Supporting Information

Force-Field Development from Electronic Structure Calculations with Periodic Boundary Conditions: Applications to Gaseous Adsorption and Transport in Metal-Organic Frameworks

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Section I: Definition of atom-types on the framework.

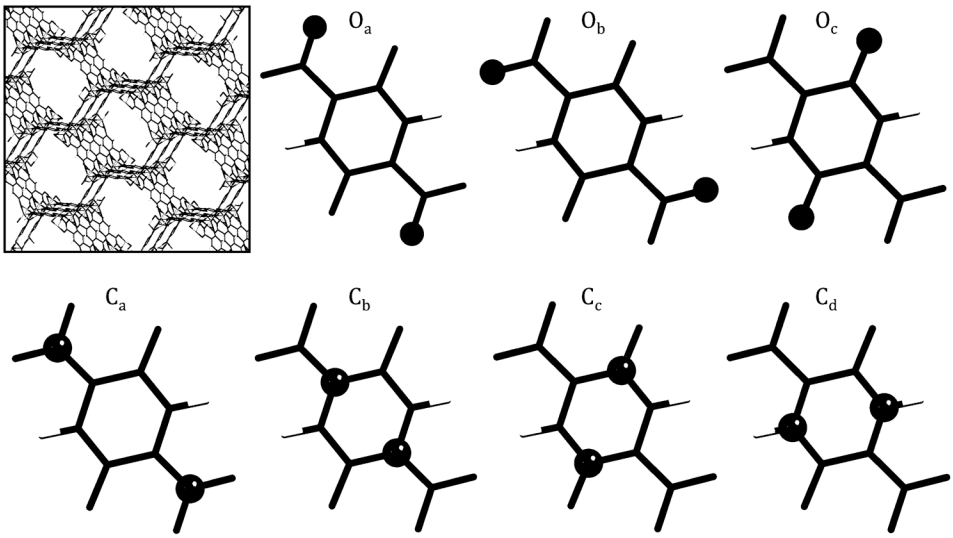


Figure S1: Image of M-MOF-74 structure (top left) where it is seen that all metal types (M) are equivalent, and BDC linker atom types considered in this work.

Section II: Referred figures in the manuscript.

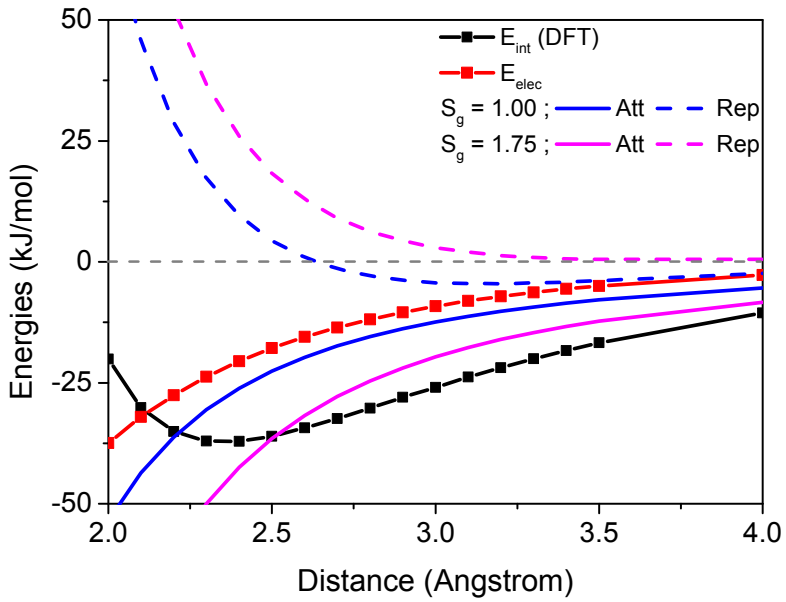


Figure S2: Demonstration of the necessity of a global scaling factor applied in the calculated dispersion contribution while performing the energy decomposition. The black squares with solid line are the DFT total energies along a given path while the red squares with solid line are the electrostatic contributions. The solid and dashed lines represent for the calculated dispersion energies and the corresponding decomposed repulsion energies, respectively. The blue and pink colors indicate the cases of the scaling factors equal to 1 and 1.75, respectively.

