**Supplementary Information**

# $C_9N_4$ and $C_2N_6S_3$ Monolayers as Promising Anchoring Materials for Lithium-Sulfur Batteries: Weakening the Shuttle Effects *via* Optimizing Lithium Bonds

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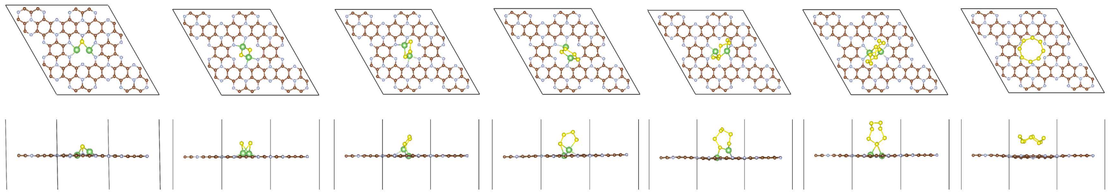
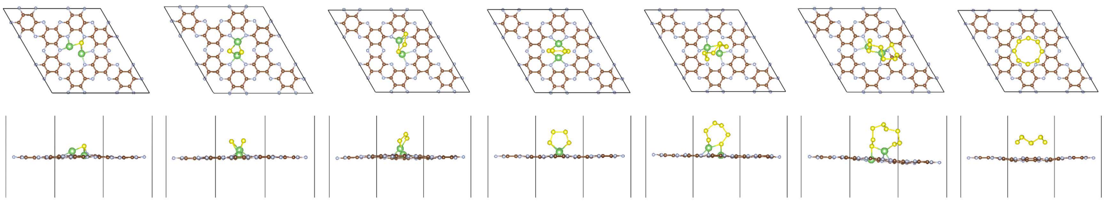
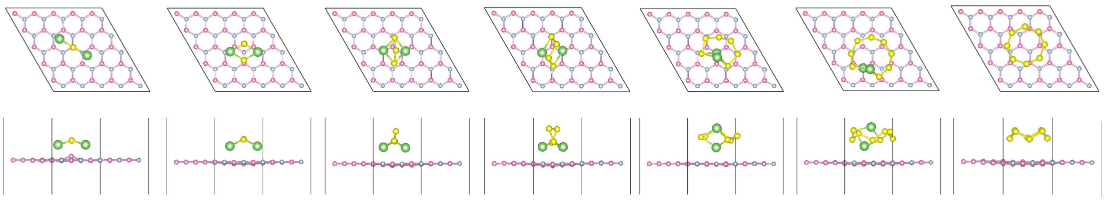


