

Supplementary Material (ESI) for Soft Matter.  
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## Supporting Information for:

# Understanding binary interactions of noble metal and semiconductor nanoparticles

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## S1 Potential parameters

**Tab. S1** Lennard-Jones (12-6 LJ) and electrostatic parameters of non-bonded interactions for Au and CdSe nanoparticles in vacuum and *n*-hexane.

Atoms	$\epsilon$ (kJ mol <sup>-1</sup> )	$\sigma$ (Å)	$q$ (e)	Refs.
Au	3.2288	2.737	0	[1, 2]
Cd	0.1397	1.98	+1.18	3
Se	0.1239	5.24	-1.18	3
H-(N)	0	0	+0.356	4
N	0.9229	3.34	-0.892	4
SH	1.6629	4.45	0	[1, 2]
CH <sub>2</sub> -(N)	0.3825	3.95	+0.18	4
CH <sub>2</sub>	0.3825	3.95	0	4
CH <sub>3</sub>	0.8148	3.75	0	4

**Tab. S2** Parameters of bonded interactions for passivating ligands (alkanethiols and alkylamines) and hexane solvent. Inter-molecular bonds are modeled using the harmonic stretching potential;  $U(r) = (1/2k_r)(r - r_0)^2$ , where  $k_r$  is the force constant and  $r_0$  is the equilibrium bond length. Bond angles are modeled using the harmonic bending potential;  $U(\theta) = (1/2k_\theta)(\theta - \theta_0)^2$ , where  $k_\theta$  is the force constant and  $\theta_0$  is the equilibrium bond angle. Torsional interactions are modeled using one of a set of cosine series potential given by;  $U(\phi) = a_0 + \sum_{i=1}^6 a_i \cos(i\phi)$ , and  $U(\phi) = 1/2A_1(1 + \cos(\phi)) + 1/2A_2(1 - \cos(2\phi)) + 1/2A_3(1 + \cos(3\phi))$ , where  $a_0, a_i, A_1, A_2, A_3$  are constants and  $\phi$  is the current dihedral angle. The gold-sulfur interaction is modeled using the pair additive Morse potential;  $U(r) = D_e((1 - \exp(-k(r - r_e)))^2 - 1)$ , where  $r_e$  is the equilibrium distance,  $D_e$  is the well depth, and  $k$  controls the width of the potential.

Interaction	Interacting group	Potential parameters <sup>a</sup>	Refs.
Bond Stretch	H-N	$k_r = 3631.71, r_0 = 1.010$	[4, 5]
	CH <sub>2</sub> -N	$k_r = 3196.58, r_0 = 1.448$	[4, 5]
	CH <sub>2</sub> -SH	$k_r = 2242.62, r_0 = 1.820$	[4, 5]
	CH <sub>2</sub> -CH <sub>x</sub>	$k_r = 2242.62, r_0 = 1.540$	[4, 5]
Bond Bending	H-N-H	$k_\theta = 365.088, \theta_0 = 106.4$	4
	CH <sub>2</sub> -N-H	$k_\theta = 519.654, \theta_0 = 112.9$	4
	CH <sub>2</sub> -CH <sub>2</sub> -N	$k_\theta = 470.599, \theta_0 = 109.5$	4
	CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>x</sub> /SH	$k_\theta = 519.654, \theta_0 = 114.0$	4
Bond Torsion	CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>x</sub> /SH	$A_1 = 5.9038, A_2 = -1.1339$ $A_3 = 13.1588$	4
	CH <sub>2</sub> -CH <sub>2</sub> -N-H	$a_0 = 1.58, a_1 = 0.40, a_2 = 0.87$ $a_3 = -0.87, a_4 = 0, a_5 = 0, a_6 = 0$	4
	CH <sub>x</sub> -CH <sub>2</sub> -CH <sub>2</sub> -N	$a_0 = 3.64, a_1 = 4.00, a_2 = 1.25$ $a_3 = -0.96, a_4 = -4.74 \times 10^{-3}$ $a_5 = 6.65 \times 10^{-4}, a_6 = -8.31 \times 10^{-5}$	4
Morse	Au-SH	$D_e = 38.6, k = 1.3, r_e = 2.9$	1

<sup>a</sup>The units of distance are in Angstrom, angles in degrees and energy in kJ/mol.

