Supporting Information

MOF-based sensors for the detection of airborne α-pinene

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1 Calibration of DVS

A calibration procedure was applied in order to evaluate the partial pressure of α-pinene in the carrier gas when using the bubbler configuration. Two sorption isotherms, considering pure vapor of α-pinene and α-pinene/Argon mixture configurations, were collected on a reference material displaying a condensation-like adsorption behavior, *i.e.,* PCN-777 (cf Figure S1). Both isotherms were adjusted until overlapping by a scaling factor (0.35). The α-pinene partial pressure in the α-pinene/Argon mixture corresponds to 281 Pa at 303 K *versus* 803 Pa in the pure phase.

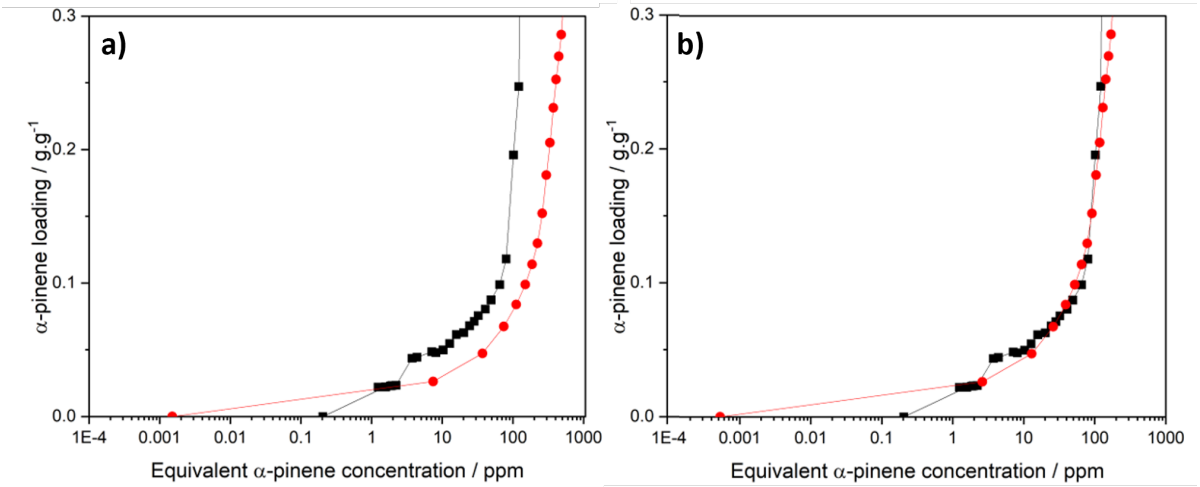

Figure S1 α-pinene adsorption isotherms recorded at 303 K for PCN-777, using the pure vapor (black squares) and α-pinene/Argon mixture (red circles) configurations **a)** before and **b)** after adjustment.

2 Characterization of the powdered DUT-4(Al) and MIL-100(Fe)

2.1 DUT-4(Al)

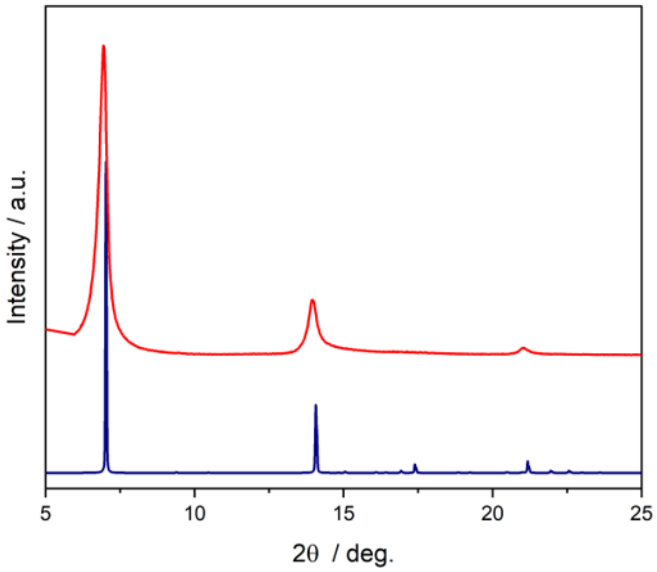

Figure S2 PXRD pattern recorded on the powdered DUT-4(Al) (red line). A simulated PXRD of the DUT-4(Al) structure is given for reference (blue line).

