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Fluorinated MOF platform for selective removal and sensing of SO₂ from flue gas and air

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Conventional SO₂ scrubbing agents, namely calcium oxide and zeolites, are often used to remove SO₂ using a strong or irreversible adsorption-based process. However, adsorbents capable of sensing and selectively capturing this toxic molecule in a reversible manner, with in-depth understanding of structure–property relationships, have been rarely explored. Here we report the selective removal and sensing of SO₂ using recently unveiled fluorinated metal–organic frameworks (MOFs). Mixed gas adsorption experiments were performed at low concentrations ranging from 250 p.p.m. to 7% of SO₂. Direct mixed gas column breakthrough and/or column desorption experiments revealed an unprecedented SO₂ affinity for KAUST-7 (NbOFFIVE-1-Ni) and KAUST-8 (AIFIVE-1-Ni) MOFs. Furthermore, MOF-coated quartz crystal microbalance transducers were used to develop sensors with the ability to detect SO₂ at low concentrations ranging from 25 to 500 p.p.m.

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Global warming and other environmental/ecological issues have forced our society to adopt stringent rules for industrial waste and be on the lookout for ways to improve indoor and outdoor air quality, including in industrial sites. One major form of industrial waste with an adverse effect on the environment is flue gas. Flue gas generated by large industries and power plants resulting from burning fossil fuel contains CO₂ (at a low percent concentration), SO₂ (500–2000 p.p.m.), NO₂ (few p.p.m.), water vapor, and nitrogen (as the dominant gas)¹. Although the concentration of SO₂ in flue gas feed is low, it could be poisonous for most liquid- or/and solid-state-based CO₂ separating agents. Therefore, the removal of SO₂ from flue gas is of prime importance². Current SO₂ removal technology involves the irreversible acid–base reaction of SO₂ with CaO to form CaSO₃³. The main drawback of this technology is its relatively low removal efficiency (<90%) associated with an almost impossible regeneration step due to its extremely energy-intensive cost. Therefore, cyclable physical sorption technology is perceived as an effective alternative approach. Hence, identification of an adsorbent that can efficiently capture SO₂, particularly at low concentration (<500 p.p.m.), is crucial.

When SO₂ is not controlled and is emitted into the atmosphere, it has adverse effects on the environment, such as acid rain, and must be monitored^{4,5}. Therefore, it is necessary to find efficient solutions to sense SO₂ at p.p.m. level (above 25 p.p.m.) in both dry and humid conditions. Recently, there have been considerable efforts in developing SO₂ sensing devices based on metal oxides (such as SnO₂, WO₃, and TiO₂) due to their excellent sensitivity, selectivity, response time, and recovery time^{6–10}. However, most of the semiconductor-based SO₂ sensors were reported to require high temperatures (200–600 °C), leading to high levels of power consumption^{11–15}. There is therefore a need for gas sensors that operate at room temperature (RT)^{16–18}, which would be an important parameter and invaluable milestone for developing alternate materials suitable for detecting SO₂.

Metal–organic frameworks (MOFs), one of the most recent classes of porous materials, have attracted immense interest due to their potential to address many enduring challenges pertaining to various key applications^{19–21} such as separation, storage, catalysis, and sensing^{22–24}. Although many of these MOFs possess good-to-excellent chemical stability (which is a prerequisite for practical industrial applications)^{25,26}, there are only a few examples of SO₂ adsorption on MOFs, mainly due to its corrosive nature^{27–36}. Many of these reported MOFs adsorb SO₂ irreversibly or undergo phase transformations and they are not suitable for SO₂–structural-adsorption-sensing relationships studies; only a handful of MOFs are proven for cyclic stability and SO₂ capture at flue gas concentration^{27–30}. In addition, designing a sensor device for reversible SO₂ sensing at p.p.m. level and in the presence of atmospheric moisture is still an ongoing challenge.

Here we report the use of isostructural fluorinated MOFs for (i) selective removal of SO₂ from synthetic flue gas and (ii) sensing of SO₂^{37,38} using a quartz crystal microbalance (QCM) as a transducer^{18,39–41}, as the coating of MOFs on the QCM electrodes can detect the change in mass of sub-nanograms upon adsorption or desorption of molecules by the MOF layer^{42,43}. We unveiled an unprecedented concurrent removal of SO₂/CO₂ from synthetic flue gas and remarkable detection capability in p.p.m. level of SO₂ concentration in both dry and humid conditions.

Results

SO₂ removal from flue gas. Recently, our exploration of fluorinated MOF platforms, namely KAUST-7 ([Ni(NbOF₅)(pyrazine)₂].2H₂O, apparent surface area 280 m² g^{−1}, estimated pore volume 0.095 cm³ g^{−1}) and KAUST-8 ([Ni(AlF₅(OH₂))

(pyrazine)₂].2H₂O, apparent surface area 258 m² g^{−1}, estimated pore volume 0.102 cm³ g^{−1}), resulted in many desirable properties that include direct air capture⁴⁴, propane-propylene separation⁴⁵, gas/vapor dehydration⁴⁶, and acid gas (H₂S, CO₂) removal⁴⁷. Although both of the MOFs are isostructural, the subtle differences in their chemical compositions, pillared by the inorganic moiety (NbOF₅)^{2−} instead of (AlF₅(OH₂))^{2−}, allowed the modulation of their properties by varying the content and intermolecular spacing of pending fluoride groups realized via different tilts of pyrazine molecules (Fig. 1). Inspired by the excellent stability and the modular nature of these MOF materials^{44–46}, we investigated their SO₂ removal and sensing in synthetic flue gas and air, respectively.