## S2 Thermal relaxation of CdSe cores and binding energy of alkylamine ligand

In the present section, we discuss the structure of thermally relaxed CdSe nanocrystals and their passivation with alkylamine ligands. To verify the force field, we reproduced the binding energy of single hexylamine ligand to the CdSe nanocrystals as reported by Schapotschnikow et al<sup>6</sup>. The initial structures of CdSe nanocrystals were generated by cutting out a sphere of given radius from the bulk wurtzite lattice of CdSe material<sup>7</sup>. Atoms at the surface with single neighbor were removed using a VMD tcl script and the structure was accepted only if the number of Cd and Se atoms were equal in the nanocrystal. Through this, five nanocrystals (CdSe)<sub>102</sub>, (CdSe)<sub>270</sub>, (CdSe)<sub>362</sub>, (CdSe)<sub>891</sub> and (CdSe)<sub>1541</sub> were generated with diameters ranging between 2.2-5.5 nm. For thermal relaxation, the initial structures of these nanocrystals were equilibrated for 3.0 ns at 450 K and gradually cooled back to 300 K in steps of 25 K, 0.1 ns. The simulations were performed in NVT ensemble without using the periodic boundary conditions. The electrostatic interactions were calculated using direct coulomb sum choosing the interaction cutoff 10 Å larger than the diameters of CdSe nanocrystals. To get an estimate of the binding energy for hexylamine

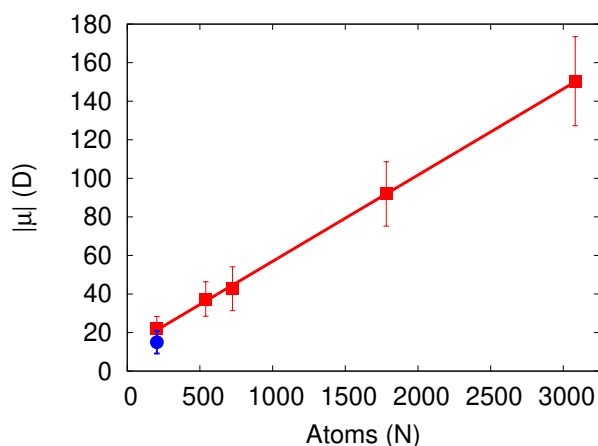
**Tab. S3** Initial diameter ( $d_0$ ), radius of gyration ( $R_g$ ), asphericity ( $A_s$ ), and the average binding energy ( $U_B$ ), of single hexylamine ligand for thermally relaxed CdSe nanocrystals at 300 K.

(CdSe) <sub>n</sub>	$d_0$ (nm)	$R_g$ (Å)	$A_s$	$U_B$ (kJ mol <sup>-1</sup> )
n = 102	2.20	8.86	$1.53 \times 10^{-2}$	82.74
270	3.09	12.11	$2.41 \times 10^{-3}$	89.62
362	3.40	13.34	$2.11 \times 10^{-4}$	85.62
891	4.59	18.07	$1.32 \times 10^{-4}$	86.94
1541	5.45	21.61	$8.79 \times 10^{-5}$	88.64

ligand, we performed 30 sets of simulations for each thermally relaxed nanocrystals by randomly placing a single ligand near the surface. Each initial configuration was equilibrated for 0.1 ns followed by data collection at every 10 steps for 0.2 ns. The binding energy was computed as the sum of coulombic and Lennard-Jones interactions between the ligand and nanocrystal atoms<sup>6</sup>.

Table S3 reports the radius of gyration,  $R_g$ , asphericity parameter,  $A_s$ , and the binding energy,  $U_B$ , of hexylamine ligand for all CdSe cores.  $d_0$  is the initial diameter, which was used to cut out the nanocrystal from the bulk CdSe lattice. It is instructive to remember that the  $R_g$  of a solid sphere relates the diameter as;  $R_g = 0.15^{1/2}d_0$ . The value of  $R_g$  of each nanocrystal is less than the

value of  $0.15^{1/2}d_0$ , which suggests that nanocrystals undergo significant structural reconstruction during thermal relaxation. The value of  $A_s$  characterizes the shape of CdSe nanocrystals and is calculated using tensors of  $R_g$ . For spherical objects,  $A_s$  tends to zero, whereas for the elongated objects, it converges to 1.  $A_s$  is found to be small and approaches to zero on increasing the size of the nanocrystals. The observation suggests that the elongated and faceted shape reduces on increasing the core radius and nanocrystals of larger diameters possess almost spherical shape. The values of  $U_B$  are found quantitatively consistent with the previous results<sup>6</sup> and do not show



