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Enabling fluorinated MOF-based membranes for simultaneous removal of H₂S and CO₂ from natural gas

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Abstract: Membrane-based gas separations are energy efficient processes; however, major challenges remain to develop high-performance membranes enabling replacement of conventional separation processes. Here, a new fluorinated MOF-based mixed-matrix membrane is reported, which is formed by incorporating the MOF crystals into selected polymers via a facile mixed-matrix approach. By finely controlling the molecular transport in the channels through MOF apertures tuned by metal pillars and at the MOF-polymer interfaces, the resulting fluorinated MOF-based membranes exhibit excellent molecular sieving properties. We show that these materials significantly outperform state-of-the-art membranes for simultaneous removal of H₂S and CO₂ from natural gas—a challenging and economically-important application. The robust fluorinated MOFs (**NbOFFIVE-1-Ni**, **AIFFIVE-1-Ni**), with tunable channel apertures provided by tuning the metal pillars and/or organic linker, pave a new avenue to efficient membrane separation processes that require precise discrimination of closely sized molecules.

Separation processes are essential in chemical industries^[1]. Membrane technology, separating mixtures without using heat, would lower global energy use and reduced carbon dioxide footprint^[2]. Alkene/alkane separation and CO₂ capture have been highlighted as chemical separations that, if improved, would gain great global benefits^[3]. The initial motivation of this work was to address both of these separations; however, we discovered instead a special approach ideally suited to natural gas purification—also a large energy consuming process. Specifically, raw natural gas typically contains CO₂ and H₂S acid gas components that currently are removed by amine scrubbing to meet pipeline specifications (< 2% CO₂ and < 4 ppm H₂S), in an

energy-intensive process with a large footprint^[4]. Membranes can provide attractive CO₂/CH₄ separation performance; however, typically show much lower efficiency in H₂S removal due to the closer molecular kinetic diameter of H₂S (3.6 Å) than CO₂ (3.3 Å) to CH₄ (3.8 Å). Due to unattractive H₂S/CH₄ separation efficiencies, reducing both CO₂ and H₂S concentration to the required level is difficult in the same membrane. Polymers, which are the dominant materials for membrane separation, are limited by a trade-off between permeability and selectivity^[5]. Crystalline molecular sieves, such as zeolites^[6] and metal-organic frameworks (MOFs)^[7], exhibit more attractive performance than polymers owing to their well-defined nanoporous structures^[8]. Unfortunately, scalable fabrication of pure zeolite or MOF membranes^[8b, 9] hasn't been developed limiting their use in large-scale membrane manufacturing. Moreover, MOF-based membranes have rarely been reported for effective removal of H₂S from natural gas, partially due to the excessively large and/or flexible apertures, and structural instability to highly corrosive H₂S in typical MOFs. Our recent work demonstrated that a properly selected polymer incorporated with H₂S-stable rare earth (RE)-**fcu**-MOF molecular sieves^[10] could realize efficient H₂S/CO₂/CH₄ separation^[11]. The hybrid mixed-matrix approach, if properly matched to transport properties and interphase compatibility between molecular sieve and polymer^[2], can provide highly desirable membranes. Such a membrane provides both high separation performance enabled by high-performing molecular sieves^[12], and economical fabrication based on a processing approach similar to that of pure polymers^[13].

A class of fluorinated MOFs — **SIFSIX**, **NbOFFIVE** and **AIFFIVE** materials^[14], offer two-dimensional nets based on linked metal nodes that are pillared via an inorganic molecular building block in the third dimension. These MOFs have received attention due to their excellent performance for adsorptive separation of CO₂^[15], acetylene separation from ethylene^[16], propylene from propane^[17] and dehydration^[18]. Highly attractive separation performance is expected in membranes based on fluorinated MOFs. In this work, we expand the use of these ultramicroporous fluorinated MOFs into membrane separation via the so-called mixed-matrix approach.