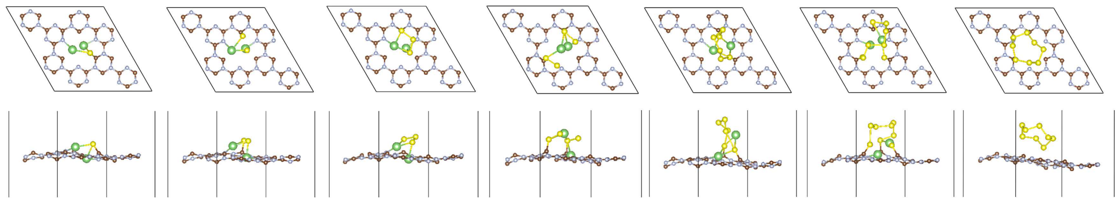
(a) $C_9N_4$



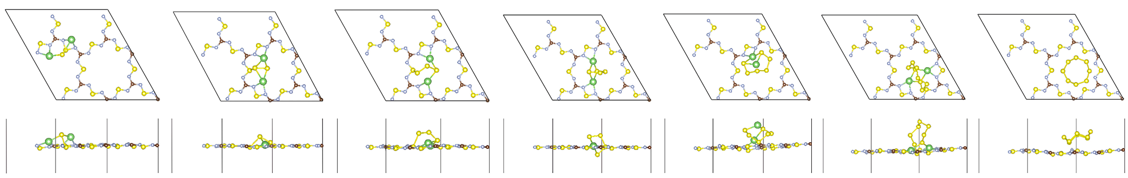
(b) $C_2N$



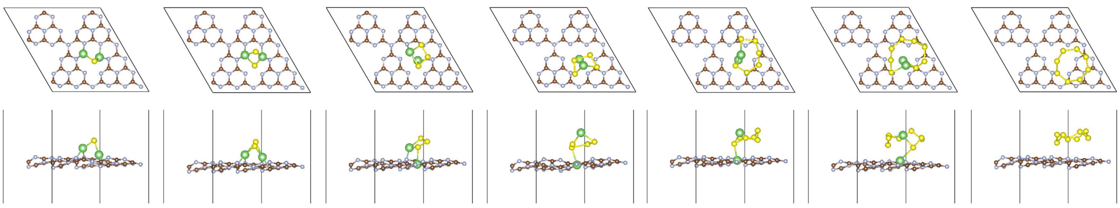
(c) BN



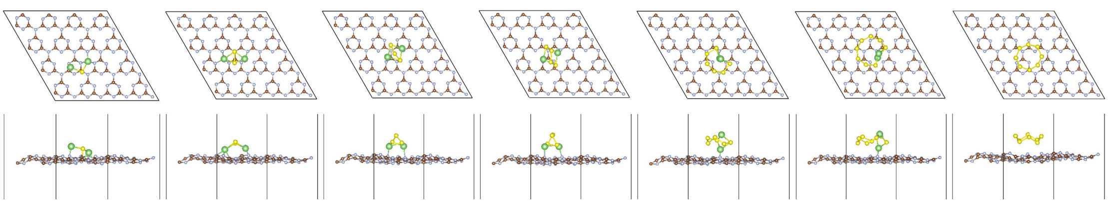
(d) CTF



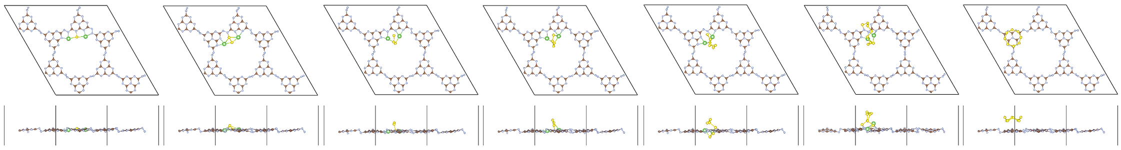
(e) $C_2N_6S_3$



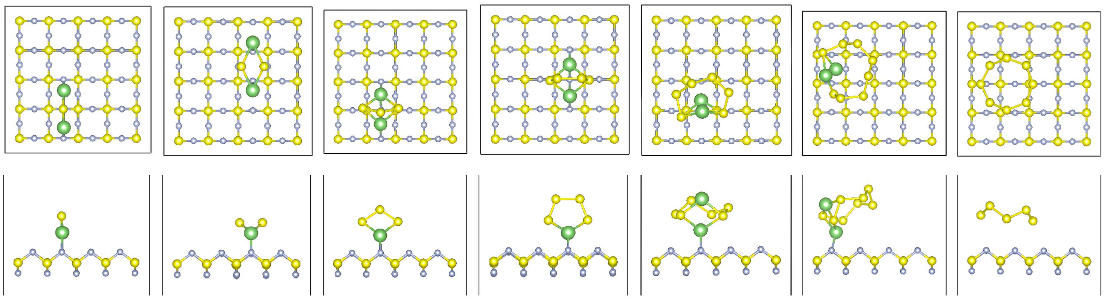
(f) *g*-$C_3N_4$



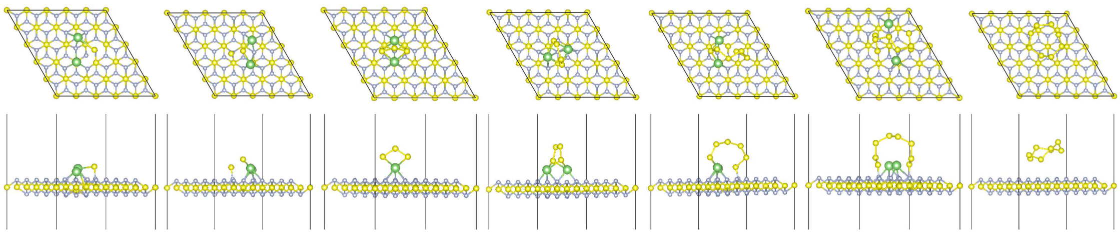
(g) *p*-$C_3N_4$



(h) $C_3N_5$

