Supplementary Information

Hierarchical Modeling of Ammonia Adsorption in Functionalized Metal-Organic Frameworks

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Fitting of NH_3 and –Cl Interaction

In the Morse potential, there are two types of interaction sites (N and H) on NH_3 and six types of interaction sites (C, HA, Cl, CA, CB and HB) on the aromatic ring. In addition, we consider two other types of sites XPC/XPCA/XPCB and XCl. XPC/XPCA/XPCB represents the π-bond electron density (pi sites) on the carbon atoms of the aromatic ring. The distance between XPC and C (also XPCA and CA, XPCB and CB) is chosen to be 0.7856 Å. XCl represents the electron density of the electron pairs on the Cl atom. The site of XCl is located on the line CA-Cl and opposite to the CA atom. The XCl-Cl distance is used as a parameter in the fitting. The partial charges of C, CA and HA are also used as parameters in the fitting, while the charge of Cl is adjusted to keep the aromatic ring charge-neutral. Since the Morse potential has three parameters and we have twenty types of interactions (2×10=20), we have 60 parameters for the Morse interactions. However, the NH_3 pi site interactions were made repulsive by choosing σ to be zero. Therefore, there are a total of 54 Morse parameters. In addition there are four other parameters for the partial charges of C, CA and HA and the XCl-Cl distance, so we have a total of 58 parameters. Because of the similarity of the two HA atoms, we have sampled a few routes around the second HA atom as shown in Figure S3 (d-f). The total number of routes sampled is 65. The fitted parameters and fitting results are shown in Table S1 and Figures S2 and S3.

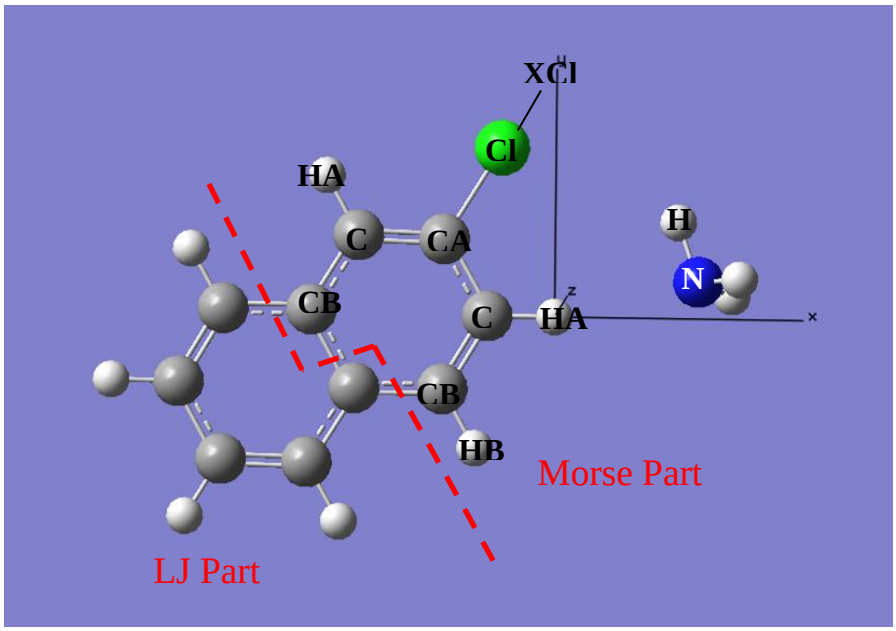


Figure S1 Schematic showing the interaction of NH_3 with the –Cl functional group. White, blue, grey, and green spheres represent H, N, C and Cl atoms, respectively.

Table S1 Fitting parameters for NH_3 interaction with –Cl group. The Cl-XCl distance is 0.2617 Å, and the charges on C, CA, HA, and Cl are −0.2945, 0.4556, 0.1745, and −0.3176, respectively.

Interactions	ε (kJ/mol)	A (1/Å)	σ (Å)
C-N	7.2500	1.0181	3.6391
HA-N	0.16494	1.9930	3.0804
Cl-N	0.23894	1.3223	4.5574
CA-N	8.0750	0.3611	2.8902
CB-N	1.9297	1.8611	2.9853
HB-N	9.5351×10^{-2}	1.5296	3.7533
XPCA-N	-5.5329×10^{-2}	5.0054	0.0000
XPC-N	-9.4508	3.7158	0.0000
XPCB-N	-2.2694	3.1849	0.0000
XCl-N	6.4562	5.9955	1.2063
C-H	0.57919	1.4699	3.1569
HA-H	8.1826×10^{-3}	1.2649	4.5099
Cl-H	4.599×10^{-3}	5.9978	0.0044
CA-H	6.0586	1.3976	2.7073
CB-H	4.3282×10^{-2}	1.0342	4.8128
HB-H	4.9120×10^{-2}	1.3495	3.5678
XPCA-H	-9.4280	0.7418	0.0000
XPC-H	-7.4992	0.4854	0.0000
XPCB-H	-1.8715	0.8131	0.0000
XCl-H	0.39390	1.3993	3.6179

