Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effect of Surface Coverage and Chemistry on Self-Assembly of Monolayer Protected Gold Nanoparticles: A Molecular Dynamics Simulation Study

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Supporting Information

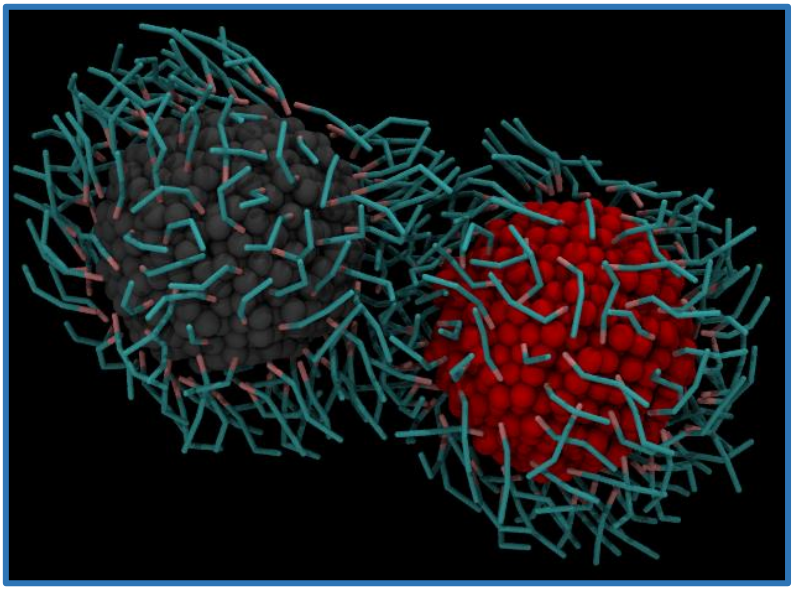

Figure S1. Entanglement between thiol chain on neutral thiol coated gold nanoparticles (AuNP) with 100% surface coverage at closest distance considered in Potential of Mean force Calculation. The nanoparticle is represented in gray and red colors in Vdw style, Sulphur atom is in pink and the Carbon chain is shown in cyan. Images are obtained using VMD Software[1]

