State-of-the-Art Chemical Sensing Using Metal-Organic Frameworks (MOFs)

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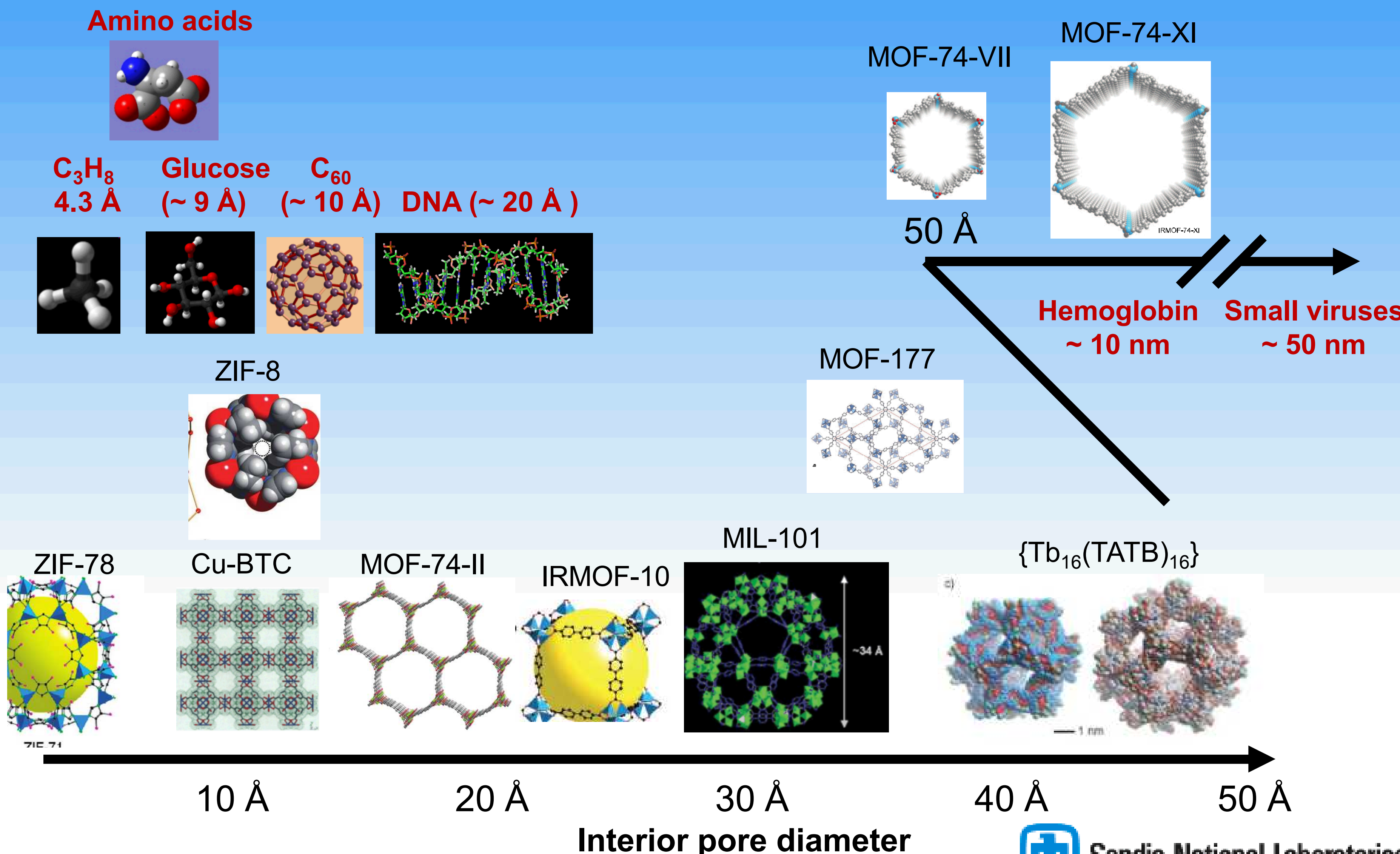
Metal-Organic Frameworks (MOFs) as Chemical Recognition Materials

Metal-Organic Frameworks (MOFs) are not inorganic oxides in the traditional sense, but are nanoporous, hybrid materials composed of metal ions typically linked to an oxygen-containing organic group. MOFs offer unprecedented opportunities to couple specific interactions between molecules adsorbed in their pores with a transduction mechanism that enables chemical sensing. A key advantage of using these materials in sensing applications is their potential to exhibit physical properties that are altered by very minor perturbations. MOF thermal stability also enables sensor regeneration and many display long-term stability under ambient conditions. In addition, their chemical selectivity is determined by framework topology and the structure of the organic linker, which can be varied easily by synthetic design. Our results demonstrate that MOF-based sensors can exhibit similar performance in terms of working temperature and response intensity to commercially available sensors and that MOFs possess much greater synthetic versatility than traditional nanoporous materials such as zeolites.

MOF porosity and chemical functionality are highly tailorable, making them ideal sensing materials



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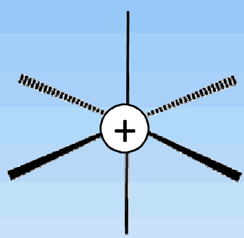
MOFs: high surface area, tailorable porosity for chemical recognition layers