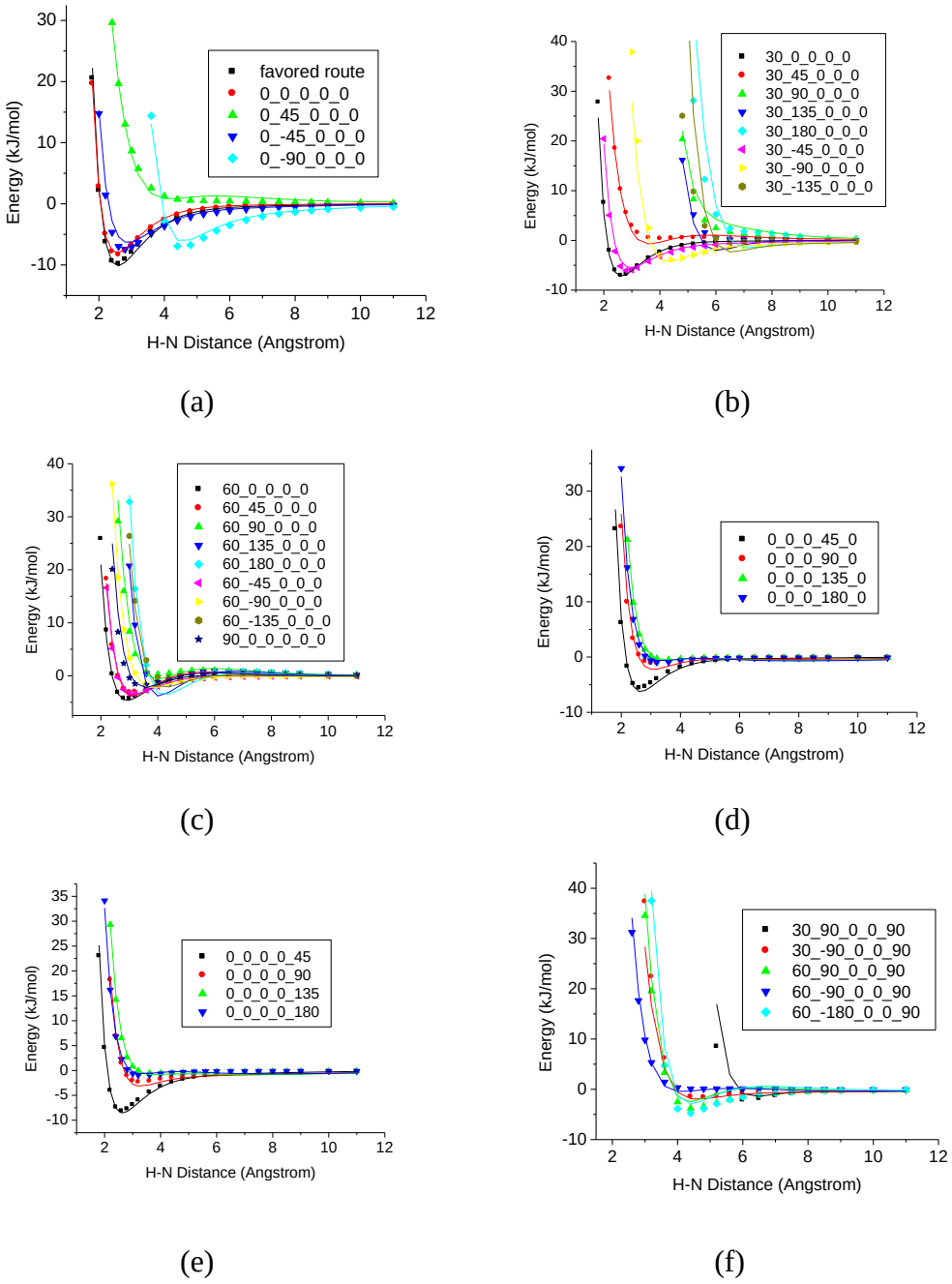


Figure S2 Fitting results of NH_3 and –Cl interaction (I). Symbols are from quantum chemistry calculations, while lines are fitting results.

