Electronic Supplementary Information

Molecular Sieving Mechanism of Polysulfide-Blocking Metal-Organic Framework Separator for Lithium-Sulfur Batteries

Taegon Jeon and Sung Chul Jung*

Department of Physics, Pukyong National University, Busan, 48513, Republic of Korea

Corresponding Author

*E-mail: scjung@pknu.ac.kr

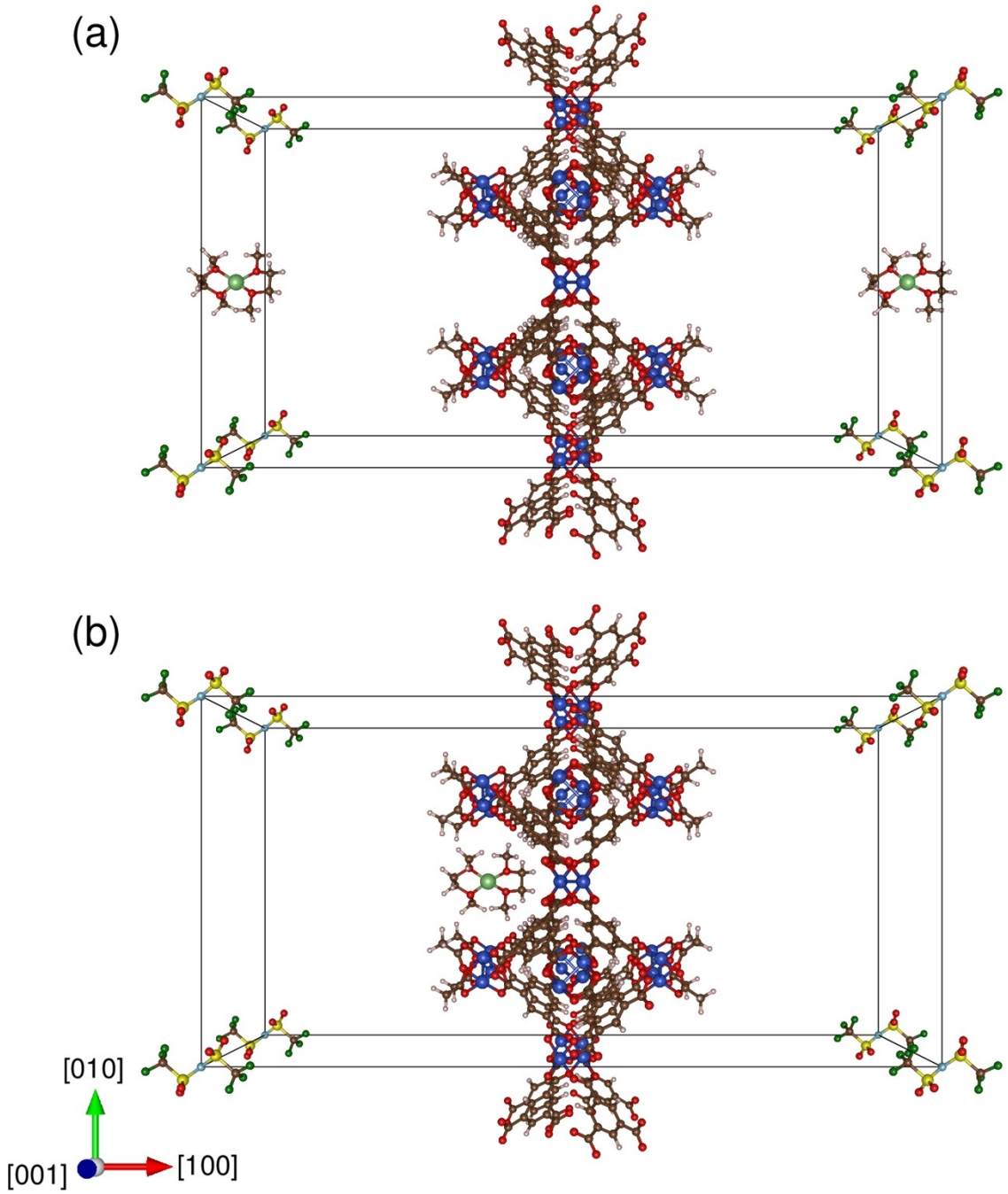
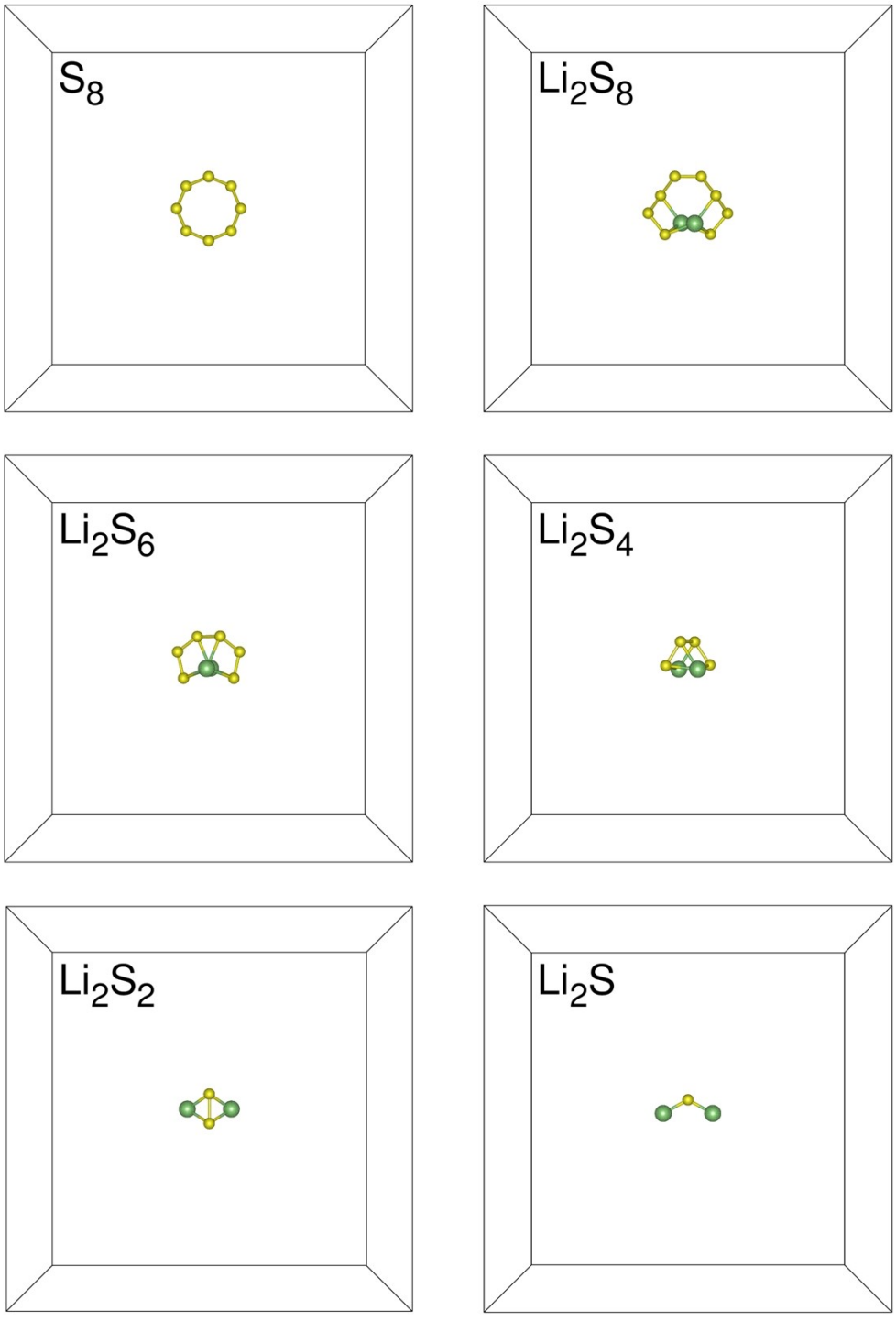
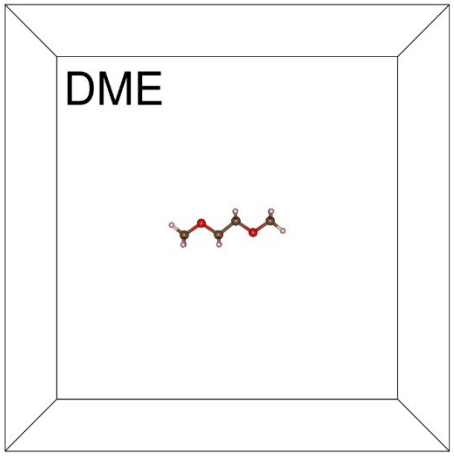


