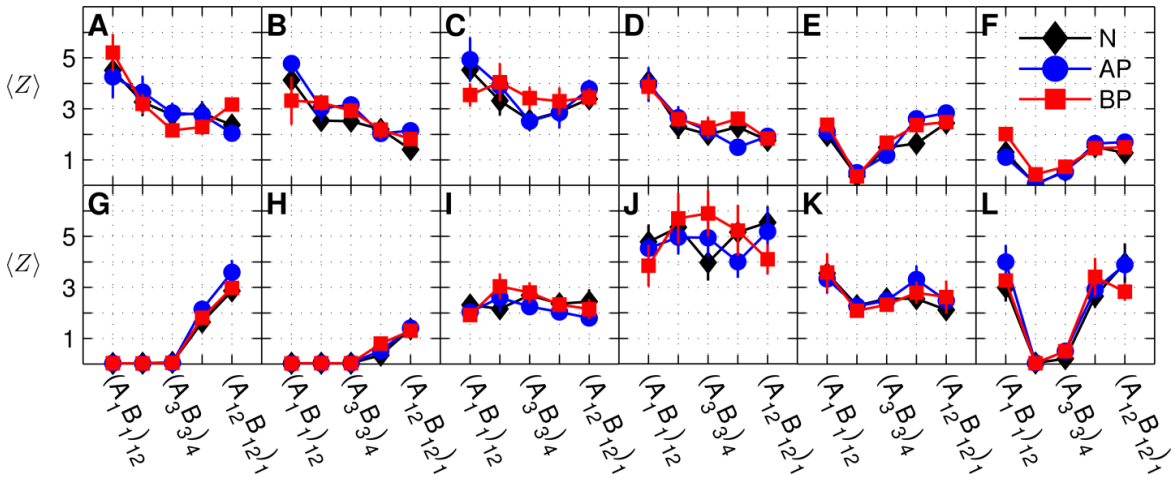

Figure S20: *Average coordination number ⟨Z⟩ as a function of monomer sequences for copolymer grafted nanoparticles of D=4d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

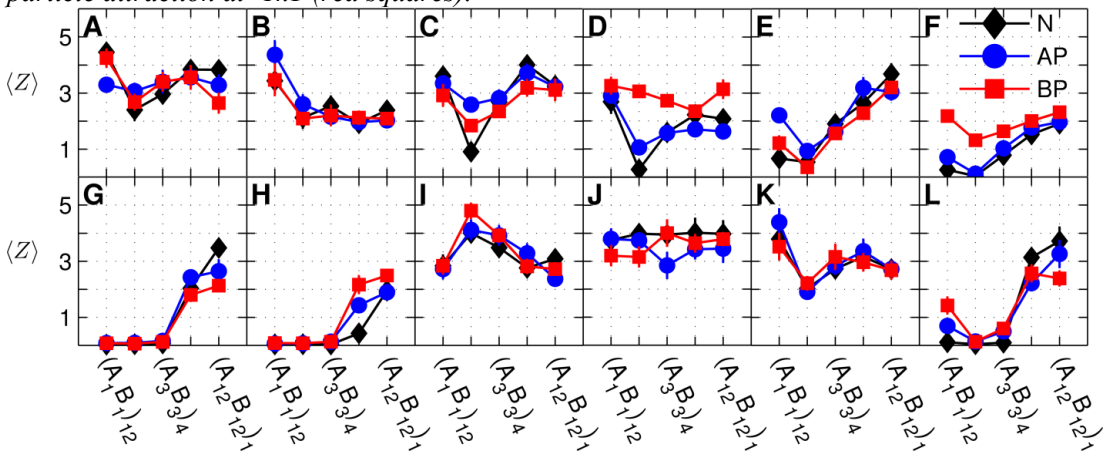

Figure S21: *Average coordination number ⟨Z⟩ as a function of monomer sequences for copolymer grafted nanoparticles of D=12d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

