Supporting Information: Flexible Force Field Parameterization through Fitting on the Ab Initio derived Elastic Tensor

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$$\mathcal{C}_{ij} = \begin{pmatrix} 33.79 & 5.05 & 3.40 & 0.00 & 0.00 & -2.24 \\ 5.05 & 69.72 & 49.46 & 0.00 & 0.00 & -1.17 \\ 3.40 & 49.46 & 36.75 & 0.00 & 0.00 & -1.08 \\ 0.00 & 0.00 & 0.00 & 44.16 & -0.22 & 0.00 \\ 0.00 & 0.00 & 0.00 & -0.22 & 9.03 & 0.00 \\ -2.24 & -1.17 & -1.08 & 0.00 & 0.00 & 9.87 \end{pmatrix} \tag{S1}$$

Flexbile force field developed in this work with the C1-C2-C3-O2 force field constant set to p_2/k_B = 601 K

$$\mathcal{C}_{ij} = \begin{pmatrix} 41.69 & 10.81 & 7.17 & 0.00 & 0.00 & 0.00 \\ 10.81 & 79.16 & 50.89 & 0.00 & 0.00 & 0.00 \\ 7.17 & 50.89 & 34.27 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 44.74 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 8.46 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 7.53 \end{pmatrix} \tag{S2}$$

Flexbile force field developed in this work without O2-V1-O1-V1 torsion.

Table S1: Flexible force field parameters for MIL-47(V). Labels are given in Fig. S1.

(a) Bonding parameters

Bond type	K (K)	r_0 (Å)
C1-C1	392459.2	1.4
C1-C2	392459.2	1.4
C2-C3	334720.0	1.49
C3-O2	476976.0	1.229
C1-H1	307105.6	1.08
V1-O1	281702.46	1.93
V1-O2	101702.46	1.81

(b) Bending parameters

Angle type	k (K)	θ_0
C1-C2-C1	63405.72	120
C2-C1-C1	63405.72	120
C1-C1-H1	35225.4	120
C2-C1-H1	35225.4	120
C1-C2-C3	85547.4	120
C2-C3-O2	80515.2	120.4
O2-C3-O2	80515.2	126
C3-O2-V1	14929.27	135.0

(c) Torsion parameters: Ryckaert-Belleman

Torsion type	p_0/k_B (K)	p_1/k_B (K)	p_2/k_B (K)	p_3/k_B (K)	p_4/k_B (K)	p_5/k_B (K)
C2-C1-C1-C2	-3648.345	0	-3648.345	0	0	0
C3-C2-C1-C1	-3648.345	0	-3648.345	0	0	0
C2-C1-C1-H1	-3648.345	0	-3648.345	0	0	0
H1-C1-C1-H1	-3648.345	0	-3648.345	0	0	0
C3-C2-C1-H1	-3648.345	0	-3648.345	0	0	0
H1-C1-C2-C1	-3648.345	0	-3648.345	0	0	0
C1-C1-C2-C1	-3648.345	0	-3648.345	0	0	0

(d) Torsion parameters: TraPPE Dihedral

Torsion type	p_0/k_B (K)	p_1/k_B (K)	p_2/k_B (K)	p_3/k_B (K)
C1-C2-C3-O2	0.0	0.0	2258.32	0.0
C2-C3-O2-V1	0.0	0.0	2012.64	0.0
O2-V1-O1-V1	0.0	0.0	1012.64	0.0

(e) Lennard-Jones parameters and atomic charges

Atom type	ϵ/k_B (K)	σ (Å)	q
O2	30.01	3.12	-0.526043092
C1	29.80	3.8068	-0.141044500
C2	29.80	3.8068	0.039468304
C3	29.80	3.8068	0.566342889
H1	19.27	2.4483	0.132130453
V1	8.05	2.801	1.491637203
O1	30.01	3.12	-0.563431035

