Supporting information to:

Optical sensor array of chiral MOF-based Fabry–Pérot films for enantioselective odor sensing

Kuo Zhan,^{a,b} Yunzhe Jiang,^a Lars Heinke^{a,*}

^a Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany

^b School of Physical Science and Engineering, Beijing Jiaotong University (BJTU), 100044 Beijing, P. R. China

1. Materials:

11-mercapto-1-undecanol (MUD, \geq 99.5%), copper acetate monohydrate (Cu(CH₃COO)₂·H₂O, \geq 99.5%), chiral (*1R,3S*)-(+)-camphoric acid (DCam, \geq 99.9%), 1,4-diazabicyclo[2.2.2]octane (dabco, \geq 99.9%), 2,2'-bipyridine (Bipy, \geq 99.9%), trimesic acid (BTC, \geq 99.9%), *R*-/*S*-1-phenylethylamine (*R*/*S*-PEA, \geq 99.9%), *R*-/*S*-1-phenylethanol (*R*/*S*-PhOH, \geq 99.9%) and *R*-/*S*-Limonene(*R*/*S*-Lim, \geq 99.9%) were obtained from Thermofisher Scientific. Absolute ethanol was purchased from VWR. Au@Si-wafer was purchased from *PVD Beschichtungen*, Silz. All solvents and chemicals were used without further purification.

SURMOF synthesis:

The SURMOF thin films were prepared in a layer-by-layer fashion, following previously optimized synthesis descriptions.¹⁻⁴ The SURMOF samples were prepared by alternatively exposing the substrate to the metal node and to the linker solutions, using a dipping robot method.³ The HKUST-1 MOF film was prepared from ethanolic 0.2mM copper acetate and ethanolic 0.1 mM trimesic acid (BTC) solutions. An isoreticular series of homochiral pillared-layer MOFs of type $Cu_2(Dcam)_2(dabco)$ and $Cu_2(Dcam)_2(Bipy)$ with identical chiral (1R,3S)-(+)-camphoric acid (Dcam) layer linker and different pillar linkers of type diazabicyclo[2.2.2]octane (dabco) and 4,4'-bipyridyl (BiPy) was prepared. The pillar-linkers (dabco or BiPy) are coordinated to the axial positions of the copper dimers, forming pillars of different lengths, perpendicular to the chiral $Cu_2(Dcam)_2$ layers. All samples were prepared in 180 synthesis cycles. Prior to SURMOF synthesis, the gold-coated Si substrates are functionalized with an 11-mercapto-1-undecanol (MUD) self-assembled monolayer (SAM). This results in a [001] crystal orientation of the SURMOF perpendicular to the substrate surface. Sketches of the synthesized SURMOF structures, which are $Cu_2(DCam)_2(dabco), Cu_2(DCam)_2(Bipy)$ and HKUST-1 are shown below, see labels.

The SURMOFs are made with 180 synthesis cycles and the films have a thickness of approximately 500nm (see Figure S3). This means that, in average, the SURMOF thickness increases by almost 3 nm per synthesis cycles. Such growth rates, which are somewhat larger than the (ideal) single-layer by single-layer growth rate are in line with thorough previous studies on the growth processes.³⁻⁷



Figure S1: The sketches of the synthesized SURMOF structures, left: Cu₂(DCam)₂(dabco), middle: Cu₂(DCam)₂(Bipy) and right: HKUST-1.

2. Characterization and sensing experiment:

The X-ray diffraction (XRD) analysis was performed using a Bruker D8-Advance diffractometer with a Bragg– Brentano (θ – θ) geometry (also referred to as out-of-plane) with a Cu-anode radiation wavelength of λ =0.154 nm. The (111) peak of the gold substrate is used as a reference, verifying the correct sample height.

A Fourier transform infrared reflection absorption spectrometer (IRRAS) Bruker Vertex 80 was used for the vibrational spectroscopy of the samples. The spectra were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal using a liquid nitrogen-cooled mercury–cadmium–telluride mid-band detector.

SEM images were recorded with a TESCAN VEGA3 tungsten heated filament scanning electron microscope. The samples were coated with a thin (\sim 10 nm) Au/Pd film to avoid charging effects. The sample was imaged under high vacuum conditions and using an acceleration voltage of 20 kV.