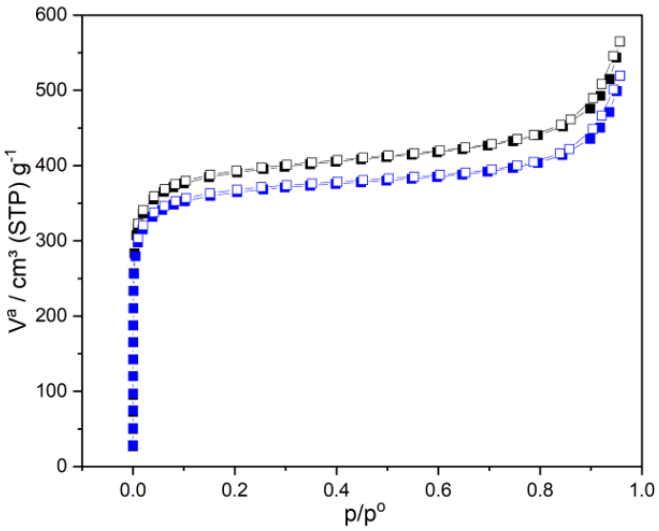

Figure S3 N_2 sorption isotherm collected at 77K on the powdered DUT-4(Al) before (black line) and after (blue line) α-pinene sorption experiments. Adsorption and desorption branches are evidenced by the filled and empty symbols, respectively.

2.2 MIL-100(Fe)

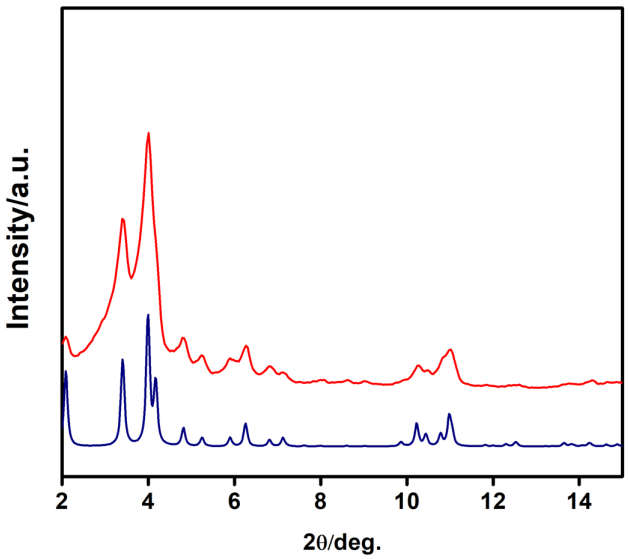

Figure S4 PXRD pattern recorded on the powdered MIL-100(Fe) (red line). A simulated PXRD of the MIL-100(Fe) structure is given for reference (blue line).

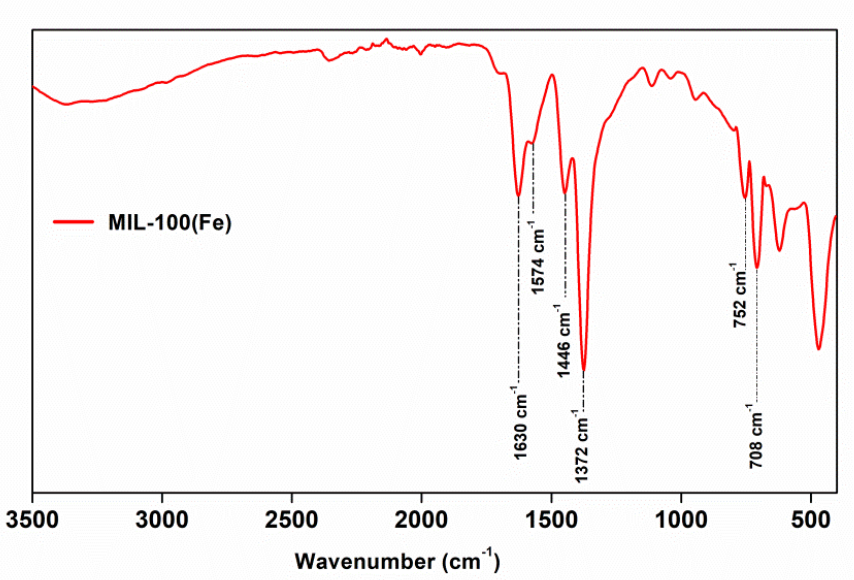

Figure S5 FT-IR spectrum of MIL-100(Fe).

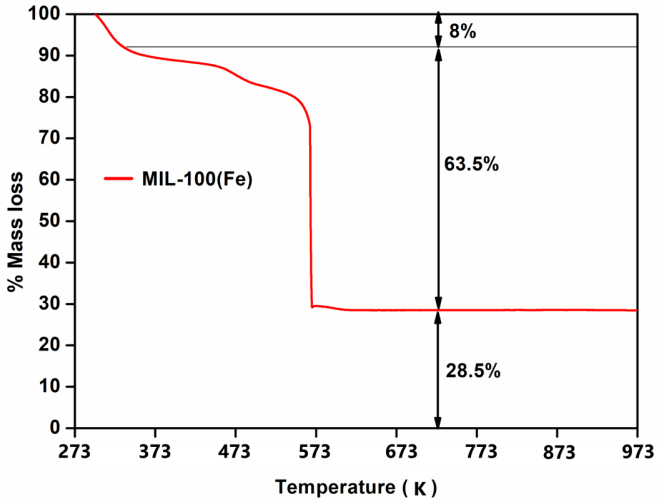

Figure S6 Thermogravimetric analysis of MIL-100(Fe).

