

Supplementary Information

**Breaking Hydrogen-bond in Aqueous Electrolyte Towards Highly Reversible**

**Zinc-ion Batteries**

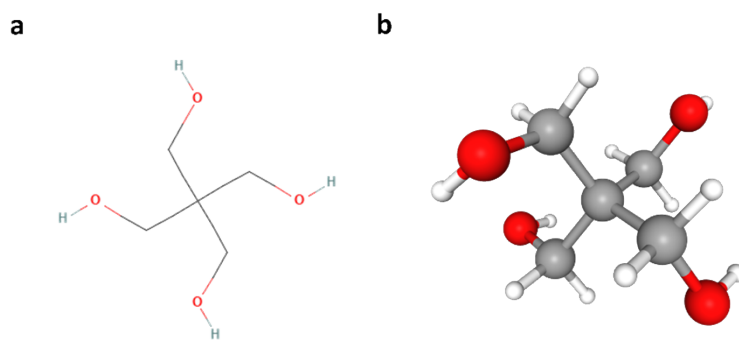
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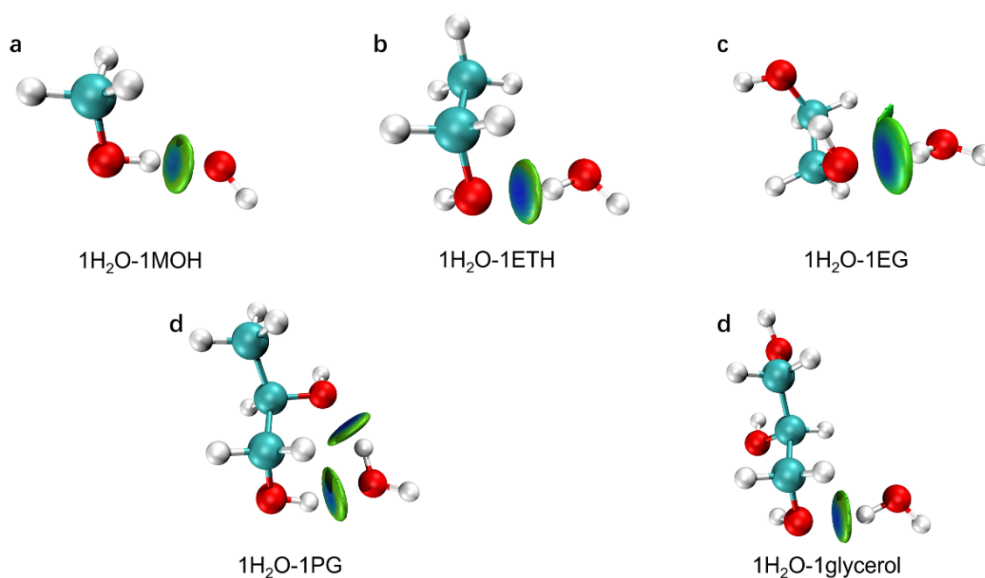
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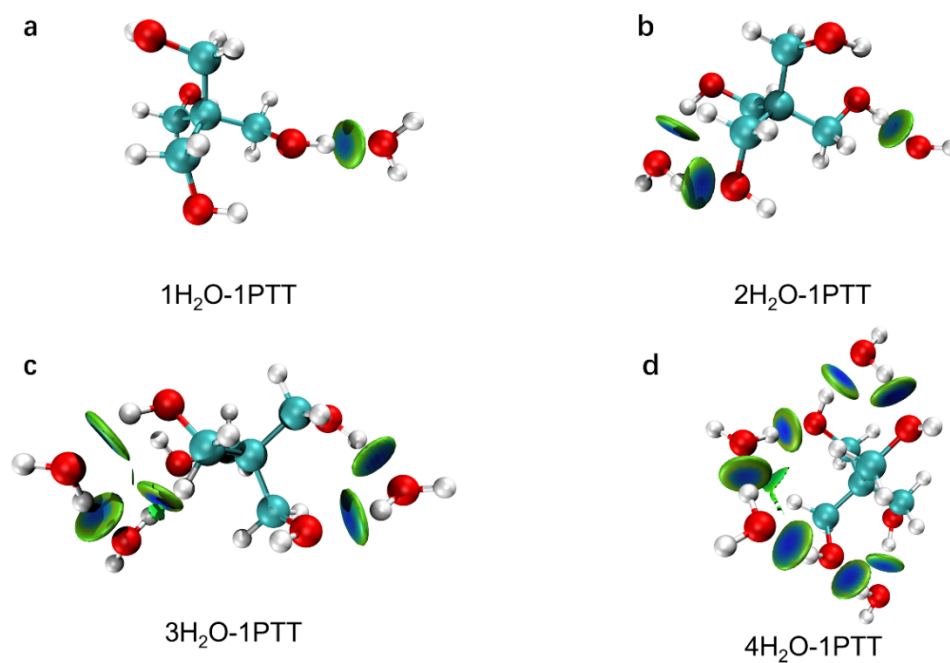
Email: [yan.jiao@adelaide.edu.au](mailto:yan.jiao@adelaide.edu.au); [junnan.hao@adelaide.edu.au](mailto:junnan.hao@adelaide.edu.au)