UV-vis reflectance spectra were recorded with an Agilent Cary 5000 spectrometer and UMA unit. The analyte vapors are detected using an Agilent Cary 5000 UV-vis spectrometer at room temperature (25°C), and the FP-chiral-SURMOF film samples are located in a cuvette with a gas in/out tube system. The wavelength resolution was set to 0.1 nm. The spectra were recorded in reflectance with an angle of 30° to the surface normal. The position of the reflectance peak wavelength was determined by fitting a Gaussian function to the data in a range of about 20 nm. The intensity of the reflectance peak (in a range of 5nm around the reflectance peak maximum) was also used as a sensor response, in addition to the peak shift. The gas inside the cuvette was controlled by two mass flow controllers (MFCs). The gas stream of the carrier gas (nitrogen) was divided into 2 streams, one stream provides a constant nitrogen flow of 300 ml min⁻¹. The other stream passes through the liquid-filled wash bottle to produce a vapor-enriched stream with a vapor pressure close to the saturated vapor pressure. Both gas streams were stored in a pure nitrogen atmosphere overnight, to realize SURMOFs with empty pores (referred to as pristine samples). The adsorption step (i.e. the analyte exposure) lasted 1h. The desorption step (i.e. the release of the analytes) in a pure nitrogen atmosphere was 2h, to ensure that all chiral odor molecules are desorbed and the pores are empty again.

The photos of the sensors for colorimetric response analysis are taken with an iPhone XR. The sensors were placed in a sealed transparent Petri dish with a gas flow going in and out (via tubes). An iPhone XR, fixed at a distance of 40 cm, was used to take the photos.

Data analysis and classification were performed using standard k-nearest neighbor (k-NN), Support Vector Machine (SVM) and Artificial Neural Network (ANN) machine learning algorithms via program codes written in Python 3 and performed in the open-source platform: Jupyter Notebook. For the k-NN, SVM, and ANN classification, a total of 50 data points of the reflectance intensity values at the reflectance peak (5nm around reflectance peak: ~466nm for $Cu_2(DCam)_2(dabco)$, ~462nm for $Cu_2(DCam)_2(Bipy)$, ~578nm for HKUST-1 FP film with resolution of 0.1nm) were collected before and after the odor exposure. Each data point for analysis includes the reflectance intensity changes of the FP-chiral-SURMOF film, thus each data point is a 3-dimensional vector. A total of 350 data points for analysis were collected for the pristine sample and the 6 analytes (i.e. the 3 pair of chiral odors). The K value in k-NN was set to 18 (which is close to the square root of 350). The kernel function in SVM was set as linear function, and the hidden layer sizes in ANN was set to 10. Data were classified using 5-fold cross validation, where 90% of the data points (i.e. 315 points) were used as the training set, and 10% were used as the test set (35 points). The outcome of the k-NN, SVM, and ANN algorithm is the grouping of the data to the different classes and the comparison of the assignments to the classes that were correct or wrong, shown in the confusion matrix. The used program codes are given in ref.⁸⁻¹⁰.

3. Principle of a Fabry-Pérot sensor:

In a Fabry-Pérot cavity, the light is reflected at both surfaces of a thin film. The different (multiplereflected and non-reflected) light beams interfere, resulting in constructive and destructive interference. More details are given in refs.¹¹⁻¹³ Briefly, the FP principle is:

The wavelengths (λ) of the reflected interference peaks are given by

$$m\,\lambda = 2\,n\,d\,\cos\theta,\tag{1}$$

where *m* is the reflection order (1, 2, 3, ...), *d* is the film thickness (here the SURMOF thickness), *n* is the refractive index (RI) of the SURMOF film, and θ is the incident angle (i.e. the angle between the surface normal and the angle of the incident and reflected light, which is 30° in the experiments).

The RI of the SURMOF film (n_{sample}) increases with the embedment of molecules (i.e. the analytes) in the porous film. The RI of the pristine SURMOF without guest molecules in the pores is $n_{\text{pristine SURMOF}}$ and the RI of the analyte is n_{analyte} . The effective RI value of the sample can be calculated by^{14, 15}:

$$n_{sample}^{2} = n_{pristine SURMOF}^{2} + (x \cdot n_{analyte})^{2}$$
(2)

where x is a factor describing the amount of analytes in the SURMOF pores. Generally, x depends on the volume fraction of the analytes and, therefore, depends on the free pore volume, the host-guest interaction and the vapor pressure. For small vapor pressures (i.e. in the Henry region of the isotherm), x is also proportional to the vapor pressure of the analytes. There, by combining eq.1 and 2, the shift of the reflectance peak is proportional to the chiral vapor concentration and to the selective adsorption behavior of the chiral SURMOFs for different analytes.

