Metal-organic frameworks (MOFs) have received much attention for their potential as chemical sensors, owing to unparalleled tunability of their host-guest response, high uptake and structural flexibility. However, because of the limited compatibility between MOF properties and sensor transduction mechanisms, very few MOFs have successfully been integrated into practical devices. We report the fabrication of the first strain-based sensor constructed from MOF nanoparticles deposited directly onto a membrane-type surface stress sensing architecture, which exhibits unprecedented response times on the order of seconds and ppm-level sensitivity towards volatile organic compounds (VOCs). Finite element analysis is used to demonstrate that the sensor response is a result of analyte-induced strain in the MOF receptor layer. We show that an array of four types of MOF nanoparticles allows for clear discrimination between different classes of VOCs and even individual gases, using principal component analysis of their response profiles. This work opens up the possibility of VOC sensing using a wide range of MOFs, beyond those that are electrically conducting or those that form oriented thin films, with the added advantages of high sensitivity and rapid response compared to existing MOF strain-based sensors.
Strain-based chemical sensing using metal-organic framework nanoparticles

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Metal-organic frameworks (MOFs) have received much attention for their potential as chemical sensors, owing to unparalleled tunability of their host-guest response, high uptake and structural flexibility. However, because of the limited compatibility between MOF properties and sensor transduction mechanisms, very few MOFs have successfully been integrated into practical devices. We report the fabrication of the first strain-based sensor constructed from MOF nanoparticles deposited directly onto a membrane-type surface stress sensing architecture, which exhibits unprecedented response times on the order of seconds and ppm-level sensitivity towards volatile organic compounds (VOCs). Finite element analysis is used to demonstrate that the sensor response is a result of analyte-induced strain in the MOF receptor layer. We show that an array of four types of MOF nanoparticles allows for clear discrimination between different classes of VOCs and even individual gases, using principal component analysis of their response profiles. This work opens up the possibility of VOC sensing using a wide range of MOFs, beyond those that are electrically conducting or those that form oriented thin films, with the added advantages of high sensitivity and rapid response compared to existing MOF strain-based sensors.

Introduction

Sensing of volatile organic compounds (VOCs) is critical to our perception of the environment around us,1 monitoring of harmful emissions,2 and healthcare analytics,3 and so is required for a wide variety of current and future technologies.4 Sensors based on metal-organic frameworks (MOFs) offer great potential, in particular towards selectivity, owing to their precisely defined pore structure and chemistry.5–8 The modular nature of MOFs allows them to be tailored with highly specific host-guest interactions to adsorb small molecules with higher uptake and selectivity than conventional materials such as polymers, zeolites and porous carbons.9,10 Luminescence and other optical transduction modes are most widely reported in the literature of MOF-based sensing;11 however, for practical usage other modes that integrate more easily with existing electronics are more viable.6,12 Whilst there have been a handful of encouraging reports of electronically-responsive MOFs,13–17 MOFs can be ideal candidates for strain-induced chemical detection because of the deformations of coordination space within their crystal structures caused by host-guest interactions and their increased flexibility compared to conventional inorganic materials.9,18–21 Micro-electromechanical systems (MEMS) sensors coated with thin films consisting of different MOFs such as ZIF-8 [ZIF, zeolitic imidazolate framework; ZIF-8 = Zn[2-methylimidazolate]2] and HKUST-1 (HKUST, Hong Kong University of Science and Technology; HKUST-1, Cu2[benzentricarboxylate]2(H2O)) have been shown to successfully respond to water, alcohols and other volatile organics, with sensitivity limits that exceed other mass-sensitive sensors.22,23 However, several challenges remain, including improving the ease of receptor layer preparation, selectivity, sensitivity and response time.24,25 Often, parameters act against one another; e.g., a thicker film may lead to increased sensitivity but at the cost of response time, owing to the time taken for analytes to diffuse through the MOF. In addition, the perceived necessity for well-adhered and defect-free, oriented thin films to effectively transmit analyte-induced strain to the sensor surface puts limits on the range of MOFs that can be used and introduces stringent, often laborious requirements to MEMS device fabrication.5,24 On the other hand, a much wider range of MOFs can now be easily synthesized in colloidal or nanoparticle (NP) form.26 Nanoparticles have been shown to be effective and simple to deposit via spray coating as receptor layer materials in MEMS sensors,27–29 and size reduction has been shown to improve the mechanical stability of multilayer NP coatings.30 Therefore, the integration of MOF NPs into MEMS devices would open up development of practical MOF-based sensors beyond those that form oriented thin films or are electronically conductive and lead to a new class of robust, selective receptor materials.

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The Membrane-type Surface stress Sensor (MSS) consists of a Si-based membrane suspended by four piezoresistive beams, composing a full Wheatstone bridge. This architecture generates potential difference upon changes to the strain state of the membrane, with approximately 100 times greater sensitivity than conventional piezoresistive microcantilevers, and can be extended to multiple sensor arrays. To induce strain on the membrane, a receptor layer bound to the membrane must undergo strain in response to an analyte. Modelling has predicted that receptor layer materials with higher Young’s moduli give better signals.

Amongst a wide range of MOF NPs available, ZIFs exhibit mechanical properties somewhat intermediate within the MOF class of materials: they are stiffer than so-called “breathing” MOFs such as MIL-53 and pillared-layer MOFs, but still exhibit measurable flexibility in their crystal structure upon gas uptake. Encouragingly for their potential sensing performance, it has been shown that particle size reduction to the nanoscale can result in rather linear gas adsorption isotherms, and improved mechanical properties. In addition, gas diffusion coefficients of bulk MOFs are often several orders of magnitude lower than that in air, therefore, it could be reasonably expected that the meso- and macro-pores within a superstructure of MOF NPs will act as channels for analytes to rapidly diffuse through the whole receptor layer. Indeed, it has been shown using environmental ellipsometry that alcohol adsorption in thin films composed of ZIF-8 NPs takes just 20 s. However, prior to this work it remained to be seen whether receptor layers built from MOF NPs would be able to induce sufficient strain in the MEMS sensors, in order to realize effective VOC sensing.

We herein report for the first time the fabrication and performance of a new MOF–MSS sensor based on NPs of the canonical ZIF family of MOFs (Fig. 1). We first demonstrate the facile sensor fabrication using ZIF-8, which exhibits hydrophobic pores with the sod network topology. We observe selectivity in its range of responses to 26 VOCs, with rapid response times of 1–30 s and ppm level sensitivity, and show that the sensor response is consistent with a mechanism of adsorbate-induced strain in the ZIF crystal lattice. Exploiting the versatility of the MSS architecture and the diversity of available MOF NPs, we use spray-coating to fabricate a 2 × 2 array of ZIF-8, ZIF-7 (Zn(benzimidazole)₃, sod), ZIF-65-Zn (Zn(2-nitroimidazole)₃, sod) and ZIF-71 (Zn(4,5-dichloroimidazole)₃, rho) MOFs. The chemical diversity of these MOFs manifests itself in a wide range of sensing profiles, which enable clear discrimination between a range of different VOC classes and individual gases via principal component analysis.

Materials and methods

Synthesis and characterisation.

All chemicals are purchased from Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co. Ltd. and Nacalai Tesque, Inc. ZIF-8 NPs were synthesized following a literature protocol, washed thrice in methanol to remove residual byproducts and resuspended in alcohol. ZIF-7, ZIF-65-Zn and ZIF-71 NPs were synthesized following similar literature routes (see ESI† Section S1 for full details). Chemical composition, particle size and phase purity of bulk samples were confirmed by powder X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), scanning electron microscopy (SEM), dynamic light scattering (DLS), zeta potential, Brunauer-Emmett-Teller (BET) surface area and thermogravimetric analysis (TGA) before and after activation under similar conditions used for sensor preparation (see ESI† Section S2–S7). Nitrogen gas sorption isotherms (ESI† Section S6) indicate significant mesoporosity and/or macroporosity in addition to the expected MOF microporosity, in line with previous reports.

Sensor preparation.

Materials were deposited directly onto the MSS membrane without any adhesive layer. For selectivity and VOC discrimination experiments, four methanolic suspensions of different ZIF NPs were deposited onto a MSS membrane array by spray coating 30 layers; a stage on which the MSS chip was mounted was held at 100 °C to rapidly evaporate the carrier solvent, and promote sintering and adhesion of the NPs to the surface. For investigation of sensitivity and response time, a ZIF-8 NP suspension was deposited on a single MSS membrane by inkjet printing; an inkjet spotter (LaboJet-500SP) and a nozzle (UHBS-300), which were purchased from the MICROJET Corporation, were utilized. The ZIF-8 NP suspension was loaded into the inkjet printer module, and up to 2500 sequential droplet depositions were performed. The inkjet stage was heated at 80 °C to control evaporation.

Sensing.

Selectivity tests using the spray-coated ZIF-8-MSS were performed under ambient temperature using the saturated vapours of 26 VOCs, including those a range of alcohols, carboxyls, arenes and alkanes (see ESI† Section S8 for details, including absolute concentrations of saturated vapours). Gases were introduced to the sensor for 30 s via a custom-built setup and purged with nitrogen gas for 30 s. Four injection-purge cycles were performed for each gas and data were recorded at
a sampling rate of 20 Hz by applying a bridge voltage of ~0.5 V to the Wheatstone bridge. Discrimination tests for the VOCs using the 2 x 2 MOF-MSS array were performed in an identical manner. Sensitivity and response time were investigated using the inkjet-printed ZIF-8-MSS for 12 VOCs under conditions of constant temperature and humidity using a separate setup (see ESI† Section S9). Gases were diluted to 2%, 5% and 10% of their saturated vapour concentrations and humidified at 0%, 10%, 40%, and 70% relative humidity (RH) prior to injection. Ten injection (10 s) - purge (10 s) cycles were performed for each measurement. Limits of detection were determined from the mean reversible response of cycles 2–4, divided by the electrical noise inherent in the MSS device (approximately 1 μV) to give the signal-to-noise ratio. The effective limit of detection was then estimated by dividing the concentration of analyte present by the signal-to-noise ratio.

