Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Appendix A. Supplementary Data

Dynamical and electronic properties of anion-pillared metal-organic frameworks for natural gas separation.

Sabrina Grigoletto, Arthur Gomes dos Santos, Guilherme Ferreira de Lima, Heitor Avelino De Abreu*

Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Avenida Antônio Carlos, 6627, Pampulha, Belo Horizonte, Minas Gerais, Brazil.

* Corresponding author: heitorabreu@ufmg.br (H. A. De Abreu)

Summary

S1. Models

To perform the GCMC and the MD calculations the crystal structures of the MOFs were optimized at PBE+D3/US level theory. The obtained unit cell parameters and bond lengths are available in Table S1 and can be compared with the respective experimental values [1], [2]. In addition to the classical simulations, we performed DFT adsorption calculations. In this case for SIFSIX-3-Cu and for SIFSIX-2-Cu, we used the same unit cells, but for SIFSIX-2-Cu-i we used a reduced primitive cell, to decrease the number of atoms to be described.

Table S1. Unit cell parameters of the MOFs SIFSIX-3-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-i and the reduced primitive form of SIFSIX-2-Cu-i. The available data is from experimental data and from DFT simulations at PBE+D3/US level theory.

MOF	Methodology	a (Å)	b (Å)	c (Å)	α°	β°	γ°
SIFSIX-3-Cu	DFT PBE+D3/US	6.921	6.921	7.945	90.00	90.00	90.00
	Experimental	6.919	6.919	7.906	90.00	90.00	90.00
SIFSIX-2-Cu	DFT PBE+D3/US	13.733	13.732	8.026	90.00	90.00	90.00
	Experimental	13.632	13.632	7.968	90.05	89.97	89.99
SIFSIX-2-Cu-i	DFT PBE+D3/US	13.755	13.755	8.227	90.00	90.00	90.00
	Experimental	13.649	13.649	8.092	90.00	90.00	90.06
Primitive SIFSIX-2-Cu-i	DFT PBE+D3/US	10.234	10.263	10.773	98.46	98.35	133.63

Table S2. Bond lengths of the MOFs SIFSIX-3-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-i and the reduced primitive form of SIFSIX-2-Cu-i. The available data is from experimental data and from DFT simulations at PBE+D3/US level theory.

MOF	Cu – F (Å)	Si – F_{axial} (Å)	Si – $F_{equatorial}$ (Å)
SIFSIX-3-Cu	2.23	1.75	1.70
	2.12	1.83	1.65
SIFSIX-2-Cu	2.28	1.73	1.71
	2.30	1.68	1.69
SIFSIX-2-Cu-i	2.38	1.74	1.71
	2.35	1.69	1.68
Primitive SIFSIX-2-Cu-i	2.30	1.74	1.71

S2.Lennard-Jones parameters for classical simulations

Table S3. Lennard-Jones parameters for MOF atoms

Atom	ε/k_b / (K)	σ / (Å)	Force field
Cu	2.5161	3.11369	Universal Force Field
Si	202.290	3.8264	Universal Force Field
C	47.8562	3.47299	DREIDING
F	36.4834	3.0932	DREIDING
N	38.9492	3.26256	DREIDING
H	7.64893	2.84642	DREIDING

Table S4. Lennard-Jones parameters from TraPPE force field for pseudo atoms of adsorbed molecules

Pseudo Atom	**ε/k_b / (K)**	**σ / (Å)**	**q**
CH_4_sp^3	148	3.73	0
CH_3_sp^3	98	3.75	0
CH_2_sp^3	46	3.95	0
CH_2_sp^2	85	3.67	0
CH_sp^2	47	3.73	0
N_N_2	36.4	3.32	-0.482
N_com (center of mass)	-	-	0.964

S3. Adsorption Energy

We performed Monte Carlo simulations in NVT ensemble to compute the variation of internal energy during adsorption process. These values can be compared with the obtained through DFT calculations.

Table S5. Computed adsorption energy

MOFs	Molecules	MC (kcal mol^{-1})
SIFSIX-3-Cu	Methane	-5.9
	Ethane	-8.1
	Ethene	-7.6
	Propane	-7.0
	Propene	-8.6
	N_2	-5.6
SIFSIX-2-Cu-i	Methane	-6.7
	Ethane	-8.9
	Ethene	-8.1
	Propane	-9.3
	Propene	-9.9
	N_2	-4.9
SIFSIX-2-Cu	Methane	-2.1
	Ethane	-3.0
	Ethene	-2.7
	Propane	-3.5
	Propene	-3.3
	N_2	-1.6

S4. Adsorption Isotherms Adjust

Grand canonical Monte Carlo simulations of the adsorption of the molecules were performed in MOFs SIFSIX-3-Cu, SIFSIX-2-Cu-I and SIFSIX-2-Cu. The simulations were performed with $1x10^6$ Cycles at 300 K. The isotherms were fitted using the Langmuir-Freudlich model as the following equation:

$$q = \frac{q_{sat} b P^{v}}{1 + b P^{v}}$$

The fitted parameters for each gas at the different MOFs are available in Tables S5, S6 and S7.

Table S5: Fitted adsorption isotherm parameters for gases in SIFSIX-3-Cu

Molecule	q_{sat} / mmol. g^{-1}	b	v
Methane	4.33362	0.0083136	0.9091390
Ethane	3.02744	0.0370561	1.0101233
Ethene	3.34954	0.0342679	0.9185464
Propane	2.81094	0.0001425	1.4386983
Propene	2.70942	0.0197164	1.4217901
N_2	3.00607	0.0030967	0.9853778

Table S6: Fitted adsorption isotherm parameters for gases in SIFSIX-2-Cu-i

Molecule	q_{sat} / mmol. g^{-1}	b	v
Methane	6.86839	0.0105370	1.0381103
Ethane	4.72678	0.2239281	0.9450387
Ethene	5.50046	0.1519167	0.7909961
Propane	3.67750	0.1194139	1.0579861
Propene	4.64105	0.5199214	0.6744319
N_2	6.66438	0.0020685	0.9766823

Table S7: Fitted adsorption isotherm parameters for gases in SIFSIX-2-Cu

Molecule	q_{sat} / mmol. g^{-1}	b	v
Methane	25.40713	1.6361e-04	1.0298374
Ethane	13.27922	1.5014e-04	1.6128207
Ethene	15.00148	1.1093e-04	1.4852562
Propane	11.16062	3.6916e-03	1.5765728
Propene	12.14805	3.1602e-03	1.4606678
N_2	21.99546	9.3059e-05	1.0049125

S5. Ideal Adsorbed Solution Theory (IAST) selectivity

Grand canonical Monte Carlo simulations of binary mixtures of different proportions of CH_4 and other molecules were used to estimate IAST selectivity. Selectivity was calculated with the following equation:

$$S = \frac{q_i}{q_j} \Big/ \frac{x_i}{x_j}$$

where q_i and q_j are the amount adsorbed and x_i and x_j are the molar fractions of each component of the binary mixture. The calculations were performed with 5.0×10^4 cycles of initialization and 1.0×10^6 cycles of simulation at 1.0×10^5 Pa and 300 K. We used binary mixtures of 0.25, 0.5, 0.75 and 0.99 molar fractions of methane with each one of the studied molecules. Calculated IAST selectivity's are presented in Figure S1.

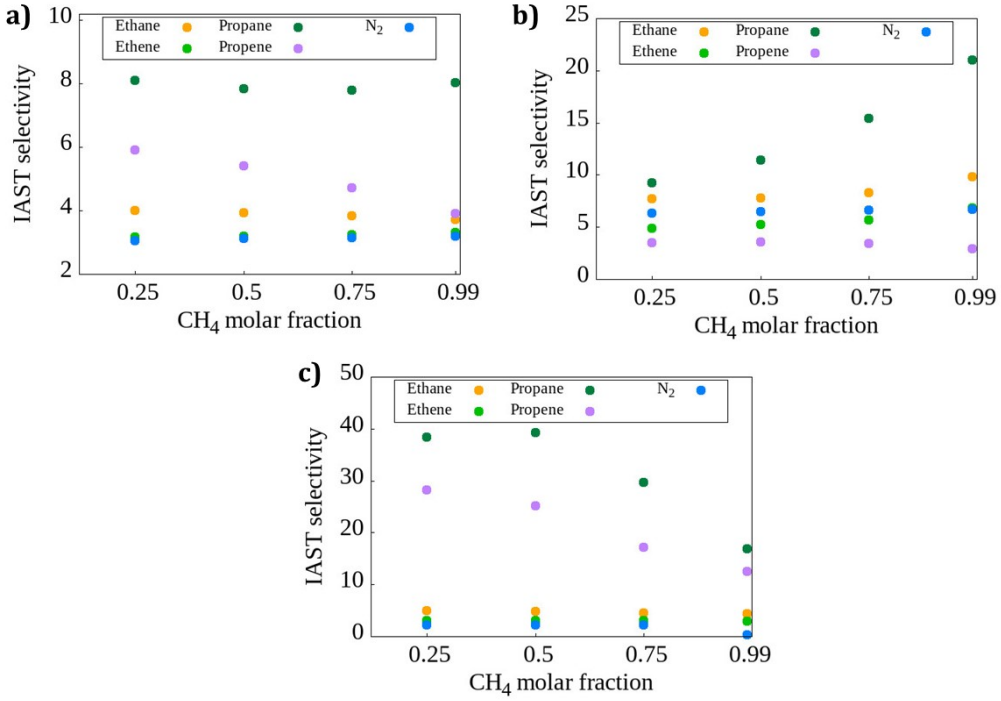

Figure S1: Calculated IAST selectivity's for binary mixtures of CH_4/C_2H_6, CH_4/C_2H_4, CH_4/C_3H_8, CH_4/C_3H_6 and CH_4/N_2 of variable molar fractions of the components in MOFs a) SIFSIX-3-Cu, b) SIFSIX-2-Cu-i and c) SIFSIX-2-Cu.