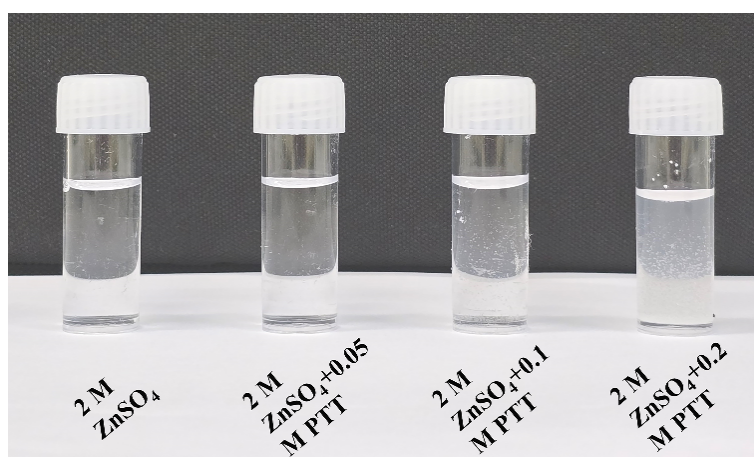
**Figure S1.** (a) The diagram of the 2D structure of PTT. (b) The corresponding 3D structure. Colour code: red, O; white, H; grey, C.



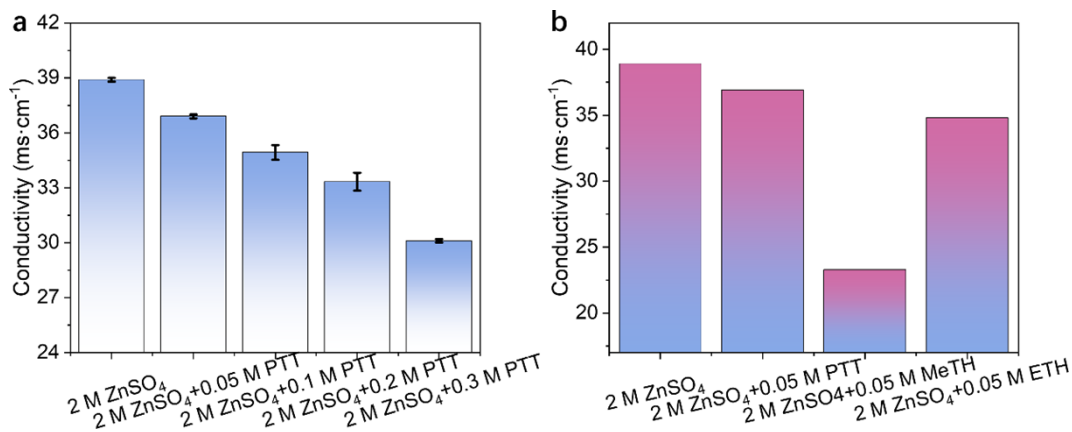
**Figure S2.** Schematic diagram of intermolecular interactions between water molecule and a) Methanol, b) Ethanol, c) Ethylene glycol, d) Propylene glycol, e) Glycerol. Colour code: red, O; white, H; cyan, C.