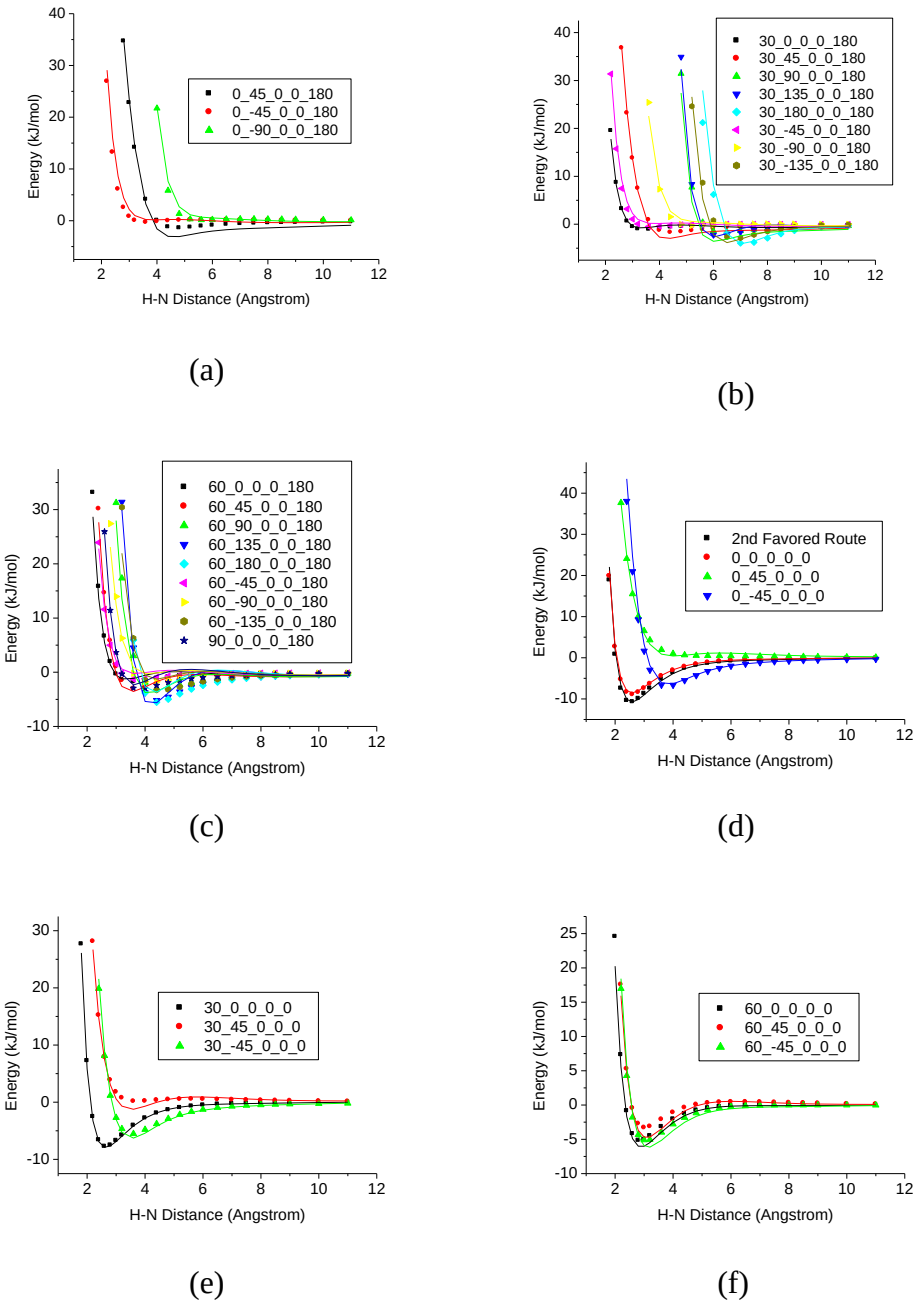


Figure S3 Fitting results of NH_3 and –Cl interaction (II). Symbols are from quantum chemistry calculations, while lines are fitting results. (d), (e) and (f) represent routes sampled around the 2nd HA atom by putting the 2nd HA atom at the origin of the coordinate system.

Fitting of NH_3 and –C=O Interaction

In the Morse potential, there are two types of interaction sites (N and H) on NH_3 and five types of interaction sites (C, HA, O, CA, and CB) on the aromatic ring. In addition, we consider two other types of sites XPC/XPCA and XO. XPC/XPCA represents the π-bond electron density (pi sites) on the carbon atoms of the aromatic ring. The distance between XPC and C (also XPCA and CA) is chosen to be 0.7856 Å. XO represents the electron density of the electron pairs on the O atom. The site of XO is located on the line CA-O and opposite to the CA atom. The XO-O distance is used as a parameter in the fitting. The partial charges of C, CA and HA are also used as parameters in the fitting, while the charge of O is adjusted to keep the aromatic ring charge-neutral. Since the Morse potential has three parameters and there are sixteen types of interactions (2×8=16), we have 48 parameters for the Morse interactions. However, the NH_3 pi site interactions were made repulsive by choosing σ to be zero. Therefore, there are a total of 44 Morse parameters. In addition there are four other parameters for the partial charges of C, CA and HA and the XO-O distance, so we have a total of 48 parameters. We have sampled a total of 51 approaching routes. The fitted parameters and fitting results are shown in Table S2 and Figures S5 and S6.

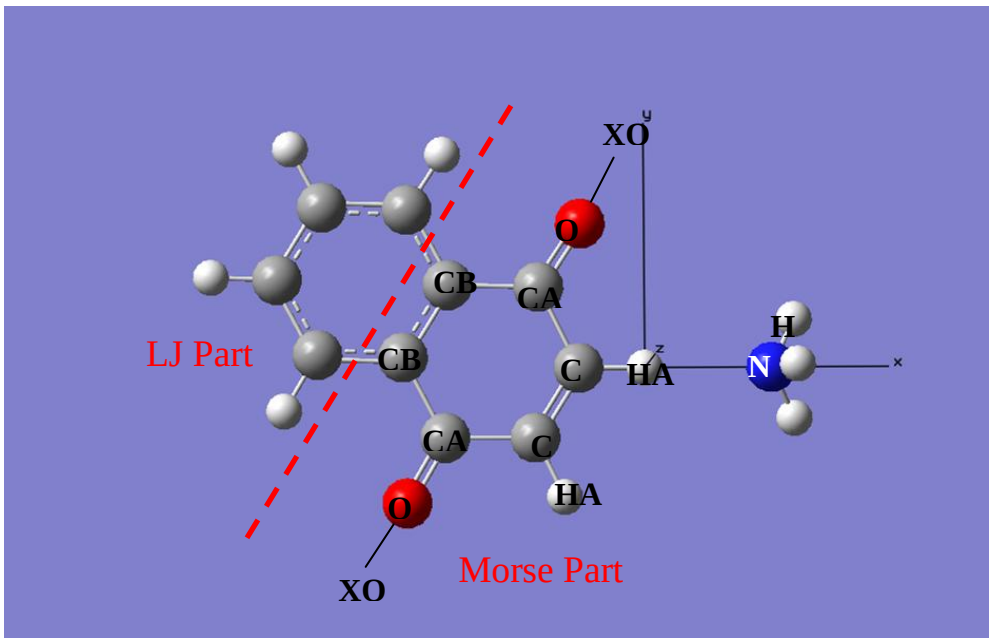
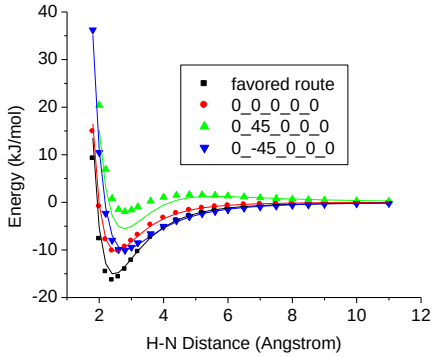