KAUST-7 was first investigated for SO₂ sorption, which is also one of the best physisorbent materials for capturing CO₂ at atmospheric concentration⁴⁴ with good water stability⁴⁵. The steep, pure SO₂ adsorption isotherm collected at 25 °C (Supplementary Figure 1) suggested a high affinity of the KAUST-7 framework for SO₂. To gain better insight on the SO₂ position within the framework and the governing interactions responsible for resultant strong affinity, we performed in situ single crystal X-ray diffraction (SCXRD) study on a suitable single crystal of KAUST-7 at 296 K under 4–5 bar of SO₂-containing atmosphere (7% SO₂, 93% N₂). The structure analysis revealed that the resultant compound crystallized in the tetragonal space group *P4/nbm* with the unit cell parameters $a = b = 9.9249(2)$ Å and $c = 7.8387(2)$ Å (Supplementary Table 1). An axial distortion of the octahedral (NbOF₅)^{2−} anion (Nb–O bond is shorter than Nb–F_{trans}, 1.82(3) and 2.03(3) Å, respectively) was observed and manifested in a disorder in the structure: the Nb atom was split over two positions, whereas the oxygen and the *trans*-fluoride were refined in the same position with equal thermal parameters (Supplementary Figure 2a). The fluorinated pillars are turned by $\varphi = \pm 8.5(2)^\circ$ from the direction toward the center of the channel (Supplementary Figure 2b) depending on the central atom position. The (NbOF₅)^{2−} anion twist is stabilized by four pairs of C–H...F hydrogen bonds with the adjacent pyrazine molecules: the H...F distances and C–H...F angles are 2.45 Å and 158° in the case of the Nb shifted toward that Ni(pyrazine)₂ layer, and 2.52 Å and 170° when in the opposite direction (Supplementary Figure 2c and 2d). The SO₂ molecule was localized in the center of the one-dimensional (1D) channel at a special position, similar to CO₂ molecule in the KAUST-7 (CO₂) structure⁴⁴. As the site symmetry ($-42m$) is higher than the symmetry of the guest molecule, the SO₂ is disordered over four positions around axis -4 with the total occupancy refined to 0.424(4). Contrary to the linear CO₂ molecule surrounded by four F-pillars, the electropositive sulfur atom of the triangular SO₂ molecule interacts with only two electronegative fluorine atoms of the adjacent (NbOF₅)^{2−} anions (S...F distances of 2.80(1) and 2.86(1) Å) shown in Fig. 2a–c. In addition, the SO₂ molecule in the MOF is stabilized by four C–H...O contacts with the hydrogen atoms of four different pyrazines (H...O distance = 2.87 Å, angle = 120°).

This observation is corroborated by density functional theory (DFT) calculations, which revealed high SO₂/KAUST-7 interaction energy of -64.8 kJ mol^{−1}. This is due to a relatively stronger interaction between the sulfur atom of SO₂ and the F-pillars with characteristic interatomic distances of 2.9 Å (Supplementary Figure 3a) along with a charge transfer between the guest and this region of the MOF. Interestingly, the SO₂/KAUST-7 interaction energy is as high as the value calculated for CO₂ (-54.5 kJ mol^{−1}). This latter molecule occupies slightly different sites than SO₂, implying an interaction of the guest molecule with both the F-pillars and the pyrazine groups (Supplementary Figure 3b). The so-predicted energetics and spatial distributions

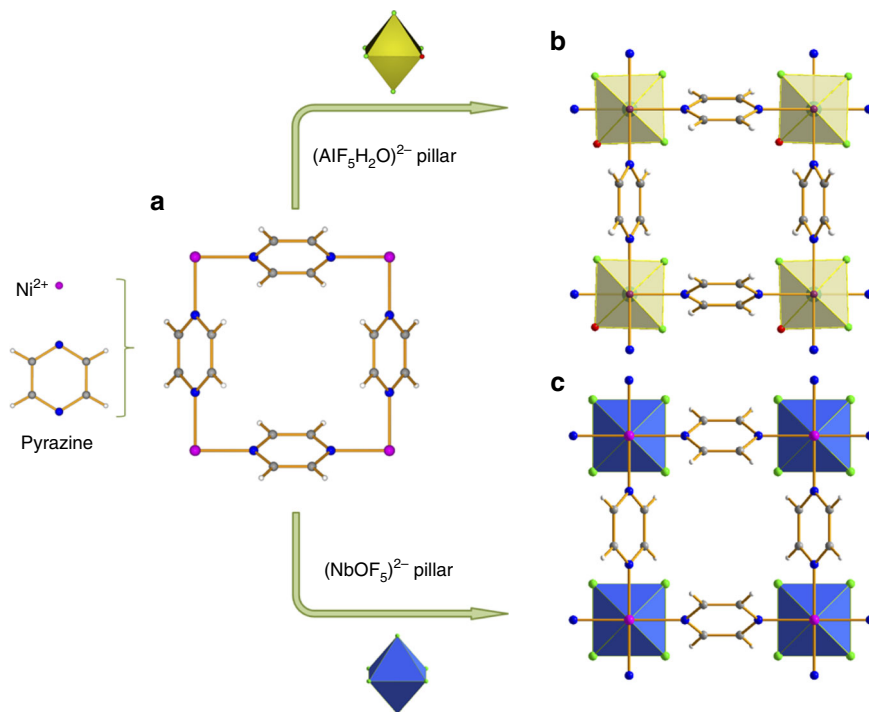


Fig. 1 Synthesis and crystal structure of KAUST-7 and KAUST-8. **a** $[\text{Ni}(\text{pyrazine})_2]^{2+}$ square grid resulting from the connection of Ni^{2+} cations and pyrazine molecules. **b** Crystal structure of KAUST-8 resulting from the pillaring of $[\text{Ni}(\text{pyrazine})_2]^{2+}$ square grid with $(\text{AlF}_5(\text{OH}_2))^{2-}$ pillar. **c** Crystal structure of KAUST-7 resulting from the pillaring of $[\text{Ni}(\text{pyrazine})_2]^{2+}$ square grid with $(\text{NbOF}_5)^{2-}$ pillar

for both molecules as single components suggest simultaneous capture of SO_2 and CO_2 .

Cyclic adsorption column breakthrough tests with SO_2/N_2 : 7/93 indicate stability and good uptake ($\approx 2.2 \text{ mmol g}^{-1}$) of SO_2 (Fig. 3a). Furthermore, adsorption column breakthrough experiments with $\text{SO}_2/\text{CO}_2/\text{N}_2$: 4/4/92 gas mixture showed simultaneous and equal retention time in the column for SO_2 and CO_2 , demonstrating identical uptake of $\approx 1.1 \text{ mmol g}^{-1}$ (Supplementary Figure 4), which is consistent with the simulated energetics trends. Upon decreasing the SO_2 concentration with nitrogen in the range commonly observed in flue gas (500 p.p.m.) (SO_2/N_2 : 0.05/99.95 mixture) and the immediately dangerous to life or health concentration (100 p.p.m.), KAUST-7 still maintains a high SO_2 uptake of about 1.4 mmol g^{-1} at 500 p.p.m. SO_2 concentration (Fig. 3b). Interestingly, adsorption column breakthrough experiments under mimicked flue gas conditions with 500 p.p.m. of SO_2 and 10% CO_2 in N_2 ($\text{SO}_2/\text{CO}_2/\text{N}_2$: 0.05/10/89.95) resulted in equal and simultaneous retention time for both SO_2 and CO_2 , leading to uptakes of $\approx 0.01 \text{ mmol g}^{-1}$ and $\approx 2.2 \text{ mmol g}^{-1}$, respectively (Fig. 3c). The direct co-adsorption experiments with different SO_2 and CO_2 compositions (4% SO_2 , 4% CO_2 , balance N_2 and 500 p.p.m. SO_2 , 10% CO_2 , balance N_2) demonstrate that KAUST-7 exhibits equal selectivity toward SO_2 and CO_2 (SO_2/CO_2 selectivity ≈ 1), which is desirable for simultaneous CO_2 and SO_2 capture in flue gas (containing low SO_2 concentrations). Nevertheless, temperature-programmed desorption (TPD) confirmed the presence of CO_2 only with an undetectable amount of SO_2 (Fig. 3d) in the adsorbed phase as the amount of SO_2 adsorbed is negligible owing to its low concentration. The performance of KAUST-7 using humid ($\approx 40\%$ Relative Humidity (RH)) 250 p.p.m. $\text{SO}_2/\text{balance N}_2$ gas mixture was also investigated (Supplementary Figure 5); it is evident that SO_2 has same breakthrough time as that of water and results in a lower SO_2 uptake under humid condition compared with the dry condition, which is not surprising

