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Supporting Information

Catalysing the Performance of Li-Sulfur Batteries with Two-Dimensional Conductive Metal Organic Frameworks

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Note 1: Selection of five combinations of MOFs ($Co_3(HITP)_2$, $Co_3(HOTP)_2$, $Co_3(THT)_2$, $Cu_3(HITP)_2$, and $Ni_3(HITP)_2$).

These MOF with such metal-linkers are experimentally synthesized and electronically conductive. The aim of this study is to show how the variation of metal ion and linker can affect the electronic properties and catalytic performance in Li-S batteries, which is well accounted by the five combinations. In one case, the variation of metal ion provides a guidance on the synergy of metal ion with Co being the best fit, and in other case, the effect of linker variation with the fixed Co metal center is analysed where THT showed the best performance.

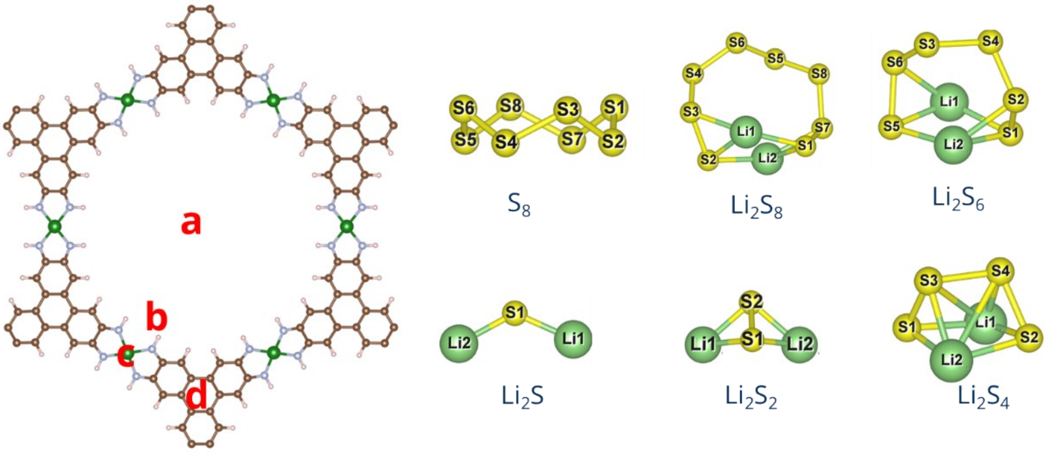

Figure S1: Possible adsorption sites and molecule configurations for Li_2S_x species from Li_2S to unlithiated S_8 at various lithiation stages.

