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Highly tunable sulfur hexafluoride separation by interpenetration control in Metal Organic Frameworks

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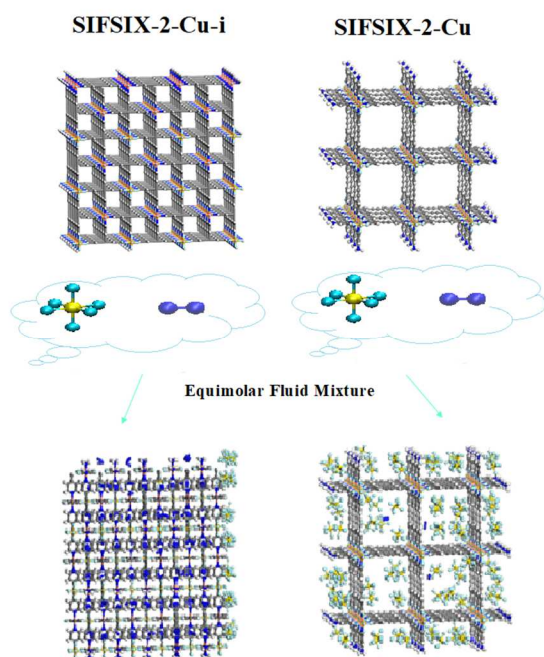
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Abstract

The separation of fluid SF₆ / N₂ mixtures using the recently synthesized metal-organic framework SIFSIX-2-Cu and its interpenetrated polymorph SIFSIX-2-Cu-i has been systematically studied by employing Monte Carlo and Molecular Dynamics simulations. These predictions revealed that SIFSIX-2-Cu shows a high thermodynamic adsorption selectivity for SF₆ over N₂ combined with one of the highest SF₆ uptakes reported so far for an adsorbent. On the other hand, the smaller pore dimensions of the interpenetrated network cause a molecular sieving effect, allowing only the adsorption of N₂. Furthermore, the self-diffusivity of the adsorbed SF₆ molecules in the SIFSIX-2-Cu framework was predicted to be significantly lower than the one corresponding to N₂, while the smaller pore channel network of SIFSIX-2-Cu-i decreases the self-diffusivity of N₂ by a factor of about 6. This study revealed that controlling the interpenetration in MOFs is an efficient way to tune their separation performances for strategic gas mixtures.

Graphical Abstract



Keywords: sulfur hexafluoride, nitrogen, gas separation, metal-organic frameworks, framework interpenetration, SIFSIX-2-Cu-i, SIFSIX-2-Cu, Monte Carlo simulations, Molecular Dynamics simulations.

Highlights

- The separation of SF₆/N₂ fluid mixtures has been studied.
- The SIFSIX-2-Cu and its interpenetrated polymorph SIFSIX-2-Cu-i have been systematically examined.
- Force field-based Monte Carlo and molecular dynamics simulation techniques have been employed.
- A high thermodynamic adsorption selectivity for SF₆ over N₂ in the case of SIFSIX-2-Cu has been revealed.
- The smaller pore dimensions of the interpenetrated SIFSIX-2-Cu-i network cause a molecular sieving effect, allowing only the adsorption of N₂.

1. Introduction

Owing to its high dielectric strength and arc-quenching properties, low toxicity and high stability, sulfur hexafluoride (SF₆) is the most widely used insulating and switching medium for electrical power transmission equipment and several other applications, especially under high voltage [1-6]. However, SF₆ is a very potent greenhouse gas due to its very long atmospheric lifetime [2] (3200 years) and its high efficiency as an infrared absorber [6]. This gas shows one of the highest global warming potentials, 24000 times higher than CO₂ and it is amongst the main anthropogenic greenhouse gases [7]. In this context, the Kyoto protocol aims to reduce its emission [7]. Furthermore, SF₆ falls also under the European F-Gas regulation limiting its use in diverse fields [5]. Therefore, there is a critical need to reduce the use of SF₆ as an insulator in high voltage and circuit breakers. The current alternative consists of considering a pressurized gas mixture, where a low content of SF₆ is mixed with ordinary gases such as N₂, CO₂ or air [8]. It was demonstrated that when mixing SF₆ with N₂, the fluid mixture maintains the high dielectric strength of pure SF₆, even at high N₂ concentration [9]. However, when mixing these two fluids the complexity of recovering and recycling SF₆ increases [4] and this holds even more true when the amount of SF₆ in the mixture decreases [9]. In this case, the development of efficient processes for the separation of SF₆/ N₂ mixtures is required.

Adsorption [4-6,10-17] and membrane [8,18-21] based-separation have been recently proposed as low energy and cost alternative recovery methods to liquefaction using refrigeration [13]. The efficiency of such processes strongly relies on the choice of the optimal adsorbents combining fast permeability and high thermodynamic selectivity for the gas of interest. Several porous materials, such as zeolites, metal-organic frameworks (MOFs), carbon nanopores and porous organic cages have been envisaged for the separation of SF₆/ N₂ mixtures. The most selective materials reported so far are zeolites FAU-ZTC [4] and 13X [10], a series of isostructural M-MOF-74 materials with a high density of unsaturated metal sites [11] and the CC3 porous organic cage [15]. The SF₆/ N₂ separation ability of these materials was attributed to a combination of fluid/pore interactions and pore dimensions, as well as to the flexible nature of the molecular cage crystal.

