Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

Li-Doped 2D Aza-Fused Covalent Organic Framework: A Promising Avenue for Hydrogen Storage

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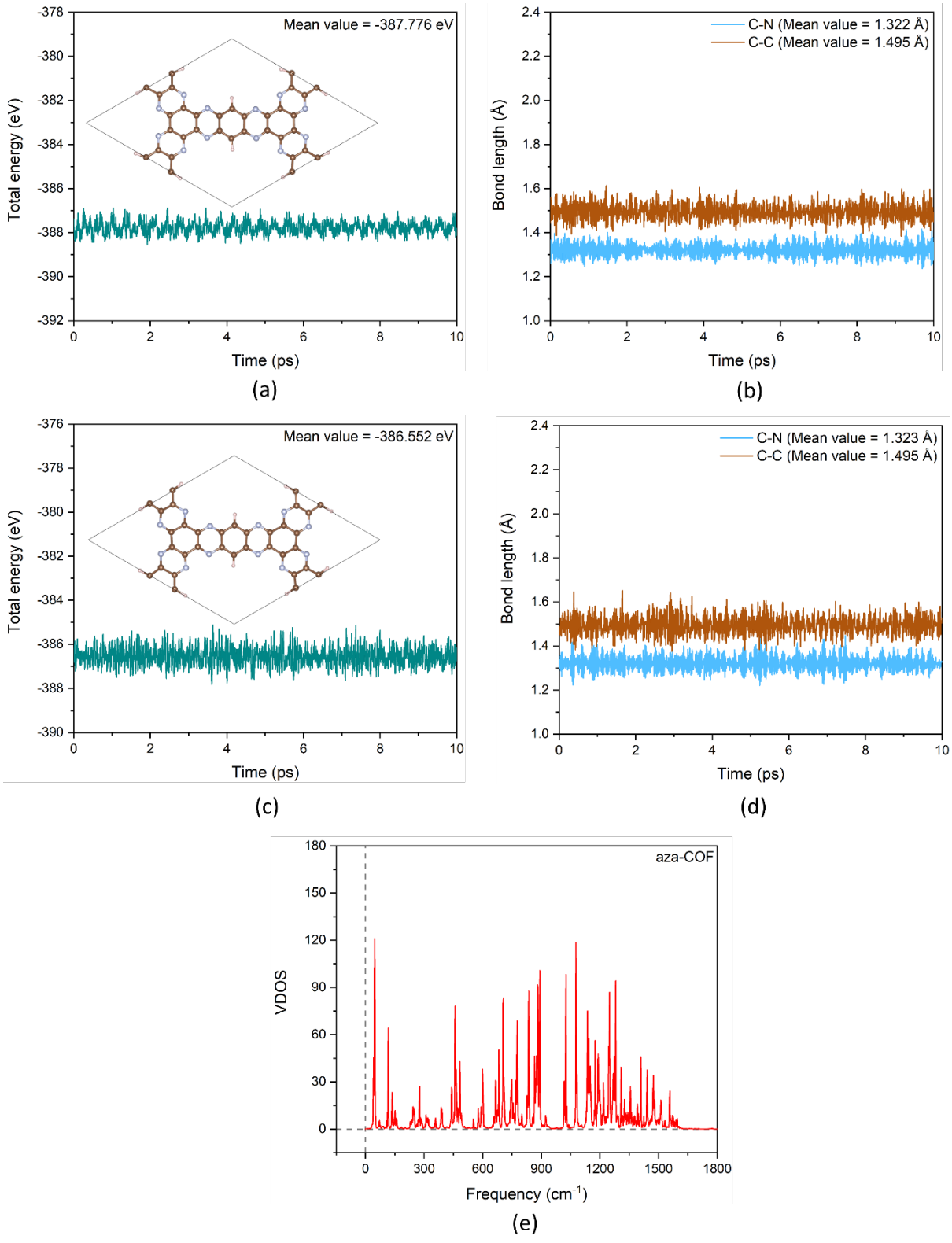
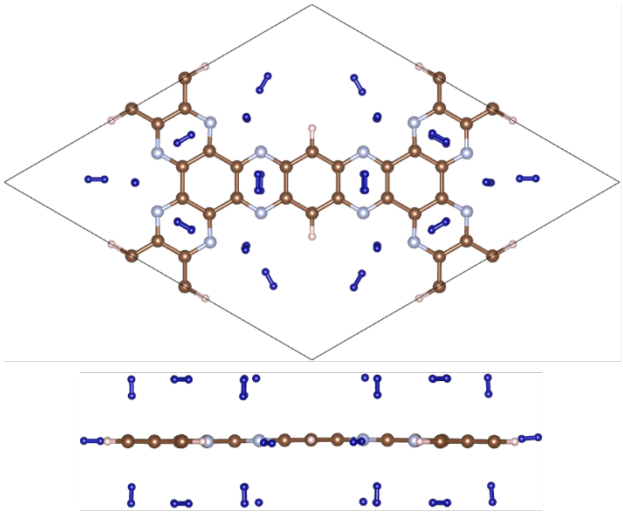
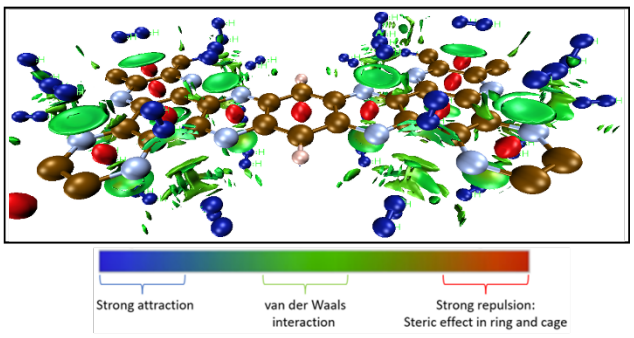