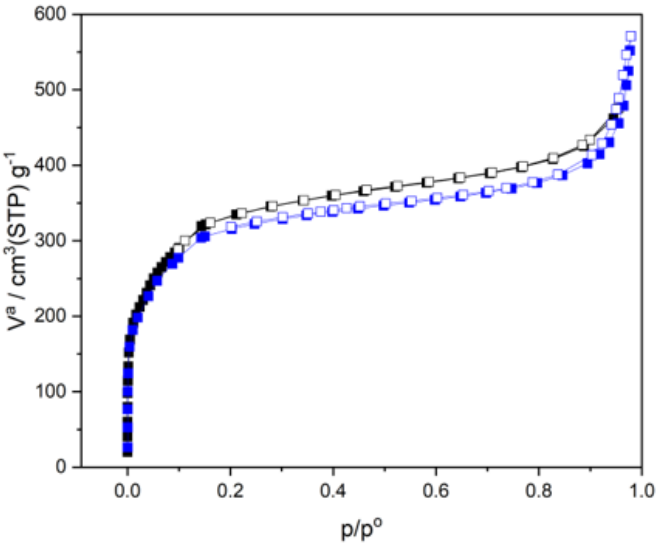

Figure S7 N_2 sorption isotherm collected at 77K on the powdered MIL-100(Fe) before (black line) and after (blue line) α-pinene sorption experiments. Adsorption and desorption branches are evidenced by the filled and empty symbols, respectively.

Table S1 Textural properties of DUT-4(Al) and MIL-100(Fe) deduced from N_2 sorption experiments.

MOF Structures	S_{BET} / m^2g^{-1}		V_{pore} / cm^3g^{-1}	
	Before α-pinene sorption	After α-pinene sorption	Before α-pinene sorption	After α-pinene sorption
DUT-4(Al)[a]	1198	1115	0.63	0.58
MIL-100(Fe)[a]	1223	1194	0.56	0.53

[a]Samples were activated at 423 K for 8 hr

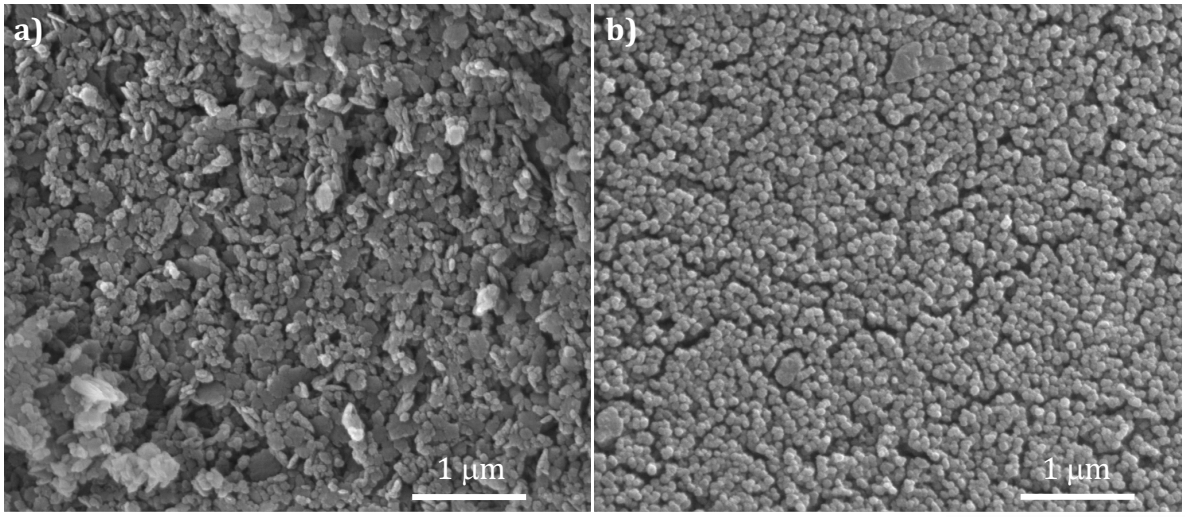

Figure S8 SEM images of the powdered **a)** DUT-4(Al) and **b)** MIL-100(Fe). They evidence the small size of the agglomerates of DUT-4(Al) and MIL-100(Fe), consistent with DLS analysis (Figure S9).