More specifically, MOFs appear as a promising family of custom-designed adsorbents able to efficiently capture strategic gases of utmost importance in diverse energy and environment-related applications [22,23]. The large variety of metal ions and organic ligands presents tremendous opportunities to design novel and fascinating entangled architectures, toward task-specific applications. MOFs showing interpenetrated networks correspond to the sub-class of MOFs that have been by far much less investigated for their potential uses in diverse applications [24,25]. Indeed, the structural interpenetration, closely associated with the pore shape/dimension of the adsorbent is expected to play a predominant role in the molecular separation process by favoring (i) a thermodynamically-driven capture via a subtle control of the degree of confinement and hence of the strength of the host/guest interactions, and/or (ii) a size exclusion via a strict control of the pore size to selectively adsorb only the smaller molecule of the mixture.

In this context, Eddaoudi *et al* reported recently a crystal engineering strategy controlling the pore functionality and size in a series of MOFs, by pillaring two-dimensional nets of organic ligands and metal nodes with hexafluorosilicate (SiF_6^{2-}) anions to form three-dimensional networks with primitive cubic (pcu) topology [26]. The pore size of this family of fluorinated MOFs, resembling pillared square grids, was tuned by either changing the length of the organic linker and/or the metal node, or using the framework interpenetration approach. In this study, $[\text{Cu}(4,4'\text{-dipyridylacetylene})_2(\text{SiF}_6)]_n$, named as SIFSIX-2-Cu, was reported as a one-dimensional square channel-like MOF with a pore dimension of 13.05 Å. Interestingly an interpenetrated polymorph isostructural to SIFSIX-2-Cu, named as SIFSIX-2-Cu-i, composed of double interpenetrated nets was also discovered. The independent nets are staggered with respect to one another, significantly reducing the dimension of the one-dimensional square pore channels to 5.15 Å. SIFSIX-2-Cu-i was demonstrated earlier [26] to remain in its pristine interpenetrated form after evacuation of solvent. This material, with a permanent porosity associated with an apparent BET area of 735 m²/g, as well as all this family of fluorinated MOFs was shown to be an ideal platform for the selective capture of CO₂ over a wide range of mixtures including CO₂/CH₄, CO₂/N₂ and CO₂/H₂ [26,27]. These findings motivated us to perform a computational exploration of the efficiency of this SIFSIX series of materials for the separation of the SF₆/N₂ mixtures at ambient conditions, particularly

focusing on the impact of the interpenetrated network. Note that although only a few MOFs have been tested so far for the separation of SF₆/ N₂ mixtures [4-6,10-17], some of them outperform other adsorbents such as zeolites and carbon-based materials [6]. Indeed some studies suggested that MOFs with small pore sizes might be adequate for trapping SF₆ at low concentrations whereas MOFs with larger pore sizes will be adequate for the storage of this molecule [6].

2. Computational Methods

A combination of force field-based Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations was employed in order to explore the adsorption of SF₆ and N₂ as single fluids in the SIFSIX-2-Cu and SIFSIX-2-Cu-i MOFs and the separation of the SF₆/ N₂ binary mixtures (two bulk molar compositions SF₆/N₂: 1:1 and 1:9) at 303 K, and in the pressure range 0.1-10 bar. Well-established all-atom rigid potential models for SF₆ [28] and N₂ [29] have been selected. The microscopic models for the MOFs, including the force field parameters, were defined following the same strategy than in our previous works [27,30]. More specifically, the CHELPG atomic charges were extracted from cluster-based density functional theory (DFT) calculations [27] while the sigma and epsilon 12-6 Lennard-Jones (LJ) parameters were taken from the literature, the LJ parameters from the DREIDING [31] and the UFF [32] force fields being assigned to the atoms of the organic and inorganic building blocks of the MOF, respectively (see Ref. 27 for more details). Lorentz-Berthelot combining rules were employed for the LJ interactions between the different atoms of the MOF/guest pairs. The SIFSIX-2-Cu-i supercell used in our simulation studies has been taken from our previous work [27] and comprised 3x3x5 unit cells. The SIFSIX-2-Cu supercell constituted by a 3x3x5 replica of its unit cell, which was initially geometry optimized at the periodic DFT level. The employed density functional was the PBE [33] with the D3 dispersion correction introduced by Grimme [34]. A hybrid Gaussian and plane waves approach, as implemented in the Quickstep module [35] of the cp2k code [36] was employed, using the DZVP-MOLOPT basis set [37] and the Goedecker-Teter-Hutter pseudopotentials [38] for the electronic structure calculations. The density cut-off was set to 500 Ry to yield well converged calculations. The supercell was saturated by adding terminal -NH₂ groups and the charges of the terminal atoms were adjusted in order to give a total zero charge to the supercell. The names of the different

interaction sites corresponding to a model building block of SIFSIX-2-Cu are presented in Figure 1. The force field parameters are also provided in Tables 1-3.

