Electronic Supplementary Material

Effects of functional groups for CO_2 capture using metal organic frameworks

Chenkai Gu[1], Yang Liu[2], Weizhou Wang[3], Jing Liu(✉)[1], Jianbo Hu[1]

1 State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

2 School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, USA

3 Henan Key Laboratory of Function-Oriented Porous Materials, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, China

E-mail: liujing27@mail.hust.edu.cn

List of Figures Captions

Fig. S1 Cluster used for calculating partial charges on MOF-177 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S2 Cluster used for calculating partial charges on MOF-177-F atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S3 Cluster used for calculating partial charges on MOF-177-CH_3 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S4 Cluster used for calculating partial charges on MOF-177-CN atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S5 Cluster used for calculating partial charges on MOF-177-OH atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S6 Cluster used for calculating partial charges on MOF-177-NH_2 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S7 Cluster used for calculating partial charges on MOF-177-COOH atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S8 Cluster used for calculating partial charges on MOF-177-SO_3H atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Fig. S9 Comparisons between the CO_2 binding energy on organic linkers calculated by DFT and the CO_2 adsorption heat in periodic MOFs at infinite dilution.

Fig. S10 DFT optimized structures of the CO_2-linkers modified with $–SO_3H$ (S, yellow spheres; O, red spheres; C, gray spheres and H, white spheres).

Fig. S11 DFT optimized structures of the CO_2-linkers modified with -COOH (O, red spheres; C, gray spheres and H, white spheres).

Fig. S12 DFT optimized structures of the CO_2-linkers modified with $–NH_2$ (O, red spheres; C, gray spheres; N, dark blue spheres and H, white spheres).

Fig. S13 DFT optimized structures of the CO_2-linkers modified with -OH (O, red spheres; C, gray spheres and H, white spheres).

Fig. S14 DFT optimized structures of the CO_2-linkers modified with -CN (O, red spheres; C, gray spheres; N, dark blue spheres and H, white spheres).

Fig. S15 DFT optimized structures of the CO_2-linkers modified with $-CH_3$ (O, red spheres; C, gray spheres and H, white spheres).

Fig. S16 DFT optimized structures of the CO_2-linkers modified with -F (O, red spheres; C, gray spheres; H, white spheres and F, cyan spheres).

Fig. S17 DFT optimized structures of the CO_2-linkers in MOF-177 (O, red spheres; C, gray spheres and H, white spheres).

Fig. S18 DFT optimized structures of the CO_2-clusters in functionalized MOF-177 (Zn, light blue

spheres; O, red spheres; C, gray spheres and H, white spheres).

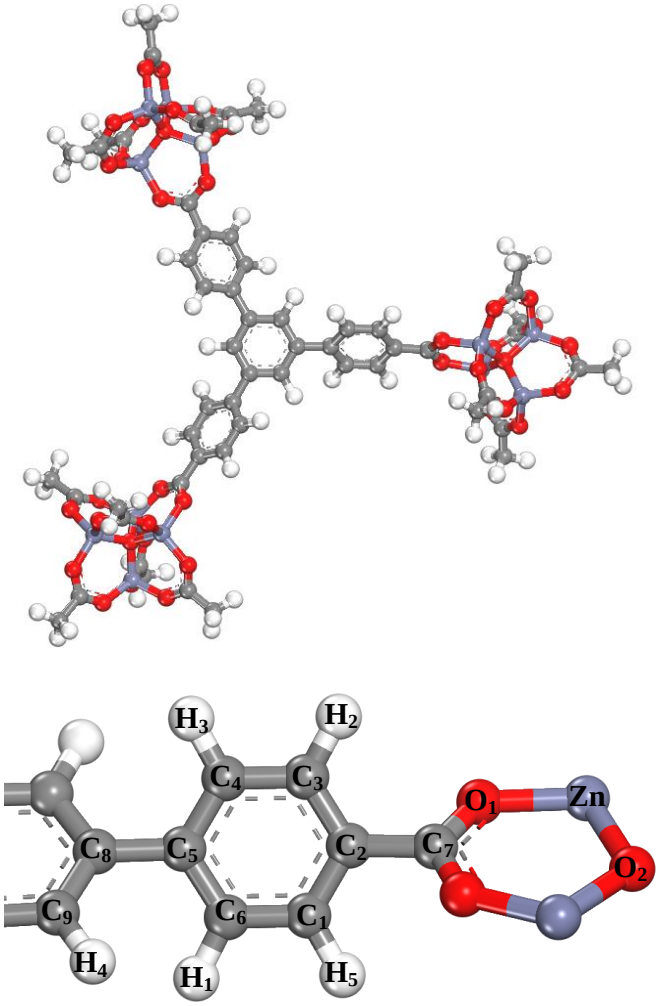


Fig. S1 Cluster used for calculating partial charges on MOF-177 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S1 Atomic partial charge (e) for the MOF-177 structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.137	-0.267	0.202	-0.267	-0.107	0.100	-0.107	0.505	-0.049
Atom	**C_9**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**	
Charge	-0.096	0.125	0.154	0.125	0.110	0.154	-0.543	-1.524	

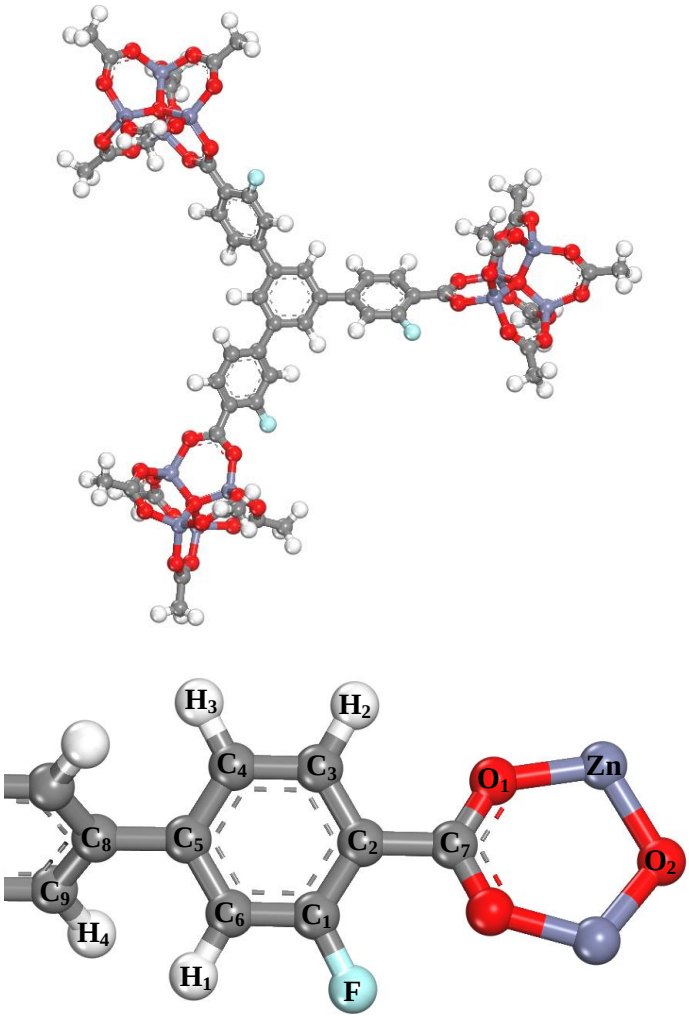


Fig. S2 Cluster used for calculating partial charges on MOF-177-F atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S2 Atomic partial charge (e) for the MOF-177-F structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.120	0.269	-0.014	-0.188	-0.193	0.138	-0.299	0.569	0.047
Atom	**C_9**	**H_1**	**H_2**	**H_3**	**H_4**	**O_1**	**O_2**	**F**	
Charge	-0.178	0.169	0.163	0.156	0.130	-0.531	-1.554	-0.168	

