Supplementary Information

Interactions between Calcium Ion and Functional Groups of Organic Scale Inhibitors in Aqueous Solutions: An Ab Initio Study

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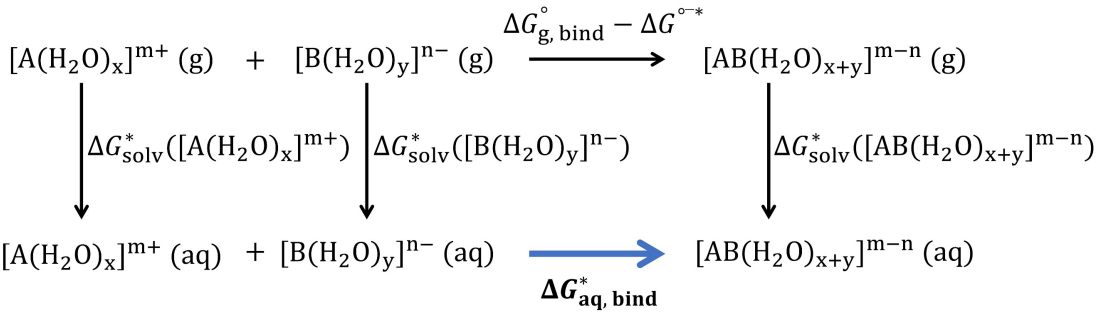
S1. Pairwise interaction calculation

The pairwise interactions were investigated using a mixed explicit/implicit solvation method. As illustrated in previous studies [1-3], the binding free energies ($\Delta G^{*}_{\mathrm{aq,\,bind}}$) between $[\mathrm{A(H_2O)_x}]^{m+}$ and $[\mathrm{B(H_2O)_y}]^{n-}$ species can be calculated using the thermodynamic cycle depicted in Scheme S1:

Scheme S1



Therefore, $\Delta G^{*}_{\mathrm{aq,\,bind}}$ can be expressed as:

$$\Delta G^{*}_{\mathrm{aq,\,bind}} = \Delta G^{\circ}_{\mathrm{g,\,bind}} + \Delta G^{*}_{\mathrm{solv}}\left([\mathrm{AB(H_2O)_{x+y}}]^{m-n}\right) - \Delta G^{*}_{\mathrm{solv}}([\mathrm{A(H_2O)_x}]^{m+}) - \Delta G^{*}_{\mathrm{solv}}\left([\mathrm{B(H_2O)_y}]^{n-}\right) - \Delta G^{\circ\text{-}*} \quad \text{(S1)}$$

$\Delta G^{\circ}_{\mathrm{g,\,bind}}$ is the gas-phase binding free energy at 298.15 K and 1 atm (denoted by the superscript "°"), written as:

$$\Delta G^{\circ}_{\mathrm{g,\,bind}} = G^{\circ}_{\mathrm{g}}\left([\mathrm{AB(H_2O)_{x+y}}]^{m-n}\right) - G^{\circ}_{\mathrm{g}}([\mathrm{A(H_2O)_x}]^{m+}) - G^{\circ}_{\mathrm{g}}\left([\mathrm{B(H_2O)_y}]^{n-}\right) \quad \text{(S2)}$$

$\Delta G^{*}_{\mathrm{solv}}$ is the standard-state solvation free energy corresponding to the 1 mol/L (gas) → 1 mol/L (solution) process (denoted by the superscript "*"). $\Delta G^{\circ\text{-}*}$ is the free energy change associated with moving the gas-phase standard state from 1 atm to 1 mol/L. The ideal-gas law yields [2]:

$$\Delta G^{\circ\text{-}*} = RT\ln(24.46) = 7.91 \text{ kJ/mol (298.15 K)} \quad \text{(S3)}$$

Following Scheme S1, we can calculate the binding free energies between $[\mathrm{A(H_2O)_x}]^{\mathrm{m+}}$ and $\left[\mathrm{B(H_2O)_y}\right]^{\mathrm{n-}}$ species. In addition, given that the formation of a cluster of a solvated ion in liquid water (55.34 mol/L) does not involve any change in free energy, the standard free energies of solvation (1 mol/L) can be calculated by adding correction terms [3], i.e.,

$$\mathrm{A^{m+}\ (aq) + xH_2O\ (aq)} \xrightarrow{\mathrm{x}RT\ln(55.34)} \mathrm{[A(H_2O)_x]^{m+}\ (aq)} \quad \text{(S4)}$$

$$\mathrm{B^{n-}\ (aq) + yH_2O\ (aq)} \xrightarrow{\mathrm{y}RT\ln(55.34)} \mathrm{\left[B(H_2O)_y\right]^{n-}\ (aq)} \quad \text{(S5)}$$

$$\mathrm{AB^{m-n}\ (aq) + (x+y)H_2O\ (aq)} \xrightarrow{(\mathrm{x+y})RT\ln(55.34)} \mathrm{\left[AB(H_2O)_{x+y}\right]^{m-n}\ (aq)} \quad \text{(S6)}$$

By combining equations S4−S6, one can notice that the binding free energy between $[\mathrm{A(H_2O)_x}]^{\mathrm{m+}}$ and $\left[\mathrm{B(H_2O)_y}\right]^{\mathrm{n-}}$ is equivalent to that between $\mathrm{A^{m+}}$ and $\mathrm{B^{n-}}$ in aqueous solutions.

S2. Influence of the system charge on the calculated results

Properly specifying the system charge is fundamental to ensuring the accuracy and reliability of the calculation. In this section, we discussed the influence of the system charge on the calculated results, including both the structure and ion pairing free energy. In Gaussian 16, a charged system is defined by adjusting the total number of electrons and constructing the corresponding spin state. Using a mixed explicit/implicit solvation method, the ion pairing free energy for the Ca^{2+}–HCO_3^- pair was predicted to be −8.1 kJ/mol, which agrees well with previous experimental and theoretical values, as shown in Table 1. Scrutinizing the structure, Ca^{2+} favors to coordinate with one O atom from HCO_3^- in a monodentate mode.

Moreover, we examined the structural and thermodynamic properties of the neutral system, i.e., the Ca−HCO_3 pair, using the same method. In this case, the ion pairing free energy was calculated to be −1190 kJ/mol. This result is unreasonable and inconsistent with previous studies. For the Ca−HCO_3 pair, the bidentate configuration is more stable than the monodentate counterpart, in contrast to the result obtained in the charged system.

S3. MetaD convergence tests

Fig. S1 shows the time evolutions of calcium−anion distances during the simulation time for Ca^{2+}–CO_3^{2-}, Ca^{2+}–HCO_3^{-}, Ca^{2+}–ACE^{-}, Ca^{2+}–MP^{2-}, Ca^{2+}–MP^{-}, and Ca^{2+}–MES^{-} systems. As time goes by, all systems are pushed by the well-tempered MetaD bias potentials to visit the entire configuration space. Fig. S2 shows the free energy surfaces (FESs) as a function of calcium−anion distances every 6 ps (200 Gaussian kernels deposited) along the last 90 ps simulation time for all systems. We have to acknowledge that some CVs, for example, the calcium−anion distance in Ca^{2+}–MP^{2-}, do not freely move through the CV space, suggesting that the FESs have not been fully converged. Nonetheless, considering the expensive cost of ab initio MetaD simulation and the slight differences of FESs from 210 ps to 240 ps, we can believe that the obtained FESs after the 240 ps run have been roughly converged.

