

Supporting Information

The Facet Selectivity of Ligands on Silver Nanoplates: A Molecular Mechanics Study

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1. Partial Charge Model

Experiments suggested that the surface of the silver nano-plate should carry partial positive charges. In this study, a partial charge model in which all silver atoms were assigned a +0.5 partial charge was used to parameterize the silver plate. In addition to that, we also performed the same calculations with several other partial charge models, i.e. in which the silver atoms were assigned +0.2, +0.3 or +0.4 partial charge, respectively.

The calculated binding affinities are summarized in Table S1 (+0.2 charge), Table S2 (+0.3 charge), and Table S3 (+0.4 charge).

COO-group number	Ligand	Surface	ΔG	$\Delta E_{\text{potential}}$	ΔE_{Bonded}	ΔE_{vdW}	ΔE_{Elec}	$-T\Delta S$	$\Delta G_{111} - \Delta G_{100}$
1	acetic	111	-50.25	-52.07	0.00	-0.51	-51.56	1.82	-0.35
		100	-49.90	-51.19	0.02	-0.56	-50.65	1.30	
2	oxalate	111	-93.34	-97.64	0.09	-1.09	-96.78	4.30	-3.97
		100	-89.37	-93.20	0.11	-0.97	-92.45	3.83	
	malonate	111	-97.18	-101.77	0.02	-1.27	-100.52	4.59	-2.84
		100	-94.34	-98.32	0.01	-1.20	-97.16	3.98	
	succinate	111	-96.64	-101.30	0.12	-1.30	-100.13	4.66	-3.43
		100	-93.21	-98.42	0.14	-1.16	-97.43	5.21	
	glutarate	111	-95.34	-100.78	0.31	-2.56	-98.57	5.44	-2.91
		100	-92.43	-97.89	0.30	-2.54	-95.72	5.46	
	pimelate	111	-93.60	-100.10	0.07	-2.26	-97.92	6.51	-2.82
		100	-90.78	-99.19	0.08	-2.20	-97.07	8.41	
3	citrate	111	-134.51	-143.45	2.74	-2.08	-144.12	8.93	-2.78
		100	-131.73	-139.62	1.42	-1.81	-139.25	7.89	
	isocitrate	111	-134.23	-140.98	4.01	-1.37	-143.64	6.75	-1.53
		100	-132.70	-138.90	1.33	-1.07	-139.18	6.20	
	trimesic	111	-133.68	-141.73	1.04	-4.18	-138.77	8.05	-5.67
		100	-128.01	-134.65	1.38	-4.10	-132.09	6.64	

Table S1. Binding energy components of ligands with +0.2 partial charge set. The unit of binding energy terms and entropy loss are kcal/mol.

COO-group number	Ligand	Surface	ΔG	$\Delta E_{\text{potential}}$	ΔE_{Bonded}	ΔE_{vdW}	ΔE_{Elec}	$-T\Delta S$	$\Delta G_{111} - \Delta G_{100}$
1	acetic	111	-77.28	-78.12	-0.04	0.65	-78.73	0.84	-2.56
		100	-74.72	-76.88	-0.05	0.64	-77.45	2.16	
2	oxalate	111	-141.38	-146.85	0.03	1.05	-148.25	5.47	-6.50
		100	-134.88	-139.75	0.02	1.03	-141.03	4.87	
	malonate	111	-147.00	-152.79	-0.04	0.94	-153.75	5.78	-3.80
		100	-143.20	-147.80	-0.08	0.95	-148.79	4.60	
	succinate	111	-146.83	-152.83	0.04	1.08	-153.98	6.00	-4.76
		100	-142.07	-148.68	0.14	1.37	-150.24	6.60	
	glutarate	111	-145.36	-151.35	0.35	0.16	-151.89	5.99	-4.55
		100	-140.81	-148.29	0.74	0.56	-149.60	7.47	
	pimelate	111	-142.86	-150.57	0.10	0.11	-150.78	7.71	-4.27
		100	-138.59	-148.37	0.11	0.13	-148.62	9.78	
3	citrate	111	-208.22	-219.86	3.97	1.93	-225.76	11.64	-5.51
		100	-202.71	-212.59	2.89	3.37	-218.87	9.89	
	isocitrate	111	-207.82	-217.42	5.45	1.93	-224.79	9.60	-4.61
		100	-203.21	-211.18	3.37	3.92	-218.52	7.97	
	trimesic	111	-202.19	-212.45	2.62	-1.06	-214.42	10.25	-8.12
		100	-194.07	-202.06	2.70	-1.64	-203.47	7.99	

Table S2. Binding energy components of ligands with +0.3 partial charge set. The unit of binding energy terms and entropy loss are kcal/mol.