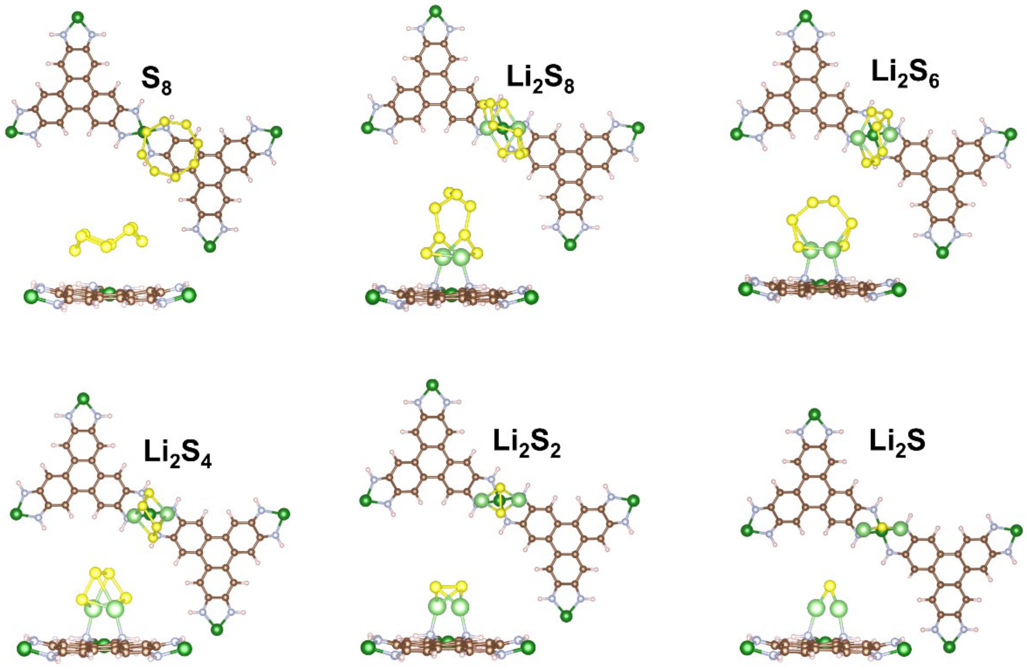

Figure S2: Illustration of stable adsorption configurations of Li_2S_x (x = 1, 2, 4, 6, or 8) series and S_8 adsorbed on the surface of MOF $Cu_3(HITP)_2$.

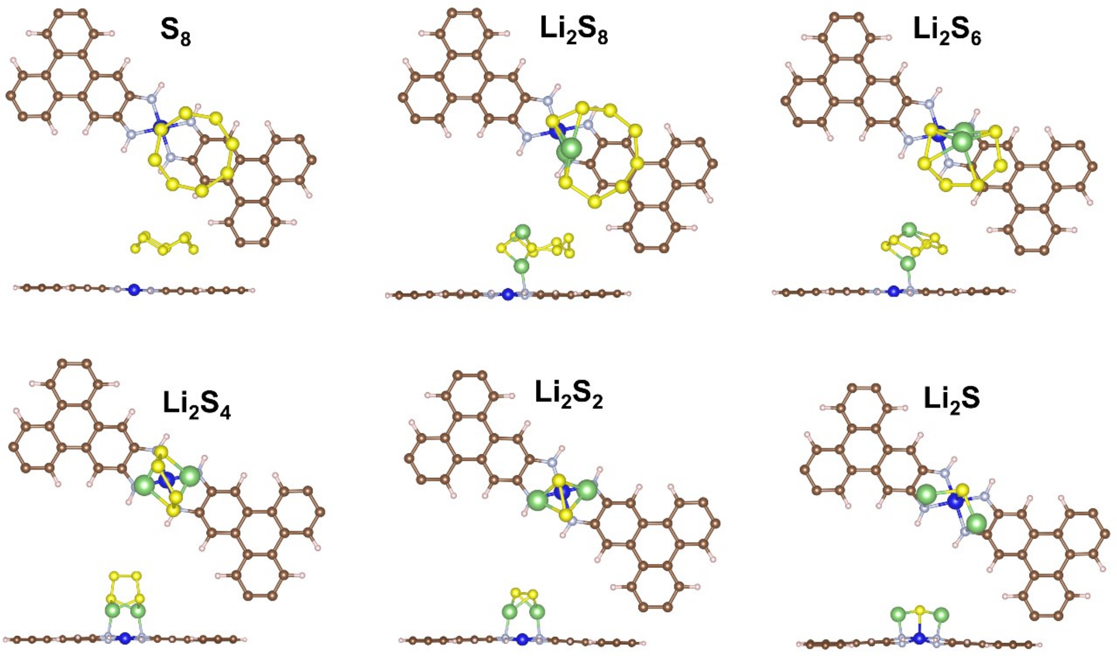

Figure S3: Illustration of stable adsorption configurations of Li_2S_x (x = 1, 2, 4, 6, or 8) series and S_8 adsorbed on the surface of $Ni_3(HITP)_2$.