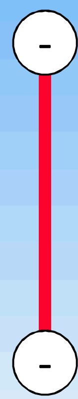
Crystalline (ordered) structure

Metal cation or C,Si,B

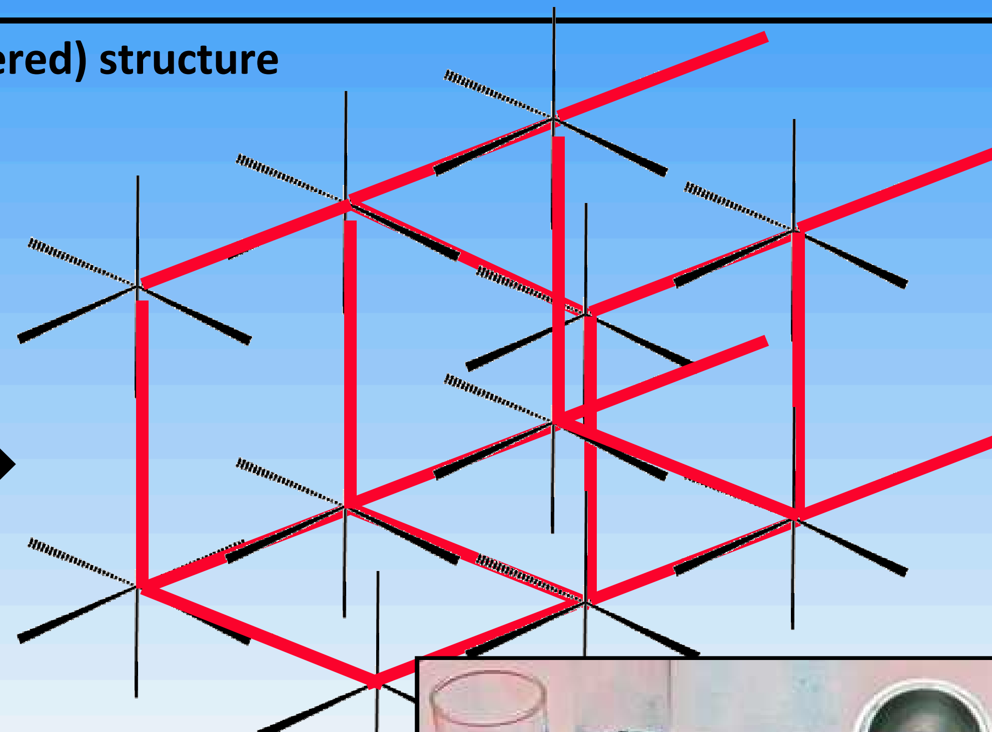


+

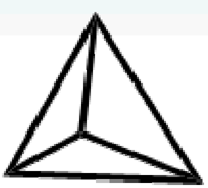
Organic anion or e^- donor



Self assembly

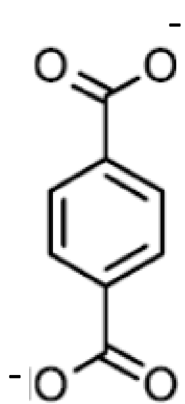


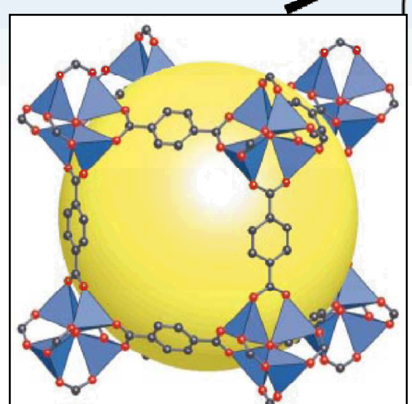
Example: Synthesis of IRMOF-1:



$Zn^{+2}(NO_3)_2$

+





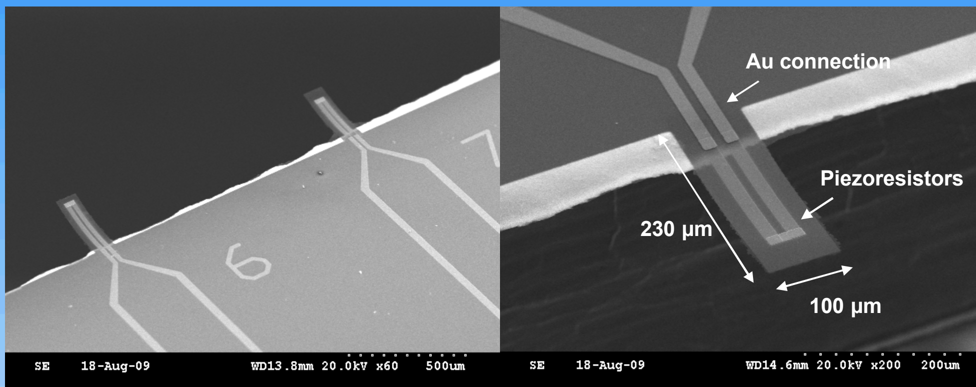
IRMOF-1

Ultrahigh surface areas (record ~ 7000 m^2/g)

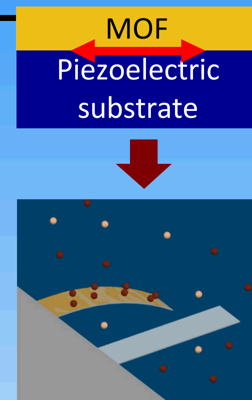
Integration of MOF Thin Films with MEMS Devices

Deposition of MOF thin films is key to development of MOF-based sensors. We integrated more than a dozen MOFs with various Micro-Electro-Mechcanical Systems (MEMS) sensing platforms, such as Quartz Crystal Microbalances and Surface Acoustic Wave (SAW) sensors. These devices can be used to detect a wide range of small molecules, including water, hydrocarbons, ketones and alcohols. For example, we demonstrated sensitivity to sub-ppm water vapor concentrations using a MOF-coated SAW device, which is competitive with state-of-the-art commercial sensors.

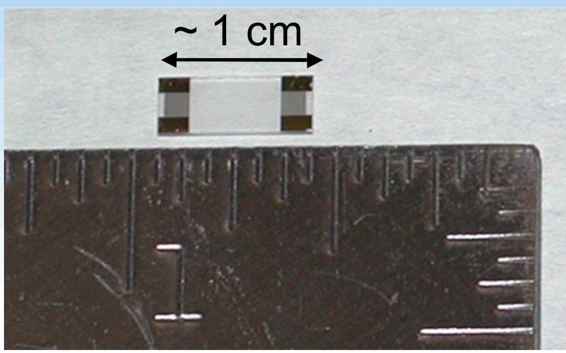
Sensing platforms for detection by mass uptake



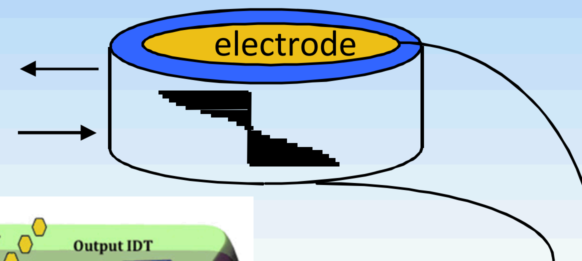
Microcantilevers (fg sensitivity)