S6. Molecular Dynamics calculations

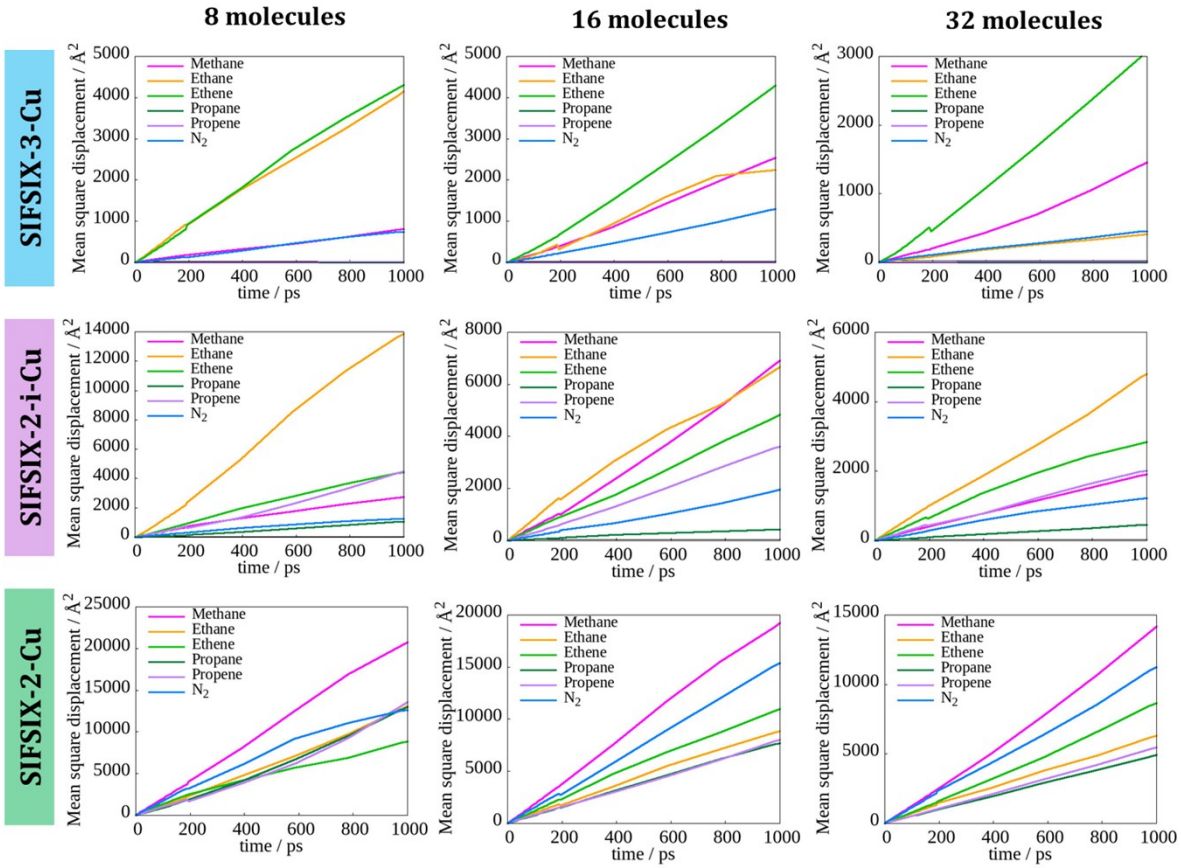

Figure S2: Plots of the mean square displacement in function of time for 8, 16 and 32 molecules of the guest molecules methane (pink), ethane (orange), ethene (light green), propane (dark green), propene (purple) and N_2 (light blue) in SIFSIX-3-Cu, SIFSIX-2-Cu-i and SIFSIX-2-Cu.

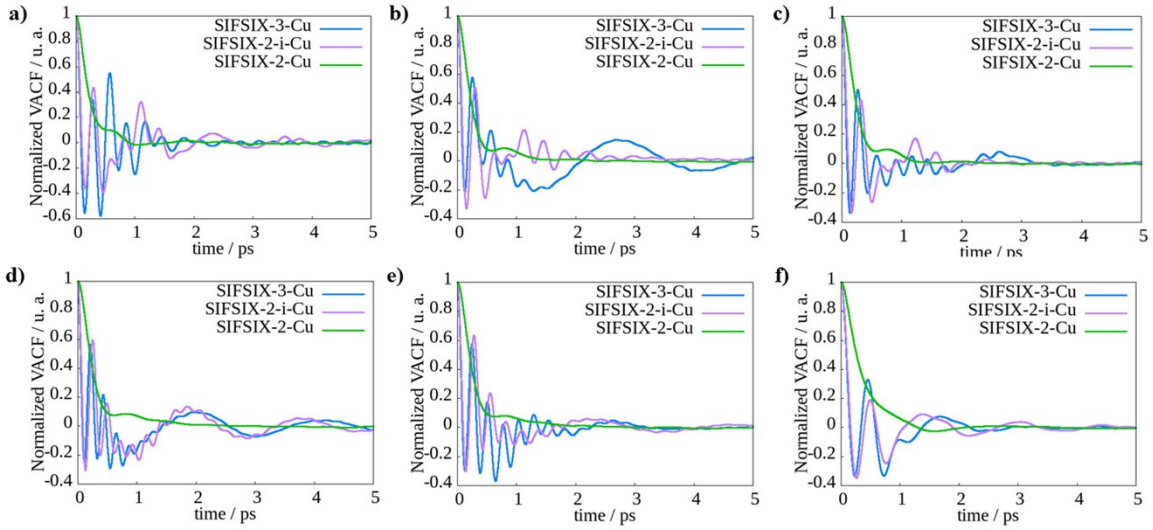

Figure S3: Plots of the normalized velocity autocorrelation function in function of time for 8 molecules of a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 in SIFSIX-3-Cu, SIFSIX-2-Cu-i and SIFSIX-2-Cu.

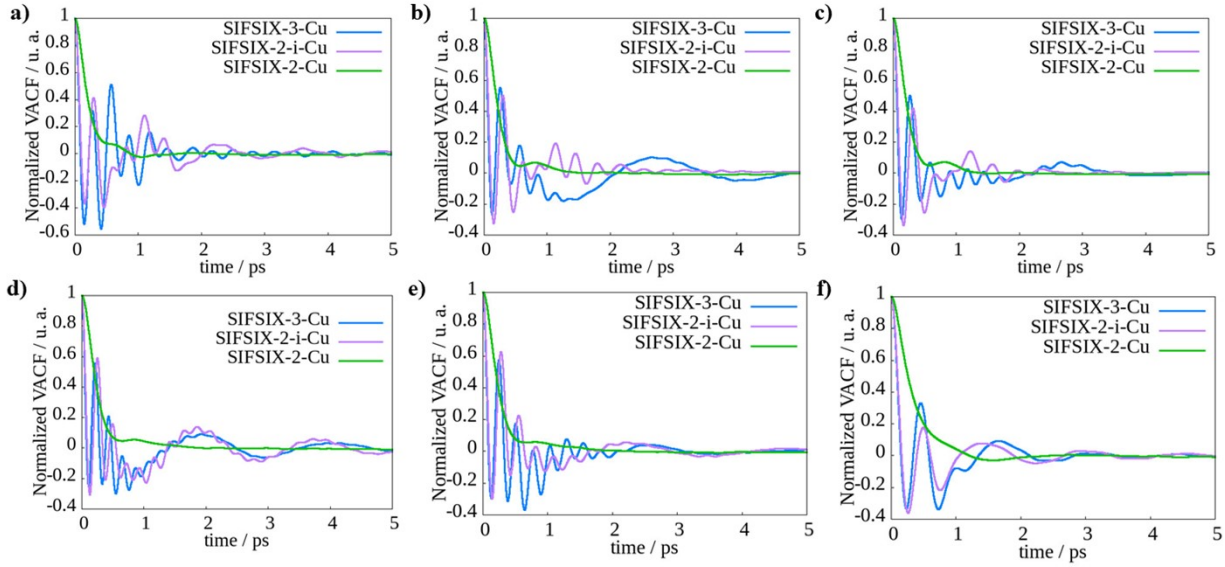

Figure S4: Plots of the normalized velocity autocorrelation function in function of time for 16 molecules of a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 in SIFSIX-3-Cu, SIFSIX-2-Cu-I and SIFSIX-2-Cu.