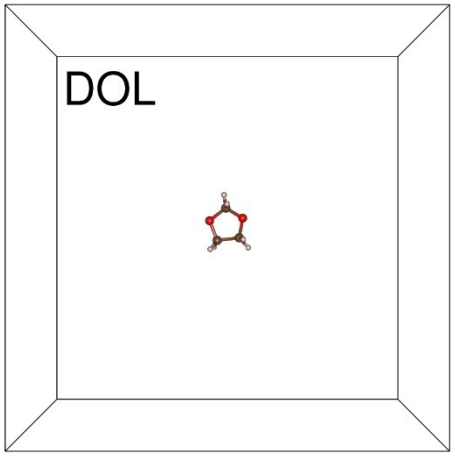
Fig. S1 Optimized structures of (a) the unbound and (b) bound states of $Li^+(DME)_2$ with MOF. Solid lines represent tetragonal supercells, containing the MOF nanosheet, a $Li^+(DME)_2$ cation, and a $[(CF_3SO_2)_2N]^-$ (TFSI) anion. The TFSI anion is fixed at the edge of the supercell. The blue, red, brown, pink, skyblue, yellow, and green balls represent Cu, O, C, H, N, S, and F atoms, respectively.

(a)

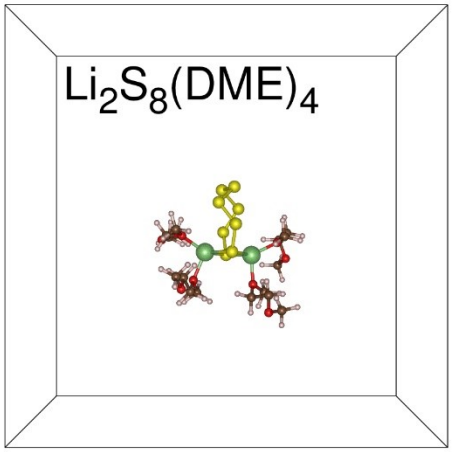


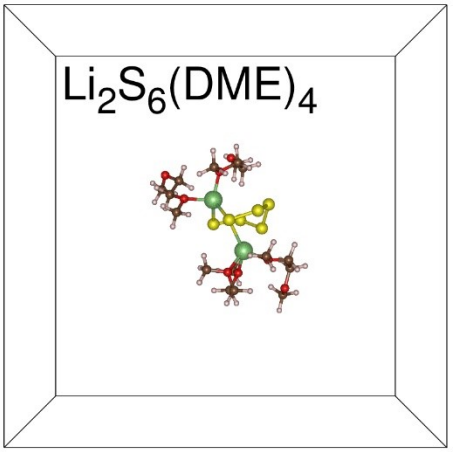
(b)

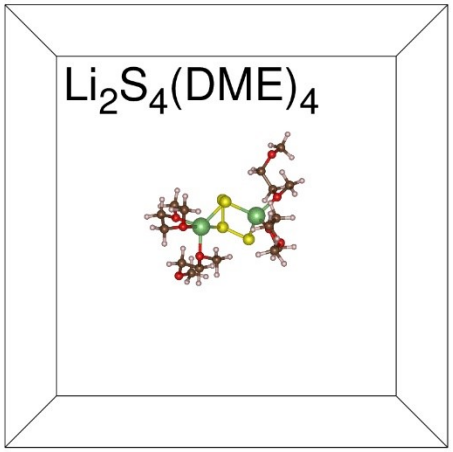


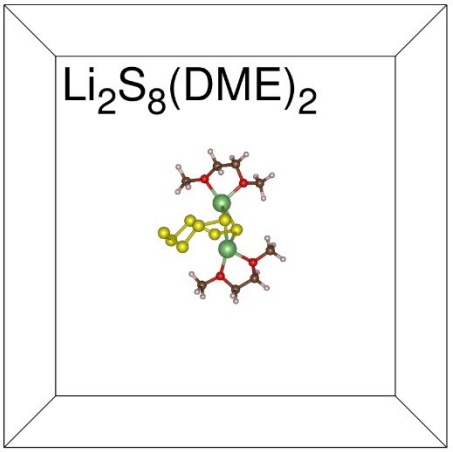


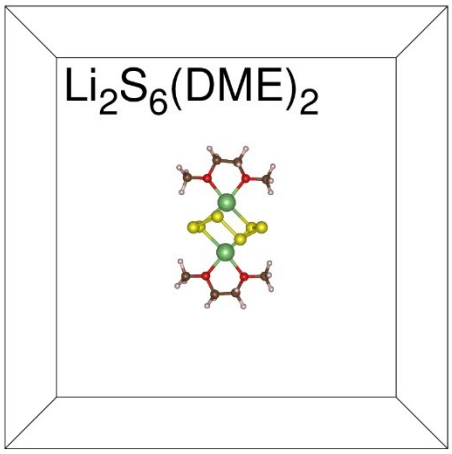
(c)