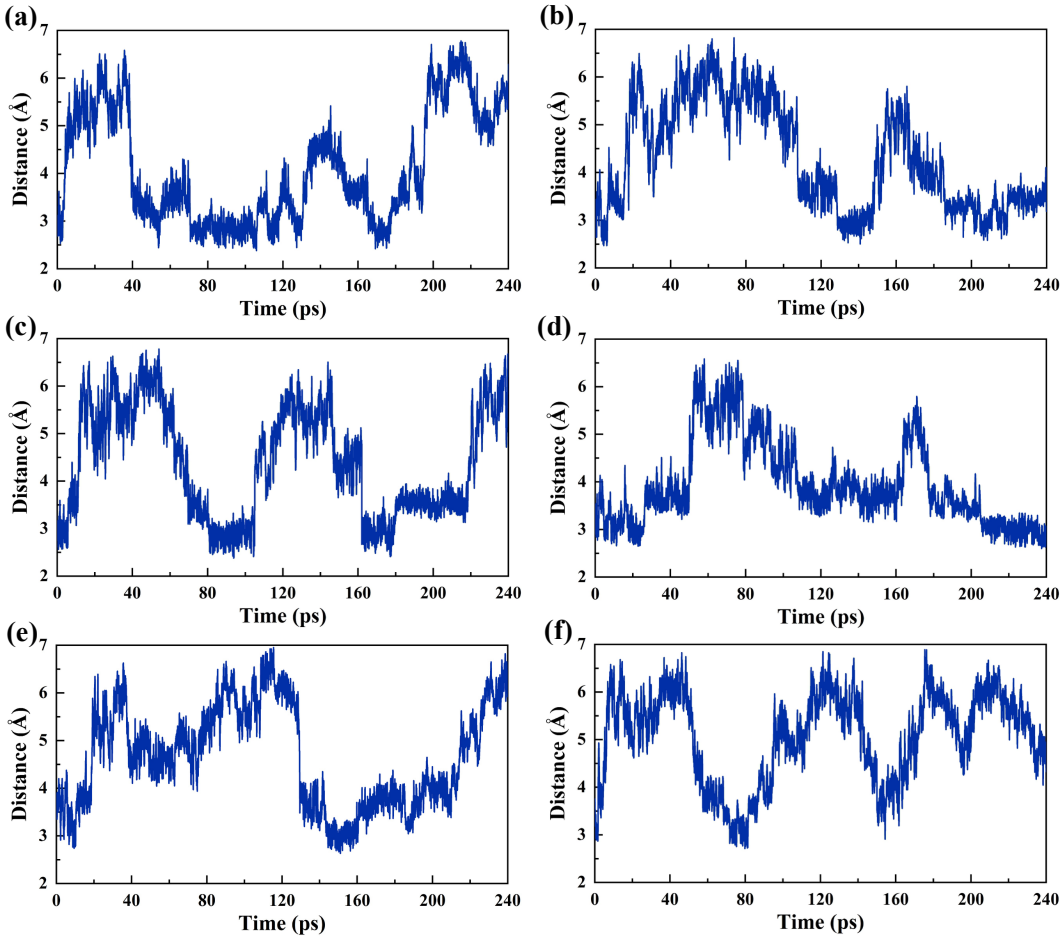


Figure S1. Time evolutions of the distances between Ca^{2+} and the central atom of

anionic groups during the simulation time for (a) Ca^{2+}–CO_3^{2-}, (b) Ca^{2+}–HCO_3^{-}, (c) Ca^{2+}–ACE^{-}, (d) Ca^{2+}–MP^{2-}, (e) Ca^{2+}–MP^{-}, and (f) Ca^{2+}–MES^{-} systems.

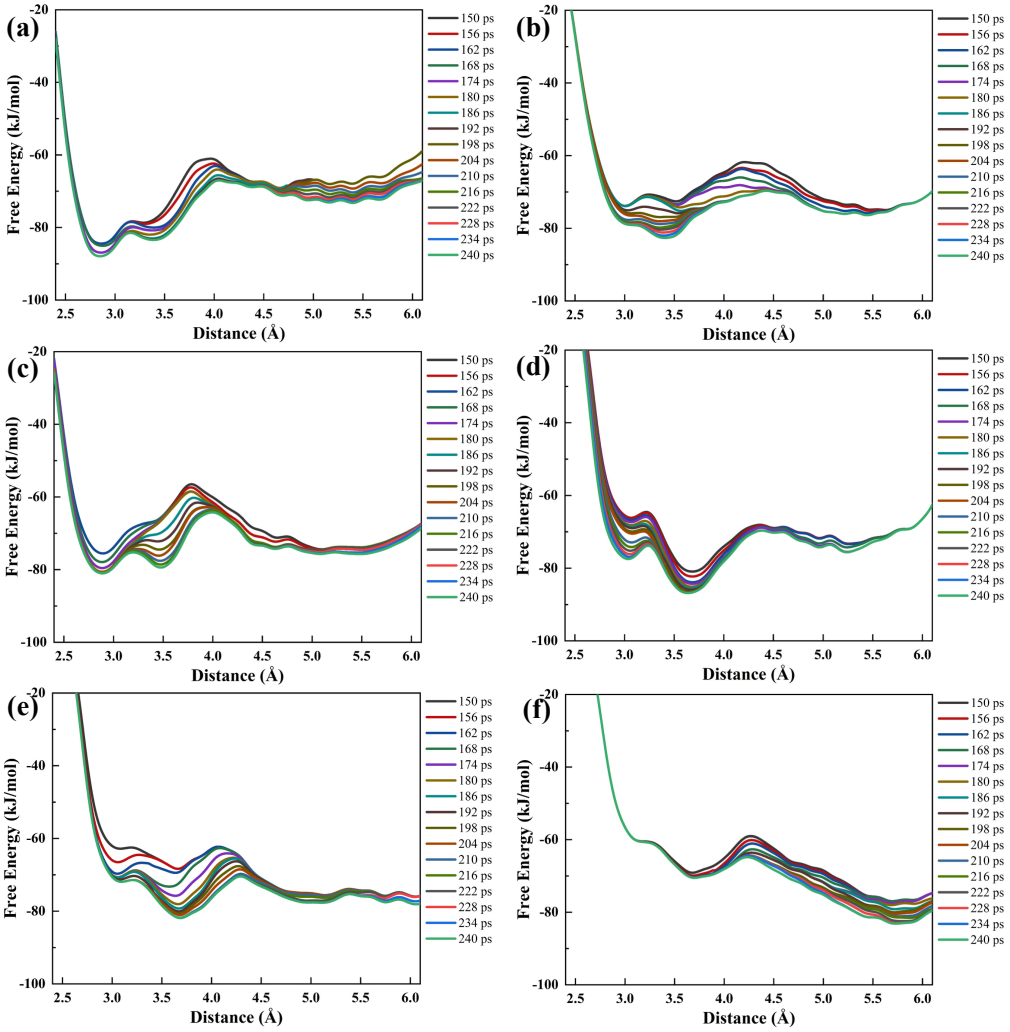


Figure S2. Free energy surfaces as a function of calcium−anion distances every 6 ps (200 Gaussian kernels deposited) along the last 90 ps simulation time for (a) Ca^{2+}–CO_3^{2-}, (b) Ca^{2+}–HCO_3^{-}, (c) Ca^{2+}–ACE^{-}, (d) Ca^{2+}–MP^{2-}, (e) Ca^{2+}–MP^{-}, and (f) Ca^{2+}–MES^{-} systems.

S4. Influence of the number of explicit water molecules on the calculated results

A mixed explicit/implicit solvation method captures both local and bulk solvent effects and thus enhances accuracy for thermodynamic properties. However, determining the appropriate number of explicit water molecules has always been a challenging and somewhat tricky problem. On one hand, from a theoretical standpoint, increasing the number of explicit water molecules provides a more realistic representation of the hydration environment surrounding the ion pair, leading to improved accuracy in the calculated results. On the other hand, from a practical computational standpoint, increasing the number of explicit water molecules introduces additional uncertainty and raises the difficulty of structural optimization, making it challenging to identify the lowest-energy configuration. In this section, we take the Ca^{2+}–CO_3^{2-} system as an example to illustrate the influence of the number of explicit water molecules on the calculated results.