considering the concentration of water is around 50 times higher than that of SO_2 . In addition to previously reported excellent water stability^{44,45}, SO_2 stability of the KAUST-7 was proven by powder X-ray diffraction (PXRD) comparison of the materials before and after dry and humid SO_2 exposure (Supplementary Figure 6), CO_2 breakthrough study before and after 7% SO_2 breakthrough experiments (Supplementary Figure 7), and CO_2 adsorption isotherm after the humid SO_2 breakthrough experiment (Supplementary Figure 8).

In our quest for a material with a more favorable selectivity for SO_2 removal from flue gas than CO_2 (at 500 p.p.m. of SO_2), we opted to investigate an analog of KAUST-7 with lower CO_2 interactions and potentially higher SO_2 interactions. Inspired by our results with KAUST-8 for dehydration of gases⁴⁶ and simultaneous removal of $\text{H}_2\text{S}/\text{CO}_2$ ⁴⁷, we found it compelling to explore the structural SO_2/CO_2 co-adsorption property. KAUST-8 exhibits three pendant fluoride groups with slightly higher F...F distance (3.613 \AA) and one potential open metal site, whereas KAUST-7 contains four pendants fluoride with smaller F...F distance ($3.210(8) \text{ \AA}$) and no open metal site. Such minute differences in structural features led us to realize equal selectivity for CO_2 and H_2S over a wide range of concentrations and temperatures⁴⁷. Encouraged by this structure–property tuning of H_2S and CO_2 adsorption affinity using this MOF, we expected KAUST-8 to be more selective toward SO_2 than CO_2 . Similar to gain better insight of the KAUST-8 system, SCXRD data were collected on the SO_2 -loaded KAUST-8 crystal. The structure analysis revealed the resultant compound crystallized in the tetragonal space group $P4/mmm$ with the unit cell parameters $a = b = 6.9996(2) \text{ \AA}$ and $c = 7.7033(2) \text{ \AA}$ (Fig. 2b–d, Supplementary Table 2). Contrary to KAUST-7, a rotational disorder of the $(\text{AlF}_5)^{2-}$ is caused by trigonal bipyramidal shape of the anions located at the axis 4 among four 1D channels in the structure. When one fluorine atom of a pillar is directed perfectly to the channel center ($\varphi = 0^\circ$), in the two other adjacent channels Al–F

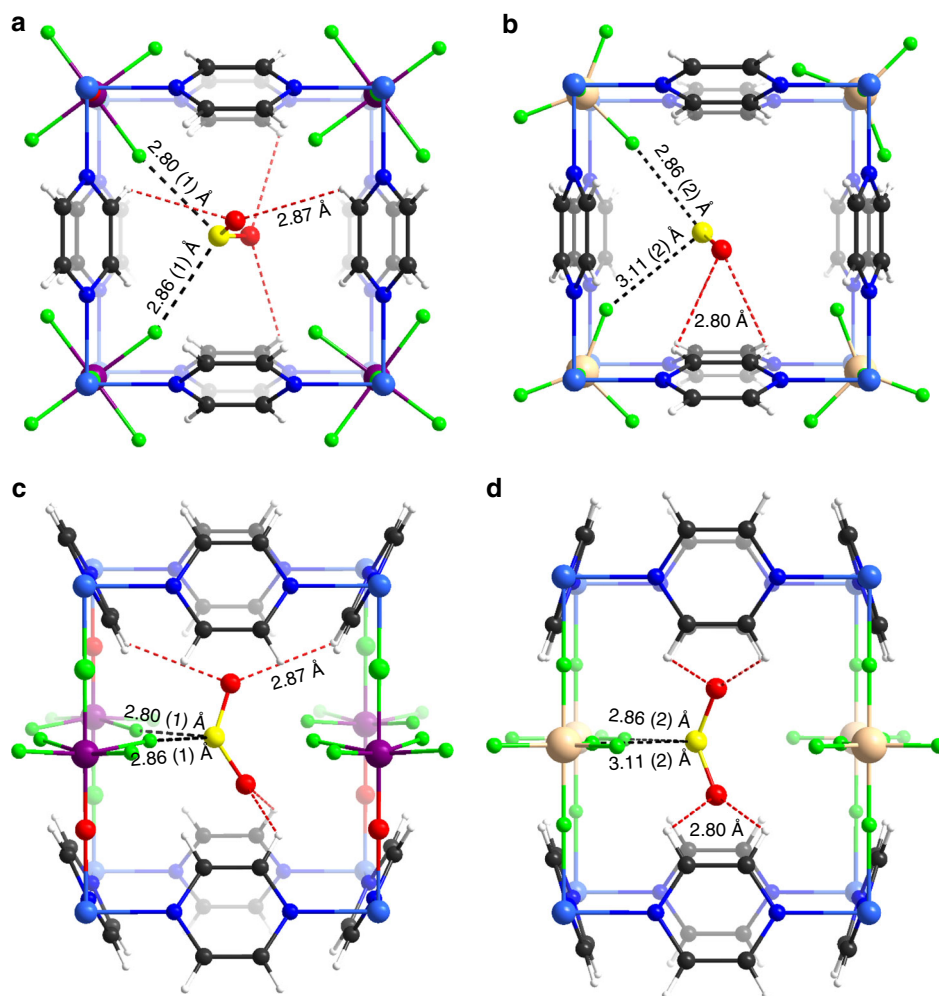


Fig. 2 In situ visualization of SO_2 in host frameworks. Intermolecular host-guest interactions in SO_2 loaded crystal structures of **a, c** KAUST-7 and **b, d** KAUST-8

