

# Supporting Information for

## Exploring Methane Storage Capacities of $M_2(\text{BDC})_2(\text{DABCO})$ sorbents: A Multiscale Computational Study

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### Contents of Tables

<b>Table S1.</b> Several well-known MOFs for gravimetric CH <sub>4</sub> adsorption capacity at 298 K so far.	S2
<b>Table S2.</b> Excess gravimetric and volumetric CH <sub>4</sub> uptakes adsorbed on M(DABCO) at room temperatures.	S2
<b>Table S3.</b> The amount of CH <sub>4</sub> adsorption in M(DABCO) at 100 bar, 298 K in many different units compared to the molar mass of M(DABCO).	S4
<b>Table S4.</b> Formation enthalpy ( $\Delta H_f$ ) of $M_2(\text{BDC})_2(\text{TED})$ or M(DABCO) compounds	S5

### Contents of Figures

<b>Figure S1.</b> Isotherms for methane compared with available experimental (exp.) data.	S3
<b>Figure S2.</b> The correlation between the surface area ( $A_{\text{BET}}$ ) and the pore volume ( $V_p$ ) of M(DABCO) sorbents. Points indicate the pairs of $V_p$ and $A_{\text{BET}}$ . The solid line indicates the linear fitting.	S3
<b>Figure S3.</b> The simulated CH <sub>4</sub> adsorption isotherms of M(DABCO) with the total uptake (solid lines) and the excess uptake (dash lines) at 298 K and pressures up to 100 bar (in mmol/g).	S4
<b>Figure S4.</b> The most stable CH <sub>4</sub> adsorption sites on the metal cluster of M(DABCO).	S6
<b>Figure S5.</b> The most stable CH <sub>4</sub> adsorption sites on the interface between the M-O-C cluster and TED of M(DABCO).	S7
<b>Figure S6.</b> The symbols for the atoms (C1, C2, C3, O, N, and M) of M(DABCO) with M = Mg, Co, Ni, Cu, or Zn. Here, H atoms are omitted.	S8
<b>Figure S7.</b> The overlap between the DOS of CH <sub>4</sub> and the atoms of M(DABCO) on the adsorption site of the metal cluster.;	S9
<b>Figure S8.</b> The overlap between the DOS of CH <sub>4</sub> and the atoms of M(DABCO) on the adsorption site of the M-O-C cluster – TED interface.	S10

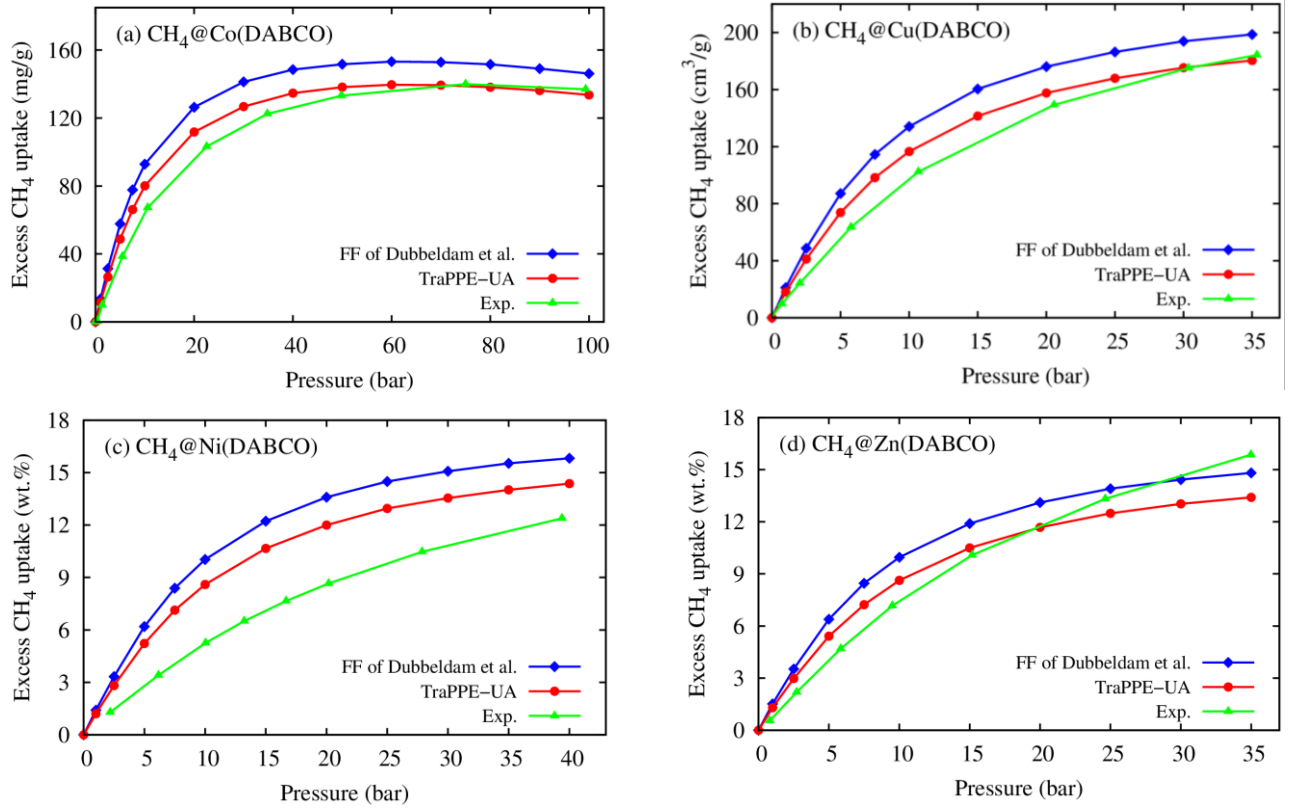
**Table S1.** Several well-known MOFs for gravimetric CH<sub>4</sub> adsorption capacity at 298 K so far.