Principal component analysis (PCA).

The responses of the 2 x 2 MOF-MSS array were analysed following the methodology of Shiba et al. (see ESI† Section S10). Briefly, the features of each response profile were decomposed into four parameters, defined as the rise rate, plateau rate, recovery rate and response magnitude. Parameters from the latter three of four cycles were used as inputs for PCA using Origin software, which determined the projection weights for a set of orthogonal principal components to maximise the total response variance.

Results and discussion

MOF-MSS sensor concept.

We fabricated a MOF-MSS by spray-coating ZIF-8 NPs directly onto one of the membranes of the MSS array. Its response to the saturated vapour of 26 VOCs is shown in Fig. 2a (for details see ESI† section S11). All gases were found to elicit a measurable response within seconds, including a range of alcohols, carbonyls, arenes, and alkanes. The irreversible signal—which we attribute to residual molecules that remain in the MOF pores on the timescale of these experiments—apparent in the first cycle for most gases is largely absent from the second cycle onwards. Whilst these irreversible signals in the first cycle can be also caused by the enhanced concentration of VOC vapours in the head space of the vial prior to the measurements, they are not included in the following analyses.

Different classes of VOCs give rise to quite distinct response profiles. Water and alcohols, such as methanol (Fig. 2b) and ethanol (Fig. 2c) give amongst the highest output voltages and profiles that typically reach saturation within 30 s. Molecules with carbonyl functionality, such as ketones, esters and amides, including acetone (Fig. 2d), as well as chloroform and tetrahydrofuran also give large responses. The response of acetic acid (Fig. 2e) is unusual amongst the VOCs studied in that it is almost entirely irreversible on these timescales. We expect that this is due to the known instability of ZIFs in acidic conditions, which may degrade the receptor layer. Aromatic compounds, such as toluene (Fig. 2f), elicit intermediate responses that typically do not reach saturation within 30 s, whilst linear alkanes, including hexane (Fig. 2g), give rise to small responses that rapidly reach saturation and then decrease. We attribute the different saturation rates to the different diffusivities of these class of VOCs in ZIF-8; larger molecules will generally pass through the structure more slowly. We also note that the responses of the ZIF-8-based MSS do not necessarily correlate with previously reported isotherms. Clearly, the response is a complex function of many factors, including host-guest interactions, diffusion through the receptor layer, mechanical properties and analyte-induced framework distortion. These factors are influenced by the structure of the MOF receptor layers on different levels, including composition, network topology, porosity (both within and between NPs), and particle-particle and particle-MSS interactions.

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Fig. 2. Responses of the ZIF-8-MSS to saturated vapours at ambient temperature: (a) first three ON-OFF cycles for 26 VOCs, coloured according to class (alcohols – purple, carbonyls – green, arenes – orange, alkanes – blue, other – grey); representative response profiles (0–150 s) for methanol (165507 ppm), ethanol (86294 ppm), acetone (302523 ppm), acetic acid (11026 ppm), toluene (38156 ppm) and hexane (194341 ppm), are shown in (b–g) respectively. (h) Relative mean response magnitudes calculated from three measurements for each gas; error bars represent two standard deviations. Colours correspond to those used in (a).
Optimisation of response magnitude and time.

In order to determine the detection limits of the ZIF-8-MSS, the response magnitude and time were first optimized by investigating the effect of receptor layer volume (see ESI† Section S12). Devices were fabricated by inkjet printing between 100 and 2500 droplets of a ZIF-8 NP suspension onto the MSS membrane. A device fabricated from 2100 inkjet droplets exhibited the best compromise between high output voltages and fast response times for selected gases from the five VOC classes investigated previously (methanol-alcohol, acetone-carbonyl, toluene-arene, heptane-alkane and water-other). Notably, for most receptor layer volumes, the response times for methanol, acetone and heptane were found to be less than 5 s, whilst for toluene and water they were consistently below 30 s. The device deposited with 2100 droplets was therefore chosen for the subsequent investigation of detection limits.

Detection limits.

The sensitivity of the 2100-droplet ZIF-8-MSS was determined for 12 VOCs under variable humidity at 298 K (Fig. 3). The sensor response typically decreased as the gases were diluted from 10 % to 5 % and then 2 % saturated vapour. To calculate the limit of detection (LOD), the VOC concentration corresponding to 2 % saturated vapour was multiplied by the ratio of 1 µV (the noise inherent to the MSS architecture; the experimental noise level can be higher depending on the measurement conditions)\textsuperscript{31,32} and the average output voltage of three ON-OFF cycles. The sensor exhibited LODs for most gases well below 10 ppm and sub-ppm LODs to some, including 1-hexanol and n-heptane. Interestingly, sensitivity appears to improve with increasing humidity in some cases, suggesting that cooperative analyte-water interactions may be beneficial to the sensing mechanism. Increasing temperature typically results in reduced output. This is most likely because the receptor layer becomes softer\textsuperscript{25} and the adsorption capacity of the MOF decreases.\textsuperscript{47} It should be also noted that longer exposure to the vapors than the current cycles can yield even higher signal levels than the presented results, especially for the gas species with low concentrations. Such trends can be observed in some response signals that are not saturated in the current cycles. Accordingly, the detection limits depend also on the measurement conditions as the saturated signal levels are determined by the partial pressure of each gas in the case of chemical gas sensors based on the gas-solid equilibrium, including the present MOF-MSS as well as common chemoresistive sensors.\textsuperscript{48,49}

Sensing mechanism.

The MOF-MSS response was shown to be consistent with a mechanism of adsorbate-induced strain in the MOF receptor layer using Finite Element Analysis (FEA). The response is linear with respect to strain and depends on the Young’s modulus, $E_p$, and, to a lesser extent, on the Poisson’s ratio, $\nu_p$, of the MOF receptor layer (see ESI† Section S13). It increases with receptor layer thickness up to a threshold value before decreasing at greater thickness. The thickness at which the response is maximised decreases as $E_p$ and $\nu_p$ increase. Using representative values for $E_p$\textsuperscript{39,50} and $\nu_p$\textsuperscript{51} of ZIF-8, the highest responses are calculated for receptor layer thicknesses between 8 µm and 10 µm. This range agrees favourably with the thickness calculated for the optimised 2100-droplet ZIF-8-MSS, which is 10.4 µm (see ESI† Section S14). FEA further indicates that it takes a strain of $1 \times 10^{-4}$–2 $\times 10^{-3}$ in a ZIF-8-MSS with such a thickness to generate the range of observed responses, i.e., 1–10 mV (Fig. S31a†). For example, methanol induces an output voltage of 10 mV in the 2100-droplet sensor (Fig. S28†), whilst the response of the spray-coated sensor to 1-butanol is around 5 mV (Fig. S34†). This is broadly consistent with previous analysis by powder XRD, which shows that full adsorption of 1-butanol induces a strain of 1.8 $\times 10^{-3}$ in the lattice parameter of ZIF-8.\textsuperscript{52} Such a lattice strain is just an order of magnitude greater than the calculated strain in the ZIF-8 receptor layer overall. We attribute this difference to inhomogeneous coverage and imperfect interparticle and particle-surface adhesion, which are important to strain transduction in the sensor device and remain to be optimized in future work.

Multichannel array sensing.

Despite reasonable selectivity that differentiates somewhat between VOCs, cross-sensitivity means that ZIF-8 is unable to unambiguously discriminate between multiple analytes. We adopted an multichannel array approach previously demonstrated for chemoresistive carbon nanotubes\textsuperscript{53} and 2-D MOFs,\textsuperscript{14} and exploited the versatility of the MOF-MSS concept to spray-coat a 2 $\times$ 2 array of MSS channels\textsuperscript{31,32} with NPs of four ZIFs, ZIF-8,\textsuperscript{54} ZIF-7,\textsuperscript{45} ZIF-65-Zn and ZIF-71\textsuperscript{46} (Fig. 4). These particular MOFs were chosen because of their variety in composition, network topology, pore aperture, and diameter (Table 1); which may be expected to affect the adsorption of gases according to size, shape and/or functionality in different

Fig. 3. Limit of detection (LOD) of a 2100 droplet nanoparticle ZIF-8-MSS sensor fabricated by inkjet printing towards various analytes determined at 298 K and humidity levels from 0 % RH (light blue) to 70 % RH. MCH = methycyclohexane; EtOAc = ethyl acetate; prop.acid = propionic acid.
ways, thus leading to a diversity of responses and thus improved VOC discrimination.

Table 1. Compositions, nets and pore aperture diameters ($d_1$), and pore diameters ($d_2$) of four ZIFs used in the 2 × 2 MOF-MSS array.

| MOF       | Composition                        | Net    | $d_1$ / Å | $d_2$ / Å |
|-----------|------------------------------------|--------|-----------|-----------|
| ZIF-7     | Zn(benzimidazole)$_2$             | sod    | ~3        | 4.3       |
| ZIF-8     | Zn(2-methylimidazole)$_2$         | sod    | 3.0       | 11.6      |
| ZIF-65-Zn | Zn(2-nitroimidazole)$_2$          | sod    | 3.2       | 10.4      |
| ZIF-71    | Zn(4,5-dichloroimidazole)$_2$     | rho    | 4.2       | 16.5      |

Simultaneous sensing experiments using the MOF-MSS array reveal a wide variety of responses of the four ZIFs to 26 VOCs (Figs. 2h and 5; see also ESI† Section S15). The relative responses of the sod structures ZIF-7, ZIF-8 and ZIF-65 are qualitatively similar, reflecting the similarity in their network topologies and pore apertures. However, certain differences are apparent in, for example, response magnitudes (e.g., acetic acid) or the relative responses of related compounds (e.g., methanol vs. ethanol; acetic acid vs. acetone). Like in ZIF-8, arenes and linear alkanes elicit medium and low responses, respectively, in ZIF-7 and ZIF-65-Zn. It is particularly interesting that the responses of ZIF-65-Zn to both alkanes and arenes tend to decrease as molecular size increases. Its pore aperture is slightly bigger than the other sod analogues; perhaps this allows for more linear discrimination between compounds. The relative responses of ZIF-71 are qualitatively different to its sod analogues. Arenes and alkanes elicit higher responses, whilst methanol and ethanol give rise to lower responses. In this case, the response to alcohols appears to increase with increasing size of the molecules. ZIF-71 also gives a more uniform response across all VOCs. We tentatively assign this to the openness of the rho net, which increases the reversibility of gas sorption compared to the other ZIFs, all of which exhibit the denser sod net. The relative decrease in response to short chain alcohols, such as methanol and ethanol, may be due to the hydrophobic nature of the dichloroimidazolate linker.

