Supplementary Information

Computational Prediction of Solvation Structure in Calcium Battery Electrolytes

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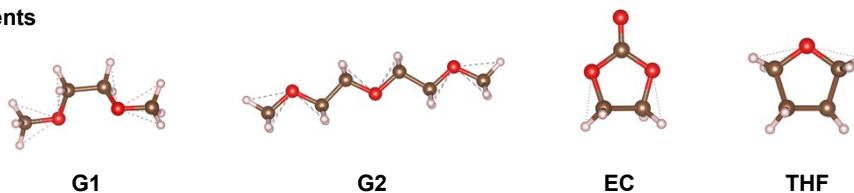
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Supplementary Figures

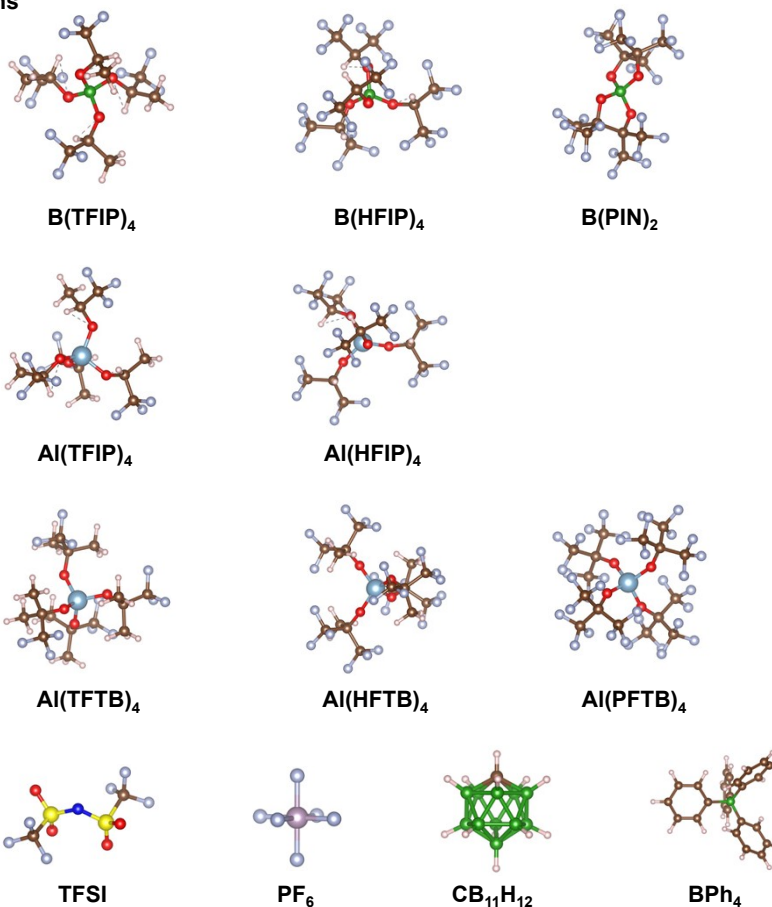| Solvents	Anions											
	Fluorinated Alkoxy Anions								Other Anions			
	Borates			Aluminates								
	B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$
G1												
G2												
EC												
THF												

Figure S1. Schematics and atomistic structures of solvents and anions that make up the Ca battery electrolytes. The colors assigned to the atoms: red for O, brown for C, white for H, yellow for S, blue for N, light blue for F, cyan for Al, green for B, and light purple for P.

