

Supporting Information: *Ab initio* molecular dynamics simulations and
vibrational frequency calculations of species in liquid-liquid phase separated
MgSO₄ solution at 543 K

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1. Formulas for vibrational frequency calculation

The vibration of molecules are regarded as harmonic classical oscillators similar to quantum oscillators in static quantum chemical calculations. By performing Fourier transforms of the molecular motion changing with time, the frequency of this motion could be derived.^{1, 2}

1.1 Autocorrelation function of velocity for Power spectra

The intensity $P(\omega)$ of Power spectra is defined by the Fourier transform of,

$$P(\omega) = m \int \langle \dot{r}(\tau) \dot{r}(t + \tau) \rangle_{\tau} e^{-i\omega t} dt,$$

where $\langle \dot{r}(\tau) \dot{r}(t + \tau) \rangle_{\tau}$ denotes the autocorrelation of velocities.

1.2 Autocorrelation function of Dipole for Infrared spectra

In order to get dipole moment μ , the localization of electron is interpreted by Wannier centers and μ is calculated as:

$$\mu = -2e \sum_i r_i + e \sum_j Z_j R_j,$$

where R_j is the position of nuclear and Z_j is their charges. r_i is the location of Wannier Centers.

The intensity of Infrared spectra is,

$$A(\omega) = \int \langle \dot{\mu}(\tau) \dot{\mu}(t + \tau) \rangle_{\tau} e^{-i\omega t} dt.$$

1.3 Autocorrelation function of polarizability for Infrared spectra

The deduced dipole moment μ_{ind} under the influence of external electric field E is,

$$\mu_{ind} = \alpha E,$$

where α is the polarizability and it can be written in matrix form:

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}.$$

Only the isotropic polarizability (elements along the diagonal) is considered in our work. So the intensity of Raman spectra is,

$$I_{isotropic}(\omega) = \frac{(\omega_{in} - \omega)^4}{\omega} \frac{1}{1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)} \int \langle \dot{\alpha}_{xx}(\tau) \dot{\alpha}_{xx}(t + \tau) \rangle_{\tau} e^{-i\omega t} dt,$$

where ω_{in} is the wavenumber of laser light, k_B is the Boltzman constant and \hbar is the reduced Planck constant.

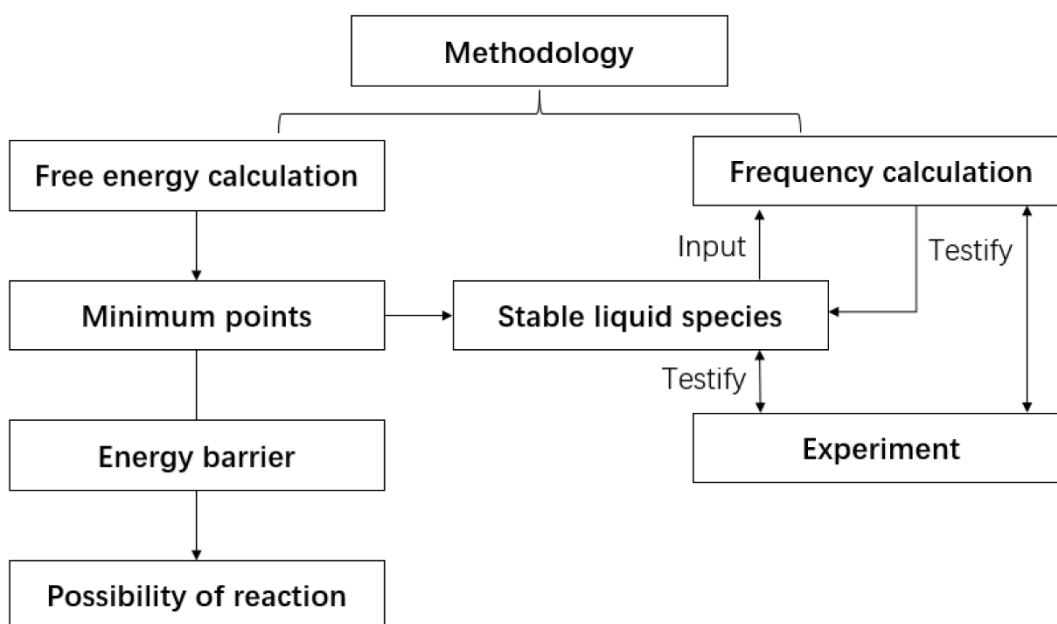


Figure S1. A flowchart of relationship between free energy calculation, frequency calculation and experiment.