MOFs	BET surface area (m <sup>2</sup> /g)	Total (excess) CH <sub>4</sub> adsorption		Pressure (bar)
		Gravimetric uptake (mg/g)	Volumetric uptake (cc(STP)/cc)	
Al-soc-MOF-1 [19], [8]	5585	ca. 420 (579 cm <sup>3</sup> /g)	197	65
		ca. 263 (362 cm <sup>3</sup> /g)	123	35
DUT-49 [22], [23]	5476	260	113	35
PCN-68 [22], [23]	5109	240	126	35
NU-111 [22], [6]	4930	241 (191)	138 (109)	35

**Table S2.** Excess gravimetric and volumetric CH<sub>4</sub> uptakes adsorbed on M(DABCO) at room temperatures.

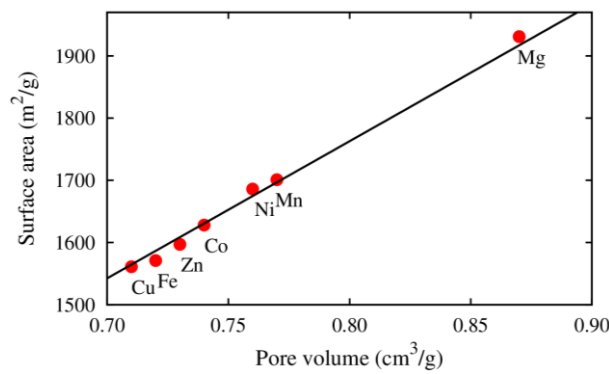
MOFs;	CH <sub>4</sub> adsorption		volumetric uptake cc(STP)/cc	Temperature (K); Pressure (bar)	Ref.
	gravimetric uptake				
	mg/g	cm <sup>3</sup> /g			
Cu(DABCO)	216	302		298; 35	[38]
Co(DABCO)	122 <sup>a</sup>	197	161	303; 35	[39]
	140 <sup>a</sup>			303; 75	[39]
Zn(DABCO)	125 <sup>a</sup>	199	164	303; 35	[40]
	143 <sup>a</sup>			303; 75	[40]
	170 <sup>a</sup>	242		298; 40	[41]
Ni(DABCO)	124 <sup>a</sup>			298; 40	[41]

<sup>a</sup>  $m_{exc}$  (mg/g) = 10 ·  $m_{exc}$  (wt.%).