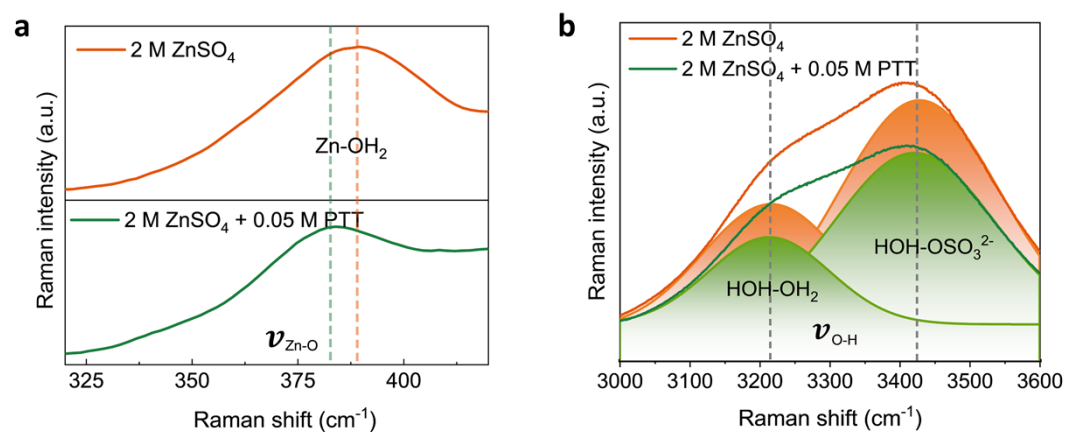
**Figure S3.** Schematic diagram of intermolecular interactions between PTT and a)  $1\text{H}_2\text{O}$ , b)  $2\text{H}_2\text{O}$ , c)  $3\text{H}_2\text{O}$ , d)  $4\text{H}_2\text{O}$ . Colour code: red, O; white, H; cyan, C.



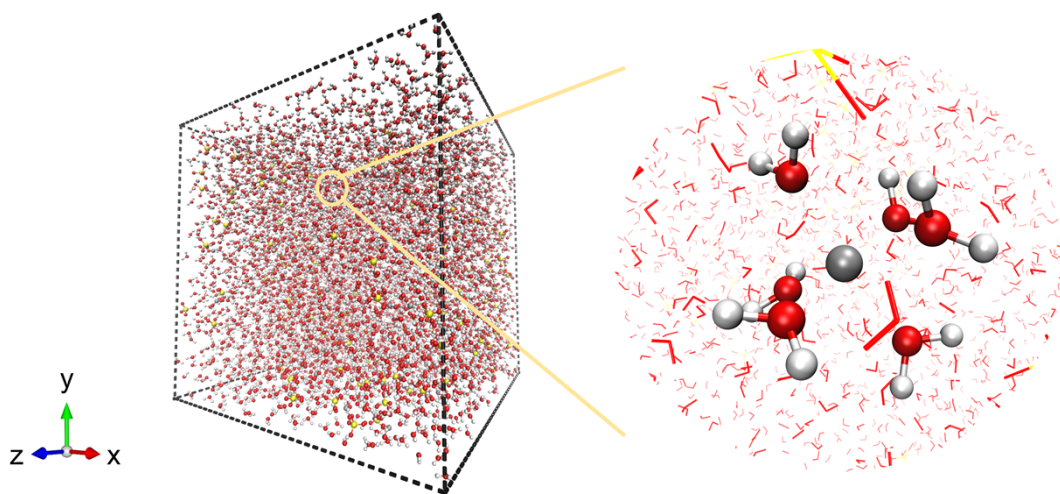
**Figure S4.** Snapshot of 2 M  $\text{ZnSO}_4$  electrolyte with different concentrations of PTT addition after 7 days.