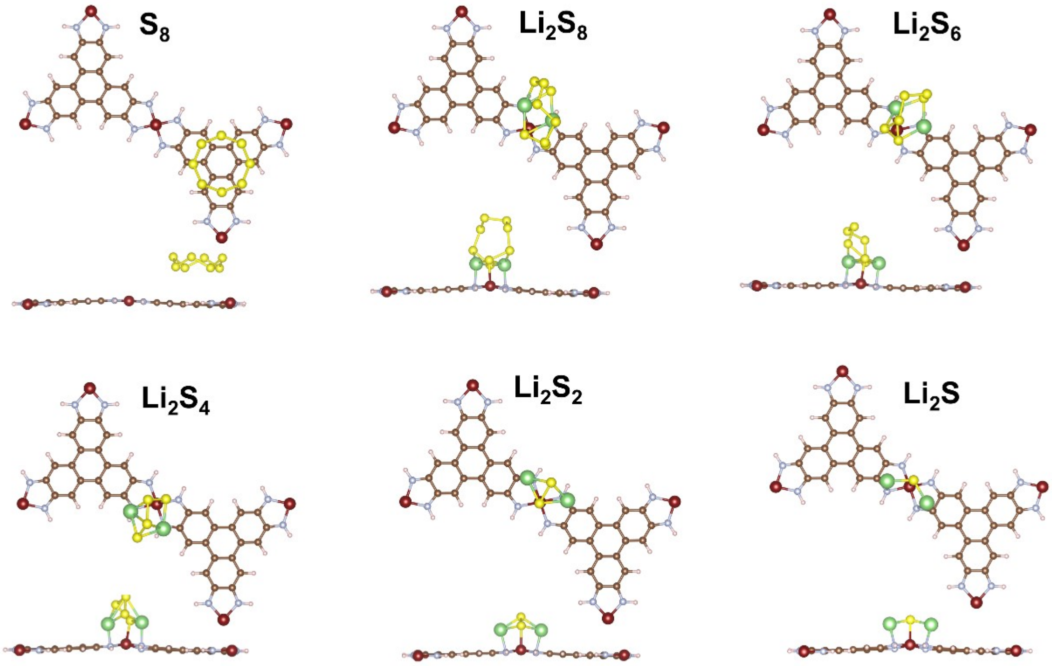

Figure S4: Illustration of stable adsorption configurations of Li_2S_x (x = 1, 2, 4, 6, or 8) series and S_8 adsorbed on the surface of MOF $Co_3(HITP)_2$.

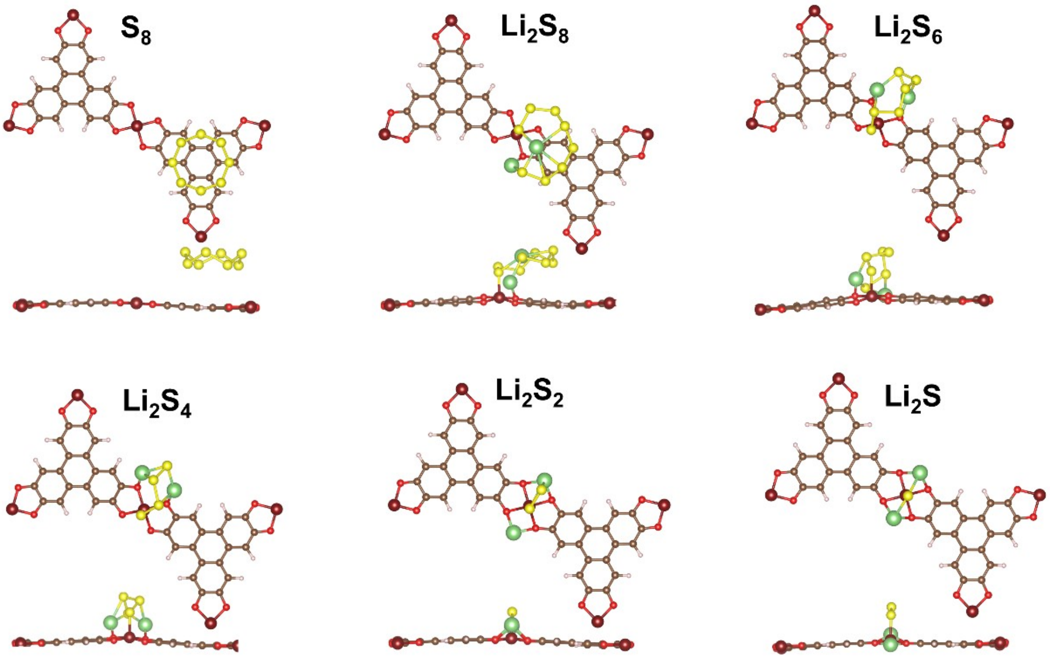

Figure S5: Illustration of stable adsorption configurations of Li_2S_x (x = 1, 2, 4, 6, or 8) series and S_8 adsorbed on the surface of MOF $Co_3(HOTP)_2$.