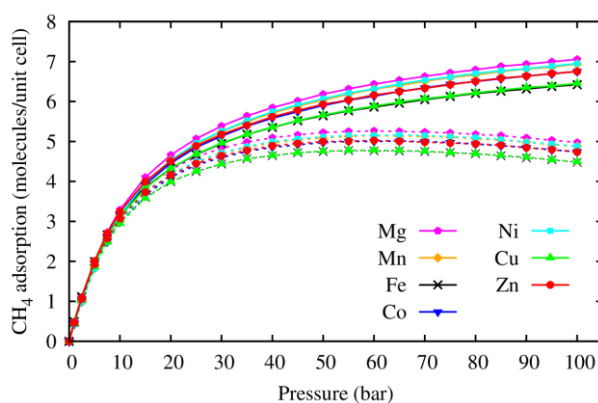


**Figure S1.** The simulated isotherms for methane compared with available experimental (exp.) data: (a) CH<sub>4</sub>@Co(DABCO) at 303 K: GCMC simulations vs experimental data from ref. [39], (b) CH<sub>4</sub>@Cu(DABCO) at 298 K: GCMC simulations vs experimental data from ref. [38], (c) CH<sub>4</sub>@Cu(DABCO) and (d) CH<sub>4</sub>@Cu(DABCO) at 298 K (in wt.% unit): GCMC simulations vs experimental data from ref. [41]. Note that wt.% in our simulation calculated by

$$m \text{ (wt. \%)} = \frac{100 \cdot m_{\text{CH}_4}(\text{g})}{(m_{\text{CH}_4} + m_{\text{MOF}})(\text{g})}, \text{ and unknown by Lee et al. [41].}$$



**Figure S2.** The correlation between the simulated surface area ( $A_{\text{BET}}$ ) and the pore volume ( $V_p$ ) of M(DABCO) sorbents. Points indicate the pairs of  $V_p$  and  $A_{\text{BET}}$ . The solid line indicates the linear fitting.



**Figure S3.** The simulated CH<sub>4</sub> adsorption isotherms of M(DABCO) with the total uptake (solid lines) and the excess uptake (dash lines) at 298 K and pressures up to 100 bar (in CH<sub>4</sub> molecules/unit cell).

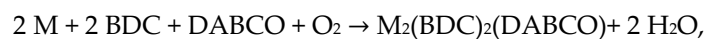
**Table S3.** The amount of CH<sub>4</sub> adsorption in M(DABCO) at 100 bar, 298 K in many different units compared to the molar mass of M(DABCO).

M(DABCO) compounds	Molar mass of M(DABCO) (g/mol)	Total CH <sub>4</sub> uptake (mg/g)	CH <sub>4</sub> molecules per unit cell	Mass of CH <sub>4</sub> (g) per mol of M(DABCO)
M = Cu	463.29	182.39	6.452	103.35
M = Fe	447.89	186.58	6.421	102.74
M = Zn	466.96	189.59	6.751	109.24
M = Co	454.06	194.05	6.753	109.32
M = Ni	453.58	199.9	6.951	113.32
M = Mn	446.07	202.22	6.936	113.07
M = Mg	384.81	231.39	7.053	115.85

**Table S4.** Formation enthalpy ( $\Delta H_f$ ) of  $M_2(BDC)_2(TED)$  or  $M(DABCO)$  compounds.

<b>M(DABCO)</b>	<b>M = Mg</b>	<b>M = Mn</b>	<b>M = Fe</b>	<b>M = Co</b>	<b>M = Ni</b>	<b>M = Zn</b>
$\Delta H_f$ (kJ/mol)	-1532	-1369	-1497	-1458	-1351	-902