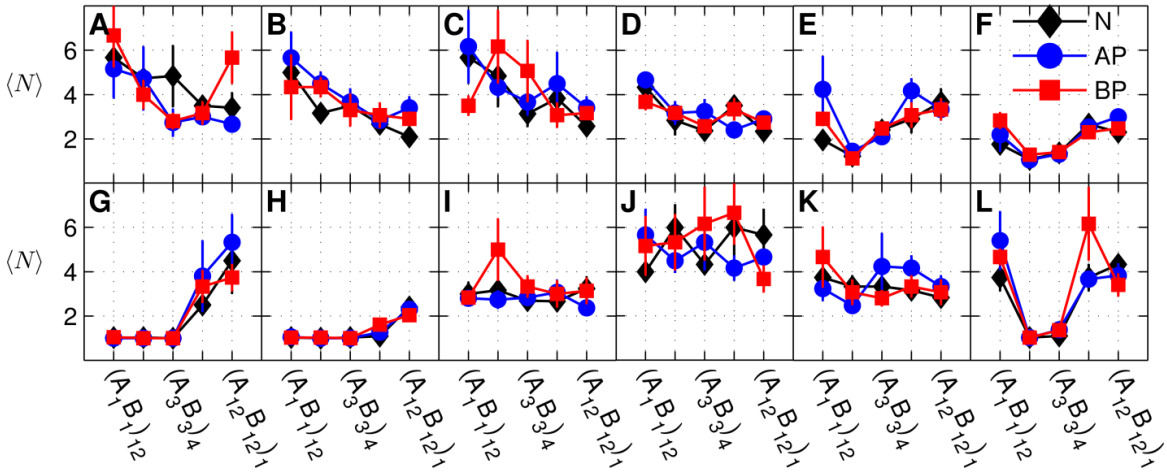

Figure S22: *Average number of particles per cluster* ⟨N⟩ *as a function of monomer sequences for copolymer grafted nanoparticles of D=4d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

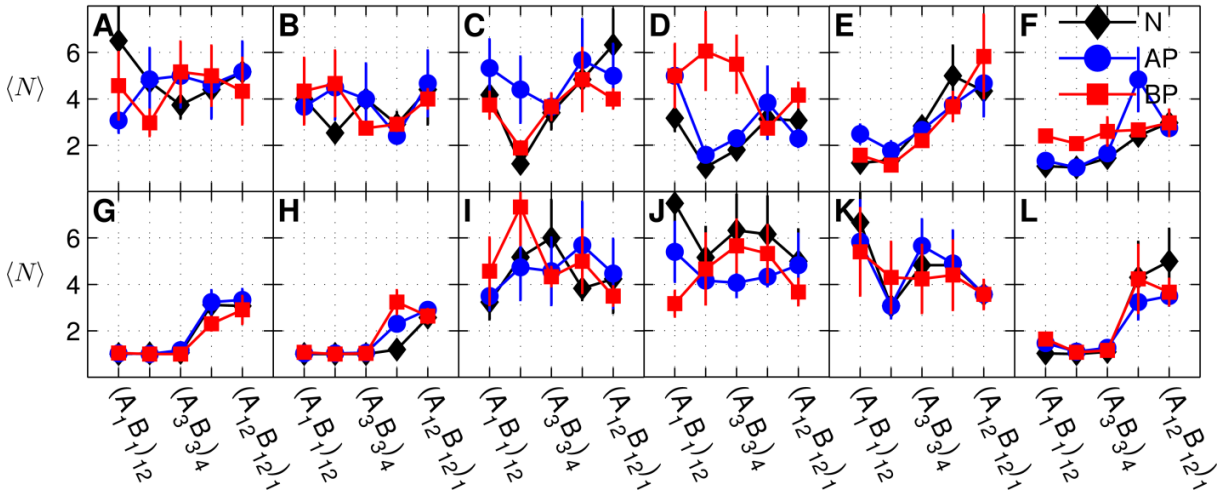

Figure S23: *Average number of particles per cluster* ⟨N⟩ *as a function of monomer sequences for copolymer grafted nanoparticles of D=12d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