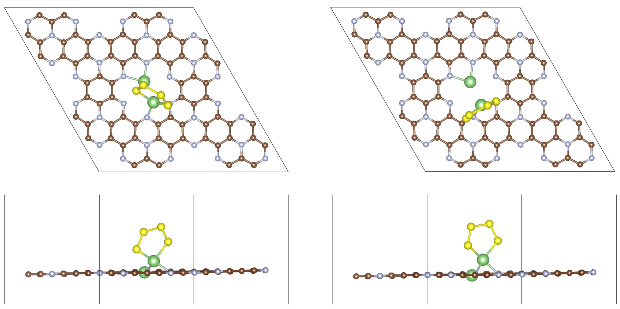


(i) *S*-$N_2S$



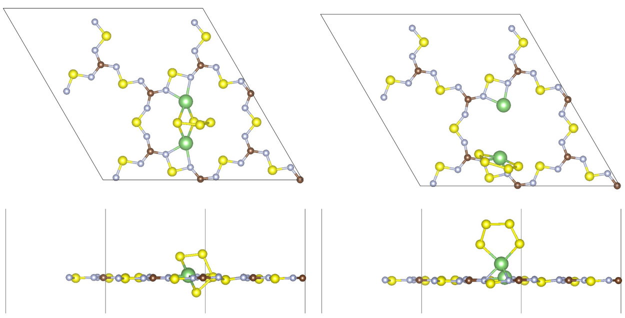
(j) *T*-$N_2S$

**Fig. S1** The most stable configurations of $Li_2S_n$ and $S_8$ on the ten examined 2D AMs.



**E = 0.00 eV** **E = 0.83 eV**

(a)



**E = 0.00 eV** **E = 1.24 eV**

(b)

**Fig. S2** Top and sides views of the “intact” and decomposed $Li_2S_4$ on the $C_9N_4$ (a) and $C_2N_6S_3$ (b), as well as their relative energies.