In addition to calculating the self-diffusion coefficients through linear regression of the mean square displacement and the Einstein equation, as presented in the manuscript, we have also determined them by integrating the Velocity Autocorrelation Function (VACF) curves. The corresponding results are provided in Table S8. The integration of the VACF curves is computed in RASPA software using a generalization of the Simpson's rule in which it is exact for cubic polynomials and is valid for an odd as well as even number of intervals[3].

Table S8. Self diffusion coefficients for 8, 16 and 32 molecules of methane, ethane, ethene, propane, propene and N_2 at SIFSIX-3-Cu, SIFSIX-2-Cu-i and SIFSIX-2-Cu.

Diffusion x 10^{-9} / $m^2 s^{-1}$							
MOFs	N° of molecules	Methane	Ethane	Ethene	Propane	Propene	N_2
SIFSIX-3-CU	8	2.26	7.29	6.27	-	-	1.03
	16	3.83	2.46	5.14	-	-	1.85
	32	2.56	0.83	3.76	-	-	1.23
SIFSIX-2-CU-i	8	6.40	17.7	7.75	1.27	6.28	3.25
	16	9.50	14.4	7.98	1.04	5.13	3.17
	32	3.94	9.14	5.94	0.89	4.12	2.34
SIFSIX-2-Cu	8	33.5	20.5	25.4	15.1	17.1	30.1
	16	29.9	19.0	19.4	13.2	14.6	26.1
	32	21.2	13.2	14.2	9.33	4.67	19.6

S7. Converged adsorption structures

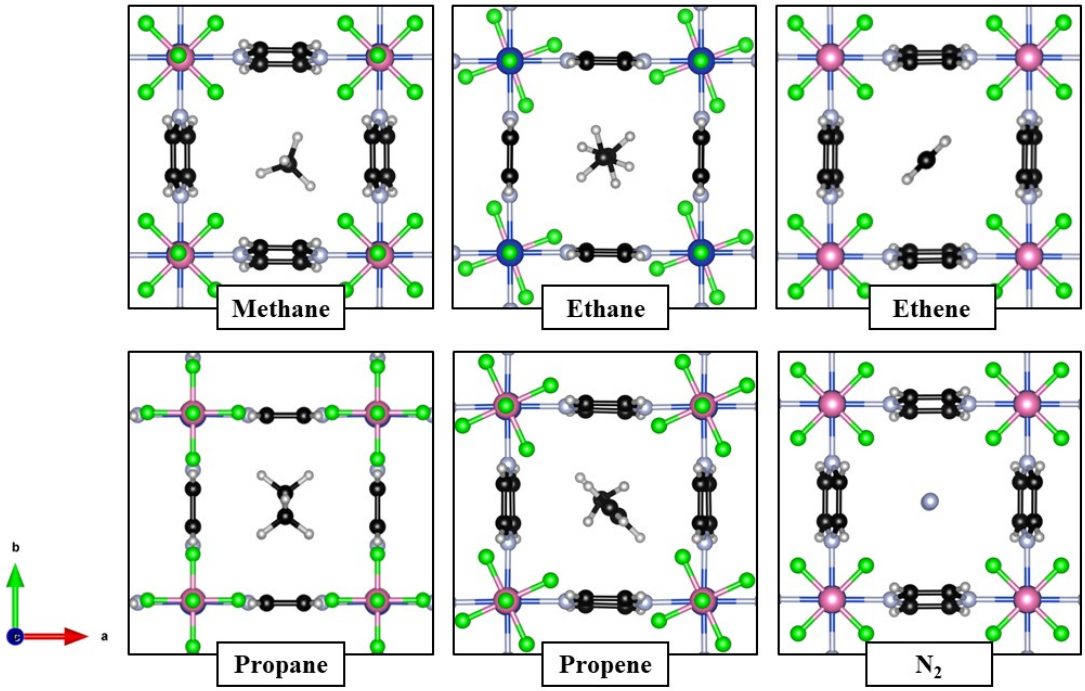

Figure S5: Converged structures for the adsorption of gas molecules in SIFSIX-3-Cu.

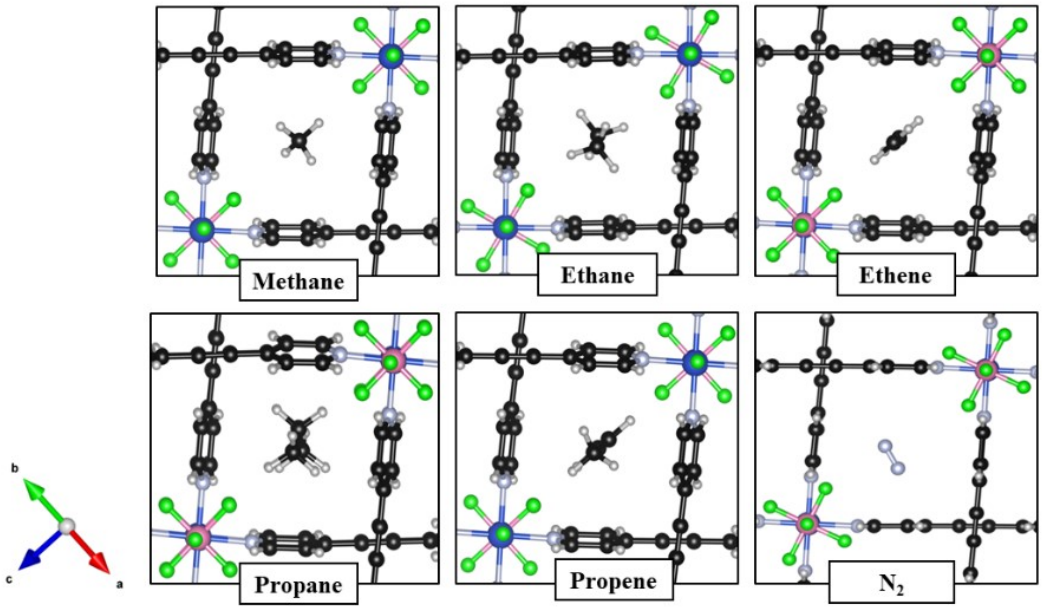

Figure S6: Converged structures for the adsorption of gas molecules in SIFSIX-2-Cu-i

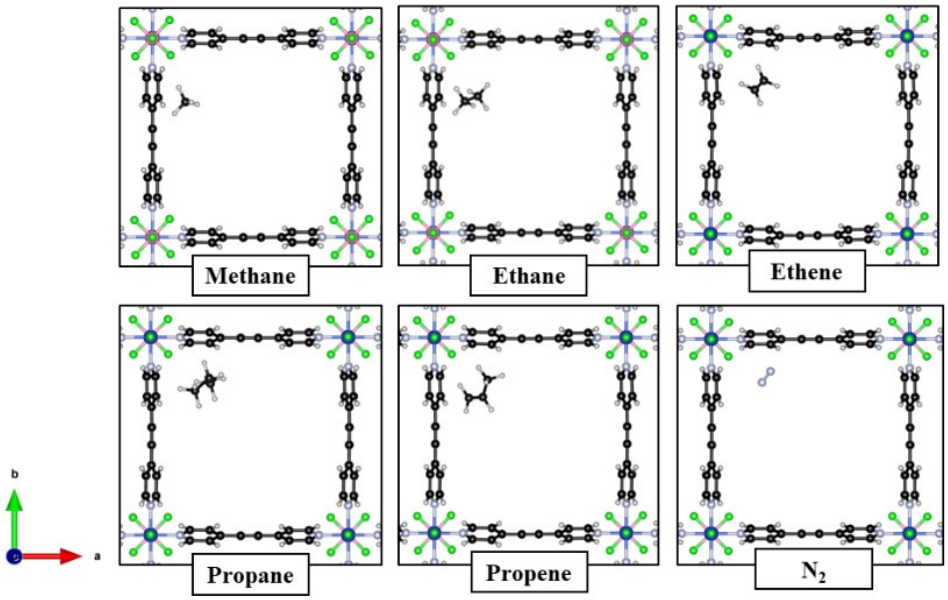

Figure S7: Converged structures for the adsorption of gas molecules in SIFSIX-2-Cu.

S8. Noncovalent interaction analysis

The noncovalent interaction (NCI) analysis calculations were performed in CRITIC2 software using the converged electronic density from DFT calculations. The visualization of NCI analysis was done in Visual Molecular Dynamics (VMD) software. Intramolecular interactions were not accounted.