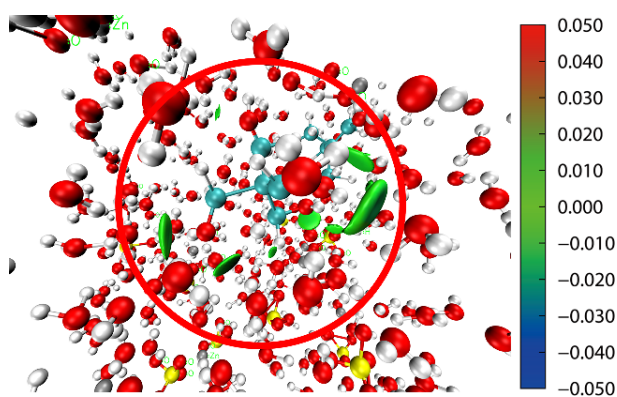
**Figure S5.** Conductivity of ZnSO<sub>4</sub> solutions containing different concentrations of PTT (a) and containing different additives, including PTT, MeTH (Methanol) and ETH (ethanol) at the same concentration (b).



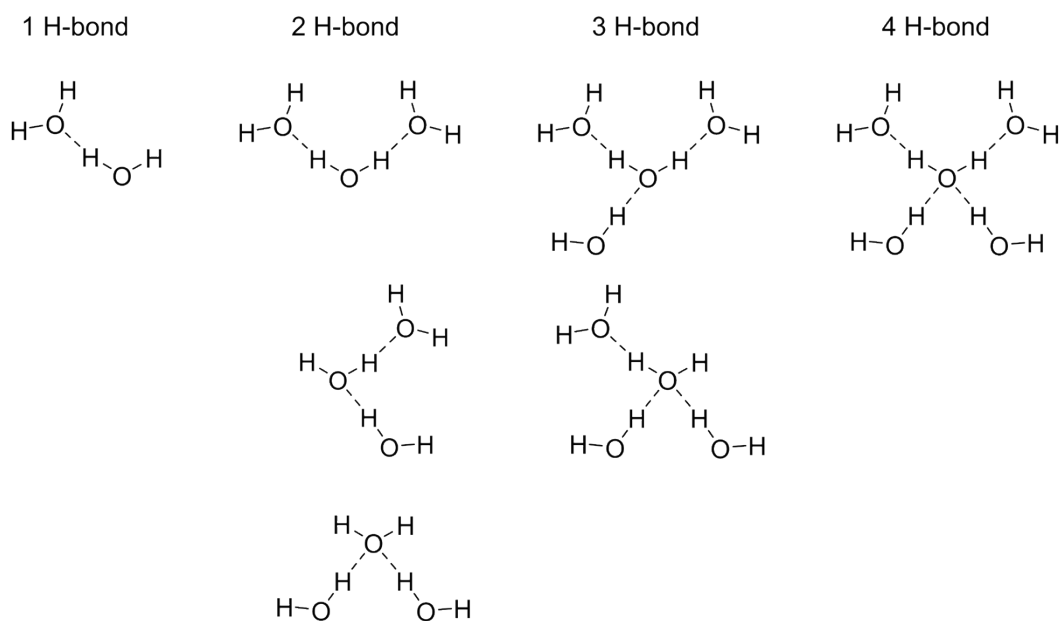
**Figure S6.** Raman spectroscopy of pure 2 M ZnSO<sub>4</sub> electrolyte and 2 M ZnSO<sub>4</sub> with 0.05 M PTT electrolyte. (a) Zn-O stretch vibration; (b) O-H stretch vibration deconvoluted with Gaussian function.