3 Characterization of DUT-4(Al) and MIL-100(Fe) ethanolic suspensions

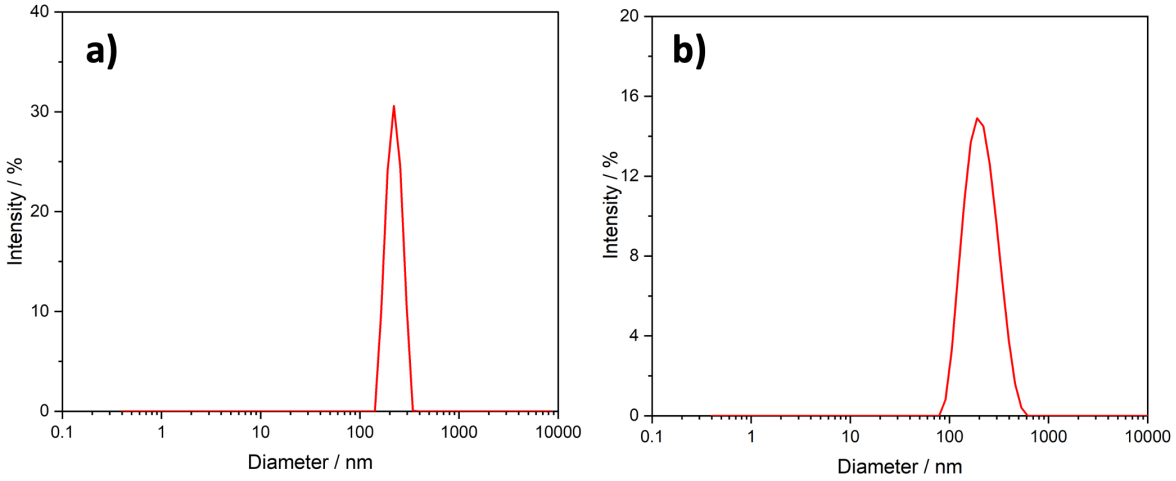

Figure S9 Dynamic light scattering curve for the **a)** DUT-4(Al) colloidal suspension (7.0 $g.L^{-1}$) and **b)** MIL-100(Fe) colloidal suspension (11.5 $g.L^{-1}$) in absolute ethanol. The average hydrodynamic diameter is around 200 nm for both suspensions.

4 Characterization of MOF@QCM

4.1 DUT-4(Al)@QCM

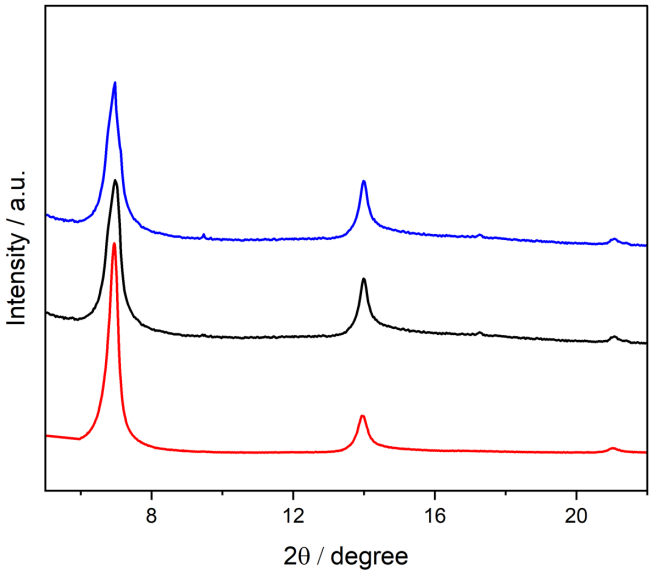

Figure S10 PXRD pattern recorded on DUT-4(Al)@QCM film as-deposited (black line) and after α-pinene sorption experiments (blue line). PXRD pattern of the powdered DUT-4(Al) is given for reference (red line).

