

## Experimental

### Synthesis of fluorinated MOF crystals.

#### (1) SIFSIX-3-Cu:

The SIFSIX-3-Cu was synthesized by layering a methanol solution of pyrazine (3.0 mmol) in a glass tube onto a methanol solution of  $\text{CuSiF}_6 \times \text{H}_2\text{O}$  (0.325 mmol). Upon layering. The layering led to a fast formation of light violet powder, that was left for another 24 h in the mother solution. The powder was then collected and washed extensively with methanol then dried under vacuum.

#### (2) NbOFFIVE-1-Ni:

Pyrazine (384.40 mg, 4.80 mmol),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (174.50 mg, 0.60 mmol),  $\text{Nb}_2\text{O}_5$  (79.70 mg, 0.30 mmol), and HF (aqueous, 48%, 0.26 mL, 7.15 mmol) were mixed in a 20 mL Teflon liner. The mixture was diluted with 3 mL of deionized water, and then the autoclave was sealed and heated to 130 °C for 24 h. After cooling down the reaction mixture to room temperature, the resultant violet square-shaped crystals, suitable for single crystal X-ray structure determination, were collected by filtration, washed with ethanol and dried in air.

#### (3) AIOFFIVE-1-Ni:

Pyrazine (384.40 mg, 4.80 mmol),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (174.50 mg, 0.60 mmol),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (225.0 mg, 0.6 mmol) and  $\text{HF}_{\text{aq}}$  48% (0.26 ml, 7.15 mmol) were mixed in a 20 ml Teflon liner. The mixture was diluted with 3 ml deionized water and then the autoclave was sealed and heated to 85 °C for 24h. After cooling down the reaction mixture to room temperature, the resultant blue-violet square-shaped crystals, suitable for single crystal X-ray structure determination, were collected by filtration, washed with 5 ethanol and dried in air.

#### (4) functionalization of NbOFFIVE-1-Ni:

The particles were functionalized with the 4-cyanopyridine at first separately and not after the incorporation in the mixed matrix with the polymer. This approach is called surface coordination modulation, which simply involves the introduction of a monodentate ligand (i.e 4-cyanopyridine in this case), which possesses similar chemical functionality to the existing multidentate organic ligand (i.e pyrazine in this case) used in the MOF. Using this way the monodentate ligand will covalently coordinate to the unsaturated surface exposed  $\text{Ni}^{2+}$  and saturate it. This approach will lead to change the surface functionality of the MOFs and allow to change its surface properties depending on the new exposed functionality from the monodentate ligand.

The surface modification was done as follows: NbOFFIVE-1-Ni MOF particles were functionalized first with the 4-cyanopyridine by immersing the dried particles in a 1 mM methanol solution of 4-cyanopyridine at 55 °C for 48 hours. The functionalized particles were then washed extensively with methanol for 4 times and then dried and fully characterized. Later on these functionalized particles were used as the filler and mixed with polymer solution to fabricate the membrane.

**Synthesis of polymers.** Polyimide polymers were synthesized via condensation of dianhydride

monomers with a diamine. Typically, stoichiometric amounts of monomers and diamines were agitated and reacted in a 20 wt% 1-methyl-2-pyrrolidinone (NMP) solution under N<sub>2</sub> purge at low temperature (~5°C) for 24 h to produce a high molecular weight PAA solution. Then chemical imidization was achieved in the presence of beta picoline and acetic anhydride at ambient temperature for 24 h under N<sub>2</sub> purge, and the resulting polyimide was precipitated and washed with methanol and dried at 210 °C under vacuum for 24 h. Monomers comprising (4,4'-hexafluoroisopropylidene) diphthalic anhydride (6FDA) and diamine 2,4,6-trimethyl-1,3-diaminobenzene (DAM) were used to synthesize 6FDA-DAM polymer. The Mw of the synthesized 6FDA-DAM was 210,000 g/mol with a polydispersity index (PDI) of 2.55. Also, monomers comprising 6FDA, DAM and 3,5-diaminobenzoic acid (DABA) were used to synthesize 6FDA-DAM-DABA with the DAM/DABA molar ratio of 3:2. The Mw of the synthesized 6FDA-DAM-DABA was 226,000 g/mol with a polydispersity index (PDI) of 2.46. The 6FDA-DAM-DABA(3:2) was monoesterified by using 1,3-propanediol to produce the crosslinkable PDMC. The 6FDA-DAM-DABA(3:2) polymer was dissolved in NMP (10 wt %) in a reaction flask with an inert nitrogen atmosphere. The catalyst, *p*-toluene sulfonic acid (0.25 mg of catalyst per gram polyimide), was added into the mixture. Then, the solution was heated to 130 °C, and 1,3-propanediol was added slowly (in 3 hours) in a 70-fold excess of the stoichiometric amount required, and allowed to react for 18 h. Finally, the polymer was precipitated into methanol, washed with methanol three times, and dried over several days under vacuum at 120 °C to get PDMC polymer.

**Membrane preparation.** Polyimides (6FDA-DAM or PDMC) were dried in a vacuum oven at 110 °C overnight before being dissolved in THF to form 15 wt% polyimide/THF solution. The solution was mixed on a rolling mixer overnight to dissolve the polymer. The resulting casting solution was poured onto a glass plate, which was placed in a glove bag pre-saturated with THF vapor for at least 4 h. Pure 6FDA-DAM or PDMC dense films were formed on a glass plate by casting the solution into desired thickness (typically 75 μm) using a draw knife with appropriate specific clearance. The film was left in the glove bag overnight to let the THF solvent evaporate slowly. The film was further dried in a vacuum oven at 120 °C overnight to remove any remaining solvent. For mixed-matrix dense film formation, MOF/THF suspension was added to 10 wt% polyimide/THF solution to form a mixed-matrix solution, which was mixed on a rolling mixer overnight. The excess solvent in the mixed-matrix solution was removed by slowly purging dry nitrogen to obtain ~15 wt% mixed-matrix/THF solution. **SIFSIX-3-Cu/6FDA-DAM**, **NbOFFIVE-1-Ni/6FDA-DAM**, **NbOFFIVE-1-Ni/PDMC** and **AIFFIVE-1-Ni/6FDA-DAM** mixed matrix dense films were formed by casting the mixed-matrix solution in the same condition with the pure 6FDA-DAM or PDMC dense films. The crosslinking of pure PDMC film or **NbOFFIVE-1-Ni/PDMC** mixed-matrix dense film was performed at 200 °C under vacuum for 2 hours. The MOF loading in the film is controlled at ~20 wt% by keeping a fixed MOF/polymer weight ratio in the casting solution.