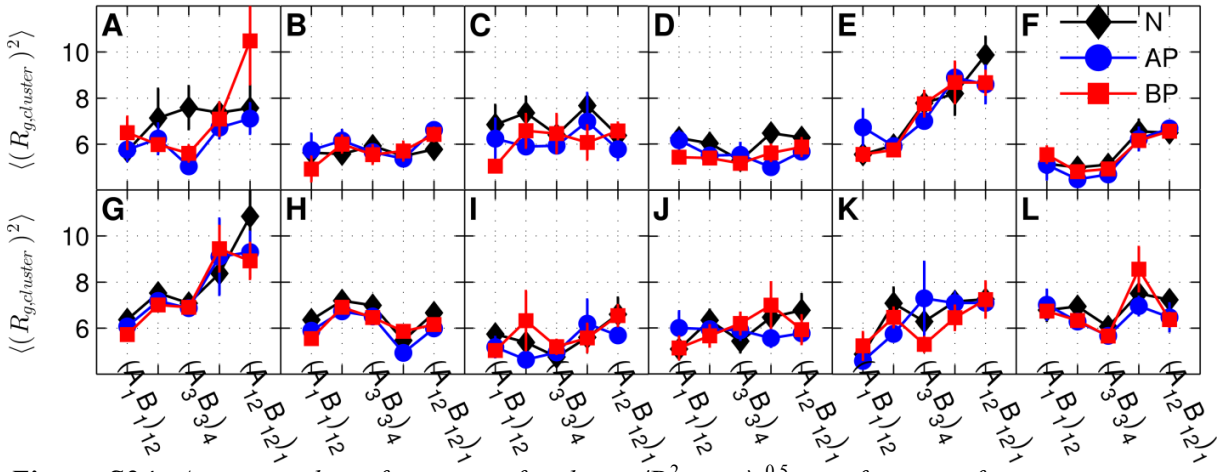

Figure S24: *Average radius of gyration of a cluster* $\langle R^2_{g,cluster} \rangle^{0.5}$ *as a function of monomer sequences for copolymer grafted nanoparticles of D=4d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

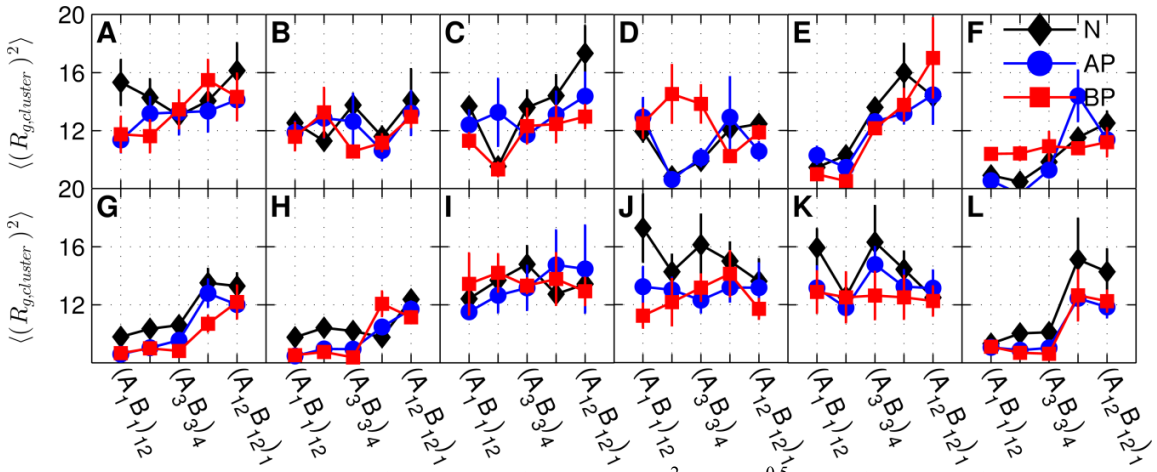

Figure S25: *Average radius of gyration of a cluster* $\langle R^2_{g,cluster} \rangle^{0.5}$ *as a function of monomer sequences for copolymer grafted nanoparticles of D=12d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares). to interaction set 12, and lines on plot L correspond to interaction set 11.*