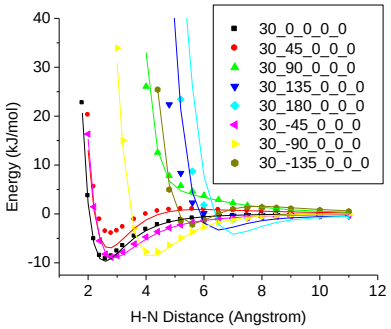
Figure S4 Schematic showing the interaction of NH_3 with the naphthoquinone group. White, blue, red, and grey spheres represent H, N, C and O atoms, respectively.

Table S2 Parameters for NH_3 interaction with the naphthoquinone group. The O-XO distance is 0.1329 Å, and the charges on C, CA, HA, and O are −0.3179, 0.6085, 0.2241, and −0.4998, respectively.

Interactions	ε (kJ/mol)	A (1/Å)	σ (Å)
C-N	1.1943	1.1102	4.0700
HA-N	0.18550	1.6640	3.4104
O-N	2.5009×10^{-2}	3.9205	0.0129
CA-N	0.78756	1.1947	3.5742
CB-N	1.8323	1.2750	3.7012
XPC-N	-9.6140	5.9105	0.0000
XPCA-N	-9.3367	4.5061	0.0000
XO-N	1.8633	1.7064	3.2951
C-H	1.2793×10^{-2}	1.5834	4.2553
HA-H	0.10516	1.4273	3.1536
O-H	2.2944×10^{-2}	0.5814	0.8121
CA-H	6.6338×10^{-3}	2.4270	3.6911
CB-H	1.9297	3.9562	2.5893
XPC-H	-8.4049	5.3381	0.0000
XPCA-H	-8.6402	0.9239	0.0000
XO-H	0.13685	2.1368	2.9220



(a)



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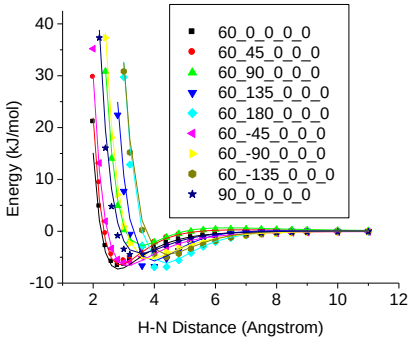
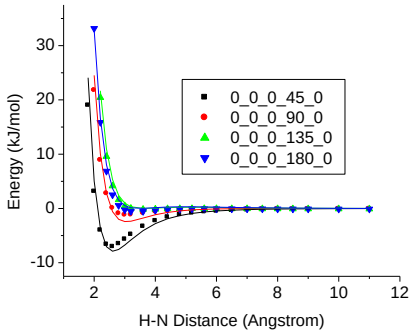
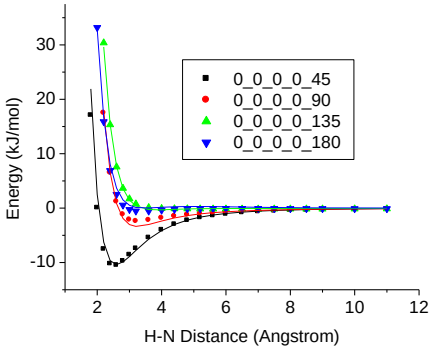


(c)

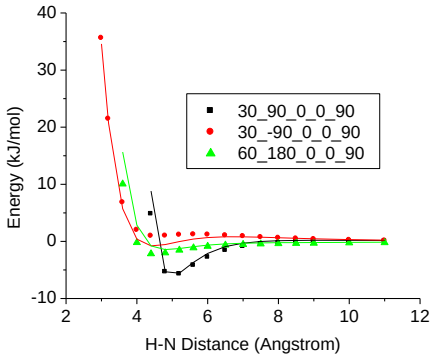


(d)

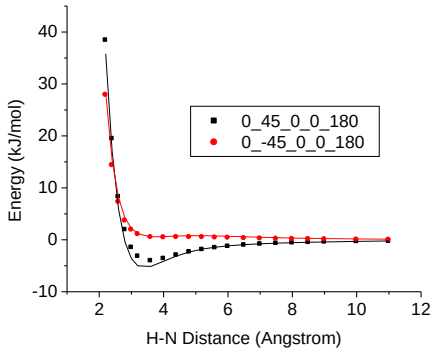


(e)

Figure S5 Fitting results of NH_3 interaction with naphthoquinone group (I). Symbols are from quantum chemistry calculations, while lines are fitting results.