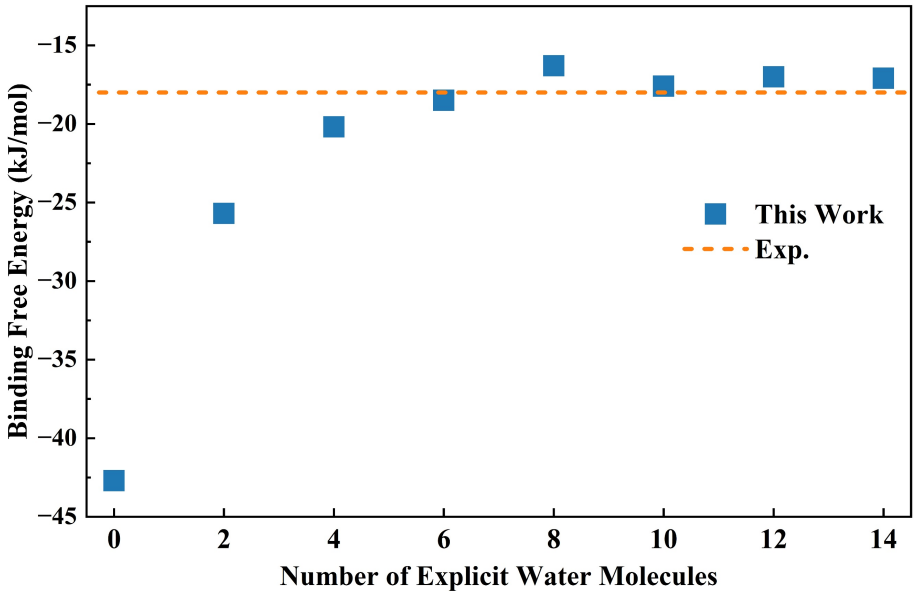


Figure S3. Binding free energies for the Ca^{2+}–CO_3^{2-} pair as a function of the number of explicit water molecules. Experimental data are from Ref. [4].

As shown in Fig. S3, the binding free energy for the Ca^{2+}–CO_3^{2-} pair is significantly underestimated in a purely implicit solvent. The introduction of explicit water molecules, even just two, can effectively alleviate this trend. When the number of water molecules exceeds six, the calculated results converge toward the

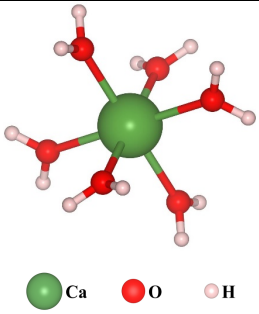
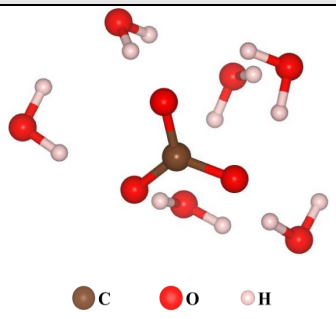
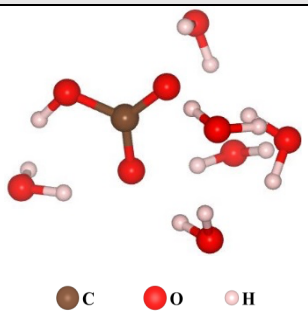
experimentally observed value. Meanwhile, we discovered that adding more explicit solvent molecules introduces many low-frequency vibrational modes, which increases the difficulty of structural optimization. This phenomenon has also been reported in recent literature [5]. Overall, we opted to incorporate twelve water molecules in all systems, achieving a balance between theoretical accuracy and computational feasibility. As shown in Table 1, the calculated results for Ca^{2+}–CO_3^{2-}, Ca^{2+}–HCO_3^{-}, and Ca^{2+}–ACE^{-} pairs agree well with available experimental and theoretical data, indicating the reliability of our calculation.

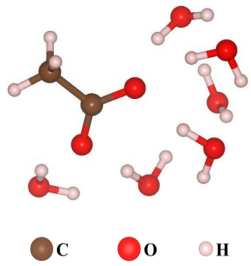
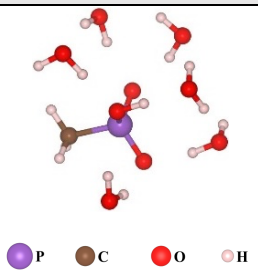
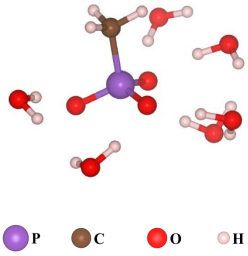
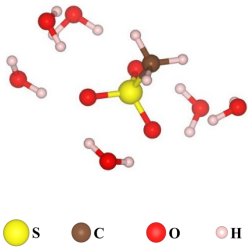
S5. Optimized structures and atomic coordinates of ion complexes

In the present DFT study, we first placed anionic groups around Ca^{2+} via a monodentate or bidentate binding mode. Afterwards, 12 explicit water molecules were randomly introduced into the systems using the PACKMOL code [6] to generate solvation shells around ion pairs. The reason for this strategy is that we do not want to impose a predefined pattern that might constrain the structural relaxation of the ion pairs. For each ion pair, we performed many independent calculations starting from different geometries. The most stable ion pairs were then placed in a 14.41 × 14.41 × 14.41 $Å^3$ periodic cubic box. Given that our AIMD simulations include 100 water molecules, the remaining 88 water molecules were again introduced using the PACKMOL code [6] to fill the box. Since the ion pairs already have a reasonable hydration structure, the equilibrium time required in the AIMD simulations is significantly shortened. Notably, we selected one monodentate and one bidentate configuration from the AIMD snapshots and performed structural optimization to verify whether we have obtained the most stable configuration in the static DFT study. Finally, the overall lowest-energy configuration was used to calculate the binding free energy.

The most stable configurations of all aqueous calcium−anion complexes after optimization are illustrated in Table S1. The structural and energetic information of several representative less stable calcium−anion complexes is displayed in Table S2.

Table S1. The most stable structures and corresponding atomic coordinates (Å) of ion complexes.

$Ca(H_2O)_6^{2+}$	$CO_3(H_2O)_6^{2-}$	$HCO_3(H_2O)_6^{-}$
		
Ca -0.0003 0.0004 0.0002	O -1.2154 0.0336 -1.3952	O 1.5845 -1.0279 -1.4525
O 1.6717 0.1170 1.7058	O 0.8319 0.9291 -1.3545	O -0.3557 0.0142 -1.2407
H 2.6307 0.1517 1.5822	O 0.5622 -1.2654 -0.9576	O 0.7538 -0.6321 0.6028
H 1.5312 0.1399 2.6629	O 3.2037 -1.3395 -0.0956	H 2.3035 -1.3590 -0.8821
O -1.6740 -0.1208 -1.7036	H 2.3007 -1.3726 -0.5022	O 0.3554 2.0457 1.5856
H -2.6330 -0.1525 -1.5790	H 3.1486 -0.4898 0.3702	H 0.5648 1.1108 1.4032
H -1.5344 -0.1476 -2.6607	O 2.2809 1.3497 0.8597	H -0.6029 2.0774 1.4242
O -0.0903 2.3889 -0.0789	H 1.8462 1.1897 -0.0274	O -2.2363 1.2283 0.5243
H -0.6508 2.9342 -0.6488	H 1.5502 1.1636 1.4710	H -1.5725 0.9559 -0.1424
H 0.4248 3.0117 0.4530	O -3.0893 -1.0842 -0.0348	H -2.2513 0.4570 1.1213
O 0.0929 -2.3880 0.0744	H -2.3287 -0.7687 -0.6488	O 1.1062 2.7432 -1.1579
H -0.4237 -3.0102 -0.4568	H -3.1653 -0.3371 0.5691	H 0.9282 2.6586 -0.2043
H 0.6547 -2.9338 0.6423	O -0.4816 0.8426 2.1792	H 0.6409 1.9853 -1.5365
O -1.7087 -0.0107 1.6737	H -0.5081 -0.0996 1.9066	O -1.8121 -1.4075 1.6011
H -2.0976 -0.7832 2.1076	H -0.7968 1.3468 1.4042	H -0.8776 -1.2220 1.3832
H -2.1547 0.7567 2.0589	O -0.6588 -1.9140 1.3369	H -2.1967 -1.6879 0.7540
O 1.7092 0.0127 -1.6718	H -1.5661 -1.8611 0.9903	O 3.2927 -1.4964 0.8354
H 2.1569 -0.7540 -2.0564	H -0.1246 -1.7706 0.5022	H 3.7905 -0.6748 0.9020
H 2.0965 0.7857 -2.1062	O -1.3046 2.4023 -0.2108	H 2.3564 -1.2268 1.0043
	H -0.3679 2.4394 -0.4761	O -2.8726 -1.2806 -1.1758
	H -1.5048 1.5602 -0.7177	H -3.2704 -0.4636 -0.8458
	C 0.0806 -0.1058 -1.2433	H -1.9778 -0.9828 -1.4289
		C 0.6061 -0.5207 -0.6550