The GCMC simulations were carried out with the Complex Adsorption and Diffusion Simulation Suite (CADSS) code [39]. The fugacities for each adsorbed species at the investigated thermodynamic conditions were calculated using the Peng-Robinson equation of state [40]. For each simulated state point, 2×10^8 Monte Carlo steps were used for the equilibration and production runs. Several types of trial molecular moves were taken into account: translation or rotation, creation or deletion and exchange of molecular identity. MD simulations were further performed in the canonical NVT ensemble to explore the diffusivity of the guest molecules in both SIFSIX-2-Cu and SIFSIX-2-Cu-i. The equations of motion were integrated using a leapfrog-type Verlet algorithm [14] and the integration time step was set to 1 fs. The intramolecular geometry of SF₆ and N₂ molecules was constrained using the quaternion formalism [41]. A Nose-Hoover thermostat [42] with a temperature relaxation time of 0.2 ps was used to constrain the temperature during the simulations. All MD simulations were run for 20 ns, after a 10 ns equilibration period, using the DL_POLY simulation code [43].

3. Results and Discussion

The simulated isotherms of SF₆ and N₂ as single components are first reported for both SIFSIX materials in Figure 2a. These data evidence that SIFSIX-2-Cu-i only adsorbs N₂ since the pore size of this interpenetrated framework is small enough to exclude the adsorption of the bulkiest SF₆ molecule. Further, the adsorption profile for SIFSIX-2-Cu suggests that this MOF shows a much higher affinity for SF₆ vs N₂ leading to only a negligible amount of N₂ adsorbed in its pores. This trend was further supported by the calculated adsorption enthalpies at low coverage, which are -22.1 kJ/mol and -9.1 kJ/mol for SF₆ and N₂ respectively. As a further step, the co-adsorption isotherms were simulated for two SF₆/N₂ molar mixtures (1:1 and 1:9) in both SIFSIX materials as reported Figures 2b-c, respectively. **Note that in all cases the pressure in the x-axis is the total pressure of the system.** These results confirmed the higher affinity for SF₆ adsorption in SIFSIX-2-Cu. This behavior is again supported by a much higher adsorption enthalpy at low coverage for SF₆ (-21.4 kJ/mol, 1:1 bulk molar mixture) vs N₂ (-9.2 kJ/mol, 1:1 bulk molar mixture) that supports a

thermodynamic-driven separation mechanism. A high SF₆/N₂ selectivity was simulated in the whole range of pressures (Figure 3), with a maximum of about 43 (bulk molar mixture 1:1) and 41 (bulk molar mixture 1:9) at pressures of 1.5 bar and 7 bar respectively. Again, in this case, as in Figure 2, the pressure in the x-axis is the total pressure of the mixture. The presence of this maximum for both mixture compositions can be interpreted as a result of a competitive adsorption at high pressures, where due to packing effects the adsorption of N₂ in the pore becomes easier, whereas at lower pressures the thermodynamic-driven separation mechanism is the predominant one. The shift of the selectivity maximum at higher pressures in the case of the 1:9 bulk molar mixture can be explained in terms of the lower bulk composition of SF₆, leading to a lower uptake of SF₆ and a higher uptake of N₂, as observed in Figure 2 c. Due to the lower SF₆ uptake, packing effects are more important at higher pressures, leading therefore to this shift of the selectivity maximum.

Note that for the 1:9 molar composition, the selectivity obtained for SIFSIX-2-Cu at 1 bar (~25) is similar than the values reported for the Mg-, Co- and Zn-MOF-74 at 308 K [11] (~20, 30 and 40, respectively). The selectivity for the 1:1 composition at ambient pressure is also comparable to the previously reported ones for Mg- and Co-MOF-74 [11] (~30 and 60, respectively) and the EMT-ZTC zeolite (~60) [4], while still remaining lower than that reported for other porous solids including the CC3 porous organic cage [15] (~200) and the FAU-ZTC zeolite [4] (~130). However, interestingly SIFSIX-2-Cu shows a much larger SF₆ uptake as compared with other materials [6,11], while the relatively moderate SF₆ adsorption enthalpy suggests a rather easy regeneration. A very recent publication [44] lists the most efficient adsorbents in terms of SF₆ uptake and SF₆/N₂ selectivity. It comes that SIFSIX-2-Cu is one the most efficient adsorbents reported so the capture of SF₆ combining an extremely large SF₆ uptake and a high SF₆/N₂ selectivity. All together, these features make this material as a promising candidate to selectively adsorb SF₆ from N₂ via a thermodynamic-driven separation mechanism. On the other hand, the interpenetrated SIFSIX-2-Cu-i allows a complete exclusion of SF₆ via a molecular sieving effect with only N₂ entering the pores leading to an infinite N₂/SF₆ selectivity.