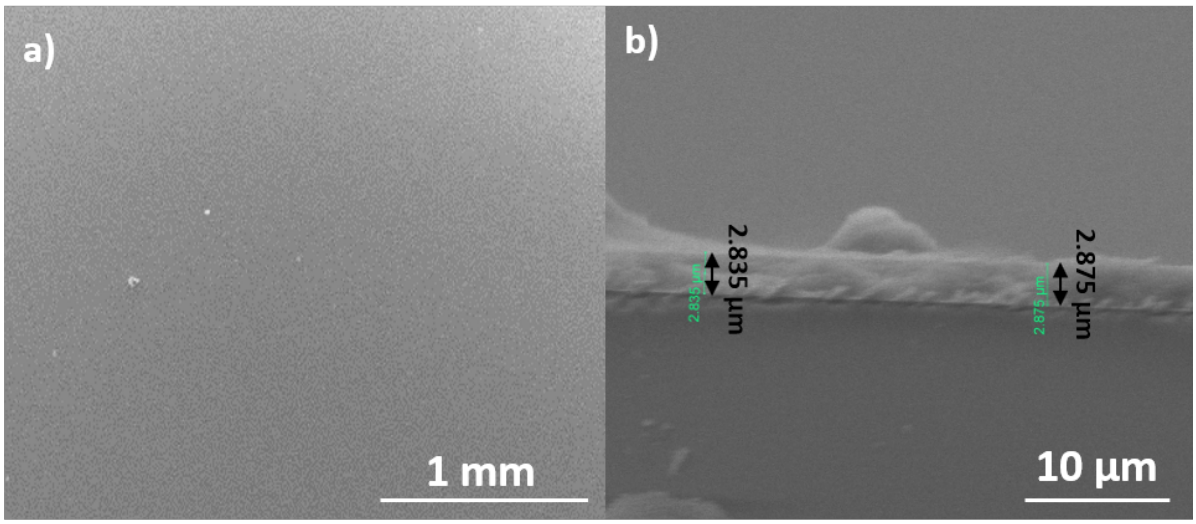

Figure S11 SEM images of DUT-4(Al)@QCM: **a)** top and **b)** cross-sectional views. The film thickness is close to 2.85 µm.

4.2 MIL-100(Fe)@QCM

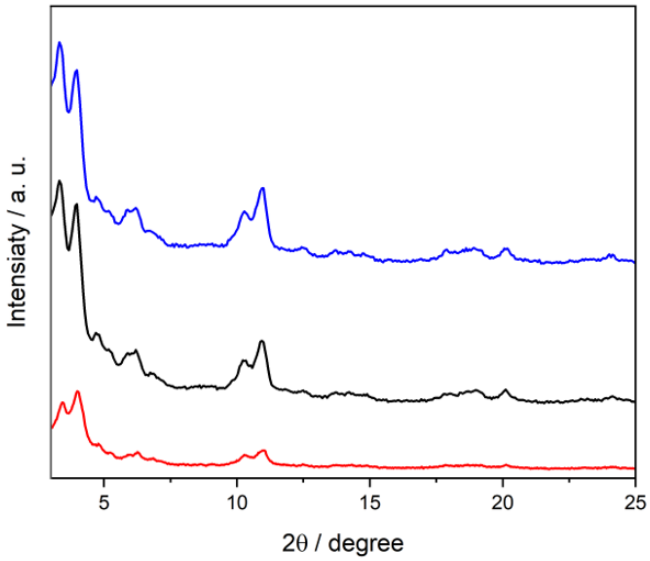

Figure S12 PXRD pattern recorded on MIL-100(Fe)@QCM film as-deposited (black line) and after α-pinene sorption experiments (blue line). PXRD pattern of the pristine powdered MIL-100(Fe) is given for reference (red line).

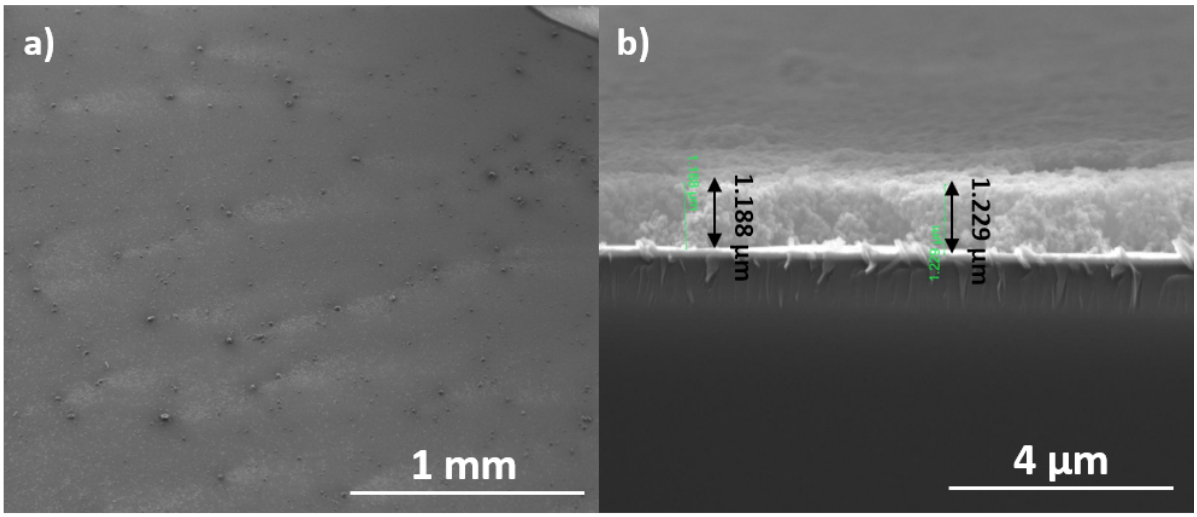

Figure S13 SEM images of MIL-100(Fe)@QCM: **a)** top and **b)** cross-sectional views. The film thickness is close to 1.21 µm.