bonds of the same anion are directed $\pm 24.1(4)^\circ$ out the diagonal direction, and in the fourth channel there are no F-atoms from this pillar (Supplementary Figure 9a). Therefore, the single average cage aperture is formed by fluorine atoms of three adjacent $(\text{AlF}_5)^{2-}$ anions only. The pillar twist is stabilized by three pairs of C-H...F hydrogen bonds between the pyrazine molecules and the fluorine atoms with H...F distances and C-H...F angles of 2.38 Å and 178° , 2.48 Å and 134° , and 2.17 Å and 161° , respectively (Supplementary Figure 9b and 9c). Similar to SO_2 -loaded KAUST-7 structure, the guest SO_2 molecule is disordered in the center of the 1D channel (the special position symmetry is $4/mmm$) of the KAUST-8 MOF. The distances between electropositive sulfur atom of the SO_2 molecule and fluorine atoms of adjacent F-pillars equals 2.86(2), 3.11(2), or 3.25(1) Å depending on the $(\text{AlF}_5)^{2-}$ orientation ($\varphi = 0^\circ$ or $\pm 24.1(4)^\circ$, Supplementary Figure 9d) and each of them is less than the sum of the S and F van der Waals radii (3.27 Å). Contrary to the KAUST-7 structure, the SO_2 molecule participates in four C-H...O contacts with only two neighboring pyrazines (H...O distance = 2.80 Å, angle = 105°). These observations were supported by DFT calculations and it revealed a lowering of the host/guest interaction energy of CO_2 for KAUST-8 compared with KAUST-7 ($-47.0 \text{ kJ mol}^{-1}$ vs. $-54.5 \text{ kJ mol}^{-1}$). In the case of KAUST-8, the trigonal bipyramidal-like Al^{3+} environment does not allow for further optimal interactions between a carbon atom in CO_2 and four F-pillars (Supplementary figure 3d), as seen

in KAUST-7. DFT calculations were further performed starting with the SO_2 -loaded crystal structure model elucidated from SCD data. Interestingly, the simulated preferential location of SO_2 is slightly pushed toward the pore wall, as compared with the scenario in KAUST-7, with the formation of a dual interaction between its sulfur atoms and the two nearby F-pillars, as well as its oxygen atoms interacting with the pyrazine linker with shorter interacting distances (Supplementary Figure 3c). The resulting geometry led to a slight enhancement of the SO_2 /host interaction energy ($-73.9 \text{ kJ mol}^{-1}$) and reduced affinity toward CO_2 , making KAUST-8 a promising candidate to selectively adsorb SO_2 over CO_2 .

Investigation of single component SO_2 adsorption showed that KAUST-8 also exhibits steep adsorption isotherm at 25°C (Supplementary Figure 10). The corresponding adsorption column breakthrough experiment with SO_2/N_2 : 7/93 mixture showed a higher uptake of 2.2 mmol g^{-1} (Fig. 4a). KAUST-8 can be completely regenerated by heating at 105°C in a vacuum or inert gas environment (Supplementary Figure 11), confirming SO_2 stability and recyclability. During the adsorption column breakthrough experiments carried out with low SO_2 (SO_2/N_2 : 0.05/99.95) mixture, KAUST-8 still maintained a high uptake of SO_2 (1.6 mmol g^{-1}) (Fig. 4b, Supplementary Table 3). Subsequent TPD analysis of the adsorbed phase confirmed the adsorption of SO_2 (Supplementary Figure 12) at p.p.m. level. Supplementary Table 3 compares SO_2 uptake of different benchmark MOFs at

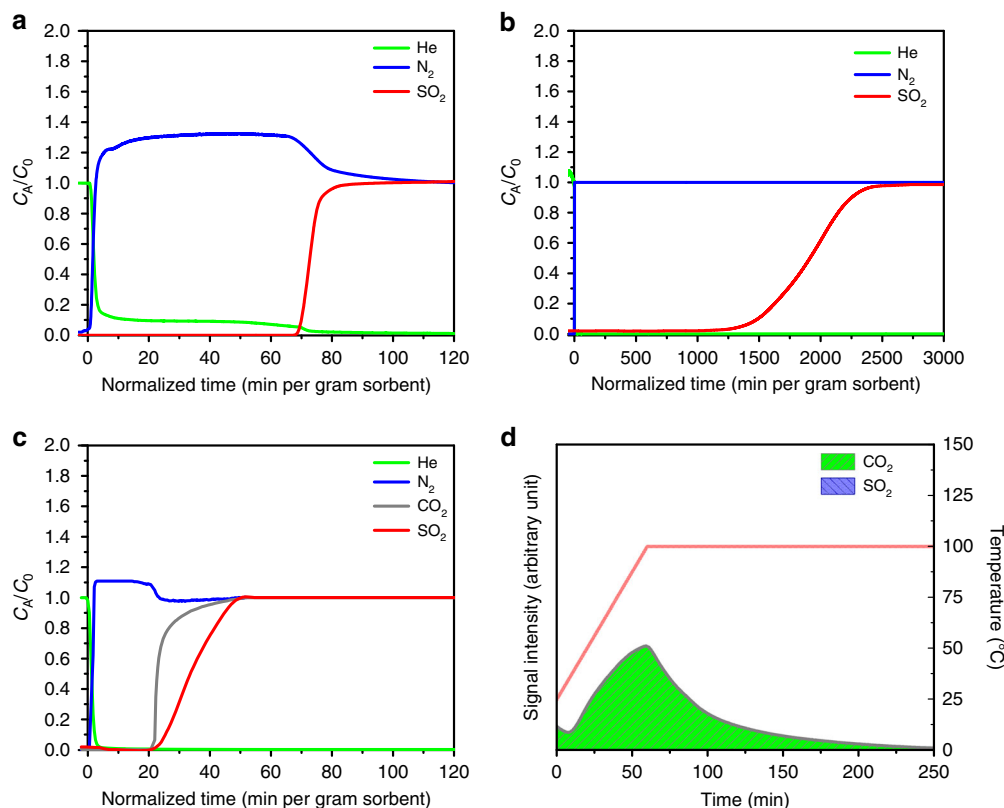


Fig. 3 CO_2/SO_2 capture performance of KAUST-7. Adsorption column breakthrough experiments for KAUST-7 with **a** SO_2/N_2 : 7/93 mixture ($10 \text{ cm}^3 \text{ min}^{-1}$, flow rate), **b** SO_2/N_2 : 0.05/99.95 mixture ($40 \text{ cm}^3 \text{ min}^{-1}$, flow rate), and **c** $\text{SO}_2/\text{CO}_2/\text{N}_2$: 0.05/10/89.95 mixture ($25 \text{ cm}^3 \text{ min}^{-1}$, flow rate). **d** Temperature-programmed desorption after initial adsorption in the column using a mixture akin to flue gas ($\text{SO}_2/\text{CO}_2/\text{N}_2$: 0.05/10/89.95), suggesting an adsorbed phase composition dominated by CO_2