Figure S2. Electrolytes of 0.5 M Ca[PF$_6$]$_2$ in the presence of solvent species with a density of 1 g/ml. (a)-(c) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in G1 solvent species after AIMD simulations. (d)-(f) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in EC solvent species after AIMD simulations. In the snapshots, the colors assigned to the atoms: red for O, brown for C, white for H, blue for Ca, light pink for P, and light blue for F.
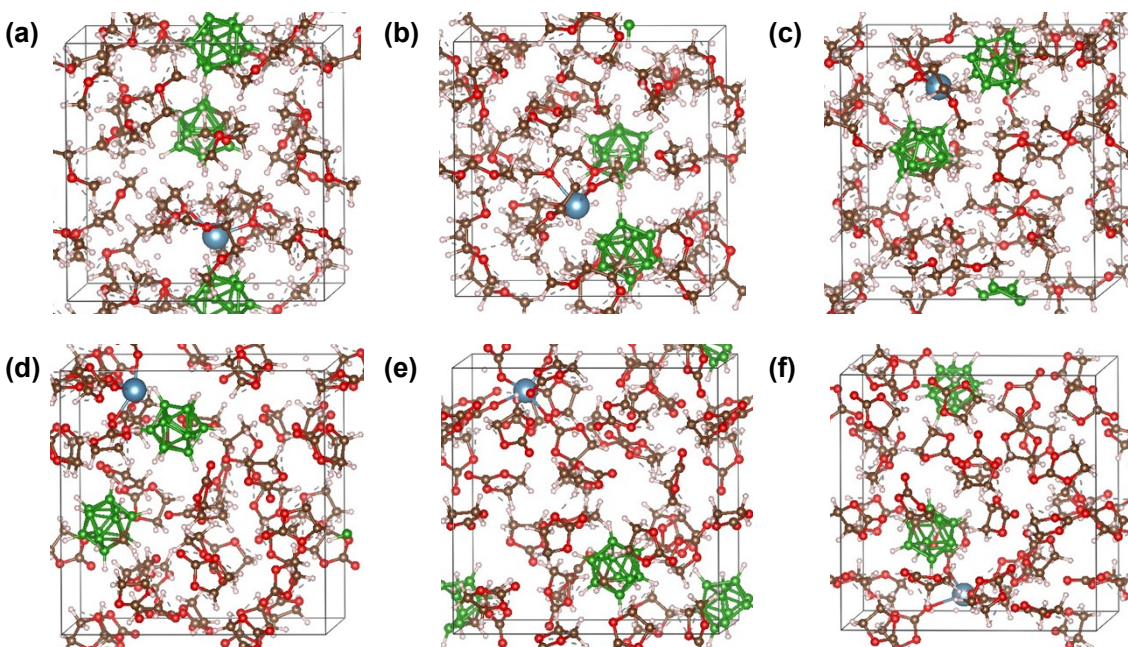
Figure S3. Electrolytes of 0.5 M Ca[CB$_{11}$H$_{12}$]$_2$ in the presence of solvent species with a density of 1 g/ml. (a)-(c) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in G1 solvent species after AIMD simulations. (d)-(f) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in EC solvent species after AIMD simulations. In the snapshots, the colors assigned to the atoms: red for O, brown for C, white for H, blue for Ca, and green for B.