(a)



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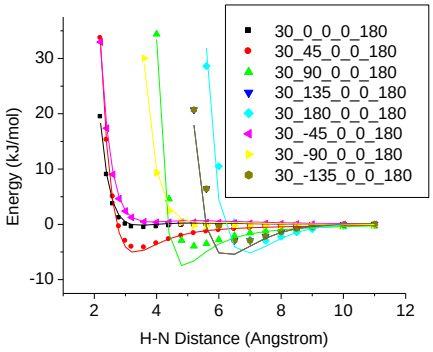

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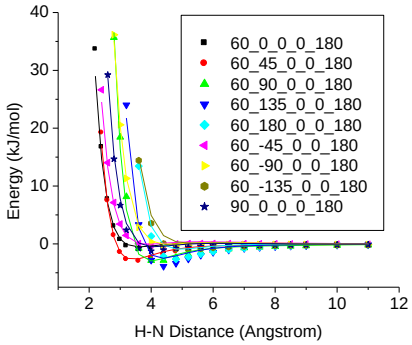


(d)

Figure S6 Fitting results of NH_3 interaction with naphthoquinone group (II). Symbols are from quantum chemistry calculations, while lines are fitting results.

Fitting of NH_3 and –COOH Interaction

In the Morse potential, there are two types of interaction sites (N and H) on NH_3 and six types of interaction sites (C, O, OA, HA, HB and CA) on the aromatic ring. In addition, we consider two other types of sites XPC/XPCA/XPO and XO/XOA. XPC/XPCA/XPO represents the π-bond electron density (pi sites) on the carbon (C and CA) or oxygen (O) atoms. The distance between XPC and C (also XPCA and CA, XPO and O) is chosen to be 0.7856 Å. XO/XOA represents the electron density of the electron pairs on the O atom. The site of XO is located on the line C-O and opposite to the C atom. The XO-O distance is used as a parameter in the fitting. The site of XOA is located on the line bisecting the angle C-OA-HA and opposite to the C and HA atoms. The XOA-OA distance is used as a parameter in the fitting. The partial charges of C, OA and HA are also used as parameters in the fitting, while the charge of O is adjusted to keep the aromatic ring charge-neutral. Since the Morse potential has three parameters and we have twenty types of interactions (2×10=20), we have 60 parameters for the Morse interactions. The parameters of XPC and XPCA are chosen to be the same. However, the NH_3 pi sites interactions were made repulsive by choosing σ to be zero. Also we ignored NH_3–HB interactions. Therefore, there are a total of 50 Morse parameters. In addition there are five other parameters for the partial charges of C, OA and HA and the XO-O, XOA-OA distances, so we have a total of 55 parameters. We have sampled a total of 50 approaching routes. The fitted parameters and fitting results are shown in Table S3 and Figures S8 and S9. It is noted that the lowest binding energy obtained from the rigid structures is -38.4 kJ/mol, which is 3.5 kJ/mol higher than that from the relaxed structures.

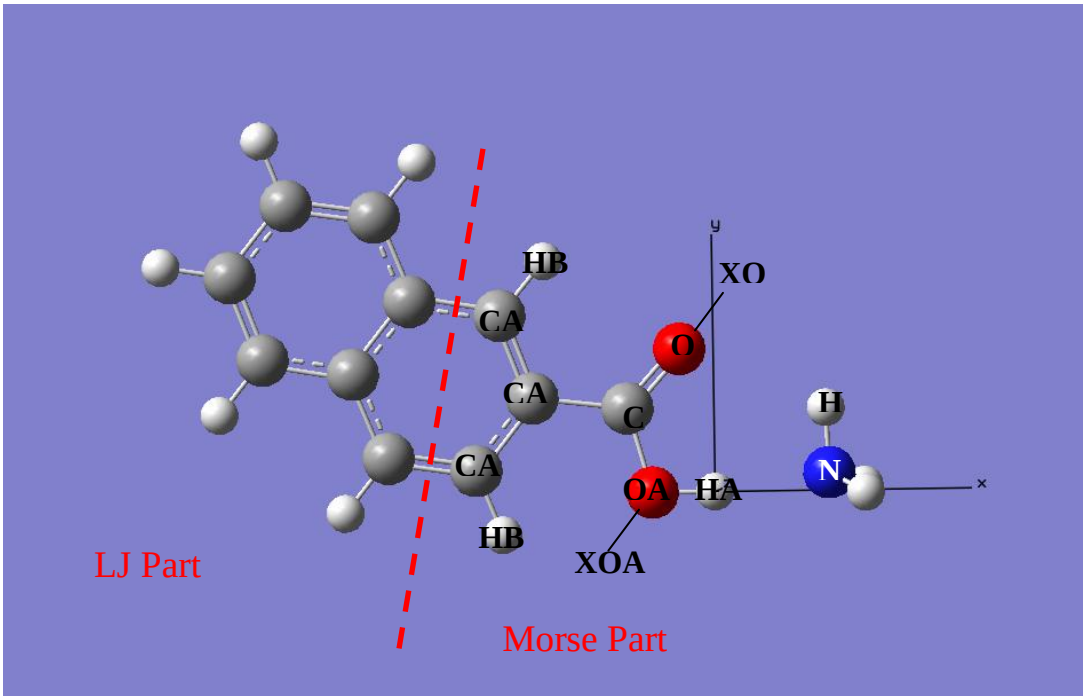
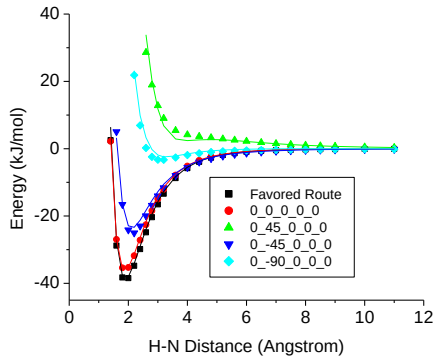


