Supplementary Information (SI) for New Journal of Chemistry.

A theoretical study on metal doping for enhancing the structure stability and CO_2 adsorption selectivity in defective UiO-66

Zewei Liu, [a] *Changbin Xu,* [a] *Haolong Zheng,* [a] *Daofei Lv,*[a] *Junjie Peng,* [a] *Xin Chen,* [a] *Chongxiong Duan,* [b] *Hongxia Xi,* [c] *Xun Wang* [*a]

[a] School of Environmental and Chemical Engineering, Foshan University, Foshan 528225, China

[b] School of Materials Science and Hydrogen Engineering, Foshan University, Foshan, 528225, China

[c] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

[*] Corresponding author. E-mail: cexunwang@fosu.edu.cn (Xun Wang).

Table S1. Force field parameters for adsorbate and adsorbent

Atom types	σ(Å)	ε/k_b(K)
C	3.47	47.86
H	2.85	7.65
O	3.03	48.16
Be	2.45	42.74
Mg	2.69	55.86
Ca	3.03	119.77
Sr	3.24	118.17
Ba	3.30	183.04
Zr	2.78	34.70
O_CO_2	3.05	79.00
C_CO_2	2.80	27.00
N_N_2	3.31	36.00
Com_N_2	0	0
CH_4	3.73	148.00

Table S2. Parameters for calculating selectivities using IAST

	UiO-66			OH-UiO-66		
parameters	CO_2	CH_4	N_2	CO_2	CH_4	N_2
q1	1.747	1.205	0.499	6.837	3.349	3.608
b1	0.048	0.013	0.007	0.009	0.004	$8.310 \cdot 10^{-4}$
c1	1.040	0.996	1.032	0.978	0.975	0.995
q2	2.678	1.880	0.199	0.106	0.018	0.018
b2	0.003	0.001	$1.470 \cdot 10^{-5}$	$9.660 \cdot 10^{-5}$	$2.420 \cdot 10^{-17}$	$2.420 \cdot 10^{-17}$
c2	1.281	1.047	2.365	2.895	1	1
R^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
	OBe-UiO-66			OMg-UiO-66		
	CO_2	CH_4	N_2	CO_2	CH_4	N_2
q1	3.558	3.133	2.655	10.324	0.011	0.005
b1	0.120	0.004	0.001	0.052	0.073	$1.38 \cdot 10^{-9}$
c1	1	0.982	1.015	0.561	1	4.896
q2	5.980	0.018	0.018	1.348	2.870	3.010
b2	0.003	$2.420 \cdot 10^{-17}$	$2.420 \cdot 10^{-17}$	0.620	0.004	0.001
c2	1	1	1	1	1	1
R^2	0.9997	0.9999	0.9999	0.9999	0.9999	0.9999
	OCa-UiO-66			OSr-UiO-66		
	CO_2	CH_4	N_2	CO_2	CH_4	N_2
q1	3.910	5.820	3.073	2.963	2.600	0.099
b1	0.027	$5.48 \cdot 10^{-4}$	0.002	2.173	0.002	0.002
c1	1	1.000	1.001	1	1	1
q2	2.900	1.214	-	4.086	0.441	2.634
b2	1.954	0.007	-	0.030	0.010	0.002
c2	1	1	-	1	1	1
R^2	0.9991	0.9999	0.9999	0.9992	0.9999	0.9998
	OBa-UiO-66					
	CO_2	CH_4	N_2			
q1	2.772	2.485	2.645			
b1	3.011	0.003	0.003			
c1	1	1	0.989			
q2	3.882	0.403	0			
b2	0.033	0.011	1			
c2	1	1	1			
R^2	0.9984	0.9999	0.9999			