**Membrane characterizations.** The dense films for scanning electron microscope (SEM, Hitachi, SU8010) test were prepared by cryogenically fracturing film in liquid nitrogen to preserve their microstructures. Wide-angle X-ray diffraction (WAXD) was measured on a Panalytical Empyrean diffractometer operating with a Cu K $\alpha$  radiation at a wavelength of 1.54 Å, in a 2 $\theta$  range of 5–45°. Attenuated total reflectance fourier transform infrared (ATR-FTIR) spectra were recorded by a Thermo Scientific iS50 spectrophotometer at a resolution of 4 cm<sup>-1</sup> with 64 scans in the spectral range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) and derivative weight data were recorded on a TA Q-500

analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere, using ~10 mg sample.

**Gas permeation measurement.** The gas permeation was conducted in a variable pressure, constant-volume apparatus described in detail in earlier work<sup>[1]</sup> (Scheme S1). The membrane was housed between an upstream, capable of high-pressure gas introduction, and a downstream, which is kept under vacuum until experiments were initiated. Modifications to the standard system configuration were made to ensure safe handling of the toxic H<sub>2</sub>S-containing gases. Specifically, two pneumatically-actuated valves were used in place of standard hand-operated valves. These are located between the upstream volume and the membrane-containing cell and between the downstream volume and the gas chromatograph sampling line, which is normally under vacuum. These valves were controlled by LabVIEW program that was used for data collection to prevent over-pressurization of the downstream, which can damage the downstream pressure transducer, and also to avoid the unintended release of large quantities of H<sub>2</sub>S gas and minimizes operator risk when handling H<sub>2</sub>S. The permeation temperature for all gases was kept at 35 °C.

A 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixture were used for mixed-gas permeation. The downstream composition was determined using a gas chromatograph (Varian 450-GC). The stage cut (the flow rate ratio of permeate to feed) was maintained below 1% to avoid concentration polarization on the upstream side of the permeation cell, keeping the driving force across the membrane constant throughout the course of the experiment. For permeation 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, a syringe pump and metering valve were used to maintain the feed pressure and control the retentate flow, respectively. The syringe pump is operated isobarically to replenish the feed gas at the same rate as retentate vents through the metering valve.

**Gas sorption measurement.** Gas sorption isotherms at feed pressure up to 20 bar were measured using a pressure decay method<sup>[2]</sup> (Scheme S2). The method and apparatus have been described in detail elsewhere. Gas adsorption amount in MOFs and dense films was calculated from the pressure change before and after sorption. A small experimental error of less than ±5 % is expected from the accurate pressure measurement and volume calibration. The sorption of all gases was carried out at 35 °C.

Films or MOF particles were activated at 200 °C under vacuum for 24 h and then loaded into the cell (B) and degassed for overnight. A differential amount of sorption gas was first introduced into the reservoir (A), then the connecting valve was quickly open for 1 second and closed. The pressure signal in both volume (A) and volume (B) were recorded continuously. The gas adsorption concentration in films or MOFs was calculated through molar balance: adsorbed amount equals to the decreased amount in the reservoir (A) minus the increased amount of the gas in the cell (B), as below:

$$C = \frac{\frac{V_A}{R \cdot T} \left( \frac{P_{A,i}}{Z_{A,i}} - \frac{P_{A,f}}{Z_{A,f}} \right) - \frac{V_B}{R \cdot T} \left( \frac{P_{B,f}}{Z_{B,f}} - \frac{P_{B,i}}{Z_{B,i}} \right)}{V_{sample}} \quad (1)$$

**Calculations of permeability, solubility and diffusivity.** Permeability (or permance) and selectivity are used to characterize the membrane separation performance. The permeability,  $P_i$ , describes the intrinsic gas separation productivity of a dense film membrane and is defined by the flux of penetrant  $i$ ,  $n_i$ , normalized by the membrane thickness,  $l$ , and the partial pressure or fugacity difference,  $\Delta p_i$ , across the membrane, as shown in the following equation:

$$P_i = \frac{n_i \cdot l}{\Delta p_i} \quad (2)$$

To obtain permeability from the constant volume, variable pressure permeation system, the following quantities can be used: slope of the permeate pressure vs. time ( $dp/dt$ ); membrane thickness ( $l$ ); downstream volume ( $V$ ); operating temperature ( $T$ ); and transmembrane pressure or fugacity difference ( $\Delta p$ ), and can be plugged into equation 2 to obtain the permeability ( $P$ ):

$$P = \frac{\frac{dp}{dt} \cdot l \cdot V}{A \cdot T \cdot \Delta p} \quad (3)$$

In the mixed-gas permeation, the permeability of component  $i$  ( $P_i$ ) is calculated by using its molar fraction in the permeate ( $x_i$ ) and the transmembrane fugacity difference ( $\Delta p_i$ ):

$$P_i = \frac{\frac{dp}{dt} \cdot x_i \cdot l \cdot V}{A \cdot T \cdot \Delta p_i} \quad (4)$$

The fugacity coefficients of H<sub>2</sub>S, CO<sub>2</sub> and CH<sub>4</sub> in gas mixtures can be calculated using the Peng-Robinson equation-of-state and the SUPERTRAPP program developed by NIST.

The permeance of hollow fiber composite membranes is calculated as:

$$\frac{P}{l} = \frac{\frac{dp}{dt} \cdot V}{A \cdot T \cdot \Delta p} \quad (5)$$

The membrane selectivity,  $\alpha_{ij}$ , is determined by the ratio of the fast gas ( $i$ ) permeability or permeance to the slow gas ( $j$ ):

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{P_i/l}{P_j/l} \quad (6)$$

Permeability can also be expressed as the product of the effective diffusion coefficient ( $D$ ) and sorption coefficient ( $S$ ) of a given gas  $i$  within the membrane:

$$P_i = D_i \cdot S_i \quad (7)$$

The sorption coefficient represents the thermodynamic contribution to transport, and it can be measured independently by pressure-decay sorption, the sorption coefficient can be expressed as:

$$S_i = \frac{c_i}{f_i} \quad (8)$$

where  $c_i$  is the concentration of a gas adsorbed in the sample, and  $f_i$  is the corresponding upstream fugacity driving force of component  $i$ .