low concentration. Materials with relatively more open structure such as MFM-300(In, Al) have very high SO_2 uptake at higher SO_2 concentration; however, they have lower SO_2 uptake at lower concentrations close to 500 p.p.m. (of interest for application such as SO_2 capture from flue gas and SO_2 sensing) compared with KAUST-7, KAUST-8, and some SIF_6^{2-} based MOFs. Materials such as MFM-300(In, Al) with very high SO_2 uptake at higher SO_2 concentration could have many important applications. MFM-300(In, Al) (very high uptake at higher concentration), and KAUST-7 and KAUST-8 (high uptake at very low concentration) are complementary to each other and their uses depend upon nature of the application. Adsorption column breakthrough experiments with synthetic flue gas using a $\text{SO}_2/\text{CO}_2/\text{N}_2$: 0.05/10/89.95 mixture showed that SO_2 continues to be adsorbed for long durations past the CO_2 breakthrough time (Fig. 4c). This indicates that the adsorbed CO_2 is replaced by SO_2 from the gas mixture, which is consistent with a much higher estimated interaction energy of SO_2 over CO_2 . Subsequent TPD analysis suggests an adsorbed phase composition of 1.5 mmol g^{-1} for CO_2 and 0.5 mmol g^{-1} for SO_2 , which is remarkable considering the large difference in concentrations of CO_2 and SO_2 in the synthetic flue gas (Fig. 4d). A selectivity of $\text{SO}_2/\text{CO}_2 \approx 66$ obtained from the combination of breakthrough and TPD experiment shows that KAUST-8 is a highly efficient material for SO_2 removal at a p.p.m. level and is promising for selectively removing SO_2 from flue gas. The performance of KAUST-8 using humid ($\approx 40\% \text{ RH}$) 250 p.p.m. $\text{SO}_2/\text{balance N}_2$ gas mixture was also investigated (Supplementary Figure 13). For KAUST-8, also SO_2 has almost the same breakthrough time as that of water; however, owing to its higher water adsorbing capacity than KAUST-7, it can adsorb more SO_2 compared with KAUST-7 under the same conditions.

Uptake of SO_2 by KAUST-8 in humid condition is notable considering in the above experiment gas stream contained almost 50 times higher concentration of water than SO_2 . In addition to previously reported excellent water stability⁴⁶, SO_2 stability of the KAUST-8 was proven by PXRD comparison of the materials before and after dry and humid SO_2 exposure (Supplementary Figure 14), CO_2 breakthrough study before and after 7% SO_2 breakthrough experiments (Supplementary Figure 15) and CO_2 adsorption isotherm after the humid SO_2 breakthrough experiment (Supplementary Figure 16).

Selective SO_2 detection from air. From the adsorptive separation study above, KAUST-8 and KAUST-7 were shown to exhibit tunable $\text{CO}_2/\text{H}_2\text{S}$ selectivity, molecules that are present in environments contaminated with SO_2 . To benefit from the outstanding properties of this platform, we found it compelling to explore the feasibility of depositing KAUST-8 and KAUST-7 on a QCM electrode and unveiling their SO_2 sensing properties in the presence and absence of humidity to mimic atmospheric conditions. Weight-detectable sensor such as QCM has been used in this study to detect SO_2 accurately when the disturbing presence of moisture is involved. These imply that QCM device can be an alternative to IDE⁴⁸ when testing for a gas in the presence of humidity. Part of the reason for this difference is that IDE sensors are based on the change in dielectric constant ($\epsilon_{\text{H}_2\text{O}} = 80$ and $\epsilon_{\text{SO}_2} = 16$) and in order to detect SO_2 accurately in the presence of moisture the deposited materials on the IDE-type electrode has to overcome the high dielectric constant for H_2O .

The surface morphology of KAUST-8 and KAUST-7 coated on QCM (see inset) was studied using scanning electron microscopy.