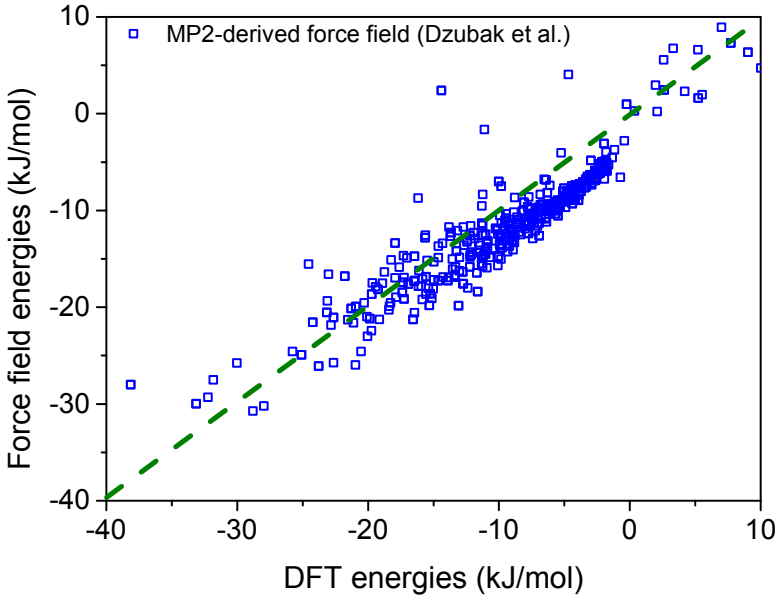


Figure S3: Comparison of the interaction energies of CO_2-framework obtained from the DFT calculations with ones computed from the MP2-derived force field (Dzubak *et al*.) (open blue squares) for a set of 600 CO_2 configurations inside the accessible pore volume of Mg-MOF-74. The green-dashed line indicates perfect agreement between the energies computed by DFT and by force field.