In a previous study based on experiments with a quartz crystal microbalance², it was found that the enantioselective uptake of chiral guest molecules by SURMOFs $Cu_2(Dcam)_2(dabco)$ and $Cu_2(Dcam)_2(Bipy)$ differ significantly, although the chiral centers in both MOFs are identical. There, it was found that the uptake of *S*-lim is significantly larger than of *R*-lim in both MOFs, $Cu_2(Dcam)_2(Bipy)$ and $Cu_2(Dcam)_2(dabco)$. This is in line with the data in Figures 2 and S5. Moreover, as expected for the achiral HKUST-1 SURMOF, a clear difference between the different molecules (Lim, PEA or PhOH) was found but no difference between the isomers (*S* or *R*). A similar selectivity has been found in our previous study using a gravimetric transducer technique.¹⁶



Figure S2: The Fourier Transform Infrared Reflection Absorption Spectra (IRRAS) of the SURMOFs films: **a**) $Cu_2(DCam)_2(dabco)$: The absorption bands at 1624 cm⁻¹ and 1467~1401 cm⁻¹ are ascribed to the v_{as} and v_s stretching bands of COO⁻ groups, according to refs.^{17, 18} **c**) $Cu_2(DCam)_2(Bipy)$: The bands at 1614 cm⁻¹ are assigned to stretching bands of COO⁻ groups, according to refs.¹⁸ **e**) HKUST-1: The symmetric COO⁻ stretch vibration at ~1390 cm⁻¹, C-H stretch vibration at 1452 cm⁻¹, and asymmetric COO⁻ stretch vibration at 1640 cm⁻¹ are assigned according to refs.¹⁹⁻²¹



Figure S3: The cross-section SEM images of the $Cu_2(DCam)_2(dabco)$ film (**a**) and **d**), left), $Cu_2(DCam)_2(Bipy)$ film (**b**) and **e**), middle), and HKUST-1 film (**c**) and **f**), right).



Figure S4: The intensity changes of the reflectance peak of the FP-Cu₂(DCam)₂(dabco) film versus concentration.



Figure S5: The reflectance spectra of the FP-Cu₂(DCam)₂(dabco) film in different analyte vapors. The analytes and concentrations are labeled. The insets show the peaks with the Gauss fittings (lines) in the range of 460-490nm.



Figure S6: a) The reflectance spectra of the FP-Cu₂(DCam)₂(Bipy) in different saturated analyte vapors. **b)** The wavelength shift of the reflectance peak of the FP-Cu₂(DCam)₂(Bipy) film *versus* vapor concentration. **c)** The intensity changes of the reflectance peak of the FP-Cu₂(DCam)₂(Bipy) film *versus* concentration. **d)** The wavelength shift of the reflectance peak of the FP-Cu₂(DCam)₂(Bipy) film for *R*-Lim at a concentration of 300 ppm. Different odor exposures were repeated, testing the repeatability and reproducibility.



Figure S7: The reflectance spectra of the FP-Cu₂(DCam)₂(Bipy) film in different analyte vapors. The analytes and concentrations are labeled. The insets show the peaks with the Gauss fittings (lines) in the range of 460-490nm.



Figure S8: a) The reflectance spectra of the FP-HKUST-1 film in different saturated analyte vapors. **b)** The wavelength shift of the reflectance peak of the FP-HKUST-1 film *versus* concentration. **c)** The intensity changes of the reflectance peak of the FP-HKUST-1 film *versus* concentration. **d)** The wavelength shift of the reflectance peak of the FP-Cu₂(DCam)₂(Bipy) film for *R*-Lim at a concentration of 300 ppm. Different odor exposures were repeated, testing the repeatability and reproducibility.



Figure S9: The reflectance spectra of FP-HKUST-1 film in different analyte vapors. The analytes and concentrations are labeled. The insets show the peaks with the Gauss fittings (lines) in the range of 570-600nm.



Figure S10: The k-NN confusion matrices of FP-SURMOFs for the 6 analytes (i.e. 3 pairs of chiral odors) at a concentration of a) 100ppm, b) 200ppm and c) 300ppm.



Figure S11: The SVM confusion matrices of FP-SURMOFs for the 6 analytes (i.e. 3 pairs of chiral odors) at a concentration of a) 100ppm, b) 200ppm and c) 300ppm.



Figure S12: The ANN confusion matrices of FP-SURMOFs for the 6 analytes (i.e. 3 pairs of chiral odors) at a concentration of a) 200ppm and b) 300ppm.



