Supporting Information

for

Long-term entrapment and temperature-controlled-release of SF$_6$ gas in metal–organic frameworks (MOFs)

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Additional results of SF$_6$-loading and SF$_6$-release experiments (TGA, FTIR and powder XRD measurements), and an example of an input file for the computation simulations
**Figure S1:** SEM micrographs of MFU-4 crystals before (left) and after (right, Sample 3a) the loading of SF₆; scale bar: 10 μm.

**Figure S2:** TG analysis of MFU-4 loaded with SF₆ (Samples 1–4 shown in Table 1) measured under a nitrogen atmosphere at a heating rate of 10 K min⁻¹.
**Figure S3:** Temperature induced gas release study from MFU-4 loaded with SF₆ (Sample 3b) carried out under a helium atmosphere followed by mass spectrometry (EI).

Signals detected (m/z): 127 (SF₅), 108 (SF₄) and 89 (SF₃). Signals not detected (m/z), for instance: 146 (SF₆); 124 (SOF₄), 102 (SO₂F₂) and 86 (SOF₂); 34 (H₂S) and 20 (HF); 119 (C₂F₆) and 69 (CF₄).

**Figure S4:** Temperature-modulated TG analysis of MFU-4 loaded with SF₆ (Samples 3) measured under a helium atmosphere at a heating rate of 1.5 K min⁻¹, amplitude of ± 5 °C and period of 200 s.

Modulated thermogravimetric analysis (MTGA™ by TA Instruments) is an analytical technique used for obtaining continuous kinetic information for decomposition and volatilization reactions. The method makes use of an oscillation temperature program to obtain kinetic parameters during a mass loss [1].
The continuous activation energy curve resulting from the linear heating rate is shown in Figure S3. When there is no mass loss, the activation energy is set to zero. Once the onset of mass loss is observed, calculation of kinetic parameters is initiated. Because it takes several cycles to produce reliable data, the first few data points are unrealistically high.

Figure S5: FTIR spectra of MFU-4 before (black) and after (Sample 3a, blue) the loading of SF$_6$.

Figure S6: XRPD analysis of MFU-4 before (black) and after (Sample 3a, blue) the loading of SF$_6$. 
**Figure S7:** FTIR spectra of MFU-4 loaded with SF₆ (Sample 3a) after 0, 1, 3, 7, 14, and 60 days. Bands attributed to SF₆ are marked with lines; bands attributed to H₂O are marked with an asterisk.

**Table S1:** Release of SF₆ from MFU-4 followed by FTIR spectroscopy (Figure S7).

| Time  | MFU-4 band (\(v_{\text{max}} = 1316 \text{ cm}^{-1}\)) | SF₆ band (\(v_{\text{max}} = 935 \text{ cm}^{-1}\)) | Area I / Area II |
|-------|--------------------------------------------------|--------------------------------------------------|------------------|
|       | Area I (1334 – 1285 cm\(^{-1}\)) | Area II (960 – 899 cm\(^{-1}\)) |                   |
| Day 0 | 0.43010                                          | 0.98704                                          | 0.436            |
| Day 1 | 0.29790                                          | 0.68587                                          | 0.434            |
| Day 3 | 0.24544                                          | 0.53837                                          | 0.456            |
| Day 7 | 0.44067                                          | 1.01079                                          | 0.436            |
| Day 14| 0.90495                                          | 2.03386                                          | 0.445            |
| Day 60| 1.04635                                          | 2.30517                                          | 0.454            |
Figure S8: FTIR spectra of MFU-4 loaded with SF₆ (Sample 3a) after 0, 1, 3, 7, 14, and 60 days showing integration of the bands at $v_{\text{max}} = 1316$ cm$^{-1}$ (MFU-4, yellow) and $v_{\text{max}} = 935$ cm$^{-1}$ (SF₆, blue).
Figure S9: VT XRPD analysis of MFU-4 loaded with SF₆ (Sample 3b) carried out under a nitrogen atmosphere.