COO-group number	Ligand	Surface	ΔG	$\Delta E_{\text{potential}}$	ΔE_{Bonded}	ΔE_{vdW}	ΔE_{Elec}	$-T\Delta S$	$\Delta G_{111} - \Delta G_{100}$
1	acetic	111	-102.96	-104.50	-0.20	1.93	-106.23	1.54	-2.86
		100	-100.10	-102.77	-0.24	1.93	-104.45	2.66	
2	oxalate	111	-190.35	-196.68	-0.21	3.39	-200.41	6.32	-8.78
		100	-181.58	-187.37	-0.28	3.15	-190.63	5.80	
	malonate	111	-198.37	-204.58	-0.34	3.39	-207.79	6.21	-5.91
		100	-192.46	-197.90	-0.32	3.32	-201.16	5.44	
	succinate	111	-197.91	-205.03	-0.21	3.68	-208.57	7.12	-5.40
		100	-192.51	-200.28	-0.03	4.15	-204.51	7.77	
	glutarate	111	-196.33	-203.36	0.03	2.83	-206.23	7.03	-5.23
		100	-191.10	-199.78	0.37	3.24	-203.39	8.68	
	pimelate	111	-193.15	-201.68	-0.21	2.61	-204.08	8.53	-4.18
		100	-188.98	-199.24	-0.22	2.64	-201.66	10.26	
3	citrate	111	-284.36	-296.93	3.53	5.83	-306.29	12.57	-8.05
		100	-276.31	-287.55	2.80	7.77	-298.17	11.24	
	isocitrate	111	-283.95	-294.71	4.75	6.44	-305.90	10.76	-6.72
		100	-277.23	-286.61	3.83	9.05	-299.56	9.38	
	trimesic	111	-273.10	-284.82	3.78	2.45	-291.77	11.73	-11.07
		100	-262.03	-271.18	3.53	1.27	-276.59	9.15	

Table S3. Binding energy components of ligands with +0.4 partial charge set. The unit of binding energy terms and entropy loss are kcal/mol.

In +0.2 charge model, the relative binding affinities in di-carboxylate group holds the basic trend of that interpreted from the experimental yields except that malonate has a stronger binding affinity than succinate. This is similar to the result from +0.5 partial charge, but the difference of the values are smaller than the report +0.5 partial charge set. In addition, in the tri-carboxylate group, the binding affinities of citrate and isocitrate match the experimental yields, but trimesic acid is the singularity.

Similar behaviors can be observed in the +0.3 and +0.4 partial charge model, but the difference in relative binding affinities in di-carboxylate group becomes larger and larger. Furthermore, the higher partial charge on silver atoms start to differentiate the trimesic acid from the other two ligand in tri-carboxylate group.

This results from the ratio of contributions from the Columbic interactions and vdW interactions between the ligand and the surface. The Columbic attraction between silver surface and the ligand is mainly from the Columbic attraction between the oxygen atoms on the ligands and the silver atoms, while the vdW attraction is mainly from the interaction between carbon and hydrogen atoms on the ligands and the silver atoms. By

comparing the +0.2, +0.3 and +0.4 charge, one can see that the columbic interaction becomes stronger and stronger. This higher positive partial charge makes oxygen-silver attraction more favorable, but in turn, makes the columbic repulsion between positively charged silver atoms and carbon, hydrogen atoms stronger. So higher positive charge will lead to the behavior of glutarate in Figure S1. In +0.2 charge model, the middle carbon in the chain stays on the surface, but in +0.3 and +0.4 charge models, it is push away from the surface, due to the stronger repulsion. This behavior weakens the vdW interaction from +0.2 to +0.4 partial charge. Also in the case of trimesic acid, the rigid molecule is unable to adjust itself to maximize the columbic attraction between oxygen and silver atoms and at the same time minimize the columbic repulsion between the silver atoms and the carbon or hydrogen. This is the intrinsic reason for trimesic acid to be a weak surfactant, and only with high positive charge model the behavior appears. Based on experimental data and existing studies, we selected +0.5 partial charge model for this study that yield both more accurate experimental trends and conformations.