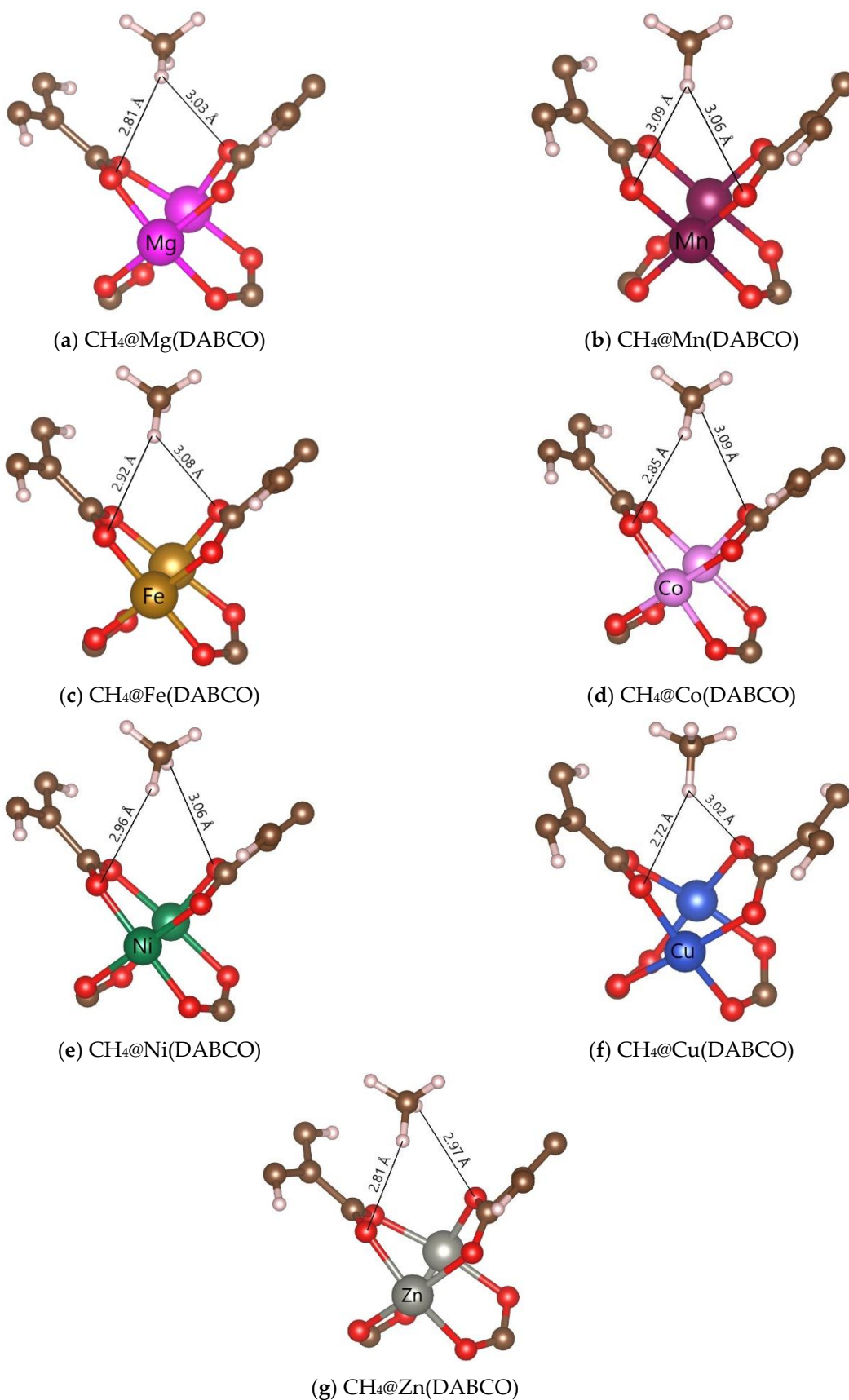
Here,  $\Delta H_f$  is the enthalpy of formation of the optimized  $M_2(BDC)_2(TED)$  compounds. It means that the more negative  $\Delta H_f$  is, the more stable the structure is.  $\Delta H_f$  is computed by the formula