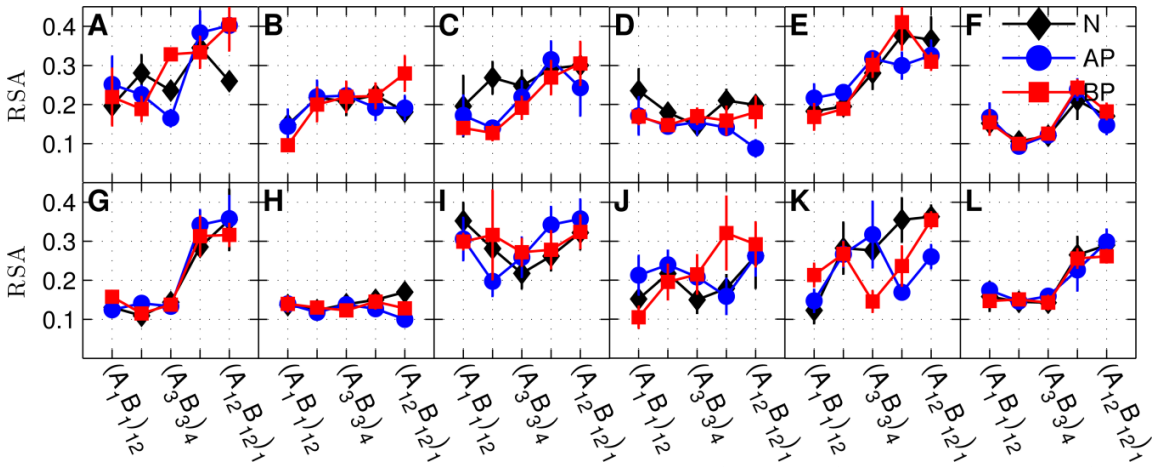

Figure S26: *Average relative square anisotropy (RSA) as a function of monomer sequences for copolymer grafted nanoparticles of D=4d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

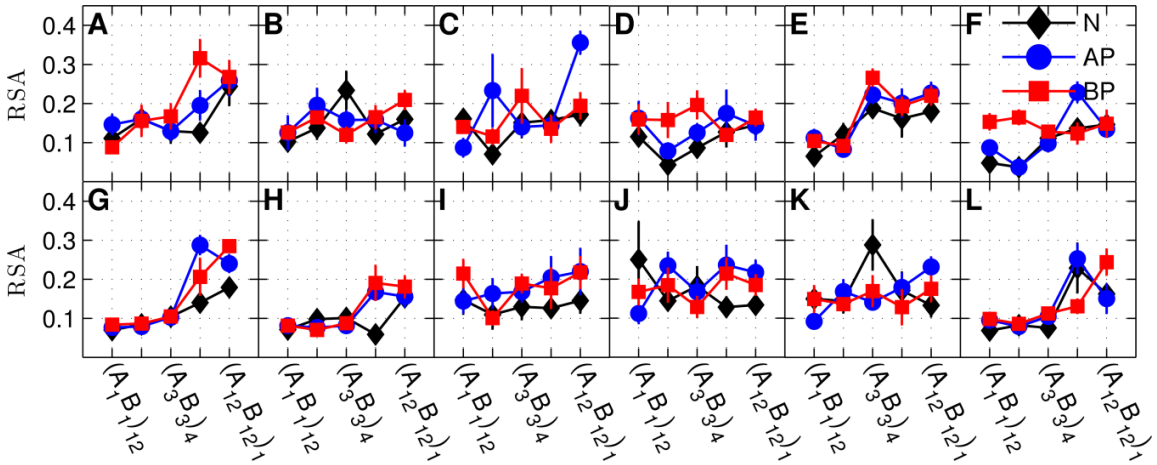

Figure S27*: Average relative square anisotropy (RSA) as a function of monomer sequences for copolymer grafted nanoparticles of D=12d with six grafts of length N=24 for systems with no particle monomer interactions (black diamonds), A-monomer to particle attraction at -1kT (blue circles), and B-monomer to particle attraction at -1kT (red squares).*