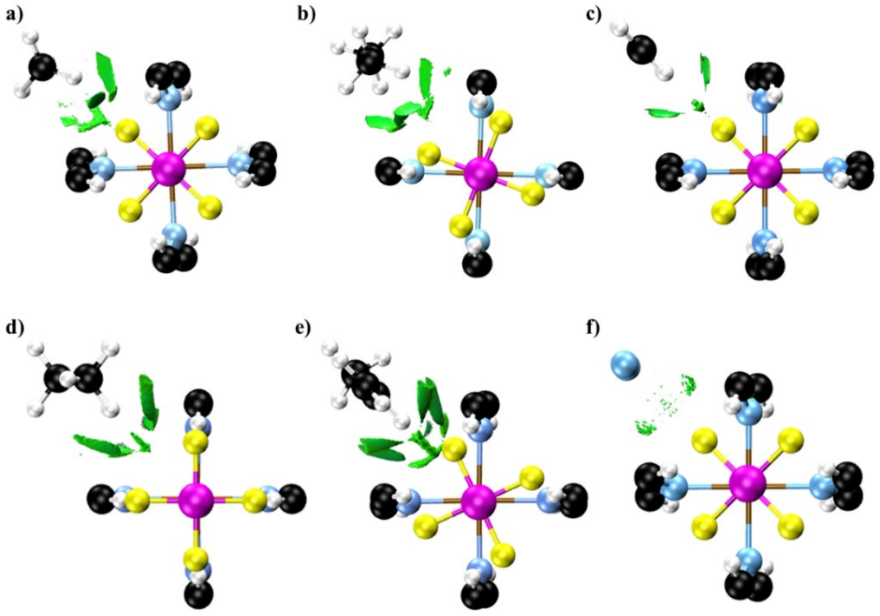

Figure S8: NCI plots of the adsorption of a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 in SIFSIX-3-Cu. The value of s for the isosurface level illustrated is 0.5 a.u. and the colour scale is $0.03 < \rho < 0.03$ a.u. Legend of atoms: carbon (black), hydrogen (white), nitrogen (light blue), copper (brown) and silicon (pink).

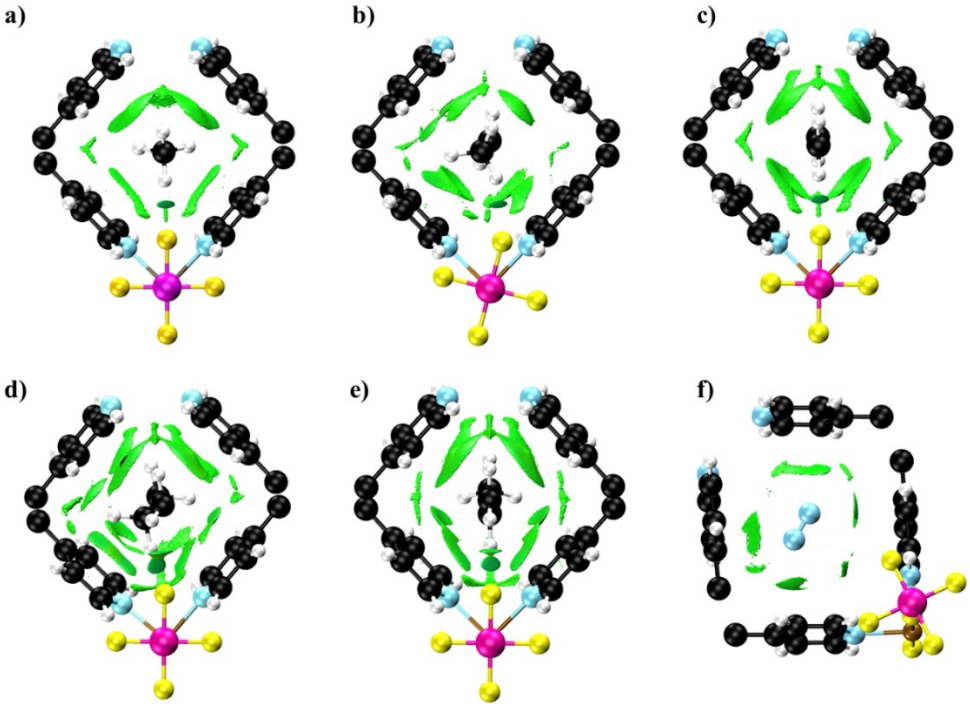

Figure S9: NCI plots of the adsorption of a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 in SIFSIX-2-Cu-i. The value of s for the isosurface level illustrated is 0.5 a.u. and the colour scale is $0.03 < \rho < 0.03$ a.u. Legend of atoms: carbon (black), hydrogen (white), nitrogen (light blue), copper (brown) and silicon (pink).

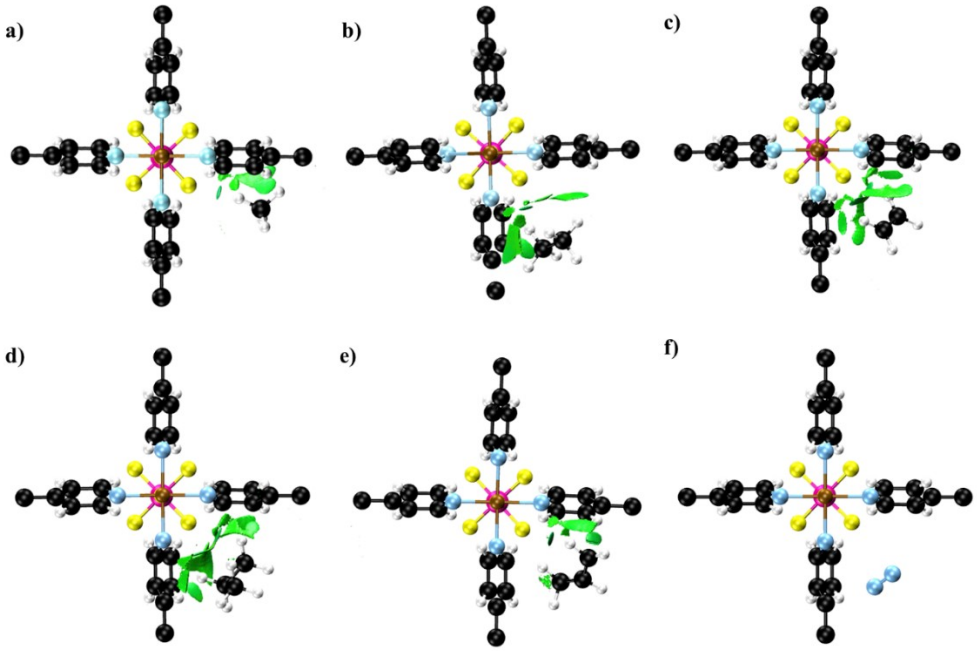

Figure S10: NCI plots of the adsorption of a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 in SIFSIX-2-Cu. The value of s for the isosurface level illustrated is 0.5 a.u. and the colour scale is $0.03 < \rho < 0.03$ a.u. Legend of atoms: carbon (black), hydrogen (white), nitrogen (light blue), copper (brown) and silicon (pink).