The adsorbed gas concentration in the films was described by the dual-mode sorption model, which is given as:

$$c_i = c_{D,i} + c_{H,i} = k_{D,i} \cdot f_i + \frac{C'_{H,i} \cdot b_i \cdot f_i}{1 + b_i \cdot f_i} \quad (9)$$

where  $c_{D,i}$  is the Henry's law or dissolved mode penetrant concentration,  $c_{H,i}$  is the penetrant concentration in the Langmuir mode or hole-filling sorption mode,  $k_{D,i}$  is the Henry's law sorption coefficient,  $C'_{H,i}$  is the Langmuir capacity constant, and  $b_i$  is the Langmuir affinity constant.

The effective diffusion coefficient ( $D$ ) in the membrane can be calculated from the independently measured permeability ( $P$ ) and sorption coefficient ( $S$ ):

$$D_i = \frac{P_i}{S_i} \quad (12)$$

The Maxwell model is used to mathematically describe the gas transport in mixed-matrix materials<sup>[3]</sup>. The model was initially derived by James C. Maxwell to describe dielectric properties in a conducting dilution suspension of identical particles<sup>[4]</sup>. This model can also be used to describe gas transport in mixed-matrix materials based on the close analogy between electrical conduction and gas permeation. Maxwell model is given by:

$$P_{MMM} = P_p \left[ \frac{P_s + 2P_p - 2\phi_s(P_p - P_s)}{P_s + 2P_p + \phi_s(P_p - P_s)} \right] \quad (13)$$

where is  $P_{MMM}$  permeability in the mixed matrix material;  $P_p$  is permeability in the polymer matrix;  $P_s$  is permeability in dispersed molecular sieve particles; and  $\phi_s$  is volume fraction of molecular sieve particles in the mixed matrix material.

The theoretical limit of permeation in MMM can be predicted by using Maxwell model. For instance:

$$\text{If: } P_s \gg P_p, P_{MMM} = P_p \frac{1+2\phi_s}{1-\phi_s}; \text{ and if: } P_s \ll P_p, P_{MMM} = P_p \frac{2-2\phi_s}{2+\phi_s},$$

$$\text{So: } P_p \frac{1+2\phi_s}{1-\phi_s} \leq P_{MMM} \leq P_p \frac{2-2\phi_s}{2+\phi_s}$$

$$\text{As: } \phi_s = 20\%, 0.73 P_p \leq P_{MMM} \leq 1.75 P_p, \text{ and } 0.42 \alpha_p \leq \alpha_{MMM} \leq 2.4 \alpha_p.$$

**If:**

(1) MOF has infinite **high**  $C_3H_6$  permeability and  $C_3H_6/C_3H_8$  selectivity, namely:  $P_{MOF}(C_3H_6) = \infty$  ( $P_s \gg P_p$ ),  $P_{MOF}(C_3H_8) = 0$  ( $P_s \ll P_p$ ),  $\alpha_{MOF}(C_3H_6/C_3H_8) = \infty$ .

By inputting the permeation property of a known polymer matrix, e.g., 6FDA-DAM:

$$P_{polymer}(C_3H_6) = 12.5 \text{ barrer}, P_{polymer}(C_3H_8) = 1.4 \text{ barrer}, \text{ and } \alpha_{polymer}(C_3H_6/C_3H_8) = 8.93,$$

A theoretically **highest** permeation performance of 20% MOF/6FDA-DAM MMM for  $C_3H_6/C_3H_8$  permeation can be calculated as:

$$P_{MMM}(C_3H_6) = 1.75 \times P_{polymer}(C_3H_6) = 1.75 \times 12.5 = 21.88 \text{ barrer}, P_{MMM}(C_3H_8) = 0.73 \times P_{polymer}(C_3H_8) = 0.73 \times 1.4 = 1.02 \text{ barrer}, \alpha_{MMM}(C_3H_6/C_3H_8) = P_{MMM}(C_3H_6)/P_{MMM}(C_3H_8) = 21.6, \text{ or } = 2.4 \times \alpha_{polymer}(C_3H_6/C_3H_8) = 2.4 \times 8.93 = 21.4.$$

**Alternatively, if:**

(2) MOF has infinite **low**  $C_3H_6$  permeability and  $C_3H_6/C_3H_8$  selectivity, namely:  $P_{MOF}(C_3H_6) = 0$  ( $P_s \ll P_p$ ),  $P_{MOF}(C_3H_8) = \infty$  ( $P_s \gg P_p$ ),  $\alpha_{MOF}(C_3H_6/C_3H_8) = 0$ .

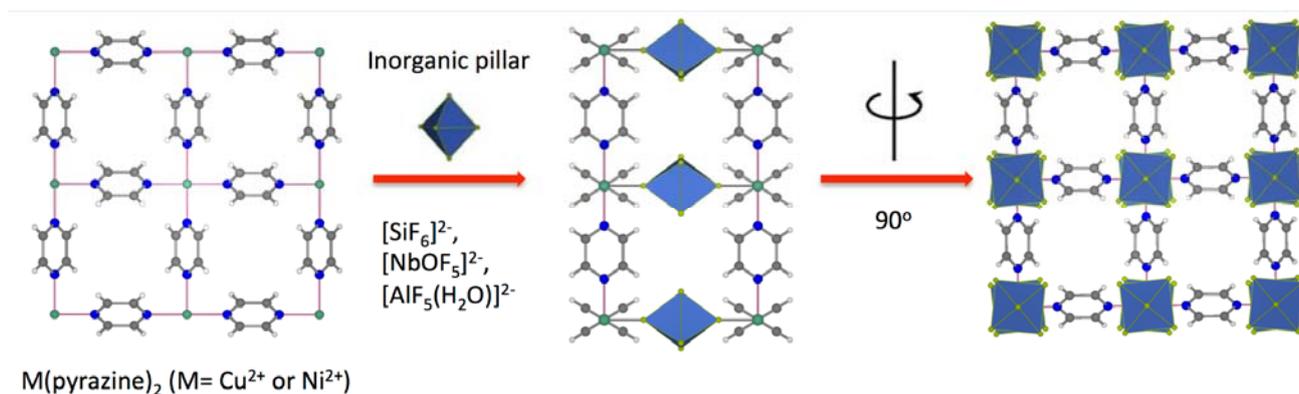
By inputting the permeation property of a known polymer matrix, e.g., 6FDA-DAM:

$$P_{polymer}(C_3H_6) = 12.5 \text{ barrer}, P_{polymer}(C_3H_8) = 1.4 \text{ barrer}, \text{ and } \alpha_{polymer}(C_3H_6/C_3H_8) = 9,$$