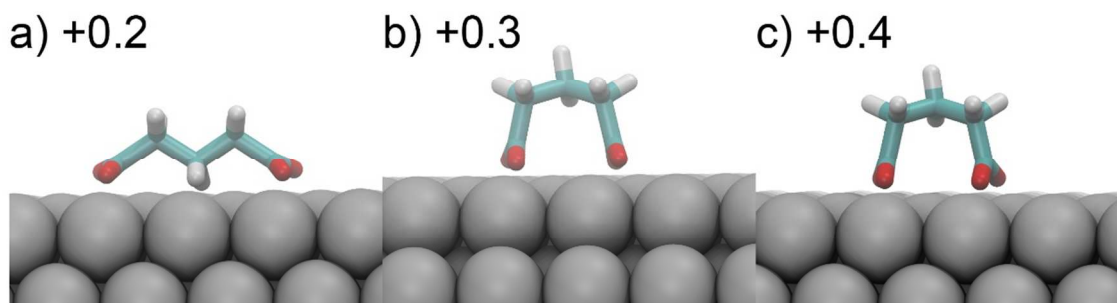


Figure S1. Binding pose of glutarate on silver plate in +0.2, +0.3 and +0.4 partial charge model.

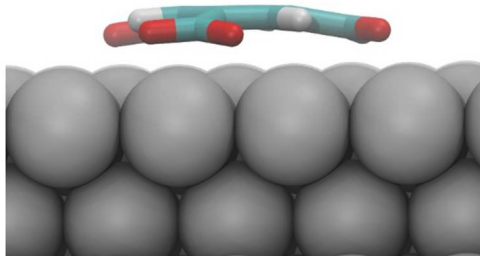


Figure S2. Binding pose of trimesic acid on silver plate in +0.2 partial charge model.

2. Solvent Effects

MD simulation was performed to optimize the arrangements of water molecules on the silver plate-ligand complex binding region, in order to investigate how many water molecules are replaced by the ligand upon binding. Releasing bound waters from the Ag surface may gain solvent entropy but lose solvent enthalpy upon ligand binding. However, the implicit solvent model may not be able to capture the effects for different ligand binding.

a. Method

The global energy minima of each silver plate-ligand complex are used as an initial conformation for MD simulations using NAMD 2.9¹. A complex conformation is solvated by a TIP3P water box, which is about 21 Å from the complex. In order to focus on water replacement, no counterions were placed on the Ag surface. The plate and ligand were held fixed during the simulations. The system is gradually heated at 50K, 100K, 150K, 200K, 250K and 298K in NPT for 10 ps. Finally a product run in NPT for 20 ps is performed and a trajectory is saved every 20 fs. This 1000 frame trajectory was processed to count how many water molecules on average were present at the first layer (defined by a distance 3.2 Å from the plate) on the silver plate within a region with radius 10 Å from the projection of the center of geometry of the ligand on the plate.