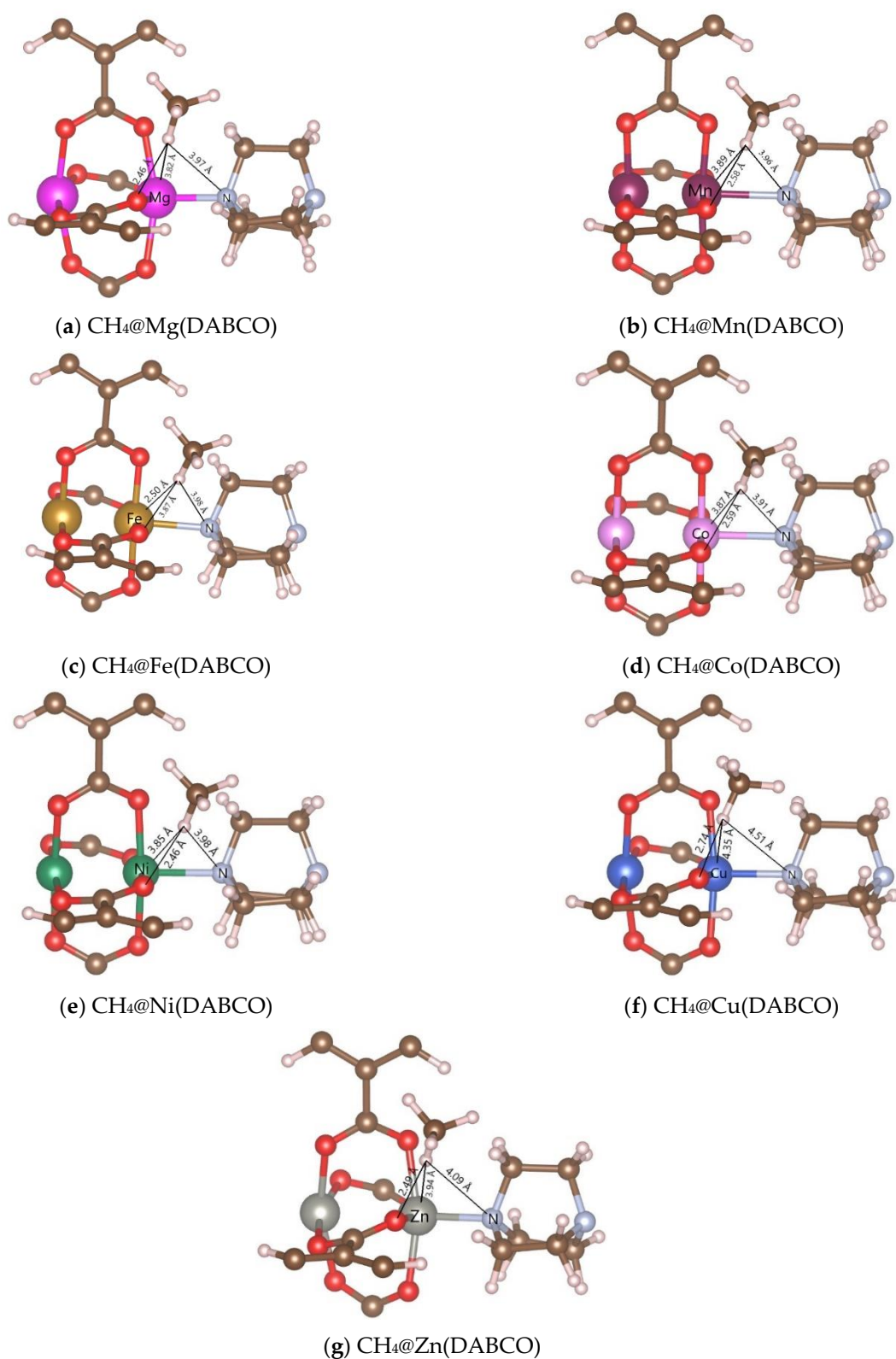
here, M = metal element, BDC = COOH – C<sub>6</sub>H<sub>4</sub> – COOH [C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>] and DABCO or TED = C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>,  $M(DABCO) = M_2(BDC)_2(DABCO)$

$$\Delta H_f = E_{tot}[M(DABCO)] + 2E_{tot}[H_2O] - \{2E_{tot}[M] + 2E_{tot}[BDC] + E_{tot}[DABCO] + E_{tot}[O_2]\}$$

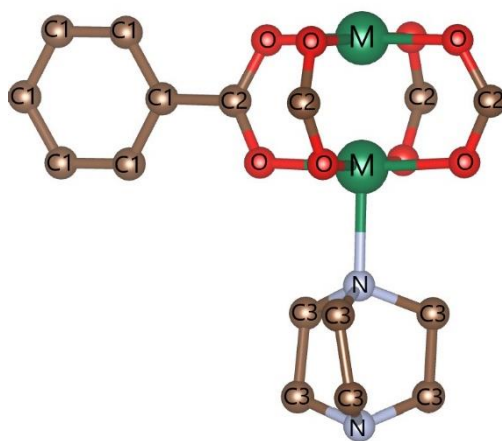
where  $E_{tot}$  is the total energy of compounds, obtained using vdW-DF calculations.