The membrane design approach we used is shown in Figure 1a. The pore structure of the MOF, with a general formula [M₁(M₂F_x)(pyrazine)₂]_n, was finely tuned by varying the metal M₁ (Ni or Cu) and the pillar ([NbOF₅]²⁻, [AlF₅]²⁻ or [SiF₆]²⁻) while using the same ligand (pyrazine, pyz), resulting in three kinds of fluorinated MOFs: [Ni(NbOF₅)(pyz)₂]_n (**NbOFFIVE-1-Ni**); [Ni(AlF₅)(pyz)₂]_n (**AIFFIVE-1-Ni**) and [Cu(SiF₆)(pyz)₂]_n (**SIFSIX-3-Cu**). Through the fine tuning of MOF structures and interfaces with the selected polymer matrices, we demonstrate [M₁(M₂F_x)(Ligand)₂]_n MOFs-based membranes for simultaneous removal of H₂S and CO₂ from natural gas with performance far

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beyond the polymer membrane state-of-the-art. Challenges in using the $[M_1(M_2F_x)(\text{Ligand})_2]_n$ MOFs for C_3H_6/C_3H_8 separation are also considered to illustrate the subtle balance needed to implement the mixed matrix paradigm. Two typical 6FDA-based polyimide polymer matrices^[4b], highly permeable 6FDA-DAM

[6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; DAM: 2,4,6-trimethyl-1,3-diaminobenzene] and crosslinkable PDMC (propane-diol monoesterified crosslinkable 6FDA/DAM:DABA), are selected to match molecular transport properties of the $[M_1(M_2F_x)(\text{Ligand})_2]_n$ MOF filler.

Figure 1. (a) Schematic of design approach using fluorinated MOF-based membranes for selective permeation of CO_2 and H_2S over CH_4 . More detailed information about molecular structures of the fluorinated MOFs and kinetic diameter of the gases are given in Figure S1 and Table S1. Sorption isotherms at 35 °C: (b) CO_2 and CH_4 for **NbOFFIVE-1-Ni** and **SIFSIX-3-Cu** (c) C_3H_6 and C_3H_8 for **NbOFFIVE-1-Ni** and (d) H_2S for **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni**. (e) PXRD patterns of for **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** crystals before and after long-term exposure to pure and high-pressure H_2S . SEM images: (f) **SIFSIX-3-Cu** nanocrystals; (g) cross-section of **SIFSIX-3-Cu/6FDA-DAM** MMM; (h) 4-cyanopyridine modified **NbOFFIVE-1-Ni** nanocrystals; and (i) cross-section of modified **NbOFFIVE-1-Ni/6FDA-DAM** MMM.

Before assessing these $[M_1(M_2F_x)(\text{Ligand})_2]_n$ MOFs as potential fillers for mixed matrix membrane materials, we evaluated their gas sorption properties to characterize their pore structures as a function of different metal clusters. Figure 1b compares CO_2 and CH_4 sorption isotherms of **NbOFFIVE-1-Ni** and **SIFSIX-3-Cu**, and the CO_2/CH_4 sorption selectivity (from pure gas adsorption) under each pressure was calculated and is shown in Figure S2 (Supporting Information). Compared with **SIFSIX-3-Cu**, **NbOFFIVE-1-Ni** shows a similar CO_2 sorption capacity with lower CH_4 uptake under the same condition, thus providing higher CO_2/CH_4 sorption selectivity. The higher sorption selectivity presumably reflects the larger $(NbOF_5)^{2-}$ than $(SiF_6)^{2-}$ pillars that

generate smaller aperture partially excluding sorption of CH_4 molecules^[17]. The CO_2 and CH_4 sorption properties of **AIFFIVE-1-Ni** crystals at high relative pressures is more or less similar to that of **NbOFFIVE-1-Ni** (Figure S3). The effect of the aperture size of **NbOFFIVE-1-Ni**, caused by steric hindrance between pyrazine molecules and $(NbOF_5)^{2-}$ pillars, is demonstrated by the adsorption cut-off between propylene (C_3H_6) and propane (C_3H_8) up to 2 bar, shown in Figure 1c. Figure 1d shows the sorption isotherms of pure H_2S in **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** with pressure up to 14 bar. Both MOFs exhibited very high H_2S sorption capacity, exceeding that of CO_2 in the MOF pore framework. The higher H_2S sorption in **AIFFIVE-1-Ni** than in