Figure S1: (a) Total energy and (b) different bond lengths fluctuations during the AIMD simulation at 300 K of aza-COF. (c) Total energy and (d) different bond lengths fluctuations during the AIMD simulation at 500 K of aza-COF. Insets of Figure S1a and S1c displays the final snapshot of aza-COF after 10 ps at 300 K and 500 K, respectively. (e) VDOS vs frequency plot at 300 K of aza-COF.



aza-COF+30H_2 (-0.17 eV)

(a)



(b)

Figure S2: (a) Optimized structure of aza-COF+30H_2. (b) NCI isosurface mapped for aza-COF+30H_2.

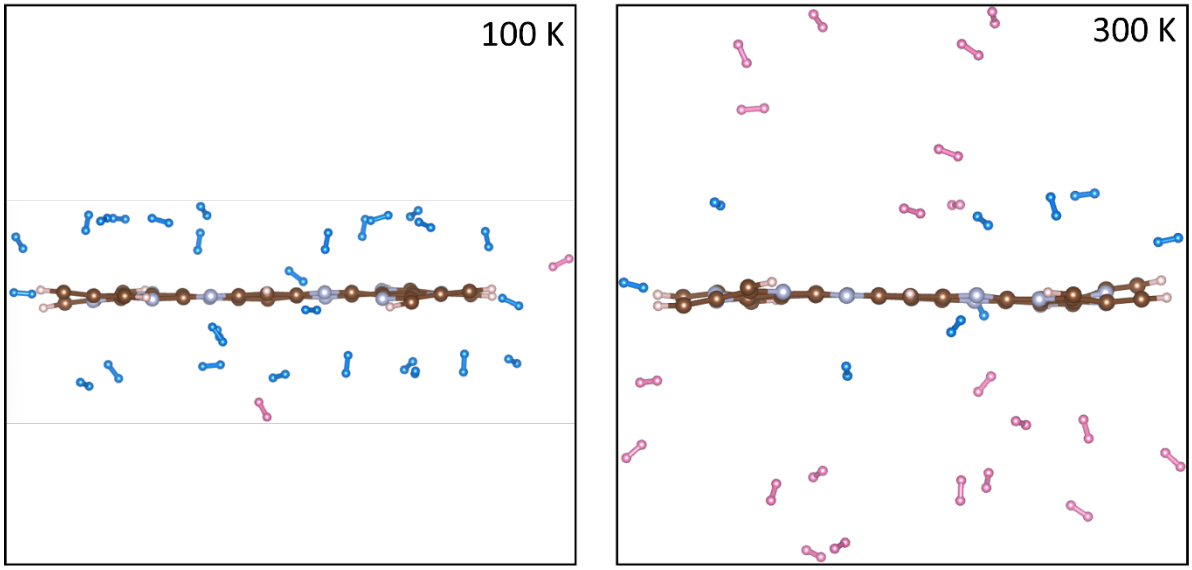
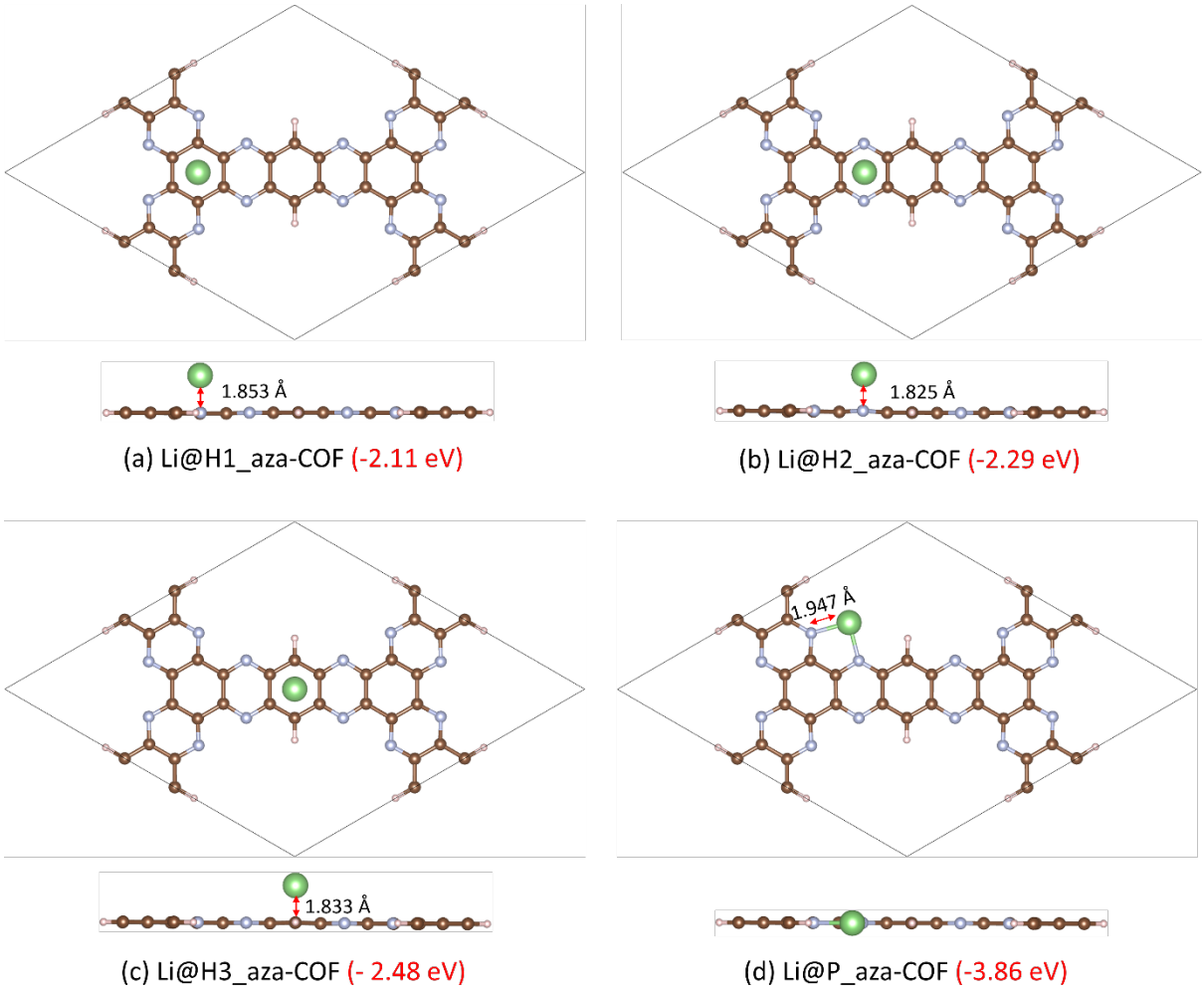


Figure S3: Snapshot of aza-COF+30H_2 after 10 ps of AIMD simulations at (a) 100 K and (b) 300 K. H_2 molecule color representation: Cyan-2.5 < d < 4.0 Å and pink- d > 4.0 Å. d denotes the distance of H_2 molecules from the surface of framework.