A theoretically **lowest** permeation performance of 20% MOF/6FDA-DAM MMM for  $C_3H_6/C_3H_8$  permeation can be calculated as:

$$P_{MMM}(C_3H_6) = 0.73 \times P_{polymer}(C_3H_6) = 0.73 \times 12.5 = 9.13 \text{ barrer}, P_{MMM}(C_3H_8) = 1.75 \times P_{polymer}(C_3H_8) = 1.75 \times 1.4 = 2.45 \text{ barrer}, \alpha_{MMM}(C_3H_6/C_3H_8) = P_{MMM}(C_3H_6)/P_{MMM}(C_3H_8) = 3.72, \text{ or } = 0.42 \times \alpha_{polymer}(C_3H_6/C_3H_8) = 0.42 \times 9 = 3.75.$$

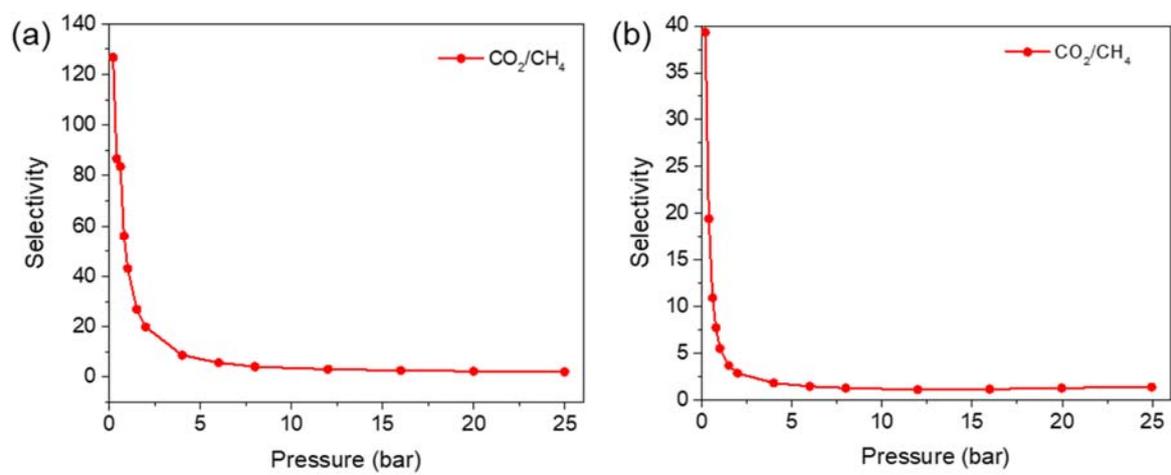
The above two limiting cases were used to define the gray boxes termed “theoretical area” shown in Figure 2b to define the range of performance possible without additional factors such as poor interfacial adhesion or bypass.



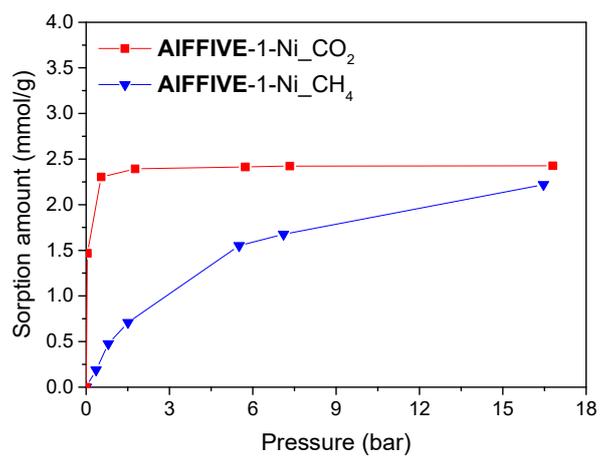
**Figure S1.**  $M$  ( $M = \text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ ) cations are associated with pyrazine molecules to form a two-dimensional square lattice (left) that is further pillared by an inorganic building block, i.e.  $[\text{SiF}_6]^{2-}$ ,  $[\text{NbOF}_5]^{2-}$  or  $[\text{AlF}_5(\text{H}_2\text{O})]^{2-}$  (middle) to generate a fluorinated MOF with square-shaped channels (right)

**Table S1.** Aperture size of the fluorinated MOFs and kinetic diameter of gas molecules

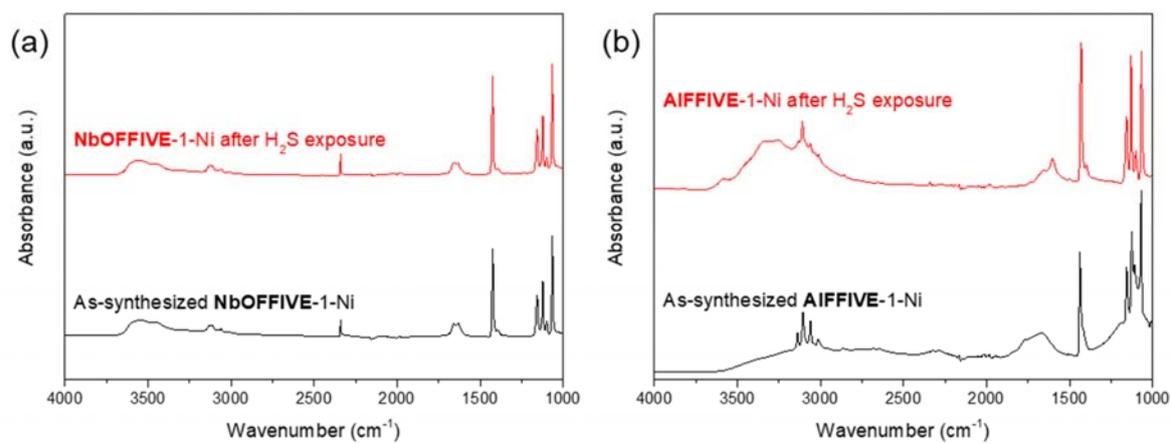
Fluorinated MOF	Aperture size (Å)
<b>NbOFFIVE-1-Ni</b>	≈ 3.2
<b>AlFFIVE-1-Ni</b>	≈ 3.2
<b>SIFSIX-3-Cu</b>	≈ 4.7
Gas molecule	Kinetic diameter (Å)
$\text{CO}_2$	3.3
$\text{H}_2\text{S}$	3.6
$\text{CH}_4$	3.8