Statistical analysis.

Further investigation of the multichannel data by principal component analysis (PCA) reveals that the 2 × 2 MOF-MSS array is able to group VOCs by chemical class and even discriminate between individual gases. PCA is an unsupervised method of classifying multi-sensor data, which reduces the dimensionality of the dataset by representing the sensor contributions as linear combinations of the original variables in typically, two or three principal components (PCs). Noting that the MOF-MSS response profiles contain a wealth of information beyond the simple magnitudes of response, we extracted parameters to describe the reversible response, uptake rate, plateau gradient and recovery rate of each ZIF in the 2 × 2 array as input data for PCA (see ESI† Section S10). It was found that the four classes of VOCs could successfully be discriminated using just two PCs, with only small ambiguities in the case of overlaps between alcohols and carbonyls (e.g., acetone), and arenes and alkanes (e.g., shorter chain alkanes and dichlorobenzenes) (Fig. 6).
Interestingly, alcohols appear to be subdivided into two groups, one with the smallest molecules (methanol and ethanol) and the other with larger molecules. The weightings of PC1 and PC2 were 55.9 % and 20.1 %, respectively, and together they describe 75.0 % of the total variance. A third principal component (PC3 = 8.2 %) was found to improve the description to 83.2 % and, when viewed with PC1, suggests a much closer grouping of the alcohols (see ESI† Section S16). Within each class, the repeatability of our measurements is apparent in the ability to clearly discriminate between different VOCs. This is an advantage for VOC identification applications, for which there is prior knowledge of a given analyte’s response. For example, methanol and ethanol are clearly distinguishable from each other, as are methylethylketone and acetone, both pairs of which differ by just one CH$_2$ group. Alkanes and aromatic molecules follow clear trends with molecular size, which could be useful in monitoring separation processes.

Conclusions

We have demonstrated for the first time that MOF NPs as a receptor layer on the MSS platform can be highly effective for strain-based chemical sensing. Response times of 1–30 s represent an order of magnitude improvement over existing MOF strain-based sensors (see ESI† Section S17). Sub-ppm sensitivity towards a range of VOCs again represents an improvement in strain-based sensing using MOFs, bringing it on par with hard-to-fabricate photonic crystal thin films, interdigitated electrode devices, and colorimetric sensors, the latter of which was limited in analyte scope to water. Importantly, we have demonstrated that, in principle, any MOF that can be made in NP form can now be employed in strain-based sensing, which allows for an enormous diversity of chemistries and VOC selectivities. We constructed a 2 x 2 MSS array using four ZIFs, which have different responses to a range of VOCs and, when their combined responses are subjected to PCA, are able to successfully group the VOCs by class and discriminate between them. Whilst the performance of the reported MOF-MSS is extremely promising, other aspects, such as particle-particle adhesion, particle-surface adhesion and mesoporosity, remain to be optimized in further work. These and many other factors may affect the sensing performance. Therefore, fundamental studies in areas such as MOF-guest interaction energetics, diffusion and flexibility will undoubtedly aid progress in this regard.

Conflicts of interest

The authors hold a patent related to the described work (JP 06544744, US 10564082).

Acknowledgements

We thank the World Premier International Research Center Initiative on Materials Nanoarchitectonics (WPI-MANA) from MEXT, Japan for financial and technical support. This work was also supported by JSPS KAKENHI Grant Number JP19KK0141, MEXT, Japan; a Grant-in-Aid for Scientific Research (A), 18H04168, MEXT, Japan; the Public/Private R&D Investment Strategic Expansion Program (PRISM), Cabinet Office, Japan; the Center for Functional Sensor and Actuator (CFSN). HHMY acknowledges support from the Glasstone Bequest for financial support through the provision of a Glasstone Fellowship and the University of Birmingham for startup funds. We thank Mr. Makito Nakatsu for performing BET measurements and Ms. Yuko Kameyama, Ms. Keiko Koda, Ms. Eri Sakon and Ms. Ikumi Nakakubo (WPI-MANA, NIMS) for coating the ZIFs and collecting all the sensing data. This work was born out of many fruitful discussions at the International Center for Young Scientists (ICYS) at NIMS.

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Fig. 6. Principal component analysis of response profile data from the 2 x 2 MSS array of ZIF NPs, using 26 VOCs.
Electronic Supplementary Information

Strain-based chemical detection using metal-organic framework nanoparticles

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S1. Synthesis

**ZIF-7 nanoparticles.** Nanoparticles of ZIF-7, Zn(bIm)$_2$ in sod topology, were synthesized by adapting the method of Li et al.$^1$ In detail, zinc nitrate hexahydrate (302 mg, 1 mmol) was dissolved in $N,N$-dimethylformamide (10 mL) and poured rapidly into a solution of benzimidazole (769 mg, 6.4 mmol) in $N,N$-dimethylformamide (10 mL) under stirring at room temperature. Stirring continued for 12 hours after which the milky suspension was centrifuged at 15000 g for 30 minutes. The supernatant was decanted and replaced by methanol and the mixture sonicated for one minute to redisperse the particulate matter. The centrifuge / washing process was repeated thrice more. Half the resulting suspension was kept for further use, and half was dried (60 °C in air, then 180 °C under active vacuum overnight), yielding an off-white solid, 104 mg (71 % yield based on Zn).

**ZIF-8 nanoparticles.** Nanoparticles of ZIF-8, Zn(mIm)$_2$ in sod topology, were synthesized by adapting the method of Cravillon et al.$^2$ In detail, zinc nitrate hexahydrate (297 mg, 1 mmol) was dissolved in methanol (20 mL) and poured rapidly into a solution of 2-methylimidazole (649 mg, 7.9 mmol) in methanol (20 mL) under stirring at room temperature. Stirring continued for 6.5 hours, after which the milky suspension was centrifuged at 15000 g for one hour. The supernatant was decanted and replaced by fresh methanol and the mixture sonicated for 5 minutes to redisperse the particulate matter. The centrifuge / washing process was repeated twice more. Half the resulting suspension was kept for further use, and half was dried (90 °C in air, then 180 °C under active vacuum overnight), yielding a pale yellow solid, 38 mg (35 % yield based on Zn).

**ZIF-65-Zn nanoparticles.** Nanoparticles of ZIF-65-Zn, Zn(nIm)$_2$ in sod topology, were synthesized by adapting the method of Tu et al.$^3$ In detail, zinc acetate dihydrate (110 mg, 0.5 mmol) was dissolved in $N,N$-dimethylformamide (5 mL) and poured rapidly into a solution of 2-nitroimidazole (113 mg, 1.0 mmol) in $N,N$-dimethylformamide (5 mL) under stirring at room temperature. Stirring continued overnight, after which the yellow milky suspension was centrifuged at 15000 g for 30 minutes. The supernatant was decanted and replaced by $N,N$-dimethylformamide and the mixture sonicated for one minute to redisperse the particulate matter. The centrifuge / washing process was repeated thrice more, using methanol as the fresh solvent. For the final centrifugation, the suspension was split into two equal fractions. One half was dried under vacuum at 55 °C overnight, yielding a yellow solid, 22.3 mg (39 % based on Zn). The other half was redispersed in IPA for sensing experiments.

**ZIF-71 nanoparticles.** Nanoparticles of ZIF-71, Zn(dClm)$_2$ in rho topology, were synthesized by adapting the method of Tu et al.$^3$ In detail, zinc acetate dihydrate (220 mg, 1 mmol) was dissolved in $N,N$-dimethylformamide (10 mL) and poured rapidly into a solution of 4,5-dichloroimidazole (960 mg, 6 mmol) in $N,N$-dimethylformamide (10 mL) under stirring at room temperature. Stirring continued for four hours after which the milky suspension was centrifuged at 15000 g for 30 minutes. The supernatant was decanted and replaced by methanol and the mixture sonicated for one minute to redisperse the particulate matter. The centrifuge / washing process was repeated thrice more. Three quarters of the resulting suspension was kept for further use, and one
quarter was dried (60 °C in air, then 180 °C under active vacuum overnight), yielding a brown powder, 75 mg (92 % yield based on Zn).
S2. Powder X-ray diffraction
Samples were analysed on Rigaku Ultima3 or RINT2000 instruments in a $\theta$-2$\theta$ flat plate geometry using Cu K-\(\alpha\) radiation. Data were collected from 2° to 50° 2$\theta$.

**ZIF-7 nanoparticles** (Fig. S1) exhibited reasonable crystallinity when as-synthesized and washed, with peak positions consistent with the theoretical pattern simulated using data from Zhao et al.$^4$ Upon heating at 180 °C under vacuum—conditions that are much harsher than those used for device fabrication—crystallinity was largely lost, as evident from the reduction of definition and intensity of the diffraction peaks.

**ZIF-8 nanoparticles** (Fig. S2) exhibited a good match to the pattern simulated using data from Park et al.$^5$ and very little difference between XRD patterns as-synthesized and washed and dried. The crystal structure was maintained even when activated at 180 °C under vacuum.

**ZIF-65-Zn nanoparticles** (Fig. S3) also exhibited a close match to the pattern simulated using data from Banerjee et al.$^6$ Very little difference was observed between the patterns of as-synthesized, washed and dried, and activated material.