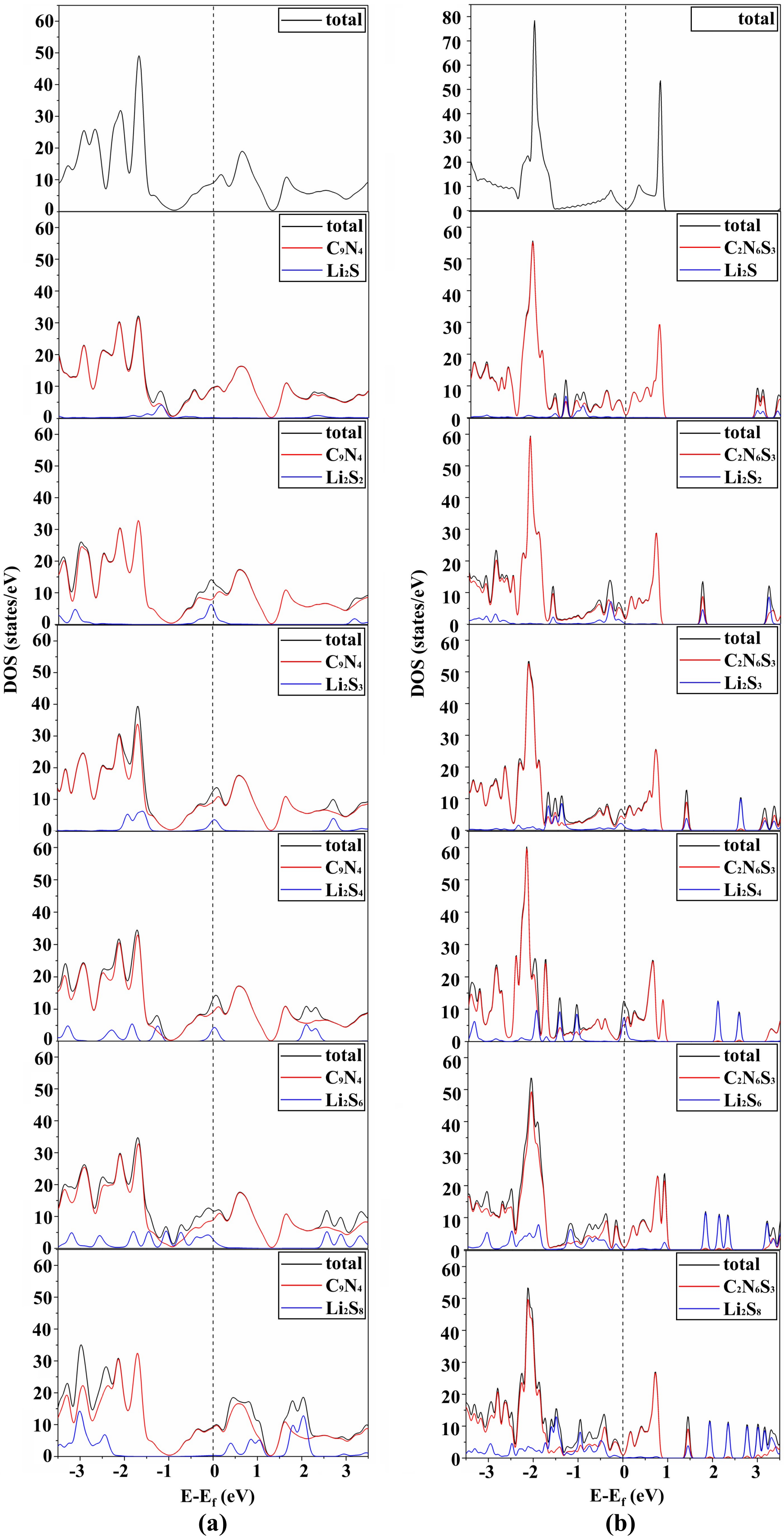



**Fig. S3** Density of states for $C_9N_4$ (a) and $C_2N_6S_3$ (b) before and after adsorption of $Li_2S_n$ ($n$ = 1, 2, 3, 4, 6, 8).

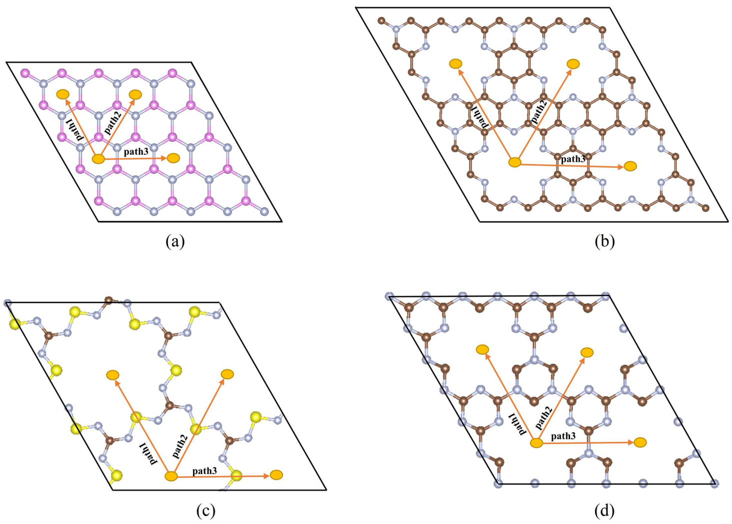