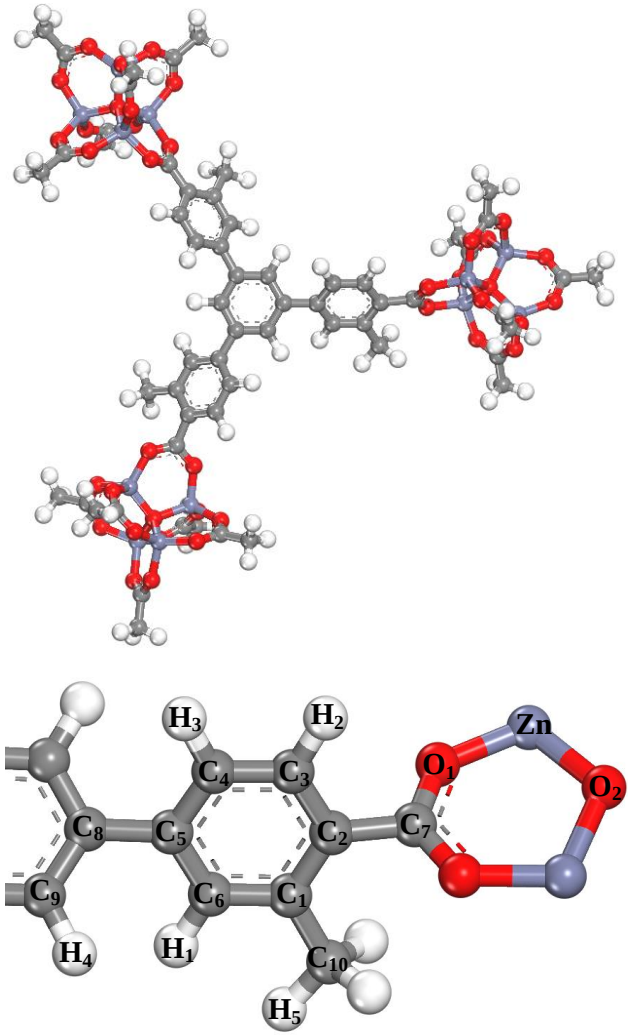


Fig. S3 Cluster used for calculating partial charges on MOF-177-CH_3 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S3 Atomic partial charge (e) for the MOF-177-CH_3 structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.155	0.549	-0.158	-0.152	-0.208	0.130	-0.347	0.647	0.086
Atom	**C_9**	**C_{10}**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**
Charge	-0.220	-0.895	0.161	0.145	0.138	0.132	0.223	-0.548	-1.566

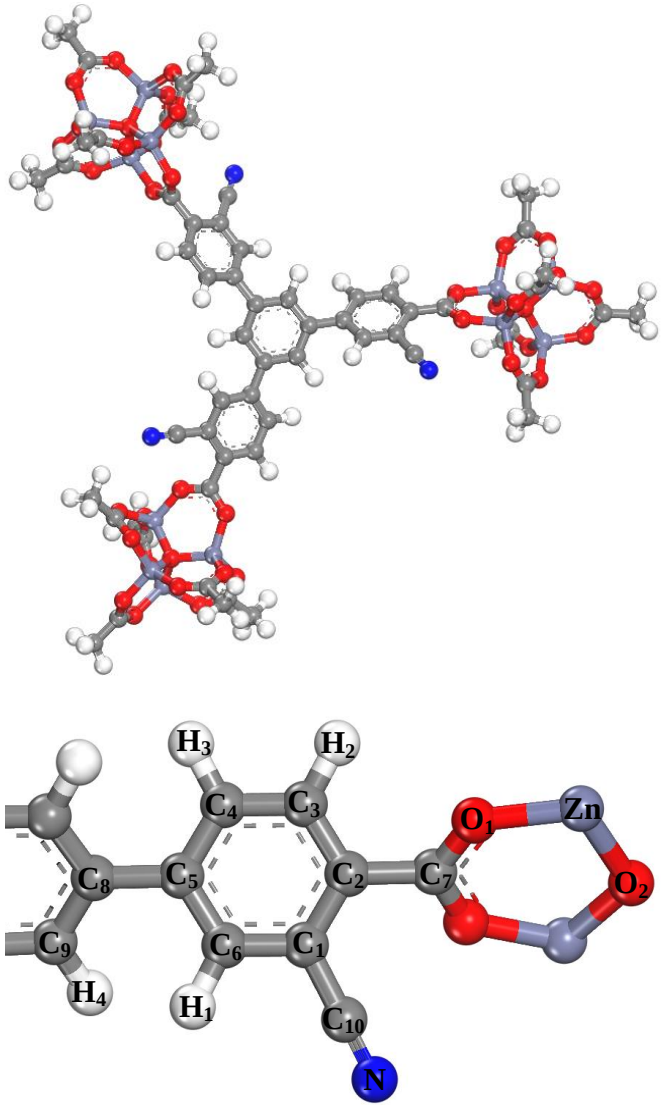


Fig. S4 Cluster used for calculating partial charges on MOF-177-CN atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S4 Atomic partial charge (e) for the MOF-177-CN structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.174	0.012	0.058	-0.207	-0.145	0.157	-0.218	0.597	-0.004
Atom	**C_9**	**C_{10}**	**H_1**	**H_2**	**H_3**	**H_4**	**O_1**	**O_2**	**N**
Charge	-0.141	0.268	0.163	0.169	0.141	0.124	-0.557	-1.624	-0.372

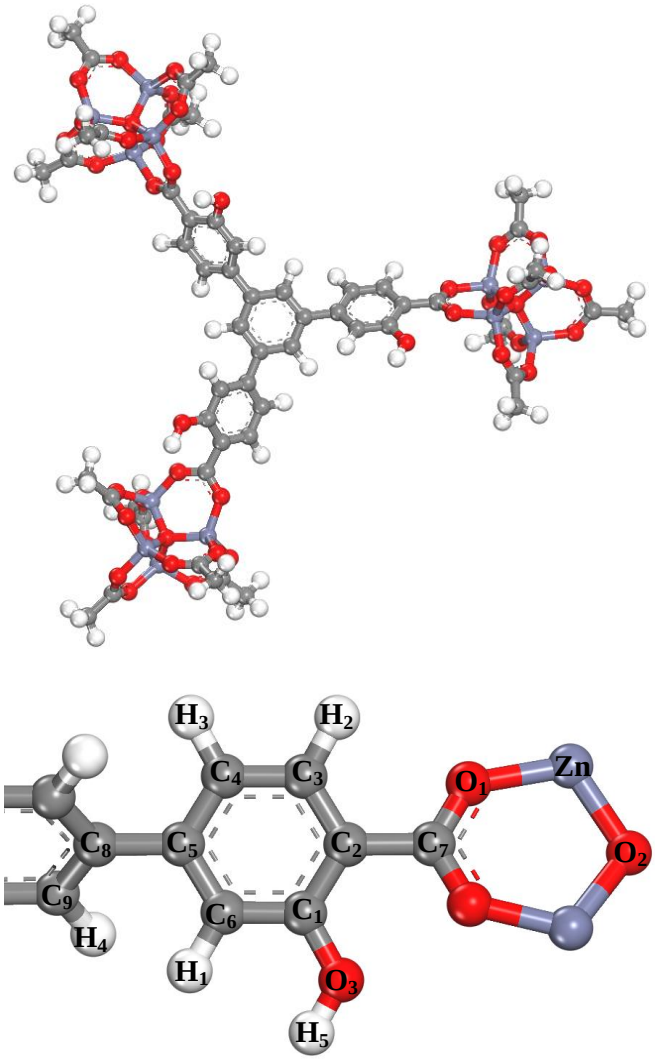


Fig. S5 Cluster used for calculating partial charges on MOF-177-OH atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S5 Atomic partial charge (e) for the MOF-177-OH structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.129	0.384	-0.079	-0.179	-0.232	0.178	-0.371	0.614	0.054
Atom	**C_9**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**	**O_3**
Charge	-0.191	0.166	0.164	0.143	0.137	0.420	-0.551	-1.594	-0.562