Figure S13: The reflectance spectra of the **a**) $\text{FP-Cu}_2(\text{DCam})_2(\text{dabco})$, **b**) $\text{FP-Cu}_2(\text{DCam})_2(\text{dabco})$, and **c**) FP-HKUST-1 films in different analyte vapors. The analytes and concentrations are labeled. The total concentration (*R*+*S*) is always 300 ppm. **d**) Radar plot of the intensity changes of the reflectance peak of the FP-chiral-SURMOF films, the analytes are labeled. The units of the axes are nm.



Figure S14: The X-ray diffraction (XRD) data of the FP-SURMOF-films samples, before and after the sensing experiments. The data indicate that the samples are stable and the crystallinity is not affected by the analyte exposure.

Table S1: The RGB values of the FP-SURMOF sensors in saturated vapors of the chiral odors. The RGB numbers are averaged from 10 measurements (i.e. 10 consecutive photos).

	Cu ₂ (DCam) ₂ (dabco)	Cu ₂ (DCam) ₂ (dabco)	HKUST-1
Pristine	(115,145,92)	(57,67,42)	(200,172,37)
<i>R</i> -PEA	(131,137,63)	(47,47,30)	(170,147,41)
S-PEA	(119,131,78)	(42,55,31)	(170,145,41)
<i>R</i> -PhOH	(127,133,65)	(31,42,28)	(165,140,43)
S-PhOH	(123,135,70)	(38,45,29)	(165,141,42)
<i>R</i> -Lim	(115,142,86)	(52,54,31)	(175,148,36)
S-Lim	(117,139,82)	(50,56,32)	(175,148,38)

Table S2. Sensor parameters of the FP-chiral-SURMOF film. The limit of detections (LODs) are calculated by the (wavelength or intensity) sensitivities divided by 3 times the standard deviations. The wavelength standard deviation was determined by the variation of the peak intensity of the pristine sample in three subsequent measurements, which is 0.1nm. The intensity standard deviation was determined by the variation of the pristine sample in three subsequent measurements, which is 0.01%.

Analyte	FP-SURMOF film	Wavelength- sensitivity in 10 ⁻² nm /ppm	Wavelength-LOD in ppm	Intensity- sensitivity in 10 ⁻⁴ / ppm	Intensity-LOD in ppm
<i>R</i> -PEA	Cu ₂ (DCam) ₂ (dabco)	3.2	9.4	-2.0	15
	Cu ₂ (DCam) ₂ (Bipy)	2.4	12.5	-1.5	20
	HKUST-1	2.9	10.3	-1.1	27.3
S-PEA	Cu ₂ (DCam) ₂ (dabco)	2.4	12.5	-1.6	18.8
	Cu ₂ (DCam) ₂ (Bipy)	2.1	14.3	-1.2	25
	HKUST-1	2.9	10.3	-1.1	27.3
R-PhOH	Cu ₂ (DCam) ₂ (dabco)	2.9	10.3	-1.8	16.7
	Cu ₂ (DCam) ₂ (Bipy)	3.4	8.8	-1.8	16.7
	HKUST-1	3.4	8.8	-1.4	21.4
S-PhOH	Cu ₂ (DCam) ₂ (dabco)	2.7	11.1	-1.7	17.6
	Cu ₂ (DCam) ₂ (Bipy)	2.7	11.1	-1.7	17.6
	HKUST-1	3.4	8.8	-1.4	21.4
<i>R</i> -Lim	Cu ₂ (DCam) ₂ (dabco)	1.0	30	-0.8	37.5
	Cu ₂ (DCam) ₂ (Bipy)	1.4	21.4	-0.9	33.3
	HKUST-1	2.1	14.3	-0.7	42.9
S-Lim	Cu ₂ (DCam) ₂ (dabco)	1.6	18.8	-1.1	18.8
	Cu ₂ (DCam) ₂ (Bipy)	1.8	16.7	-1.0	30
	HKUST-1	2.1	14.3	-0.7	42.9

Reference

1. Shekhah, O.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Wöll, C., Stepby-step route for the synthesis of metal-organic frameworks. J. Am. Chem. Soc. 2007, 129 (49), 15118-15119.

2. Gu, Z.-G.; Grosjean, S.; Bräse, S.; Wöll, C.; Heinke, L., Enantioselective adsorption in homochiral metal-organic frameworks: the pore size influence. Chemical Communications 2015, 51 (43), 8998-9001.

Gu, Z.-G.; Pfriem, A.; Hamsch, S.; Breitwieser, H.; Wohlgemuth, J.; Heinke, L.; Gliemann, H.; Wöll, C., Transparent films of metal-organic 3. frameworks for optical applications. Micropor. Mesopor. Mat. 2015, 211, 82-87.