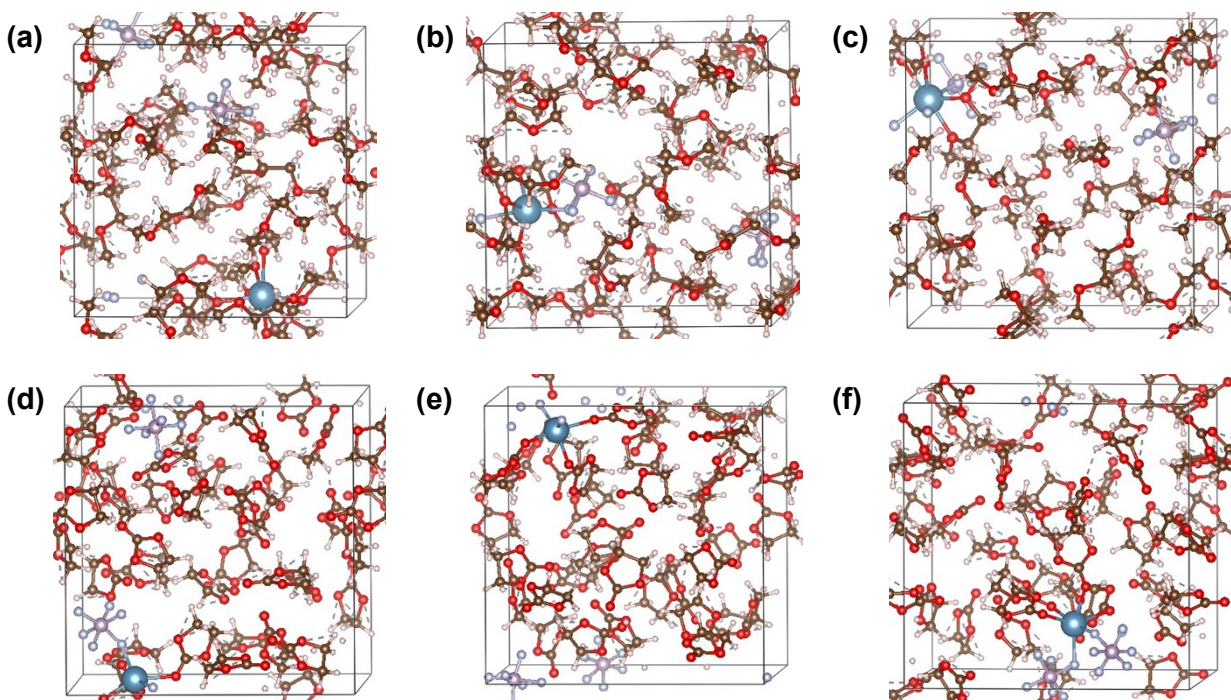**Figure S4.** Electrolytes of 0.5 M Ca[BPh$_4$]$_2$ in the presence of solvent species with a density of 1 g/ml. (a)-(c) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in G1 solvent species after AIMD simulations. (d)-(f) present the snapshots for the final structure of SSIP, CIP-A1, and CIP-A2 in EC solvent species after AIMD simulations. In the snapshots, the colors assigned to the atoms: red for O, brown for C, white for H, blue for Ca, and green for B.