$ACE(H_2O)_6^-$	$MP(H_2O)_6^-$	$MP(H_2O)_6^{2-}$	$MES(H_2O)_6^-$
			
C 0.9113 -2.8931 -0.2766	C -0.4830 -2.1924 1.1876	C 0.6102 -1.5877 1.3825	C -0.6422 -0.6276 -1.7234
C 0.6755 -1.4792 0.2451	H -0.7117 -2.2709 2.2503	H 0.4301 -2.5985 1.0097	H 0.2220 -0.3247 -2.3120
O -0.5356 -1.0937 0.2873	H -1.2424 -2.7248 0.6147	H 1.6030 -1.5423 1.8350	H -0.7726 -1.7081 -1.7578
O 1.6578 -0.7898 0.5809	H 0.5028 -2.6225 1.0069	H -0.1470 -1.3445 2.1312	H -1.5459 -0.1178 -2.0534
H 0.2946 -3.5982 0.2833	H -0.1452 0.3304 -1.3059	P 0.5225 -0.3836 -0.0074	S -0.3466 -0.1784 -0.0221
H 0.5934 -2.9426 -1.3205	P -0.4972 -0.4414 0.7263	O 0.6966 1.0071 0.6326	O 0.8698 -0.9144 0.3726
H 1.9612 -3.1705 -0.2029	O -0.1870 -0.5786 -0.8774	O -0.9086 -0.5643 -0.5829	O -1.5364 -0.6046 0.7264
O 1.4617 1.9933 0.4687	O 0.6392 0.2848 1.4002	O 1.6339 -0.7528 -0.9812	O -0.1556 1.2807 -0.0066
H 0.8205 2.1665 -0.2430	O -1.8885 0.1182 0.8995	O -2.6011 1.3118 -1.6227	O -2.6171 2.2695 1.0559
H 1.4734 1.0153 0.5623	O -3.2085 -1.5002 -1.0495	H -1.8440 0.6915 -1.4611	H -2.6284 1.4435 1.5566
O 3.9871 0.5723 -0.4949	H -2.4059 -1.4200 -1.5783	H -3.2059 1.0089 -0.9306	H -1.7429 2.2149 0.6294
H 3.4076 -0.1431 -0.1887	H -3.0014 -0.9098 -0.2987	O -2.9197 0.1259 1.1529	O 3.3180 0.1185 1.5470
H 3.4409 1.3529 -0.3225	O -0.0106 1.9163 -1.7855	H -2.1591 -0.2127 0.6128	H 2.4043 -0.2031 1.4579
O -1.0341 2.3940 -1.0622	H 0.8130 2.1426 -1.2993	H -2.5870 1.0165 1.3692	H 3.7315 -0.2261 0.7413
H -1.3125 2.1503 -0.1619	H -0.7173 2.3274 -1.2444	O 4.1624 -0.9480 0.0650	O 2.5280 2.1999 -0.3675
H -1.3165 1.6213 -1.5850	O 2.0340 2.2491 0.0760	H 3.2541 -1.0685 -0.3158	H 1.5696 2.0369 -0.2982
O -3.3389 -0.6765 0.7159	H 2.7867 1.6457 -0.0323	H 4.1448 0.0086 0.2142	H 2.8768 1.8046 0.4492
H -3.0903 0.1430 1.1652	H 1.4545 1.7105 0.6617	O 3.0534 1.8319 -0.4869	O -0.7022 -3.4888 0.6845
H -2.4929 -1.1536 0.6719	O -1.8160 2.7400 0.2395	H 2.2331 1.7161 0.0592	H 0.1389 -3.0129 0.6512
O -1.1799 1.2212 1.5931	H -1.1814 3.0558 0.8923	H 2.8774 1.1208 -1.1237	H -1.3191 -2.7642 0.8613
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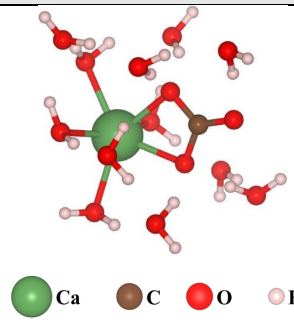
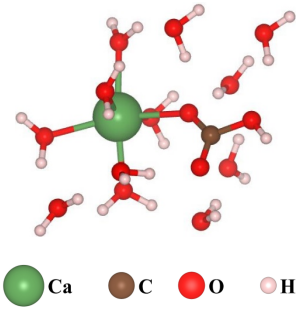
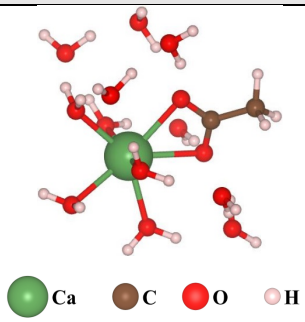
H -1.3525 -0.5909 -1.3233	H 3.0857 -0.9640 -0.1829	O -2.7448 -2.6069 -0.5456	O 3.1548 -0.4152 -1.4238
H -2.8041 -0.2046 -1.3703	O 2.0800 -2.0519 -1.5194	H -1.9676 -2.0132 -0.6964	H 3.0167 0.5446 -1.3119
	H 1.2592 -1.5300 -1.3818	H -3.2466 -2.0927 0.0973	H 2.3825 -0.7950 -0.9764
	H 1.8635 -2.9331 -1.2003		

$CaCO_3(H_2O)_{12}$	$CaHCO_3(H_2O)_{12}^+$	$CaACE(H_2O)_{12}^+$
		
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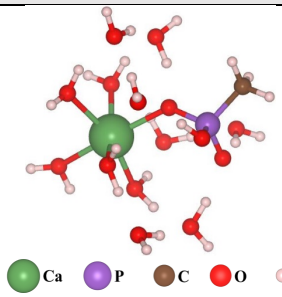	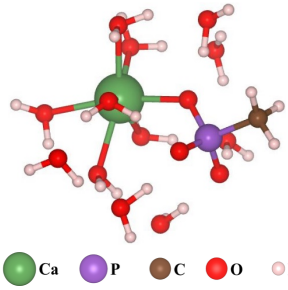	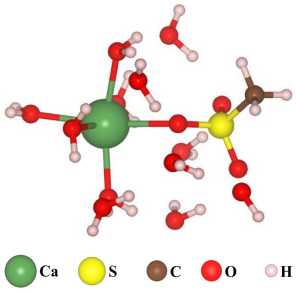
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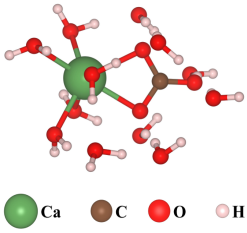
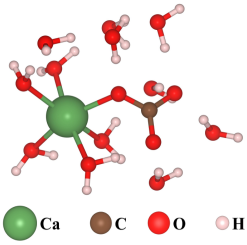
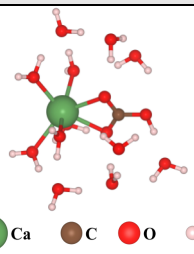
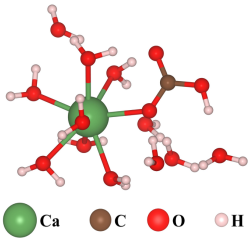
Table S2. The representative less stable structures and corresponding atomic coordinates (Å) of contact ion pairs. ΔG denotes the free energy difference between the given configuration and the most stable counterpart listed in Table S1.