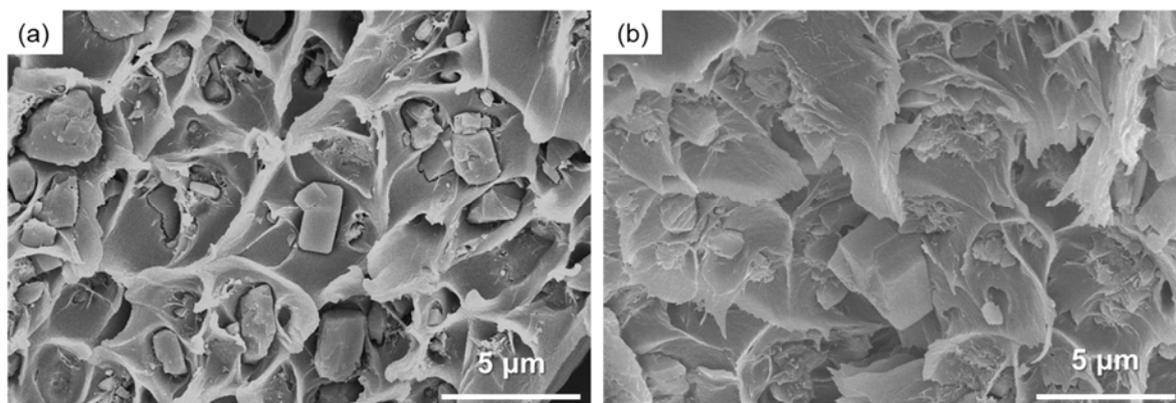
**Figure S2.** High-pressure sorption selectivity for CO<sub>2</sub>/CH<sub>4</sub> at 35 °C for (a) NbOFFIVE-1-Ni and (b) SIFSIX-3-Cu crystals.



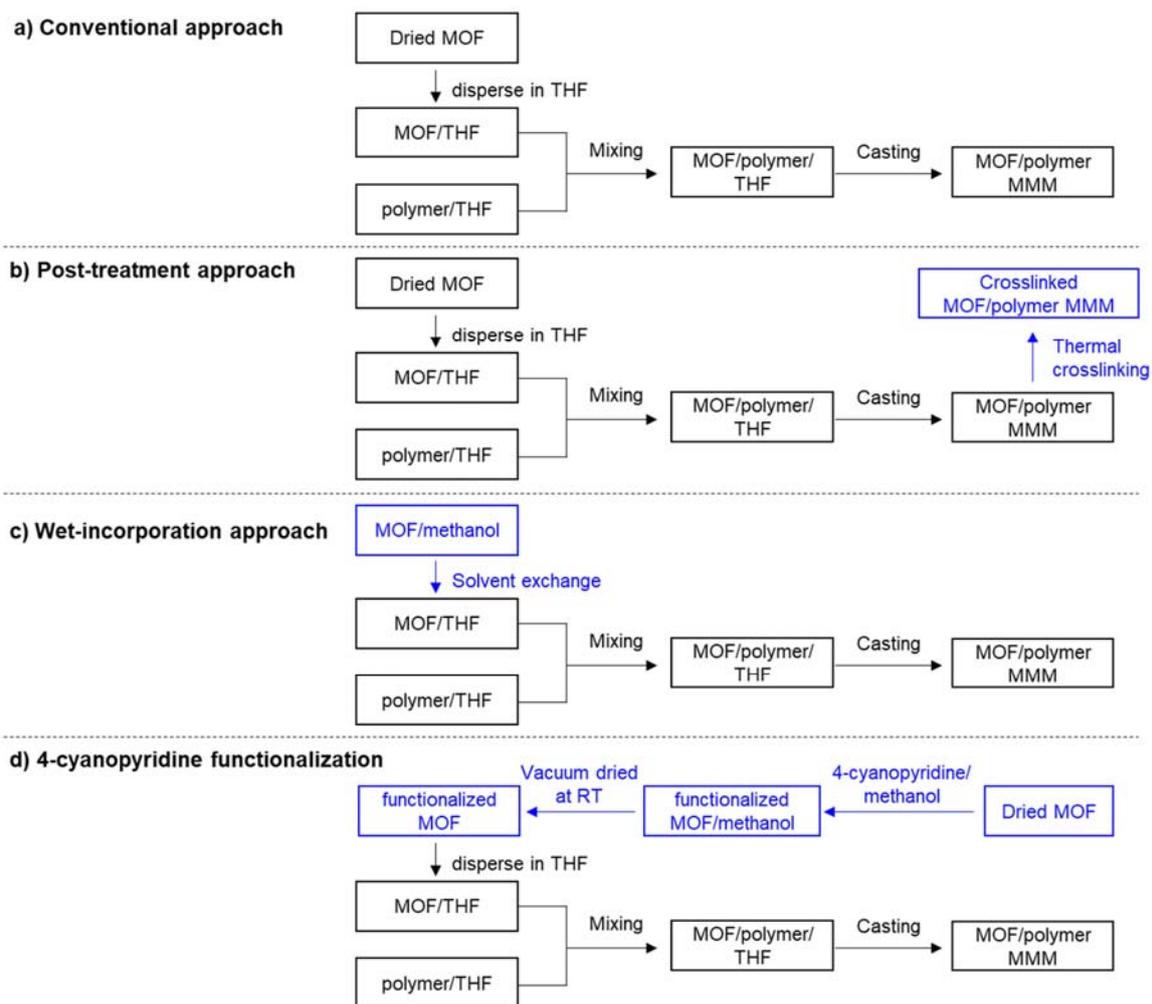
**Figure S3.** CO<sub>2</sub> and CH<sub>4</sub> adsorption isotherms of AIFVIVE-1-Ni crystals at 35 °C.