5 DUT-4(Al)@QCM and MIL-100(Fe)@QCM sensor response

5.1 Repeatability

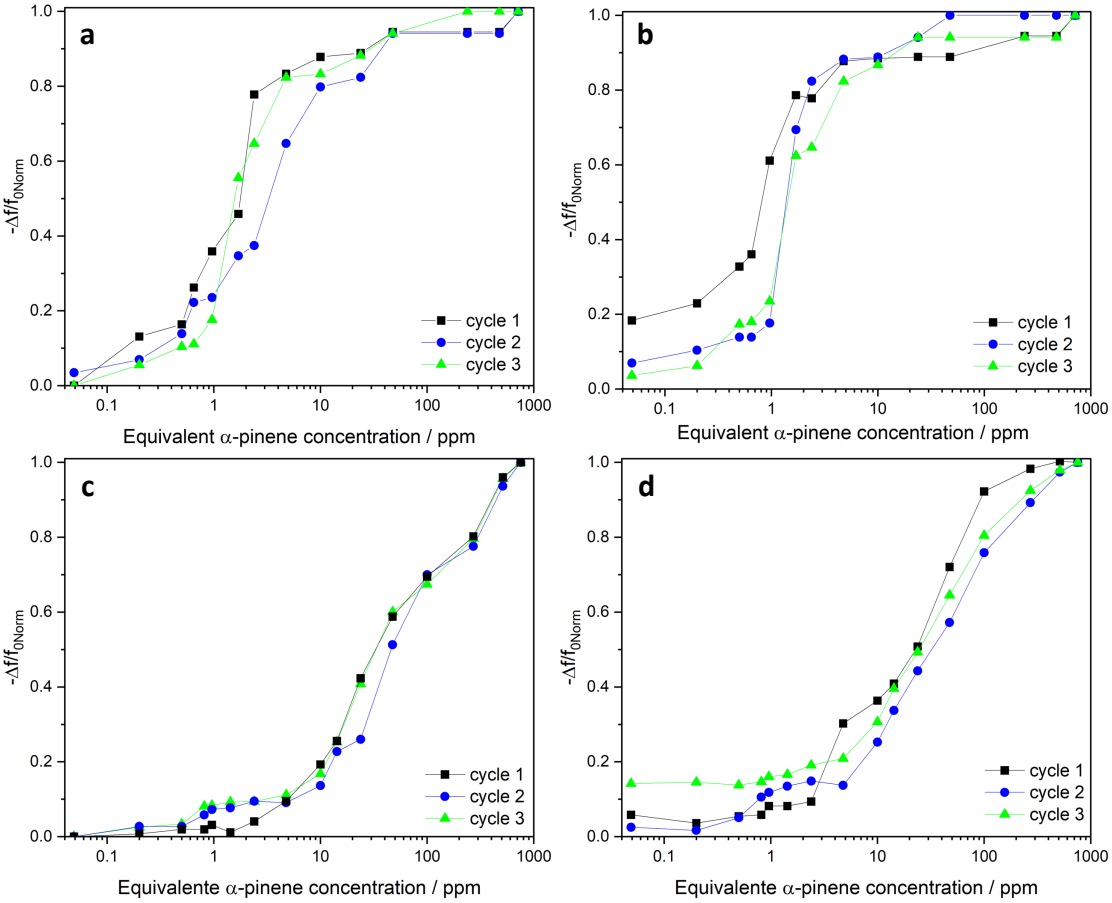

Figure S14 Normalized relative frequency shift [$\Delta f/f_{0Norm} = (\Delta f/f_0)/(\Delta f/f_0)_{max}$] for DUT-4(Al)@QCM with **a)** increasing and **b)** decreasing α-pinene concentration over three sorption cycles. Normalized relative frequency shift [$\Delta f/f_{0Norm} = (\Delta f/f_0)/(\Delta f/f_0)_{max}$] for MIL-100(Fe)@QCM with **a)** increasing and **b)** decreasing α-pinene concentration over three sorption cycles. Lines are guide for the eyes.

5.2 Recovery time

Table S2 Recovery time for DUT-4(Al)@QCM and MIL-100(Fe)@QCM, as defined by the time to achieve 90 % total change of frequency shift to reach the baseline for α-pinene concentration switch back to 2 ppm.