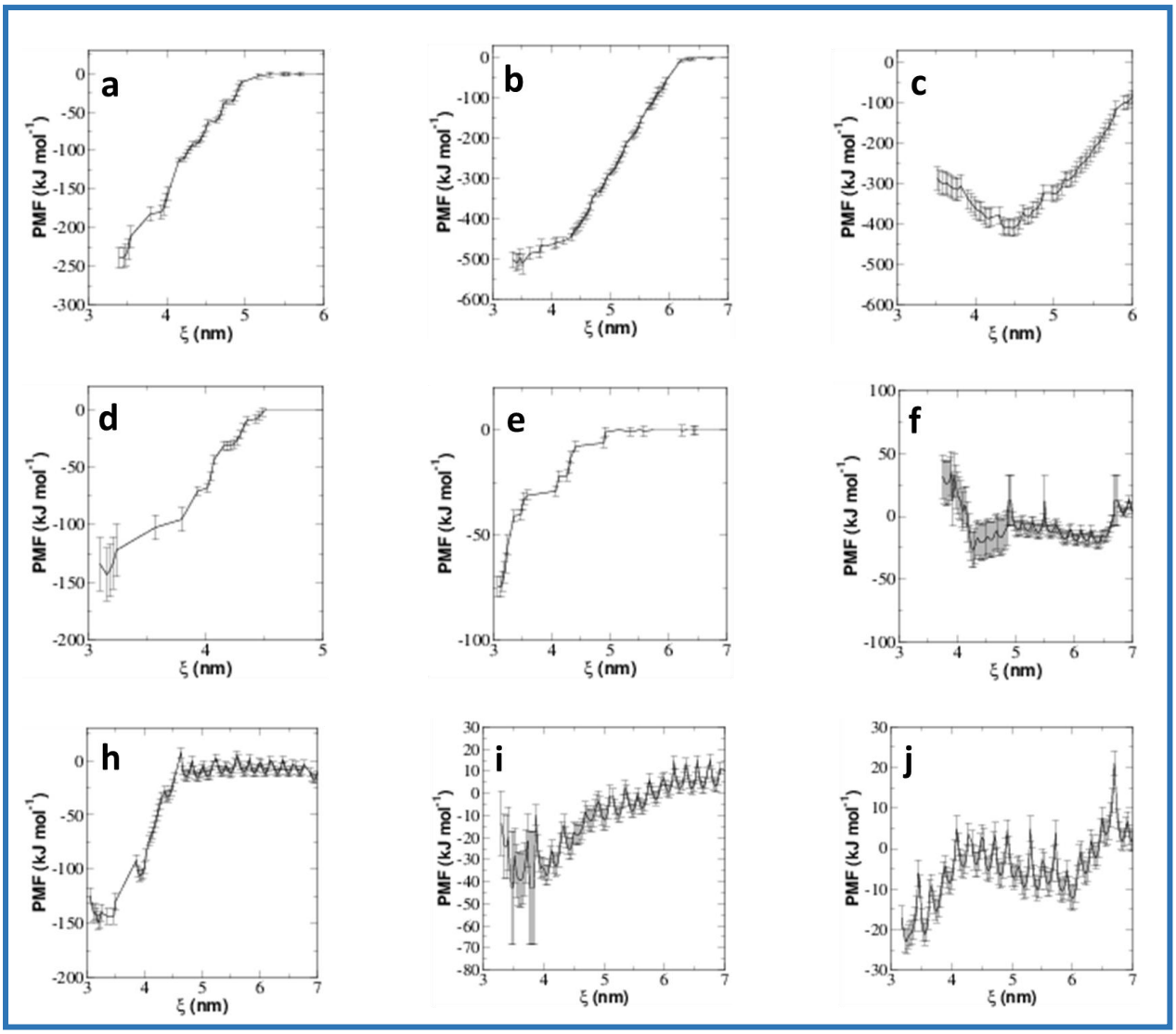

Figure S2. Potential of Mean Force (with error bars obtained using Boot-Strapping) between two nanoparticles in aqueous medium for, a-c – Neutral thiol coated AuNP with 20, 60 and 100 % surface coverage respectively, d-f – Cationic thiol coated AuNP with 20, 60 and 100 % surface coverage respectively, and, h-j – Anionic thiol coated AuNP with 20, 60 and 100 % surface coverage respectively

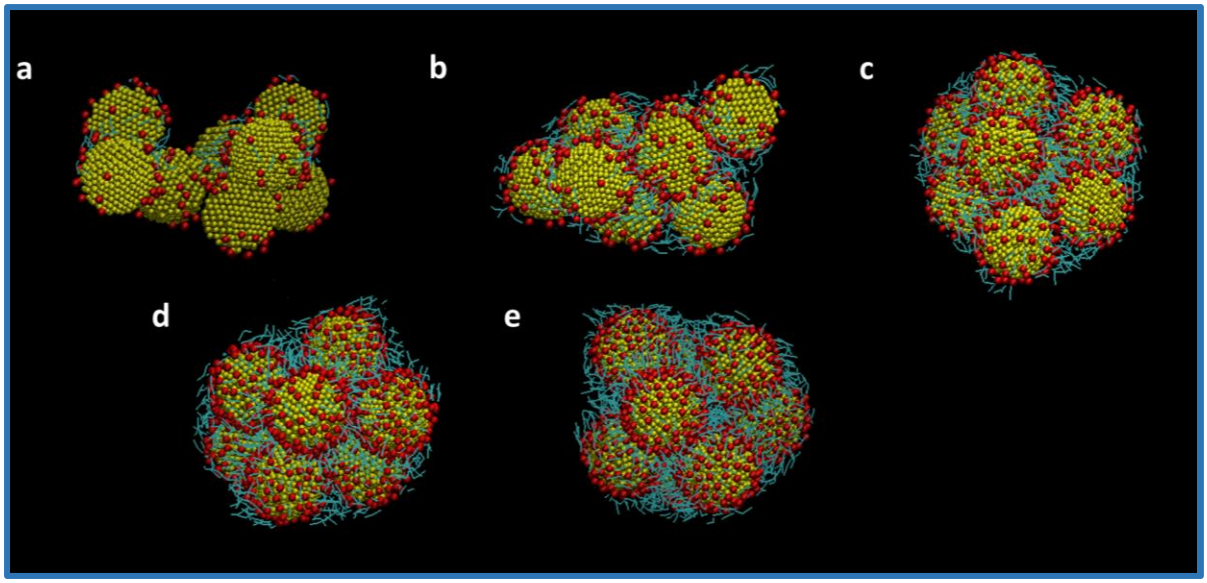

Figure S3. Structures of the 8 AuNP system formed at the end of 500 ns of simulation for neutral thiol coated AuNP with a. 20%, b. 40%, c. 60%, d. 80% and e. 100% surface coverage respectively. The nanoparticle is represented in yellow in Vdw style, Sulphur atom is in red and the Carbon chain is shown in cyan. Images are obtained using VMD Software[1]