The GCMC simulations allowed us to shed light in the co-adsorption mechanism at the microscopic level. The preferential adsorption of SF₆ over N₂ in the SIFSIX-2-Cu

MOF was confirmed by the shape and intensities of the calculated guest-pore atom-atom radial distribution functions (RDF). Some representative RDF, corresponding to the thermodynamically adsorbed fluids (equimolar bulk mixture composition) at 1 bar and 303 K in the SIFSIX-2-Cu and SIFSIX-2-Cu-i nanopores, are presented in Figure 4. Note that these plotted data illustrate the most representative interactions observed in the system.

These RDFs clearly confirm that the different adsorption sites of SIFSIX-2-Cu, particularly the C₁ and C₄ atoms of the pyridine rings, preferentially interact with SF₆ since the intensities of the main peaks, which are correlated with the strength of interactions, are higher than that corresponding to N₂ (Figures 4a, b). This can be clearly observed especially in the shape of the C₁-F and C₁-N RDFs for which two sharp peaks are located at 3.5 and 5.5 Å in the case of the C₁-F RDF (Figure 4a) and a low-intensity peak is present at 4.4 Å in the case of the C₁-N RDF (Figure 4b). This behavior is consistent with the higher adsorption enthalpy calculated for SF₆. When also comparing the RDFs for the N₂/MOF pair (Figures 4b, c), it can be clearly seen that the peaks become sharper and with a higher intensity in the case of the interpenetrated framework, exhibiting the strongest interaction with the C₁ atoms of the pyridine rings but also more pronounced interactions with the fluorine atoms, as it can be seen in Figure 4c. In the case of SIFSIX-2-Cu-i, the F-N RDF exhibits a sharp peak located at 3.4 Å, whereas in the case of SIFSIX-2-Cu (Figure 4b) the corresponding RDF exhibits a relatively low-intensity peak. This increase of the peak intensity of all the RDFs can be interpreted in terms of the higher confinement degree felt by N₂ in the small pore diameter of SIFSIX-2-Cu-i, which is also consistent with the significant increase of the adsorption enthalpy of N₂ at low coverage (-24.5 kJ/mol) as compared to the value obtained in the non-interpenetrated phase (-9.2 kJ/mol). Analysis of these data explains the higher N₂ uptake in the interpenetrated SIFSIX-2-Cu-i MOF, in comparison with SIFSIX-2-Cu, for all investigated bulk fluid compositions, as depicted in Figure 2.

Representative snapshots of the GCMC simulations, depicting the preferential adsorption of SF₆ in the SIFSIX-2-Cu material and the exclusion of SF₆ molecules via molecular sieving in the case of the interpenetrated SIFSIX-2-Cu-i framework are presented in Figure 5 for the case of the equimolar bulk mixture. As it can be clearly observed in Figure 5a, the large pores of SIFSIX-2-Cu allow the adsorption of both

SF₆ and N₂ molecules and the thermodynamic-driven separation mechanism determines the preferential adsorption of SF₆. Figure 5b illustrates the preferential interaction between SF₆ and the carbon atoms of the organic linker with characteristic host/guest distances of about 3 Å consistent with the corresponding RDFs reported in Figure 4. On the other hand, as it can be clearly observed from Figure 5c, the small pore size of SIFSIX-2-Cu-i causes the complete exclusion of the larger size SF₆ molecules, allowing only the adsorption of N₂.

Molecular Dynamics simulations were further performed in the canonical NVT ensemble, using the calculated SF₆ and N₂ uptakes corresponding to 1 bar and an equimolar bulk mixture composition, to explore the diffusivity of the guest molecules in both SIFSIX-2-Cu and SIFSIX-2-Cu-i. The self-diffusion coefficients of SF₆ and N₂ were calculated using the well-known Einstein relation applied to the mean-square displacements (MSDs) for both guests averaged over all the MD trajectories and using a multi-time step origin. The corresponding MSDs are presented in Figure 6. In the case of SIFSIX-2-Cu, this led to $D_s(\text{SF}_6)$ and $D_s(\text{N}_2)$ values of $2.50 \cdot 10^{-9}$ and $14.90 \cdot 10^{-9}$ m²/s, respectively, resulting in a self-diffusivity ratio of ~6. This finding indicates that SIFSIX-2-Cu equally exhibits a satisfactory kinetic selectivity. Interestingly, the self-diffusivity for N₂ in the interpenetrated SIFSIX-2-Cu-i framework drops down to the value of $2.59 \cdot 10^{-9}$ m²/s. These differences are clearly reflected on the calculated MSDs (Figure 6). The combination of the decrease of the pore dimensions of SIFSIX-2-Cu-i with the strengthening of the fluid-pore interactions, can be considered as the main reason for this significant decrease of the self-diffusion coefficient for N₂.