Heinke, L.; Gu, Z.; Wöll, C., The surface barrier phenomenon at the loading of metal-organic frameworks. Nat. Comm. 2014, 5, 4562. 4. 5.

Shekhah, O.; Liu, J.; Fischer, R. A.; Wöll, C., MOF thin films: existing and future applications. Chem. Soc. Rev. 2011, 40 (2), 1081-1106.

Shekhah, O., Layer-by-Layer Method for the Synthesis and Growth of Surface Mounted Metal-Organic Frameworks (SURMOFs). Materials 6. (Basel) 2010, 3 (2), 1302-1315.

Wang, Z.; Wöll, C., Fabrication of Metal-Organic Framework Thin Films Using Programmed Layer-by-Layer Assembly Techniques. Advanced 7 Materials Technologies 2019, 4 (5), 1800413.

Qin, P.; Day, B. A.; Okur, S.; Li, C.; Chandresh, A.; Wilmer, C. E.; Heinke, L., VOC mixture sensing with a MOF film sensor array: Detection 8. and discrimination of Xylene Isomers and their Ternary Blends. ACS. Sens. 2022, 7 (6), 1666-1675.

Qin, P.; Okur, S.; Li, C.; Chandresh, A.; Mutruc, D.; Hecht, S.; Heinke, L., A photoprogrammable electronic nose with switchable selectivity for 9 VOCs using MOF films. Chem. Sci. 2021, 12 (47), 15700-15709.

Okur, S.; Zhang, Z.; Sarheed, M.; Nick, P.; Lemmer, U.; Heinke, L., Towards a MOF e-Nose: A SURMOF sensor array for detection and 10. discrimination of plant oil scents and their mixtures. Sensor Atuat B-Chem. 2020, 306, 127502.

Guenther, B. D., Modern optics. OUP Oxford: 2015. 11.

12. Zhang, Y.; Carvalho, W. S.; Fang, C.; Serpe, M. J., Volatile organic compound vapor detection with responsive microgel-based etalons. Sensors Actuators B: Chemical 2019, 290, 520-526.

Lu, G.; Hupp, J. T., Metal- organic frameworks as sensors: a ZIF-8 based Fabry- Pérot device as a selective sensor for chemical vapors and gases. 13. J. Am. Chem. Soc. 2010, 132 (23), 7832-7833.

Xu, H.; Wu, P.; Zhu, C.; Elbaz, A.; Gu, Z. Z. J. J. o. M. C. C., Photonic crystal for gas sensing. 2013, 1 (38), 6087-6098. 14.

Park, S. H.; Xia, Y., Assembly of mesoscale particles over large areas and its application in fabricating tunable optical filters. Langmuir 1999, 15 15. (1), 266-273

Okur, S.; Qin, P.; Chandresh, A.; Li, C.; Zhang, Z.; Lemmer, U.; Heinke, L., An enantioselective e - nose: an array of nanoporous homochiral 16. MOF films for stereospecific sensing of chiral odors. Angewandte Chemie International Edition 2021, 60 (7), 3566-3571.

Gu, Z.-G.; Grosjean, S.; Bräse, S.; Wöll, C.; Heinke, L., Enantioselective adsorption in homochiral metal-organic frameworks: the pore size 17. influence. Chem. Commun. 2015, 51 (43), 8998-9001.

18. Gu, Z.-G. Synthesis and Characterization of Surface Mounted Chiral Metal-Organic Frameworks. Karlsruhe, Karlsruher Institut für Technologie (KIT), Diss., 2014, 2014.

19. Müller, K.; Malhi, J. S.; Wohlgemuth, J.; Fischer, R. A.; Wöll, C.; Gliemann, H.; Heinke, L., Water as a modulator in the synthesis of surfacemounted metal-organic framework films of type HKUST-1. Dalton Trans. 2018, 47 (46), 16474-16479.

20. Gu, Z.-G.; Heinke, L.; Wöll, C.; Neumann, T.; Wenzel, W.; Li, Q.; Fink, K.; Gordan, O. D.; Zahn, D. R., Experimental and theoretical investigations of the electronic band structure of metal-organic frameworks of HKUST-1 type. Appl Phys Lett. 2015, 107 (18), 102_1.

Wang, Z.; Liu, J.; Arslan, H. K.; Grosjean, S.; Hagendorn, T.; Gliemann, H.; Bräse, S.; Wöll, C., Post-synthetic modification of metal-organic 21. framework thin films using click chemistry: the importance of strained C-C triple bonds. Langmuir. 2013, 29 (51), 15958-15964.