2. The distribution diagram of HB

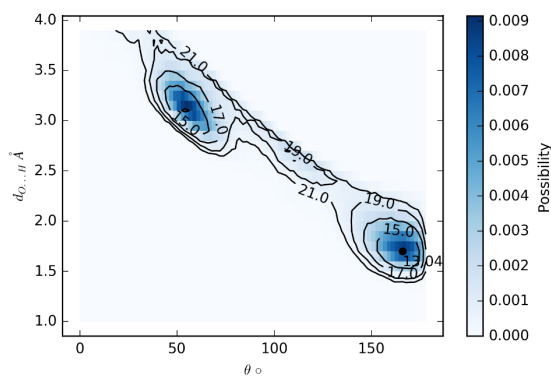
The diagrams of $d_{O...H}$ and θ distribution shows below, (Figure S2) which presents the comfort of our HB standard ($1.2 \leq d_{O...H} \leq 2.3 \text{ \AA}$ and $\theta \geq 130^\circ$).

From Figure S1, average number of hydrogen bonds of water-water and sulfate-water can be counted. Under the precondition that $d_{O...H}$ and θ can walk through the phase space ergodically, Helmholtz free energy of HB is derived from the following formula,

$$e^{\frac{\Delta E}{RT}} = P$$

where P is the possibility at a certain region of phase diagram. By drawing the isopotential energy surface on the diagram, the free energy change of breaking one HB between sulfate-water (s-w) or water-water (w-w) is $\sim 5 \text{ kJ/mol}$.

Hydrogen bond distribution of sulfate-water at 330K



Hydrogen bond distribution of water-water at 330K

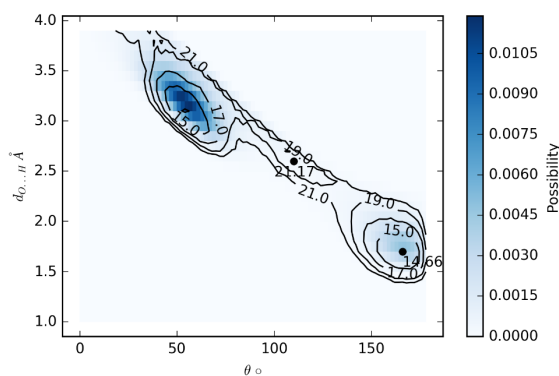


Figure S2. The HB distribution of sulfate-water and water-water at 330K under PBE0 (the unit of isopotential energy surface is kJ/mol)

3. The fitting parameters of HB lifetime

Three parameters (A_1 , k_1 , k_2) need to be fitted for the following formula^{3, 4},

$$C(t) = A_1 e^{-k_1 t} + (1 - A_1) e^{-k_2 t}.$$

It was done by Python Library scipy Function curve_fit. The detailed parameters for lifetime calculation is listed in Table S1. The lifetime and Number of HB for calculated ensembles are listed in Table S2.

Table S1. The fitting parameters of HB lifetime (s-w represents sulfate anion to water, w-w represents water to water)

Parameters	A_1		k_1		k_2	
	s-w	w-w	s-w	w-w	s-w	w-w
330K/PBE0						
Free SO ₄	0.11	0.26	12.58	5.90	1.23	1.05
Mono-CIP	0.61	0.39	2.32	3.82	0.58	0.78
Bi-CIP	0.51	0.39	3.82	4.30	0.58	0.84
S-M-S	1.23	1.17	1.66	1.68	1.65	1.68
M-S-M	0.51	1.31	4.16	1.82	0.82	1.82
543K/PBE0						
Free SO ₄	1.77	1.78	4.54	8.56	4.54	8.56
Mono-CIP	1.86	0.75	4.88	9.10	4.88	3.26

M-S-M	0.37	0.76	10.61	9.22	5.14	4.10
<hr/>						
PBE/Free SO ₄						
330K	0.79	0.65	0.55	0.48	4.10	2.39
543K	1.55	2.04	3.94	8.16	3.94	8.17

Table S2. The lifetime and Number of HB for calculated ensembles (data* is from direct integration. The other is from fitting of 3 parameters)