4. Conclusions

In summary, the present study revealed the predominant effect of the interpenetration of the MOF network on the separation of the SF₆/N₂ mixture. A high thermodynamic and kinetic adsorption selectivity for SF₆ over N₂ has been observed in the case of SIFSIX-2-Cu, whereas the steric hindrance due to the much smaller pore dimensions of the interpenetrated SIFSIX-2-Cu-i framework induces a molecular sieving effect, allowing only the adsorption of N₂. This computational exploration paves the way towards the identification of adsorbents highly selective for this strategic gas mixture

that has been only rarely explored so far using a physisorption-based separation process.

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TABLES

Table 1: Partial charges and Lennard-Jones parameters corresponding to each type of atoms in the SIFSIX-2-Cu-i and SIFSIX-2-Cu supercells. For the terminal nitrogen and hydrogen atoms the symbols NT and HT have been used, respectively. The charges of the terminal nitrogen atoms NT of the SIFSIX-2-Cu supercell have been slightly adjusted to give a total zero charge to the supercell. The different carbon types C₁-C₄ are depicted in Figure 1 in the manuscript.

Interaction Site	q (e)	σ (Å)	ϵ (K)
Cu	0.700	3.2950	2.5178
Si	0.734	3.8264	202.2900
F	-0.370	3.0930	36.4830
N	-0.182	3.6621	38.9750
NT (SIFSIX-2-Cu-i)	-0.69635	3.6621	38.9750
NT (SIFSIX-2-Cu)	-0.561875	3.6621	38.9750
H	0.136	2.8464	7.6490
HT	0.276	2.8464	7.6490
C₁	-0.226	3.4730	47.8570
C₂	0.088	3.4730	47.8570
C₃	-0.140	3.4730	47.8570
C₄	0.300	3.4730	47.8570

Table 2: Partial charges and Lennard-Jones parameters corresponding to each type of interaction sites in the SF₆ molecule.

Interaction Site	q (e)	σ (Å)	ε (K)
S	0.66	3.228	165.14
F	-0.11	2.947	27.02

S-F Bond Length: 1.564 Å

Table 3: Partial charges and Lennard-Jones parameters corresponding to each type of interaction sites in the N₂ molecule.

Interaction Site	q (e)	σ (Å)	ε (K)
N	-0.482	3.32	36.4
C.O.M. (center of mass)	0.964	-	-

N-N Bond Length: 1.098 Å

FIGURES

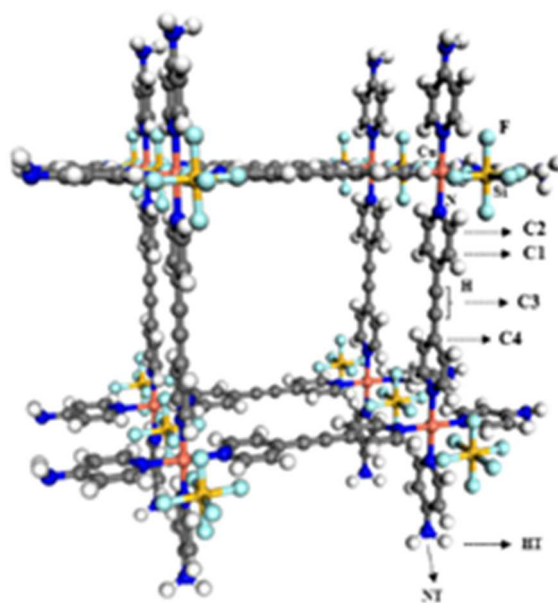


Figure 1

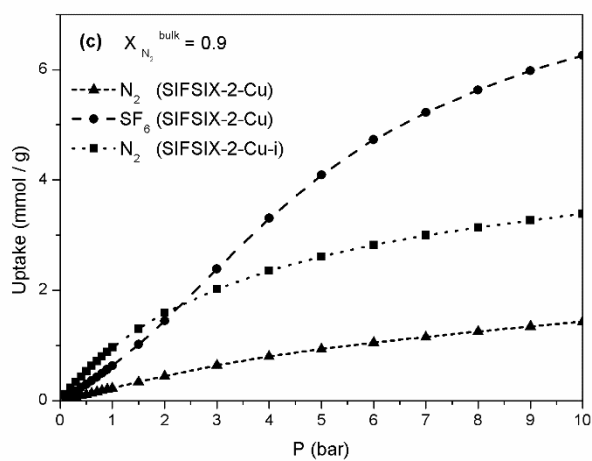
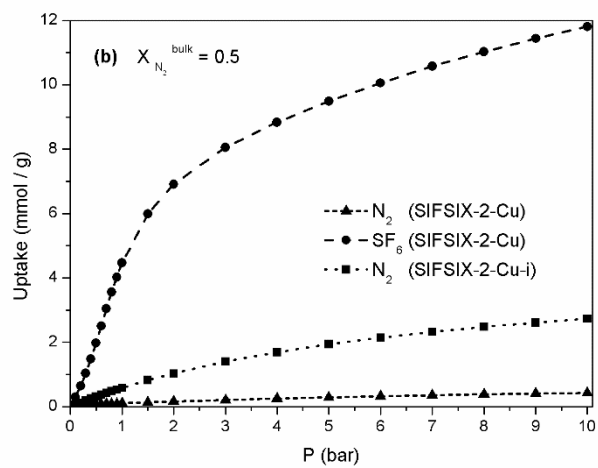
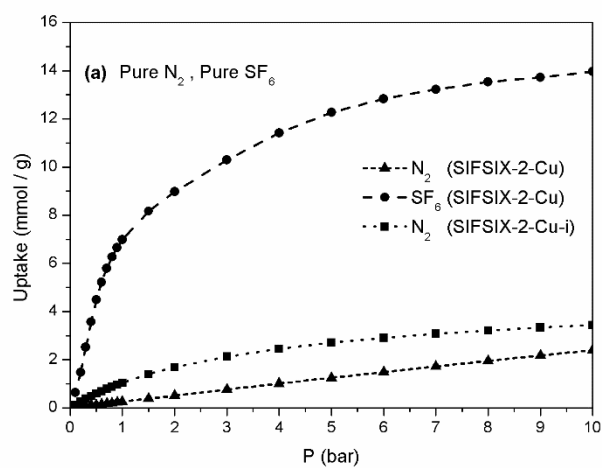