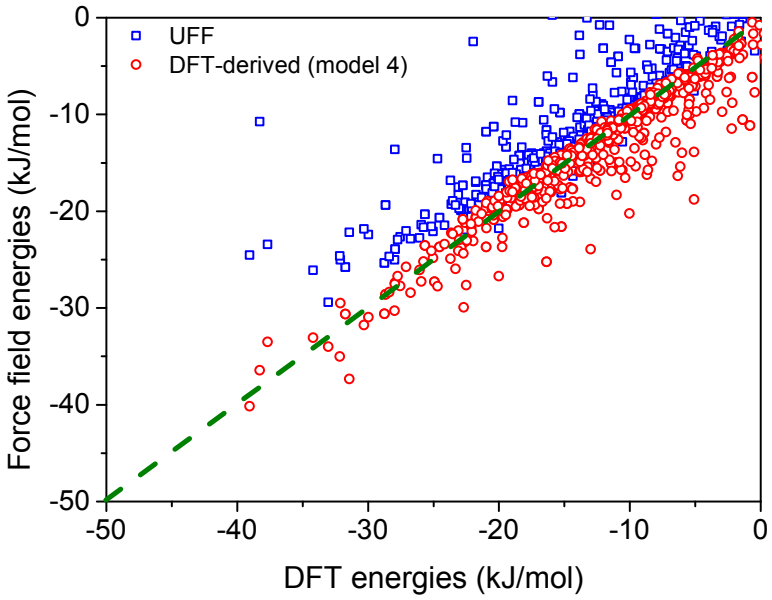
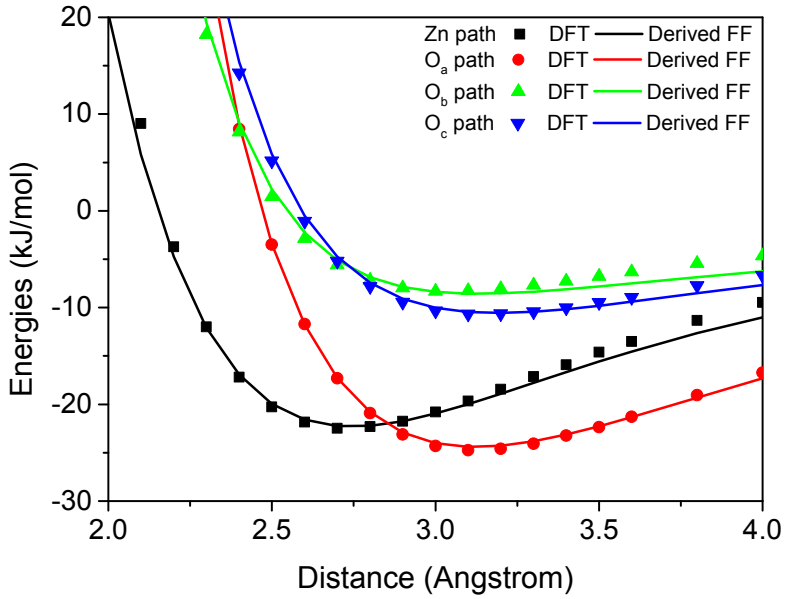
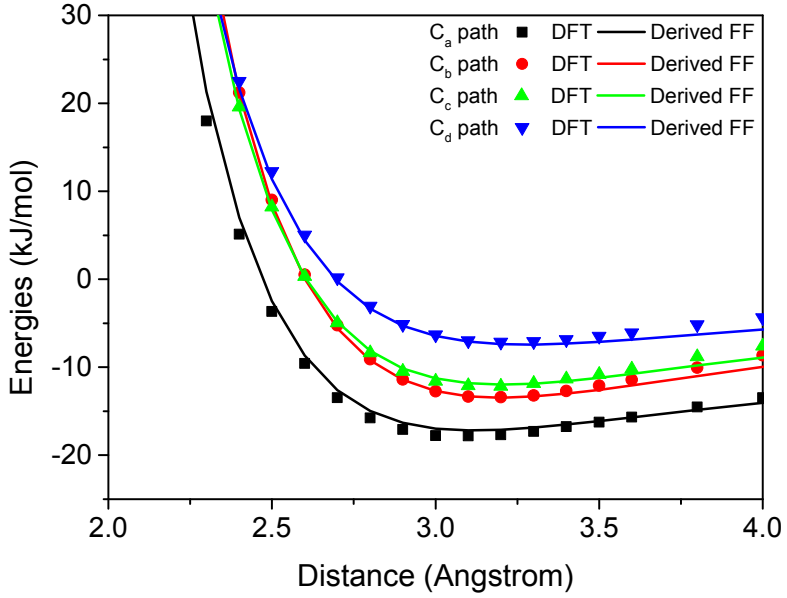


Figure S4: Comparison of the interaction energies of CO_2-framework obtained from the DFT calculations with ones computed from the UFF (open blue squares) and the DFT-derived force field (model 4) (open red circles) for a set of 1200 CO_2 configurations inside the accessible pore volume of Mg-MOF-74. The green-dashed line indicates perfect agreement between the energies computed by DFT and by force fields.



(a)



(b)

Figure S5: Comparisons of CO_2-framework Interaction energies as a function of distance inside Zn-MOF-74 obtained from the DFT calculations (closed symbol) with ones computed from the DFT-derived force field (solid line) along (a) Mg and O and (b) C paths. The DFT-derived force field demonstrated here was built upon the model 4 of CO_2 inside the Mg-MOF-74.

Section III: Force-field parameters

Table S1: Atomic charges (e) of the framework atoms

Atom types	Mg-MOF-74	Zn-MOF-74
Metal	1.560	1.209
O_a	-0.899	-0.719
O_b	-0.752	-0.671
O_c	-0.903	-0.740
C_a	0.900	0.841
C_b	-0.314	-0.298
C_c	0.456	0.376
C_d	-0.234	-0.170
H	0.186	0.172

Table S2: Atomic charges (e) of the guest molecules

Atom	Charges (e)
$O(CO_2)^a$	-0.35
$C(CO_2)^a$	0.70
$O(CO_2)^b$	-0.3256
$C(CO_2)^b$	0.6512
$O(H_2O)^c$	0.000
$H(H_2O)^c$	0.52422
$M(H_2O)^c$	-1.04844