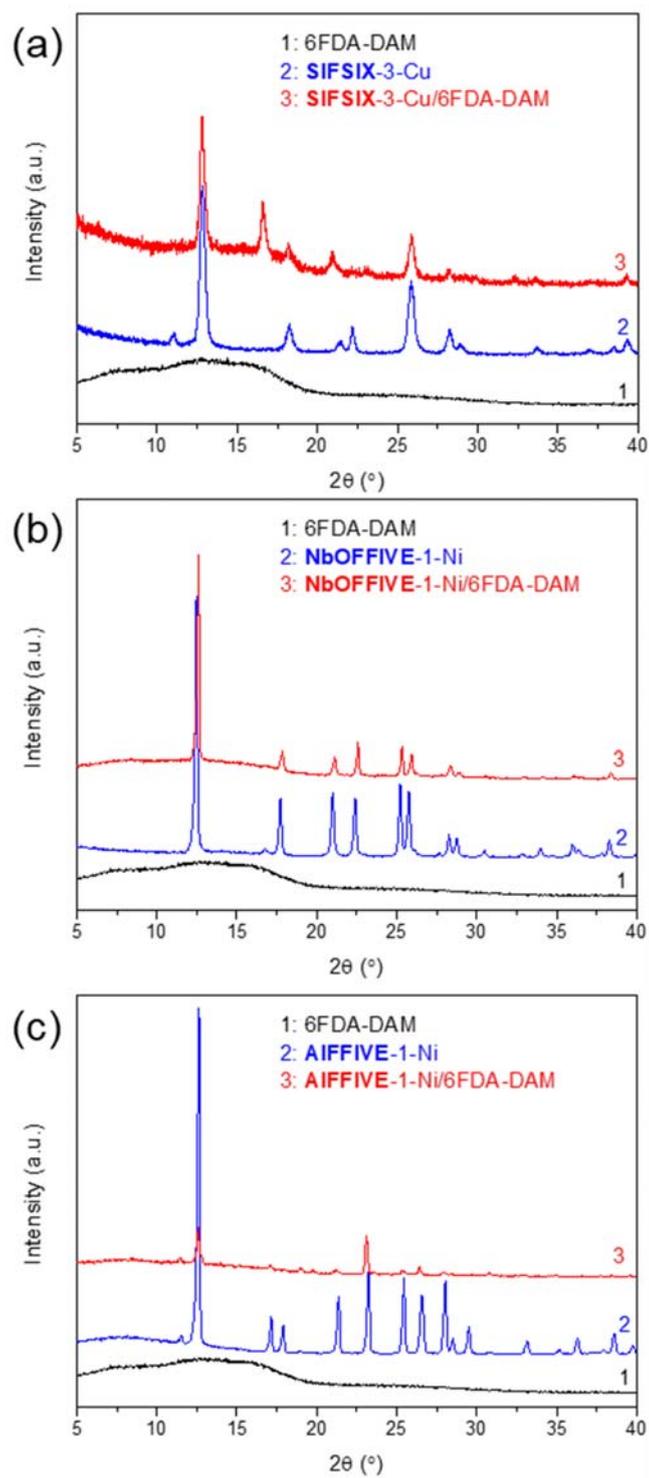
**Figure S4.** IR spectra of (a) NbOFFIVE-1-Ni and (b) AlFFIVE-1-Ni crystals before and after long-term exposure to pure and high-pressure H<sub>2</sub>S



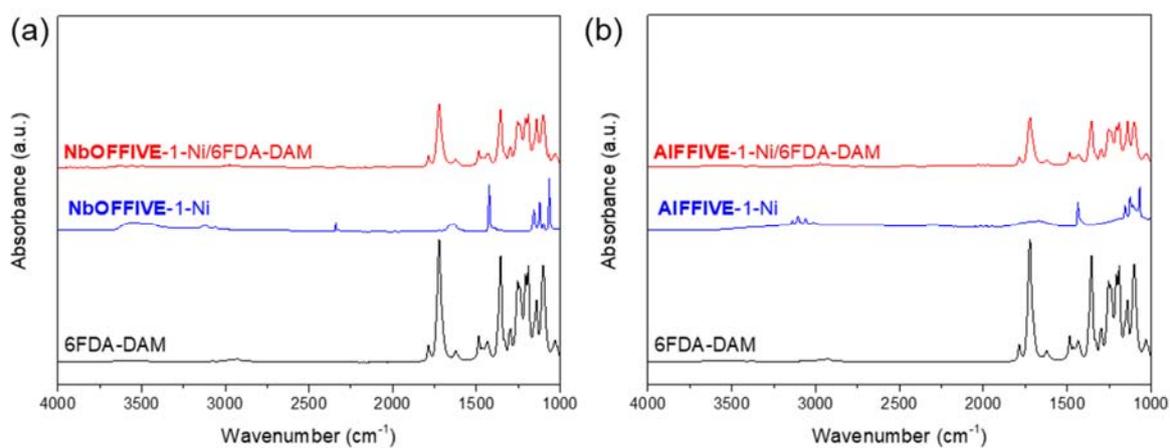
**Figure S5.** Cross-sectional SEM images of (a) dried **NbOFFIVE-1-Ni/6FDA-DAM** MMM and (b) crosslinked **NbOFFIVE-1-Ni/PDMC** MMM.



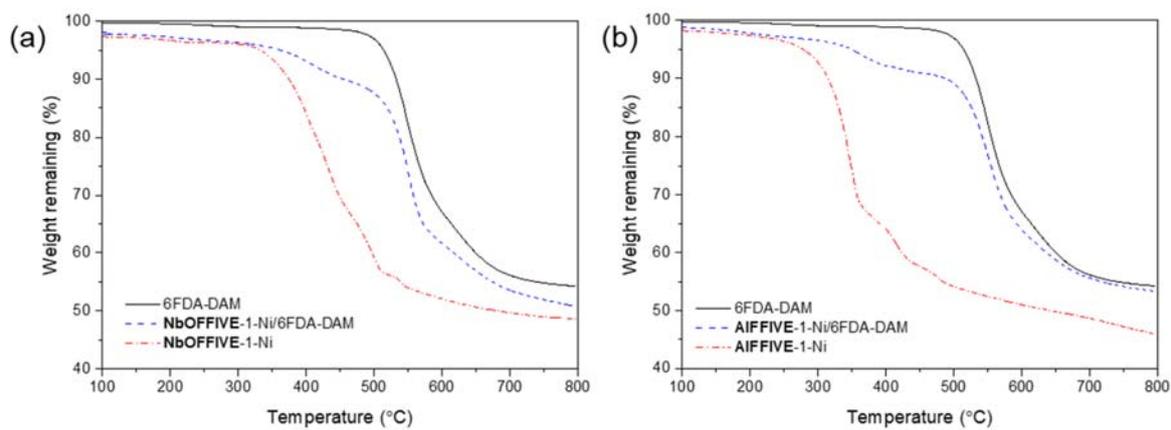
**Figure S6.** Schematic of preparing MOF/polymer MMM via various functionalization approaches