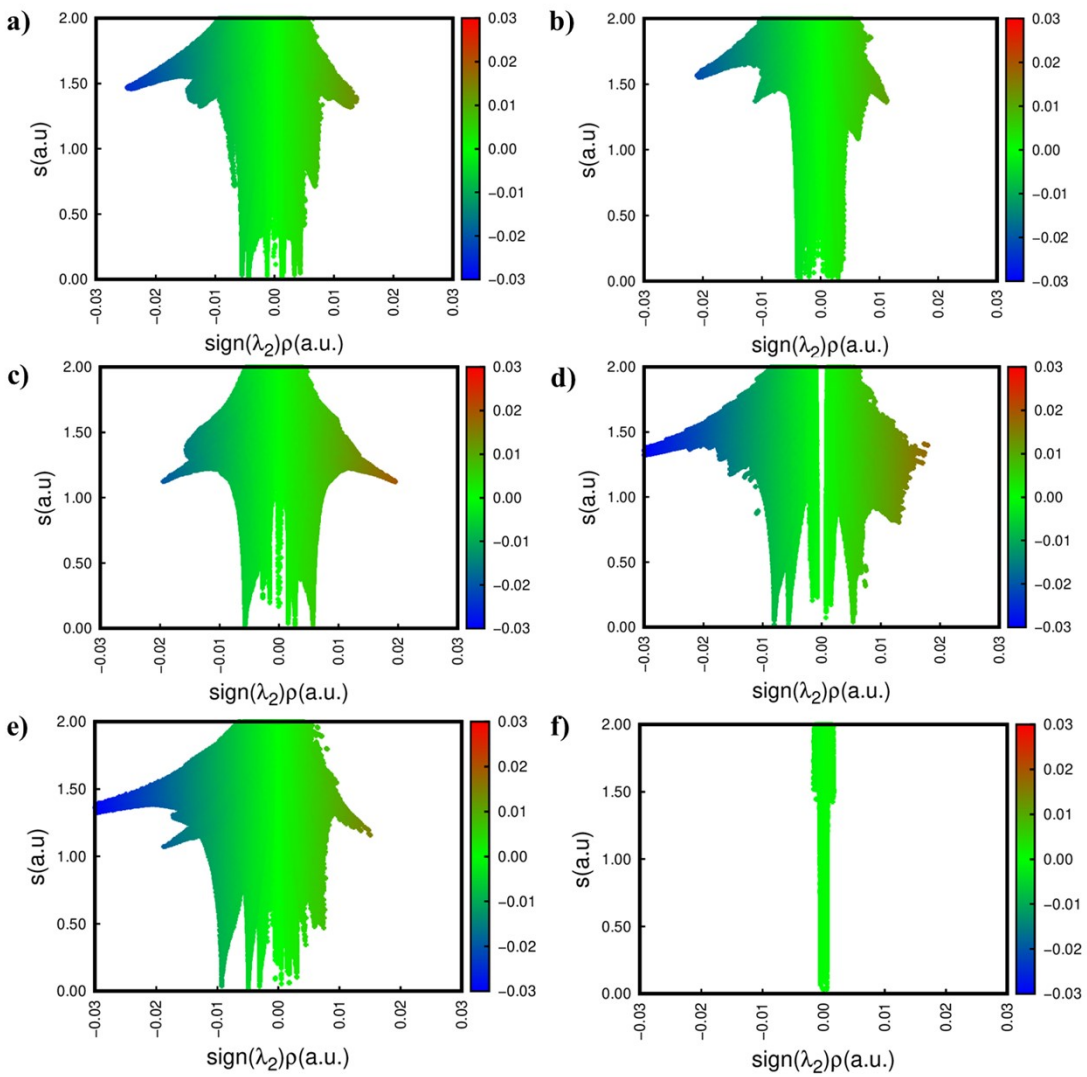

Figure S11: NCI colour maps for the adsorption a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 at SIFSIX-3-Cu MOF. The values of s and sign(λ_2)ρ which characterize ionic interactions, van der Waals interactions and steric clashes are in blue, green and red, respectively.

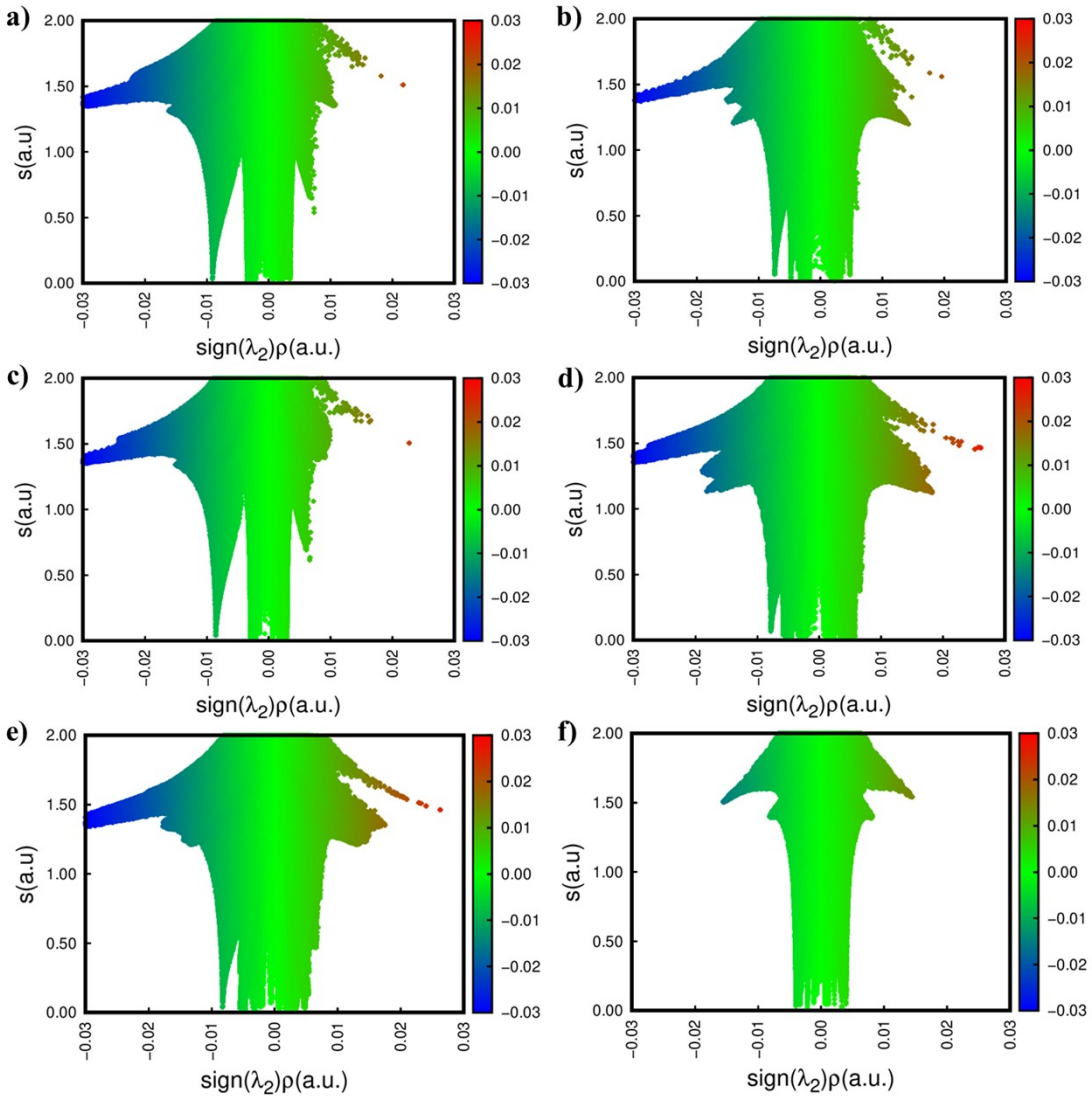

Figure S12: NCI colour maps for the adsorption a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 at SIFSIX-2-Cu-i MOF. The values of s and sign(λ_2)ρ which characterize ionic interactions, van der Waals interactions and steric clashes are in blue, green and red, respectively.