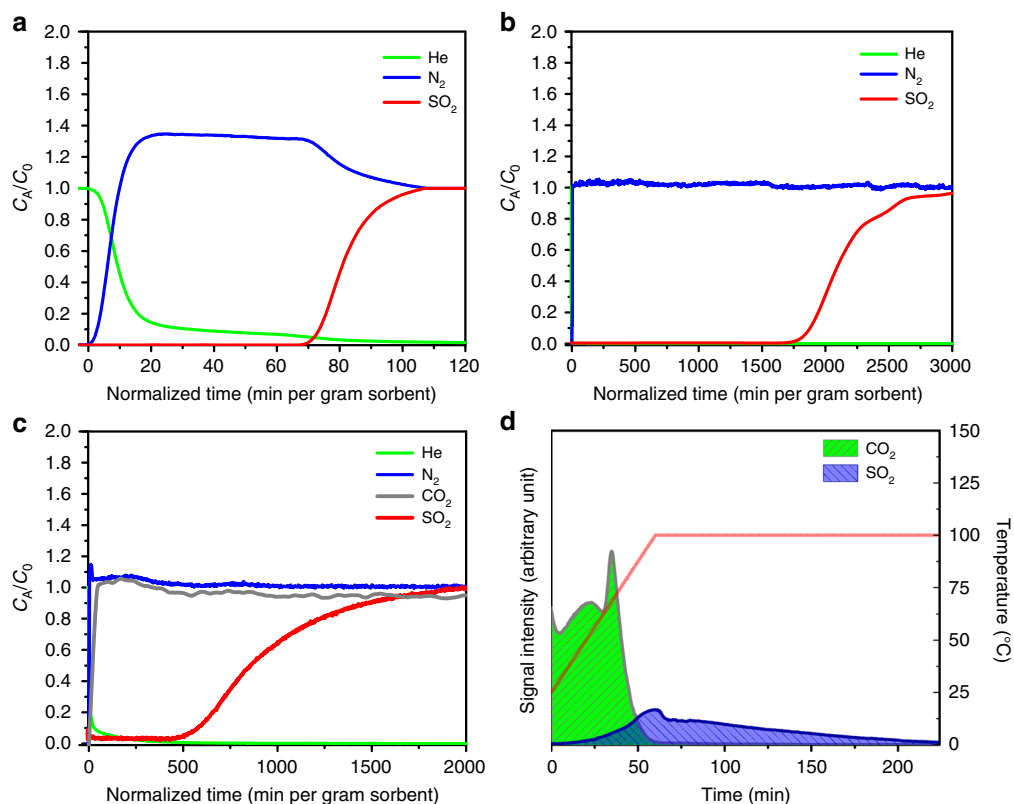


Fig. 4 CO_2/SO_2 capture performance of KAUST-8. Adsorption column breakthrough experiments for KAUST-8 with **a** SO_2/N_2 : 7/93 ($10 \text{ cm}^3 \text{ min}^{-1}$, flow rate), **b** SO_2/N_2 : 0.05/99.95 mixture ($40 \text{ cm}^3 \text{ min}^{-1}$, flow rate), and **c** $\text{SO}_2/\text{CO}_2/\text{N}_2$: 0.05/10/89.95 ($40 \text{ cm}^3 \text{ min}^{-1}$, flow rate). **d** TPD experiment suggests a considerable amount of SO_2 along with CO_2 as adsorbed phase after a breakthrough experiment with 500 p.p.m. SO_2 in the presence of 10% CO_2 and balance N_2

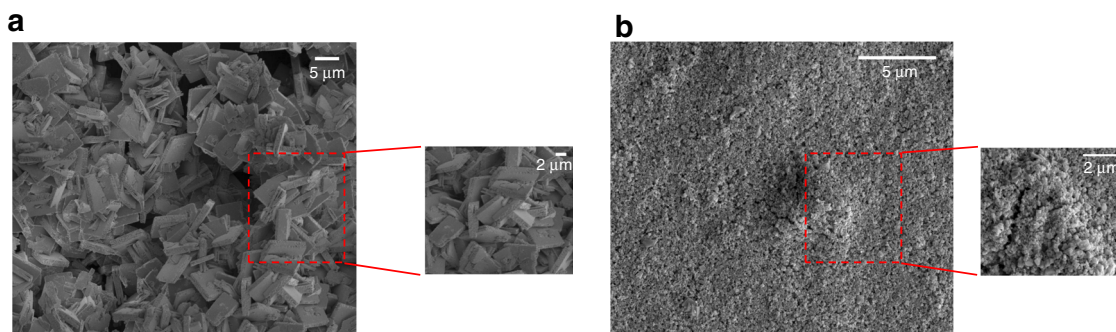


Fig. 5 Scanning electron microscopy of thin films. SEM micrographs at a high and low magnification of **a** KAUST-7 and **b** KAUST-8 thin films coated on the gold electrode of QCM

The thin films of both MOFs were found to be compact and uniform. The densely packed MOFs crystals were uniformly deposited on the QCM substrate with low intergranular voids and random orientation. As illustrated in Fig. 5, the coating of KAUST-7 led to cubic crystallites of $\sim 150 \text{ nm}$, whereas for the KAUST-8 films the size of the crystallites is significantly larger at $\sim 30 \mu\text{m}$. PXRD experiments were carried out to confirm the purity and crystallinity of the deposited MOFs (Supplementary Figure 17).

The sensitivity ($\Delta f/f$) of KAUST-8- and KAUST-7-coated QCM devices were measured for different concentrations of SO_2 , ranging from 0 to 500 p.p.m. in balance with nitrogen¹⁸. Uncoated QCM showed a negligible response to SO_2 . With the increase in the concentration of SO_2 , both MOF-coated sensors

responded with a nonlinear decrease in sensitivity (Fig. 6) and (Supplementary Figure 18). The lowest detection limit, defined theoretically using a largely accepted methodology by the sensing community⁴², was estimated to be about 100 p.p.b. (with noise drift in the resonance frequency of $\pm 1.5 \text{ Hz}$)⁴⁹. By optimizing the device parameters, drift in the sensors resonance frequency, this detection limit can be reduced to below 0.2 Hz^{50,51} and thereby improving the detection limit to $< 15 \text{ p.p.b.}$ This discrepancy/gap between the theoretical and experimental detection limits (15 p.p.b. and 5 p.p.m.) was never discussed previously in the open literature.

After each exposure cycle, the device was in situ heated at 105°C in ambient nitrogen for 4 h, allowing the reactivation of the evaluated MOF thin film for another sensing cycle.

Humidity is present in most environments, and so it is important to understand a sensors response in its presence. Therefore, mixed gas experiments were performed, exposing KAUST-7 and KAUST-8 to SO₂ in humid conditions mimicking real-world conditions for SO₂ detection. Figure 7 shows the

sensor sensitivity as a function of SO₂ concentration in humid conditions (60% RH) at RT for uncoated and coated KAUST-7 and KAUST-8 QCMs. Uncoated QCM has a near-zero response to humidity and SO₂. This corroborates that the sensing response to SO₂ under humid conditions is due to its affinity to KAUST-7 and KAUST-8 films.

The responses of the two kinds of sensors were different. As seen in Fig. 7 and (Supplementary Figure 19), the resonance frequency of the QCMs initially decreased when the ambience was changed from dry to humid SO₂ conditions. The most prominent difference is the inversion in the sensor output due to the introduction of SO₂ at 60% RH but not in the same manner as compared with the dry SO₂ case. Interestingly, when exposed to 25 p.p.m. of SO₂ in the above-mentioned humid conditions, the sensor resonance frequency for SO₂ was reduced. Under humid conditions, the sensitivity of the two MOFs slightly reduced when compared with dry conditions. However, KAUST-7 films demonstrated a four-time higher sensitivity toward SO₂ in the presence of humidity compared with KAUST-8.

To further analyze the results obtained, it is necessary to consider the specific features of the adsorption of SO₂ and water on the surface of KAUST-7 and KAUST-8. As seen in Fig. 7, the presence of humidity (60% RH) did not significantly affect the KAUST-7-based sensors response to the SO₂ analyte. This may be due to the affinity of SO₂ molecules to replace some of the adsorbed water molecules or/and coexist in the highly confined pore system. In the case of KAUST-8-based sensor, which is isomorphous to the KAUST-7, lower sensitivity to SO₂ in the presence of humidity was observed. Although SO₂ has the affinity to replace water molecules, the reduced sensitivity is attributed to the absence of accessible ultra-microporous morphology. The number of SO₂-adsorbing active sites is reduced by the pre-adsorbed water, thereby limiting the available space in the pore system for adsorption. This observation is supported by the fact that the water molecules strongly interact with Al³⁺⁴⁶ with higher host/guest interaction energy as compared with SO₂. The TPD experiment results (Supplementary Figure 20) show that in the case of KAUST-7, the SO₂ can replace the already adsorbed water molecules relatively easy as compared with the KAUST-8, which has stronger water affinity. These results are in agreement with the conclusion reported in the literature for the simultaneous capture of CO₂ and H₂O using KAUST-8⁴⁶.