**ZIF-71 nanoparticles** (Fig. S4) exhibited lower crystallinity when as-synthesized than the other materials investigated, although the positions of the XRD peaks match the pattern simulated using data from Banerjee et al.$^6$ well. A similar degree of crystallinity is retained after washing and drying, and after activation.

![XRD patterns](image)

**Fig. S1.** XRD patterns of ZIF-7 nanoparticles: as-synthesized, washed and dried in vacuo at room temperature, and activated at 180 °C in vacuo. The theoretical, simulated pattern is shown below for comparison.
Fig. S2. XRD patterns of ZIF-8 nanoparticles: as-synthesized, washed and dried in vacuo at room temperature, and activated at 180 °C in vacuo. The theoretical, simulated pattern is shown below for comparison.

Fig. S3. XRD patterns of ZIF-65-Zn nanoparticles: as-synthesized, washed and dried in vacuo at room temperature, and activated at 180 °C in vacuo. The theoretical, simulated pattern is shown below for comparison.
Fig. S4. XRD patterns of ZIF-71 nanoparticles: as-synthesized, washed and dried in vacuo at room temperature, and activated at 180 °C in vacuo. The theoretical, simulated pattern is shown below for comparison.
S3. Infrared spectra

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet spectrometer with ATR attachment, under a flow of nitrogen, for each material after washing and drying under vacuum at room temperature, and after activation at 180 °C under vacuum. In the spectra of samples that have been washed and dried at room temperature, broad peaks in the region 2700–3500 cm\(^{-1}\) (O-H stretching, methanol), strong peaks at around 1700 cm\(^{-1}\) (C=O stretching, DMF) and 2800–3000 cm\(^{-1}\) (CH\(_3\) stretching, methanol/DMF) are suggestive of solvent that remains in the pores after washing. The peak at around 1400 cm\(^{-1}\) in the spectrum of ZIF-71 corresponds to precursor acetate ions (antisymmetric stretch). All these peaks are not present in the activated sample spectra, indicating that the solvents have been removed.

Fig. S5. Infrared spectrum of ZIF-7 nanoparticles, after washing and drying in vacuo at room temperature, and after activation in vacuo at 180 °C.
Fig. S6. Infrared spectrum of ZIF-8 nanoparticles, after washing and drying in vacuo at room temperature, and after activation in vacuo at 180 °C.

Fig. S7. Infrared spectrum of ZIF-65-Zn nanoparticles, after washing and drying in vacuo at room temperature, and after activation in vacuo at 180 °C.
**Fig. S8.** Infrared spectrum of ZIF-71 nanoparticles, after washing and drying in vacuo at room temperature, and after activation in vacuo at 180 °C.
S4. Scanning electron microscopy
Scanning electron microscopy (SEM) images were acquired at magnifications between 20,000× and 200,000×, using a Hitachi SU8000 FE-SEM in backscattered electron imaging mode. Working distances between 4.6 and 8.0 mm were used, with 2.5 kV and 1.5 kV acceleration and deceleration voltages, respectively. The images show that each sample consists of agglomerated particles with sizes ranging from 50 nm to 200 nm; the most monodisperse were ZIF-8 particles, which had the most well-defined rhombic dodecahedral morphology.

**Fig. S9.** SEM images of ZIF-7 nanoparticles.
Fig. S10. SEM images of ZIF-8 nanoparticles.
Fig. S11. SEM images of ZIF-65-Zn nanoparticles.
Fig. S12. SEM images of ZIF-71 nanoparticles.
S5. Dynamic light scattering and zeta potential
Dynamic light scattering (DLS) and zeta potential measurements were performed on diluted nanoparticle suspensions using an Otsuka Electronics ELSZ-2000 instrument. Comparing the SEM results to the particle diameters obtained in this way suggests that, after washing, the suspended particles are made up of several agglomerated smaller particles.

Table S1. Dynamic light scattering data for the ZIF nanoparticle suspensions.

|           | Suspension medium | Mean particle diameter / nm | Polydispersity index | Zeta potential / mV | Mobility / cm²/Vs |
|-----------|-------------------|-----------------------------|----------------------|---------------------|-------------------|
| ZIF-7     | IPA               | 90                          | 0.153                | 46                  | 3.443 × 10⁻⁵      |
| ZIF-8     | Methanol          | 186                         | 0.102                | 31.2                | 1.695 × 10⁻⁴      |
| ZIF-65-Zn | IPA               | 374                         | 0.216                | 307                 | 2.292 × 10⁻⁴      |
| ZIF-71    | IPA               | 196                         | 0.239                | –55                 | -4.1 × 10⁻⁵       |
S6. Nitrogen sorption
Nitrogen sorption isotherms were collected at 77 K on samples activated at 180 °C for 48 hours in the pressure range $10^{-6} < P/P_0 < 1$, using a Quantachrome Autosorb iQ instrument. Surface areas were calculated from Brunauer-Emmett-Teller (BET) theory using data in the region $0.05 < P/P_0 < 0.3$. The data (Figs. S13–15) are broadly consistent with existing literature; notably evidence for the two-step isotherm can be seen for ZIF-8, and ZIF-7 exhibits very little adsorption owing to structure collapse upon activation.

| Table S2. BET surface areas for ZIF nanoparticles. |
|----------------------------------|
| ZIF-7   | 224.3 |
| ZIF-8   | 1269.7 |
| ZIF-65-Zn | 642.4 |
| ZIF-71  | 803.3 |

Fig. S13. Nitrogen sorption isotherms for ZIF nanoparticles, showing the full pressure range.
Fig. S14. Nitrogen sorption isotherms for ZIF nanoparticles, showing the *meso-* and microporous adsorption regime enlarged.

Fig. S15. Nitrogen sorption isotherms for ZIF nanoparticles, showing the low pressure region using a semi-log scale.
S7. Thermogravimetry
Thermogravimetric analysis was performed using a Perkin Elmer Diamond combined TG/DTA instrument. Activated samples were heated at a heating rate of 10 °C/minute under a constant air flow and differential thermal analysis was simultaneously conducted with reference to Al₂O₃ powder. Mass change data are plotted below as a function of time (a) and temperature (b) for each of ZIF-7, ZIF-8, ZIF-65-Zn and ZIF-71, for which the starting masses were 7.21 mg, 6.86 mg, 6.53 mg and 7.11 mg, respectively. Final masses were 1.97 mg for ZIF-7 (corresponding to ZnO, calculated 2.01 mg), 2.32 mg for ZIF-8 (corresponding to ZnO, calculated 2.55 mg), -0.09 mg for ZIF-65-Zn (corresponding to full evaporation) and 0.34 mg for ZIF-71 (corresponding to near-complete evaporation).
Where the mass change vs. temperature data turn back on themselves, we attribute this to the strongly exothermic decomposition process observed in the DTA signal for each material and the subsequent need for cooling the samples to return to the programmed temperature ramp profile. The actual temperature and deviation from programmed temperature data are plotted as a function of time in (c) for each ZIF.
Fig. S16. Thermogravimetry and differential thermal analysis of ZIF-7 nanoparticles post-activation, shown as a function of time (a) and temperature (b). Sample temperature data and deviation from programmed temperature profile are shown in (c).
Fig. S17. Thermogravimetry and differential thermal analysis of ZIF-8 nanoparticles post-activation, shown as a function of time (a) and temperature (b). Sample temperature data and deviation from programmed temperature profile are shown in (c).
Fig. S18. Thermogravimetry and differential thermal analysis of ZIF-65-Zn nanoparticles post-activation as a function of time (a) and temperature (b). Sample temperature data and deviation from programmed temperature profile are shown in (c).
Fig. S19. Thermogravimetry and differential thermal analysis of ZIF-71 nanoparticles post-activation as a function of time (a) and temperature (b). Sample temperature data and deviation from programmed temperature profile are shown in (c).
S8. Sensing experiments: selectivity and VOC discrimination.

Saturated vapour sensing was performed with the following experimental setup. The MSS coated with various ZIFs was mounted on a chamber and the chamber was carefully sealed with an O-ring. Two mass flow controllers (MFCs; FCST1005C-4F2-F100-N2, purchased from Fujikin Inc.) were utilized to introduce nitrogen into the chamber at the flow rate of 100 mL/min. One MFC was for purging (i.e. accelerating desorption of adsorbents), and the other one was for introducing sample vapor together with nitrogen as a carrier. In the present case, 1 mL of 26 sample liquids (pure water, formaldehyde solution (35–38%), acetic acid, methanol, ethanol, isopropanol, 1-butanol, 1-pentanol, acetone, methyl ethyl ketone, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, benzene, toluene, xylene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, chloroform, ethyl acetate, tetrahydrofuran and N,N-dimethylformamide; vapour pressures are given in Table S3) was added into a small vial capped with a rubber lid. Two needles connected to a PTFE tube was stuck into the headspace of the vial through the rubber lid. One end of the PTFE was connected to MFC and the other end of the PTFE tube was connected to a vacant vial, so-called ‘mixing vial’ to make the mixed gas sample homogeneous. Another PTFE tube stuck into the mixing vial was connected to the chamber. Another MFC and vacant vial were set in the same way and connected to the mixing vial. The two MFCs were switched every 30 seconds to perform a sample introduction-purging cycle. This cycle was repeated four times, and the data were recorded at the bridge voltage of –0.5 V and sampling rate of 20 Hz. The data collection program was designed by LabVIEW (National Instruments Corporation). All the above experiments were conducted under an ambient condition without any temperature/humidity control.