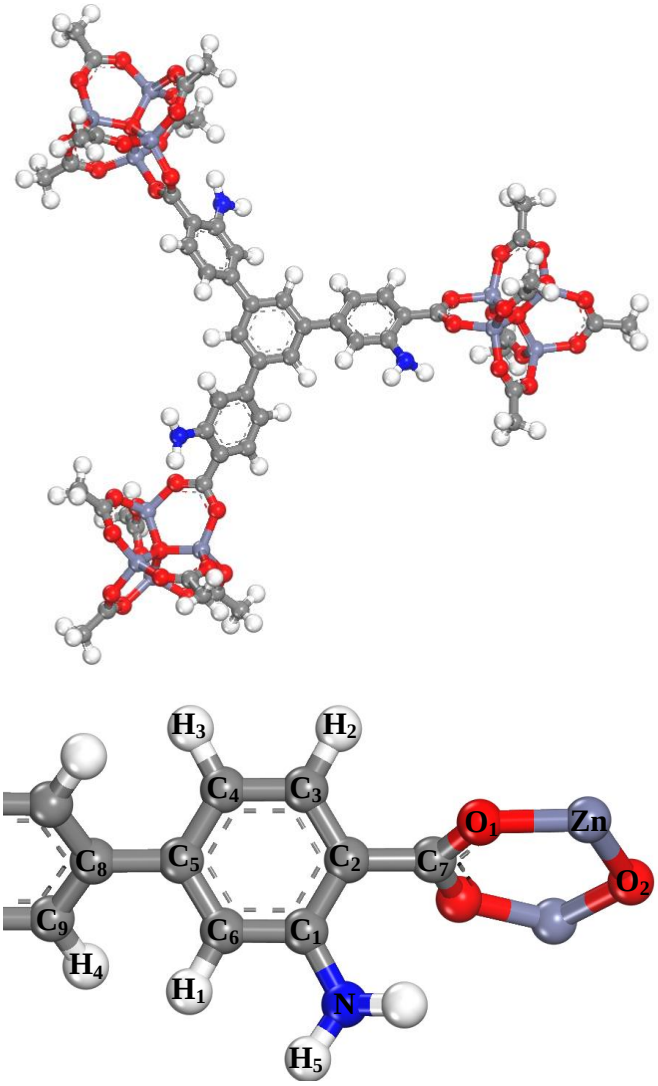


Fig. S6 Cluster used for calculating partial charges on MOF-177-NH_2 atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S6 Atomic partial charge (e) for the MOF-177-NH_2 structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.142	0.435	-0.180	-0.173	-0.233	0.183	-0.392	0.695	0.043
Atom	**C_9**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**	**N**
Charge	-0.200	0.165	0.161	0.131	0.133	0.357	-0.574	-1.583	-0.832

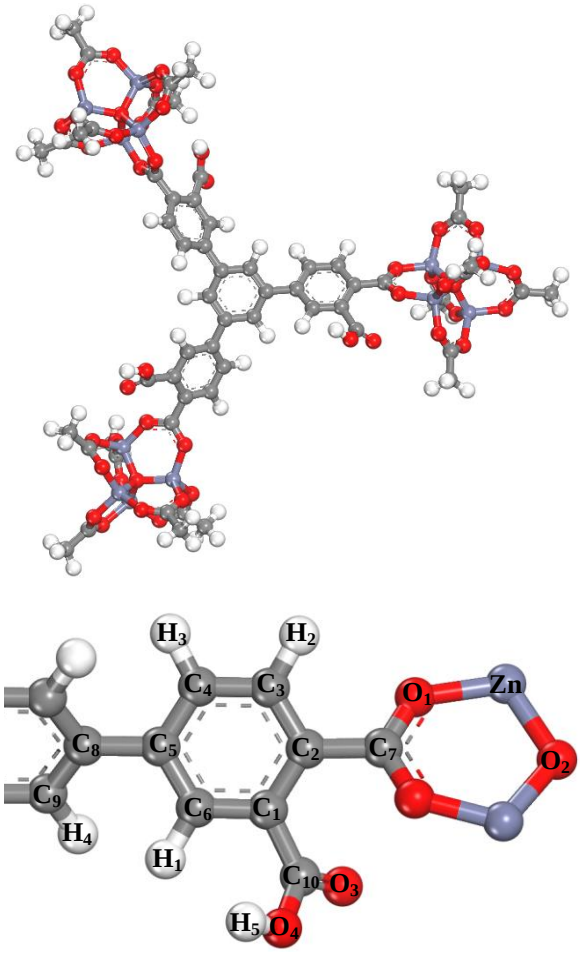


Fig. S7 Cluster used for calculating partial charges on MOF-177-COOH atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S7 Atomic partial charge (e) for the MOF-177-COOH structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.160	-0.068	0.034	-0.208	-0.131	0.150	-0.299	0.640	-0.007
Atom	**C_9**	**C_{10}**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**
Charge	-0.141	0.559	0.154	0.207	0.135	0.132	0.410	-0.560	-1.610
Atom	**O_3**	**O_4**							
Charge	-0.423	-0.529							

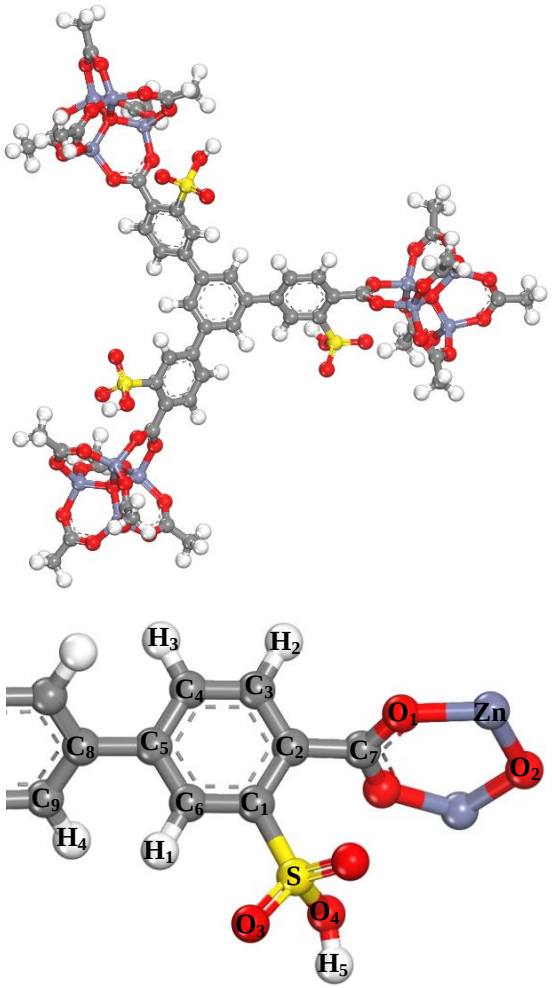


Fig. S8 Cluster used for calculating partial charges on MOF-177-SO_3H atoms. The terminations of cluster were saturated with methyl groups to minimize the boundary effects.