(a) Li@H1_aza-COF (-2.11 eV)

(b) Li@H2_aza-COF (-2.29 eV)

(c) Li@H3_aza-COF (- 2.48 eV)

(d) Li@P_aza-COF (-3.86 eV)

Figure S4: Optimized structures of Li doped at different binding sites of aza-COF: (a) H1, (b) H2, (c) H3, and (d) P, with respective binding energy.

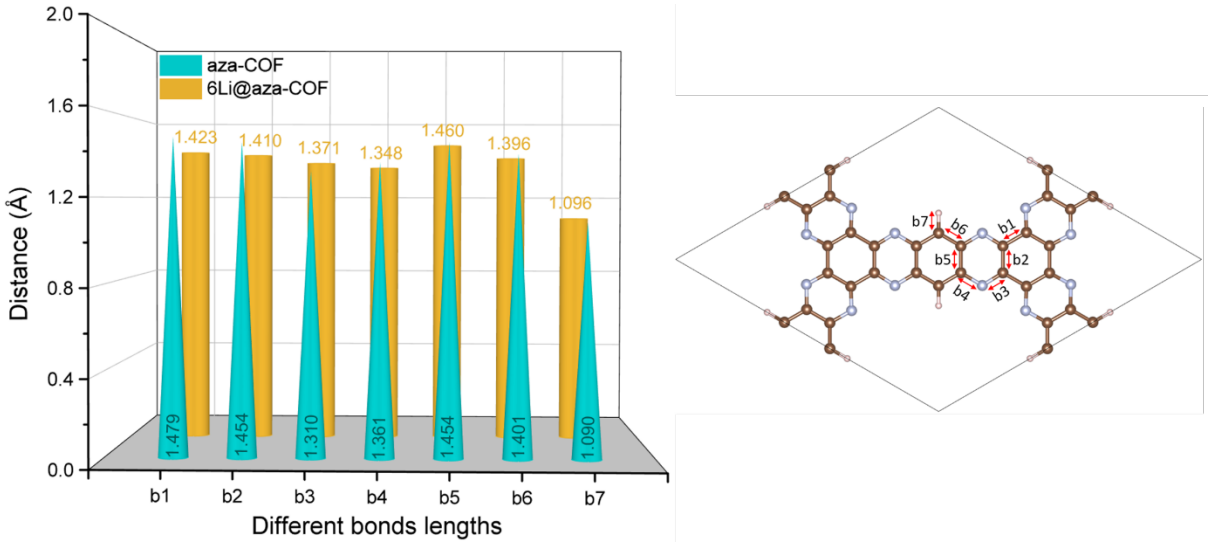
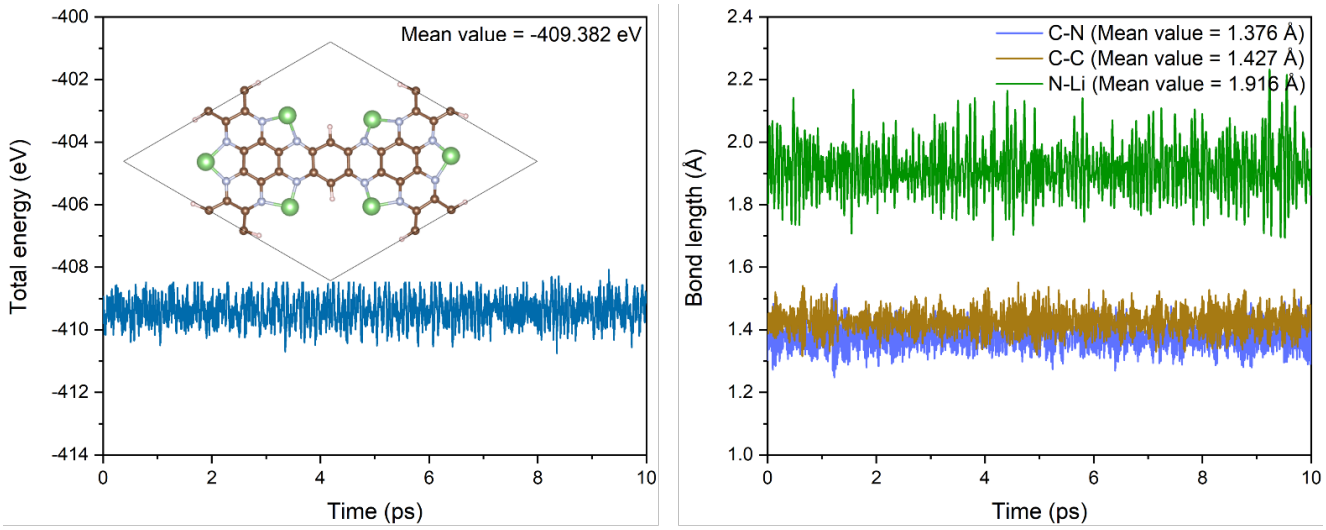
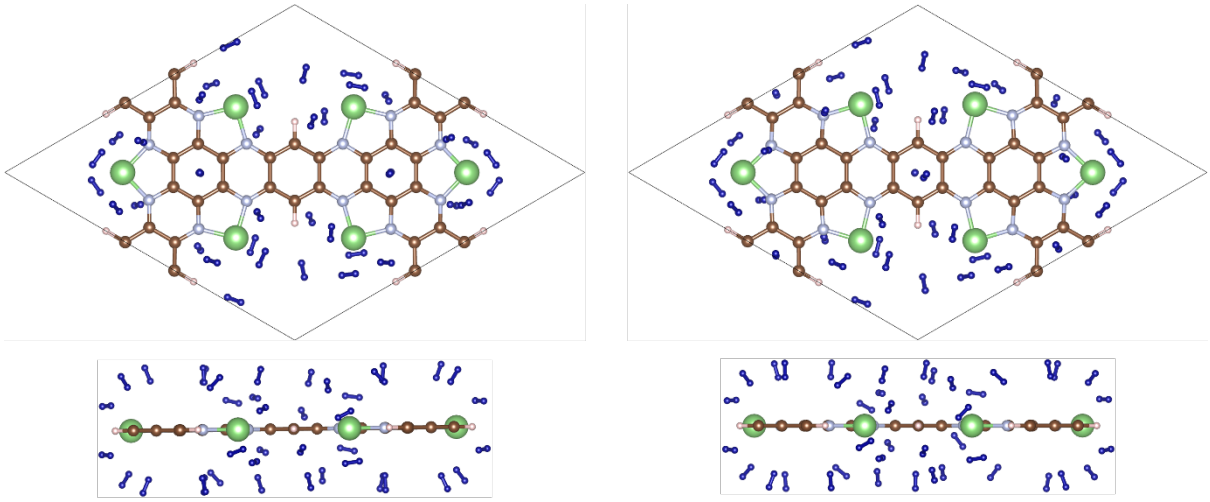