The most important parameters for a sensing device are its stability and reproducibility. These parameters were investigated by cyclic exposure of the sensor to different SO₂ concentrations after every 48 h at RT over a period of 12 days (Fig. 8). The three results demonstrated the stability of the sensors exposed to 50, 100, and 157 p.p.m. SO₂ gas with no significant change in the resonant frequency over time.

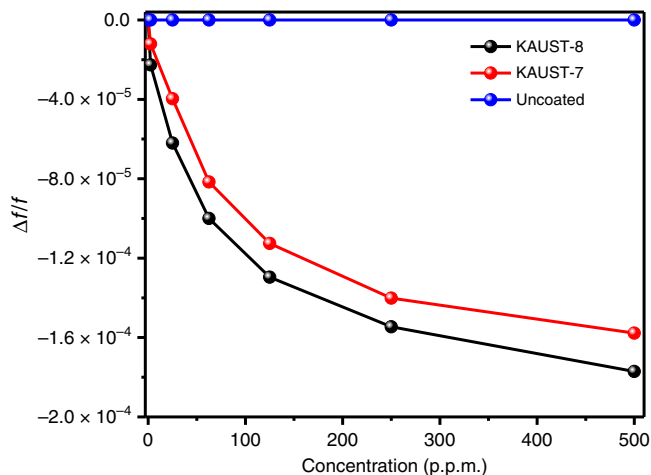


Fig. 6 Frequency shift comparisons. Frequency shift as a function of the SO₂ concentration for the uncoated and KAUST-7- or KAUST-8-coated QCM sensors

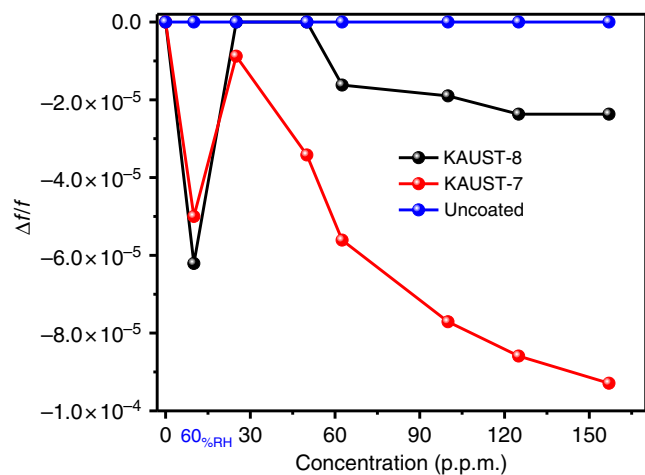


Fig. 7 Sensor responses. Plots of sensors responses as a function of SO₂ concentration in synthetic air

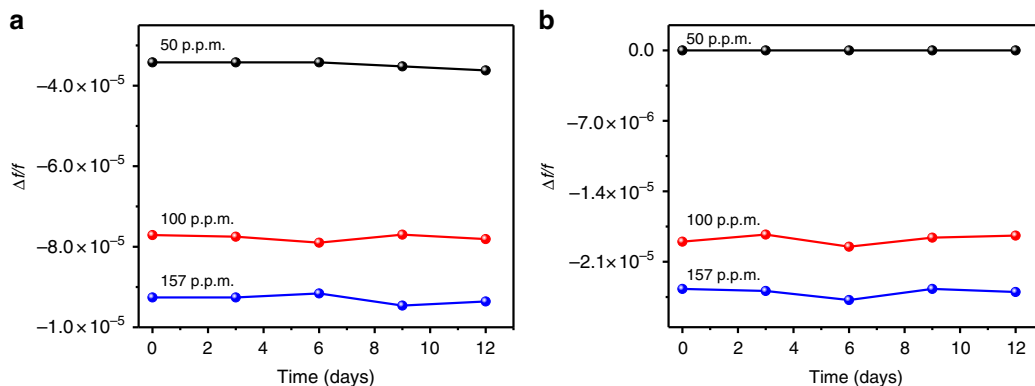


Fig. 8 Stability and reproducibility. Long-term stability property of the **a** KAUST-7 and **b** KAUST-8 sensors exposed to 50, 100, and 157 p.p.m. SO₂ gas

Discussion

In this report, we successfully demonstrated the superior performance of two fluorinated MOFs, namely KAUST-7 and KAUST-8, for the capture of SO₂ from flue gas. Combined mixed gas breakthrough experiments and molecular simulation confirmed that simultaneous capture of SO₂ and CO₂ occurs using KAUST-7, whereas KAUST-8 displays a higher affinity for SO₂ with SO₂/CO₂ selectivity ≈66. Based on this performance, QCM-based sensors were successfully fabricated for sensing SO₂ from air using this fluorinated MOF platform (Supplementary Figure 21). Both MOF materials confirmed their potential, revealing good SO₂ detection capabilities above 25 p.p.m., the range of SO₂ concentrations in the air-inducing nose and eye irritation. This remarkable performance of sensing makes these materials highly desirable for the fabrication of new advanced devices to improve health and environmental conditions.

Methods

Materials. All reagents were used as received from commercial suppliers without further purification.

KAUST-7^{44,45} and KAUST-8⁴⁶ were synthesized according to literature procedures.

Powder X-ray diffraction. The PXRD data were collected over the 2θ range 4–40° or 6–80° on a high-resolution PANalytical X'Pert MPD-PRO diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV/40 mA).

Single crystal X-ray diffraction. The SCXRD data were collected using a Bruker X8 PROSPECTOR APEX2 CCD diffractometer (Cu K α , $\lambda = 1.54178 \text{ \AA}$). Indexings were performed using APEX2 (Difference Vectors method)⁵². Data integration and reduction were performed using SAINTplus⁵³. Absorption corrections were performed by multi-scan method implemented in SADABS⁵⁴. Space groups were determined using XPREP implemented in APEX2⁵². Both structures were solved using Direct Methods (SHELXS-97) and refined using SHELXL-2018/3 (full-matrix least-squares on F^2) contained WinGX v1.70.01^{55–57}.