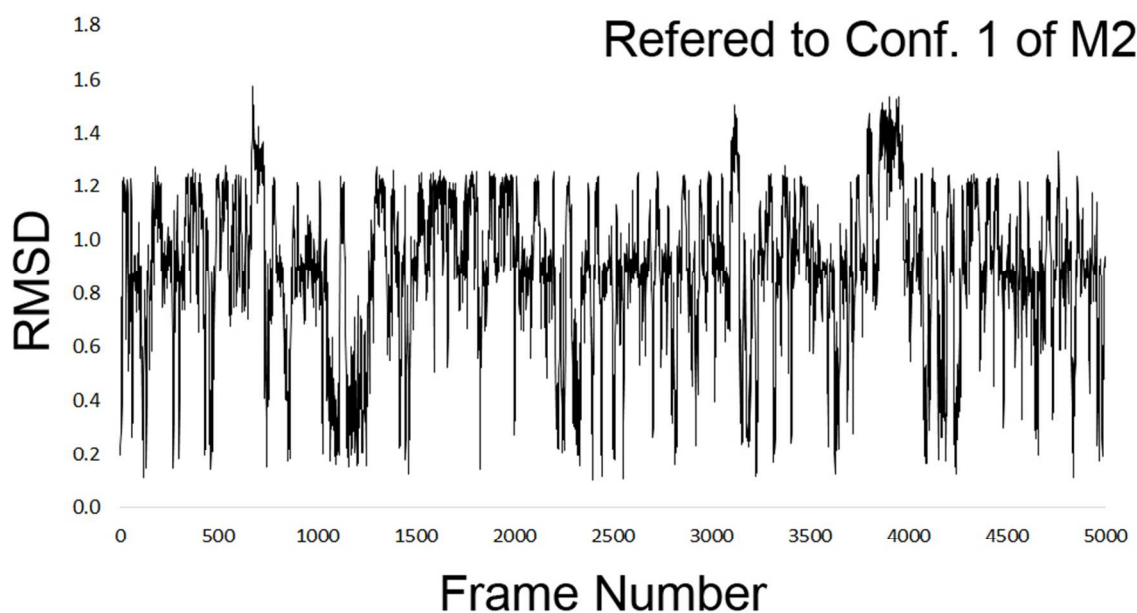
b. Discussion

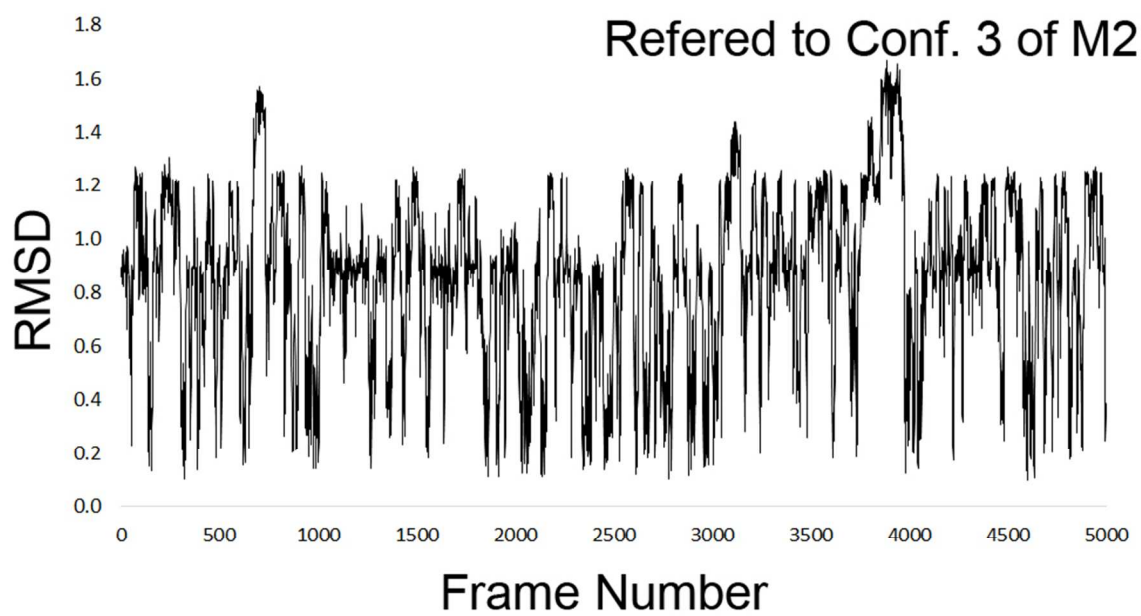
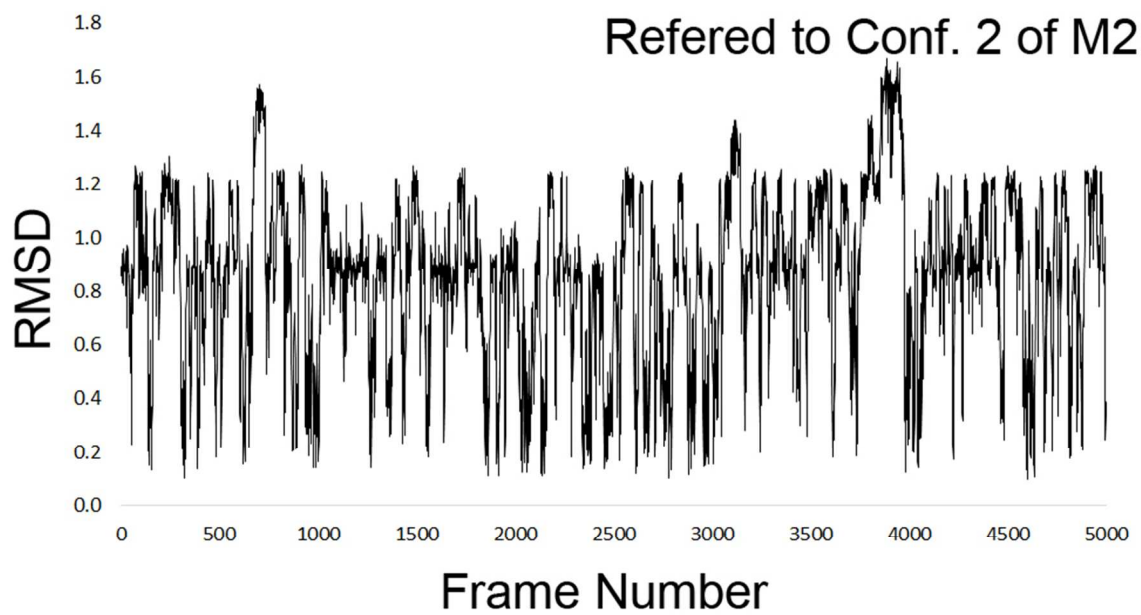
The result of number of waters in defined region is given in Table S4. The differences in numbers of water in defined region reveal the differences of number of waters replaced by two different ligands. For example, comparing with ligands within the di-carboxylate and tri-carboxylate groups, the differences are lesser than 5.5 and 2.3 waters, respectively. Considering the standard deviation, the difference is insignificant. We therefore concluded that the solvent effects from releasing waters on the surface are similar among ligands in each group; therefore, this term does not affect results of related binding affinities.