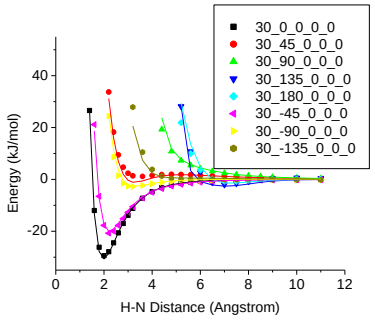
Figure S7 Schematic showing interaction of NH_3 with –COOH group. White, blue, red, and grey spheres represent H, N, O and C atoms, respectively.

Table S3 Parameters for NH_3 interaction with –COOH group. The O-XO distance is 0.2605 Å and the OA-XOA distance is 0.2265 Å. The charges on C, O, OA, and HA are 0.7928, −0.6098, −0.7764, and 05364, respectively.

Interactions	ε (kJ/mol)	A (1/Å)	σ (Å)
C-N	4.4368	1.4087	3.1953
O-N	0.34376	0.3000	5.0000
OA-N	0.85966	1.7655	3.6427
HA-N	8.3516×10^{-4}	1.8150	4.4305
HB-N	0	0	0
CA-N	6.3085	3.6391	2.7744
XPC(XPCA)-N	-0.45797	0.3760	0.0000
XPO-N	-38.595	1.8259	0.0000
XO-N	38.595	5.6615	2.1537
XOA-N	1.7403	1.8088	3.2293
C-H	3.4654	3.5707	2.3892
O-H	38.363	6.0000	1.3666
OA-H	0.19502	0.8503	4.9975
HA-H	2.3354	1.8012	1.9975
HB-H	0	0	0
CA-H	9.2107×10^{-4}	2.0557	4.8099
XPC(XPCA)-H	-10.241	5.9547	0.0000
XPO-H	-38.595	1.4969	0.0000
XO-H	11.106	1.8065	1.6307
XOA-H	0.50349	2.1712	2.5964



(a)



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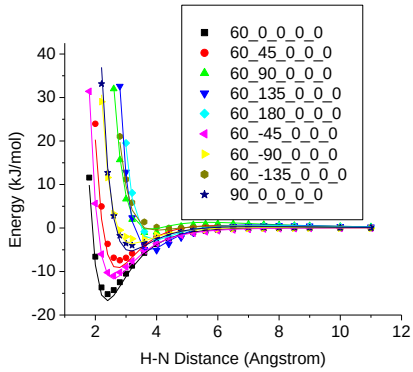

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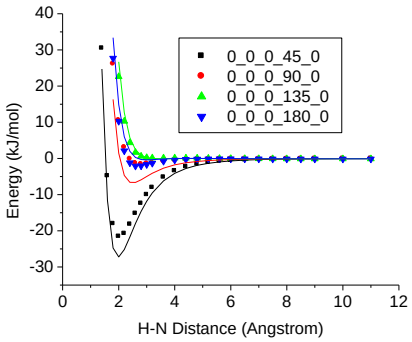

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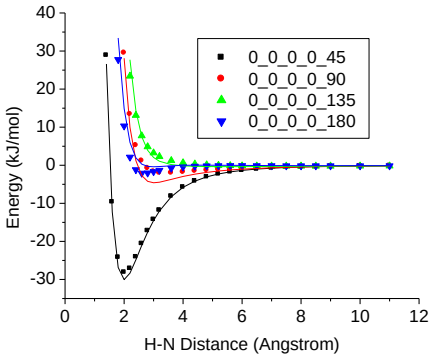


(e)

Figure S8 Fitting results of NH_3 interaction with –COOH group (I). Symbols are from quantum chemistry calculations, while lines are fitting results.