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NbOFFIVE-1-Ni is due to stronger dual interactions between hydrogen atoms of H₂S and the two nearby pillar-F atoms of the MOF framework. The results indicate that these fluorinated MOFs are highly and preferentially adsorptive toward CO₂ and even H₂S over CH₄, which offers an exciting opportunity for the selective transport of CO₂ and H₂S from CH₄ via membrane process. Moreover, Ni-based analogue provide better stability than **SIFSIX-3-Cu** in the presence of H₂S^[19]. The **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** are proven to be highly stable to corrosive H₂S, as evidenced from the PXRD patterns and IR spectra after long-term exposure of these crystals to pure and high-pressure H₂S (Figures 1e, S4). There are a few minor changes in XRD pattern and IR spectrum of the **AIFFIVE-1-Ni** crystals after long-term exposure to pure and high-pressure H₂S, which might be due to the adsorption of traces of H₂S in the pores of **AIFFIVE-1-Ni** sample after long-term H₂S sorption test.

We then fabricate the MOF-based mixed-matrix membrane (MMM) by casting a MOF-polymer solution comprising the selected [M₁(M₂F_x)(Ligand)₂]_n MOF crystals. The successful formation of MMMs is strongly dependent on interfacial morphology between filler and polymer. Non-ideal interfaces such as matrix rigidification or sieve-in-a-cage would reduce the gas permeability or selectivity^[20]. In this work, the conventional approach for making MMM, i.e., mixing dried [M₁(M₂F_x)(Ligand)₂]_n fluorinated MOF crystals with polyimide solution lead to interfacial voids in the casted **NbOFFIVE-1-Ni/6FDA-DAM** MMM (Figure S5a). Defects presumably arose due to interfacial stress during solvent evaporation^[21]. To improve the interphase compatibility, we replaced the 6FDA-DAM with hydroxyl groups-contained PDMC matrix and crosslinked the resulting **NbOFFIVE-1-Ni/PDMC** film. It was found that the interfaces were significantly improved by this “post-treatment” approach (Figure S5b). Alternatively, we took the solvent (e.g., THF) for dissolving polymer (e.g., polyimide) to exchange the solvent (e.g., methanol) for synthesizing MOF (e.g., **SIFSIX-3-Cu**) and used the mixed solutions of solvent-exchanged MOF and polymer to cast MMM (Figure S6). With this “wet incorporation” approach, well-dispersed **SIFSIX-3-Cu** nanocrystals were produced (Figure 1f) and an excellent interfacial morphology was obtained in the **SIFSIX-3-Cu/6FDA-DAM** MMM (Figure 1g). Inspired by this result, we further used 4-cyanopyridine to functionalize the **NbOFFIVE-1-Ni** so as to highly enhance its molecular interaction with the polyimide matrix, in which the –N– could interact with the Ni²⁺ on **NbOFFIVE-1-Ni** meanwhile the –CN might form interaction with –C=O on 6FDA-DAM (more details are given in Experimental of SI). The modified **NbOFFIVE-1-Ni** fillers formed an intact interface with 6FDA-DAM matrix (Figure 1h,i). Characterization by PXRD, IR and thermogravimetric analysis (TGA) showed good physicochemical properties of the fluorinated MOFs in the MMMs (Figure S7-9).

We measured the pure gas permeation through the **SIFSIX-3-Cu/6FDA-DAM** MMM and found enhancements in both CO₂ permeability and CO₂/CH₄ selectivity (Figure S10). Unfortunately, in 50/50 CO₂/CH₄ mixed-gas permeation, the selectivity decreases from 24.0 (for pure 6FDA-DAM membrane) to 20.3 in the **SIFSIX-3-Cu/6FDA-DAM** MMM, with a 52.5% higher CO₂ permeability (Figure 2a). These latter results indicate that **SIFSIX-**