Table S8 Atomic partial charge (e) for the MOF-177-SO_3H structure

Atom	**Zn**	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**
Charge	1.168	0.035	0.099	-0.229	-0.117	0.117	-0.153	0.557	-0.032
Atom	**C_9**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**O_1**	**O_2**	**O_3**
Charge	-0.084	0.145	0.181	0.140	0.123	0.416	-0.536	-1.618	-0.338
Atom	**O_4**	**S**							
Charge	-0.443	0.484							

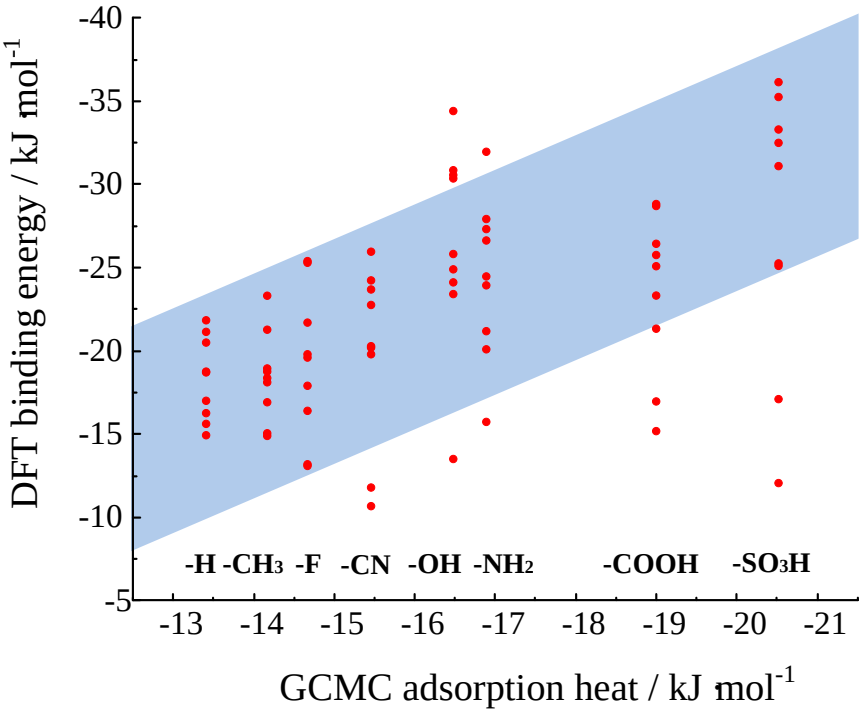


Fig. S9 Comparisons between the CO_2 binding energy on organic linkers calculated by DFT and the CO_2 adsorption heat in periodic MOFs at infinite dilution.

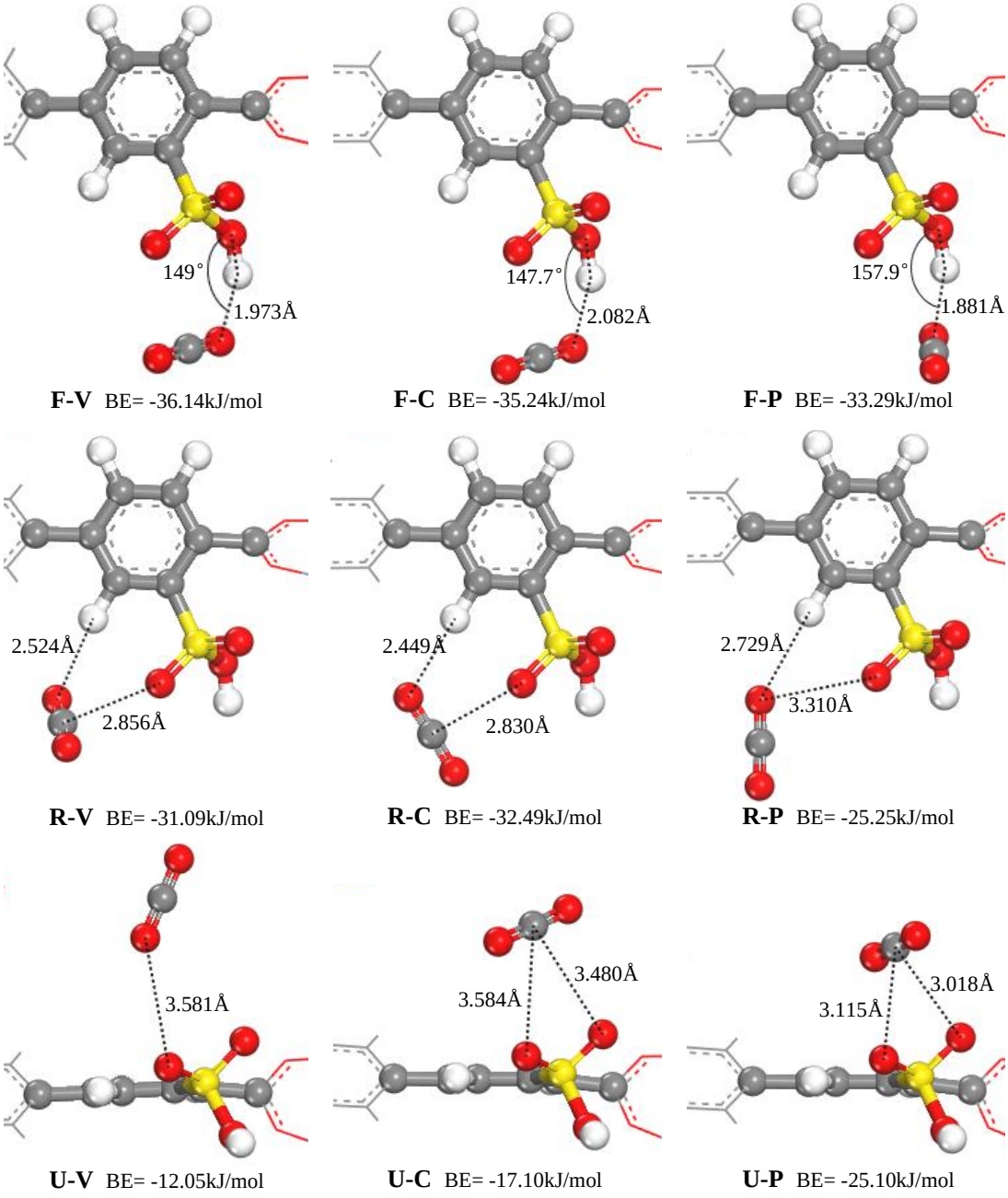


Fig. S10 DFT optimized structures of the CO_2-linkers modified with $–SO_3H$ (S, yellow spheres; O, red spheres; C, gray spheres and H, white spheres).