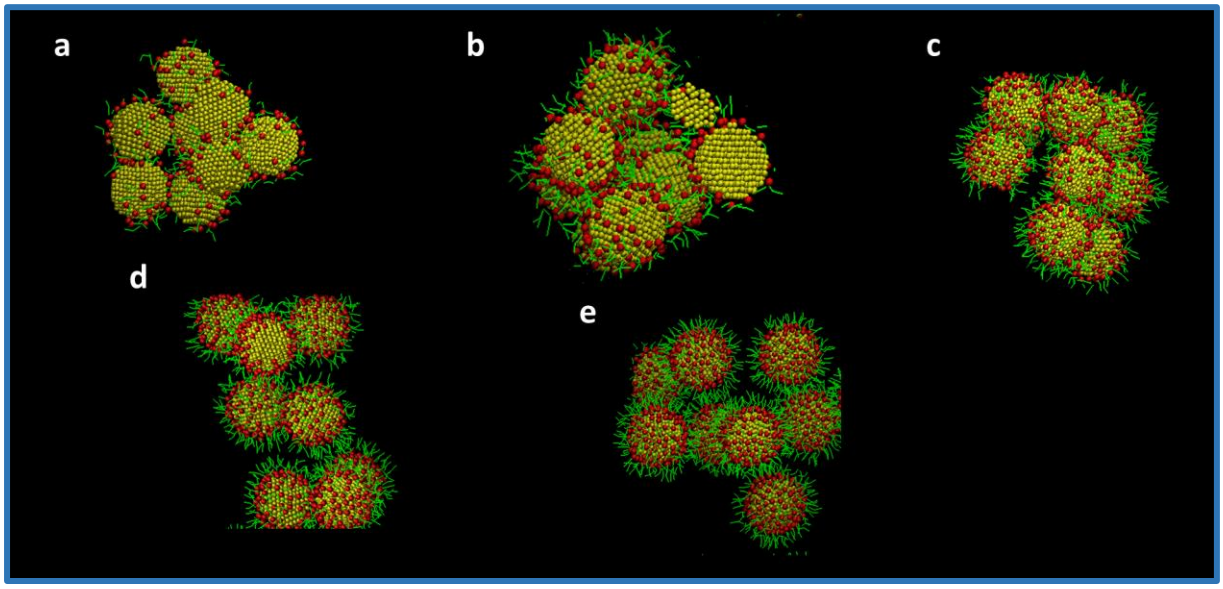

Figure S4. Structures of the 8 AuNP system formed at the end of 500 ns of simulation for cationic thiol coated AuNP with a. 20%, b. 40%, c. 60%, d. 80% and e. 100% surface coverage respectively. The nanoparticle is represented in yellow in Vdw style, Sulphur atom is in red and the Carbon chain is shown in green. Images are obtained using VMD Software[1]

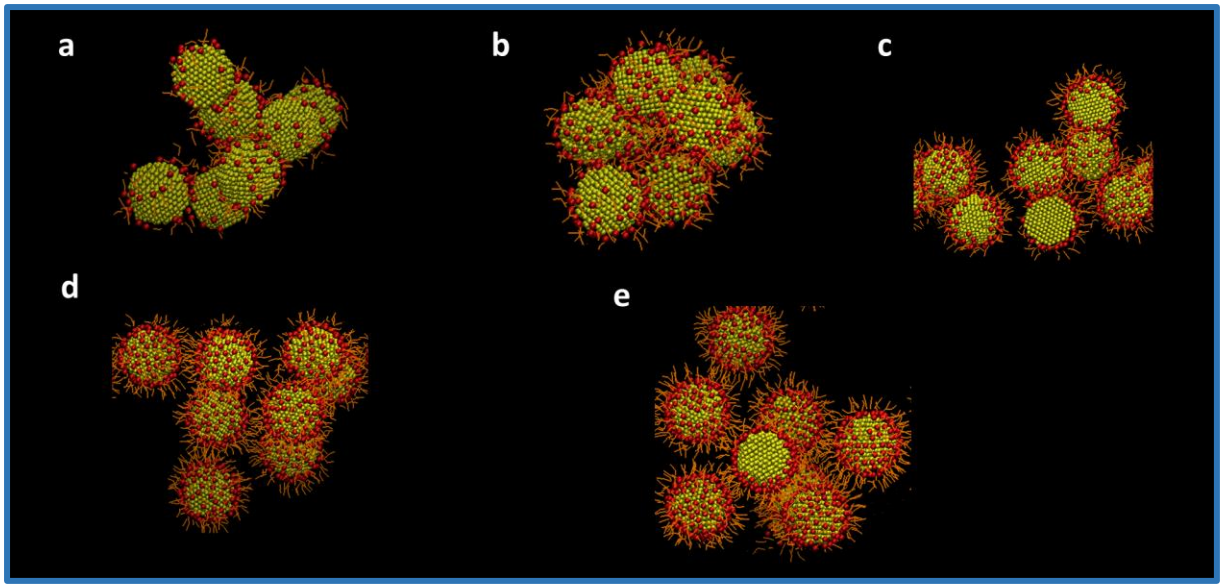

Figure S5. Structures of the 8 AuNP system formed at the end of 500 ns of simulation for anionic thiol coated AuNP with a. 20%, b. 40%, c. 60%, d. 80% and e. 100% surface coverage respectively. The nanoparticle is represented in yellow in Vdw style, Sulphur atom is in red and the Carbon chain is shown in red. Images are obtained using VMD Software[1]

System Details and Forcefield Information:

The number of ligands at different densities are shown in Table S1.