Ensembles	Values	Average bond number		Relevant Lifetime (ps)	
		s-w	w-w	s-w	w-w
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Free SO ₄					
PBE0/330K		9.0	3.0	0.72*, 0.73	0.75*, 0.75
PBE0/543K		6.7	1.2	0.23*, 0.22	0.12*, 0.12
PBE/330K		8.0	3.3	1.46*, 1.48	1.54*, 1.54
PBE/543K		6.6	1.4	0.26*, 0.25	0.13*, 0.13
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Mono-CIP					
PBE0/330K		7.4	3.0	0.94*, 0.94	0.88*, 0.88
PBE0/543K		5.0	1.4	0.21*, 0.20	0.16*, 0.16
<hr/>					
Bi-CIP					
PBE0/330K		6.2	3.0	0.83*, 0.85	0.83*, 0.81
<hr/>					
S-M-S					
PBE0/330K		7.2	2.9	0.64*, 0.60	0.64*, 0.59
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M-S-M					
PBE0/330K		5.7	2.9	0.71*, 0.72	0.59*, 0.55
PBE0/543K		3.9	1.2	0.16*, 0.16	0.14*, 0.14

4. The mean force diagram

The PMF is integrated from the mean force $f(r)$ (Figure S3). The error for every r point is defined as the average $f(r)$ of latter half steps minus the average $f(r)$ of the beginning half steps.

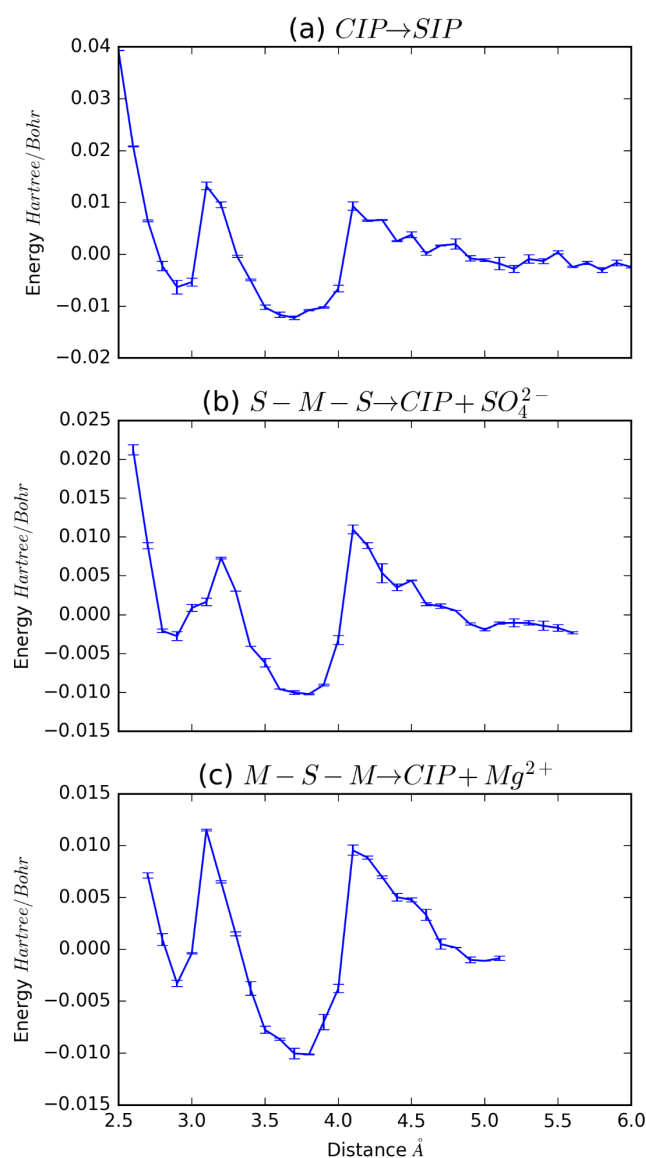


Figure S3. The mean force of process (a), (b) and (c)

5. The performance between PBE and PBE0

5.1 The calculated frequencies

The calculated frequencies of PBE shows a systemic decrease ~ 100 cm⁻¹ compared to PBE0 and Exp. results (Table S3, Figure S4(a)(b)(c)). Same underestimation of ~ 100 cm⁻¹ was also reported for water frequencies.⁵

The difference between those two functional is whether the Hartree-Fock (HF) exchange is involved. PBE0 contains 25% HF exchange term, 75% PBE exchange term and 100% PBE correlation term. The point for mixing the exchange term is because pure GGA functional like PBE, BLYP always overestimates the total electron energy due to the integration of electron-electron potential containing itself. The term of HF exchange can to some extent compensate such effect. The intrinsic description of the sulfate anion electron structure caused the wide deviation of vibration frequency.