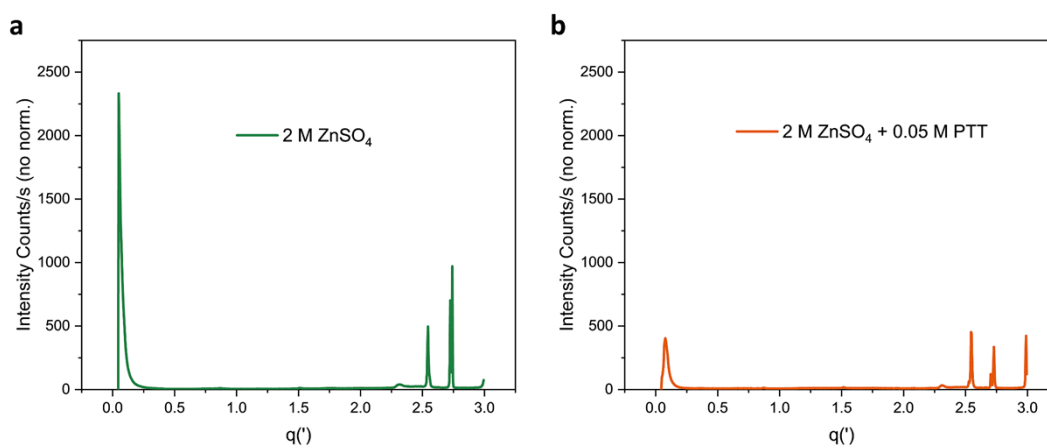
**Figure S7.** Snapshot of the model for 2 M  $\text{ZnSO}_4$  after theoretical MD simulation. Colour code: red, O; white, H; yellow, S; grey, Zn.



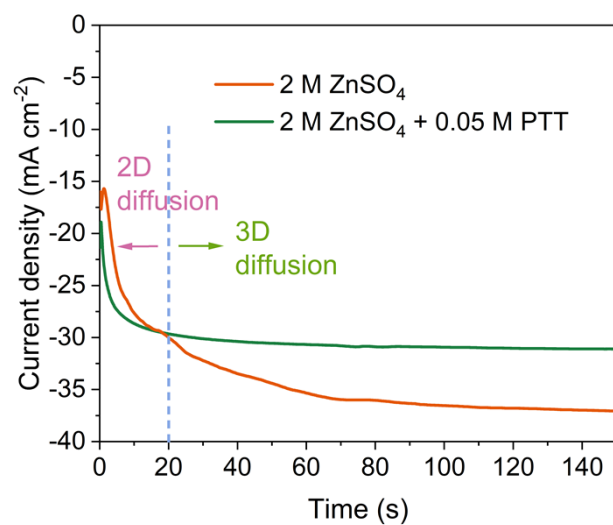
**Figure S8.** Snapshot of the intermolecular interactions between PTT and surrounding  $\text{ZnSO}_4$  molecules in the model of 2 M  $\text{ZnSO}_4$  with 0.05 M PTT. Colour code: red, O; white, H; yellow, S; cyan, C; grey, Zn.



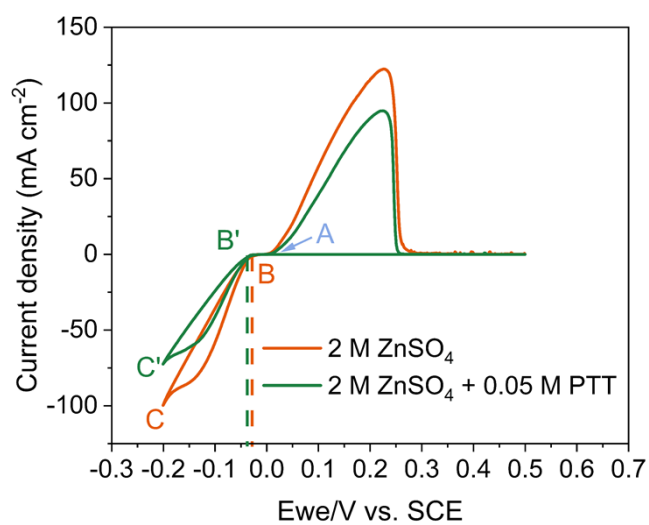
**Figure S9.** Classification of different numbers of H-bonds between water molecules.