$CaCO_3(H_2O)_{12}$		$CaHCO_3(H_2O)_{12}^+$	
			
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C 0.6201 1.2261 -0.2356	C -0.9595 0.7028 -1.2598	C -0.2799 1.3787 -0.0621	C 1.4532 -1.5752 -1.0128
O 0.7281 0.4259 -1.2563	O 0.2508 0.5982 -0.7850	O 0.5877 0.8790 -0.8214	O 0.5698 -2.3713 -1.3697
O 0.0297 0.7330 0.8192	O -1.3506 -0.0823 -2.1810	O -0.9067 0.6701 0.7959	O 1.2068 -0.3881 -0.5492
O 1.0697 2.4065 -0.2549	O -1.7417 1.5819 -0.7314	O -0.5372 2.6766 -0.1627	O 2.7205 -1.9601 -1.0867
O 3.2904 -0.3913 -1.5527	O -1.2416 -1.773 0.9118	H -1.3408 2.9082 0.3753	H 3.3249 -1.2793 -0.7113
H 2.4293 0.0694 -1.6748	H -1.9559 -1.8855 0.2193	O 2.4022 -0.3461 1.3866	O 0.7551 2.2564 0.8276
H 3.7265 0.1516 -0.8755	H -1.5699 -1.0133 1.4382	H 2.5657 -0.6022 2.3018	H 1.1394 1.9107 1.6477
O -2.3139 -0.7156 -1.1492	O 3.3947 -0.9179 0.0495	H 3.2464 -0.4092 0.8836	H 1.5092 2.3541 0.2088
H -2.1696 0.0915 -1.7136	H 3.6613 -0.7074 0.9528	O 2.1469 -2.3136 -0.9412	O -1.3408 0.6964 2.3248
H -2.9559 -0.4617 -0.4583	H 3.7987 -0.1952 -0.5131	H 2.2218 -3.0343 -1.5730	H -0.9281 -0.0105 2.8640
O 2.1174 0.4165 2.6007	O 0.3336 -2.0212 -2.0604	H 2.9958 -1.8014 -0.9652	H -2.2751 0.7216 2.5603
H 1.3076 0.7687 2.1761	H -0.3191 -1.2605 -2.2784	O 0.0974 -1.1344 2.7756	O 2.1261 -0.0312 2.0116
H 2.8311 0.8171 2.0735	H 0.0494 -2.8015 -2.5417	H -0.5070 -1.7923 3.1401	H 1.9093 -0.1912 1.0656
O 3.6033 1.6971 0.4742	O 0.1431 1.7630 2.7903	H -0.3346 -0.2765 2.8964	H 3.0921 -0.0635 2.0351
H 4.2662 2.3912 0.5374	H -0.7834 1.4649 2.7452	O -1.0154 -1.6027 -1.7195	O -0.4019 1.8535 -2.1487
H 2.7705 2.1320 0.1651	H 0.1952 2.4253 2.0688	H -0.7668 -1.9109 -2.5969	H -0.7212 1.2946 -2.8720
O -1.2918 -3.1925 -1.4206	O 1.4203 -0.4630 2.2718	H -1.9333 -1.9017 -1.5414	H -0.8319 2.7134 -2.2346
H -2.0171 -2.5628 -1.6004	H 1.3570 -1.0039 3.0647	O -1.1597 -3.0300 0.9474	O -1.4805 -0.7502 -2.1099
H -1.6929 -3.9800 -1.0394	H 0.9961 0.4249 2.4918	H -1.0578 -3.9794 1.0690	H -2.3172 -1.2375 -2.1052
O -1.5463 1.4334 -2.5623	O -3.1313 -1.7486 -0.9729	H -2.0600 -2.8787 0.5784	H -0.7729 -1.4378 -2.0756
H -0.6148 1.1787 -2.4160	H -3.8036 -1.1133 -0.6677	O 3.1895 1.6753 -1.4784	O -3.4074 0.4972 0.0629
H -1.6295 2.2771 -2.0823	H -2.6043 -1.1958 -1.5937	H 2.2313 1.5031 -1.5389	H -3.7471 -0.4042 -0.1416
O -1.2722 3.6615 -0.7255	O 2.0503 2.5657 -1.1666	H 3.2353 2.2691 -0.7041	H -4.0460 1.1265 -0.2860
H -0.3417 3.3834 -0.5262	H 1.3757 1.8482 -1.1185	O 2.5253 2.6991 1.0587	O -1.1709 -1.8486 0.6473
H -1.2392 4.5951 -0.9541	H 1.6945 3.2234 -0.5532	H 1.6981 3.1763 0.9178	H -0.7935 -1.9993 1.5342
O -2.1526 2.1320 1.5388	O 0.8089 -3.4241 1.2874	H 2.2729 1.8009 1.3164	H -0.5574 -2.2674 -0.0032
H -1.2740 1.6936 1.4223	H -0.1458 -3.2425 1.4011	O -3.5103 0.4677 0.0305	O 0.1342 -1.4646 3.1198
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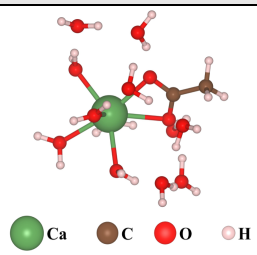
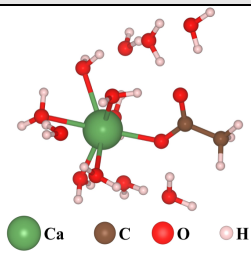
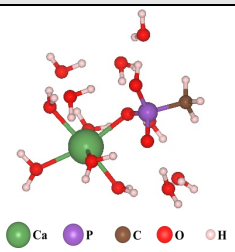
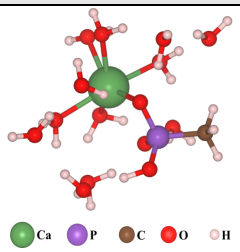
O 1.8536 -2.5517 -0.9970	O -0.1491 3.4069 0.5455	H -3.2861 0.7697 -0.8762	H 1.0056 -1.0687 2.8762
H 1.8082 -3.1107 -1.7790	H -0.7257 2.7860 0.0249	O -2.8880 3.1565 1.0663	O -1.7069 3.0511 0.1299
H 2.5327 -1.8434 -1.1890	H -0.6432 4.2291 0.6192	H -3.3633 3.9933 1.1003	H -2.4315 3.4984 0.5780
O -1.7212 -1.9737 1.6584	O -2.2274 0.6733 1.7874	H -3.5329 2.4638 0.8550	H -0.8902 3.2885 0.6039
H -2.4558 -1.3225 1.7166	H -3.1937 0.6946 1.7760	O -2.2222 1.0766 -2.3565	O 4.3611 -0.0447 0.0976
H -1.2711 -1.9891 2.5109	H -1.9866 1.0665 0.9090	H -1.4693 0.4720 -2.2894	H 5.3153 -0.1472 0.0093
H -4.4836 0.0730 1.5328	O 4.3052 1.1899 -1.2277	H -1.8406 1.9538 -2.4813	H 4.1140 0.7912 -0.3414
O -3.5743 -0.0151 1.2332	H 3.5273 1.8113 -1.1835	O -3.3536 -2.1417 -0.4180	O 2.6815 1.8049 -1.0924
H -3.1180 0.8786 1.3645	H 4.6087 1.1994 -2.1403	H -4.1798 -2.5901 -0.6290	H 2.1211 0.9966 -1.1587
H 2.0079 -2.5704 1.5369	O -4.2854 0.7777 -0.3168	H -3.5753 -1.1901 -0.1952	H 2.6448 2.2475 -1.9474
O 1.2911 -1.9825 1.8002	H -4.9986 1.1809 -0.8201	O 4.1461 -0.5699 -0.6486	O -3.6022 -2.0990 -0.5760
H 1.7152 -1.1634 2.1834	H -3.4409 1.1565 -0.6705	H 5.0983 -0.6636 -0.7573	H -4.2314 -2.8264 -0.5328
Bidentate mode	Monodentate mode	H 3.8647 0.3197 -1.0562	H -2.8385 -2.3170 -0.0034
ΔG = +1.7 kJ/mol	ΔG = +5.6 kJ/mol	Bidentate mode	Monodentate mode
		ΔG = +6.3 kJ/mol	ΔG = +0.8 kJ/mol