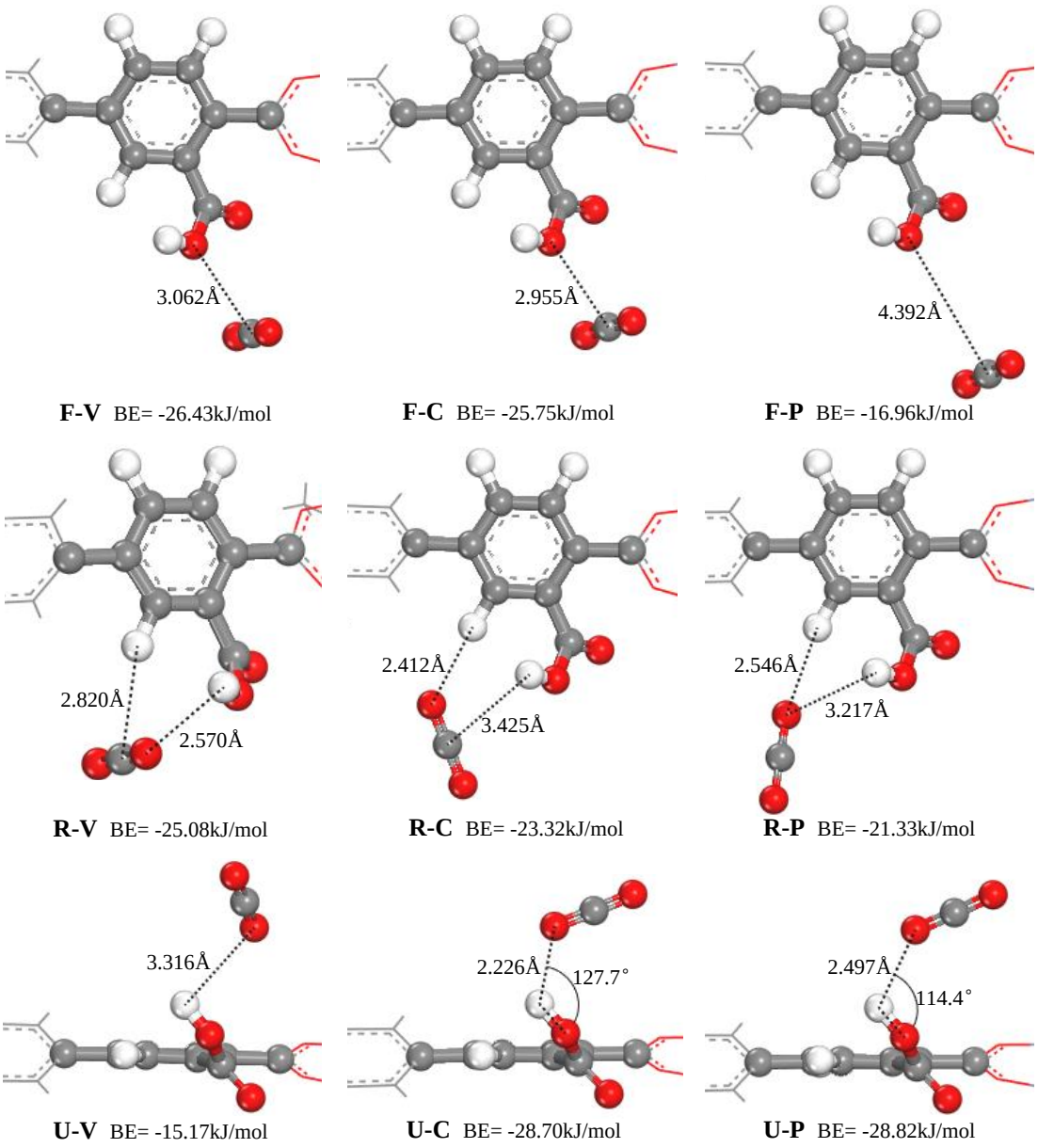


Fig. S11 DFT optimized structures of the CO_2-linkers modified with -COOH (O, red spheres; C, gray spheres and H, white spheres).

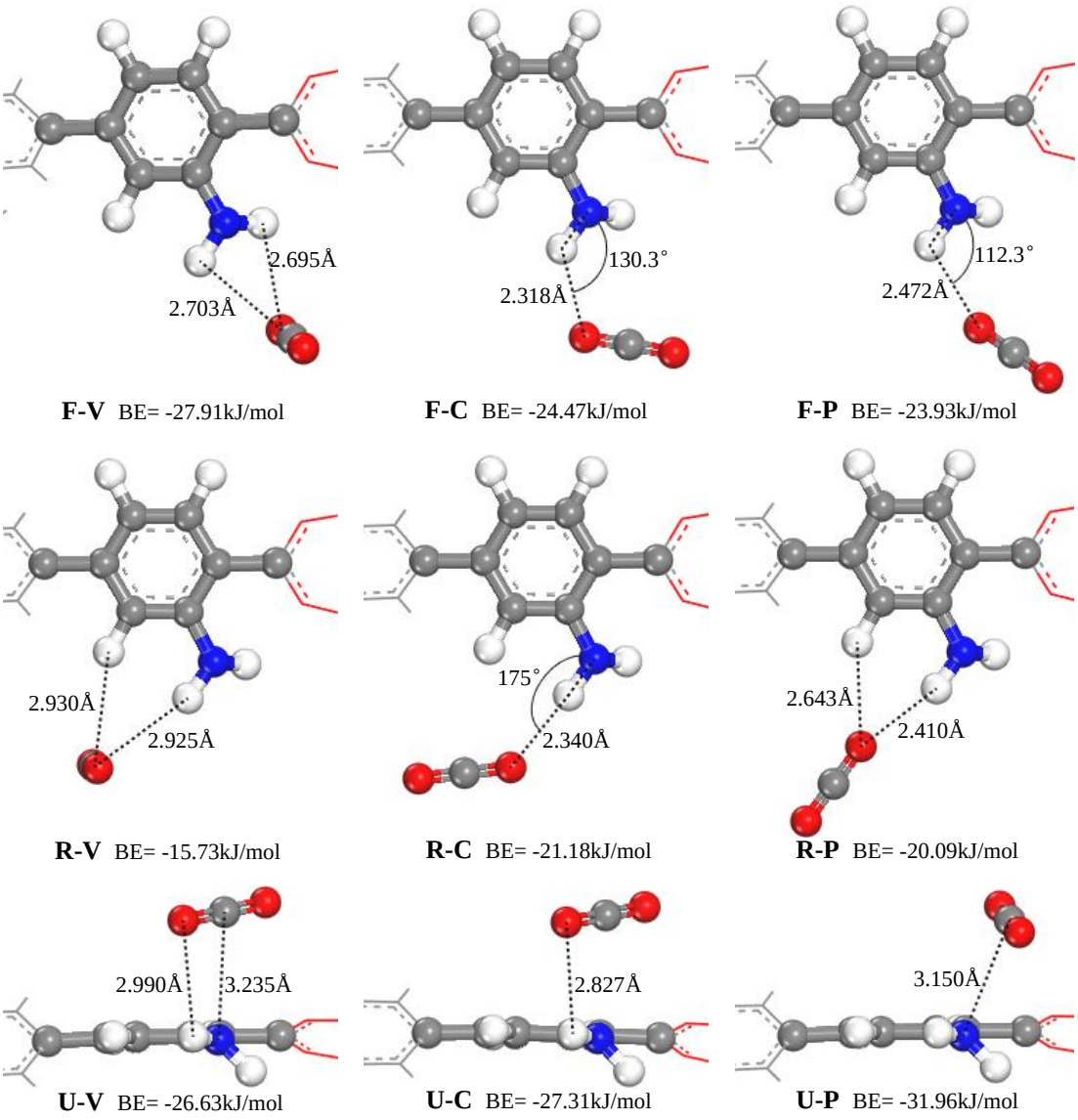


Fig. S12 DFT optimized structures of the CO_2-linkers modified with $–NH_2$ (O, red spheres; C, gray spheres; N, dark blue spheres and H, white spheres).