**Figure S10.** Intensity Counts for Zn electrodes in ZnSO<sub>4</sub> electrolyte (a) and ZnSO<sub>4</sub> electrolyte with PTT addition (b) after the 100<sup>th</sup> plating.

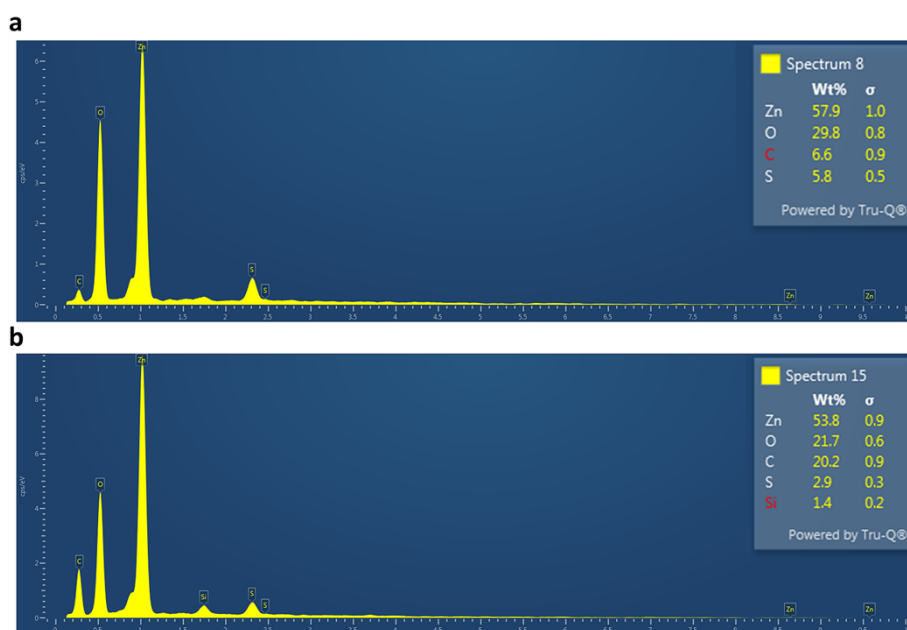


**Figure S11.** Chronoamperometry (CA) curves of Zn/Cu coin cells containing pure 2 M ZnSO<sub>4</sub> electrolyte and 2 M ZnSO<sub>4</sub> with 0.05 M PTT at a constant potential of -150 mV.

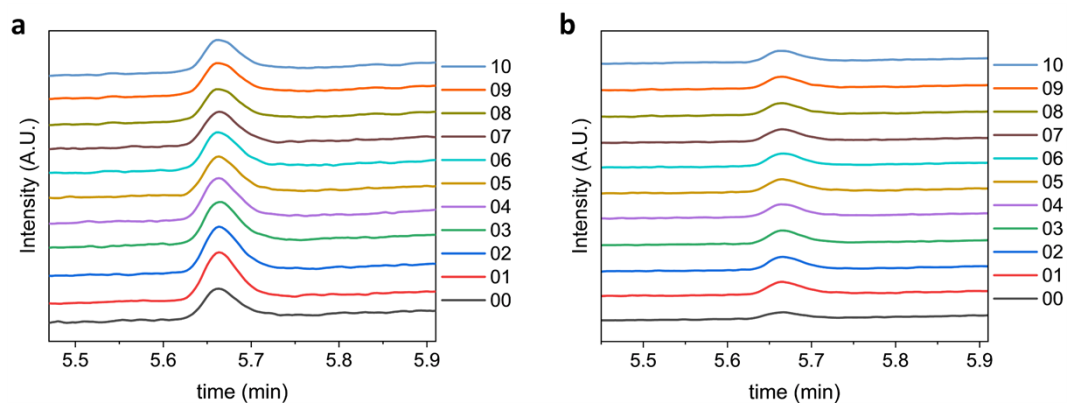


**Figure S12.** Chronoamperometry (CA) curves of Zn/Cu coin cells containing 2 M

ZnSO<sub>4</sub> and 2 M ZnSO<sub>4</sub> with 0.05 M PTT at 0.5 mV s<sup>-1</sup>.