QCM	Recovery time / s		
	5 ppm to 2 ppm	24 ppm to 2 ppm	47 ppm to 2 ppm
DUT-4(Al)	28	24	20
MIL-100(Fe)	54	51	70

5.3 Sensitivity

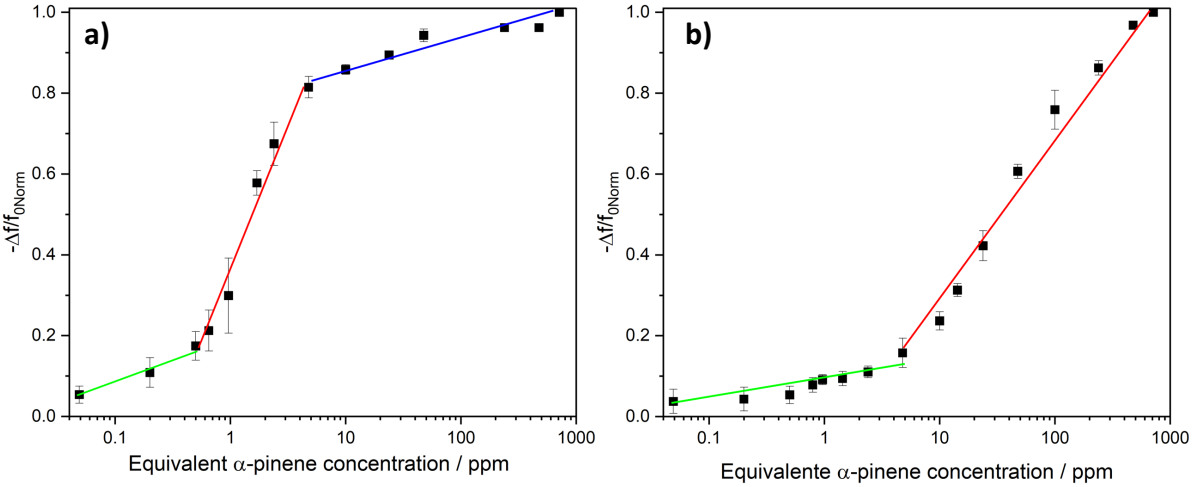

Figure S15 Normalized relative frequency shift for **a)** DUT-4(Al)@QCM and **b)** MIL-100(Fe)@QCM *versus* the equivalent α-pinene concentration. For the sake of visibility, each point corresponds to the average of the data collected with increasing and decreasing α-pinene concentration and error bars represent 3 standard deviations. Linear regressions were considered to evaluate the sensitivity, S, of both sensors with respect to the equivalent α-pinene concentration.

Table S3 Sensitivity of DUT-4(Al)@QCM and MIL-100(Fe)@QCM according to the equivalent α-pinene concentration

QCM	α-pinene concentration / ppm	Sensitivity in $log_{10}(ppm)^{-1}$
DUT-4(Al)	0.05 – 0.6	1×10^{-4}
	0.6 - 4.8	1×10^{-3}
	≥ 4.8	2×10^{-4}
MIL-100(Fe)	≤ 4.8	7×10^{-5}
	≥ 4.8	5×10^{-4}

6 Characterization of DUT-4(Al)/MIL-100(Fe)@QCM

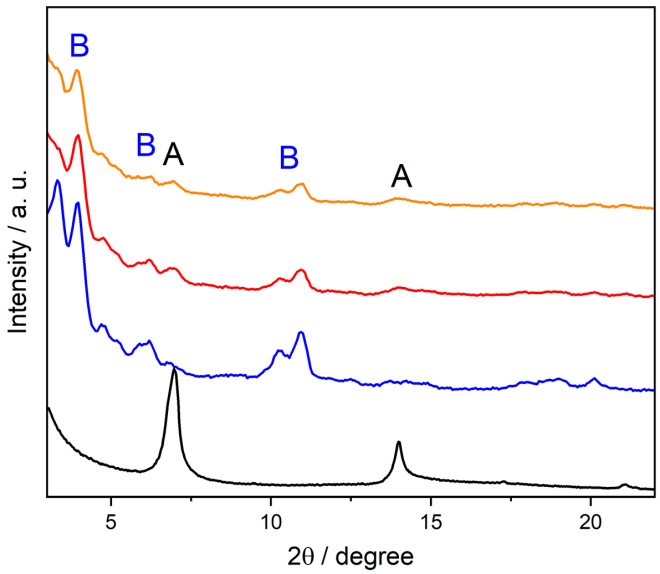

Figure S16 PXRD pattern recorded on DUT-4(Al)/MIL-100(Fe)@QCM film as-deposited (red line) and after α-pinene sorption experiments (orange line). PXRD patterns of DUT-4(Al)@QCM (black line) and MIL-100(Fe)@QCM (blue line) are given for reference. The typical brag peaks of DUT-4(Al) and MIL-100(Fe) in DUT-4(Al)/MIL-100(Fe)@QCM are highlighted by letters A and B, respectively.