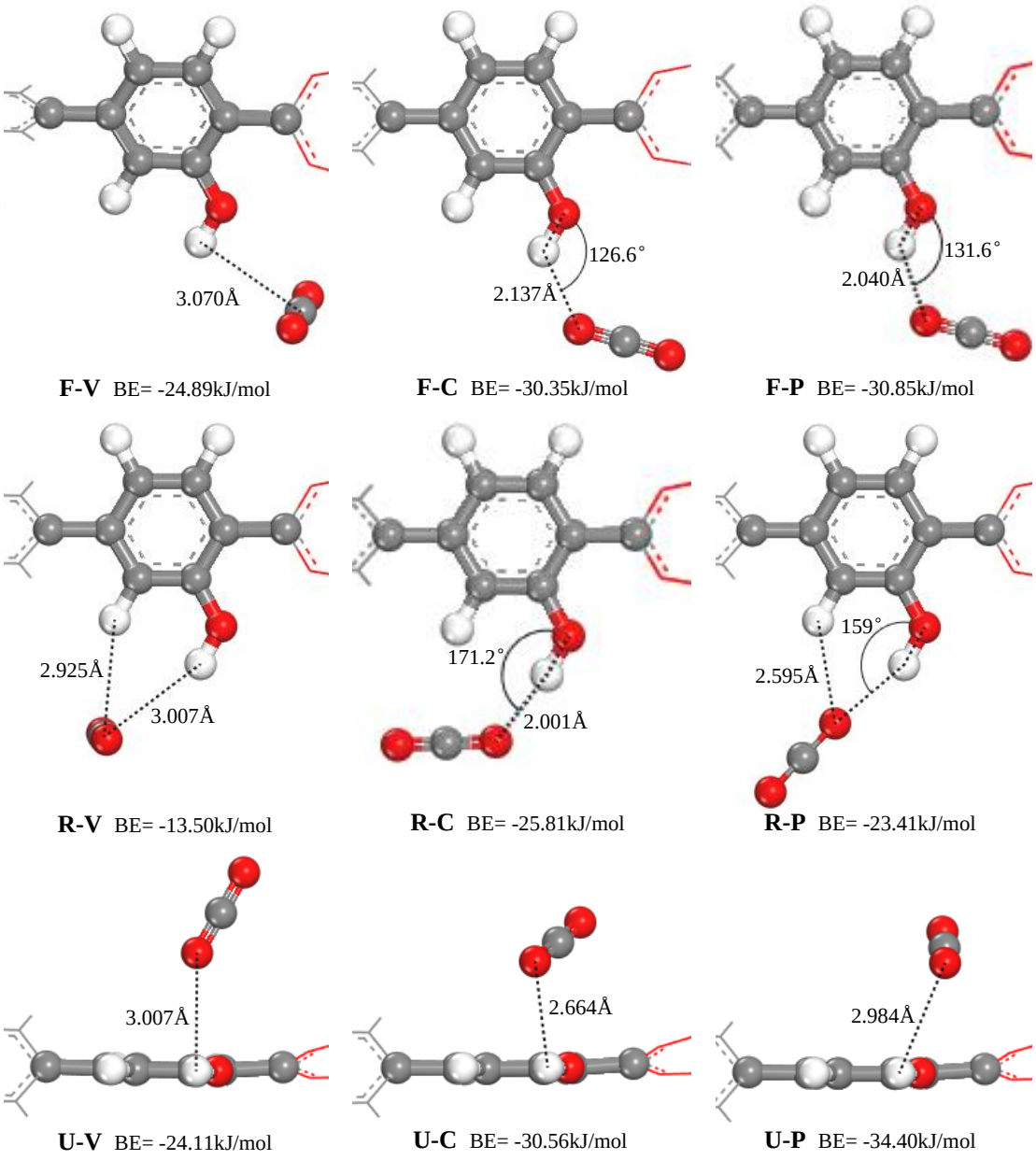


Fig. S13 DFT optimized structures of the CO_2-linkers modified with -OH (O, red spheres; C, gray spheres and H, white spheres).

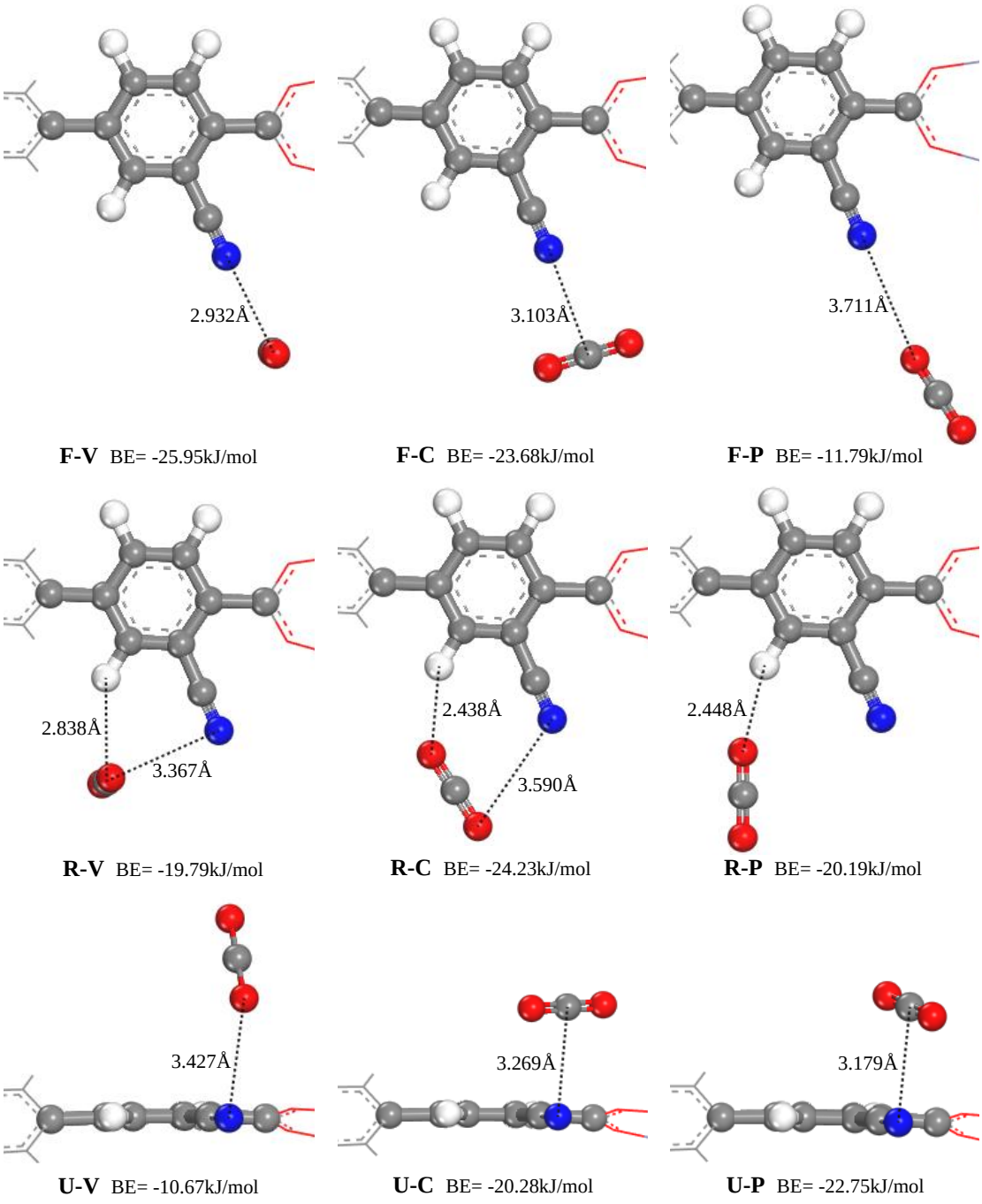


Fig. S14 DFT optimized structures of the CO_2-linkers modified with -CN (O, red spheres; C, gray spheres; N, dark blue spheres and H, white spheres).