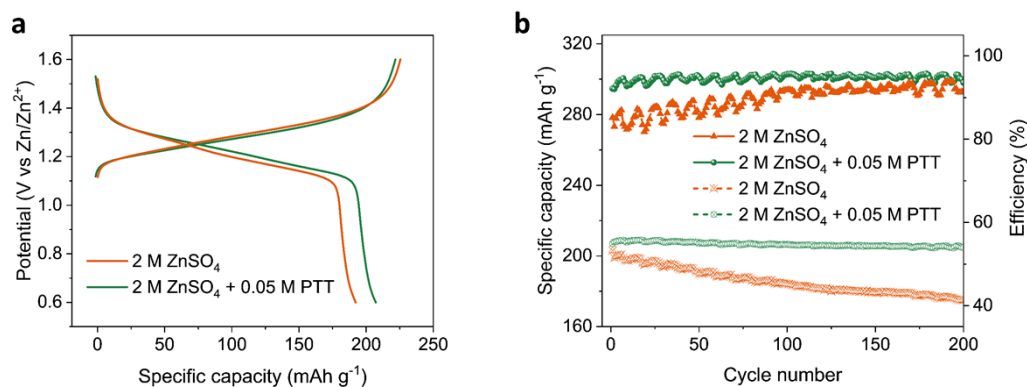
**Figure S13.** Energy dispersive X-ray spectroscopy (EDX) analysis of Zn electrode in ZnSO<sub>4</sub> electrolyte (a) and ZnSO<sub>4</sub> electrolyte with PTT addition (b) after the 100<sup>th</sup> plating.



**Figure S14.** *In situ* GC curves to dynamically evaluate the H<sub>2</sub> amount during the Zn plating/stripping (a) in pure ZnSO<sub>4</sub> electrolytes and (b) in ZnSO<sub>4</sub> electrolyte with PTT



addition.



**Figure S15.** (a) Galvanostatic charge/discharge curves of Zn-I<sub>2</sub> full cells with containing 2 M ZnSO<sub>4</sub> electrolyte and 2 M ZnSO<sub>4</sub> with 0.05 M PTT at 0.2 A g<sup>-1</sup>. (b) Cycling performance of Zn-I<sub>2</sub> full cells with containing 2 M ZnSO<sub>4</sub> electrolyte and 2 M ZnSO<sub>4</sub> with 0.05 M PTT at 0.2 A g<sup>-1</sup>.

**Table S1.** Dihedral angles of common configurations of PTT molecules.

□	Omega (H-O-C-C) (degree, °)							
	Sequence	1	2	3	4	5	6	7
	<b>O1</b>	111.82	179.94	72.66	179.60	66.89	64.12	73.03
	<b>O2</b>	74.85	73.36	69.98	63.81	178.67	179.27	74.70
	<b>O3</b>	69.42	69.69	178.93	75.47	79.03	75.79	76.58

**O4**    179.99    70.56    70.77    79.65    76.81    75.12    179.49

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**Table S2.** Numbers of molecules in different solution models.

<b>System</b>	<b>Nº of water molecules</b>	<b>Nº of ZnSO<sub>4</sub></b>	<b>Nº of PTT molecules</b>
Pure ZnSO <sub>4</sub> solution	5000	200	–
ZnSO <sub>4</sub> solution with PTT addition	5000	200	5

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**Table S3.** Periodic boundary size of different system cells.

<b>System</b>	<b>Cell length (Å)</b>	<b>Cell length (Å)</b>	<b>Cell length (Å)</b>
Pure ZnSO <sub>4</sub> solution	52.435	52.434	52.435
ZnSO <sub>4</sub> solution with PTT	54.930	54.931	54.931

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