**Fig. S4** Diffusion paths for $Li_2S_6$ on the BN (a) $C_9N_4$ (b) $C_2N_6S_3$ (c) and CTF (d) monolayers.

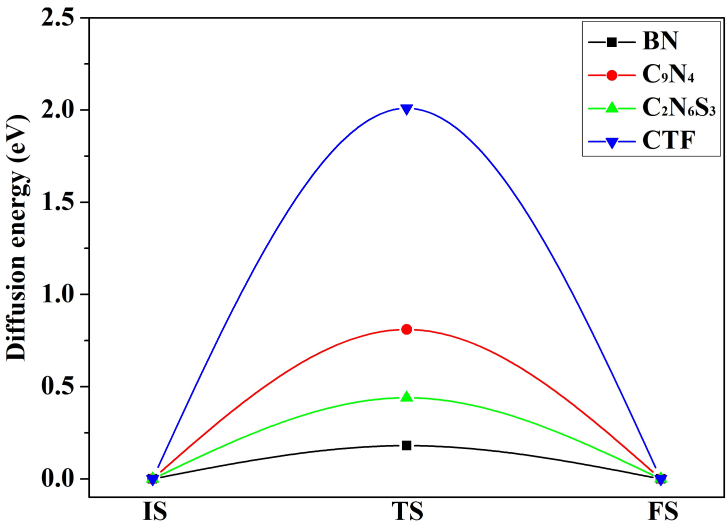
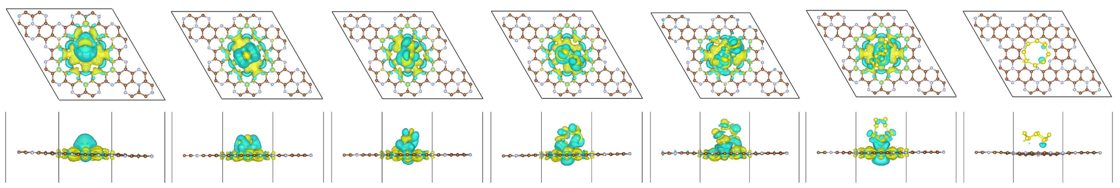
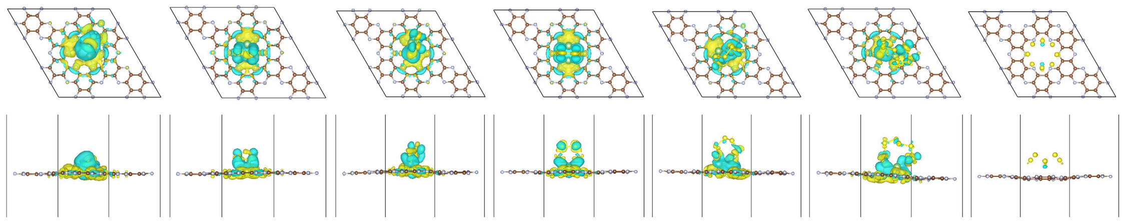