VII. Relative Strength of Monomer-Particle and Monomer-Monomer Interactions for D-4d and D=12d

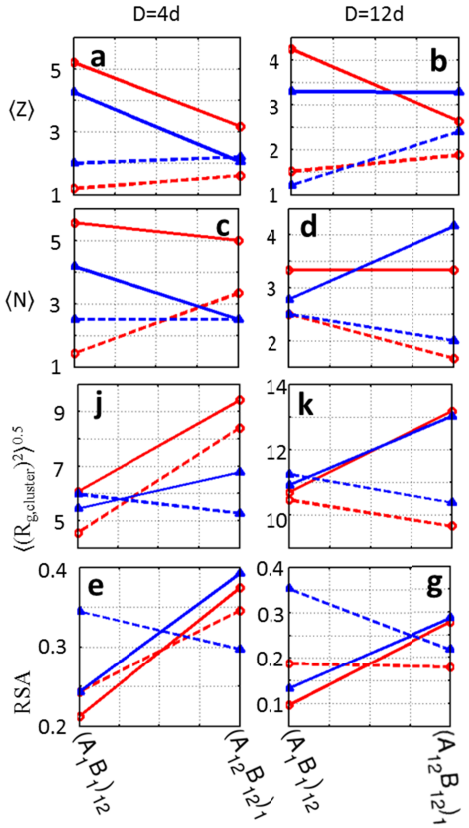

Figure S28: *Average coordination number (⟨Z⟩), average number of particles per cluster (⟨N⟩), average cluster radius of gyration* $\langle R^2_{g,cluster} \rangle^{0.5}$*, and relative square anisotropy (RSA) as a function of monomer sequences for copolymer grafted nanoparticles of D=4d (left column) and D=12d (right column) each with six grafts of length N=24. The solid blue lines represent a system where A-A attraction is 1kT and A-particle attraction is 1kT. The dashed blue lines represent a system where A-A attraction is 1kT and A-particle attraction is 16kT. The solid red lines represent a system where B-B attraction is 1kT and B-particle attraction is 1kT. The dashed red lines represent a system where B-B attraction is 1kT and B-particle attraction is -16kT.*

In the main manuscript in section III C, we described the effect of particle-monomer interactions on the assembly of copolymer grafted nanoparticles. We concluded that the effect of these interactions on nanoparticle assembly is minimal due to the limited surface area on particles of size D=4d and 12d, but there is also an effect from the 2-dimensional nature of particle-monomer contacts versus 3-dimensional nature of monomer-monomer contacts. In a polymer grafted particle, while a grafted monomer can have many monomer-monomer interacting neighbors within the square well width of √2d each monomer can only have one particle-monomer interaction within the square well depth of (D+d)/2. When we compare systems with monomer-monomer interactions that are equal in magnitude to particle-monomer interactions (Figure 8a,b) with systems with monomer-monomer interactions that are half the magnitude of particle-monomer interactions (Figure 8c,d) we are effectively "doubling" the particle-monomer interaction strength. Because the number of possible monomer-monomer contacts is still significantly higher than particle-monomer contacts, we still do not observe an appreciable increase in the effect of particle-monomer interactions on characteristics of the assembled cluster.

In our lattice model, to make the particle-monomer contacts to significantly affect the assembly, the monomer-monomer epsilons ($\varepsilon_{AB}, \varepsilon_{AA}, \varepsilon_{BB}$) would have to be approximately 1/16 of the particle-monomer epsilons ($\varepsilon_{BP}, \varepsilon_{AP}$). This large increase in interaction strength effectively makes one *particle-monomer* contact equal to 16 *monomer-monomer* contacts, therefore approximately equating their enthalpic potential. In Figure S28 we present data for ⟨Z⟩, ⟨N⟩, $\langle R^2_{g,cluster}\rangle^{0.5}$, and RSA at both D=4d (left column) and D=12d (right column) for both $(A_1B_1)_{12}$ and $(A_{12}B_{12})_1$ that compares the effect of particle monomer interactions at a strength of 1kT (solid lines) and 16kT (dashed lines). We observe a drastic increase in the effect of particle monomer interactions for all of the data, especially for D=12d. In particular, nearly all of the trends in the data from $(A_1B_1)_{12}$ to $(A_{12}B_{12})_1$ are reversed when the particle monomer-interactions are raised from -1kT to -16kT. These data demonstrate that particle-monomer interactions have the potential to dramatically affect the assembly of copolymer grafted nanoparticles, but they must have extremely large interaction strengths in order to do so.