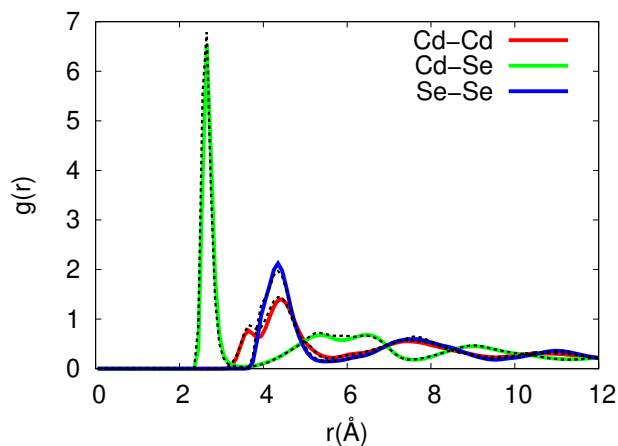
**Fig. S1** Magnitude of dipole moment,  $|\mu|$ , of thermally relaxed bare CdSe nanocrystals in the Debye (D) units as a function of number of atoms,  $N$ , in the nanocrystals at 300 K. The  $|\mu|$  of the SNP10 in vacuum is additionally shown in the plot by blue point for comparison.

any correlation with the nanocrystal size. This validates our computational setup and force field for the simulation of CdSe nanoparticles. The positive sign of binding energy indicates that CdSe cores gain energy by adsorption of ligands.

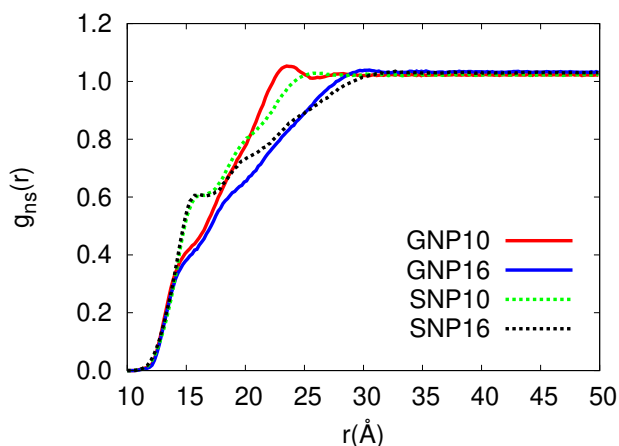
In Fig. S1, we show the magnitude of dipole moment,  $|\mu|$ , of thermally relaxed bare CdSe nanocores as a function of number of atoms,  $N$ , of nanocrystal in vacuum. The permanent dipole in nanocrystals originates due to the anisotropy in the wurtzite unit cell of CdSe material *i.e.*,  $c$ -axis of the unit cell is different from  $a$  and  $b$  axes.  $|\mu|$  shows a linear relationship with the  $N$  as noted earlier<sup>6,8</sup>. In the figure, we also show the  $|\mu|$  of  $(\text{CdSe})_{102}$  nanoparticle passivated with the decylamine ligands (blue point) for the comparison. As expected<sup>9</sup>, the magnitude is slightly lower than the bare nanocrystal. For computational efficiency,  $(\text{CdSe})_{102}$  core is chosen in the study of solvation and PMF calculations. While doing the passivation, the alkylamines primarily bind with the Cd atoms present at the nanocrystal surface. However, it was found that the excess ligands adsorb on the surface through weakly supported Se...H...N type hydrogen

bonding interactions. These excess ligands were systematically removed from the surface (see computational details) to get the nanoparticle having stable capping monolayer primarily bound with the Cd atoms.