Table S1: The binding energies E_b (eV) of Li_2S_8 - Li_2S_4, Li^+ diffusion barrier (eV) and Li_2S decomposition barrier (eV) molecules on cathode hosts investigated in our study and previous studies.

Cathode Host	Li_2S_8 -Li_2S Binding Energy Range (eV)	Li^+ Diffusion Barrier (eV)	Li_2S Decomposition Barrier (eV)
Graphene[36]	-0.67 (Li_2S_6)	0.30	1.81
Anatase TiO_2(101)[37]	-3.09 to -4.48	0.73	-
Transition-metal nitride[38]	-1.97 to -3.61	0.16−0.27	0.95-2.18
Cu-BHT[39]	-1.58 to -3.12	-	0.61
MoS_2[35]	-0.77 to -1.00	-	-
Single atom V@NG[40]	-3.38 (Li_2S_6)	0.23	1.10
$Fe_3C_{12}S_{12}$[41]	-1.44 to -3.68	-	0.67
M_2(2,5-dioxido-1,4-benzene dicarboxylate)[7]	-1.94 to -2.00	-	-
MPc-COFs, M = Mn, Cu, and Zn[42]	-1.30 to -4.07	-	1.10-1.80
$Co_3(HITP)_2$	-0.85 to -1.98	0.26	1.18
$Cu_3(HITP)_2$	-1.14 to -1.60	0.76	0.73
$Ni_3(HITP)_2$	-0.98 to -1.44	0.22	1.08
$Co_3(HOTP)_2$	-1.93 to -3.54	1.08	1.27
$Co_3(THT)_2$	-1.40 to -2.68	0.68	1.06

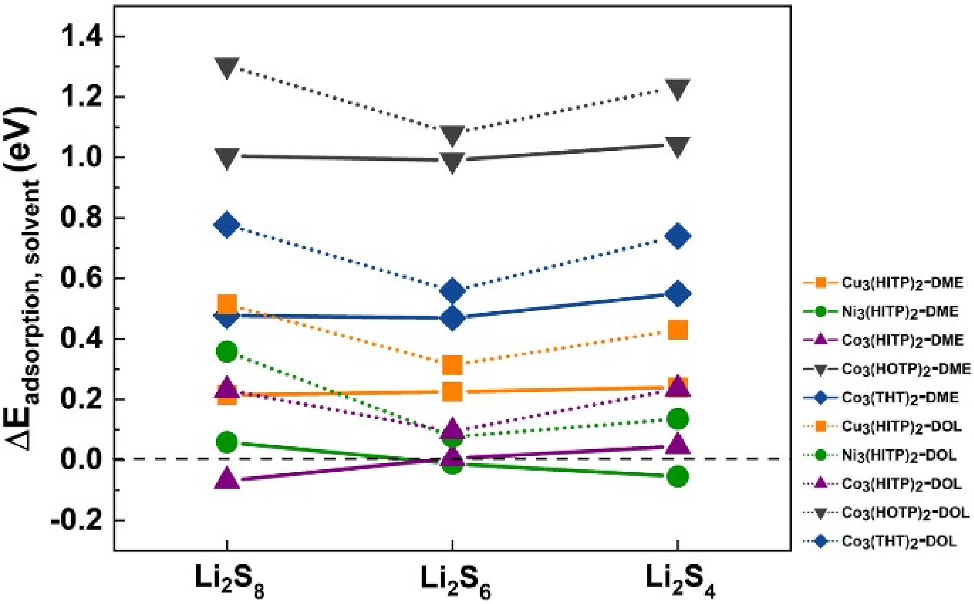

Figure S6: Adsorption energy curves of higher order Li_2S_x (x = 4, 6, 8) series adsorbed on MOFs in DME and DOL solvents.