3-Cu channels enhanced the CO₂ transport through the membrane, while the sorption competition between CO₂ and CH₄ in the **SIFSIX-3-Cu** may decrease the perm-selectivity for CO₂/CH₄ mixtures. The 6FDA-DAM MMM with ~20 wt% **NbOFFIVE-1-Ni**, whose aperture size is smaller and CH₄ sorption is lower than **SIFSIX-3-Cu**, gave higher mixed-gas CO₂/CH₄ selectivity and lower CO₂ permeability compared to **SIFSIX-3-Cu/6FDA-DAM** MMM at equivalent loading (Figure 2a). In fact, the CO₂/CH₄ selectivity of the **NbOFFIVE-1-Ni/6FDA-DAM** MMM (22.6) is even lower than that of the pure 6FDA-DAM membrane, which we attribute to by-pass gas transport through the non-selective interfacial voids^[20] (Figure S5a).

To explore the bypass transport pathway mechanism, we further measured 50/50 C₃H₆/C₃H₈ mixed-gas permeation performance of the **NbOFFIVE-1-Ni/6FDA-DAM** MMM. Theoretically, **NbOFFIVE-1-Ni** allows C₃H₆ entrance but should fully exclude C₃H₈ according to the steady-state sorption measurement (Figure 1d) and the previous study^[17]. Such exclusion should greatly enhance the selective permeation of C₃H₆ over C₃H₈ in the 6FDA-DAM membrane incorporated by **NbOFFIVE-1-Ni** in the absence of a bypass. In fact, we observed a reduced C₃H₆/C₃H₈ selectivity and 9 times higher C₃H₆ permeability in the pristine **NbOFFIVE-1-Ni/6FDA-DAM** MMM. The Maxwell model^[11] without bypass was used to predict theoretical performance limit of 6FDA-DAM (see Experimental in Supporting Information), indicated by the gray rectangle in Figure 2b. As expected, the C₃H₆/C₃H₈ separation performance of **NbOFFIVE-1-Ni/6FDA-DAM** MMM is inconsistent with Maxwell predictions, suggesting the existence of by-pass caused by interfacial voids^[20]. We notice that the increase in CO₂ permeability is less significant than for the C₃ case, suggesting that by-pass permeation for CO₂ is not much faster than through the polymer matrix and **NbOFFIVE-1-Ni** (Figure 2c).

These observations lead us to speculate that the high C₃ permeability reflects excessive swelling of interface voids by the more condensable C₃ molecules with higher swelling potential (Figure 2d). Indeed, the C₃ swelling for 6FDA-DAM is much stronger than CO₂ under the same conditions (e.g., 2-7 bar, 35°C). The **NbOFFIVE-1-Ni** shows much lower diffusivity for C₃ than CO₂. We believe that these facts make the C₃ molecules tend to permeate through the swelled interfacial voids, while CO₂ diffuses primarily through the 6FDA-DAM matrix, **NbOFFIVE-1-Ni** and less swollen interface with comparable rates (Figure 2c-d). The above combined complex factors led to a dramatic discrepancy of results of the high C₃ permeability and normal CO₂ permeability predicted by the Maxwell model.

Crosslinking is an efficient approach to suppress polymer swelling^[22]. As expected, the crosslinked **NbOFFIVE-1-Ni/PDMC** MMM shows more normal higher C₃H₆ permeability, but the C₃H₆/C₃H₈ selectivity is still highly inconsistent with Maxwell model predictions. It appears that despite improved interface adhesion by crosslinking the polymer matrix (Figure S5), molecular-scale incompatibility exists even without excessive swelling. We speculate that such subtle incompatibility enables by-pass transport in the **NbOFFIVE-1-Ni/PDMC** MMM, leading to reduced selectivity for C₃H₆/C₃H₈ and CO₂/CH₄ (Figures 2b, S11). Fortunately, incorporation of 4-cyanopyridine modified

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NbOFFIVE-1-Ni, which shows an excellent interfacial morphology characterized by SEM (Figure 1i), successfully enhanced both the permeability and selectivity of 6FDA-DAM membrane for CO₂/CH₄ mixtures (Figure 2a). This fact notwithstanding, C₃H₆/C₃H₈ permeation through the modified **NbOFFIVE-1-Ni**/6FDA-DAM MMM failed to fit within the Maxwell prediction area,

suggesting the lack of a suitable molecular level MMM interface. The surface fluorine of the fluorinated MOFs is believed to be responsible for the molecular incompatibility, but transport through **NbOFFIVE-1-Ni** and the MOF-polymer interfaces still provides substantial enhancement for CO₂/CH₄ separation performance.