The response of four blank MSS membranes was measured to confirm that the observed responses of the MOF–MSS were due to the MOF receptor layers. As can be seen in Figs. S20 and S21, the outputs of the blank devices change by 0.01–0.02 mV upon introduction of 20% saturated water or methanol vapour, and the drift of the signals over the course of the 270 s experiment is 0.01–0.06 mV. These values are small compared with output signals of 0.5–8 mV from the MOF–MSS.
| VOC class | VOC                  | Vapour pressure (mm Hg) | Vapour pressure (ppm) |
|-----------|----------------------|-------------------------|-----------------------|
| Alcohols  | Methanol             | 125.79                  | 165507                |
|           | Ethanol              | 65.58                   | 86294                 |
|           | Isopropanol          | 51.41                   | 67651                 |
|           | 1-Butanol            | 6.60                    | 8681                  |
|           | 1-Pentanol           | 2.34                    | 3081                  |
|           | Acetone              | 229.92                  | 302523                |
|           | N,N-dimethylformamide | 3.47                 | 4564                  |
|           | Acetic acid          | 8.38                    | 11026                 |
|           | Methyl ethyl ketone  | 87.69                   | 115383                |
|           | Formaldehyde         | 52.00                   | 68421                 |
|           | Ethyl acetate        | 95.94                   | 126241                |
|           | Benzene              | 80.48                   | 105897                |
|           | Toluene              | 29.00                   | 38156                 |
|           | 1,2-Dichlorobenzene  | 1.48                    | 1951                  |
|           | 1,3-Dichlorobenzene  | 2.28                    | 2994                  |
|           | Xylene               | 6.66                    | 8769                  |
|           | Hexane               | 147.70                  | 194341                |
| Arenes    | Heptane              | 44.85                   | 59019                 |
|           | Octane               | 14.80                   | 19480                 |
|           | Nonane               | 4.91                    | 6458                  |
|           | Decane               | 1.59                    | 2095                  |
|           | Undecane             | 0.42                    | 558                   |
|           | Dodecane             | 0.15                    | 196                   |
| Alkanes   | Water                | 0.03                    | 41.67                 |
|           | Tetrahydrofuran (THF)| 165.26                  | 217452                |
|           | Chloroform           | 191.14                  | 251496                |

*Values calculated from Antoine coefficients obtained from The Yaws’ Handbook of Vapor Pressure.*

*Estimate; temperature lies outside valid range for coefficients.*

*Based on data at 37 °C from sigmaaldrich.com.*

*Values calculated by NIST based on data from Bridgeman et al.*
Fig. S20. Response of blank MSS membranes to 20 % saturated water vapour: (a) output voltage as a function of time over four ON-OFF cycles for four different membranes (grey, navy, yellow, light blue), and (b) the response of one blank membrane, scaled to match Fig. 2a in the main manuscript.
Fig. S21. Response of blank MSS membranes to 20 % saturated methanol vapour: (a) output voltage as a function of time over four ON-OFF cycles for four different membranes (grey, navy, yellow, light blue), and (b) the response of one blank membrane, scaled to match Fig. 2a in the main manuscript.
S9. Sensing experiments: sensitivity and response time.

For sensing experiments in much lower concentration ranges, we designed another measurement system. The MSS chip coated with various ZIFs was mounted in a Teflon chamber, and the chamber was carefully sealed with O-rings. The chamber was placed in a constant temperature bath kept at 25 °C. The sample gases—the vapors of the 12 solvents (pure water, ethanol, 1-hexanol, hexanal, n-heptane, methylecyclohexane, toluene, ethyl acetate, acetone, chloroform, aniline and propionic acid) generated via bubbling—were injected into the chamber with a gas flow system equipped with three MFCs. Nitrogen was used as a carrier gas. The concentrations of the sample gases were calibrated by measuring the decrease in the weight of the solvents before and after a gas flow. The relative humidity (RH) was controlled by providing a saturated water vapor to the gas flow line. The concentration of the sample gases and the humidity of the carrier gas were adjusted by controlling the flow rates of the three MFCs. The total gas flow rate of the three MFCs was set at 100 mL/min. The surface stress caused by the gas adsorption/desorption in the ZIF layer was electrically read by a Wheatstone bridge circuit consisting of the piezoresistors embedded on the bridges. In the present study, a voltage of –0.5 V was applied to the circuit, and the relative resistance changes of piezoresistors were detected as output signals. Each measurement was performed through 10 cycles of 10 seconds sample injection and 10 seconds nitrogen purge. The sample gases were diluted to 2, 5 and 10% of their saturated vapor concentration. The carrier gas was humidified at 0%, 10%, 40%, and 70% RH.
S10. Principal component analysis for VOC discrimination

Principal component analysis (PCA) was performed for discrimination of the 26 samples, following the methodology of Shiba et al.\textsuperscript{10} To perform PCA, features of a signal measured by the MSS were expressed by four parameters which are defined as follows:

Parameter 1: \((b - a)/(t_b - t_a)\) \hspace{1cm} (1)
Parameter 2: \((c - b)/(t_c - t_b)\) \hspace{1cm} (2)
Parameter 3: \((d - c)/(t_d - t_c)\) \hspace{1cm} (3)
Parameter 4: \((c - a)\) \hspace{1cm} (4)

where \(a, b, c, d, e, t_a, t_b, t_c,\) and \(t_d\) are denoted in Fig. S22. In this case, \(t_b = t_a + 5\) [s], \(t_c = t_a + 30\) [s], and \(t_d = t_a + 35\) [s] were used. Three sets of the parameters were extracted from the latter three signals where \(t_a = 90, 150\) and \(210\) out of the four repeated curves in the response signals, since the latter cycles could provide reproducible signals without initial fluctuations such as mixing of sample gases and pre-adsorbed gases. Then, \textit{Origin} software (ver. 2017) was used to perform PCA. PCA finds projection weights for sensor response data that maximize the total response variance in principal components (PCs), where the dimension capturing the greatest variance is given by PC1, and the second greatest variance (subject to being orthogonal to PC1) is given by PC2.

Fig. S22. Schematic of a feature extraction of a signal measured by the MSS. Four parameters are defined as features by using \(a, b, c, d, e, t_a, t_b, t_c,\) and \(t_d\). Figure reproduced with permission from Shiba \textit{et al.}\textsuperscript{10}
S11. ZIF-8 response to 26 VOCs – detailed plots

**Water and alcohols**

- H2O
- MeOH
- EtOH
- IPA
- 1-BuOH
- 1-PeOH

**Fig. S23.** Response profiles of ZIF-8-MSS fabricated by spray-coating to saturated vapour of water and alcohols.

**Aromatics**

- Benzene
- Toluene
- Xylene
- 1,2-dichlorobenzene
- 1,3-dichlorobenzene

**Fig. S24.** Response profiles of ZIF-8-MSS fabricated by spray-coating to saturated vapour of aromatic VOCs.
**Fig. S25.** Response profiles of ZIF-8-MSS fabricated by spray-coating to saturated vapour of linear chain alkanes.

**Fig. S26.** Response profiles of ZIF-8-MSS fabricated by spray-coating to saturated vapour of ketones, esters and amides. HCHO = formaldehyde (aq.); MEK = methyl ethyl ketone; AcOEt = ethyl acetate; DMF = N,N-dimethylformamide.
Fig. S27. Response profiles of ZIF-8-MSS fabricated by spray-coating to saturated vapour of other VOCs. CHCl3 = chloroform; THF = tetrahydrofuran; CH3COOH = acetic acid.
S12. Optimisation of receptor layer volume
The receptor layer volume was optimized by measuring the sensor response to selected VOCs as a function of the number of inkjet droplets deposited. The magnitude of responses (Fig. S28) to water, methanol, acetone, heptane and toluene appear to increase linearly with respect to mass up to 900 droplets. Thereafter, maxima are found around 1700–2100 droplets in each case. Response time, defined here as the time taken to reach 80% of the maximum output voltage, was found to be less than 10 s in most cases without a linear trend with respect to layer volume (Fig. S29). With the exception of the layer of 2500 droplets, both acetone and heptane elicit response times less than 5 s.

![Graph showing output voltage as a function of receptor layer volume](image)

**Fig. S28.** Output voltage as a function of receptor layer volume, measured as number of inkjet printed droplets, for selected VOCs.
Fig. S29. Output response time (defined here as the time taken to reach 80% of the maximum response) as a function of receptor layer volume, measured as number of inkjet printed droplets, for selected VOCs.
S13. Finite element Analysis

To examine the effects of ZIF-8 receptor layer thickness, $t_f$, on nanomechanical sensing, we performed numerical calculations through Finite Element Analysis (FEA) using COMSOL Multiphysics® 5.5 with the Structural Mechanics module. The dimensions for the MSS were set as illustrated in Fig. S30. The diameter and thickness of the membrane are 300 µm and 3 µm, respectively. The membrane is suspended by the four sensing beams, in which piezoresistors are embedded ($R_1$–$R_4$). The dimensions of each beam in the directions $x$ and $y$ are as follows: sensing beams for $R_1$ and $R_3$, 12 µm × 18 µm; sensing beams for $R_2$ and $R_4$, 28 µm × 13 µm.

Fig. S30. Configuration of an MSS. The piezoresistor-integrated sensing beams are magnified in the insets. All images are illustrated in top-view. Numbers indicate the dimensions in µm.

A receptor layer with radius, $r_f$, of 145 µm was placed on the membrane at the center and the thickness of the receptor layer, $t_f$, was varied from 0.1 µm to 25 µm, its Young’s modulus, $E_f$, was varied with representative values of 2.973 ± 5%, 3.145 ± 5% and 7.06 ± 5% (corresponding to Young’s modulus values of ZIF-8 when evacuated, filled with DMF and in monolithic form, respectively), and its Poisson’s ratio, $\nu_f$, was varied between representative values of 0.3 and 0.45. To the receptor layer, isotropic internal strain, $\varepsilon$, ranging from $1 \times 10^{-6}$ to $3 \times 10^{-4}$ was applied. These results are shown in Figures S31 and S32.