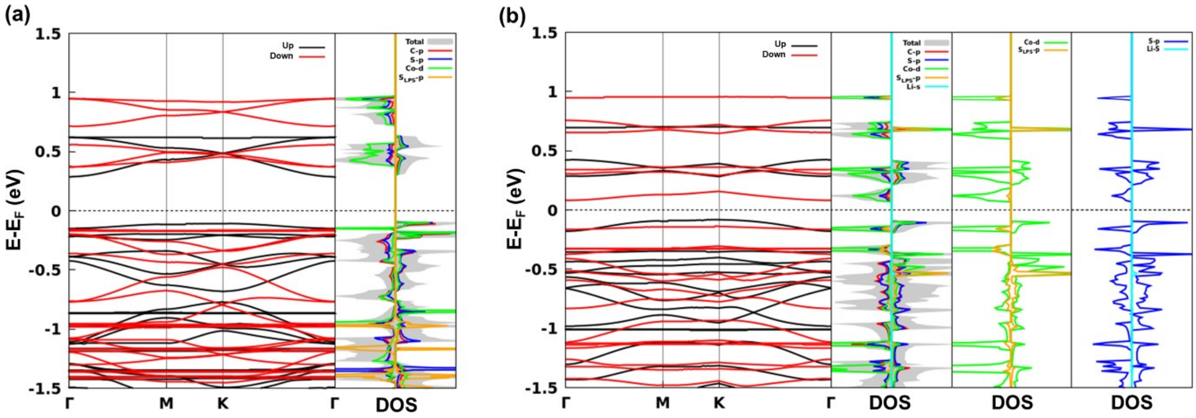

Figure S7: Computed band structures and DOS of (a) S_8 and (b) Li_2S adsorbed $Co_3(THT)_2$ monolayers with PBE-D3 calculations. The Fermi energy is set to zero.

The S_8 adsorbed $Co_3(THT)_2$ retains the similar band gap of 0.39 eV as of pristine $Co_3(THT)_2$ monolayer but with a shift of Fermi level towards the valence band. Sizable density of states is introduced by the adsorption of S_8 in the valence band after ~ -0.9 eV region due to weak adsorption interactions. In case of Li_2S adsorbed $Co_3(THT)_2$ the band gap decreases to 0.22 eV and the valence band maxima and conduction band minima are contributed by spin down channels. The partial DOS shows overlap between Co-d and S_{LPS}-p (sulfur of Li_2S) orbitals, and Li-s and S-p (sulfur of $Co_3(THT)_2$) orbital, which is more significant for Co and S_{LPS}.

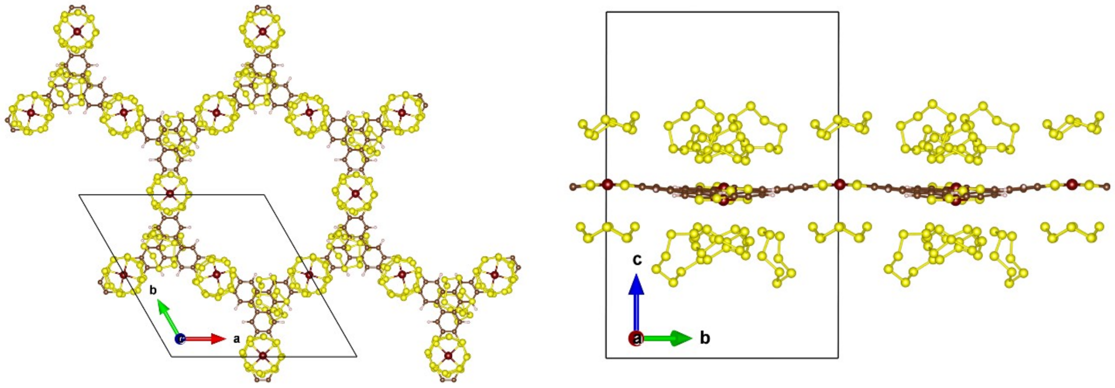

Figure S8: The side and top view of optimized stable configuration of S_8 loaded on $Co_3(THT)_2$ MOF.

To determine the maximum sulfur loading capacity, the average adsorption energy E_{avg_ads} is calculated as,

$$E_{avg\_ads} = (E_{MOF-nS_8} - E_{MOF} - nE_{S_8})/n \qquad (1)$$

where, E_{MOF}, E_{MOF-nS_8}, and E_{S_8} represent the total energy for the pristine $Co_3(THT)_2$ MOF, $Co_3(THT)_2$ MOF with n number of S_8 adsorbed and Li_2S species, respectively. The average adsorption energy is obtained to be -0.47 eV for 10 Li_2S adsorbed on both sides of unitcell. The negative value of adsorption energy suggests the feasibility of adsorption and thus $Co_3(THT)_2$ can have a maximum sulfur loading capacity of 71.8 %.