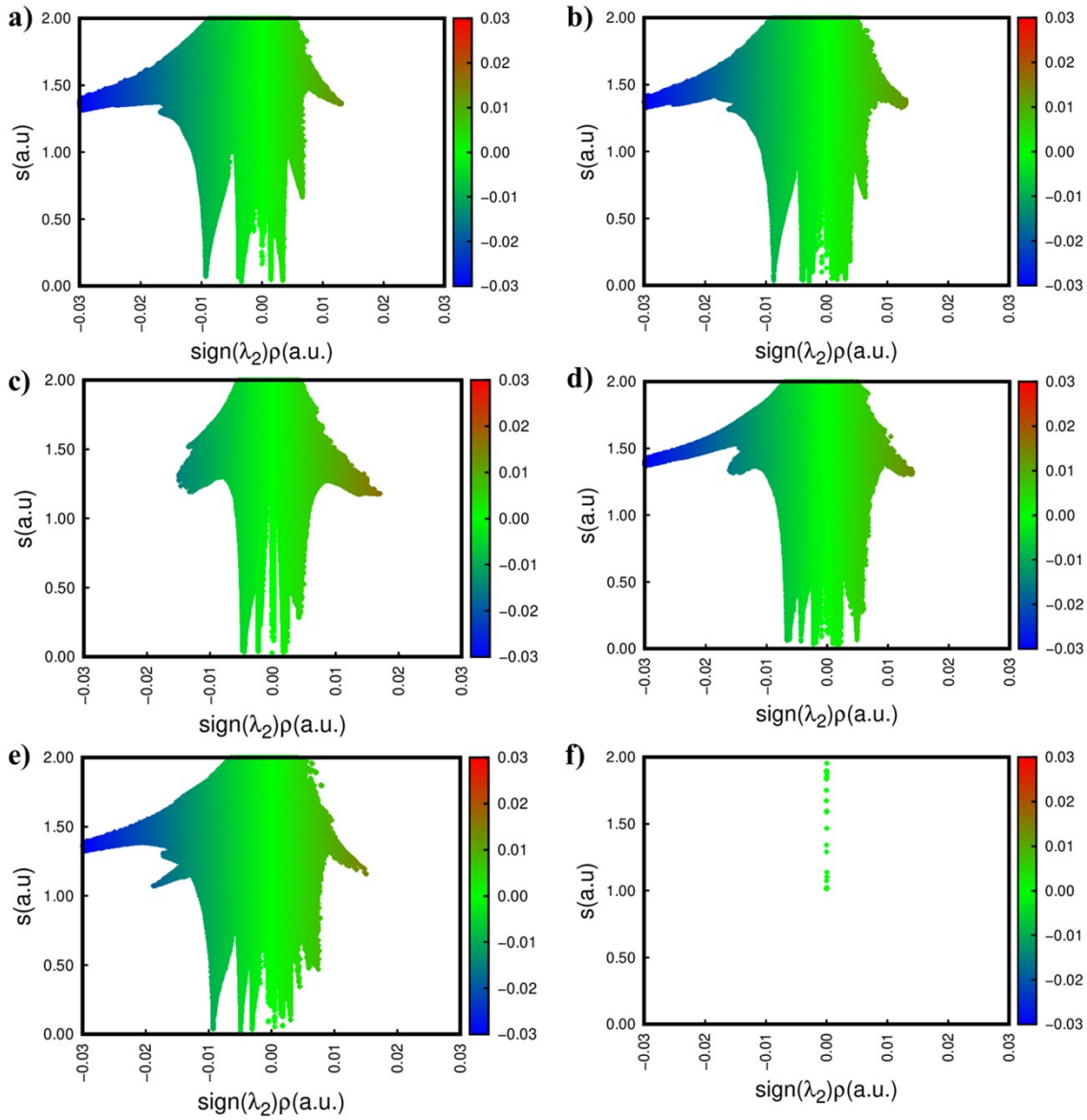

Figure S13: NCI colour maps for the adsorption a) methane, b) ethane, c) ethene, d) propane, e) propene and f) N_2 at SIFSIX-2-Cu MOF. The values of s and sign(λ_2)ρ which characterize ionic interactions, van der Waals interactions and steric clashes are in blue, green and red, respectively.

S9. Inputs

In this section, are presented the input files used for some of the performed calculations.

1. SIFSIX-3-Cu optimization input for Quantum ESPRESSO software.

```
&CONTROL
    calculation = 'vc-relax'
    title = 'SIFSIX-3-Cu'
    pseudo_dir = ''
    tprnfor = .TRUE.
    tstress = .TRUE.
    verbosity = 'high'
    nstep = 600
    etot_conv_thr = 1.0D-5
    forc_conv_thr = 1.0D-5
/
&system
    ibrav        = 6
    a            = 6.91860
    b            = 6.91860
    c            = 7.90610
    nat          = 28
    ntyp         = 6
    ecutwfc      = 60.0D0
    ecutrho      = 480.0D0
    nspin        = 1
    vdw_corr     = 'Grimme-D3'
    occupations  = 'smearing'
    degauss      = 0.02D0
    smearing     = 'gaussian'
/
&electrons
    conv_thr         = 1.0D-9
    mixing_mode      = 'local-TF'
    mixing_beta      = 0.5D0
    diagonalization  = 'david'
    startingwfc      = 'atomic+random'
    electron_maxstep = 600
/
&ions
    ion_dynamics      = 'bfgs'
    ion_positions     = 'default'
    pot_extrapolation = 'atomic'
    wfc_extrapolation = 'none'
/
&cell
    cell_dynamics = 'bfgs'
    cell_dofree   = 'all'
/
```

```
ATOMIC_SPECIES
F    18.998  f_pbe_v1.4.uspp.F.UPF
C    12.011  c_pbe_v1.2.uspp.F.UPF
H    1.008   h_pbe_v1.4.uspp.F.UPF
N    14.007  n_pbe_v1.2.uspp.F.UPF
Si   28.085  si_pbe_v1.uspp.F.UPF
Cu   63.546  cu_pbe_v1.2.uspp.F.UPF
ATOMIC_POSITIONS {crystal}
N    0.500000000000      0.217000000000     0.500000000000
C    0.500000000000      0.089300000000     0.384300000000
H    0.500000000000      0.140100000000     0.279800000000
Cu   0.500000000000      0.500000000000     0.500000000000
F    0.500000000000      0.500000000000     0.232000000000
F    0.331300000000      0.331300000000     0.000000000000
Si   0.500000000000      0.500000000000     0.000000000000
N    0.783000000000      0.500000000000     0.500000000000
C    0.910700000000      0.500000000000     0.384300000000
H    0.859900000000      0.500000000000     0.279800000000
F    0.668700000000      0.331300000000     0.000000000000
N    0.500000000000      0.783000000000     0.500000000000
C    0.500000000000      0.910700000000     0.384300000000
H    0.500000000000      0.859900000000     0.279800000000
F    0.668700000000      0.668700000000     0.000000000000
N    0.217000000000      0.500000000000     0.500000000000
C    0.089300000000      0.500000000000     0.384300000000
H    0.140100000000      0.500000000000     0.279800000000
F    0.331300000000      0.668700000000     0.000000000000
C    0.500000000000      0.910700000000     0.615700000000
H    0.500000000000      0.859900000000     0.720200000000
F    0.500000000000      0.500000000000     0.768000000000
C    0.089300000000      0.500000000000     0.615700000000
H    0.140100000000      0.500000000000     0.720200000000
C    0.500000000000      0.089300000000     0.615700000000
H    0.500000000000      0.140100000000     0.720200000000
C    0.910700000000      0.500000000000     0.615700000000
H    0.859900000000      0.500000000000     0.720200000000
K_POINTS automatic
4 4 4 1 1 1
```

2. SIFSIX-2-Cu optimization input for Quantum ESPRESSO software

```
&CONTROL
    calculation = 'vc-relax'
    title = 'SIFSIX-2'
    pseudo_dir = ''
    restart_mode = 'from_scratch'
    tprnfor = .TRUE.
    tstress = .TRUE.
    verbosity = 'high'
    nstep = 600
```

```
    etot_conv_thr = 1.0D-5
    forc_conv_thr = 1.0D-5
/
&system
    ibrav        = 6
    a            = 13.631600
    b            = 13.63160
    c            = 7.96800
    nat          = 52
    ntyp         = 6
    ecutwfc      = 50.0D0
    ecutrho      = 400.0D0
    nspin        = 1
    vdw_corr     ='Grimme-D3'
    occupations  = 'smearing'
    degauss      = 0.02D0
    smearing     = 'gaussian'
/
&electrons
    conv_thr         = 1.0D-9
    mixing_mode      = 'local-TF'
    mixing_beta      = 0.5D0
    diagonalization  = 'david'
    startingwfc      = 'atomic+random'
    electron_maxstep = 600
/
&ions
    ion_dynamics      = 'bfgs'
    ion_positions     = 'default'
    pot_extrapolation = 'atomic'
    wfc_extrapolation = 'none'
/
&cell
    cell_dynamics = 'bfgs'
    cell_dofree   = 'all'
/
ATOMIC_SPECIES
F    18.998  f_pbe_v1.4.uspp.F.UPF
C    12.011  c_pbe_v1.2.uspp.F.UPF
H    1.008   h_pbe_v1.4.uspp.F.UPF
N    14.007  n_pbe_v1.2.uspp.F.UPF
Si   28.085  si_pbe_v1.uspp.F.UPF
Cu   63.546  cu_pbe_v1.2.uspp.F.UPF
ATOMIC_POSITIONS {crystal}
Cu     0.500000000000     0.500000000000     0.000000000000
Si     0.500000000000     0.500000000000     0.500000000000
F      0.500000000000     0.500000000000     0.711300000000
C      0.500000000000     0.148600000000     0.000000000000
N      0.500000000000     0.351300000000     0.000000000000
F      0.396500000000     0.432300000000     0.500000000000
```

```
C      0.500000000000     0.044200000000     0.000000000000
C      0.851400000000     0.500000000000     0.000000000000
N      0.648700000000     0.500000000000     0.000000000000
F      0.567700000000     0.396500000000     0.500000000000
C      0.955800000000     0.500000000000     0.000000000000
C      0.698300000000     0.457500000000     0.876900000000
H      0.662800000000     0.427100000000     0.788400000000
C      0.798700000000     0.455800000000     0.872400000000
H      0.831900000000     0.424400000000     0.782400000000
C      0.500000000000     0.851400000000     0.000000000000
N      0.500000000000     0.648700000000     0.000000000000
F      0.603500000000     0.567700000000     0.500000000000
C      0.500000000000     0.955800000000     0.000000000000
C      0.542500000000     0.698300000000     0.876900000000
H      0.572900000000     0.662800000000     0.788400000000
C      0.544200000000     0.798700000000     0.872400000000
H      0.575600000000     0.831900000000     0.782400000000
C      0.148600000000     0.500000000000     0.000000000000
N      0.351300000000     0.500000000000     0.000000000000
F      0.432300000000     0.603500000000     0.500000000000
C      0.044200000000     0.500000000000     0.000000000000
C      0.301700000000     0.542500000000     0.876900000000
H      0.337200000000     0.572900000000     0.788400000000
C      0.201300000000     0.544200000000     0.872400000000
H      0.168100000000     0.575600000000     0.782400000000
F      0.500000000000     0.500000000000     0.288700000000
C      0.457500000000     0.698300000000     0.123100000000
H      0.427100000000     0.662800000000     0.211600000000
C      0.455800000000     0.798700000000     0.127600000000
H      0.424400000000     0.831900000000     0.217600000000
C      0.301700000000     0.457500000000     0.123100000000
H      0.337200000000     0.427100000000     0.211600000000
C      0.201300000000     0.455800000000     0.127600000000
H      0.168100000000     0.424400000000     0.217600000000
C      0.698300000000     0.542500000000     0.123100000000
H      0.662800000000     0.572900000000     0.211600000000
C      0.798700000000     0.544200000000     0.127600000000
H      0.831900000000     0.575600000000     0.217600000000
C      0.457500000000     0.301700000000     0.123100000000
H      0.427100000000     0.337200000000     0.211600000000
C      0.455800000000     0.201300000000     0.127600000000
H      0.424400000000     0.168100000000     0.217600000000
C      0.542500000000     0.301700000000     0.876900000000
H      0.572900000000     0.337200000000     0.788400000000
C      0.544200000000     0.201300000000     0.872400000000
H      0.575600000000     0.168100000000     0.782400000000
K_POINTS automatic
2 2 4 1 1 1
```