Each geometry was meshed over 20,000 elements, which give sufficient resolution for the present simulation. In the case of an MSS, the surface stress on the membrane is transduced to the four sensing beams as an amplified uniaxial stress, resulting in the changes in electrical resistance of the piezoresistors embedded in the beams. We calculated the total resistance change, $\Delta R/R_{\text{total}}$ obtained from the Wheatstone bridge circuit composed of the four piezoresistors, providing the sensing signals of MSS. The $p$-type piezoresistors of the MSS are fabricated by doping boron onto a single crystal Si with (100) surface to take advantage of its high piezocoefficient. Assuming in-plane stress (i.e., $\sigma_z = 0$), relative resistance change can be described as:

$$\frac{\Delta R_i}{R_i} \approx \frac{1}{2} \pi_{44} (\sigma_x - \sigma_y),$$

(5)
where $\pi_{44}$ (~138 $\times$ 10$^{-11}$ [Pa$^{-1}$]) is one of the fundamental piezoresistance coefficients of the silicon crystal, and $\sigma_x$, $\sigma_y$, and $\sigma_z$ are stresses induced on the piezoresistors in [110], [1–10] and [001] directions of the silicon crystal, respectively. The subscript of “$i$” indicates the position of the piezoresistors on the MSS can be seen in Fig. S30 and the previous literature.$^9, 14$ The total resistance change, $\Delta R/R_{\text{total}}$, of all four piezoresistors can be approximately given by the following equation:

$$\frac{\Delta R}{R_{\text{total}}} = \left(\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2} + \frac{\Delta R_3}{R_3} - \frac{\Delta R_4}{R_4}\right).$$

(6)

Due to the symmetric geometry, Eq. (6) can be reduced to the following equation:

$$\frac{\Delta R}{R_{\text{total}}} = 2\left(\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2}\right).$$

(7)

The signal output (intensity) of the full Wheatstone bridge ($V_{\text{out}}$) is given by:

$$V_{\text{out}} = \frac{V_B \Delta R}{4 R_{\text{total}}},$$

(8)

where $V_B$ is bias voltage applied to the bridge.$^9, 14$ A fixed constraint was applied on the outer edges of the four sensing beams (Fig. S30).

Fig. S31. MSS response as a function of strain (a) and thickness at Young’s modulus values of 2.973, 3.145 and 7.06 (b–d, respectively) with Poisson’s ratio values from 0.3 to 0.45.
Fig. S32. MSS response as a function of receptor layer thickness, strain, Young’s modulus and Poisson’s ratio.
S14. Estimated thickness of ZIF-8 on the membrane of MSS

When we coat $N$ droplets of ZIF-8 solution by inkjet spotter, the volume of spotted solution, $V_{\text{sol}}$ [mL], is given by:

$$V_{\text{sol}} = V_{\text{drop}} \cdot N.$$  \hspace{1cm} (9)

where $V_{\text{drop}}$ denotes the volume of one droplet [mL/droplet]. When the concentration of ZIF-8 solution is $C$ [g/mL], the volume of ZIF-8 layer on the membrane of MSS, $V_f$, is given by:

$$V_f = \frac{V_{\text{drop}} \cdot N \cdot C}{\rho},$$  \hspace{1cm} (10)

where $\rho$ denotes the density of ZIF-8 (solid) [g/mL]. When the ZIF-8 receptor layer forms a cylindrical structure, the thickness of ZIF-8 layer, $t_f$ [cm], is given by:

$$t_f = \frac{V_{\text{drop}} \cdot N \cdot C}{\rho} \frac{1}{\pi r_f^2},$$  \hspace{1cm} (11)

where $r_f$ denotes the radius of cylindrical receptor layer [cm]. The thickness, $t_f$, of the 2100 shots layer is calculated from the values given in Table S4, using eq. (11) as follows:

$$t_f [\text{cm}] = \frac{0.3 \times 10^{-6} \cdot 2100 \cdot 1.0 \times 10^{-3}}{0.92} \frac{1}{\pi \times (1.45 \times 10^{-2})^2} \approx 10.4 \times 10^{-4} [\text{cm}],$$

$$= 10.4 [\text{µm}].$$  \hspace{1cm} (12)

Table S4. Parameters for ZIF-8 receptor layer thickness calculation.

| Descriptions                  | Default values          |
|-------------------------------|-------------------------|
| Volume of one droplet $V_{\text{drop}}$ | ~0.3 [nL/shot]          |- \hspace{60pt} ~0.3 \times 10^{-6} [cm³/droplet] |
| Number of droplets $N$        | 2100 [shot]             |
| Conc. of ZIF-8 $C$           | 1.0 [mg/mL]             |- \hspace{60pt} 1.0 \times 10^{-3} [g/cm³] |
| Density of ZIF-8 $\rho$      | 0.92 [g/mL]             |- \hspace{60pt} 0.92 [g/cm³] |
| Radius of receptor $r_f$     | 145 [µm]                |- \hspace{60pt} 1.45 \times 10^{-2} [cm] |
S15. Relative responses of 2 x 2 array of ZIFs to 26 VOCs

Fig. S33. Response profiles of ZIF-7-MSS membrane to 26 VOCs.

Fig. S34. Response profiles of ZIF-8-MSS membrane to 26 VOCs.
Fig. S35. Response profiles of ZIF-65-Zn-MSS membrane to 26 VOCs.

Fig. S36. Response profiles of ZIF-71-MSS membrane to 26 VOCs.
S16. Principal component analysis plots using three PCs.

Fig. S37. Principal component analysis, showing combinations of PC1, 2 and 3. Alcohol responses are individually grouped within solid ellipses.
### S17. Comparison of selected MOF-based sensors.

#### Table S5. Comparison of selected MOF-based sensors.

| MOF                  | Fabrication method                        | Device type          | Analytes                        | Sensitivity / ppm | Response time / s | Ref. |
|----------------------|-------------------------------------------|----------------------|---------------------------------|--------------------|-------------------|------|
| **Strain-based**     |                                           |                      |                                 |                    |                   |      |
| ZIF-8                | Conversion of ZnO nanorods                | Microcantilever      | Methanol, ethanol, 1-propanol   | 3-10               | 10-100            | 19   |
| ZIF-8                | Conversion of ZnO nanorods                | Microcantilever      | Methanol, ethanol, 1-propanol   | 10-20              | 100-500           | 19   |
| HKUST-1              | Growth on self-assembled monolayer        | Microcantilever      | H₂O, methanol, ethanol, CO₂     | 1000               | 10                | 20   |
| ZIF-8, 7, 65, 71     | Inkjet printing                           | Membrane-type Surface stress Sensor (MSS) | Various VOCs | 0.1-30 | 1-30 | This work  |
| **Chemoresistive**   |                                           |                      |                                 |                    |                   |      |
| Cu₃(HITP)₂            | Drop-casting                              | Interdigitated electrodes | Ammonia | ≤ 0.5 | Not reported | 21   |
| Cu, Ni-HITP/HHTP     | Drop-casting                              | Interdigitated electrodes | Various VOCs | 20    | Not reported | 22   |
| **Photonic**         |                                           |                      |                                 |                    |                   |      |
| ZIF-8                | Direct growth on substrate                | Fabry-Perot interferometer | Propane, ethanol | 100   | > 120  | 23   |
| ZIF-8                | Sequential growth                         | Multilayer MOF/metal Bragg stack | Ethane, ethylene, propane, propylene, H₂ | 150   | Not reported | 24   |
| HKUST-1              | Step-by-step growth                       | MOF-Si colloidal crystal thin film | H₂O, Ar, ethanol, ethylene, CO₂, carbon disulfide | 0.3-2.6 | 10-60 | 25   |
| **Optical**          |                                           |                      |                                 |                    |                   |      |
| HKUST-1              | Suspension in PTFE filter                 | LED fibre optic sensor | Water                           | 0.04               | 23                | 26   |
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Strain-based chemical sensing using metal-organic framework nanoparticles

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Metal-organic frameworks (MOFs) have received much attention for their potential as chemical sensors, owing to unparalleled tunability of their host-guest response, high uptake and structural flexibility. However, because of the limited compatibility between MOF properties and sensor transduction mechanisms, very few MOFs have successfully been integrated into practical devices. We report the fabrication of the first strain-based sensor constructed from MOF nanoparticles deposited directly onto a membrane-type surface stress sensing architecture, which exhibits unprecedented response times on the order of seconds and ppm-level sensitivity towards volatile organic compounds (VOCs). Finite element analysis is used to demonstrate that the sensor response is a result of analyte-induced strain in the MOF receptor layer. We show that an array of four types of MOF nanoparticles allows for clear discrimination between different classes of VOCs and even individual gases, using principal component analysis of their response profiles. This work opens up the possibility of VOC sensing using a wide range of MOFs, beyond those that are electrically conducting or those that form oriented thin films, with the added advantages of high sensitivity and rapid response compared to existing MOF strain-based sensors.

Introduction

Sensing of volatile organic compounds (VOCs) is critical to our perception of the environment around us,1 monitoring of harmful emissions,2 and healthcare analytics,3 and so is required for a wide variety of current and future technologies.4 Sensors based on metal-organic frameworks (MOFs) offer great potential, in particular towards selectivity, owing to their precisely defined pore structure and chemistry.5–8 The modular nature of MOFs allows them to be tailored with highly specific host-guest interactions to adsorb small molecules with higher uptake and selectivity than conventional materials such as polymers, zeolites and porous carbons.9,10 Luminescence and other optical transduction modes are most widely reported in the literature of MOF-based sensing;11 however, for practical usage other modes that integrate more easily with existing electronics are more viable.6,12 Whilst there have been a handful of encouraging reports of electronically-responsive MOFs,13–17 MOFs can be ideal candidates for strain-induced chemical detection because of the deformations of coordination space within their crystal structures caused by host-guest interactions and their increased flexibility compared to conventional inorganic materials.5,18–21 Micro-electromechanical systems (MEMS) sensors coated with thin films consisting of different MOFs such as ZIF-8 (ZIF, zeolitic imidazolate framework; ZIF-8 = Zn[2-methylimidazolate])2 and HKUST-1 (HKUST, Hong Kong University of Science and Technology; HKUST-1, Cu[benzentricarboxylate]2(H2O)3) have been shown to successfully respond to water, alcohols and other volatile organics, with sensitivity limits that exceed other mass-sensitive sensors.22,23 However, several challenges remain, including improving the ease of receptor layer preparation, selectivity, sensitivity and response time.20,24 Often, parameters act against one another; e.g., a thicker film may lead to increased sensitivity but at the cost of response time, owing to the time taken for analytes to diffuse through the MOF. In addition, the perceived necessity for well-adhered and defect-free, oriented thin films to effectively transmit analyse-induced strain to the sensor surface puts limits on the range of MOFs that can be used and introduces stringent, often laborious requirements to MEMS device fabrication.24 On the other hand, a much wider range of MOFs can now be easily

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synthesized in colloidal or nanoparticle (NP) form. Nanoparticles have been shown to be effective and simple to deposit via spray coating as receptor layer materials in MEMS sensors, and size reduction has been shown to improve the mechanical stability of multilayer NP coatings. Therefore, the integration of MOF NPs into MEMS devices would open up development of practical MOF-based sensors beyond those that form oriented thin films or are electronically conductive and lead to a new class of robust, selective receptor materials.