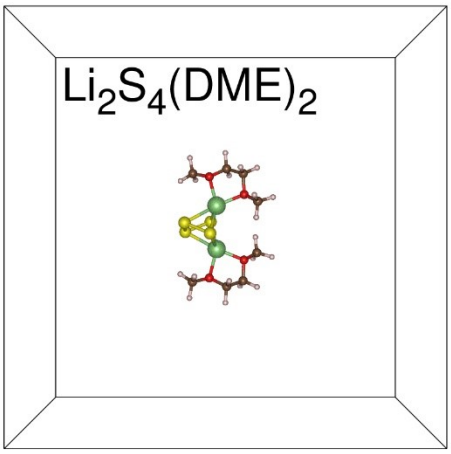









$Li_2S_6(DME)_2$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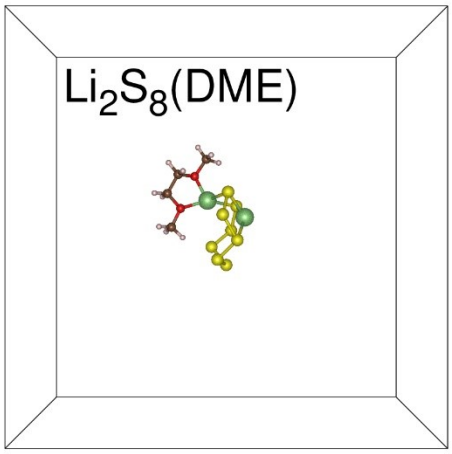
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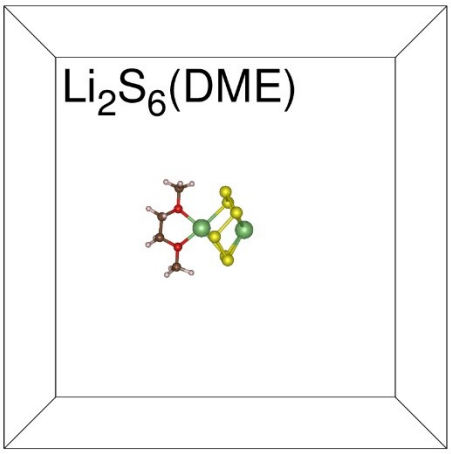
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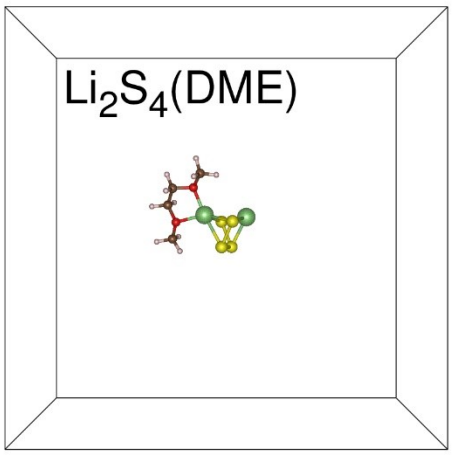
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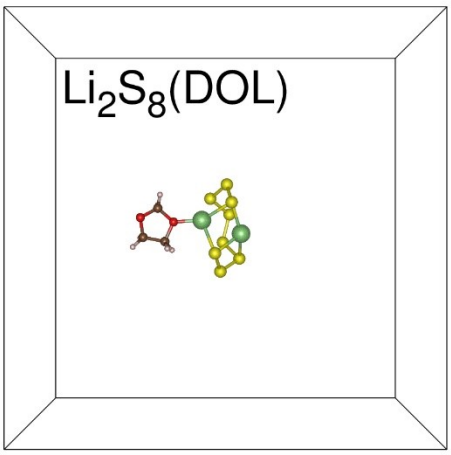

$Li_2S_8(DOL)$

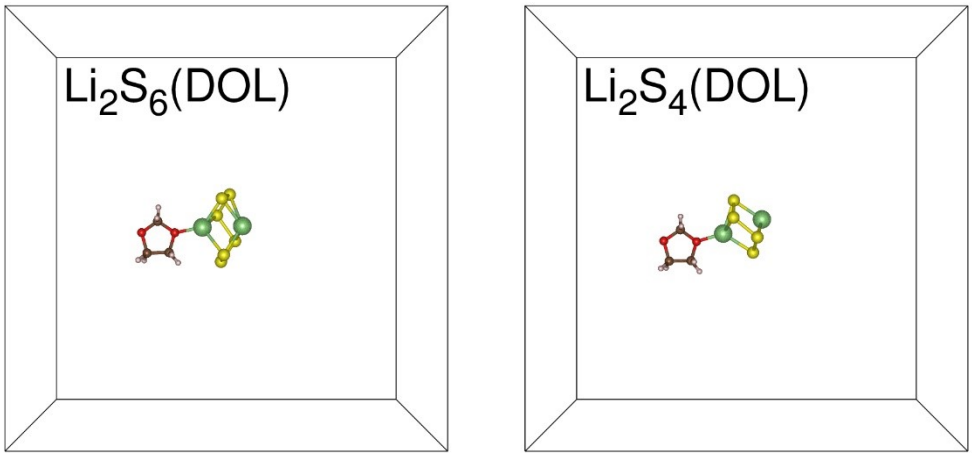


Fig. S2 Optimized structures of (a) S_8 and Li_2S_x, (b) DME and DOL, and (c) DME/DOL-solvated Li_2S_x. Solid lines represent the cubic supercells.