In situ gas loading experiment. We used commercially available Swagelok miniature quick connect with a small modification that allowed us to fix 0.3 mm glass capillary loaded with crystal above the quick connect. The selected single crystal was glued to glass fiber and placed in 0.3 mm glass capillary before attaching it to quick connect. In situ pretreatment of the crystal loaded in environmental gas cell was carried out first under dry nitrogen flow. Temperature of the crystal increased by immersing the capillary in to oil bath. Temperature of the oil bath was fixed at 140 °C for both the samples to obtain 105–120 °C effective temperature at the crystal. After 24 h, nitrogen flow was changed to dynamic vacuum keeping the temperature constant. After 12 h, crystal was allowed to cool down under dynamic vacuum and then 7% SO₂ (93% N₂) was introduced into environmental cell at 4–5 bar pressure. In case of CO₂, 100% CO₂ was introduced at 2–3 bar. The gas-loaded environmental cell was detached under pressure and allowed to equilibrate for around 8 h. After 8 h, the environmental cell was mounted on a modified goniometer for single crystal X-ray data collection.

Column breakthrough test set-up, procedure, and measurements. The experimental setup used for dynamic breakthrough measurements is shown in Supplementary Figure 22. The gas manifold consisted of three lines fitted with mass flow controllers. Line A is used to feed an inert gas, most commonly helium, to activate the sample before each experiment. The other two lines B and C feed a pure or pre-mixed gases. Whenever required, gases flowing through lines B and C may be mixed before entering a column packed with the sample using a four-way valve. In a typical experiment, 300–500 mg of adsorbent (in the column) was treated in situ at a required temperature under He flow (50 cm³ g⁻¹) for 8 h.

Before starting each experiment, helium reference gas is flushed through the column and then the gas flow is switched to the desired gas mixture at the same flow rate between 10–50 cm³ g⁻¹. The gas mixture downstream the column was monitored using a Hiden mass spectrometer.

Fabrication of KAUST-7- and KAUST-8-coated QCM. The transducer was a 10 MHz AT-cut piezoelectric QCM device with a thickness shear mode and placed between two gold electrodes for electrical connection. The QCM is rinsed with ethanol and dried in air. MOFs paste was then applied to the electrode of QCMs by spin-coating method (2 μm thick); no prior modification of the sensors surface was required.

The QCM sensor was then fixed in a sealed chamber. Before measurements, the fresh coated MOFs film was activated in situ for 4 h to have a guest free framework.

The resulting coatings are ultrathin and reproducible so that the stress upon absorption of SO₂ inducing a change in the mass change of the thin film is effective.

Sensing apparatus. Supplementary Figure 23 shows the sensing setup used in this study for real-time measurement. All the sensor measurements were carried out at RT, under a dry air total stream of 200 cm³ m⁻¹. MFCs (mass flow controllers) from Alicat Scientific, Inc. were used to control the flow rate for gases coming from certified bottles. Stainless steel delivery lines or perfluoroalkoxy alkane, Perfluoroalkoxy (PFA) tubing (in regions requiring flexibility and resistivity to volatile organic compounds (VOCs)) were used on the setup with Vernier metering valves (from Swagelok) as a flow regulator. To detect the change in humidity level inside the chamber, a commercial humidity sensor (Honeywell HIH-4000–003) was used as a reference, which has an error < 0.5% RH. The QCM sensor was exposed to the analyte stream until a stable response was obtained; a two-port network (Keysight E5071C ENA) circuit was used to monitor the change in resonance frequency. A LabVIEW interface was used for synchronization and data acquisition by controlling the LCR meter (L = Inductance, C = Capacitance, R = Resistance) and the multimeter. Hence, the possibility of data loss was minimized.

Computational methods. All simulations were performed using the codes available in the Quantum Espresso package⁵⁸, which implements the DFT under periodic boundary conditions with plane-wave functions as basis sets⁵⁹. The geometry optimizations were performed with the generalized gradient approximation (Perdew–Burke–Ernzerhof (PBE))⁶⁰ including the dispersion corrections described by the Grimme's scheme⁶¹, maintaining fixed the atomic coordinates of the F–Ni–F chains and the unit cell dimensions. The relative ion positions were relaxed until all of the force components were lower than 0.001 Ry Bohr⁻¹. The equilibrium atomic positions of all systems were found by minimizing the total energy gradient. The ion cores were described by Vanderbilt ultrasoft pseudopotential⁶² and the Kohn–Sham one-electron states were expanded in a plane-wave basis set with a kinetic cutoff energy of 50 Ry (500 Ry for the density). All the calculations were performed at the Γ -point. The Hubbard approach was also applied in order to better describe the localized d states of nickel. The Hubbard parameters (U) were taken from the calculations of Wang et al.⁶³, with a value of 6.4 eV for nickel. The Marzari–Vanderbilt smearing technique was used⁶⁴ with a broadening of 0.005 Ry in order to smooth the Fermi distribution.

The geometry optimizations of SO₂ and CO₂ in both MOFs were performed by considering one guest molecule per formula unit. The interaction energy was then calculated using the following equation: $\Delta E = E_{\text{MOF/guest molecule}} - E_{\text{guest molecule}} - E_{\text{empty MOF}}$, where $E_{\text{MOF/guest molecule}}$, $E_{\text{guest molecule}}$ and $E_{\text{empty MOF}}$ are the total energy of the loaded system (guest molecule + MOF), of the guest molecule and the single-point total energy of the MOF, respectively.

Data availability

The X-ray crystallographic data for KAUST-7 (SO₂) and KAUST-8 (SO₂) have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1871683 and 1871684, respectively. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk. All other relevant data supporting the findings of this study are available from the corresponding authors on request.

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Author contributions

K.A. and A.C. carried out the synthetic experiments. K.A. and M.R.T. contributed to the conceptual approach in designing the MOF deposition on the electrode. G.D.W., N.H., and Y.B. set, conducted, and analyzed the single component SO₂ gas adsorption experiments. P.B. and Y.B. conducted and interpreted the column breakthrough experiments. A.S. and P.B. carried out in situ SO₂-loaded single crystal X-ray diffraction study and analysis. Y.B., M.R.T., and K.A. conceptualized the set of sensing testing. Y.B., M.R.T., K.A., K.N.S., and K.N.C. conducted and interpreted the sensing results. S.T. and G.M. performed the theoretical study. K.A., Y.B., and M.E. conceived, designed, and guided the whole project. P.B., M.R.T., Y.B., K.A., M.E., K.N.C., and A.S. wrote the manuscript and all authors approved it.

Additional information

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