Figure 2. (a) CO₂/CH₄ separation performance of 6FDA-DAM membrane and 6FDA-DAM MMMs incorporated by **SIFSIX-3-Cu**, pristine **NbOFFIVE-1-Ni** and modified **NbOFFIVE-1-Ni** (feed: 50/50 CO₂/CH₄ mixtures, 6.9 bar, 35 °C). (b) C₃H₆/C₃H₈ separation performance of 6FDA-DAM membrane and its MMMs incorporated by pristine **NbOFFIVE-1-Ni** and modified **NbOFFIVE-1-Ni**; PDMC membrane and **NbOFFIVE-1-Ni**/PDMC MMM (feed: 50/50 C₃H₆/C₃H₈ mixtures, 2 bar, 35 °C). The C₃H₆/C₃H₈ mixed-gas upper-bound is adopted from reference 12c. Schematic of (c) CO₂/CH₄ and (d) C₃H₆/C₃H₈ permeation through the matrix, MOF and interface of **NbOFFIVE-1-Ni**/6FDA-DAM MMM.

The enhanced selective permeation of CO₂ over CH₄ (Figure 2a), together with highly preferential H₂S sorption (Figure 1d) achieved in **NbOFFIVE-1-Ni** motivated us to further study the 6FDA-DAM MMM with optimized (4-cyanopyridine modified) **NbOFFIVE-1-Ni** for H₂S/CO₂/CH₄ separation. Its analogue, **AIFFIVE-1-Ni** is also incorporated into 6FDA-DAM for comparison. In the pure gas permeation, it was found that introducing **NbOFFIVE-1-Ni** or **AIFFIVE-1-Ni** highly improved the separation performance of the membrane for H₂S and CO₂ over CH₄ (Figure 3a). The **NbOFFIVE-1-Ni** MMM shows higher selectivity while

lower permeability than **AIFFIVE-1-Ni** MMM, which can be explained by the larger diameter of Nb⁵⁺ than Al³⁺ resulting in a tighter aperture size in **NbOFFIVE-1-Ni** than **AIFFIVE-1-Ni**. Both CO₂ and H₂S must be removed from CH₄ to meet the pipeline specifications^[23]. This requirement led us also to explore simultaneous removal of H₂S and CO₂ from CH₄ stream using a highly aggressive model natural gas feed (20% H₂S, 20% CO₂ and 60% CH₄). Acid gas removal performance for natural gas can be conveniently evaluated in terms of the total acid gas permeability $[P(\text{CO}_2)+P(\text{H}_2\text{S})]$ and selectivity

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$[P(\text{CO}_2)+P(\text{H}_2\text{S})]/P(\text{CH}_4)]^{[23]}$. The separation performance of 6FDA-DAM membrane is highly improved by introducing **NbOFFIVE-1-Ni** or **AIFFIVE-1-Ni**. Such MMMs have properties far above the performance limit of glassy polymers such as cellulose acetate (CA), 6FDA-DAM/DABA and PIM-6FDA-OH for $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$ separation (Figure 3b, Table S2). It is also interesting to compare the performance of 6FDA-DAM MMMs

incorporated with several other MOFs at ~20 wt% particle loading. **NbOFFIVE-1-Ni** with tighter aperture size, provides much higher acid gas selectivity compared to **AIFFIVE-1-Ni** which is consistent with pure gas permeation result. The performance of **NbOFFIVE-1-Ni** MMM also exceeds RE-**fcu**-MOFs MMMs that we recently discovered for efficient $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$ separation^[11].