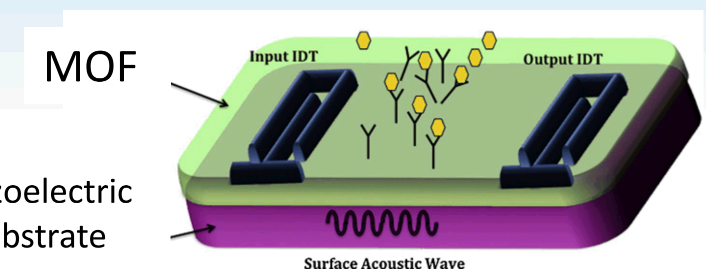
Quartz crystal microbalance (QCM) (~1 ng/cm^2 sensitivity)



Surface accoustic wave (SAW) sensors (~ 0.1 ng/cm^2 sensitivity)



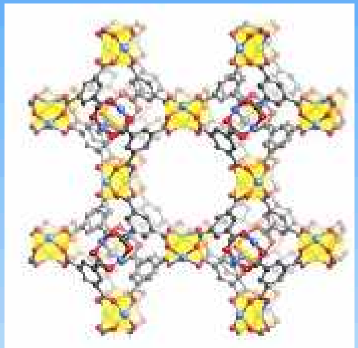
Piezoelectric substrate



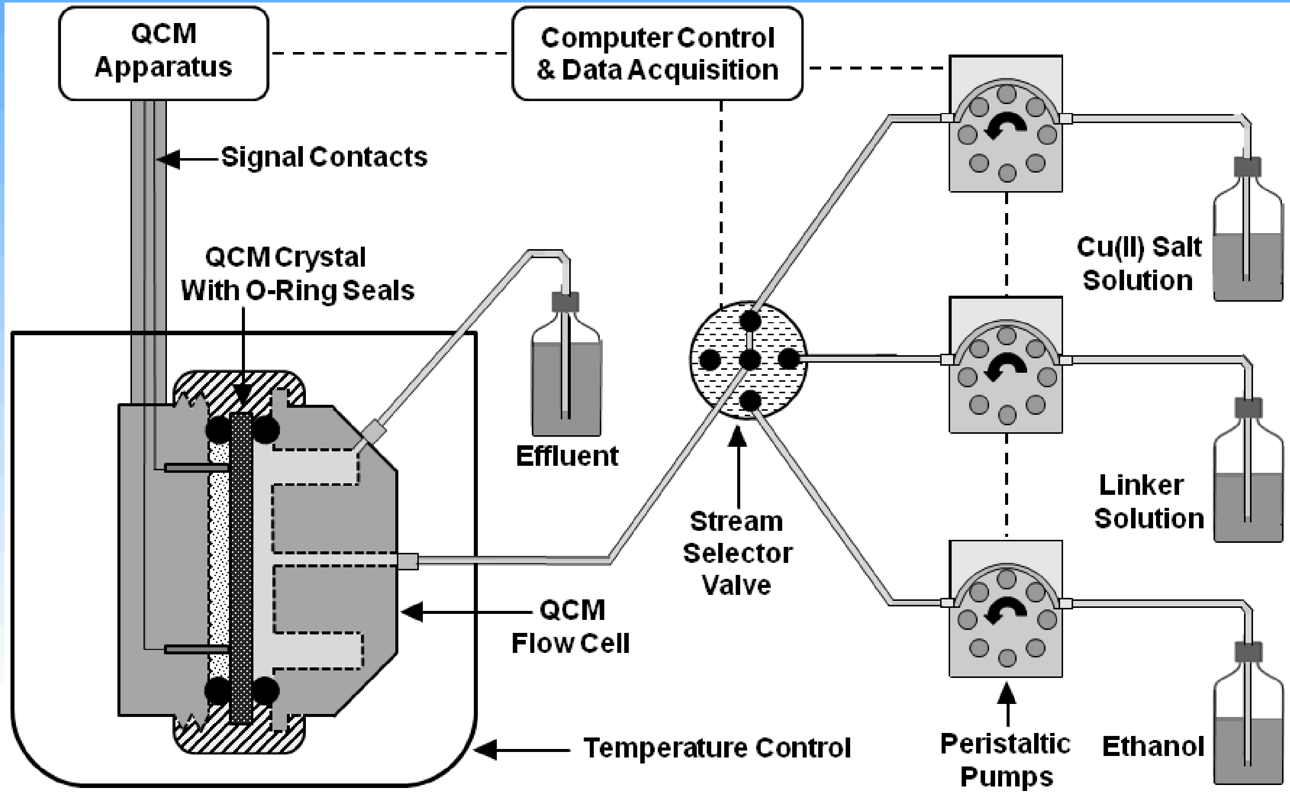
Recognition chemistries are required to enhance sensitivity and impart selectivity to the device

Quartz Crystal Microbalance : A versatile technique to monitor *in situ* the deposition of MOFs on surfaces

MOF



QCM crystal



Schematic representation of automated MOF film growth/QCM capability

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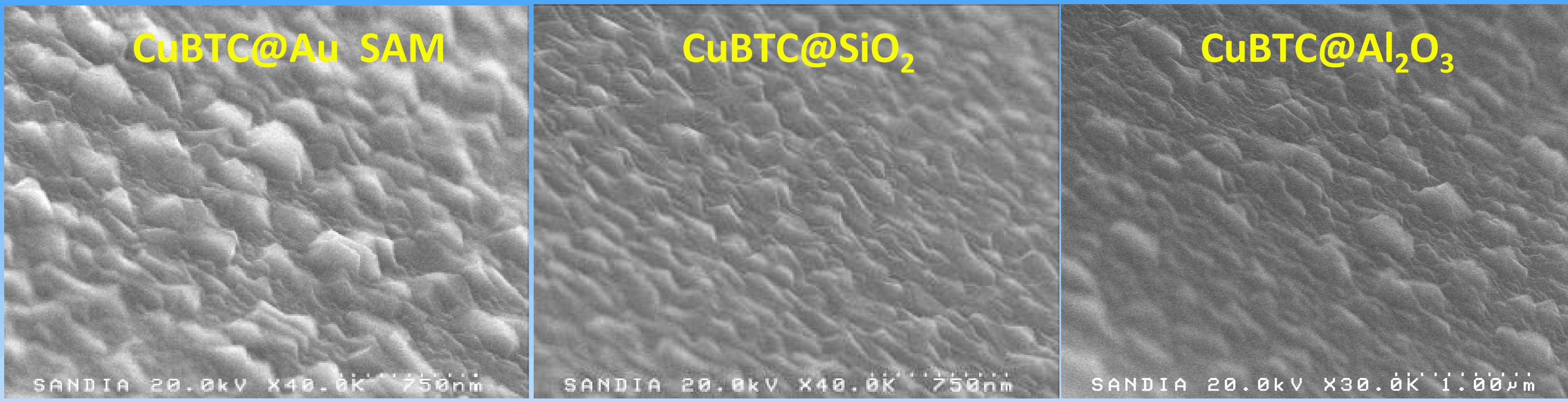
Repertoire of MOF coatings