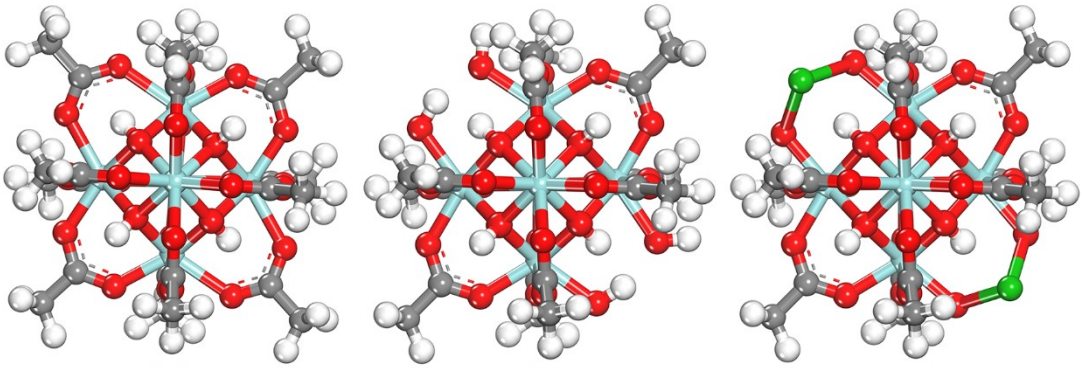

Fig. S1. The simplified metal clusters for (a) UiO-66, (b) OH-UiO-66 and (c) OM-UiO-66 (M=Be, Mg, Ca, Sr, Ba) (white: H, grey: C, red: O, cyan: Zr, green: M)

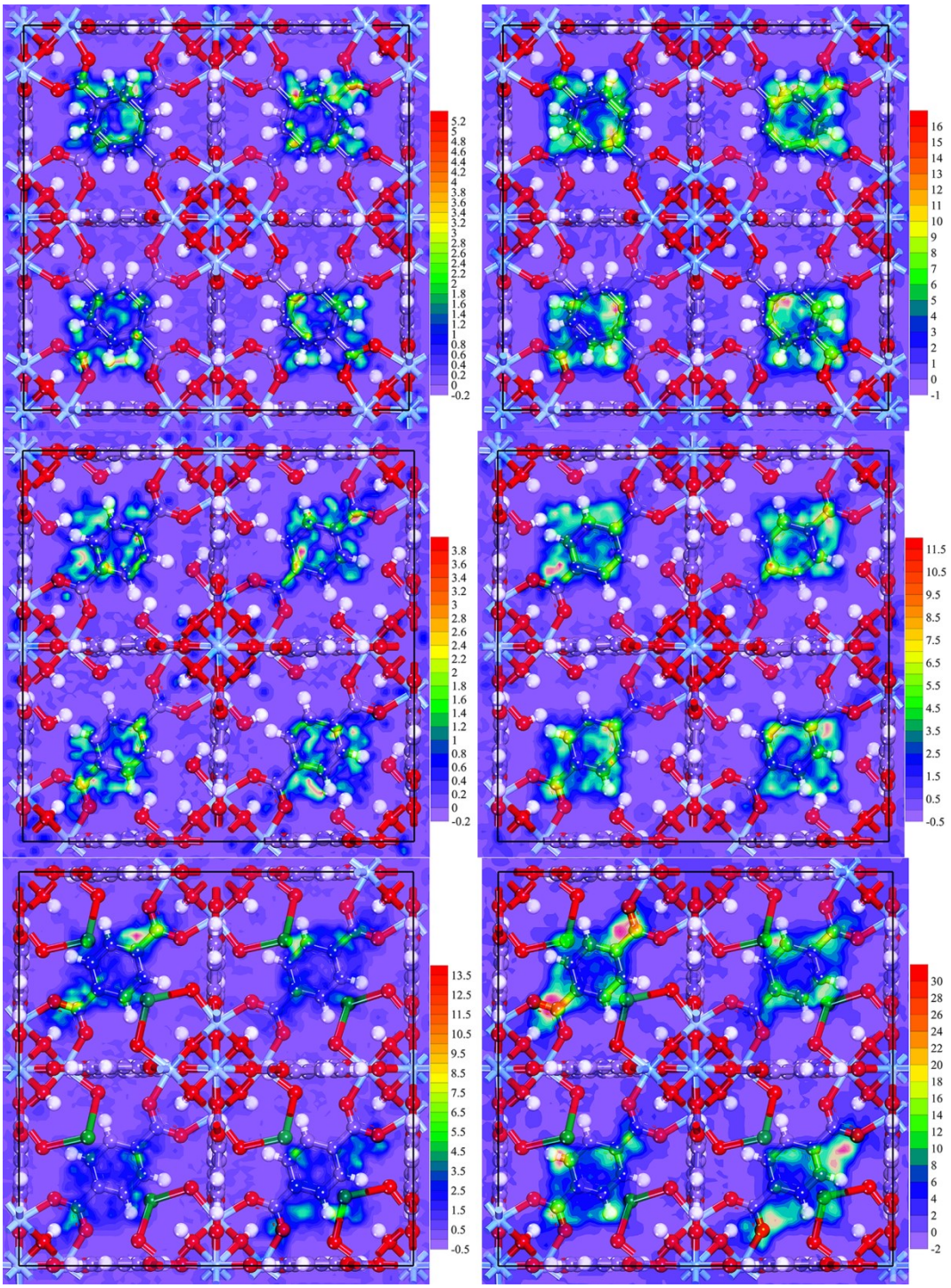

Fig. S2. The COM of N_2 molecules in (a, b) UiO-66, (c, d) OH-UiO-66 and (e,f) OBa-UiO-66 at 1kPa (a, c, e) and 4kPa (b, d, f)