No. of Carboxylate Group	Ligand	No. of Water	Standard Deviation
1	Acetate	59.33	1.79
2	Oxalate	62.81	2.20
	Malonate	61.72	2.28
	Succinate	57.27	1.82
	Glutarate	61.39	2.01
	Pimelate	58.31	2.15
3	Citrate	55.71	1.84
	Isocitrate	53.45	1.77
	Trimesic acid	53.40	2.06

Table S4. Numbers of water in the region that is the first layer (here cut off at 3.2 Å from the surface) water that is within 10 Å from the projection of center of geometry of the ligand on silver surface of silver plate-ligand complexes.

3. Plots of RMSD for Comparison of M2 and MD Conformations





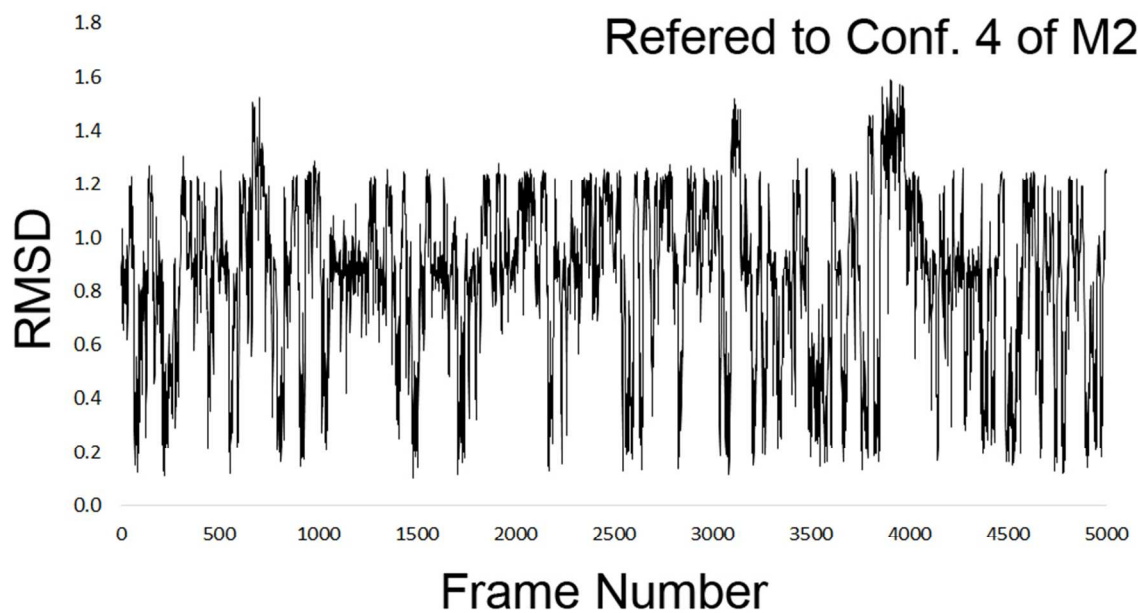


Figure S4. Plots of RMSD (in Å) computed by all atoms, including hydrogen atoms, for succinate from MD simulations. Each plot used one local energy minima found by M2 as a reference structure. . The frame was saved every 1 ps, and the MD simulation length is 5 ns.