MOF	Substrate	Conditions	Morphology
Cu-BTC	SAM@Au, Al_2O_3, SiO_2 QCM, SAW, µCL	LBL, drop-casting, Spin-coating, solvothermal	Continuous, polycrystalline films
DUT-6	Al_2O_3	Hydrothermal	Continuous films
MOF-74(Mg)	SiO_2 SAW	Drop-casting, spin casting, solvothermal	Island growth
MOF-74(Zn)	SiO_2	Solvothermal	Continuous films
Al-MIL-53	SiO_2	Drop cast	Individual crystals
PCN-14	SAW/SiO_2	Solvothermal	Continuous film (rough, semi-amorphous)
NOTT-100	SiO_2, Al_2O_3 SAW	Solvothermal; LBL	Continuous films
NOTT-101	SiO_2, Al_2O_3 SAW	Solvothermal; LBL	Continuous films
ZIF-8	SAW/SiO_2	Hupp method	Continuous films (rough)

CuBTC deposition on various substrates



Dense CuBTC coatings were prepared on Au SAMs, SiO_2 and Al_2O_3 surfaces

CuBTC@Si_3N_4 film is easily delaminated

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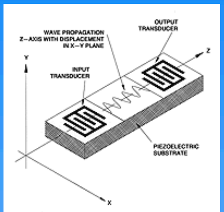
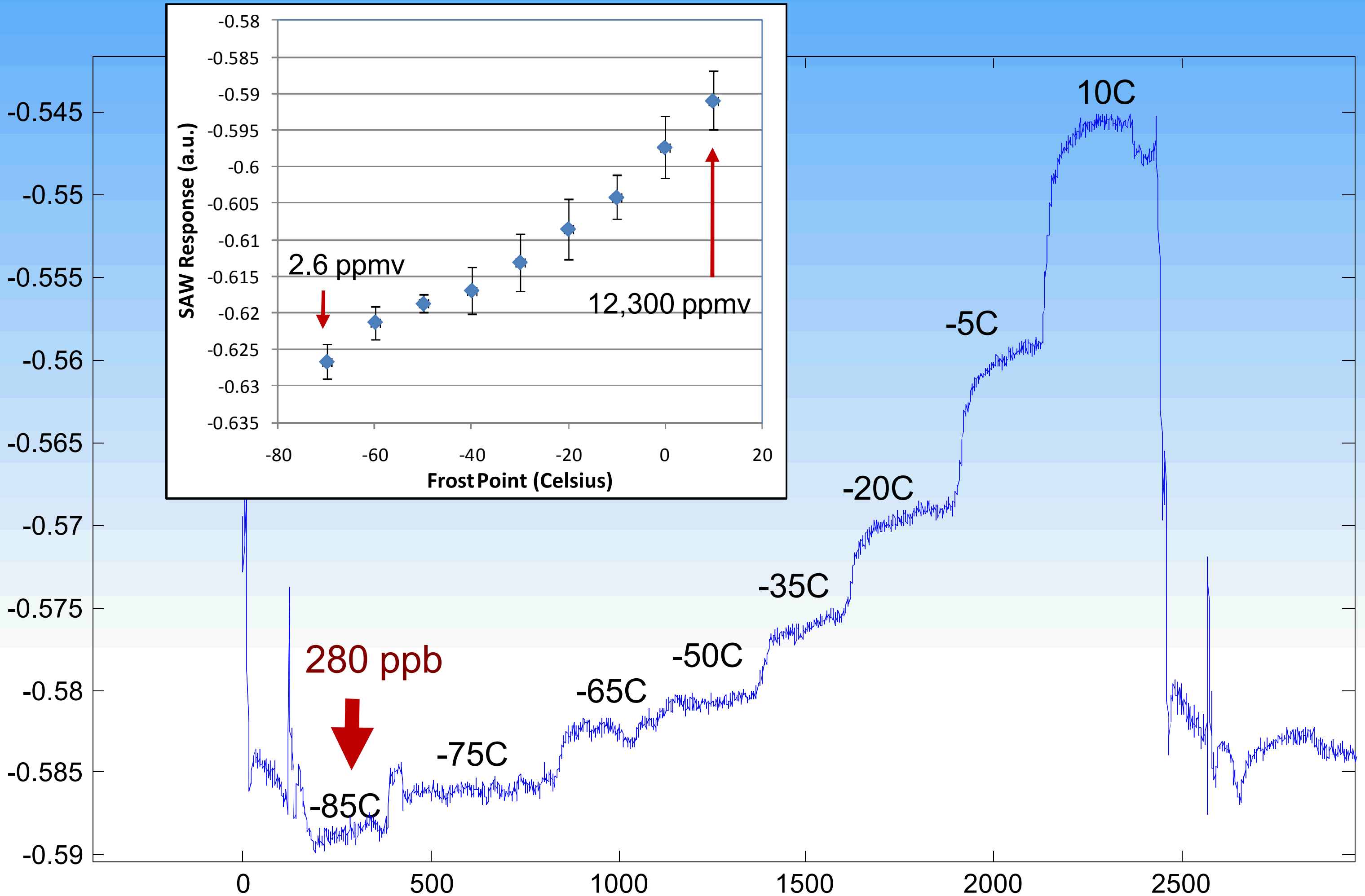
Humidity detection at sub-ppm levels is feasible