3. SIFSIX-2-Cu-i unit cell optimization input in Quantum ESPRESSO

```
&CONTROL
    calculation = 'vc-relax'
    title = 'sifsix-2-i'
    pseudo_dir = ''
    restart_mode = 'from_scratch'
    tprnfor = .TRUE.
    tstress = .TRUE.
    verbosity = 'high'
    nstep = 600
    etot_conv_thr = 1.0D-5
    forc_conv_thr = 1.0D-5
/
 &system
    ibrav        = 0
    nat          = 104
    ntyp         = 6
    ecutwfc      = 50.0D0
    ecutrho      = 400.0D0
    nspin        = 1
    vdw_corr     ='Grimme-D3'
    occupations  = 'smearing'
    degauss      = 0.02D0
    smearing     = 'gaussian'
/
&electrons
    conv_thr         = 1.0D-9
    mixing_mode      = 'local-TF'
    mixing_beta      = 0.5D0
    diagonalization  = 'david'
    startingwfc      = 'atomic+random'
    electron_maxstep = 600
/
 &ions
    ion_dynamics      = 'bfgs'
    ion_positions     = 'default'
    pot_extrapolation = 'atomic'
    wfc_extrapolation = 'none'
/
 &cell
    cell_dynamics = 'bfgs'
    cell_dofree   = 'all'
/
ATOMIC_SPECIES
Cu  63.55  cu_pbe_v1.2.uspp.F.UPF
Si  28.09  si_pbe_v1.uspp.F.UPF
F   19.00  f_pbe_v1.4.uspp.F.UPF
C   12.01  c_pbe_v1.2.uspp.F.UPF
N   14.00  n_pbe_v1.2.uspp.F.UPF
```

```
H    1.01  h_pbe_v1.4.uspp.F.UPF
CELL_PARAMETERS {angstrom}
 13.64900       0.00000       0.00000
  0.00000      13.64900       0.00000
  0.00000       0.00000       8.09200
ATOMIC_POSITIONS {crystal}
C       -0.000000   0.300100   0.354300
C       -0.000000   0.197800   0.362400
C        0.000000   0.456900   0.500000
C       -0.000000   0.351900   0.500000
C        0.699900  -0.000000   0.354300
C        0.802200  -0.000000   0.362400
C        0.543100  -0.000000   0.500000
C        0.648100  -0.000000   0.500000
C        0.000000   0.699900   0.354300
C       -0.000000   0.802200   0.362400
C       -0.000000   0.543100   0.500000
C       -0.000000   0.648100   0.500000
C        0.300100  -0.000000   0.354300
C        0.197800  -0.000000   0.362400
C        0.456900  -0.000000   0.500000
C        0.351900  -0.000000   0.500000
C        0.000000   0.699900   0.645700
C       -0.000000   0.802200   0.637600
C        0.300100  -0.000000   0.645700
C        0.197800   0.000000   0.637600
C       -0.000000   0.300100   0.645700
C        0.000000   0.197800   0.637600
C        0.699900  -0.000000   0.645700
C        0.802200   0.000000   0.637600
C        0.500000   0.800100   0.854300
C        0.500000   0.697800   0.862400
C        0.500000   0.956900   0.000000
C        0.500000   0.851900   0.000000
C        0.199900   0.500000   0.854300
C        0.302200   0.500000   0.862400
C        0.043100   0.500000   0.000000
C        0.148100   0.500000   0.000000
C        0.500000   0.199900   0.854300
C        0.500000   0.302200   0.862400
C        0.500000   0.043100   0.000000
C        0.500000   0.148100   0.000000
C        0.800100   0.500000   0.854300
C        0.697800   0.500000   0.862400
C        0.956900   0.500000   0.000000
C        0.851900   0.500000   0.000000
C        0.500000   0.199900   0.145700
C        0.500000   0.302200   0.137600
C        0.800100   0.500000   0.145700
C        0.697800   0.500000   0.137600
```

C	0.500000	0.800100	0.145700
C	0.500000	0.697800	0.137600
C	0.199900	0.500000	0.145700
C	0.302200	0.500000	0.137600
H	0.000000	0.333000	0.250800
H	0.000000	0.162400	0.261300
H	0.667000	-0.000000	0.250800
H	0.837600	0.000000	0.261300
H	0.000000	0.667000	0.250800
H	0.000000	0.837600	0.261300
H	0.333000	-0.000000	0.250800
H	0.162400	0.000000	0.261300
H	0.000000	0.667000	0.749200
H	0.000000	0.837600	0.738700
H	0.333000	0.000000	0.749200
H	0.162400	-0.000000	0.738700
H	-0.000000	0.333000	0.749200
H	-0.000000	0.162400	0.738700
H	0.667000	0.000000	0.749200
H	0.837600	-0.000000	0.738700
H	0.500000	0.833000	0.750800
H	0.500000	0.662400	0.761300
H	0.167000	0.500000	0.750800
H	0.337600	0.500000	0.761300
H	0.500000	0.167000	0.750800
H	0.500000	0.337600	0.761300
H	0.833000	0.500000	0.750800
H	0.662400	0.500000	0.761300
H	0.500000	0.167000	0.249200
H	0.500000	0.337600	0.238700
H	0.833000	0.500000	0.249200
H	0.662400	0.500000	0.238700
H	0.500000	0.833000	0.249200
H	0.500000	0.662400	0.238700
H	0.167000	0.500000	0.249200
H	0.337600	0.500000	0.238700
Cu	-0.000000	-0.000000	0.500000
Cu	0.500000	0.500000	0.000000
Si	0.000000	0.000000	0.000000
Si	0.500000	0.500000	0.500000
N	-0.000000	0.147600	0.500000
N	0.852400	-0.000000	0.500000
N	-0.000000	0.852400	0.500000
N	0.147600	-0.000000	0.500000
N	0.500000	0.647600	0.000000
N	0.352400	0.500000	0.000000
N	0.500000	0.352400	0.000000
N	0.647600	0.500000	0.000000
F	0.000000	0.000000	0.790800
F	-0.000000	-0.000000	0.209200

```
F        0.080592   0.915818   0.000000
F        0.095245   0.103300   0.000000
F        0.918680   0.088780   0.000000
F        0.912887   0.915818   0.000000
F        0.500000   0.500000   0.290800
F        0.586124   0.590007   0.500000
F        0.413626   0.417613   0.500000
F        0.500000   0.500000   0.709200
F        0.586124   0.410286   0.500000
F        0.411353   0.587977   0.500000
K_POINTS automatic
2 2 4 1 1 1
```