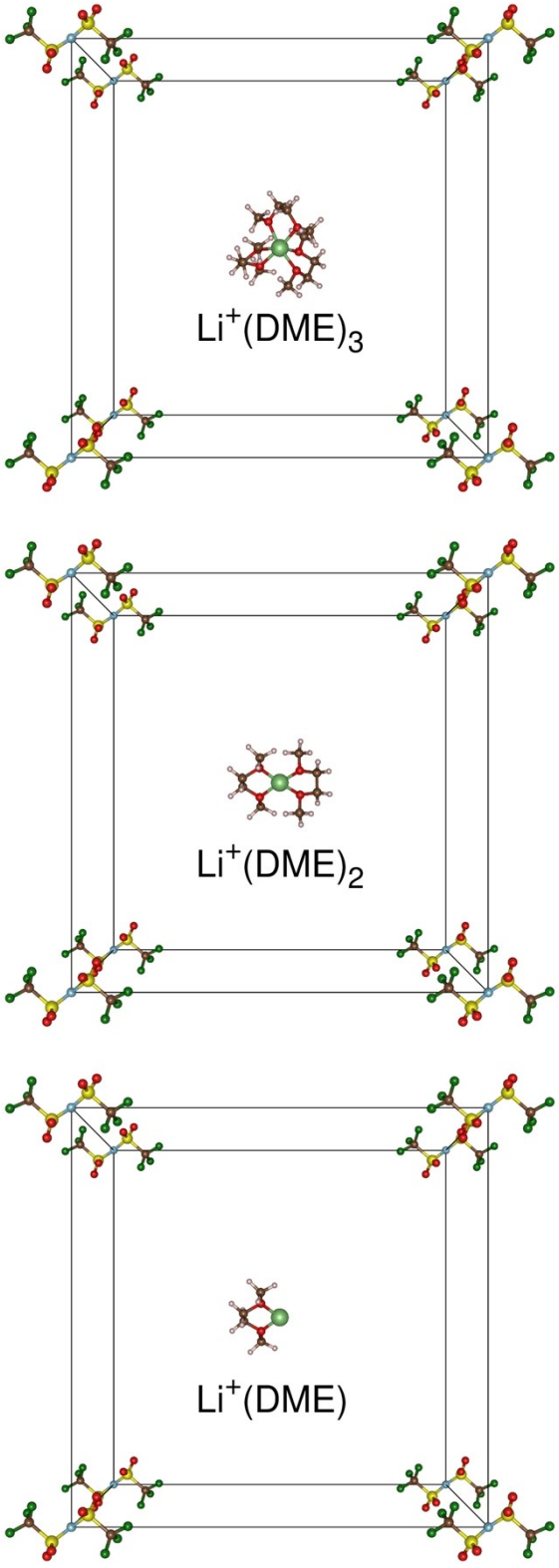


Fig. S3 Optimized structures of $Li^+(DME)_y$. Solid lines represent the cubic supercells, containing a $Li^+(DME)_y$ cation and a TFSI anion.