Cu-BTC coated SAW device

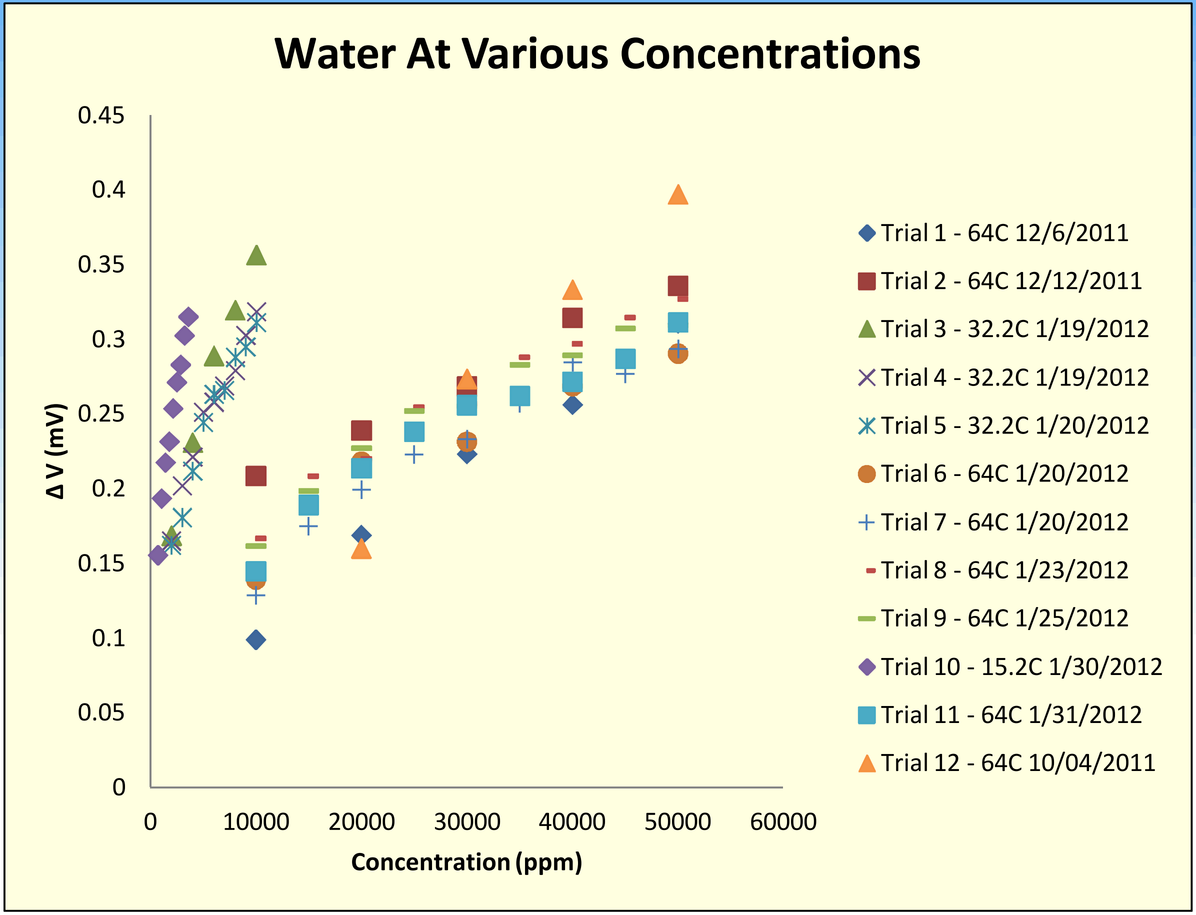


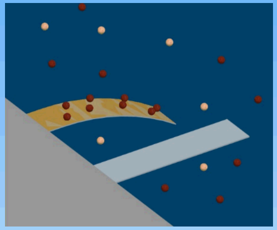
Sensor response over 4 orders of magnitude in H_2O concentration



MOF-coated microcantilever: repeatable detection of water vapor demonstrated

Sensor in continuous use for >12 months!





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MOFs for Breath Analysis

Human breath contains a number of volatile organic compounds (VOCs) that are either disease markers (e.g., acetone or nitric oxide) or indications of consumption of substances such as alcohol. The presence of a large number of potential interferents, including water vapor, carbon dioxide, and many trace species demands that chemical sensors exhibit a high degree of selectivity, as well as high sensitivity and fast response. Our synthetic effort is guided by atomistic modeling, which shows that both sensitivity (i.e., analyte uptake) and selectivity can be achieved by tuning the chemical environment of the MOF pore. Our results demonstrate that detection of acetone and alcohols is feasible using MOF-coated SAW sensors and strain-based microcantilevers. Using a hydrophilic MOF (“Cu-BTC”), we demonstrate uptake of alcohols and acetone, while the hydrophobic MOF “ZIF-8” responds to acetone and hexane, but not water vapor. In contrast, we can tune the humidity and hexane response within a common structural element by modifying the organic linker from hydrophilic (Cu-BTC) to hydrophobic (PCN-14) in a series of copper-paddlewheel MOFs.

Breath analysis

More than 1000 compounds can be found in human breath and breath condensate

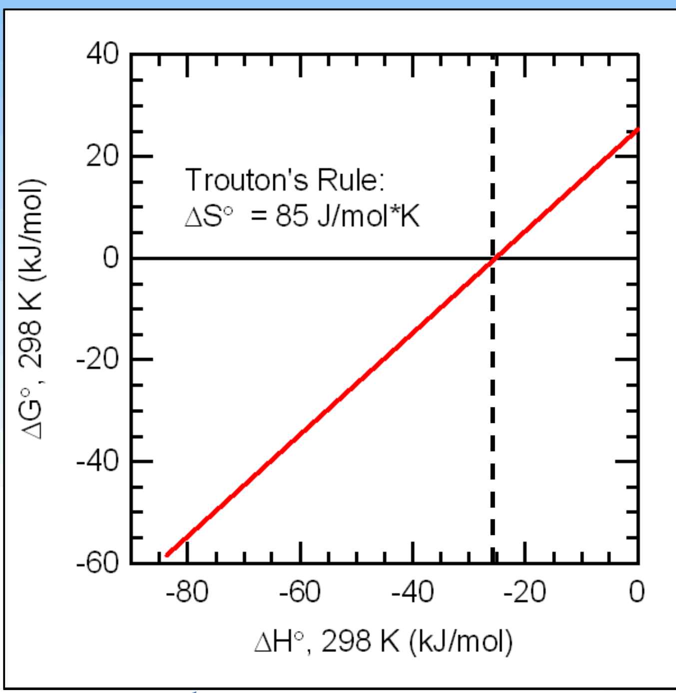
Compound	Concentration	Disease Marker
Acetone	500 ppb	Uncontrolled diabetes
Isoprene	100 ppb	Cholesterol metabolism
Ethanol	200 ppb	Alcohol consumption
Ethane, n-Pentane		Oxidative stress; lipid peroxidation
Alkanes, alkane and benzene derivatives		Lung cancer
GC/FID; PTR-MS		Bulky; expensive
Metal-oxide	Acetone: 20 ppb – 100 ppm	Operate at 100 – 400 °C Selectivity can be poor
Carbon black/polymer composites	EtOH: 600 ppb–10 ppm Acetone: 5 – 33 ppm	Broad response, low selectivity