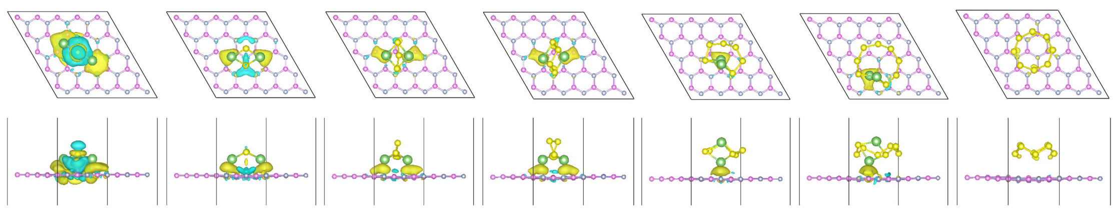

**Fig. S5** Migration energy barrier of $Li_2S_6$ on BN, $C_9N_4$, $C_2N_6S_3$ and CTF.



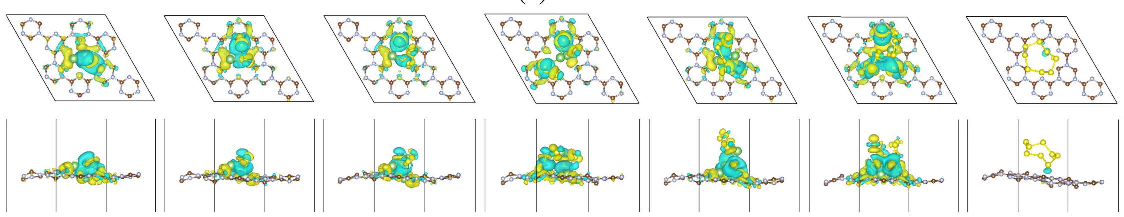
(a) $C_9N_4$



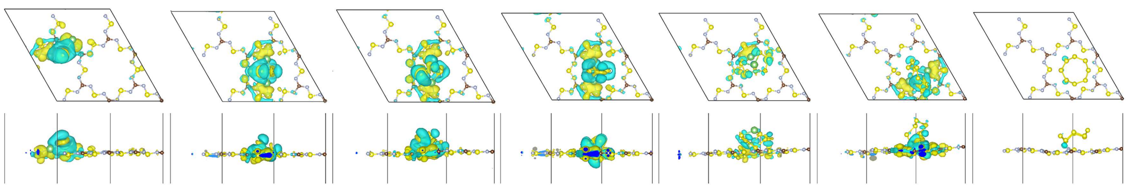
(b) $C_2N$



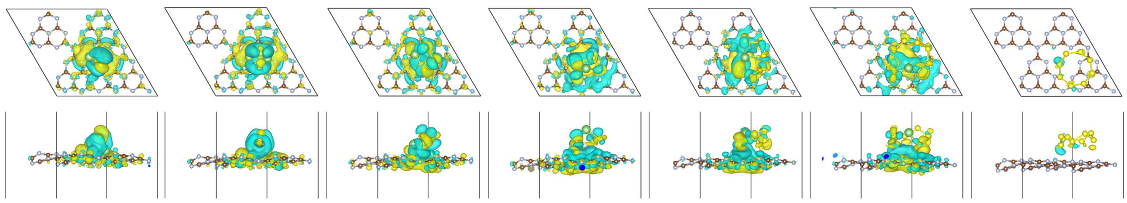
(c) BN



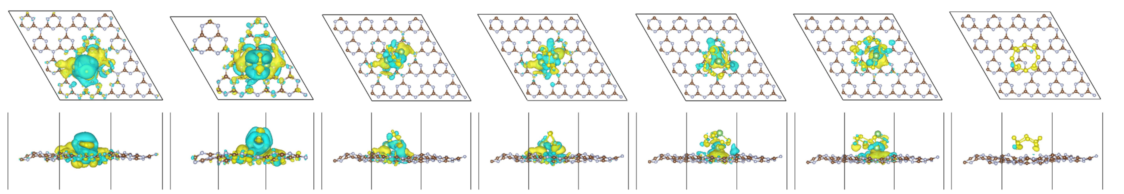
(d) CTF



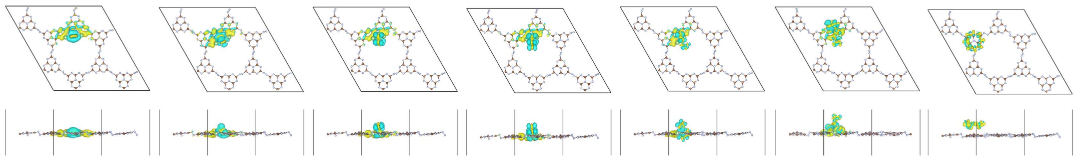
(e) $C_2N_6S_3$



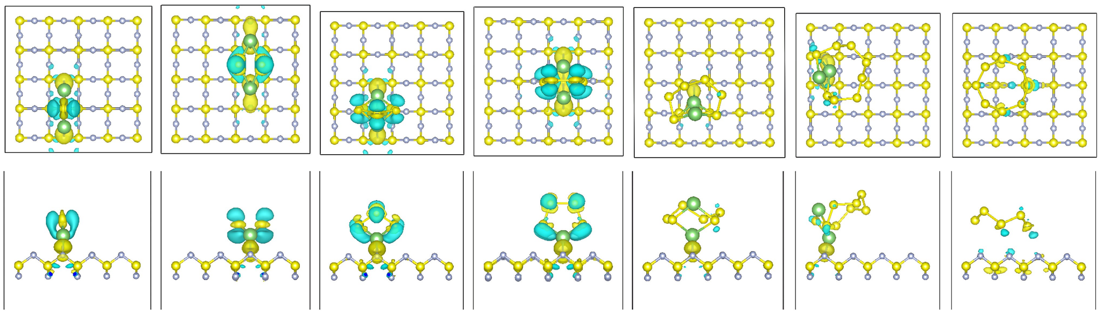
(f) *g*-$C_3N_4$



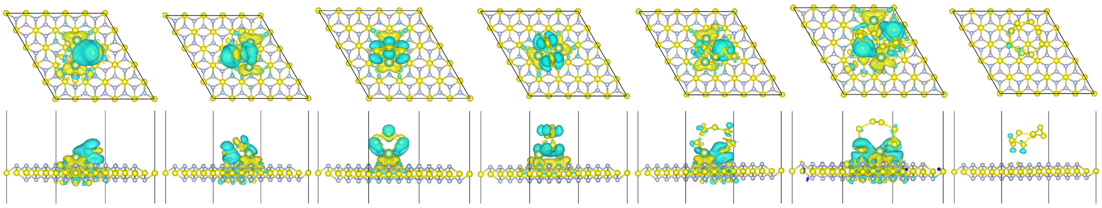
(g) *p*-$C_3N_4$



(h) $C_3N_5$



(i) *S*-$N_2S$



(j) *T*-$N_2S$

**Fig. S6** Charge density difference diagrams of the $Li_2S_n$ and $S_8$ on ten examined 2D AMs.

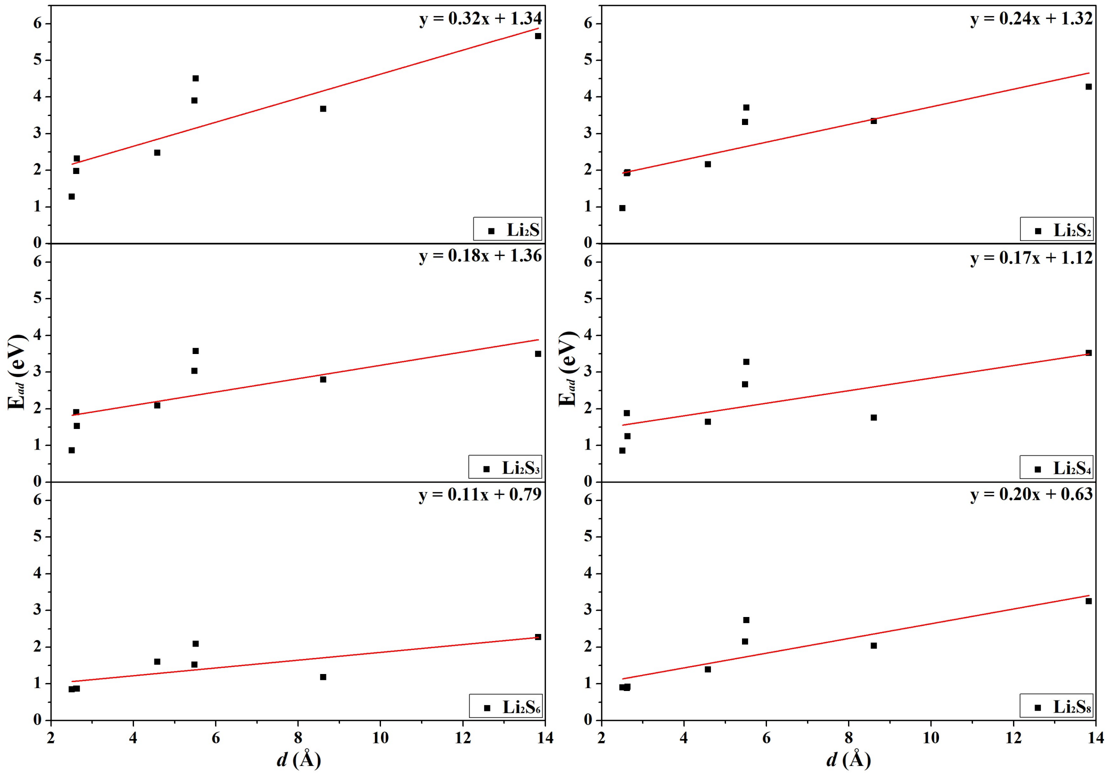



**Fig. S7** Linear fitting between the adsorption energy of $Li_2S_n$ ($n$ = 1~4, 6, 8) and the pore size of the AMs. The sequence of the AMs is the same as Fig. 6b except CTF and *T*-$N_2S$.

**Table S1** The N content ($\eta$, in %), pore size ($d$, in Å), and number of bridge N atoms in one pore ($m$) for each considered AM.

| | $\eta$ | $d$ | $m$ |
|---|---|---|---|
| $C_9N_4$ | 30.77 | 5.51 | 6 |
| $C_2N$ | 33.33 | 5.49 | 6 |
| BN | 50.00 | 2.51 | 0 |
| CTF | 50.00 | 5.29 | 3 |
| $C_2N_6S_3$ | 54.54 | 8.61 | 6 |