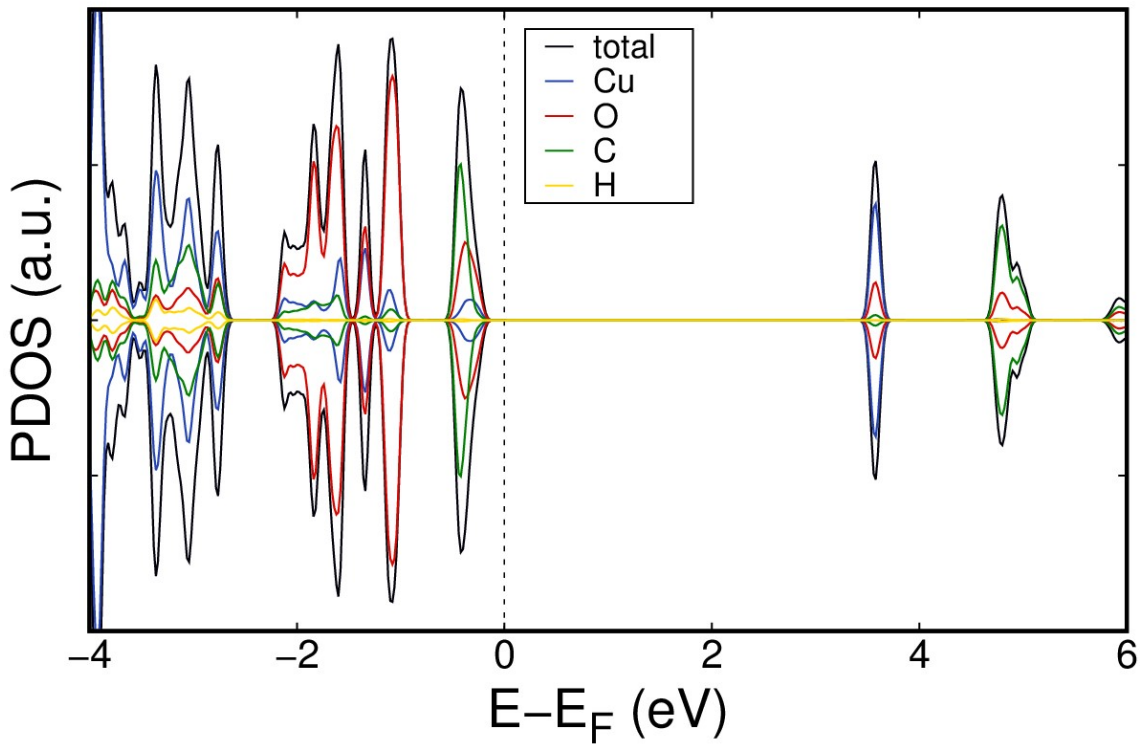
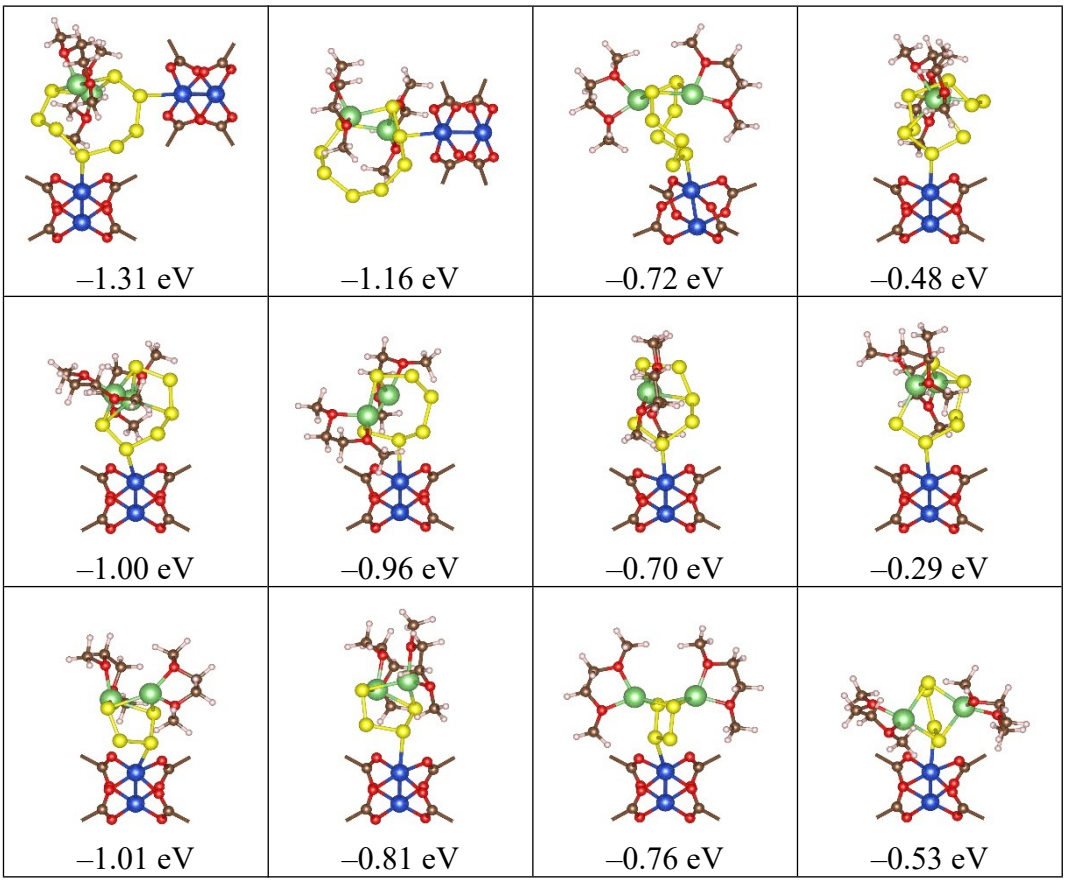
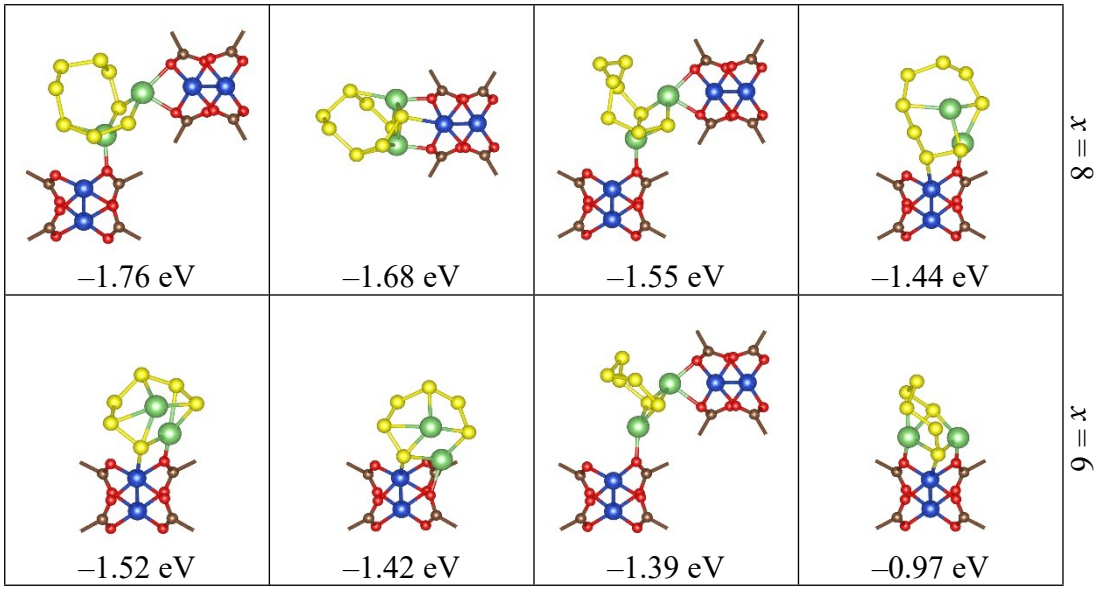


Fig. S4 Projected density of states (PDOSs) of HKUST-1 MOF obtained using the HSE06 functional.