[a]TraPPE; [b]EPM2; [c]TIP4P-Ew

Table S3: Lennard-Jones parameters for guest molecules

Atom	Lennard-Jones parameters	
	Epsilon (K)	Sigma (Å)
Mg [a]	55.85	2.69
Zn [a]	62.40	2.46
O_a [a]	30.19	3.12
O_b [a]	30.19	3.12
O_c [a]	30.19	3.12
C_a [a]	52.84	3.43
C_b [a]	52.84	3.43
C_c [a]	52.84	3.43
C_d [a]	52.84	3.43
H [a]	22.14	2.57
$O(CO_2)$[b]	79.00	3.05
$C(CO_2)$[b]	27.00	2.80
$O(CO_2)$[c]	80.507	3.033
$C(CO_2)$[c]	28.129	2.757
$O(H_2O)$[d]	81.90	3.164
$H(H_2O)$[d]	n/a	n/a
$M(H_2O)$[d]	n/a	n/a

[c]UFF; [b]TraPPE; [c]EPM2; [d]TIP4P-Ew

Table S4: (CO_2 model 1) Derived force-field parameters of CO_2 inside Mg-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, $Å^{-1}$, $KÅ^6$) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used.

Guest model: EPM2 Global Scaling factor, $\mathbf{S_g}$ =1.15									
	Mg	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
$O(CO_2)$	1.01016E8 4.915 1.6934E5	4.13513E7 3.880 1.9229E5	2.24393E7 3.680 1.9229E5	2.39923E7 3.655 1.9229E5	2.19975E7 3.690 3.4165E5	1.52973E7 3.315 3.4165E5	3.85840E7 3.890 3.4165E5	3.4804E6 2.765 3.4165E5	-*
$C(CO_2)$	-*	-*	-*	-*	-*	-*	-*	-*	-*

* Obtained directly from the Lorentz-Berthelot mixing rule with parameters given in Table S3.

Table S5: (CO_2 model 2) Derived force-field parameters of CO_2 inside Mg-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^{6}) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used.

Guest model: EPM2 Global Scaling factor, $\mathbf{S_g}$ =2.0									
	Mg	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
O(CO_2)	2.12551E7 3.840 4.80935E5	4.00264E7 3.855 1.68390E5	2.34334E7 3.705 1.68390E5	2.38227E7 3.655 1.68390E5	2.79912E7 3.840 2.66249E5	2.28405E7 3.515 2.66249E5	3.03352E7 3.815 2.66249E5	4.94048E6 2.965 2.66249E5	-*
C(CO_2)	-*	-*	-*	-*	-*	-*	-*	-*	-*

* Obtained directly from the Lorentz-Berthelot mixing rule with parameters given in Table S3.

Table S6: (CO_2 model 3) Derived force-field parameters of CO_2 inside Mg-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^{6}) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used.

Guest model: TraPPE Global Scaling factor, $\mathbf{S_g}$ =1.1									
	Mg	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
O(CO_2)	4.40825E7 4.46000 1.63331E5	3.95436E7 3.88500 1.85237E5	2.88557E7 3.81000 1.85237E5	2.51634E7 3.68500 1.85237E5	2.12871E7 3.67000 3.28865E5	1.61520E7 3.34500 3.28865E5	4.60000E7 3.97000 3.28865E5	4.05246E6 2.84500 3.28865E5	-*
C(CO_2)	-*	-*	-*	-*	-*	-*	-*	-*	-*

* Obtained directly from the Lorentz-Berthelot mixing rule with parameters given in Table S3.

Table S7: (CO_2 model 4) Derived force-field parameters of CO_2 inside Mg-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^{6}) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used with two parameters ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) in the units of (K, Å).