Table S3. The vibrational frequencies of free sulfate anion using different functional (data with* is from autocorrelation function of velocity. The other is from autocorrelation function of dipoles or polarizability)

Phase/T	Method	$V_1(\text{R})-\text{E}$	$V_2(\text{IR})-\text{T}_2$	$V_3(\text{R})-\text{A}_1$	$V_4(\text{IR})-\text{T}_2$
Free SO_4 330K	AIMD/PBE	417*, 420	584*, 576	905*, 906	1052*, 1056
	AIMD/PBE0	437*, 434	608*, 601	985*, 983	1138*, 1125
Free SO_4 543K	AIMD/PBE	409*, 406	580*, 566	895*, 896	1015*, 1011
	AIMD/PBE0	441*, 441	608*, 597	973*, 972	1117*, 1111
Na_2SO_4 (0.7 mol/L)	Exp. ⁶	449	613	981	1111

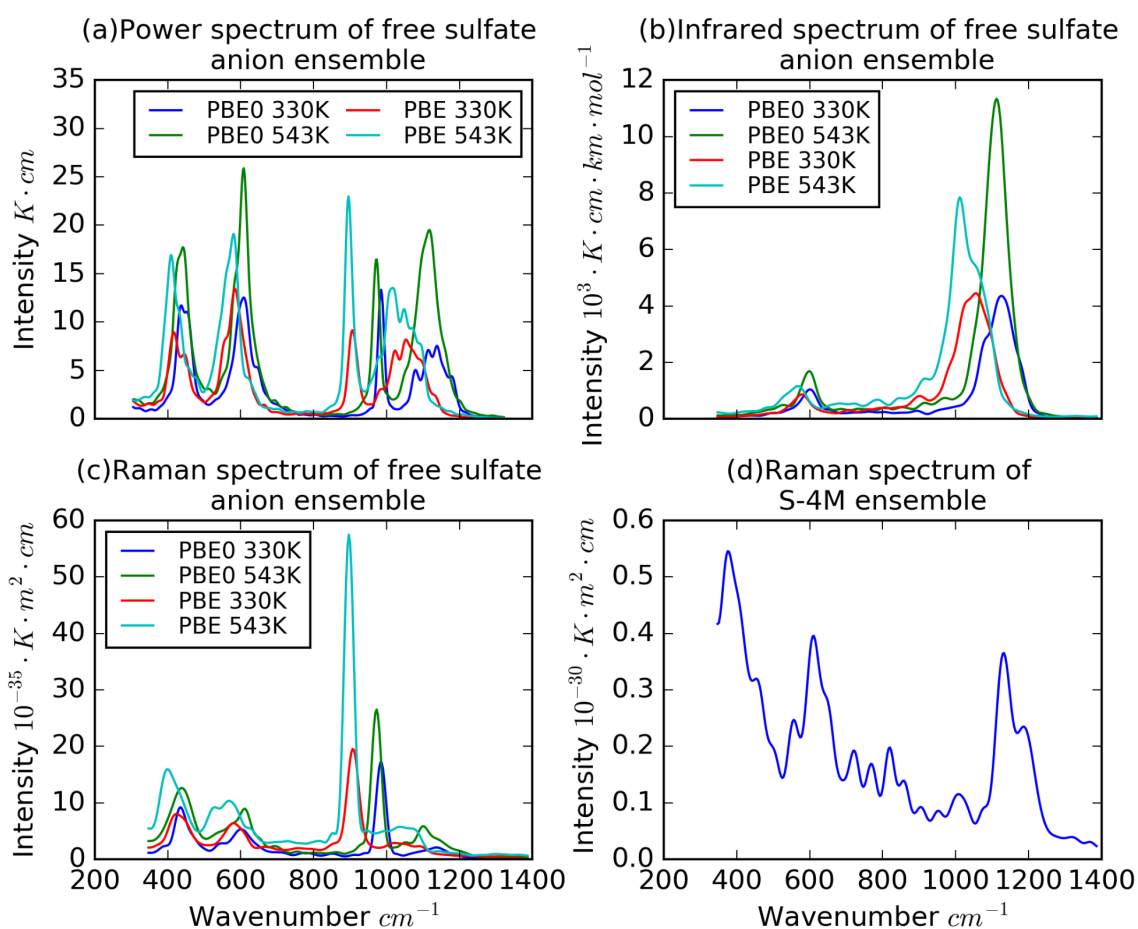


Figure S4. the Power, Infrared and Raman spectra of free sulfate anion under PBE and PBE0 and Raman spectra of S-4M at 330 K.

5.2 The water sphere around the surface anions

The first sphere water of sulfate anion at 330K has been counted and the Radial Distribution Function (RDF) between S-Ow (sulfate anion and Oxygen of water) was plotted (Figure S5). In PBE ensemble, the range from 2.95 to 4.35Å is considered to be the first water layer with a peak at 3.75Å. The peak of second layer is 5.35Å. In PBE0 ensemble, the range from 2.95 to 4.45Å is considered as the first layer. The location of the first peak is the same as PBE while the second peak is 5.75Å. X-ray