Figure S10: FTIR spectra of MFU-4 loaded with SF₆ (Sample 3c) before (black line) and after (purple line) keeping the sample under vacuum (p = 2.8 × 10⁻⁷ mbar) at room temperature for 24 h; bands attributed to SF₆ are marked with lines.
**Figure S11**: TG analysis carried out under a nitrogen atmosphere at a heating rate of 10 K min$^{-1}$ of MFU-4 loaded with SF$_6$ (Sample 3c) before (black line) and after (purple line) keeping the sample under vacuum ($p = 2.8 \times 10^{-7}$ mbar) at room temperature for 24 h; mass loss (150–390 °C): black line – 3.13 wt %, purple line – 2.81 wt %.

**Figure S12**: Acid-induced gas release from MFU-4 loaded with SF$_6$ (Sample 3c) followed by mass spectrometry (EI). The time point “0 min” corresponds to the addition of concentrated sulfuric acid. Sharp signals around the time point “6 min” correspond to the release of small visible gas bubbles (which were dispersed in the reaction solution) after manually shaking the reaction vessel. Signals detected ($m/z$): 127 (SF$_5$), 108 (SF$_4$) and 89 (SF$_3$).
**Figure S13**: Electrostatic potential-derived partial (ESP) charges for MFU-4 and for SF$_6$. Symmetry unique atoms are high-lighted as spheres. Exact values for charges are available from the exemplary GULP input file shown below.
GULP input file for a linear transition scan of SF$_6$ through the narrow pore of MFU-4:

```
opti conse qok nomod pres spat noauto
ttol 1e-005
gtol 0.0001
xtol 1e-005
maxcyc 4000

title
GULP calculation from Materials Studio for MFU-4-cryst-SF6
end

cell
21.697000 21.697000 21.697000 90.000000 90.000000 90.000000 0 0 0 0 0 0

fractional
N1 core 0.714238 0.214238 0.883241 -0.161826 1.000000 0.0 1 1 1
C1 core 0.727417 0.227417 0.943692 0.135252 1.000000 0.0 1 1 1
N1 core 0.714238 0.616759 0.285762 -0.161826 1.000000 0.0 1 1 1
C1 core 0.727417 0.556308 0.272583 0.135252 1.000000 0.0 1 1 1
N1 core 0.116759 0.714238 0.785762 -0.161826 1.000000 0.0 1 1 1
C1 core 0.056308 0.727417 0.772583 0.135252 1.000000 0.0 1 1 1
N1 core 0.556308 0.227417 0.772583 -0.161826 1.000000 0.0 1 1 1
C1 core 0.556308 0.272583 0.772583 0.135252 1.000000 0.0 1 1 1
Zn1 core 0.161331 0.661331 0.838669 0.327035 1.000000 0.0 1 1 1
Cl1 core 0.103660 0.603660 0.896340 -0.400864 1.000000 0.0 1 1 1
N1 core 0.750000 0.847778 0.250000 -0.058241 1.000000 0.0 1 1 1
N1 core 0.347778 0.750000 0.250000 -0.058241 1.000000 0.0 1 1 1
N1 core 0.847778 0.250000 0.250000 -0.058241 1.000000 0.0 1 1 1
N1 core 0.250000 0.347778 0.250000 -0.058241 1.000000 0.0 1 1 1
N1 core 0.750000 0.847778 0.250000 -0.058241 1.000000 0.0 1 1 1
N1 core 0.785762 0.714238 0.883241 -0.161826 1.000000 0.0 1 1 1
C1 core 0.272583 0.772583 0.943692 0.135252 1.000000 0.0 1 1 1
```

translate along c axis of the unit cell in 200 steps
translate 0.0 0.0 1.0 200 noise 0.05

Species
C1 core C_R
Cl core Cl
F1 core F_
H1 core H_
N1 core N_R
S1 core S_3+2
Zn1 core Zn3+2

spacegroup
P 1

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connect 3 4 resonant 0 0 0
connect 3 13 resonant 0 0 0
connect 3 229 single 0 0 0
connect 4 162 resonant 0 0 0
connect 4 377 resonant 0 0 0
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connect 6 345 resonant 0 0 0
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library uff
dump MFU-4-cryst-SF6.grs
output movie arc MFU-4-cryst-SF6

References:
[1] Blaine, R. L.; Hahn, B. K. J. Therm. Anal. Calorim 1997, 54, 695-704.