Heats of adsorption (298 K) predicted by Grand Canonical Monte Carlo simulations

A + MOF ↔ A@MOF

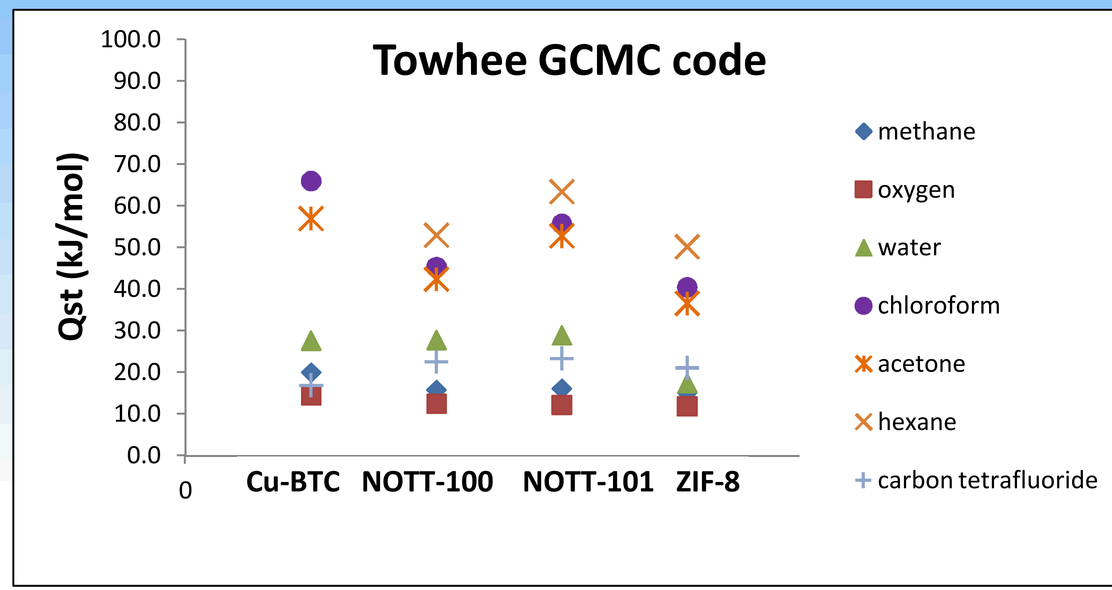
Spontaneous → **$\Delta G°$(adsorption) < 0**

Free energy of condensation



Spontaneous **Non-Spontaneous**

Predicted Heats of Adsorption



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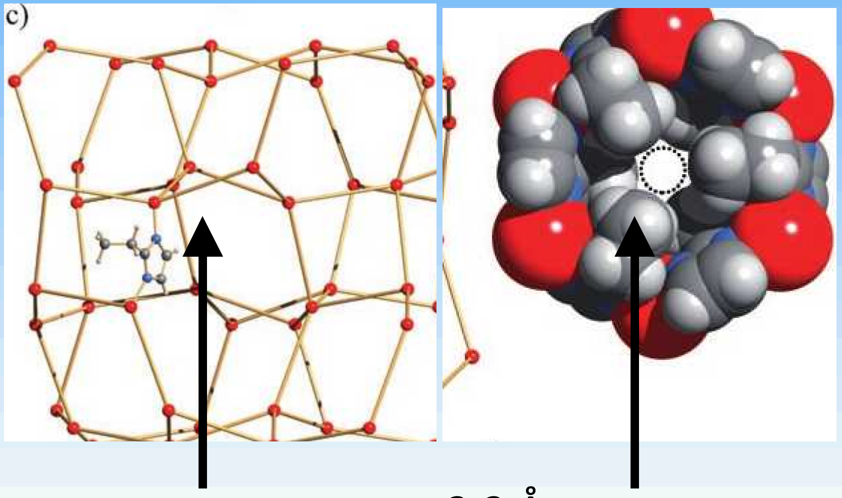
MOFs used in this study

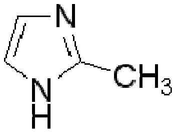
ZIF-8
Hydrophobic pores



12.5 Å pore diameter

3.3 Å pore aperture

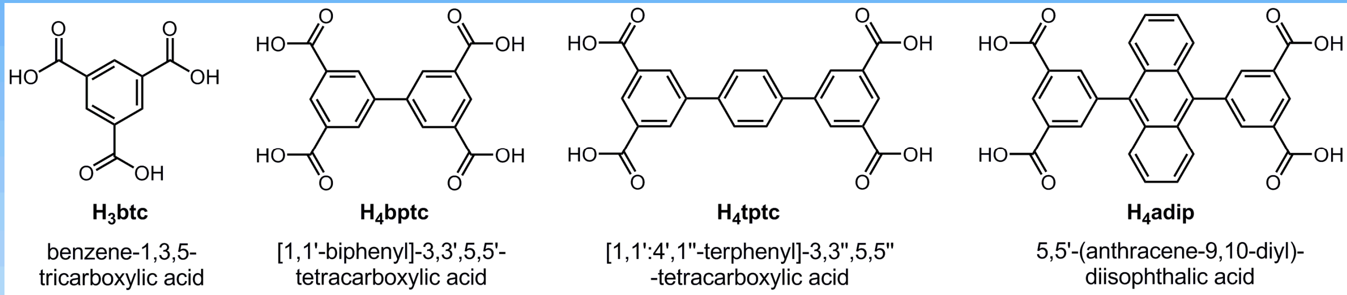
- Zn(II) ions
- Methylimidizolate linkers