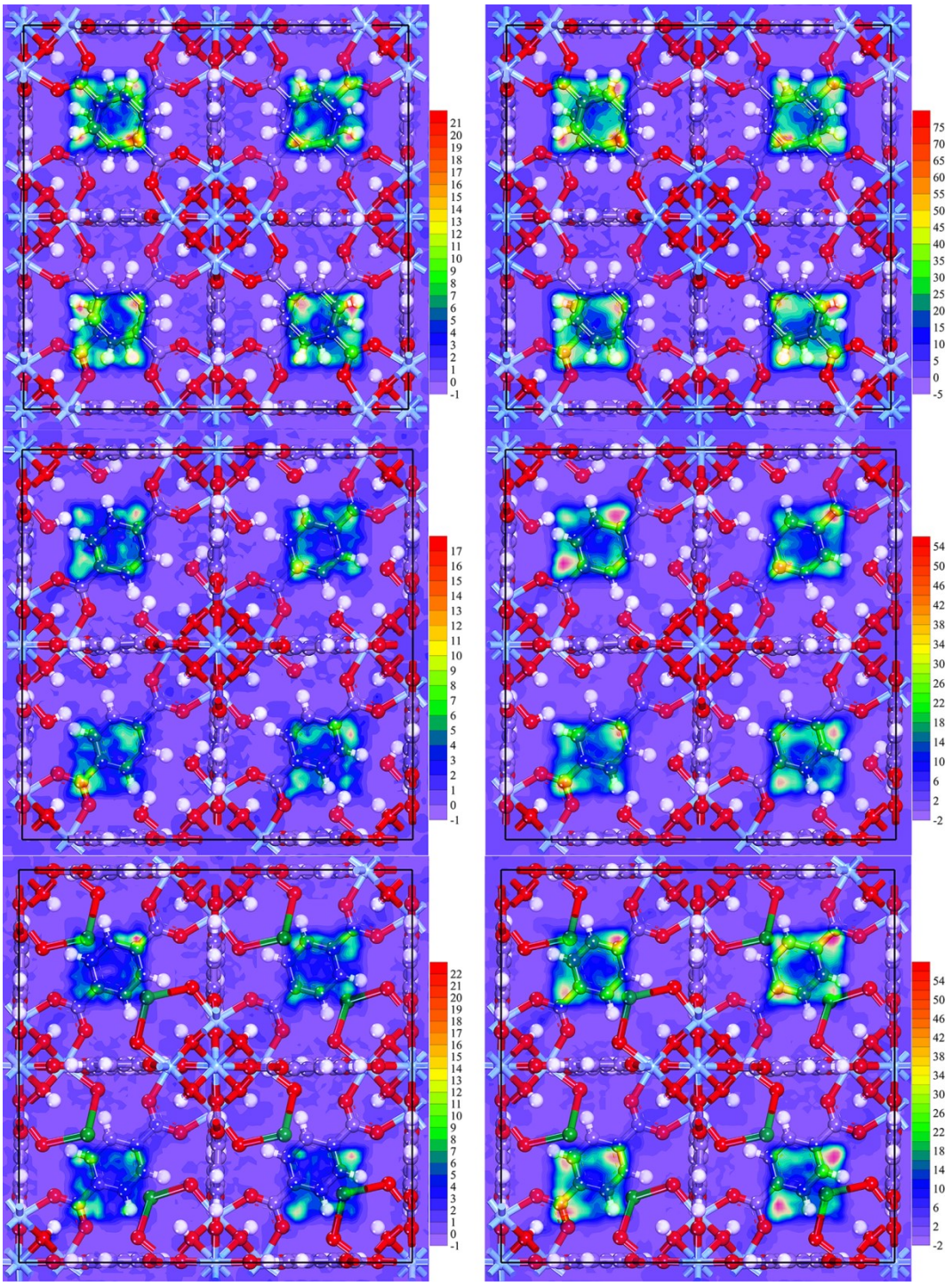

Fig. S3. The COM of CH_4 molecules in (a, b) UiO-66, (c, d) OH-UiO-66 and (e,f) OBa-UiO-66 at 1kPa (a, c, e) and 4kPa (b, d, f)