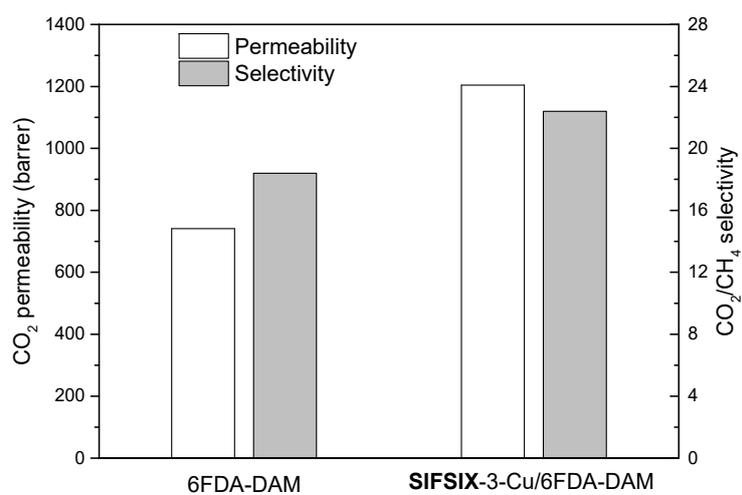
**Figure S7.** XRD patterns of (a) SIFSIX-3-Cu and SIFSIX-3-Cu/6FDA-DAM MMM; (b) NbOFFIVE-1-Ni and NbOFFIVE-1-Ni/6FDA-DAM MMM; (c) AIOFFIVE-1-Ni and AIOFFIVE-1-Ni/6FDA-DAM MMM.



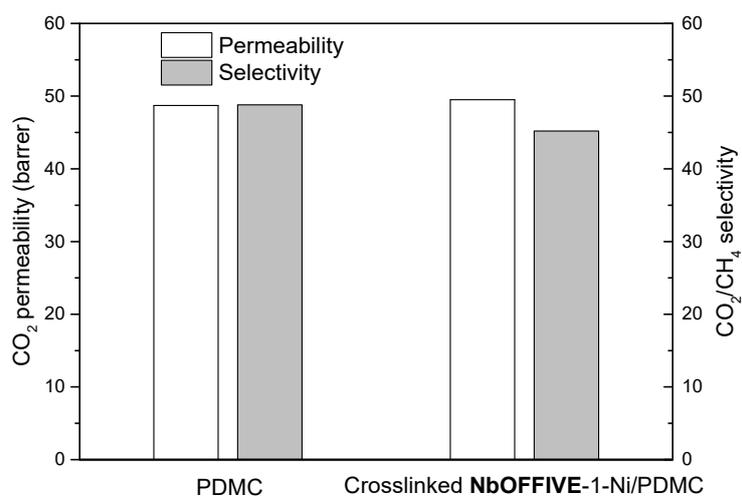
**Figure S8.** IR spectra of (a) **NbOFFIVE-1-Ni** and **NbOFFIVE-1-Ni/6FDA-DAM** MMM; and (b) **AlFFIVE-1-Ni** and **AlFFIVE-1-Ni/6FDA-DAM** MMM.



**Figure S9.** TGA curves of (a) 6FDA-DAM, NbOFFIVE-1-Ni and NbOFFIVE-1-Ni/6FDA-DAM MMM; and (b) 6FDA-DAM, AIFFIVE-1-Ni and AIFFIVE-1-Ni/6FDA-DAM MMM.



**Figure S10.** CO<sub>2</sub>/CH<sub>4</sub> pure gas permeation of pure 6FDA-DAM membrane and SIFSIX-3-Cu/6FDA-DAM MMM, feed: 3.4 bar, 35 °C.

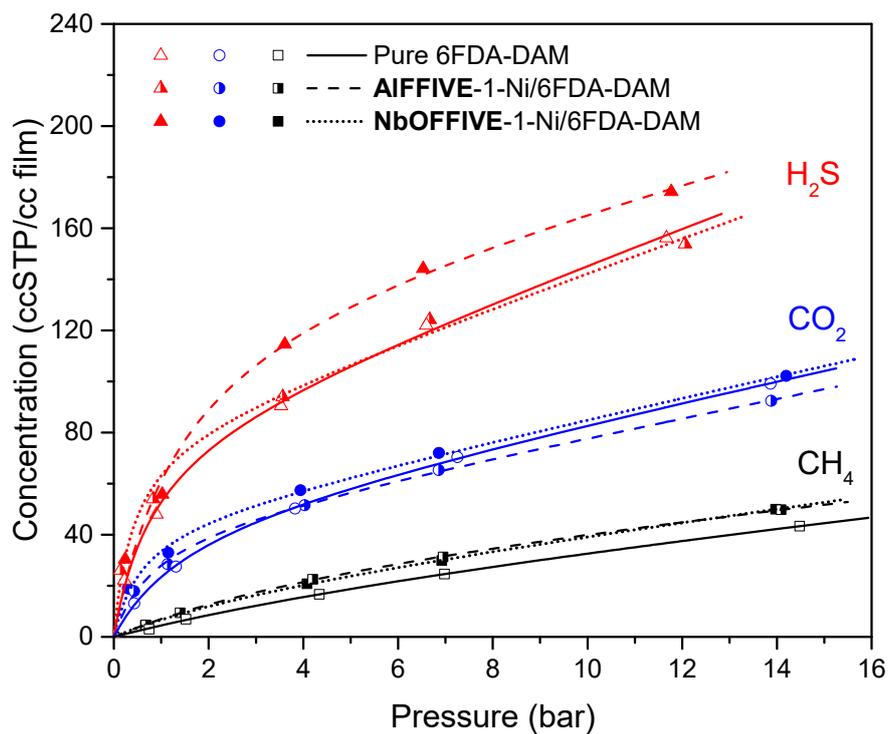


**Figure S11.** CO<sub>2</sub>/CH<sub>4</sub> mixed-gas permeation of pure crosslinked PDMC membrane and crosslinked NbOFFIVE-1-Ni/PDMC MMM, feed: 50/50 CO<sub>2</sub>/CH<sub>4</sub>, 6.9 bar, 35 °C.