Figure 2

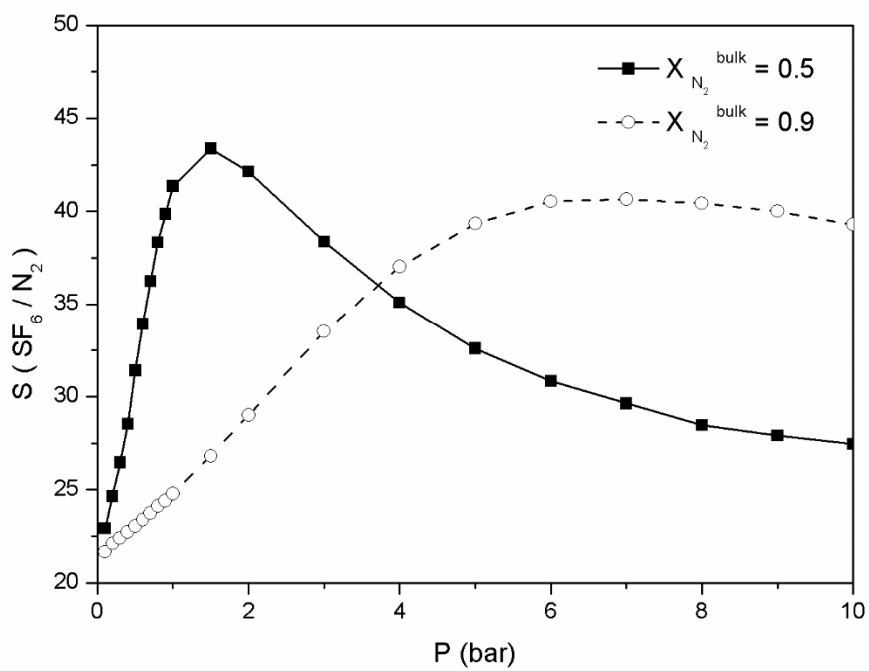


Figure 3

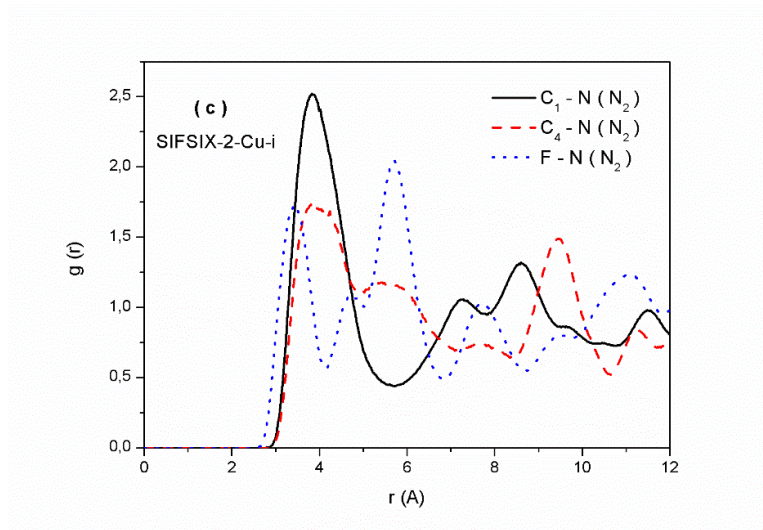
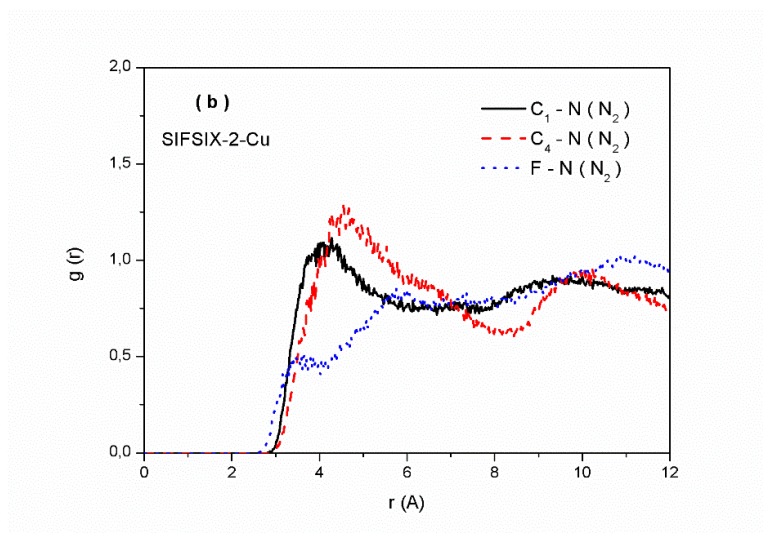