The Membrane-type Surface stress Sensor (MSS) consists of a Si-based membrane suspended by four piezoresistive beams, composing a full Wheatstone bridge. This architecture generates potential difference upon changes to the strain state of the membrane, with approximately 100 times greater sensitivity than conventional piezoresistive microcantilevers, and can be extended to multiple sensor arrays. To induce strain on the membrane, a receptor layer bound to the membrane must undergo strain in response to an analyte. Modelling has predicted that receptor layer materials with higher Young’s moduli give better signals.

Amongst a wide range of MOF NPs available, ZIFs exhibit mechanical properties somewhat intermediate within the MOF class of materials: they are stiffer than so-called “breathing” MOFs such as MIL-53 and pillared-layer MOFs, but still exhibit measurable flexibility in their crystal structure upon gas uptake. Encouragingly for their potential sensing performance, it has been shown that particle size reduction to the nanoscale can result in rather linear gas adsorption isotherms, and improved mechanical properties. In addition, gas diffusion coefficients of bulk MOFs are often several orders of magnitude lower than that in air; therefore, it could be reasonably expected that the meso- and macro-pores within a superstructure of MOF NPs will act as channels for analytes to rapidly diffuse through the whole receptor layer. Indeed, it has been shown using environmental ellipsometry that alcohol adsorption in thin films composed of ZIF-8 NPs takes just 20 s. However, prior to this work it remained to be seen whether receptor layers built from MEMS sensors, in order to realize effective VOC sensing.

We herein report for the first time the fabrication and performance of a new MOF–MSS sensor based on NPs of the canonical ZIF family of MOFs (Fig. 1). We first demonstrate the facile sensor fabrication using ZIF-8, which exhibits hydrophobic pores with the sod network topology. We observe selectivity in its range of responses to 26 VOCs, with rapid response times of 1–30 s and ppm level sensitivity, and show that the sensor response is consistent with a mechanism of adsorbate-induced strain in the ZIF crystal lattice. Exploiting the versatility of the MSS architecture and the diversity of available MOF NPs, we use spray-coating to fabricate a 2 × 2 array of ZIF-8, ZIF-7 (Zn(benzimidazole)$_2$, sod), ZIF-65-Zn (Zn(2-nitroimidazole)$_2$, sod) and ZIF-71 (Zn(4,5-dichloroimidazole)$_2$, rho). The chemical diversity of these MOFs manifests itself in a wide range of sensing profiles, which enable clear discrimination between a range of different VOC classes and individual gases via principal component analysis.

Materials and methods

Synthesis and characterisation.

All chemicals are purchased from Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co. Ltd. and Nacalai Tesque, Inc. ZIF-8 NPs were synthesized following a literature protocol, washed thrice in methanol to remove residual byproducts and resuspended in alcohol. ZIF-7, ZIF-65-Zn and ZIF-71 NPs were synthesized following similar literature routes (see ESI† Section S1 for full details). Chemical composition, particle size and phase purity of bulk samples were confirmed by powder X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), scanning electron microscopy (SEM) and dynamic light scattering (DLS) or after spray coating on the MSS chip. ZIF crystal lattice. Exploiting the versatility of the MSS architecture and the diversity of available MOF NPs, we use spray-coating to fabricate a 2 × 2 array of ZIF-8, ZIF-7 (Zn(benzimidazole)$_2$, sod), ZIF-65-Zn (Zn(2-nitroimidazole)$_2$, sod) and ZIF-71 (Zn(4,5-dichloroimidazole)$_2$, rho). The chemical diversity of these MOFs manifests itself in a wide range of sensing profiles, which enable clear discrimination between a range of different VOC classes and individual gases via principal component analysis.

Sensor preparation.

Materials were deposited directly onto the MSS membrane without any adhesive layer. For selectivity and VOC discrimination experiments, four methanolic suspensions of different ZIF NPs were deposited onto a MSS membrane array by spray coating 30 layers; a stage on which the MSS chip was mounted was held at 100 °C to rapidly evaporate the carrier solvent, and promote sintering and adhesion of the NPs to the surface. For investigation of sensitivity and response time, a ZIF-8 NP suspension was deposited on a single MSS membrane by inkjet printing; an inkjet spotter (LaboJet-500SP) and a
Principal component analysis (PCA).

the concentration of analyte present by the signal-to-noise effective limit of detection was then estimated by dividing (approximately 14, divided by the electrical noise inherent in the MSS device determined from the mean reversible response of cycles 2–injection. 10 injection (10 s) - purge (10 s) cycles were at 0 %, 10 % of their saturated vapour concentrations and humidified constant temperature and humidity using a separate setup. Sensitivity and response time were investigated using the bridge. Discrimination tests for the VOCs using the 2 x 2 applying a bridge voltage of –0.5 V to the Wheatstone and data were recorded at a sampling rate of 20 Hz by Four injection-purge cycles were performed for each gas and vapours of 26 VOCs, including those a range of alcohols, carbonyls, arenes and alkanes (see ESI† Section S8 for details, including absolute concentrations of saturated vapours). Gases were introduced to the sensor for 30 s via a custom-built setup and purged with nitrogen gas for 30 s. VCs, including those a range of alcohols, arenes and alkanes. The irreversible signal—which we attribute to residual molecules that remain in the MOF pores on the timescale of these experiments—apparent in the first cycle responses can be also caused by the enhanced concentration of VOC vapours in the head space of the vial prior to the measurements, they are not included in the following analyses. Different classes of VOCs give rise to quite distinct response profiles. Water and alcohols, such as methanol (Fig. 2b) and ethanol (Fig. 2c) give amongst the highest output voltages and profiles that typically reach saturation within 30 s. Molecules with carbonyl functionality, such as
ketones, esters and amides, including acetone (Fig. 2d), as well as chloroform and tetrahydrofuran also give large responses. The response of acetic acid (Fig. 2e) is unusual amongst the VOCs studied in that it is almost entirely irreversible on these timescales. We expect that this is due to the known instability of ZIFs in acidic conditions, which may degrade the receptor layer. Aromatic compounds, such as toluene (Fig. 2f), elicit intermediate responses that typically do not reach saturation within 30 s, whilst linear alkanes, including hexane (Fig. 2g), give rise to small responses that rapidly reach saturation and then decrease. We attribute the different saturation rates to the different diffusivities of these class of VOCs in ZIF-8; larger molecules will generally pass through the structure more slowly. We also note that the responses of the ZIF-8-based MSS do not necessarily correlate with previously reported isotherms. Clearly, the response is a complex function of many factors, including host-guest interactions, diffusion through the receptor layer, mechanical properties and analyte-induced framework distortion. These factors are influenced by the structure of the MOF receptor layers on different levels, including composition, network topology, porosity (both within and between NPs), and particle-particle and particle-MSS interactions.

**Optimisation of response magnitude and time.**

In order to determine the detection limits of the ZIF-8-MSS, the response magnitude and time were first optimized by investigating the effect of receptor layer volume (see ESI† Section S12). Devices were fabricated by inkjet printing between 100 and 2500 droplets of a ZIF-8 NP suspension onto the MSS membrane. A device fabricated from 2100 inkjet droplets exhibited the best compromise between high output voltages and fast response times for selected receptor layer volumes, the response times for methanol, acetone and heptane were found to be less than 5 s, whilst for toluene and water they were consistently below 30 s. The device deposited with 2100 droplets was therefore chosen for the subsequent investigation of detection limits.

**Detection limits.**

The sensitivity of the 2100-droplet ZIF-8-MSS was determined for 12 VOCs under variable humidity at 298 K (Fig. 3). The sensor response typically decreased as the gases were diluted from 10 % to 5 % and then 2 % saturated vapour. To calculate the limit of detection (LOD), the VOC concentration corresponding to 2 % saturated vapour was multiplied by the ratio of 1 μV (the noise inherent to the MSS architecture; the experimental noise level can be higher depending on the measurement conditions) and the average output voltage of three ON-OFF cycles. The sensor exhibited LODs for most gases well below 10 ppm and sub-ppm LODs to some, including 1-hexanol and n-heptane. Interestingly, sensitivity appears to improve with increasing humidity in some cases, suggesting that cooperative analyte-water interactions may be beneficial to the sensing mechanism. Increasing temperature typically results in reduced output. This is most likely because the receptor layer becomes softer and the adsorption capacity of the MOF decreases. It should be also noted that longer exposure to the vapors than the current cycles can yield even higher signal levels than the presented results, especially for the gas species with low concentrations. Such trends can be observed in some response signals that are not saturated in the current cycles. Accordingly, the detection limits depend also on the measurement conditions as the saturated signal levels are determined by the partial pressure of each gas in the case of chemical gas sensors based on the gas-solid equilibrium, including the present MOF-MSS as well as common chemoresistive sensors.