(a) $Li_2S_x(DME)_2$



(b) Li_2S_x



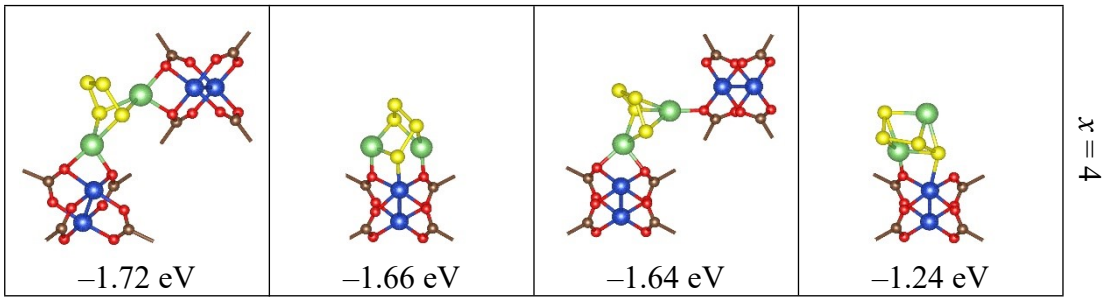


Fig. S5 Optimized structures of (a) the $Li_2S_x(DME)_2$- and (b) Li_2S_x-adsorbed MOF nanosheets. The adsorption structures, initially obtained from the AIMD simulations at 300 K, were optimized by static DFT calculations. The numbers represent the adsorption energies, defined as $E_a = E(Li_2S_x(DME)_y/MOF) - E(Li_2S_x(DME)_y) - E(MOF)$, where $E(Li_2S_x(DME)_y/MOF)$ is the energy of $Li_2S_x(DME)_y$-adsorbed MOF, $E(Li_2S_x(DME)_y)$ is the energy of isolated $Li_2S_x(DME)_y$, and $E(MOF)$ is the energy of MOF nanosheet.

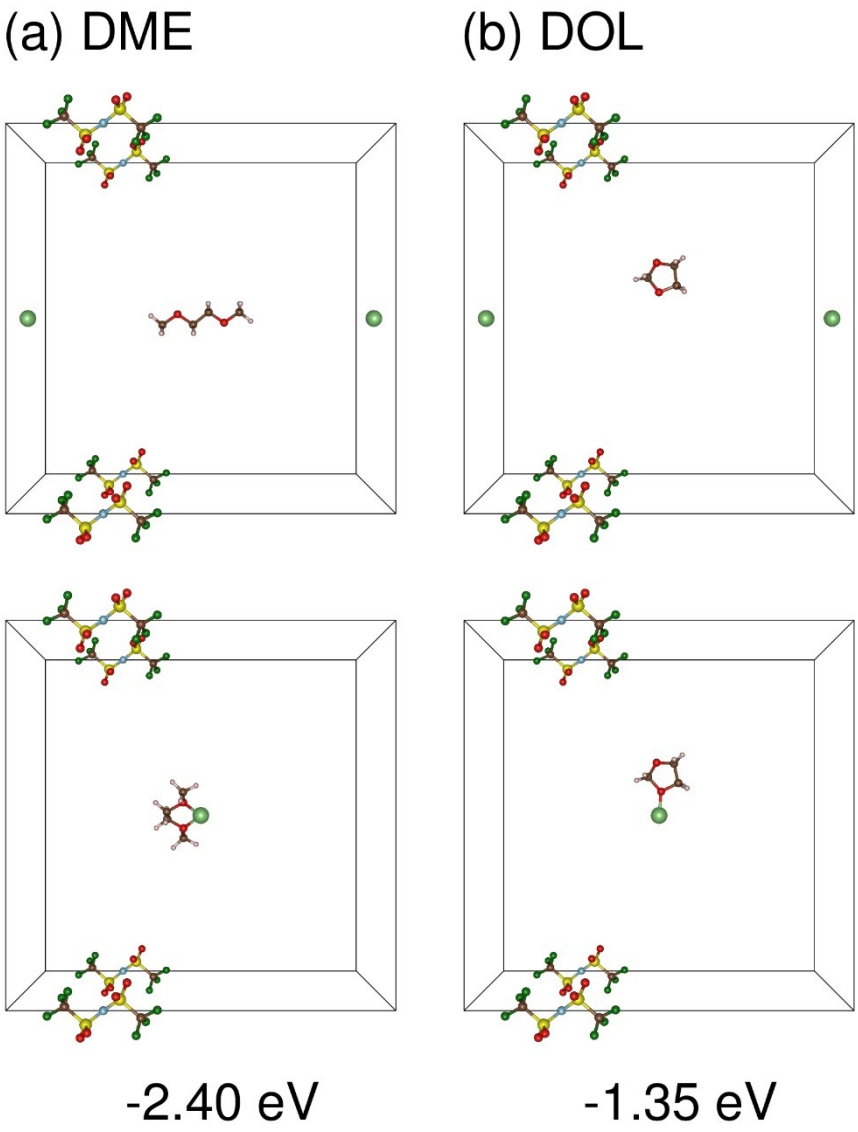


Fig. S6 Optimized structures of the unbound and bound states of Li^+ with (a) DME and (b) DOL. The numbers represent the Li^+–solvent binding energies, calculated as the energy difference between the bound and unbound states of Li^+ with DME/DOL.