**Figure S4.** The most stable  $\text{CH}_4$  adsorption sites on the metal cluster of  $\text{M}(\text{DABCO})$ .

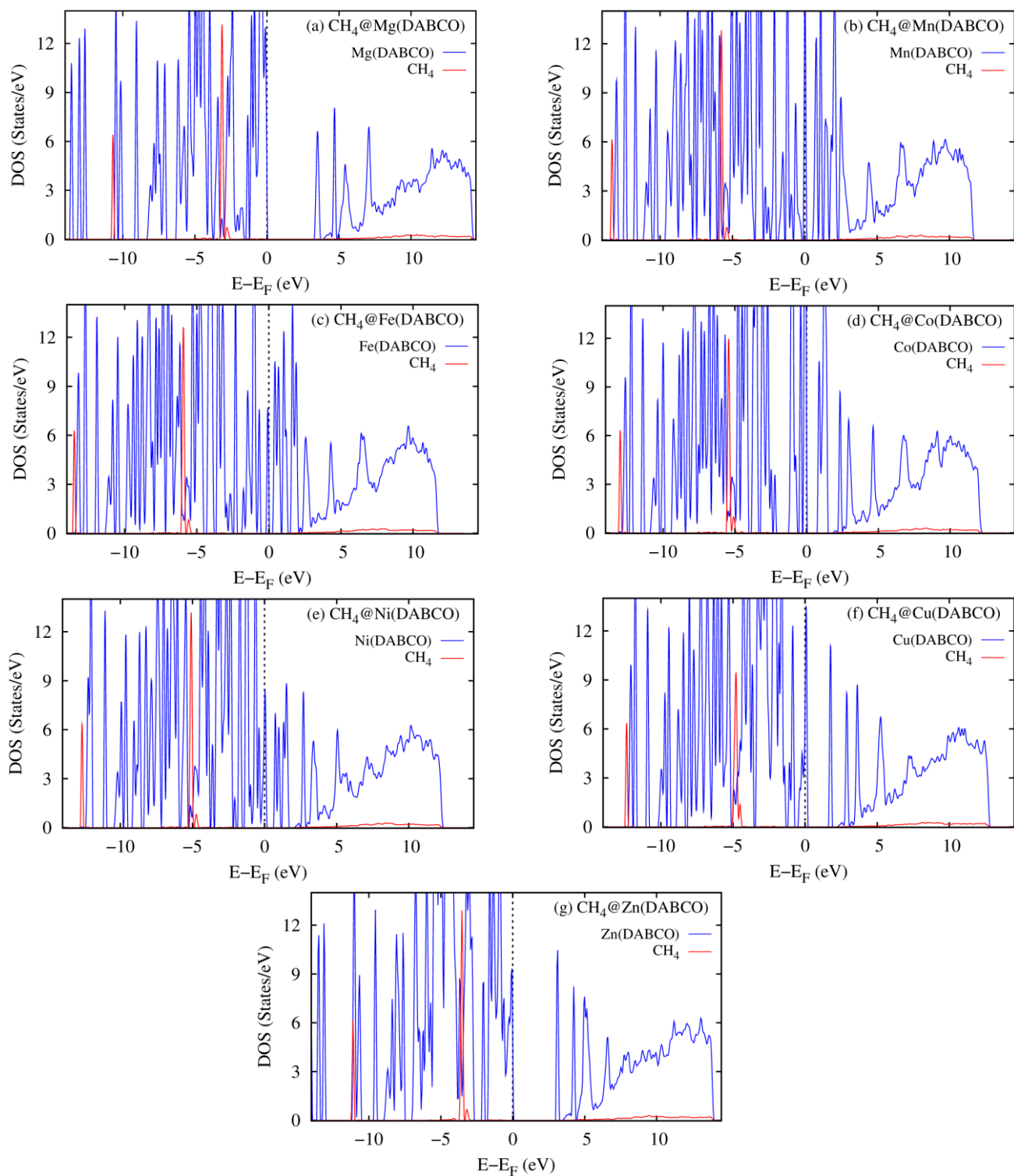


**Figure S5.** The most stable  $\text{CH}_4$  adsorption sites on the interface between the M-O-C cluster and TED of M(DABCO).