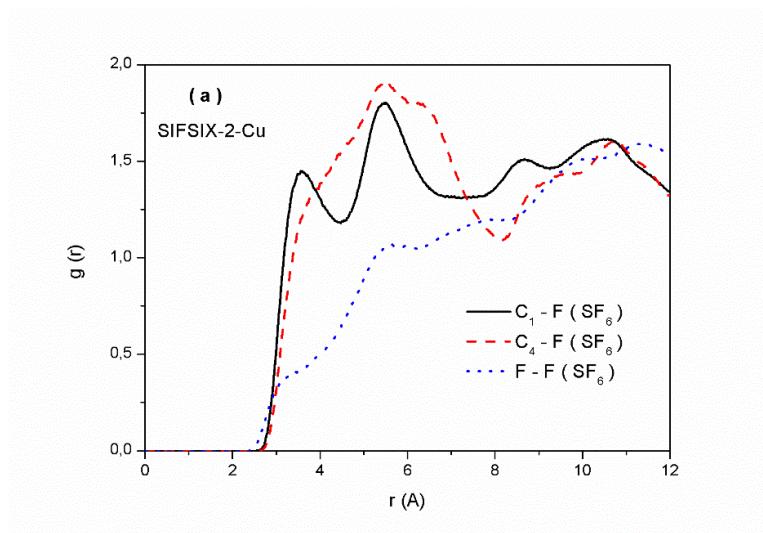


Figure 4

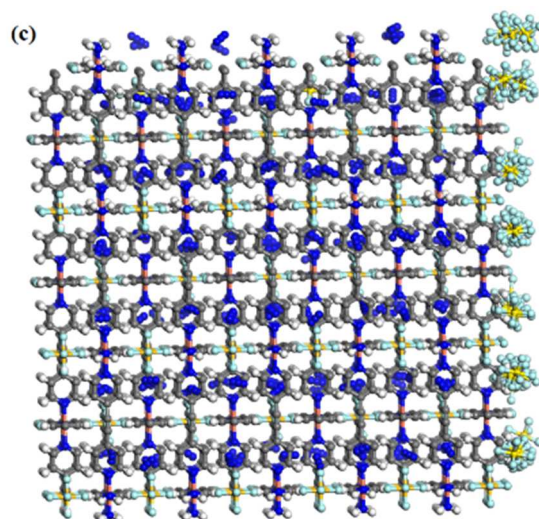
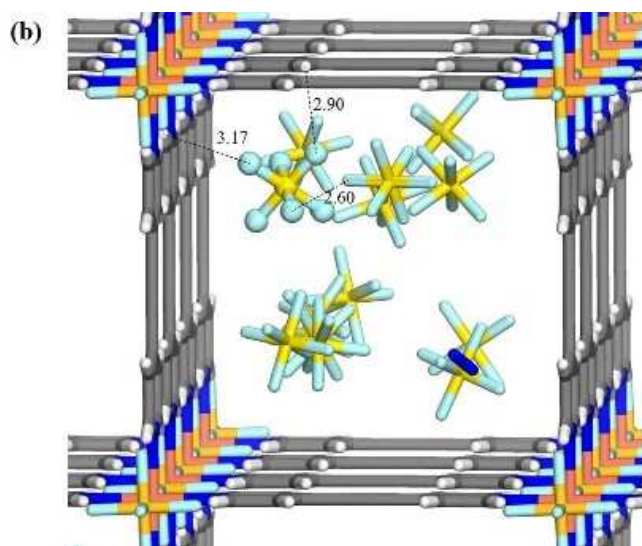
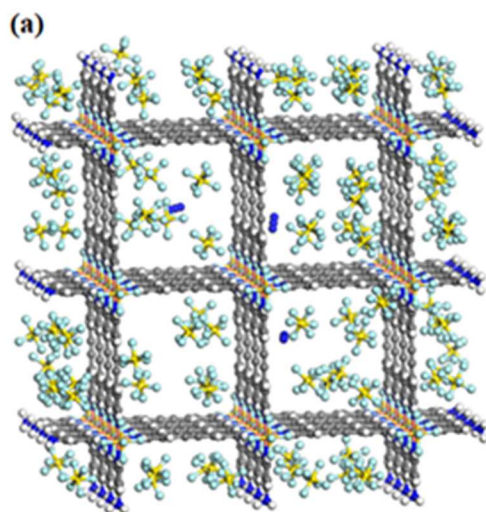