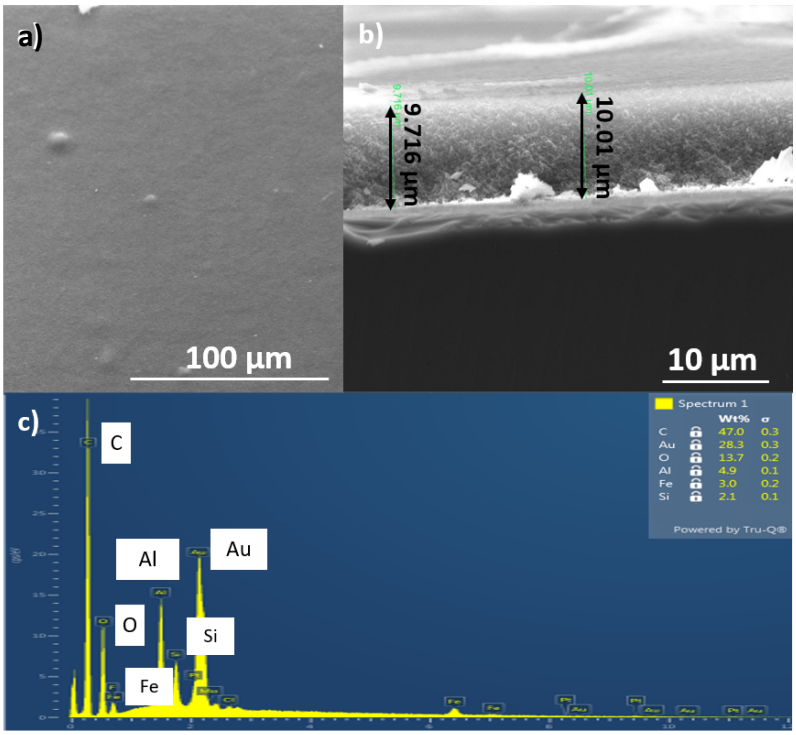

Figure S17 SEM images of DUT-4(Al)/MIL-100(Fe)@QCM: **a)** top and **b)** cross-sectional views. Film thickness is close to 9.90 µm. **c)** EDX spectrum of DUT-4(Al)/MIL-100(Fe)@QCM.

7 DUT-4(Al)/MIL-100(Fe)@QCM repeatability

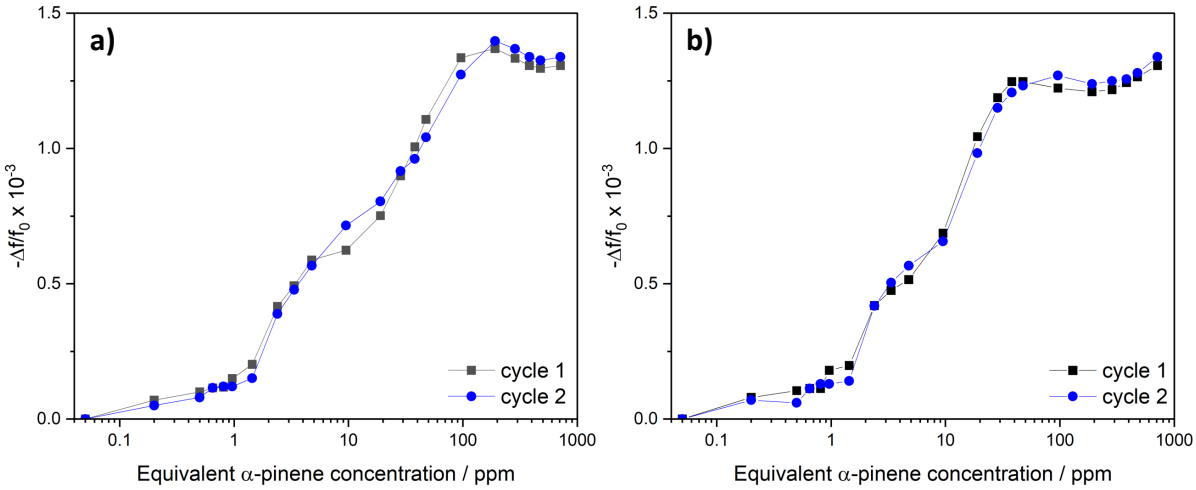

Figure S18 Relative frequency shift for DUT-4(Al)/MIL-100(Fe)@QCM with **a)** increasing and **b)** decreasing α-pinene concentration over two sorption cycles. Lines are guides for the eyes.