4. Flow Chart of M2 Method

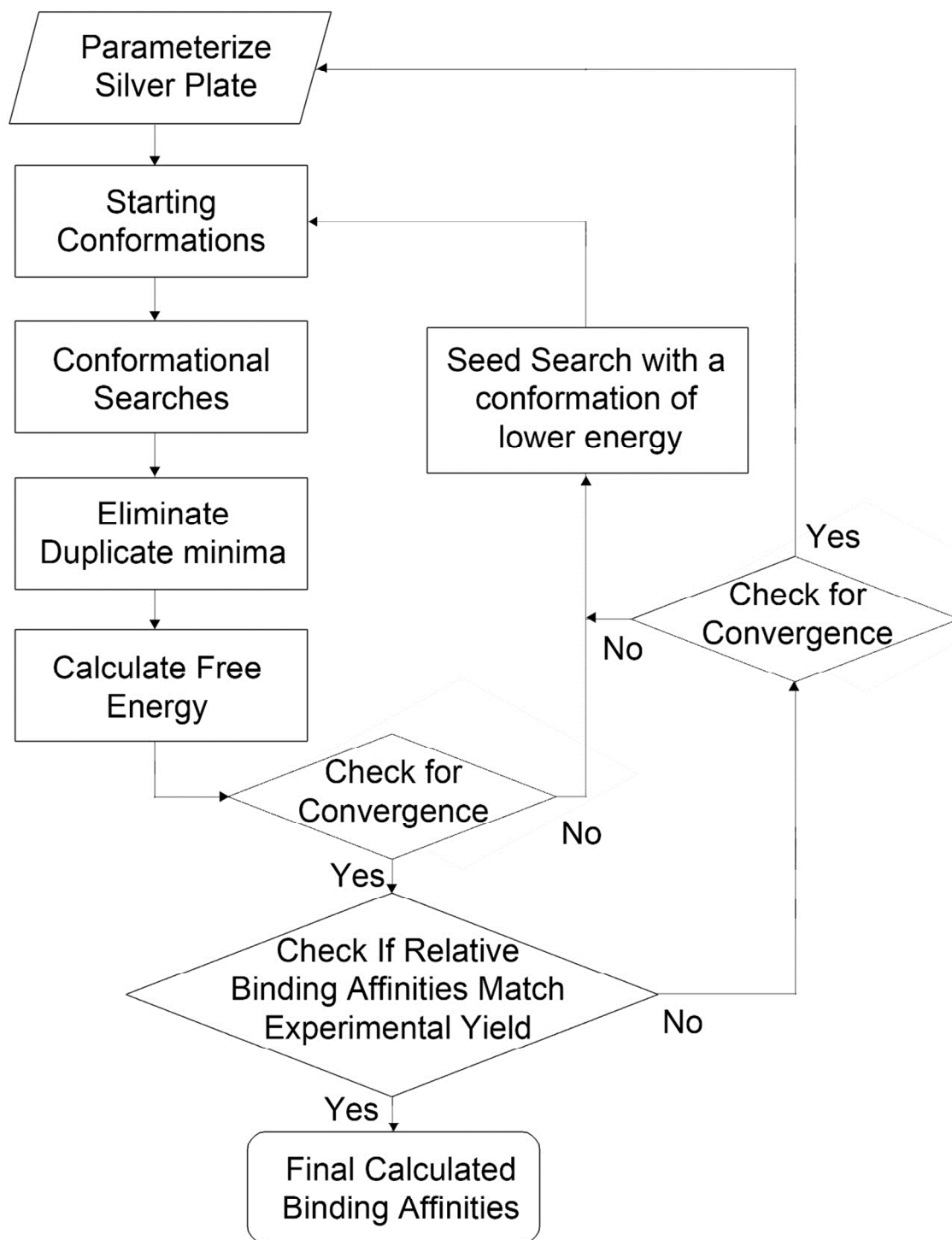


Figure S3. Flow chart of applying M2 method to silver plate-ligand systems.

5. The second generation of Mining Minima Method (M2) Calculation Details

M2 method is based on thorough conformational search and modified harmonic approximation using the bond-angle-torsion coordinates. The standard chemical potential of species X can be written as Equation 1. Q stands for canonical partition function, and V is the volume. The subscribe N,X means the system containing N solvent molecules and one solute molecule X, and similarly N,0 means the system with N solvent molecules but no solute. C° is the standard concentration. The explicit solvent molecules are replaced by an implicit solvent model, GBSA or PBSA, to avoid numerous configurations generated by the solvent molecules.

Because there are multiple local minima in the canonical ensemble, the total standard chemical potential is described by Equation 2 where $\mu_{X,i}^\circ$ is the chemical potential of each local minimum.

By introducing Rigid Rotor Approximation, the standard chemical potential $\mu_{X,i}^\circ$ of species X is given by Equation 3. In this equation, M_X is the total mass of X, $I_{X,a}, I_{X,b}, I_{X,c}$ are its principle moments of rotational inertia. n_X is the number of atom in the molecule. h and k are the Planck's and Boltzmann's constants. The first two brackets are translational and rotational contributions, and are straight forward in calculation. The most computationally intensive part is the third bracket, which is the vibrational part, and is further calculated by Equation 4. In Equation 4, U and W are the potential and solvation energies, and q is the vibrational coordinates. A more specific detailed explanation can be found in the original work².

The M2 method is different from MMPBSA or other MD based analysis method. It uses analytical integration from the diagonalized Hessian matrix (modified harmonic approximation). According to Equation 2, the total standard chemical potential of species X is the sum of those of local minima weighed by the Boltzmann factor. Therefore, there is no fluctuation or standard deviation in the results from M2 method.

Equation 1.

$$\mu_X^\circ = -RT \left(\frac{1}{V_{N,X} C^\circ} \frac{Q_{N,X}(V_{N,X})}{Q_{N,0}(V_{N,0})} \right)$$

Equation 2.

$$\mu_X^\circ = -RT \ln \sum_i e^{-\beta \mu_{X,i}^\circ}$$

Equation 3.

$$e^{-\beta\mu_{X,i}^{\circ}} = \left[\frac{1}{C^{\circ}} \left(\frac{2\pi M_X kT}{h^2} \right)^{3/2} \right] \left[8\pi^2 \left(\frac{2\pi kT}{h^2} \right)^{3/2} (I_{X,a} I_{X,b} I_{X,c})^{1/2} \right] \left[\left(\frac{2\pi kT}{h^2} \right)^{(3n_X-6)/2} Z_X^{vib} \right]$$

Equation 4.

$$Z_x^{vib} = \int e^{-\beta(U(q)+W(q))} dq$$

1. Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kale, L.; Schulten, K. Scalable molecular dynamics with NAMD. *Journal of Computational Chemistry* **2005**, 26 (16), 1781-1802.
2. Chang, C. E.; Potter, M. J.; Gilson, M. K. Calculation of molecular configuration integrals. *Journal of Physical Chemistry B* **2003**, 107 (4), 1048-1055.