Figure 5

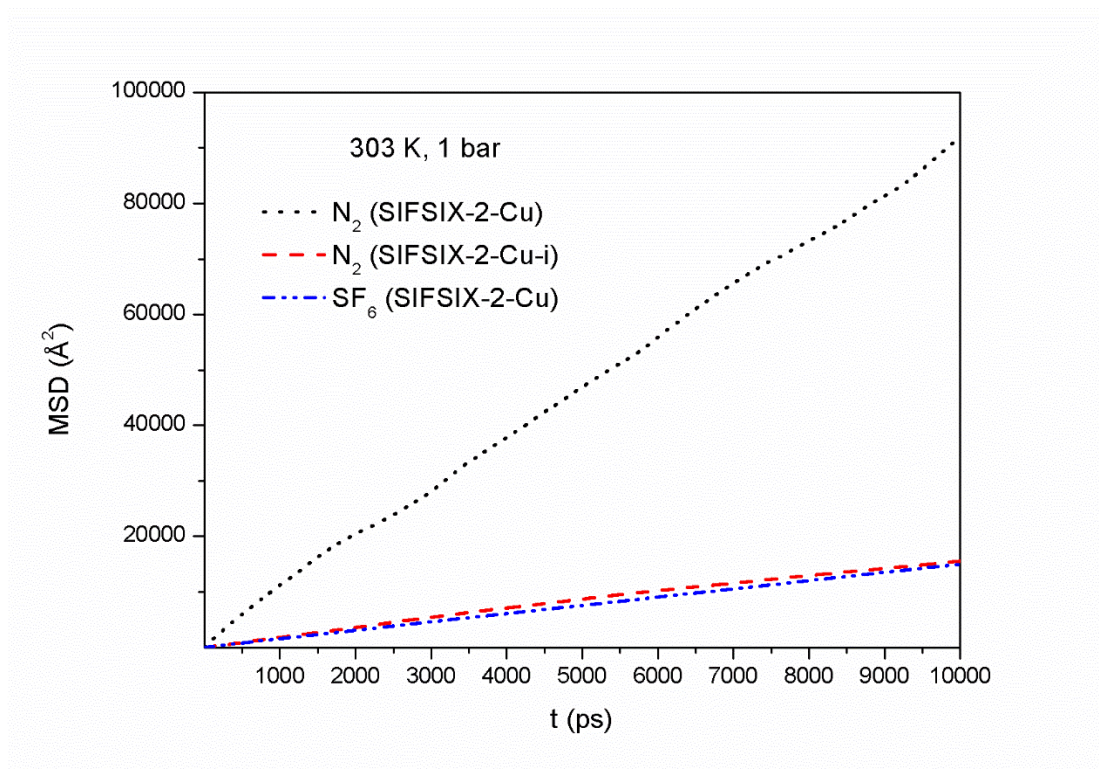


Figure 6

FIGURE CAPTIONS

Figure 1: Names of the interaction sites corresponding to a model building block of the SIFSIX-2-Cu framework.

Figure 2: The binary mixture adsorption isotherms for SF₆ and N₂ corresponding to (a) the pure fluids, (b) the equimolar (1:1) and (c) the 1:9 SF₆/N₂ bulk mixtures at 303 K for SIFSIX-2-Cu and SIFSIX-2-Cu-i.

Figure 3: The calculated thermodynamic adsorption selectivity for SF₆ over N₂, corresponding to the bulk (1:1) and (1:9) SF₆/N₂ binary mixtures, in the case of SIFSIX-2-Cu as a function of pressure.

Figure 4: Representative interatomic guest-pore radial distribution functions, corresponding to the thermodynamically adsorbed components of an equimolar bulk mixture at 1 bar and 303 K, in SIFSIX-2-Cu and SIFSIX-2-Cu-i.

Figure 5: Representative snapshots of the GCMC simulations corresponding to an equimolar bulk mixture, depicting the preferential adsorption of SF₆ in SIFSIX-2-Cu (a and b) and the molecular sieving effect, allowing only the adsorption of N₂ in the case of SIFSIX-2-Cu-i (c).

Figure 6: Mean-square displacements for the adsorbed N₂ and SF₆ molecules in the two materials, corresponding to an equimolar bulk mixture at 303 K and 1 bar. This graph does not report the plots for SF₆ in SIFSIX-2-Cu-i since this molecule cannot enter the pore of this MOF.