| *g*-$C_3N_4$ | 57.14 | 4.58 | 6 |
| *p*-$C_3N_4$ | 57.14 | 2.63 | 3 |
| $C_3N_5$ | 62.50 | 13.83 | 18 |
| *S*-$N_2S$ | 66.67 | 2.62 | 2 |
| *T*-$N_2S$ | 66.67 | 2.63 | 0 |

**Table S2** Average length of the formed S−C bonds ($d_{S\text{–}C}$, in Å) between the $Li_2S_n$ and the ten AMs. Data in parentheses denote the number of S−C bonds.

| | $Li_2S$ | $Li_2S_2$ | $Li_2S_3$ | $Li_2S_4$ | $Li_2S_6$ | $Li_2S_8$ |
|---|---|---|---|---|---|---|
| $C_9N_4$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $C_2N$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| BN | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| CTF | 1.69 | 1.77 | 1.83 | 1.65 | 1.73 | 1.74 |
| | (1) | (1) | (1) | (2) | (2) | (3) |
| $C_2N_6S_3$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *g*-$C_3N_4$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *p*-$C_3N_4$ | 2.02 | -- | -- | -- | -- | -- |
| | (1) | -- | -- | -- | -- | -- |
| $C_3N_5$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *S*-$N_2S$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *T*-$N_2S$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |

**Table S3** Li...S distances of the broken Li−S bonds ($d_{Li\cdots S}$, in Å). Data in parentheses denote the number of broken Li−S bonds.