**Sensing mechanism.**

The MOF-MSS response was shown to be consistent with a mechanism of adsorbate-induced strain in the MOF receptor layer using Finite Element Analysis (FEA). The response is linear with respect to strain and depends on the Young’s modulus, \( E_Y \), and, to a lesser extent, on the Poisson’s ratio, \( \nu \), of the MOF receptor layer (see ESI† Section S13). It increases with receptor layer thickness up to a threshold value before decreasing at greater thickness. The thickness at which the response is maximised decreases as \( E_Y \) and \( \nu \) increase. Using representative values for \( E_Y^{39,50} \) and \( \nu^{31} \) of ZIF-8, the highest responses are calculated for receptor layer thicknesses between 8 μm and 10 μm. This range agrees favourably with the thickness calculated for the optimised 2100-droplet ZIF-8-MSS, which is 10.4 μm (see ESI† Section S14). FEA further indicates that it takes a strain of \( 1 \times 10^{-5} \) to \( 2 \times 10^{-4} \) in a ZIF-8-MSS with such a thickness to generate the range of observed responses,
i.e., 1–10 mV (Fig. S31a†). For example, methanol induces an output voltage of 10 mV in the 2100-droplet sensor (Fig. S28†), whilst the response of the spray-coated sensor to 1-butanol is around 5 mV (Fig. S34†). This is broadly consistent with previous analysis by powder XRD, which shows that full adsorption of 1-butanol induces a strain of $1.8 \times 10^{-4}$ in the lattice parameter of ZIF-8.\textsuperscript{12} Such a lattice strain is just an order of magnitude greater than the calculated strain in the ZIF-8 receptor layer overall. We attribute this difference to inhomogeneous coverage and imperfect interparticle and particle-surface adhesion, which are important to strain transduction in the sensor device and remain to be optimized in future work.

### Multichannel array sensing.

Despite reasonable selectivity that differentiates somewhat between VOCs, cross-sensitivity means that ZIF-8 is unable to unambiguously discriminate between multiple analytes. We adopted a multichannel array approach previously demonstrated for chemoresistive carbon nanotubes\textsuperscript{51} and 2-D MOFs,\textsuperscript{33} and exploited the versatility of the MOF-MSS concept to spray-coat a 2 x 2 array of MSS channels\textsuperscript{31,32} with NPs of four ZIFs, ZIF-8,\textsuperscript{44} ZIF-7,\textsuperscript{45} ZIF-65-Zn and ZIF-71 (Fig. 4). These particular MOFs were chosen because of their variety in composition, network topology, pore aperture, and diameter (Table 1); which may be expected to affect the adsorption of gases according to size, shape and/or functionality in different ways, thus leading to a diversity of responses and thus improved VOC discrimination.

| MOF | Composition | Net | $d_a$ | $d_p$ |
|-----|-------------|-----|-------|-------|
| (a) | Acetic acid | Acetone | Chloroform | Water |
| (b) | Acetone | Toluene | Hexane | Alkene | Other |
| (c) | Alcohol | Carbonyl | Arenal | Other |
| (d) | Alcohol | Carbonyl | Arenal | Alkane | Other |
| (e) | Alcohol | Carbonyl | Arenal | Alkane | Other |

Simultaneous sensing experiments using the MOF-MSS array reveal a wide variety of responses of the four ZIFs to 26 VOCs (Figs. 2h and 5; see also ESIF Section S15). The relative responses of the sod structures ZIF-7, ZIF-8 and ZIF-65 are qualitatively similar, reflecting the similarity in their network topologies and pore apertures. However, certain differences are apparent in, for example, response magnitudes (e.g., acetic acid) or the relative responses of related compounds (e.g., methanol vs. ethanol; acetic acid vs. acetone). Like in ZIF-8, arenes and linear alkanes elicit medium and low responses, respectively, in ZIF-7 and ZIF-65-Zn. It is particularly interesting that the responses of ZIF-65-Zn to both arenes and alkanes tend to decrease as molecular size increases. Its pore aperture is slightly bigger than the other sod analogues; perhaps this allows for more linear discrimination between compounds. The relative responses of ZIF-71 are qualitatively different to its sod analogues. Arenes and alkanes elicit higher responses, whilst methanol and ethanol give rise to lower responses.

In this case, the response to alcohols appears to increase with increasing size of the molecules. ZIF-71 also gives a more uniform response across all VOCs. We tentatively attribute this to the openness of the rho net, which increases the reversibility of gas sorption compared to the other ZIFs, all of which exhibit the denser sod net. The relative decrease in response to short chain alcohols, such as methanol and ethanol, may be due to the hydrophobic nature of the dichloroimidazolate linker.

**Table 1.** Compositions, nets and pore aperture diameters ($d_a$), and pore diameters ($d_p$) of four ZIFs used in the 2 x 2 MOF-MSS array.

**Fig. 3.** Limit of detection (LOD) of a 2100 droplet nanoparticle ZIF-8-MSS sensor fabricated by inkjet printing towards various analytes determined at 298 K and humidity levels from 0 % RH (light blue) to 70 % RH). MCH = methylcyclohexane; EtOAc = ethyl acetate; prop.acid = propionic acid.

**Fig. 4.** Crystal structures of (a) ZIF-7, (b) ZIF-8, (c) ZIF-65-Zn and (d) ZIF-71. ZnN\textsubscript{4} tetrahedra are shown in blue; C, H, N, O and Cl atoms are shown in grey, white, blue, red and green, respectively. Methyl H atoms are not shown for clarity. Sample morphologies and device appearance of the 2 x 2 MOF-MSS array: (e-h) SEM images of representative NPs of ZIF-7, ZIF-8, ZIF-65-Zn and ZIF-71, respectively (scale bars = 200 nm); (i) optical micrograph of the MSS array spray-coated with (clockwise from top left) ZIF-7, ZIF-8, ZIF-71 and ZIF-65. Each membrane is 300 μm in diameter.

**Fig. 5.** Response of MOF-MSS array sensor membranes spray-coated with (a) ZIF-7, (b) ZIF-65-Zn, and (c) ZIF-71. Relative mean response magnitudes are calculated from three measurements for each gas; error bars represent two standard deviations. Colours correspond to those used in Fig. 2.

**Statistical analysis.**

Further investigation of the multichannel data by principal component analysis (PCA) reveals that the 2 x 2 MOF-MSS array is able to group VOCs by chemical class and even discriminate between individual gases. PCA is an
unsupervised method of classifying multi-sensor data, which reduces the dimensionality of the dataset by representing the sensor contributions as linear combinations of the original variables in typically, two or three principal components (PCs). Noting that the MOF-MSS response profiles contain a wealth of information beyond the simple magnitudes of response, we extracted parameters to describe the reversible response, uptake rate, plateau gradient and recovery rate of each ZIF in the 2 x 2 array as input data for PCA (see ESI† Section S10). It was found that the four classes of VOCs could successfully be discriminated using just two PCs, with only small ambiguities in the case of overlaps between alcohols and carbonyls (e.g., acetone), and arenes and alkanes (e.g., shorter chain alkanes and dichlorobenzenes) (Fig. 6). Interestingly, alcohols appear to be subdivided into two groups, one with the smallest molecules (methanol and ethanol) and the other with larger molecules. The weightings of PC1 and PC2 were 55.9 % and 20.1 %, respectively, and together they describe 75.0 % of the total variance. A third principal component (PC3 = 8.2 %) was found to improve the description to 83.2 % and, when viewed with PC1, suggests a much closer grouping of the alcohols (see ESI† Section S16). Within each class, the repeatability of our measurements is apparent in the ability to clearly discriminate between different VOCs. This is an advantage for VOC identification applications, for which there is prior knowledge of a given analyte's response. For example, methanol and ethanol are clearly distinguishable from each other, as are methylethylketone and acetone, both pairs of which differ by just one CH₂ group. Alkanes and aromatic molecules follow clear trends with molecular size, which could be useful in monitoring separation processes.

Conclusions

We have demonstrated for the first time that MOF NPs as a receptor layer on the MSS platform can be highly effective for strain-based chemical sensing. Response times of 1–30 s represent an order of magnitude improvement over existing MOF strain-based sensors (see ESI† Section S17). Sub-ppm sensitivity towards a range of VOCs again represents an improvement in strain-based sensing using MOFs, bringing it on par with hard-to-fabricate photonic crystal thin films, interdigitated electrode devices and colorimetric sensors, the latter of which was limited in analyte scope to water. Importantly, we have demonstrated that, in principle, any MOF that can be made in NP form can now be employed in strain-based sensing, which allows for an enormous diversity of chemistries and VOC selectivities. We constructed a 2 x 2 MSS array using four ZIFs, which have different responses to a range of VOCs and, when their combined responses are subjected to PCA, are able to successfully group the VOCs by class and discriminate between them. Whilst the performance of the reported MOF-MSS is extremely promising, other aspects, such as particle-particle adhesion, particle-surface adhesion and mesoporosity, remain to be optimized in further work. These and many other factors may affect the sensing performance. Therefore, fundamental studies in areas such as MOF-guest interaction energetics, diffusion and flexibility will undoubtedly aid progress in this regard.

Conflicts of interest

The authors hold a patent related to the described work (JP 06544744, US 10564082).

Acknowledgements

We thank the World Premier International Research Center Initiative on Materials Nanoarchitectonics (WPI-MANA) from MEXT, Japan for financial and technical support. This work was also supported by JSPS KAKENHI Grant Number JP19KK0141, MEXT, Japan; a Grant-in-Aid for Scientific Research (A), 18H04168, MEXT, Japan; the Public/Private R&D Investment Strategic Expansion Program (PRISM), Cabinet Office, Japan; the Center for Functional Sensor and Actuator (CFSN). HHMY acknowledges support from the Glasstone Bequest for financial support through the provision of a Glasstone Fellowship and the University of Birmingham for startup funds. We thank Mr. Makito Nakatsu for performing BET measurements and Ms. Yuko Kameyama, Ms. Keiko Koda, Ms. Eri Sakon and Ms. Ikumi Nakakubo (WPI-MANA, NIMS) for coating the ZIFs and collecting all the sensing data. This work was born out of many fruitful discussions at the International Center for Young Scientists (ICYS) at NIMS.

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