$CaACE(H_2O)_{12}^+$		$CaMP(H_2O)_{12}^+$	
			
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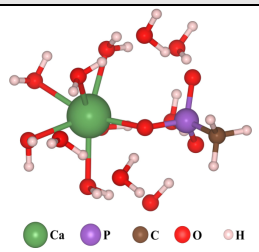
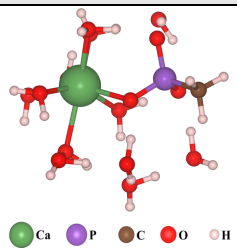
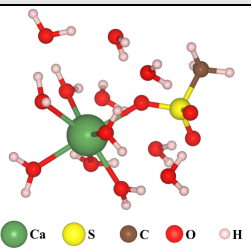
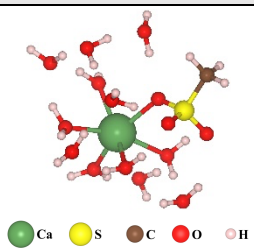
$CaMP(H_2O)_{12}$		$CaMES(H_2O)_{12}^{+}$	
			
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C 1.8077 3.0774 -0.9926	C 3.5181 0.1647 -1.2722	C -2.7662 0.2735 -2.2449	C -1.5298 3.2049 -1.4276
H 1.2602 3.2393 -1.9218	H 3.4258 0.4755 -2.3125	H -2.3855 1.1987 -2.6723	H -1.0690 3.3077 -2.4078
H 1.4278 3.7505 -0.2223	H 3.7583 1.0384 -0.6647	H -2.3931 -0.5846 -2.8009	H -2.4701 2.6640 -1.5040
H 2.8621 3.2986 -1.1556	H 4.3197 -0.5687 -1.1878	H -3.8537 0.2782 -2.2240	H -1.6659 4.1814 -0.9678
P 1.6322 1.3565 -0.4514	P 1.9624 -0.5711 -0.7184	S -2.1911 0.1634 -0.5689	S -0.4186 2.2914 -0.3938
O 2.3584 1.1937 0.8747	O 2.1464 -1.0346 0.7454	O -2.7191 -1.1048 -0.0314	O -1.0418 2.2105 0.9460
O 2.1798 0.4565 -1.5746	O 1.5849 -1.7258 -1.6463	O -2.6741 1.3338 0.1533	O 0.8666 2.9665 -0.3904
O 0.1022 1.1053 -0.2989	O 0.8777 0.5401 -0.7772	O -0.7078 0.1376 -0.6596	O -0.3195 0.9172 -0.9839
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H 1.4145 -1.7017 1.9203	H -0.1062 0.1485 2.3447	H -1.1153 -0.0557 2.8613	H 0.1512 -0.1926 2.7449
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H -0.9276 2.2188 0.0166	H -3.1817 1.4710 -2.2193	H 0.0815 -0.9036 -2.0752	H 0.5579 -2.5330 -2.6822
O 0.2912 -2.3103 -1.2456	O -0.8382 -1.2856 -2.5569	O 1.1422 2.4593 1.1681	O -2.5584 0.3035 -2.5597
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H 1.2504 -2.4105 -1.0649	H -0.8423 -0.6810 -3.3061	H 0.3277 2.9264 0.8823	H -2.5389 0.0831 -3.4962
O -3.4782 -0.6604 0.7505	O 1.2002 3.0943 -0.3257	O 2.8259 -1.6932 0.2605	O -3.5203 -1.2864 -0.5306
H -3.8350 0.0660 0.2031	H 1.1695 2.1094 -0.5180	H 3.0987 -1.7619 -0.6805	H -3.3362 -0.7016 -1.2944
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H 3.7089 -2.2331 -1.5675	H -0.8592 2.1165 1.5012	H -1.5737 4.3266 0.1967	H -0.8489 -2.2089 1.9437
H 2.8072 -0.9749 -1.2159	H -1.6585 2.7645 0.3351	H -1.7603 2.7752 0.0322	H -1.0206 -3.0138 0.5898
O -1.9135 -3.1343 0.2510	O 0.9460 -3.6806 0.0739	O 3.0418 0.1865 2.3371	O 2.9474 2.0827 1.5259
H -1.3973 -3.3973 -0.5272	H 1.4368 -3.3230 0.8265	H 3.2723 0.6841 3.1275	H 2.4384 1.5915 2.1867
H -2.8355 -3.0572 -0.0228	H 1.2881 -3.1148 -0.6676	H 3.7842 -0.3867 2.1097	H 2.3583 2.7938 1.2287
O 0.9740 1.1357 3.1736	O -3.4784 -0.2354 0.6610	O -1.1575 -3.2475 -0.7371	O 2.7969 -2.2291 0.3586
H 1.4920 1.2587 2.3326	H -3.3903 -0.9340 1.3576	H -1.8767 -2.6020 -0.5590	H 3.6588 -2.0192 -0.0851
H 1.4214 0.4197 3.6368	H -3.5287 0.6055 1.1333	H -1.5622 -4.1173 -0.8245	H 2.8654 -3.0917 0.7785
O 0.3689 -0.3845 -3.2173	O -1.1545 3.7509 -1.2308	O 1.1192 3.2932 -1.7404	O -2.0360 -3.3869 -0.8627
H 1.0910 0.0341 -2.6349	H -1.2277 4.6531 -1.5543	H 0.2321 3.4358 -1.3622	H -2.5195 -4.1939 -1.0667
H 0.6619 -0.3338 -4.1306	H -0.1960 3.5974 -0.9560	H 1.2186 3.8967 -2.4830	H -2.7002 -2.6402 -0.7338
O -1.4971 0.6589 2.2684	O 2.8723 0.8509 2.3760	O 0.2430 -2.1795 1.4195	O -3.0138 0.4811 1.7241
H -0.6242 0.7829 2.7314	H 3.7206 1.2299 2.1297	H -0.4534 -2.1788 2.0978	H -3.8069 0.9435 2.0196
H -1.6946 1.5383 1.9045	H 2.6963 0.0815 1.7442	H -0.1390 -2.7042 0.6866	H -2.3895 1.1731 1.4036
O -3.7549 1.5422 -0.9452	O 0.6137 2.1316 2.5638	O 3.0319 -1.4290 -2.4323	O -1.4227 -1.1203 3.2933
H -4.4715 2.0785 -1.2955	H 0.5630 2.5168 3.4442	H 3.5892 -1.7265 -3.1580	H -1.6975 -1.3733 4.1808
H -3.0874 2.1522 -0.5380	H 1.5224 1.7043 2.4917	H 2.0874 -1.6408 -2.6474	H -2.1316 -0.5649 2.8981
O 2.9369 -1.2565 1.7513	O -2.6418 -2.1859 2.3523	O -2.2201 -1.4494 2.6607	O 4.7455 -1.2286 -1.1071
H 2.8474 -0.3100 1.4563	H -2.4638 -2.7634 1.5915	H -2.6285 -1.3323 1.7768	H 4.3196 -0.3543 -1.1441
H 3.2261 -1.6995 0.9344	H -1.7737 -1.7657 2.4879	H -2.9115 -1.7153 3.2756	H 5.6914 -1.0909 -0.9928
Monodentate mode	Monodentate mode	Monodentate mode	Monodentate mode
ΔG = +0.3 kJ/mol	ΔG = +0.8 kJ/mol	ΔG = +1.3 kJ/mol	ΔG = +2.2 kJ/mol