| | $Li_2S$ | $Li_2S_2$ | $Li_2S_3$ | $Li_2S_4$ | $Li_2S_6$ | $Li_2S_8$ |
|---|---|---|---|---|---|---|
| $Li_2S_n$ @$C_9N_4$ | -- | -- | 4.38 | 4.61 | 4.34 | -- |
| | -- | -- | (1) | (1) | (1) | -- |
| $Li_2S_n$ @$C_2N$ | -- | -- | 4.61 | -- | 3.62 | 4.78 |
| | -- | -- | (1) | -- | (1) | (1) |
| $Li_2S_n$ @BN | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $Li_2S_n$ @CTF | -- | 3.02 | 3.77 | 4.05 | -- | 3.37 |
| | -- | (1) | (1) | (1) | -- | (2) |
| $Li_2S_n$ @$C_2N_6S_3$ | -- | -- | 3.68 | -- | -- | -- |
| | -- | -- | (1) | -- | -- | -- |
| $Li_2S_n$ @*g*-$C_3N_4$ | -- | -- | 4.47 | 3.38 | 4.45 | 4.02 |
| | -- | -- | (1) | (1) | (1) | (1) |
| $Li_2S_n$ @*p*-$C_3N_4$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $Li_2S_n$ @$C_3N_5$ | -- | -- | 3.10 | 2.88 | 3.20 | 4.62 |
| | -- | -- | (2) | (1) | (2) | (2) |
| $Li_2S_n$ @*S*-$N_2S$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $Li_2S_n$ @*T*-$N_2S$ | 2.99 | 3.27 | -- | -- | 3.02 | 3.62 |
| | (1) | (2) | -- | -- | (1) | (3) |

**Table S4** Average length of the formed S−N bond ($d_{S-N}$, in Å) between the $Li_2S_n$ and the ten AMs. Data in parentheses denote the number of S−N bonds.

| | $Li_2S$ | $Li_2S_2$ | $Li_2S_3$ | $Li_2S_4$ | $Li_2S_6$ | $Li_2S_8$ |
|---|---|---|---|---|---|---|
| $C_9N_4$ | 1.81 | -- | -- | -- | -- | -- |
| | (1) | -- | -- | -- | -- | -- |
| $C_2N$ | 1.78 | -- | -- | -- | -- | -- |
| | (1) | -- | -- | -- | -- | -- |
| BN | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| CTF | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $C_2N_6S_3$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *g*-$C_3N_4$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| *p*-$C_3N_4$ | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |
| $C_3N_5$ | 1.75 | 1.87 | -- | -- | -- | 1.83 |
| | (1) | (1) | -- | -- | -- | (1) |
| *S*-$N_2S$ | 1.63 | -- | -- | -- | -- | -- |
| | (1) | -- | -- | -- | -- | -- |
| *T*-$N_2S$ | 1.62 | 1.64 | -- | 1.61 | -- | 1.60 |
| | (1) | (1) | -- | (1) | -- | (2) |

**Table S5** Diffusion barriers ($E_a$, in eV) of $Li_2S_6$ along three paths on BN, $C_9N_4$, $C_2N_6S_3$ and CTF monolayers.

| $Li_2S_6$ | BN | $C_9N_4$ | $C_2N_6S_3$ | CTF |
|---|---|---|---|---|
| Path1 | 0.21 | 0.89 | 0.51 | 2.25 |
| Path2 | 0.18 | 0.81 | 0.44 | 2.01 |
| Path3 | 0.20 | 0.85 | 0.49 | 2.13 |

**Table S6** Variation of adsorption energies ($E_{ad}$, in eV), charger transfer ($\Delta q$, in |$e$|) and average length of Li−S/N bond ($d_{Li-S}$, $d_{Li-N}$, in Å). Data in parentheses denote the number of S−N bonds.

| @$Li_2S_8$ | $E_{ad}$ | $\Delta q$ | $d_{Li-S}$ | $d_{Li-N}$ |
|---|---|---|---|---|
| non-Li-trapped $C_9N_4$ | 2.73 | 0.75 | 2.69 | 2.03 |
| | | | (4) | (4) |
| Li-trapped $C_9N_4$ | 1.87 | 0.08 | 2.44 | 2.04 |
| | | | (4) | (2) |
| non-Li-trapped $C_2N_6S_3$ | 2.03 | 0.75 | 2.46 | 2.08 |
| | | | (4) | (4) |
| Li-trapped $C_2N_6S_3$ | 1.46 | 0.17 | 2.35 | 2.11 |
| | | | (4) | (2) |