Figure S5: Different bond lengths of aza-COF and 6Li@aza-COF.



(a) (b)

Figure S6: (a) Total energy and (b) different bond lengths fluctuations during the AIMD simulation at 500 K of 6Li@aza-COF. Inset of Figure S1a displays the final snapshot of 6Li@aza-COF after 10 ps.



(a) 6Li@aza-COF+40H2 (-0.23 eV)

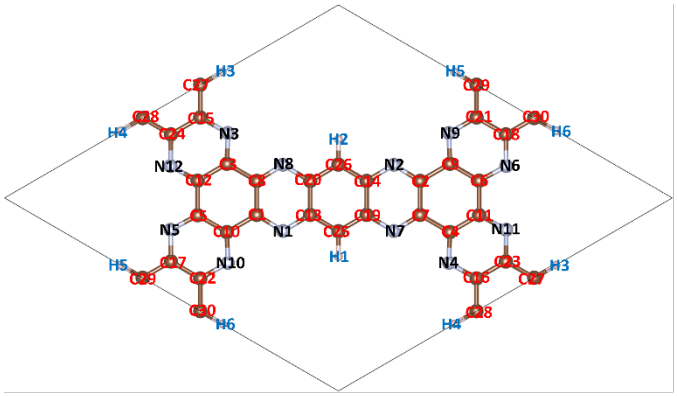
(b) 6Li@aza-COF+42H_2 (-0.22 eV)

Figure S7: Optimized structures of (a) 6Li@aza-COF+40H_2 and (b) 6Li@aza-COF+42H_2 configurations.

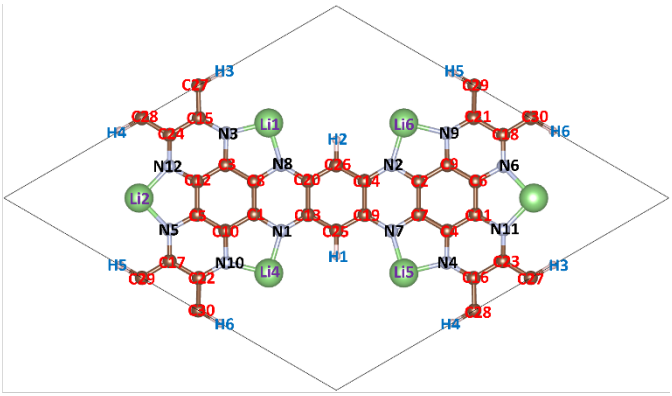
Table S1: Bader charges on C, N, H and Li atoms in aza-COF and 6Li@aza-COF.

Atoms	aza-COF	6Li@aza-COF
C1	0.57657	0.42707
C2	0.59027	0.43589
C3	0.67658	0.43028
C4	0.54243	0.44283
C5	0.57684	0.42945
C6	0.58547	0.43681
C7	0.57657	0.42716
C8	0.59027	0.43495
C9	0.67658	0.42980
C10	0.54243	0.44322
C11	0.57684	0.42944
C12	0.58548	0.43666
C13	0.43495	0.44631
C14	0.46144	0.52029
C15	0.43824	0.42128
C16	0.43733	0.47913
C17	0.47821	0.44683
C18	0.47821	0.51008
C19	0.48728	0.44599
C20	0.51286	0.52076
C21	0.43733	0.42177
C22	0.43824	0.47892
C23	0.47821	0.44705
C24	0.47821	0.50971
C25	-0.03318	-0.04294
C26	-0.03318	-0.03964
C27	0.01336	0.00051
C28	0.01336	0.00231
C29	0.01336	0.00040
C30	0.01336	0.00218
N1	-1.10694	-1.31947
N2	-1.10694	-1.32068
N3	-1.12677	-1.32603
N4	-1.12677	-1.3268
N5	-1.10690	-1.31699
N6	-1.10690	-1.32173
N7	-1.10694	-1.31918
N8	-1.10694	-1.32076
N9	-1.12677	-1.32632
N10	-1.12677	-1.32717
N11	-1.10690	-1.31741
N12	-1.10690	-1.32119
H1	0.12766	-0.03653
H2	0.12766	-0.03834
H3	0.11575	-0.04517

H4	0.11575	-0.04493
H5	0.11575	-0.04499
H6	0.11552	-0.04502
Li1		0.89082
Li2		0.89023
Li3		0.89019
Li4		0.89098
Li5		0.89099
Li6		0.89084



aza-COF



6Li@aza-COF

Table S2: Bader charges on Li and H atoms of adsorbed H_2 molecules in 6Li@aza-COF and 6Li@aza-COF+6H_2.

Configurations	Li atom	H atom (H_2 molecules)
6Li@aza-COF	0.89082	
	0.89023	
	0.89019	
	0.89098	
	0.89099	
	0.89084	
6Li@aza-COF+6H_2	0.87432	0.04097
	0.87313	-0.03889
	0.87317	-0.04417
	0.87388	0.04660
	0.87460	0.03858
	0.87434	-0.03629
		-0.03463
		0.03723
		-0.04121
		0.04331
		-0.03697
		0.03896