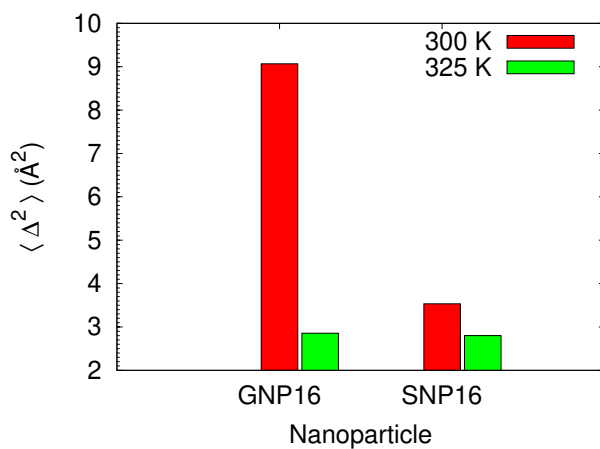
### S3 Additional Figures



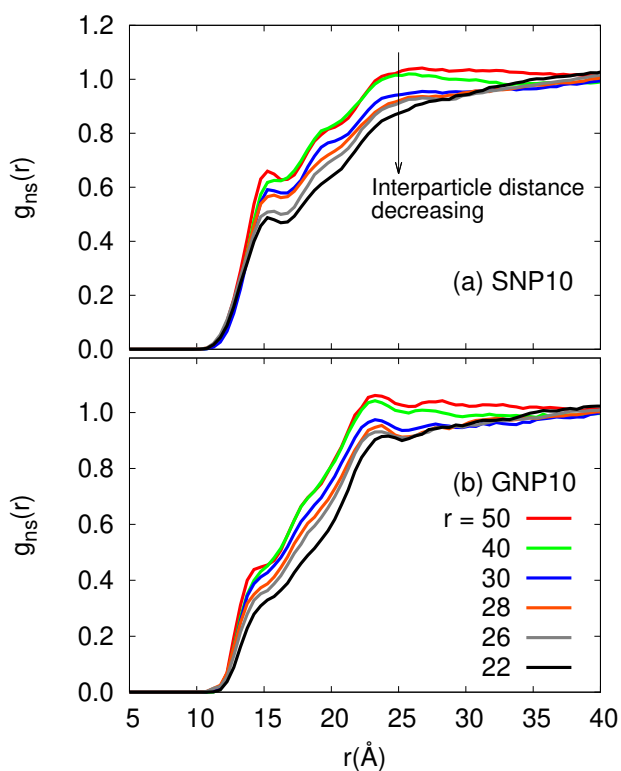
**Fig. S2** Cd-Cd, Cd-Se, and Se-Se radial distribution function of both bare (solid lines) and passivated  $(\text{CdSe})_{102}$  nanocrystal (dashed lines) at 300 K in flexible (non-rigid) model.



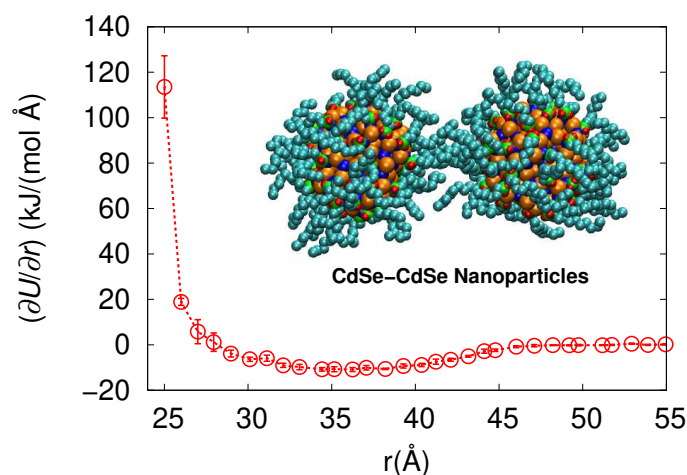
**Fig. S3** Radial distribution,  $g_{ns}(r)$ , of solvent monomers around GNP10, GNP16, SNP10, and SNP16, computed from the center of mass of inorganic core of nanoparticles.



**Fig. S4** The comparison of mean value of the  $\Delta^2$  for GNP16 and SNP16 nanoparticles in vacuum at two different temperatures.



**Fig. S5** Radial distribution,  $g_{ns}(r)$ , of solvent monomers around GNP10 and SNP10 in the pair interaction at different interparticle separations,  $r$ .



**Fig. S6** The variation of mean force as a function of pair separation,  $r$ , for SNP10-SNP10 pair interaction. The error bars were calculated by dividing the force trajectories into six blocks.

## S4 Supplementary Movie Captions

**Movie S1.** Random orientation of dipole moments in SNP10-SNP10 pair interaction at higher separation, *i.e.*, where inter-nanoparticle interaction is negligible.

**Movie S2.** Antiparallel orientation of dipole moments in SNP10-SNP10 pair interaction at closer separation, *i.e.*, at the onset of repulsion.

## References

- [1] U. Landman and W. D. Luedtke, *Faraday Discuss.*, 2004, **125**, 1–22.
- [2] K. Tay and F. Bresme, *Mol. Simulat.*, 2005, **31**, 515–526.
- [3] E. Rabani, *J. Chem. Phys.*, 2002, **116**, 258.
- [4] C. D. Wick, J. M. Stubbs, N. Rai and J. I. Siepmann, *J. Phys. Chem. B*, 2005, **109**, 18974–18982.
- [5] R. C. Rizzo and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1999, **121**, 4827–4836.
- [6] P. Schapotschnikow, B. Hommersom and T. J. H. Vlugt, *J. Phys. Chem. C*, 2009, **113**, 12690–12698.

- [7] Y.-N. Xu and W. Y. Ching, *Phys. Rev. B*, 1993, **48**, 4335–4351.
- [8] B. J. Morgan and P. A. Madden, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2355–2361.
- [9] E. Rabani, *J. Chem. Phys.*, 2001, **115**, 1493.