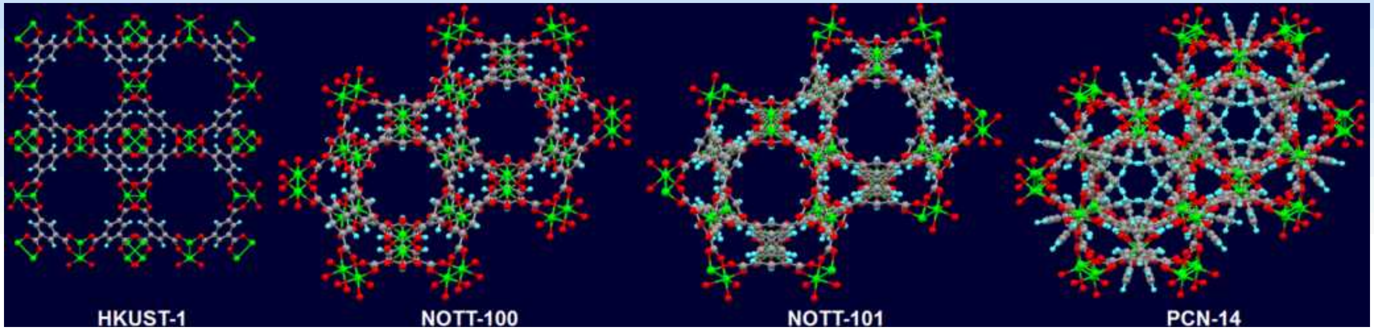


MOFs used in this study (Part 2)

Copper-paddlewheel MOFs

Variable pore size and hydrophilic to hydrophobic pore environments





	HKUST-1	NOTT-100	NOTT-101	PCN-14
Pore entrance diameter (Å):	6.5	4.8	5.5	4.5
Largest cavity diameter (Å):	11.1	10.0	11.2	11.2

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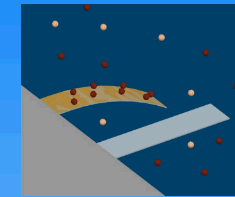
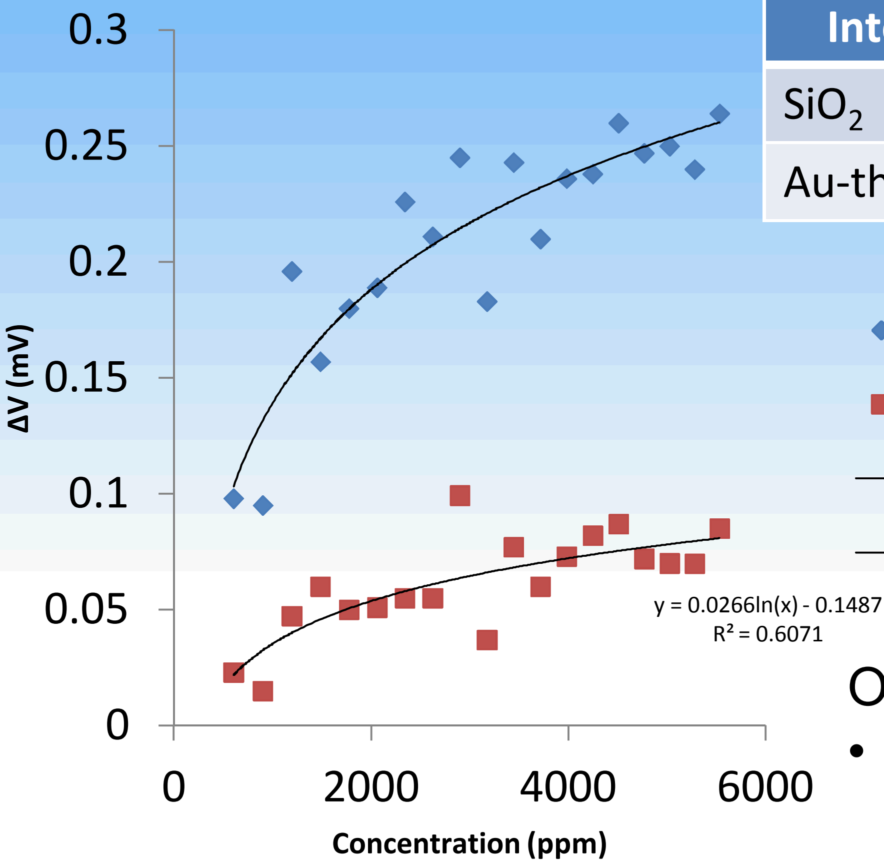
Ethanol detection:
Cu-BTC coated microcantilever