S6. Analysis of charge density difference

In this section, an analysis of the charge density difference was performed to estimate the bonding strength between Ca^{2+} and the anionic groups. For Ca^{2+}–CO_3^{2-}, Ca^{2+}–HCO_3^-, and Ca^{2+}–ACE^- pairs, both bidentate and monodentate structures exist. While for Ca^{2+}–MP^{2-}, Ca^{2+}–MP^-, and Ca^{2+}–MES^- pairs, even if the phosphonate or sulfonate group is placed in a bidentate coordination with Ca^{2+} in the initial setup, one O atom from anions is detached from Ca^{2+} during the energy minimization, forming the monodentate binding mode in the end. Therefore, in Fig. S4, we first displayed the results of the charge density difference for bidentate configurations of Ca^{2+}–CO_3^{2-}, Ca^{2+}–HCO_3^-, and Ca^{2+}–ACE^- pairs. Wherein, the yellow and cyan areas represent an increase and decrease in charge density, respectively. In general, more charge accumulation in the bonding region indicates a stronger interaction. Accordingly, we can qualitatively state that Ca^{2+}–CO_3^{2-} pair possesses the strongest Ca–O interaction, followed by Ca^{2+}–HCO_3^- and Ca^{2+}–ACE^- pairs from Fig. S4. To describe the charge accumulation in more detail, as shown in Fig. S6(a), we exported the 1D charge density differences along the Ca–O pathway. Obviously, the charge accumulation in the Ca^{2+}–CO_3^{2-} pair is the most significant.

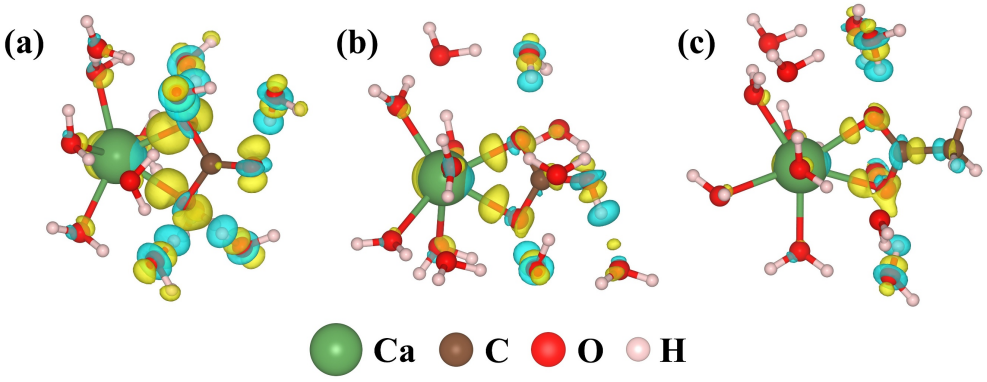

Figure S4. Charge density differences (isosurface = 0.006 e/bohr^3) for bidentate configurations of aqueous (a) Ca^{2+}–CO_3^{2-}, (b) Ca^{2+}–HCO_3^-, and (c) Ca^{2+}–ACE^- ion pairs.

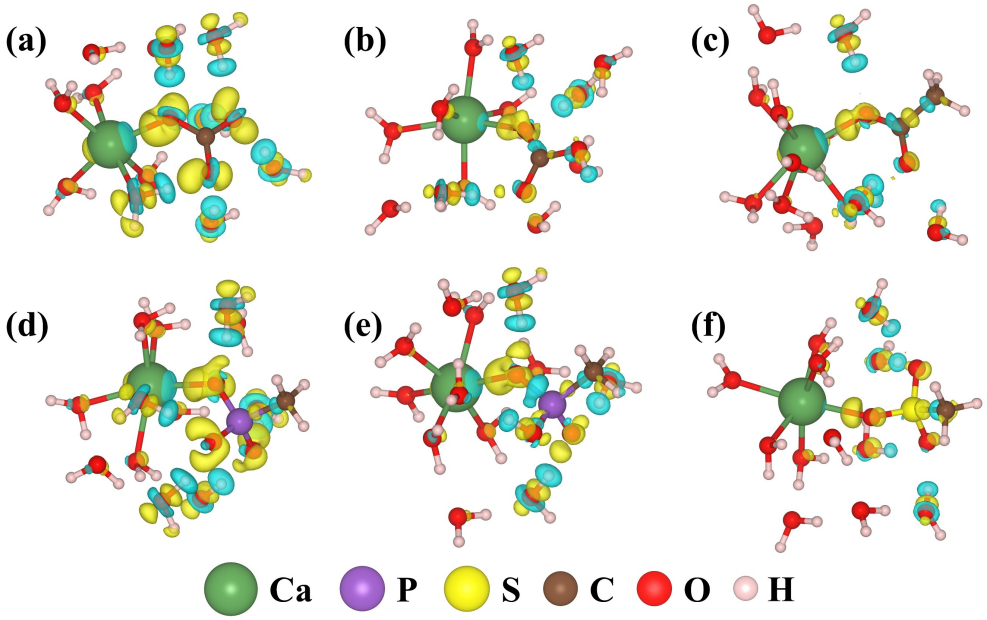

Figure S5. Charge density differences (isosurface = 0.006 e/bohr^3) for monodentate configurations of aqueous (a) Ca^{2+}–CO_3^{2-}, (b) Ca^{2+}–HCO_3^-, (c) Ca^{2+}–ACE^-, (d) Ca^{2+}–MP^{2-}, (e) Ca^{2+}–MP^-, and (f) Ca^{2+}–MES^- ion pairs.

Moreover, the results of the charge density difference for monodentate configurations and the corresponding 1D profiles were displayed in Fig. S5 and Fig. S6(b), respectively. Combined with the values of binding free energy shown in Table 1, one can notice that stronger Ca–O interactions typically result in enhanced stability. The only exception is the Ca^{2+}–MP^- pair, which exhibits a stronger Ca–O interaction but a less negative binding free energy in comparison with the Ca^{2+}–HCO_3^- pair. We attributed this phenomenon to the difference in the geometries of the functional groups. Compared to the planar (bi)carbonate/carboxylate, the attachment of the bulky trigonal pyramidal phosphonate group with Ca^{2+} squeezes the living space of water molecules in the first solvation shell of Ca^{2+} and thus weakens the stability of the contact ion pair.