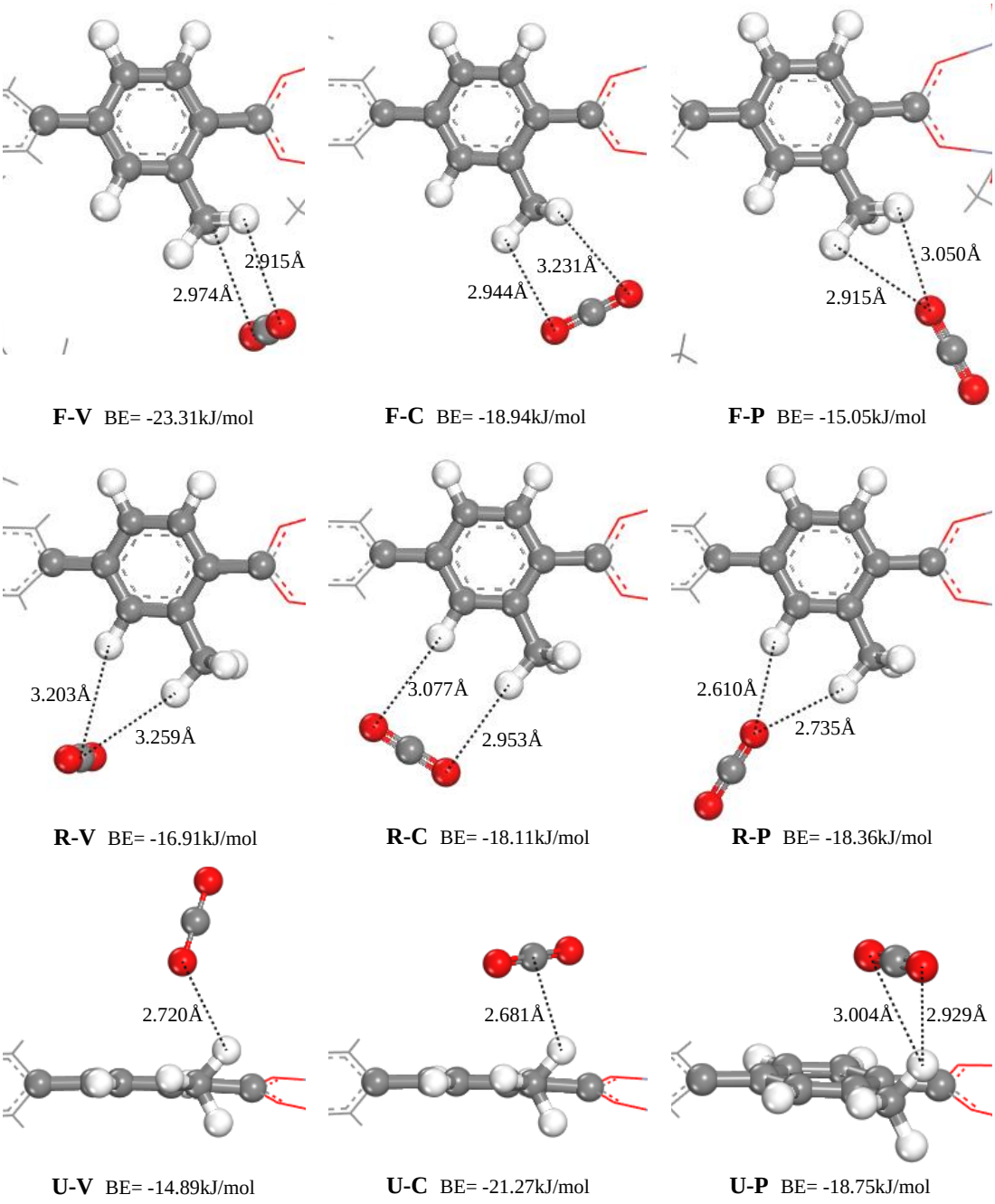


Fig. S15 DFT optimized structures of the CO_2-linkers modified with $–CH_3$ (O, red spheres; C, gray spheres and H, white spheres).

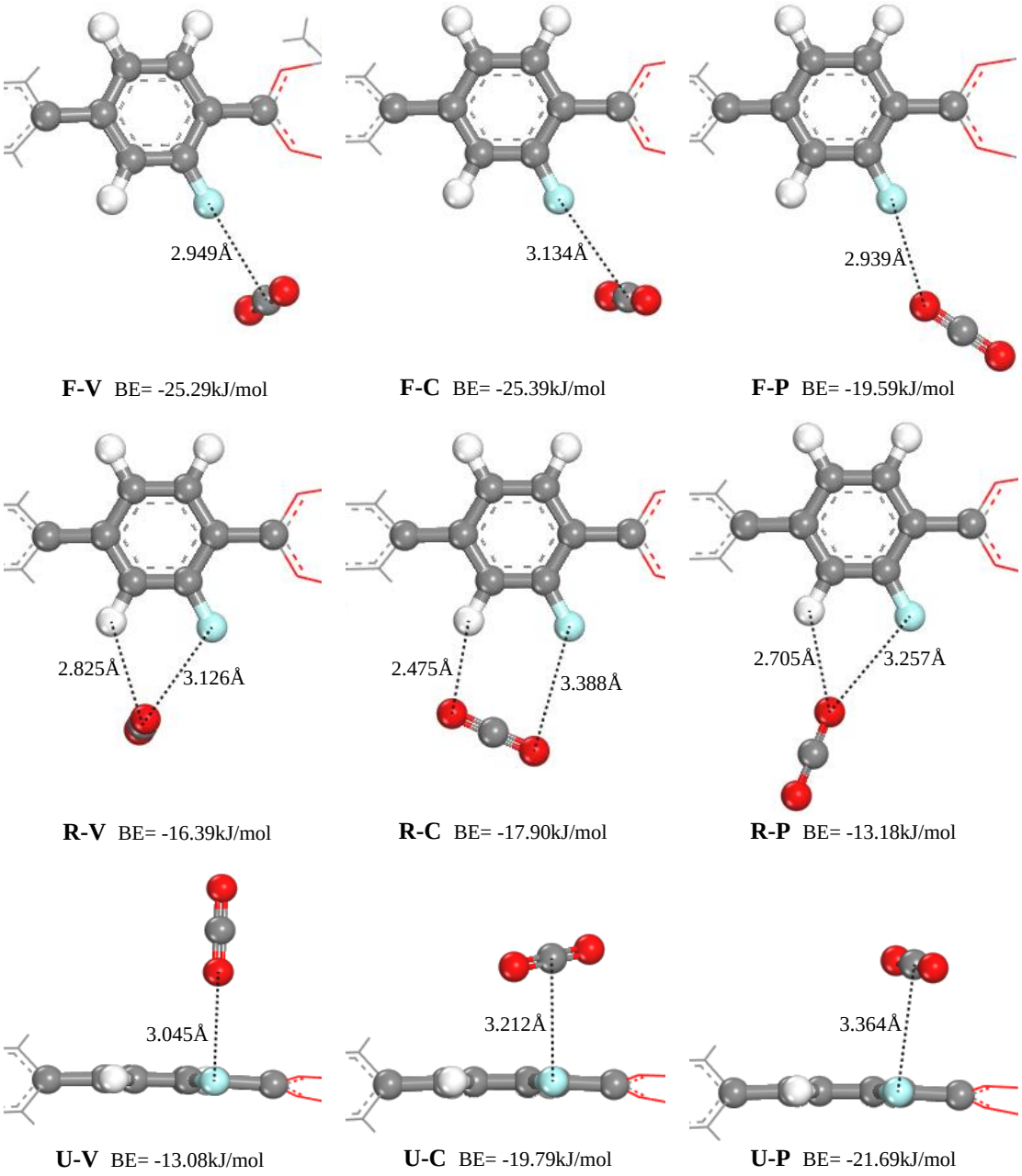


Fig. S16 DFT optimized structures of the CO_2-linkers modified with -F (O, red spheres; C, gray spheres; H, white spheres and F, cyan spheres).