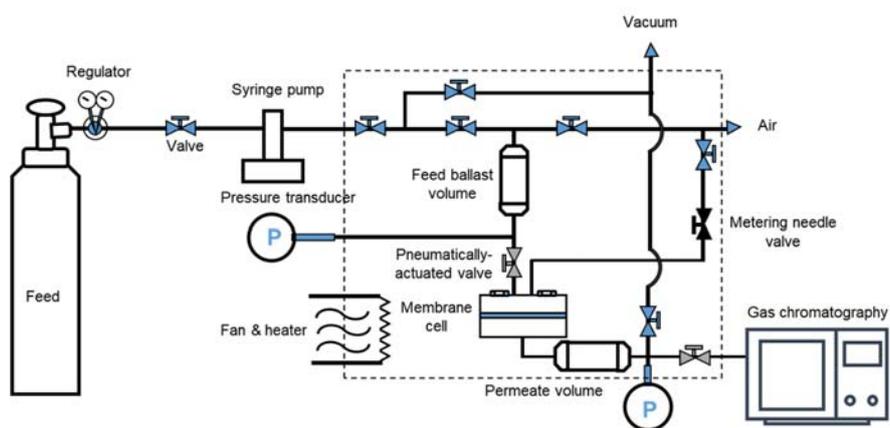
**Table S2.** H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixed-gas separation performance of dense films made of glassy polymers tested at 35 °C

Membrane	P <sub>H<sub>2</sub>S</sub> (barrer)	P <sub>CO<sub>2</sub></sub> (barrer)	$\alpha$ (H <sub>2</sub> S/CH <sub>4</sub> )	$\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> )	P <sub>H<sub>2</sub>S+CO<sub>2</sub></sub> (barrer)	$\alpha$ ((H <sub>2</sub> S+CO <sub>2</sub> )/CH <sub>4</sub> )	Ref
PIM-6FDA-OH <sup>a</sup>	36.0	54.7	18.3	27.8	90.7	46.1	[5]
Crosslinked 6FDA-DAM-DABA <sup>b</sup>	33.5	46.2	22.5	31.2	79.7	53.7	[6]
Crosslinked 6FDA-DAM-DABA <sup>b</sup>	38.2	54.6	19.3	28.4	92.8	47.7	[6]
CA (cellulose acetate) <sup>c</sup>	8.71	8.66	29.7	29.5	17.37	59.2	[7]
CA (cellulose acetate) <sup>d</sup>	39.7	27.5	27.4	19.1	67.2	46.5	[7]
6F-PAI-1 <sup>e</sup>	4.2	8.1	11	32	12.3	43	[8]
6FDA-DAM-DABA <sup>f</sup>	42.4	95.6	16.4	36.1	137.9	52.1	[9]
17.8 wt% Y- <i>fum-<b>fcu</b></i> -MOF/6FDA-DAM <sup>f</sup>	393.0	543.2	19.6	27.1	936.2	46.7	[9]
19.0 wt% Eu- <i>naph-<b>fcu</b></i> -MOF/6FDA-DAM <sup>f</sup>	287.4	460.4	18.9	30.3	747.8	49.2	[9]
6FDA-DAM <sup>f</sup>	258	414	15.3	24.4	672	39.7	
20 wt% <b>NbOFFIVE</b> -1-Ni/6FDA-DAM	401	547	20.7	28.2	948	48.9	This work
20 wt% <b>AIFFIVE</b> -1-Ni/6FDA-DAM	458	599	18.6	23.8	1047	42.4	

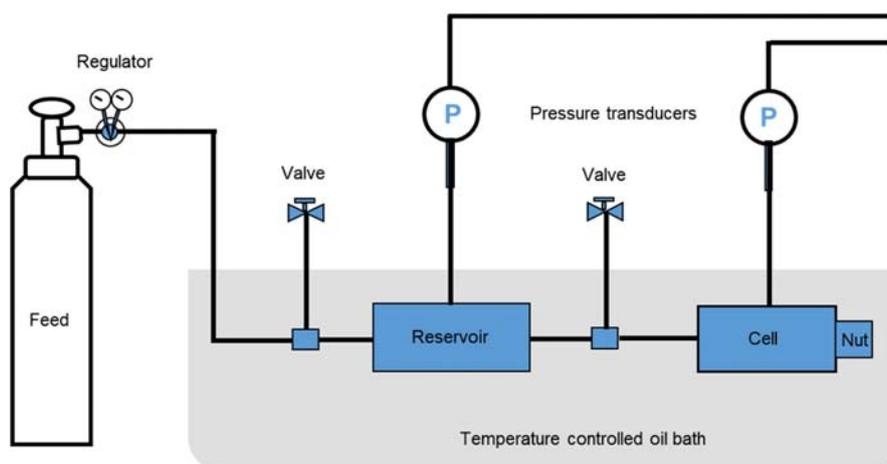
Feed conditions: <sup>a</sup> 15/15/70 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 34.5 bar; <sup>b</sup> 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 48.3 bar; <sup>c</sup> 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 34.5 bar; <sup>d</sup> 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 48.3 bar; <sup>e</sup> 10/20/70 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 63.3 bar; <sup>f</sup> 20/20/60 H<sub>2</sub>S/CO<sub>2</sub>/CH<sub>4</sub> mixtures, 6.9 bar, 35 °C.



**Figure S12.** High-pressure sorption isotherms of H<sub>2</sub>S, CO<sub>2</sub> and CH<sub>4</sub> for pure 6FDA-DAM, NbOFFIVE-1-Ni/6FDA-DAM MMM and AIFFIVE-1-Ni/6FDA-DAM MMM measured at 35 °C.



**Supplementary Scheme 1.** Constant-volume dense film permeation system for pure and mixed gases<sup>[9]</sup>.



**Supplementary Scheme 2.** Pressure decay sorption apparatus used for gas sorption experiments<sup>[9]</sup>.

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