4. SIFSIX-2-Cu-I primitive reduced unit cell optimization input in Quantum ESPRESSO

```
&control
    calculation  = 'vc-relax'
    title        = 'sifsix-2-i-cu-reduzida'
    tstress      = .TRUE.
    tprnfor      = .TRUE.
    verbosity    = 'high'
    nstep        = 600
    etot_conv_thr = 1.0D-5
    forc_conv_thr = 1.0D-5
/
&system
    ibrav       = 0
    celldm(1)   = 10.4651
    nat         = 52
    ntyp        = 6
    ecutwfc     = 50.0D0
    ecutrho     = 400.0D0
    occupations = 'smearing'
    degauss     = 0.02D0
    smearing    = 'gaussian'
    nspin       = 1
    vdw_corr    = 'Grimme-D3'
/
&electrons
    electron_maxstep = 1000
    conv_thr         = 1.0D-9
    mixing_mode      = 'local-TF'
    mixing_beta      = 0.5D0
    diagonalization  = 'david'
    startingwfc      = 'atomic+random'
/
&ions
    ion_dynamics      = 'bfgs'
    ion_positions     = 'default'
```

```
    pot_extrapolation = 'atomic'
    wfc_extrapolation = 'none'
/
&cell
    cell_dynamics  =  'bfgs'
    cell_dofree    =  'all'
/
CELL_PARAMETERS {alat}
   1.765267422   0.062575629  -0.023429445
  -1.238696108   1.260667847  -0.021865727
  -0.263886994  -0.664199310   1.897093901
ATOMIC_SPECIES
Cu  63.55  cu_pbe_v1.2.uspp.F.UPF
Si  28.09  si_pbe_v1.uspp.F.UPF
F   19.00  f_pbe_v1.4.uspp.F.UPF
C   12.01  c_pbe_v1.2.uspp.F.UPF
N   14.00  n_pbe_v1.2.uspp.F.UPF
H    1.01  h_pbe_v1.4.uspp.F.UPF
ATOMIC_POSITIONS (angstrom)
N        0.116720447   4.331915025   1.029803135
C        0.291056859   5.487493980   1.708728291
C       -0.525045827   5.843777837   2.774773633
C       -1.558735649   4.972353764   3.169606764
C       -1.745429395   3.786640793   2.435120563
C       -0.894998775   3.504962852   1.374983785
C       -2.380930922   5.271845948   4.279666741
Cu       1.462564316   3.740965463  -0.403321023
F        0.613619699   1.690527430  -0.320386862
Si       0.002299219   0.076685916  -0.260392163
F        1.606319946  -0.531179259  -0.322589323
F        0.075203437   0.102314398   1.453641582
F       -0.070197754   0.047056446  -1.976884657
F        2.307514906   5.790336256  -0.454702430
F       -1.600896024   0.686123176  -0.205548076
N        2.782374297   3.248319225   1.081901323
C        2.901832569   1.957682060   1.465155785
C        3.695986824   1.578702090   2.538443219
C        4.411459933   2.564328844   3.242269065
C        4.296403321   3.902847550   2.818692199
C        3.471623897   4.204754072   1.743242590
C        5.226441652   2.217017967   4.342051904
C        3.774665855  -1.467833129   5.366392211
C        2.964633357  -1.162947002   6.483913251
C        1.988195444  -2.065610347   6.947658705
C        1.193655070  -1.708017006   8.029366855
N        1.335659954  -0.520411093   8.659063960
C        2.288828668   0.342779272   8.242140434
C        3.113783474   0.061195134   7.162080247
N       -1.327526530   0.548605026   8.625712205
C       -1.417156552   1.830876491   8.207764948
```

```
C       -2.238405605   2.204899960   7.153684377
C       -3.010420156   1.223530840   6.505672489
C       -2.924496567  -0.104910796   6.965388879
C       -2.070872119  -0.403518446   8.019120162
C       -3.842418665   1.566169849   5.417269953
H        2.335288749   1.219079046   0.900957097
H       -0.804527212   2.564502886   8.728607684
H        3.752475543   0.529899013   2.830198043
H       -2.271393932   3.245914334   6.831271517
H        3.353964489   5.231971372   1.395123138
H       -1.969063101  -1.424048279   8.390673528
H        0.421064585  -2.378752239   8.406935683
H        1.105723727   6.134997139   1.383018871
H        3.857297019   0.790388106   6.841110472
H       -2.537948120   3.085566226   2.695661524
H        2.375272641   1.283694466   8.784098774
H       -1.006609835   2.589421395   0.794412328
H        4.844475279   4.697837753   3.325436785
H       -3.513901023  -0.895781256   6.500432852
H        1.848758363  -3.033648675   6.465151717
H       -0.357532485   6.785150976   3.299275568
K_POINTS automatic
2 2 4  1  1  1
```

5. Input for GCMC calculations in RASPA software

```
SimulationType                MonteCarlo
NumberOfCycles                1000000
NumberOfInitializationCycles  50000

Forcefield                    Local
CutOffVDW                     12.0

ChargeMethod                  Ewald
CutOff                        12.0
EwaldPrecision                1e-6

Framework 0
FrameworkName sifsix-3-cu
UnitCells 1 1 1
HeliumVoidFraction 0.32
ExternalTemperature 300
ExternalPressure $i

UseChargesFromCIFFile         yes

Component 0 MoleculeName             methane
            MoleculeDefinition       TraPPE
            IdealGasRosenbluthWeight  1.0
            TranslationProbability    0.5
```

```
            RotationProbability       0.5
            ReinsertionProbability    0.5
            SwapProbability           0.5
            CreateNumberOfMolecules   0
```

6. Input for GCMC calculations for binary adsorption in RASPA software

```
SimulationType                MonteCarlo
NumberOfCycles                1000000
NumberOfInitializationCycles  50000

Forcefield                    Local
CutOffVDW                     12.0

ChargeMethod                  Ewald
CutOff                        12.0
EwaldPrecision                1e-6

Framework 0
FrameworkName sifsix-3-cu
UnitCells 1 1 1
HeliumVoidFraction 0.32
ExternalTemperature 300
ExternalPressure 1.0e5

UseChargesFromCIFFile         yes

Component 0 MoleculeName             methane
            MoleculeDefinition       TraPPE
            MolFraction               0.5
            TranslationProbability    0.5
            IdentityChangeProbability 1.0
              NumberOfIdentityCHanges 2
              IdentityChangesList     0 1
            IdealGasRosenbluthWeight  1.0
            TranslationProbability    0.5
            RotationProbability       0.5
            ReinsertionProbability    0.5
            SwapProbability           0.5
            CreateNumberOfMolecules   0

Component 1 MoleculeName             N2
            MoleculeDefinition       TraPPE
            MolFraction               0.5
            TranslationProbability    0.5
            IdentityChangeProbability 1.0
              NumberOfIdentityCHanges 2
              IdentityChangesList     0 1
            IdealGasRosenbluthWeight  1.0
            TranslationProbability    0.5
```

```
            RotationProbability       0.5
            ReinsertionProbability    0.5
            SwapProbability           0.5
            CreateNumberOfMolecules   0
```

7. Input for MC calculations in NVT ensemble in RASPA software

```
SimulationType                MonteCarlo
NumberOfCycles                1000000
NumberOfInitializationCycles  100000
RestartFile                   no

Ensemble                      NVT

Forcefield                    GenericMOFs
UseChargesFromCIFFile         yes

Framework 0
FrameworkName sifsix-3-cu
UnitCells 1 1 1
HeliumVoidFraction 0.32
ExternalTemperature 300.0
ExternalPressure 0.0

Component 0 MoleculeName             methane
            MoleculeDefinition       TraPPE
            TranslationProbability   0.5
            RotationProbability      0.5
            ReinsertionProbability   0.5
            CreateNumberOfMolecules  1
```

8. Input for MD calculations in RASPA software

```
SimulationType                MD
NumberOfCycles                10000000
NumberOfInitializationCycles  200000
NumberOfEquilibrationCycles   500000

Ensemble                      NVT
ChargeMethod                  Ewald
CutOff                        12.0
EwaldPrecision                1e-6
TimeStep                      0.0005

Forcefield                    GenericMOFS
CutOffVDW                     12.0

Framework                     0
FrameworkName                 sifsix-3-cu
```

```
UseChargesFromCIFFile         yes
UnitCells                     1 1 1
HeliumVoidFraction            0.32
ExternalTemperature           298
ExternalPressure              0.0

ComputeMSD yes
PrintMSDEvery 100
ComputeVACF yes
WriteVACFEvery 100

Component 0 MoleculeName              methane
            StartingBead              0
            MoleculeDefinition        TraPPE
            IdealGasRosenbluthWeight  1.0
            FugacityCoefficient       1.0
            TranslationProbability    1.0
            ReinsertionProbability    1.0
            CreateNumberOfMolecules   $I
```

9. Force Field mixing rules file for methane adsorption in SIFSIX serie of MOFs employing UFF+DREIDING force fields.

```
# general rule for shifted vs truncated
truncated
# general rule tailcorrections
no
# number of defined interactions
7
# type interaction
Cu_             lennard-jones     2.5161   3.11369
N_              lennard-jones    38.9492   3.26256
C_              lennard-jones    47.8562   3.47299
H_              lennard-jones     7.6489   2.84642
Si_             lennard-jones   202.290    3.8264
F_              lennard-jones    36.4834   3.0932
CH4_sp3         lennard-jones   148.0      3.78
# general mixing rule for Lennard-Jones
Lorentz-Berthelot
```

S10. References

[1] O. Shekhah *et al.*, "Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture", *Nat Commun*, vol. 5, no. May, pp. 1–7, 2014, doi: 10.1038/ncomms5228.

[2] P. Nugent *et al.*, "Porous materials with optimal adsorption thermodynamics and kinetics for co2 separation", *Nature*, vol. 495, no. 7439, pp. 80–84, 2013, doi: 10.1038/nature11893.

[3] D. Dubbeldam, S. Calero, T. J. H. Vlugt, D. E. Ellis, and R. Q. Snurr, “RASPA 2.0.45: Molecular Software Package for Adsorption and Diffusion in (Flexible) Nanoporous Materials”, 2021.