Table S1: System Details

Surface Coverage Percentage	Number of Ligands
20	29
40	60
60	89
80	120
100	147

Figure S6 shows a schematic of the Coarse Grained (CG) model used in our simulations. For the sake of clarity, only one thiol chain is shown in the figure. This mapping scheme is based on MARTINI forcefield and more details on the types of beads can be found in the original publication[2-3]. Thiol coated AuNP were modelled using parameters taken from earlier simulation studies[4-7]. The Dodecane Thiol (DDT) chains were modelled using a 4:1 mapping (4 CH_x (x=2 or 3) entities form 1 bead), while Sulphur (S) and Gold (Au) atoms were modelled

using a 1:1 mapping. Au was modelled using bead type of C5, while sulphur was modelled using a N0 bead. The terminal DDT bead was modelled using a C1 bead in neutral thiol coating, while a Qda bead with a charge of +1 and -1 was used in case of Anionic and Cationic charged coatings respectively. Table S2 shows the bonded parameters used between different beads in our simulation.

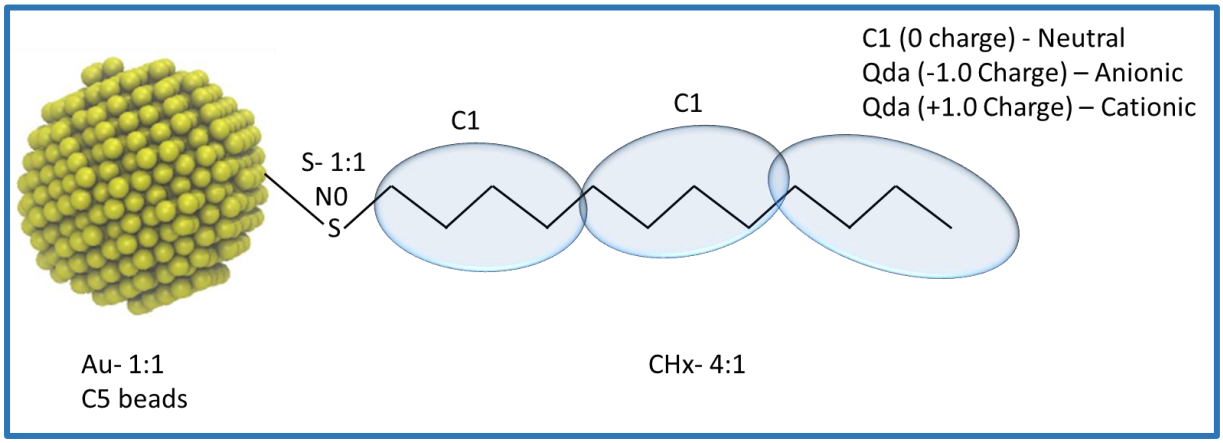

Figure S6. Schematic showing Mapping of AuNP with different thiol coatings. For the sake of clarity, only one ligand is shown. AuNP is made of Au beads that were represented by C5 bead type of Martini, with a 1:1 Mapping. Sulphur is represented with a N0 type bead in a 1:1 mapping, while the carbons were mapped using 4 heavy Carbon atoms to 1. The Terminal Carbon atoms were represented by C1 (0 Charge), Qda (-1 Charge) and Qda (+1 Charge) in the cases of neutral, anionic and cationic thiol coating systems respectively, while all other carbons are represented using a C1 type bead.

Table S2. Bonded parameters used in our simulations

Bonds			
	Bead types	b_o (nm)	K_b (KJ/mol nm^2)
b1	C5-C5	0.288	1250
b2	C5-N0	0.450	34500
b3	N0-C1	0.445	1250
b4	C1-C1/C1-Qda	0.470	1250
Angles			
		θ_o (deg)	K_θ (KJ/ mol)
a1	C5-N0-C1/N0-C1-C1/C1-C1-C1/C1-C1-Qda	180	25

References:

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2. Marrink SJ, De Vries AH, Mark AE. Coarse grained model for semiquantitative lipid simulations. The Journal of Physical Chemistry B. 2004 Jan 15;108(2):750-60.

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4. Lin J, Zhang H, Chen Z, Zheng Y. Penetration of lipid membranes by gold nanoparticles: insights into cellular uptake, cytotoxicity, and their relationship. ACS nano. 2010 Aug 27;4(9):5421-9.

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