Diffraction experiments⁷ reveal the first peak is located at 3.67-3.89Å which is in agreement with both simulation's RDF. However, the coordination number (CN) of the first shell differs a lot. The average CN of PBE is 9.7 with most occurrence number of 9 and 10. The average CN of PBE0 is 10.8 with most occurrence number of 10 and 11. Vchirawongkwin et al.⁷ has also performed QM/MM with pure HF to be its QM part. Their results of CN is 10.4.

Many studies have point out for pure water ensembles, PBE tends to overstructure hydrogen bonds among water molecules.^{8,9} In Table S2, the lifetime of HB from PBE functional is twice the value of data from PBE0 functional for both s-w and w-w. The HB interaction tends to be more stable in PBE ensembles. Because of the preference for water molecules to form HB networks with each other, the interactions between sulfate anions and water molecules are depressed, causing the difference of the first water sphere.

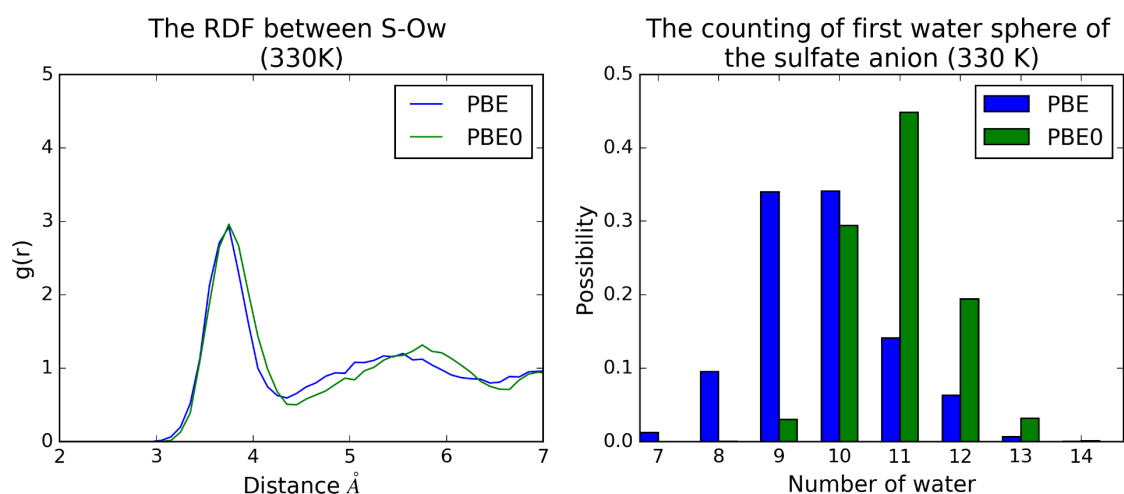


Figure S5. The RDF between S-Ow (left) and the counting of first water sphere of the sulfate anion (right)

6. Testing of classic force field

In order to preform large size ensemble of cluster aggregation, two popular classic force fields were tested: Madrid-2019¹¹ plus TIP4P water¹² and Mamatkulov 2013¹³ plus SPC/E water¹⁴.