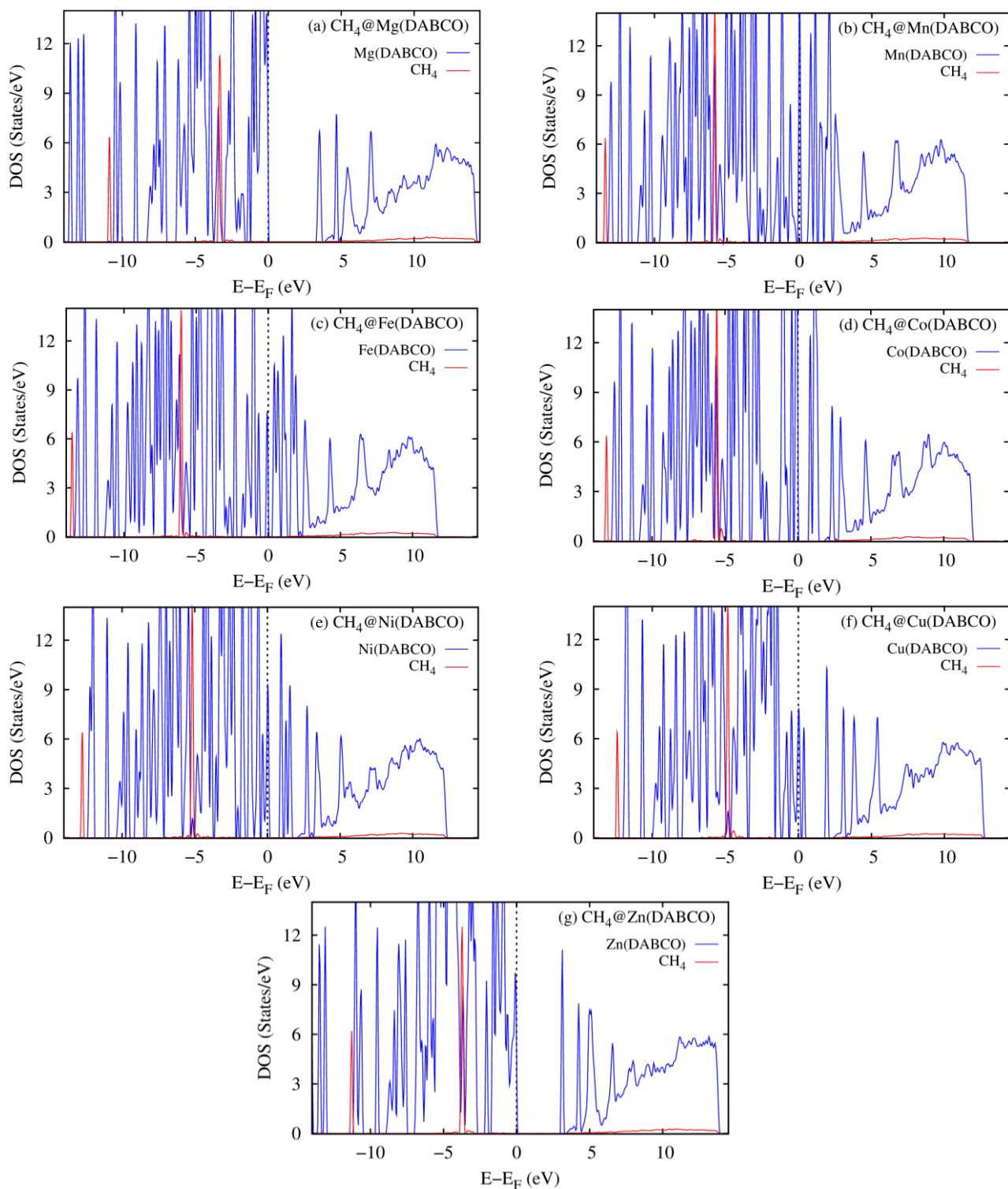


**Figure S6.** The symbols for the atoms (C1, C2, C3, O, N, and M) of M(DABCO) with M = Mg, Mn, Fe, Co, Ni, Cu, or Zn. Here, H atoms are omitted.





**Figure S7.** The overlap between the DOS of  $\text{CH}_4$  and the atoms of  $\text{M(DABCO)}$  on the adsorption site of the metal cluster.



**Figure S8.** The overlap between the DOS of  $\text{CH}_4$  and the atoms of  $\text{M}(\text{DABCO})$  on the adsorption site of the  $\text{M}-\text{O}-\text{C}$  cluster – TED interface.

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