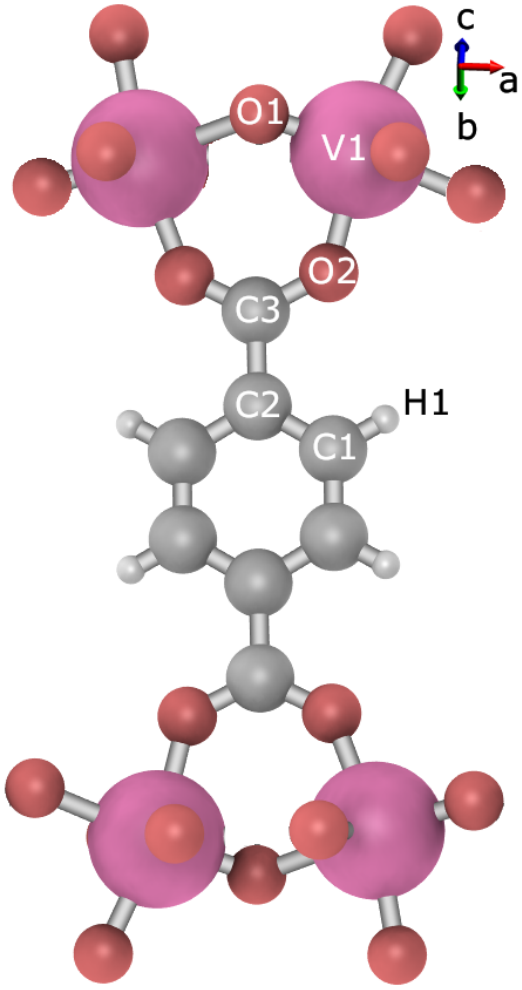

Figure S1: Labels of unit cell of MIL-47(V).

RASPA simulation input files for Baker's minimization

The force field calculations are performed with the RASPA-2.0 package.[1] Initial structure is taken from Barthelet *et al*.[2] (CCDC 166785).

Listing 1: framework.def

```
# CoreShells bond  BondDipoles UreyBradley bend  inv  tors
 0 7 0 0 8 0 10 0 0 0 0 0 0
# bond
C1 C1 HARMONIC_BOND 392459.2 1.4
C1 C2 HARMONIC_BOND 392459.2 1.4
C2 C3 HARMONIC_BOND 334720.0 1.49
C3 O2 HARMONIC_BOND 476976.0 1.229
C1 H1 HARMONIC_BOND 307105.6 1.08
V1 O1 HARMONIC_BOND 281702.46 1.93
V1 O2 HARMONIC_BOND 101702.46 1.81
# bend
C1 C2 C1 HARMONIC_BEND 63405.72 120
C2 C1 C1 HARMONIC_BEND 63405.72 120
C1 C1 H1 HARMONIC_BEND 35225.4  120
C2 C1 H1 HARMONIC_BEND 35225.4  120
C1 C2 C3 HARMONIC_BEND 85547.4  120
C2 C3 O2 HARMONIC_BEND 80515.2  120.4
O2 C3 O2 HARMONIC_BEND 80515.2  126
C3 O2 V1 HARMONIC_BEND 14929.27 135.0
# torsion
C2 C1 C1 C2 SIX_COSINE_DIHEDRAL  -3648.345  0  -3648.345 0  0 0
```

```
C3 C2 C1 C1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
C2 C1 C1 H1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
H1 C1 C1 H1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
C3 C2 C1 H1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
H1 C1 C2 C1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
C1 C1 C2 C1 SIX_COSINE_DIHEDRAL -3648.345 0 -3648.345 0 0 0
C1 C2 C3 O2 TRAPPE_DIHEDRAL 0.0 0.0 2258.32270650 0.0
C2 C3 O2 V1 TRAPPE_DIHEDRAL 0.0 0.0 2012.64 0.0
O2 V1 O1 V1 TRAPPE_DIHEDRAL 0.0 0.0 1012.64 0.0
```

Listing 2: force_field_mixing_rules.def

```
# shifted or truncated
shifted
# tail corrections
no
# amount of interactions
7
# interactions
O2 LENNARD_JONES 30.01 3.12
C1 LENNARD_JONES 29.80 3.8068
C2 LENNARD_JONES 29.80 3.8068
C3 LENNARD_JONES 29.80 3.8068
H1 LENNARD_JONES 19.27 2.4483
V1 LENNARD_JONES 8.05 3.401
O1 LENNARD_JONES 30.01 3.12
# mixing rules
```

Lorentz−Berthelot

References

(1) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. *Mol. Simul.* **2016**, *42*, 81–101.

(2) Barthelet, K.; Marrot, J.; Riou, D.; Frey, G. A Breathing Hybrid Organic-Inorganic Solid with Very Large Pores and High Magnetic Characteristics. *Angew. Chem. Int. Ed.* **2002**, *41*, 281–284.