Figure 3. Separation performance and transport properties of 6FDA-DAM membrane, **NbOFFIVE-1-Ni**/6FDA-DAM MMM and **AIFFIVE-1-Ni**/6FDA-DAM MMM for $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$: (a) pure gas permeation; (b) mixed-gas permeation and compared with literature. The $(\text{CO}_2+\text{H}_2\text{S})/\text{CH}_4$ mixed-gas upper-bound is adopted from reference 11; (c) gas solubility and diffusivity; (d) sorption selectivity and diffusion selectivity. To obtain individual permeabilities in model natural gas permeation (20/20/60 $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$ mixtures with total pressure of 6.9 bar), pure H_2S or CO_2 permeation was conducted under 1.38 bar, and pure CH_4 permeation was conducted under 4.14 bar at 35 °C.

To further understand the transport mechanism in **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** MMMs, we deconvoluted the permeability (P_i) into the product of sorption coefficient (solubility, S_i) and diffusion coefficient (diffusivity, D_i), according to the sorption-diffusion model^[24]. High-pressure sorption measurements (0-14 bar) were employed to determine the solubility and diffusivity under conditions that are identical to the membrane permeation measurements. Sorption isotherms of H_2S , CO_2 and CH_4 in 6FDA-DAM and its **NbOFFIVE-1-Ni** or **AIFFIVE-1-Ni** MMMs are shown in Figure S12 and calculated sorption and diffusion data are summarized in Figure 3c-d. The gas sorption and diffusion in 6FDA-DAM are enhanced by the incorporation of **NbOFFIVE-1-Ni** or **AIFFIVE-1-Ni**. On the one hand, this is partially owing to the higher sorption capacity of **NbOFFIVE-1-Ni**

or **AIFFIVE-1-Ni** than that of 6FDA-DAM under the permeation pressure (Figure 3c). On the other hand, the well-defined pores of **NbOFFIVE-1-Ni** or **AIFFIVE-1-Ni** provide channels for faster molecular diffusion. More importantly, these MOF apertures exhibit molecular sieving properties that increase the diffusion selectivity for both H_2S and CO_2 over CH_4 (Figure 3d). The differences in gas affinity and aperture size between **NbOFFIVE-1-Ni** and **AIFFIVE-1-Ni** account for the variation of transport properties in their MMMs.

In conclusion, we demonstrate fluorinated MOFs for membrane separation via rational incorporation of these molecular sieves into the selected polymer. The fluorinated MOF-based hybrid materials with finely tuned molecular transport channels greatly improved molecular sieving properties of the

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polymer matrices, far beyond the existing glassy polymer-based membranes for challenging *total* acid gas removal from natural gas. With versatile pore structures tailored by the size and chemistry of metal pillars and organic linkers, the robust fluorinated MOFs open a new door to efficient membrane separation processes that require precise discrimination of closely sized molecules. Additional work is underway to explore the membrane transport properties by systematically varying the fabrication parameters (e.g., MOF loading), and the operation conditions (e.g., feed pressure).

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Keywords: MOF • mixed matrix membrane • natural gas • H₂S • CO₂/CH₄

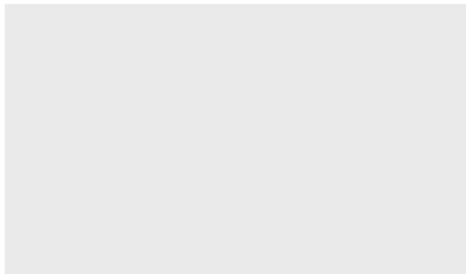
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New fluorinated MOF based mixed-matrix membranes with finely controlled molecular transport in the channels through MOF aperture exhibit excellent molecular sieving properties that significantly outperform state-of-the-art membranes for simultaneous removal of H₂S and CO₂ from natural gas.



G. Liu, A. Cadiou, Y. Liu, K. Adil, V. Chernikova, I.-D. Carja, Y. Belmabkhout, M. Karunakaran, O. Shekhah, C. Zhang, A. Itta, S. Yi, M. Eddaoudi, W.J. Koros**

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Enabling fluorinated MOF-based membranes for simultaneous removal of H₂S and CO₂ from natural gas

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