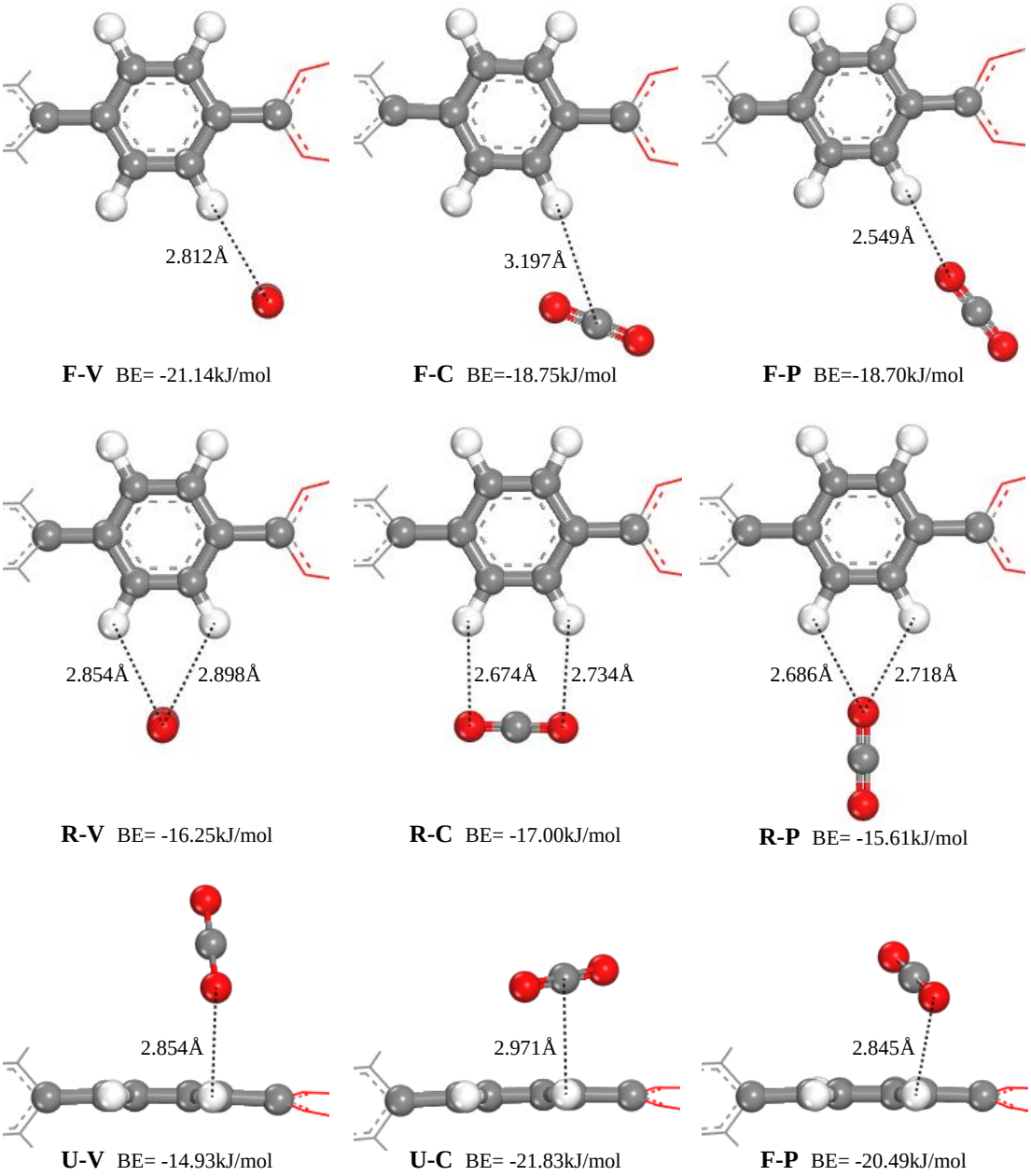
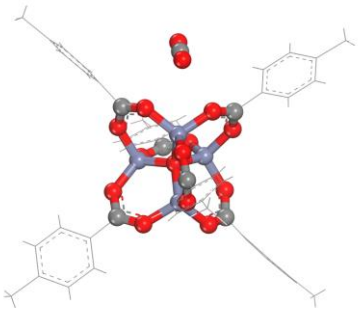
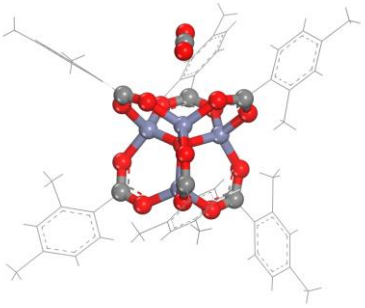


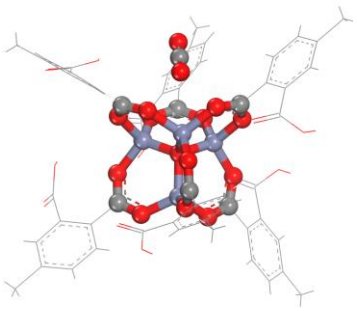
Fig. S17 DFT optimized structures of the CO_2-linkers in MOF-177 (O, red spheres; C, gray spheres and H, white spheres).



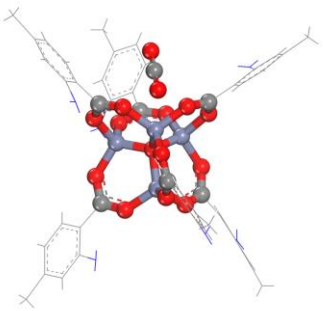
MOF-177 BE= -29.44kJ/mol



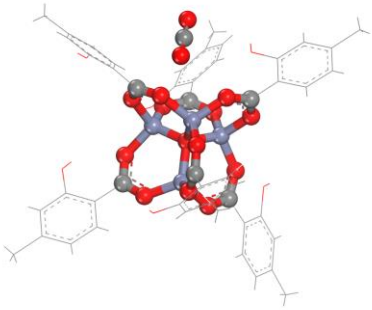
MOF-177-CH_3 BE= -32.44kJ/mol



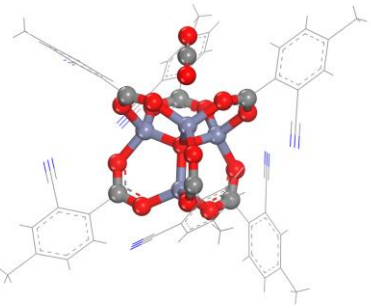
MOF-177-COOH BE= -30.84kJ/mol



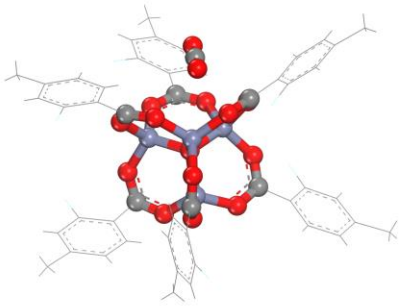
MOF-177-NH_2 BE= -33.66kJ/mol



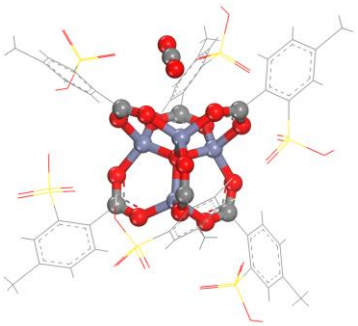
MOF-177-OH BE= -27.03kJ/mol



MOF-177-CN BE= -29.30kJ/mol



MOF-177-F BE= -29.07kJ/mol



MOF-177-SO_3H BE= -27.65kJ/mol

Fig. S18 DFT optimized structures of the CO_2-clusters in functionalized MOF-177 (Zn, light blue spheres; O, red spheres; C, gray spheres and H, white spheres).