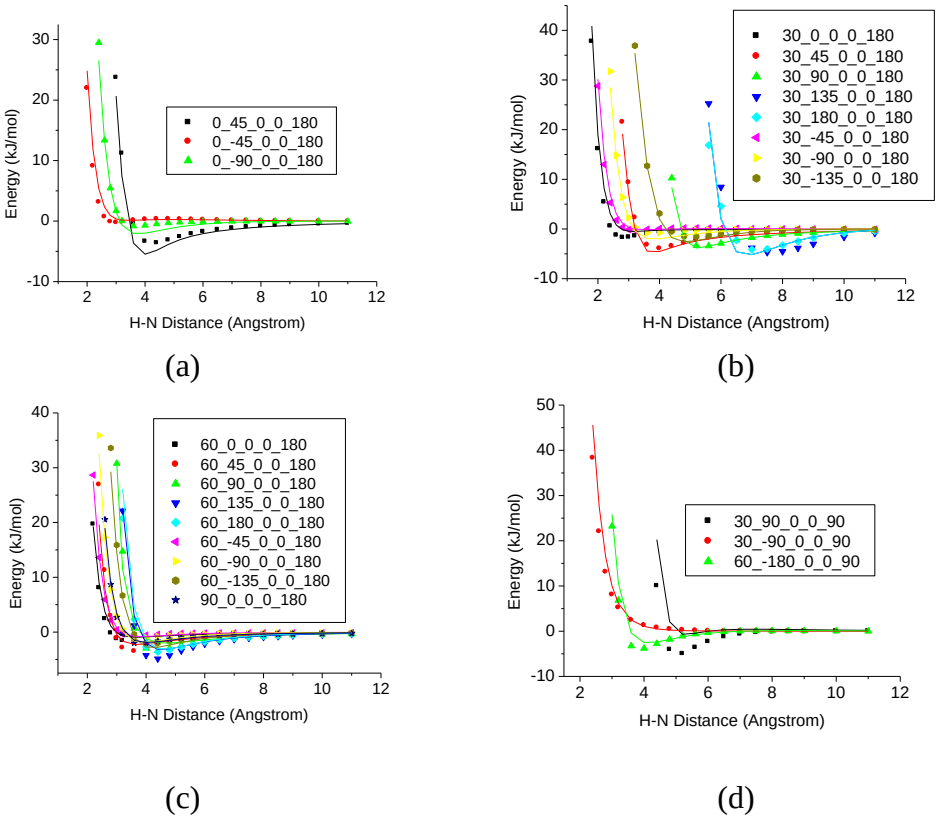
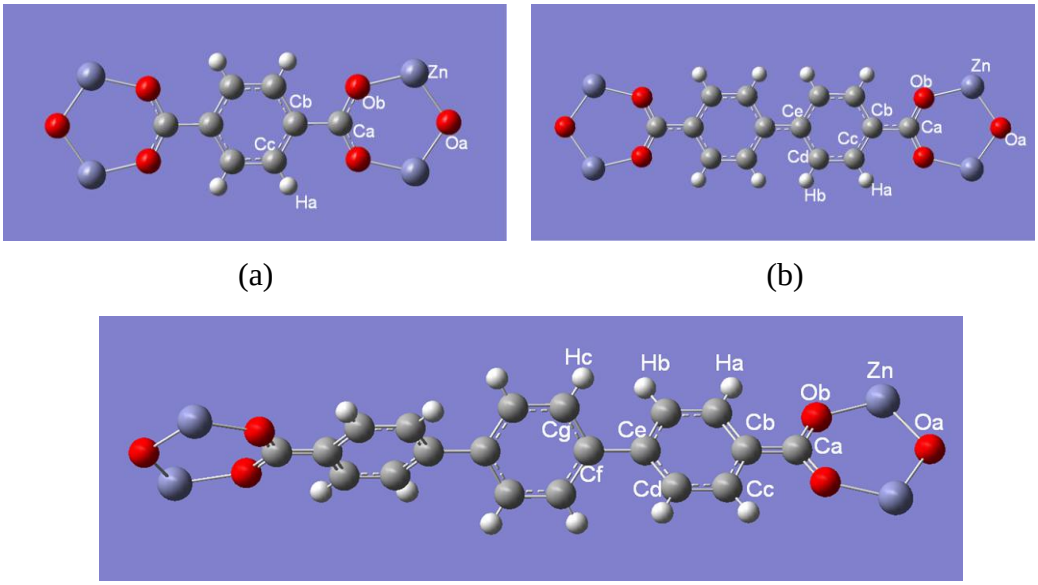


Figure S9 Fitting results of NH_3 interaction with –COOH group (II). Symbols are from quantum chemistry calculations, while lines are fitting results.

Lennard-Jones Parameters and Coulomb Charges for MOF Atoms

In this section, we list the Lennard-Jones parameters and charges for all MOF atoms that are not modeled with the Morse potential. Figures S10 and S11 define the distinct atoms in these MOF structures. Tables S4 and S5 list all of the parameters.



(a) (b)

(c)

Figure S10.The definitions of the crystallographically different atoms for (a) IRMOF-1, (b) IRMOF-10, and (c) IRMOF-16. White, red, grey and purple spheres represent H, O, C, and Zn atoms, respectively.

Table S4. The Lennard-Jones and charge parameters used for IRMOF-1, -10, and -16.