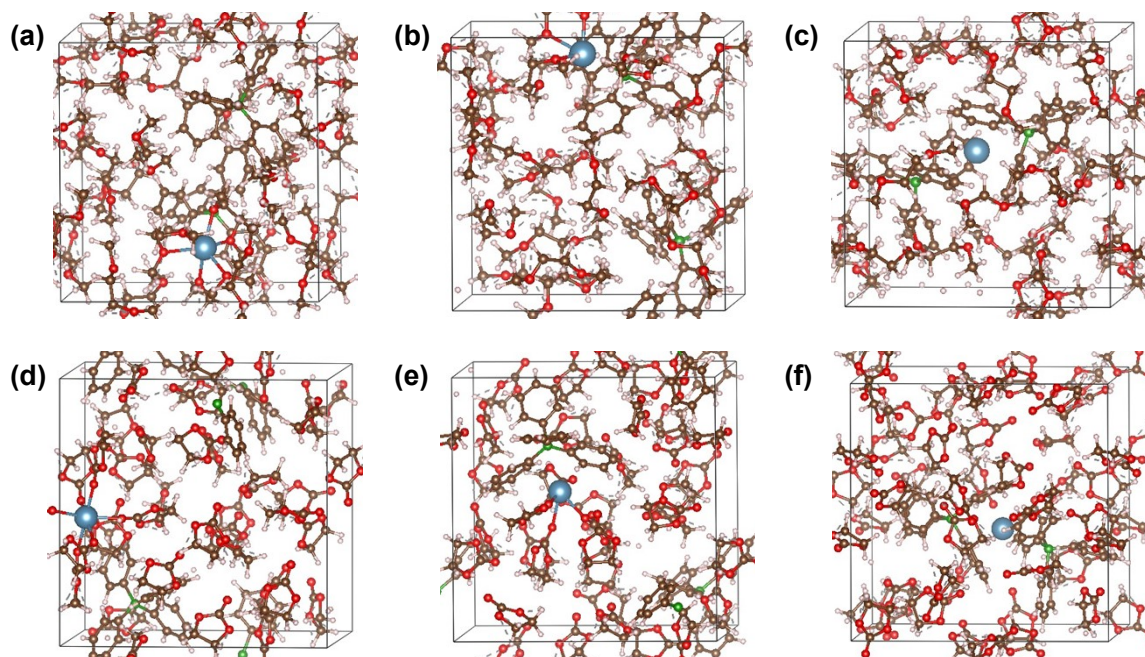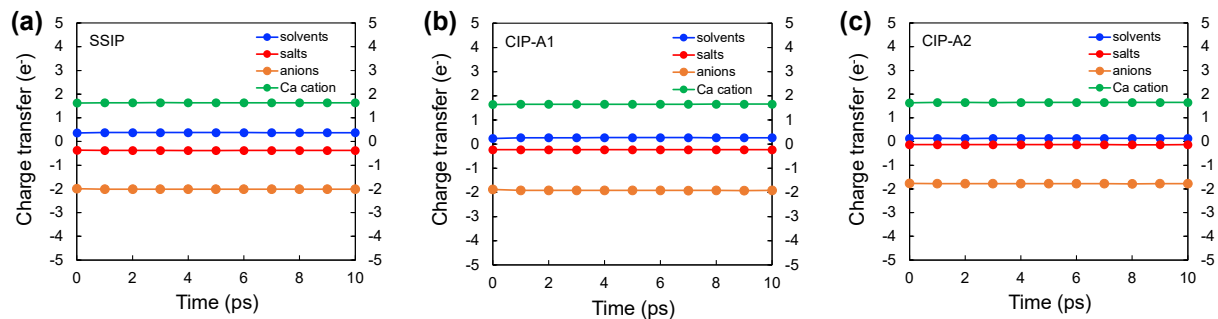**Figure S5.** Bader charge analysis for electrolytes of 0.5 M Ca[Al(TFIP)$_4$]$_2$ with a density of 1 g/ml. The diagram shows the initial structure of (a) SSIP, (b) CIP-A1, and (c) CIP-A2 in G1 solvent species.

(a)

$$G(\text{Ca(anion)}_2) + G(n(\text{solvent})) \overset{\Delta G}{\to} G(\text{Ca(solvent)}_n^{2+}) + G(2(\text{anion}^-))$$

Number of solvents	B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$
1												
2												

Formation energy ΔG (eV): 1, 0, -1, -2, -3, -4

(b)

$$G(\text{Ca(anion)}^+) + G(n(\text{solvent})) \overset{\Delta G}{\to} G(\text{Ca(solvent)}_n^{2+}) + G((\text{anion}^-))$$

Number of solvents	B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$
1												
2												

Formation energy ΔG (eV): 1, 0, -1, -2

(c)

$$G(\text{Ca(anion)}^+) + G((\text{anion}^-)) \overset{\Delta G}{\to} G(\text{Ca(anion)}_2)$$

B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$

Formation energy ΔG (eV): 0.1, 0, -0.1

Figure S6. Heat map illustrating the formation free energies (ΔG) among electrolyte solvation structures with G2 solvents: (a) SSIP formation energy transformation from CIP-A2, (b) SSIP formation energy transformation from CIP-A1, and (c) CIP-A2 formation energy transformation from CIP-A1.

(a)

$$G(\mathrm{Ca(anion)_2}) + G(\mathrm{n(solvent)}) \xrightarrow{\Delta G} G(\mathrm{Ca(solvent)_n^{2+}}) + G(\mathrm{2(anion)^-})$$

Number of solvents	B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$
1												
2												
3												
4												
5												
6												

Formation energy ΔG (eV): 3, 2, 1, 0, -1, -2, -3

(b)

$$G(\mathrm{Ca(anion)^+}) + G(\mathrm{n(solvent)}) \xrightarrow{\Delta G} G(\mathrm{Ca(solvent)_n^{2+}}) + G(\mathrm{(anion)^-})$$