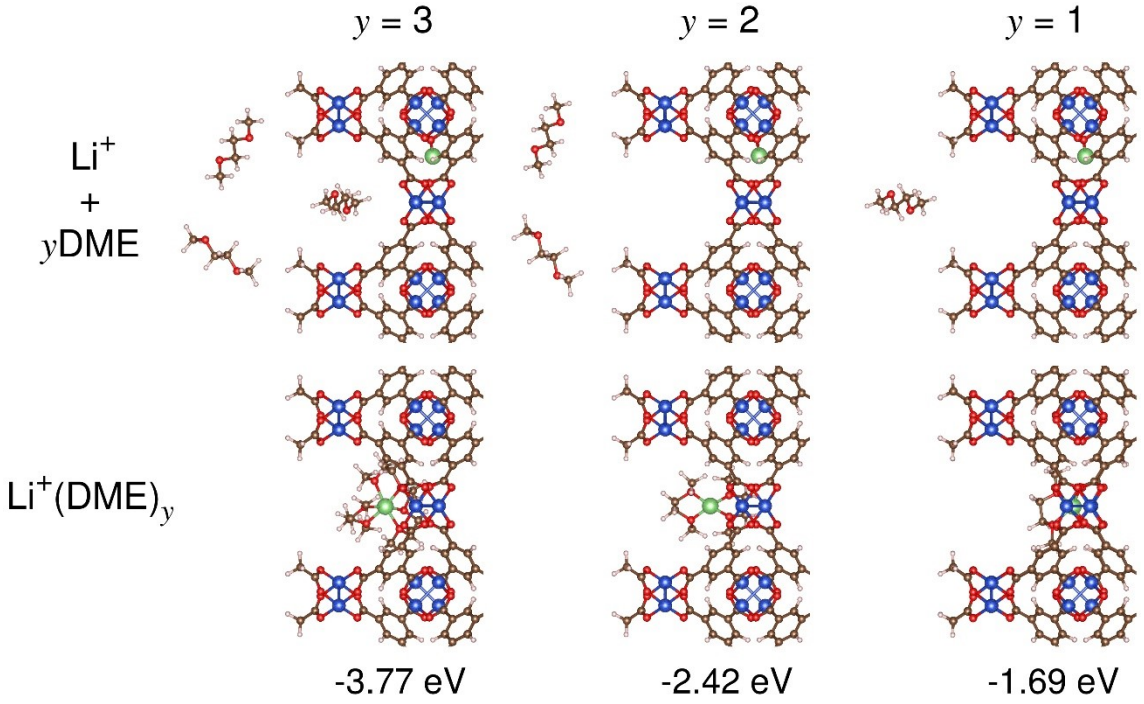


Fig. S7 Optimized structures of the $Li^+(DME)_y$-adsorbed MOF nanosheet and the Li^+-adsorbed MOF nanosheet with y surrounding DMEs. The numbers represent the relative energies between the solvated and bare states of Li^+ in MOF, defined as $E(Li^+) = E(Li^+(DME)_y/MOF) - E(Li^+/MOF + yDMEs)$, where $E(Li^+(DME)_y/MOF)$ is the energy of $Li^+(DME)_y$-adsorbed MOF and $E(Li^+/MOF + yDMEs)$ is the energy of Li^+-adsorbed MOF with y DMEs separated from Li^+.

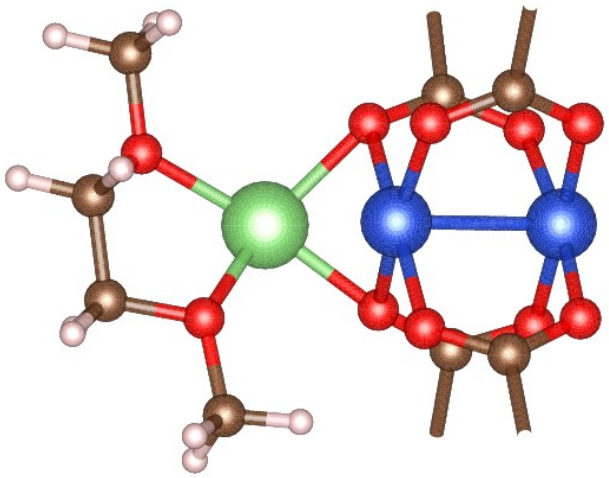


Fig. S8 Optimized structure of the Li^+(DME)-adsorbed MOF nanosheet. The number represents the adsorption energy, which is calculated as the energy difference between the above configuration and a configuration where Li^+(DME) in the supercell is the farthest from the MOF nanosheet (e.g., $Li^+(DME)_2$ in Fig. S1a).

Table S1 Bader charges of the Cu–S and Li–O bond atoms in the $Li_2S_x(DME)_2$- and Li_2S_x-adsorbed structures shown in Fig. 3b.

	atom	$x = 8$	$x = 6$	$x = 4$
$y = 2$	Cu	+1.08, +1.08	+1.10	+1.08
	S	–0.05, –0.11	–0.06	–0.07
$y = 0$	Cu		+1.07	
	S		–0.61	
	Li	+0.89, +0.90	+0.89	+0.90, +0.90
	O	–1.17, –1.17, –1.15	–1.18	–1.18, –1.17, –1.19, –1.18

Table S2 Adsorption energies (eV) of the $Li_2S_x(DME)_2$- and Li_2S_x-adsorbed structures shown in Fig. 3b.

	$x = 8$	$x = 6$	$x = 4$
$y = 2$	–1.31	–1.00	–1.01
$y = 0$	–1.76	–1.52	–1.72

[a] The presented structures in each x and y are the most stable among the adsorption structures in Fig. S5.