Guest model: EPM2 Global Scaling factor, $\mathbf{S_g}$ =1.7									
	Mg	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
O(CO_2)	2.47320E7 3.965 4.08795E5	3.37882E7 3.805 1.43132E5	2.67786E7 3.780 1.43132E5	2.63432E7 3.705 1.43132E5	2.76500E7 3.840 2.26311E5	2.14836E7 3.515 2.26311E5	2.99216E7 3.840 2.26311E5	1.31469E7 3.315 2.26311E5	56.900 2.343
C(CO_2)	190.6212 2.816	69.958 2.794	69.958 2.794	69.958 2.794	87.738 2.904	87.738 2.904	87.738 2.904	87.738 2.904	68.317 2.453

Table S8: Derived force-field parameters of CO_2 inside Zn-MOF-74 (build upon model 4 as shown in Table S7). Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^6) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used with two parameters ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) in the units of (K, Å).

Guest model: EPM2 Global Scaling factor, $\mathbf{S_g}$ =1.7									
	Zn	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
$O(CO_2)$	6.87804E6 3.065 5.62211E5	3.37882E7 3.805 1.43132E5	2.67786E7 3.780 1.43132E5	2.63432E7 3.705 1.43132E5	2.76500E7 3.840 2.26311E5	2.14836E7 3.515 2.26311E5	2.99216E7 3.840 2.26311E5	1.31469E7 3.315 2.26311E5	56.900 2.343
$C(CO_2)$	174.382 3.014	69.958 2.794	69.958 2.794	69.958 2.794	87.738 2.904	87.738 2.904	87.738 2.904	87.738 2.904	68.317 2.453

Table S9: (H_2O model B) Derived force-field parameters of H_2O inside Mg-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^6) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used.

Guest model: TIP4P-Ew Global Scaling factor, $\mathbf{S_g}$ =1.0									
	Mg	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
$O(H_2O)$	2.19311E7 3.945 1.70117E5	-*	2.93687E7 3.810 1.91368E5	1.31946E7 3.310 1.91368E5	8.27745E6 3.200 3.37984E5	1.71280E7 3.350 3.37984E5	8.93584E7 4.275 3.37984E5	5.24596E6 3.025 3.37984E5	-*
$H(H_2O)$	-**	3.91009E6 3.960 5.49046E4	3.91009E6 3.960 5.49046E4	3.91009E6 3.960 5.49046E4	2.77748E6 3.475 9.98541E4	2.77748E6 3.475 9.98541E4	2.77748E6 3.475 9.98541E4	2.77748E6 3.475 9.98541E4	-**
$M(H_2O)$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

* Obtained directly from the Lorentz-Berthelot mixing rule with parameters given in Table S3. ** The parameters of $H(H_2O)$ were taken from UFF, and the Lorentz-Berthelot mixing rule was applied for the inter-molecular interaction.

Table S10: (H_2O model B) Derived force-field parameters of H_2O inside Zn-MOF-74. Three parameters ($\boldsymbol{A_{ij}}$, $\boldsymbol{B_{ij}}$, $\boldsymbol{C_{ij}}$) with the units of (K, Å^{-1}, KÅ^6) are displayed while the Buckingham potential is adopted. Otherwise, the 12-6 Lennard Jones potential is used. The parameters provided here were not partially transferred from the Model B of Mg-MOF-74 but directly parameterized all the approached pairs from all generated paths since that all the DFT energies along all the paths were computed already.

Guest model: TIP4P-Ew Global Scaling factor, $\mathbf{S_g}$ =1.0									
	Zn	O_a	O_b	O_c	C_a	C_b	C_c	C_d	H
$O(H_2O)$	1.25926E7 3.560 1.41379E5	-*	3.88088E7 3.935 1.91368E5	1.30727E7 3.310 1.91368E5	1.62829E7 3.600 3.37984E5	1.58036E7 3.300 3.37984E5	1.26622E8 4.475 3.37984E5	4.99772E6 2.975 3.37984E5	-*
$H(H_2O)$	-**	3.73560E6 3.935 5.4904E4	3.73560E6 3.935 5.4904E4	3.73560E6 3.935 5.4904E4	2.38591E6 3.375 9.9854E4	2.38591E6 3.375 9.9854E4	2.38591E6 3.375 9.9854E4	2.38591E6 3.375 9.9854E4	-**
$M(H_2O)$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

* Obtained directly from the Lorentz-Berthelot mixing rule with parameters given in Table S3. ** The parameters of $H(H_2O)$ were taken from UFF, and the Lorentz-Berthelot mixing rule was applied for the inter-molecular interaction.