Number of solvents	B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$
1												
2												
3												
4												
5												
6												

Formation energy ΔG (eV): 2, 1, 0, -1, -2, -3

(c)

$$G(\mathrm{Ca(anion)^+}) + G(\mathrm{(anion)^-}) \xrightarrow{\Delta G} G(\mathrm{Ca(anion)_2})$$

B(TFIP)$_4$	B(HFIP)$_4$	B(PIN)$_2$	Al(TFIP)$_4$	Al(HFIP)$_4$	Al(TFTB)$_4$	Al(HFTB)$_4$	Al(PFTB)$_4$	TFSI	PF$_6$	CB$_{11}$H$_{12}$	BPh$_4$

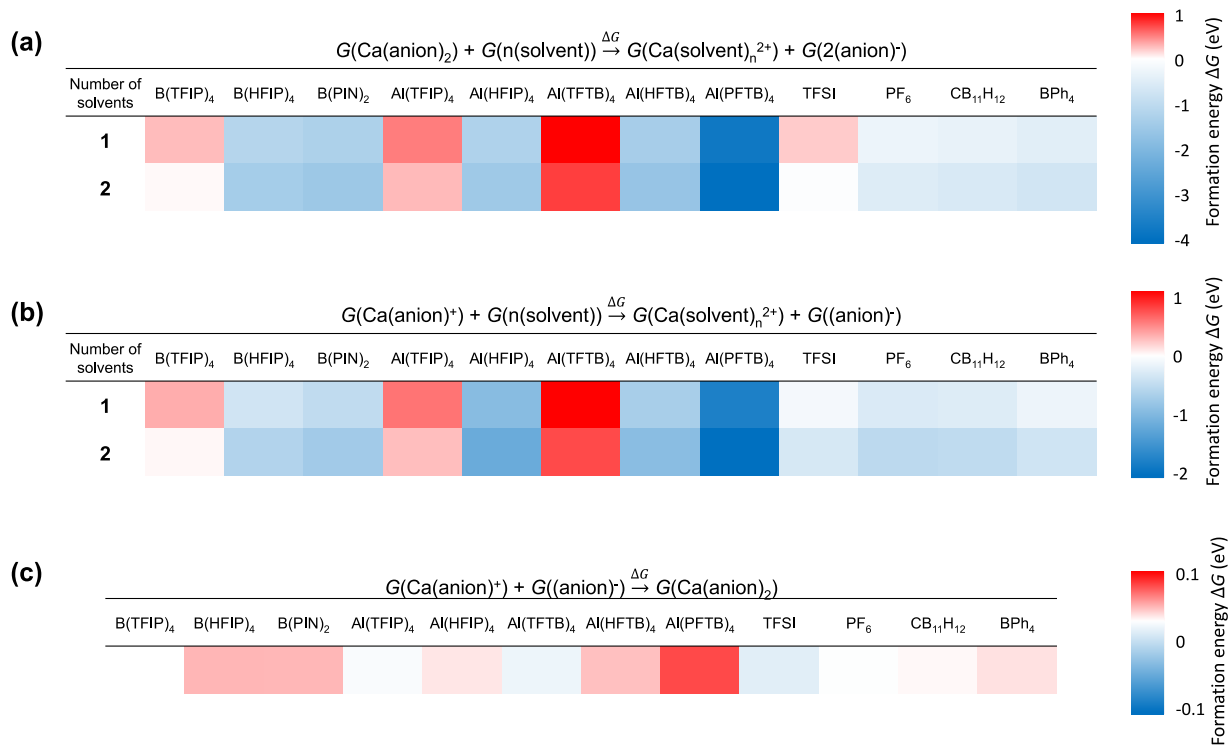Formation energy ΔG (eV): 0.1, 0, -0.1, -0.2