As demonstrated in the Figure S6, the free energy curve of CMD differs significantly from the AIMD results (Figure 2a). Figure S6a indicates Mg^{2+} and SO_4^{2-} wouldn't form CIP at 543K.

The free energy difference between SIP and CIP in Figure S6) is over 15 kcal/mol compared to

4.04 kcal/mol in AIMD results, which means that the formation of CIP is greatly overestimated. Balasubramanian et al.¹⁵ calculated MgSO₄ in water by using the CMD method. Their radial distribution figure shows that bidentate complexing is favored over monodentate complexing, which conflicts with our AIMD results. The accuracy of CMD cannot be guaranteed by current available force field.

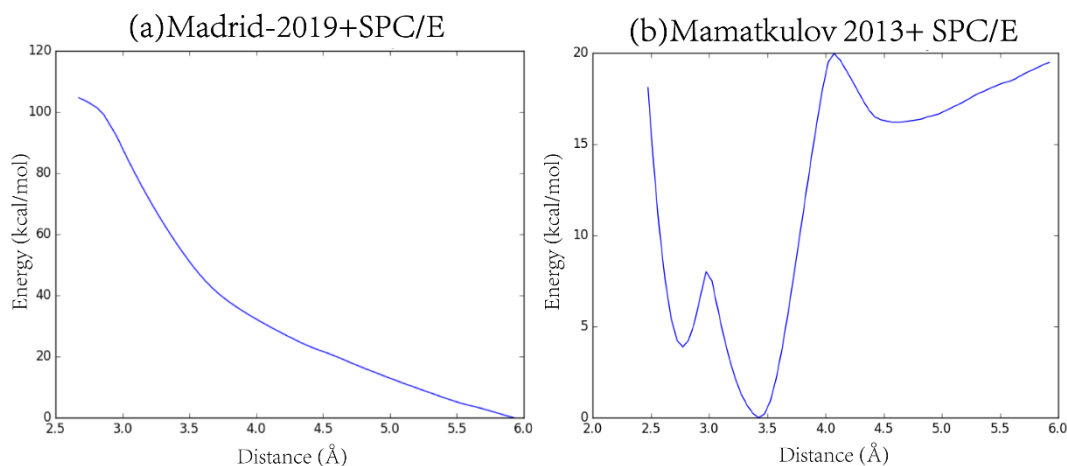


Figure S6. The PMF of CIP to SIP. (a) Madrid-2019+SPC/E (b) Mamatkulov 2013+ SPC/E. The distance between Mg and S was chosen as the reaction coordinate.

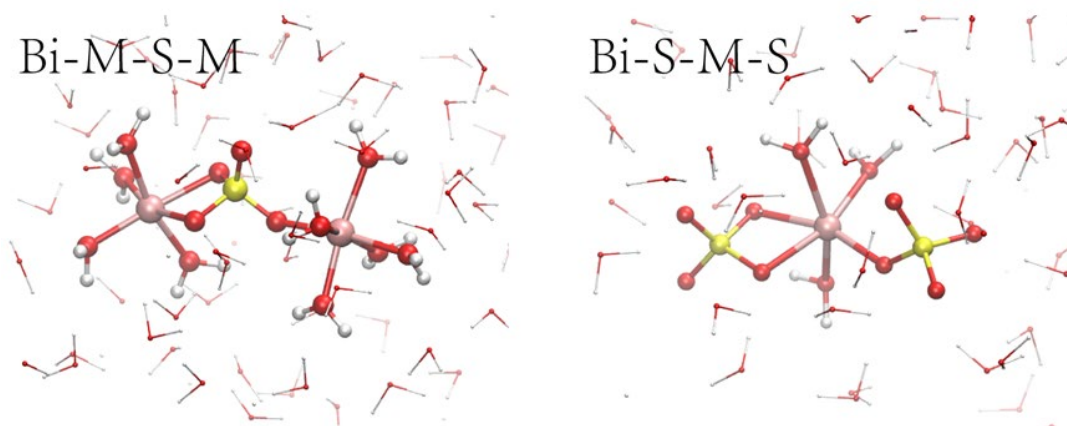


Figure S7. The snapshot of Bi-M-S-M and Bi-S-M-S. Not all water molecules are expressed. The figures of Mono-M-S-M and Mono-S-M-S are in Figure 1.

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