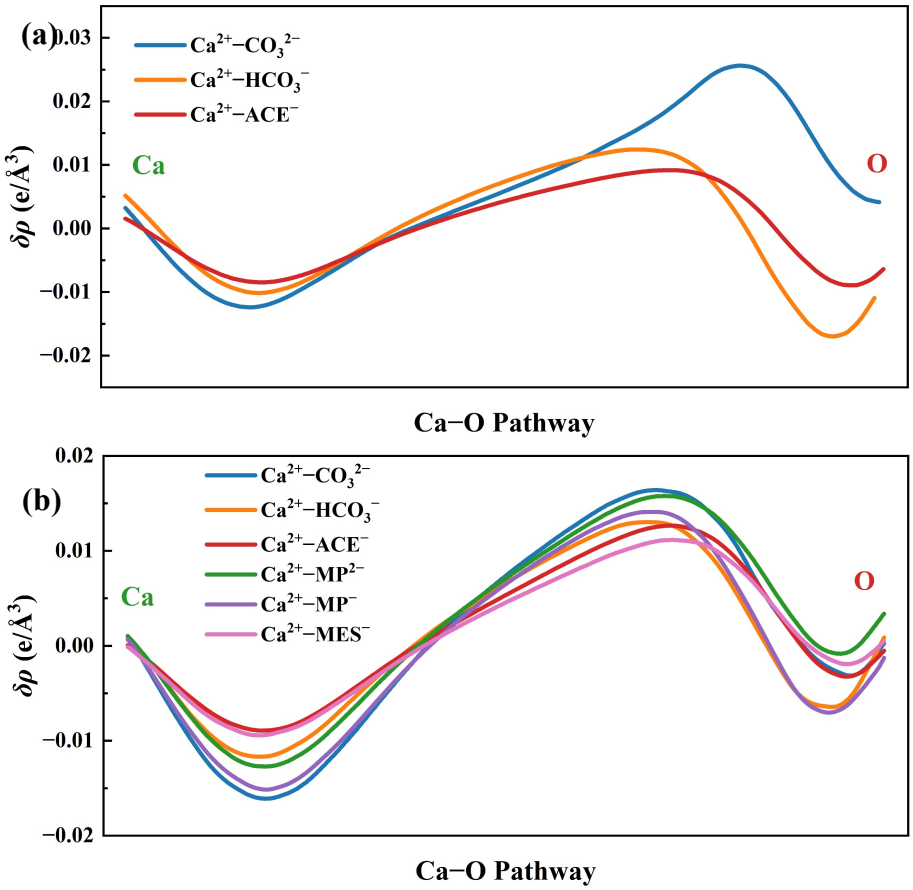

Figure S6. 1D charge density differences along the Ca−O pathway for (a) bidentate and (b) monodentate configurations.

S7. Effects of initial structures on simulation results

We conducted three independent ab initio MetaD simulations for the Ca^{2+}–CO_3^{2-} system to confirm the consistency of our calculations within the given methodological framework. The snapshots of the system after 20, 30, and 40 ps NVT run were selected the initial structures in Test_1, Test_2, and Test_3 as shown in Fig. S7. Although there are some differences between free energy profiles, especially at the calcium–anion distances above 5 Å, the most important property for the contact ion pair, namely the activation barrier for decomposition, falls within the range of 20.9 ± 1 kJ/mol. The errors induced by the limited time scale of AIMD simulation are acceptable.

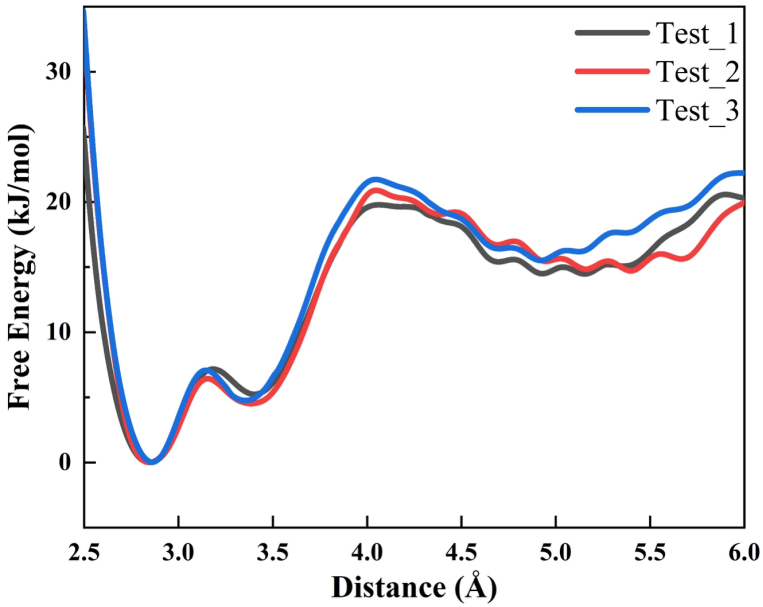

Figure S7. Free energy profiles as a function of calcium–anion distance for the Ca^{2+}–CO_3^{2-} system with different initial structures.

S8. Spatial distributions of Ca^{2+} around the anionic groups

In Fig. S8, we displayed the 3D spatial distributions of Ca^{2+} around the anionic groups for the contact ion pairs.

For each AIMD frame, the reference anionic group, e.g., ACE^{-}, is assigned a local coordinate frame that remains fixed relative to its internal geometry. Typically, the carbon atom of the group is placed at the origin, one C−O bond defines the x-axis, and the plane of the group defines the y- and z-axes. This transformation eliminates the effects of global translation and rotation, ensuring that the spatial distribution reflects the intrinsic molecular environment rather than overall system motion. Afterwards, the position of the target ion, i.e., Ca^{2+}, is re-expressed in the newly defined coordinate system for every frame of the trajectory. Repeating this over all snapshots yields a large set of ion coordinates that describe how the Ca^{2+} is distributed relative to the anionic group across the entire simulation. In this work, for simplicity, we only presented the results for contact ion pairs.

The 3D spatial distribution can be visualized as an isosurface. High-density regions correspond to preferred binding sites or stable coordination geometries.

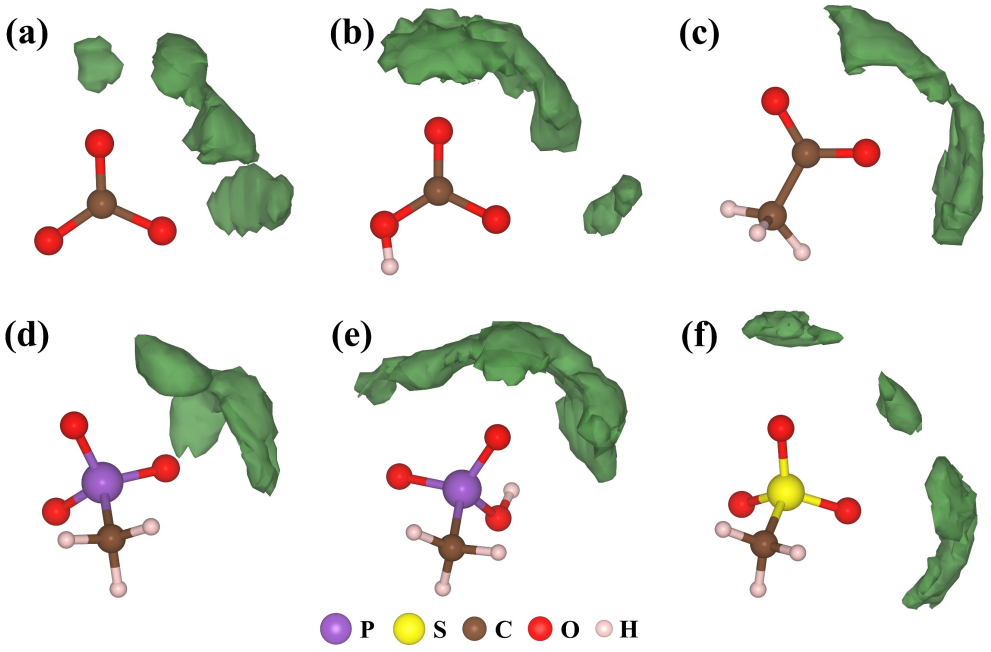

Figure S8. Spatial distributions of Ca^{2+} around (a) CO_3^{2-}, (b) HCO_3^{-}, (c) ACE^{-}, (d) MP^{2-}, (e) MP^{-}, and (f) MES^{-} groups for contact ion pairs.

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