Figure S7. Heat map illustrating the formation free energies (ΔG) among electrolyte solvation structures with THF solvents: (a) SSIP formation energy transformation from CIP-A2, (b) SSIP formation energy transformation from CIP-A1, and (c) CIP-A2 formati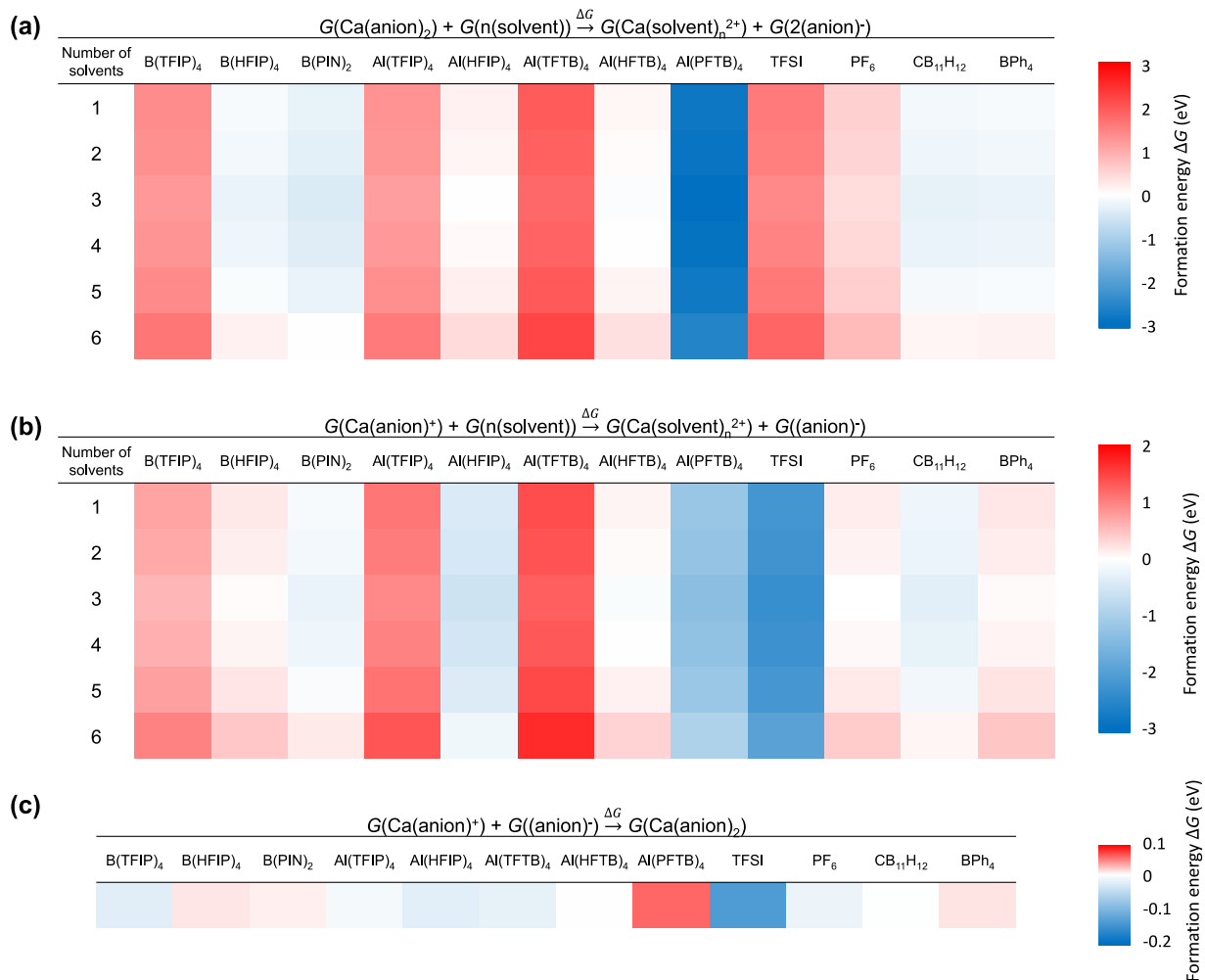on energy transformation from CIP-A1.