Atom type	ε/k_B (K)	σ (Å)	Charge (e)
Zn	0.42	2.7	1.275
Oa	700	2.98	-1.5
Ob	70.5	3.11	-0.6
Ca	47.0	3.74	0.475
Cb	47.86	3.47	0.125
Cc	47.86	3.47	-0.15
Cd	47.86	3.47	-0.15
Ce	47.86	3.47	0.0
Cf	47.86	3.47	0.0
Cg	47.86	3.47	-0.15
Ha	7.65	2.85	0.15
Hb	7.65	2.85	0.15
Hc	7.65	2.85	0.15

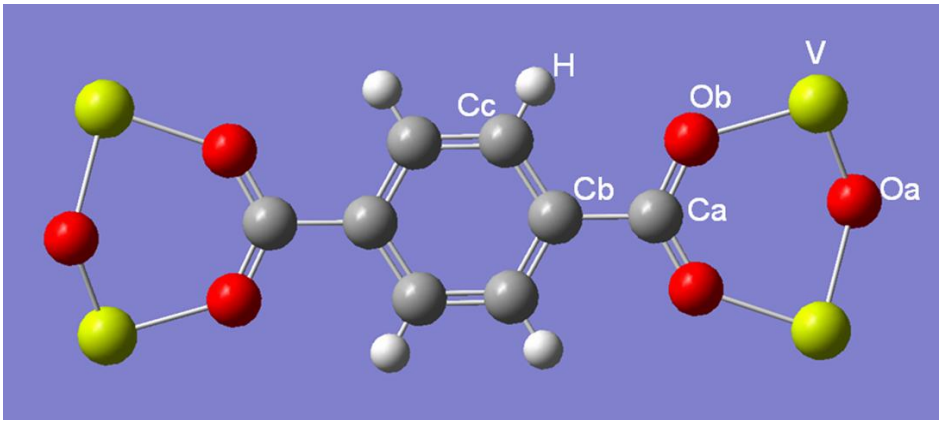


Figure S11. The definitions of the crystallographically different atoms for MIL-47. White, red, grey and yellow spheres represent H, O, C, and V atoms, respectively.

Table S5. The Lennard-Jones and charge parameters used for MIL-47.

Atom type	ε/k_B (K)	σ (Å)	Charge (e)
V	8.051	2.801	1.770
Oa	45.158	3.033	-0.662
Ob	45.158	3.033	-0.611
Ca	47.856	3.473	0.644
Cb	47.856	3.473	0.032
Cc	47.856	3.473	-0.153
H	7.649	2.846	0.149

Additional Results

In the main text, the adsorption isotherms are presented in volumetric units. Here, we also plot some of the isotherms using mg/g instead of mg/cm^3 for ammonia uptake.

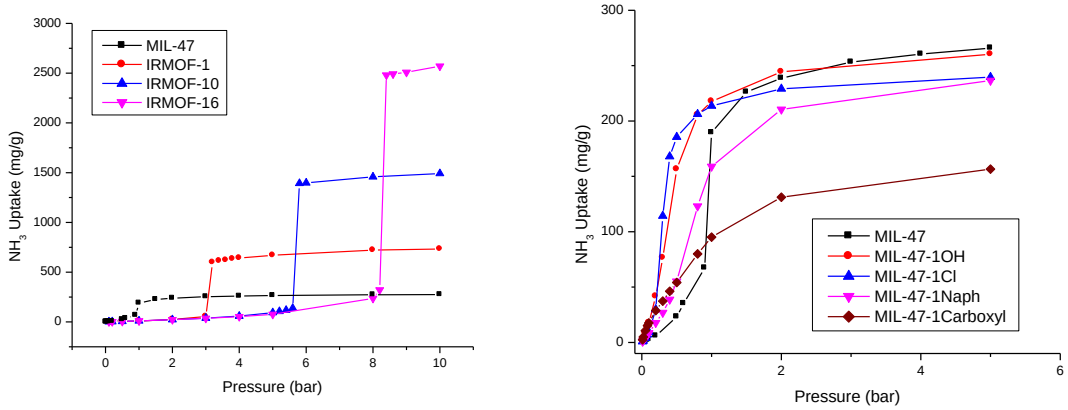


Figure S12. Ammonia adsorption isotherms at 298 K corresponding to Figures 8a (left) and 9a (right) in gravimetric units.

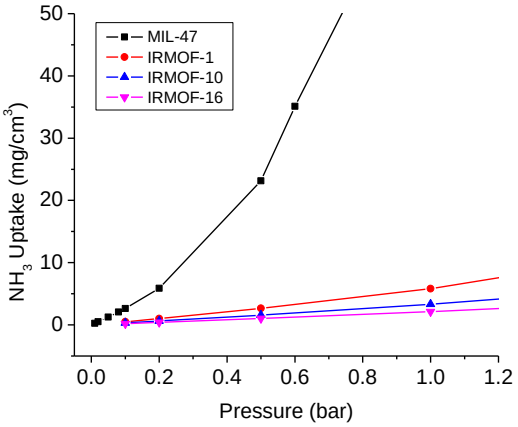


Figure S13. Effect of pore size on the adsorption of NH_3 at 298 K (low pressure region of Figure 8 in the main text).

Table S6. Void fraction of four metal organic frameworks and their functionalized forms (100% functionalization).

Functional Groups	No Functional Group	Alcohol	Chlorine	Naphthoquinone	Carboxyl
MIL-47	0.530	0.515	0.503	0.515	0.466
IRMOF-1	0.737	0.723	0.717	0.727	0.692
IRMOF-10	0.833	0.827	0.826	0.829	0.814
IRMOF-16	0.886	0.882	0.881	0.883	0.876