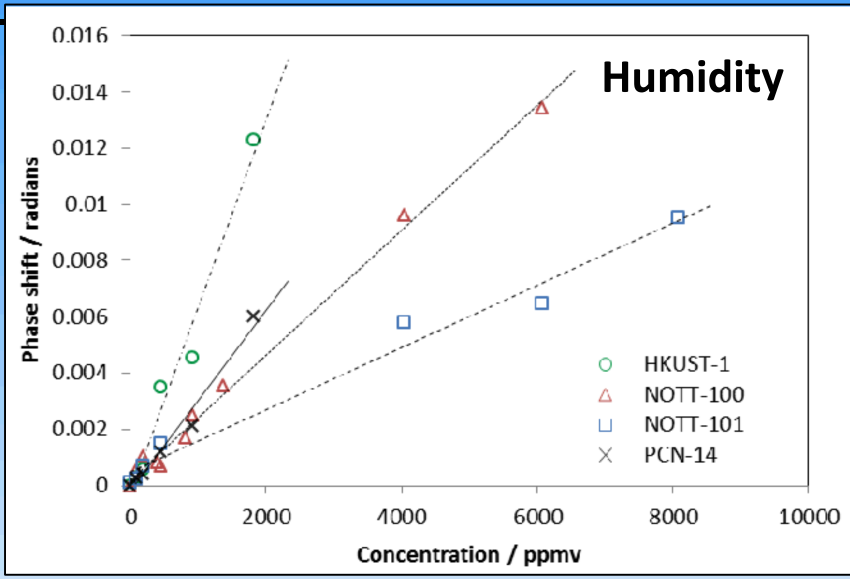


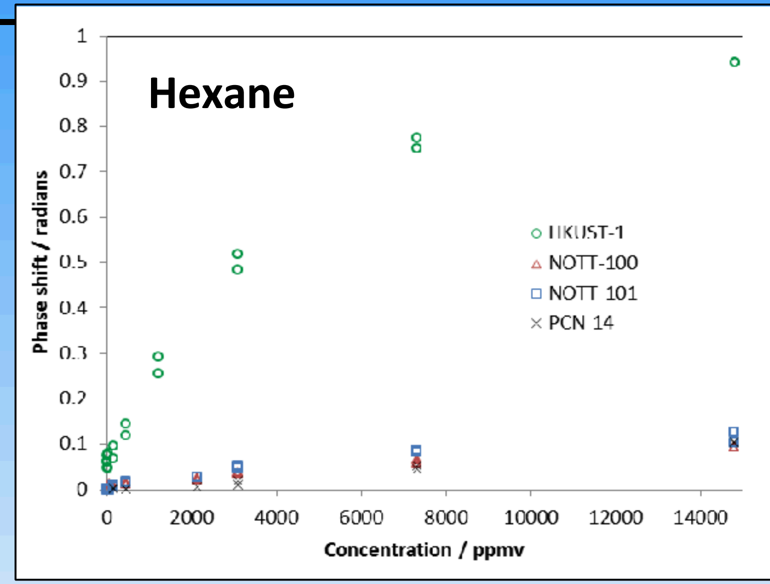
Interface	Thickness	LOD (ppm)
SiO_2	~200 nm	20
Au-thiol SAM	~150 nm	50

Other gases:

- No response to N_2, CH_4, CO_2

Response of MOF-coated SAWS to humidity and hexane, tuned by pore chemical environment





MOF Coating	Hexane Response (µ-rad/ppm)	Water Response (µ-rad/ppm)	Coating thickness (nm)	Normalized Hexane Response (µ-rad /ppm/nm)	Normalized Water Response (µ-rad/ppm/nm)
Cu-BTC	6.6	174	173	0.038	1.0
NOTT-100	2.2	10	130	0.017	0.076
NOTT-101	1.1	13	200	0.0055	0.066
PCN-14	3.2	7.9	150	0.021	0.052

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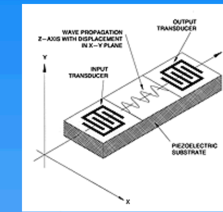
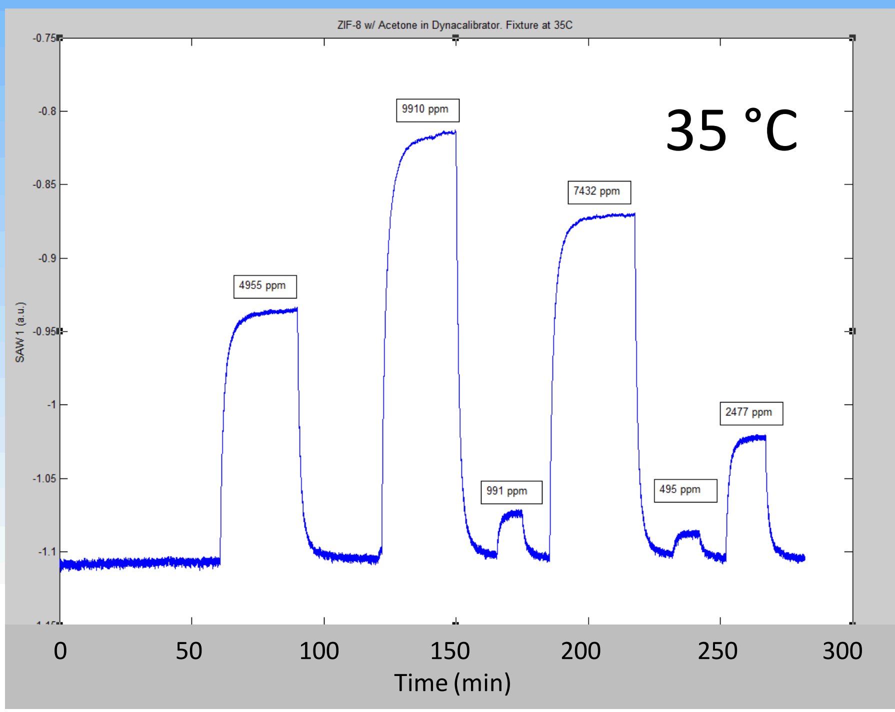
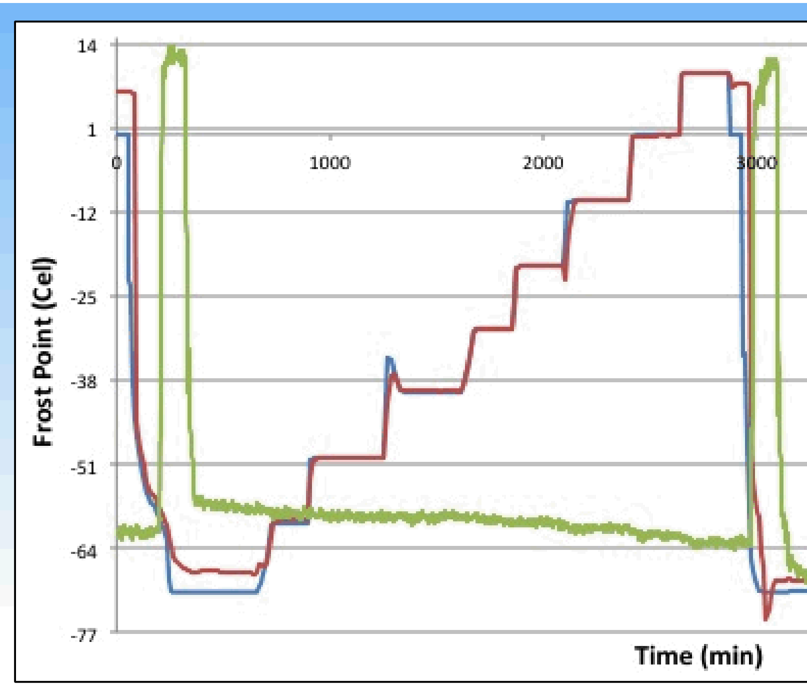
Response to acetone:
ZIF-8 coated SAW device



Interface	Thickness	LOD (ppm)
SiO_2	~450 nm	~30





Other gases:

- No response to water vapor (above)
- No response to N_2, CH_4, CO_2

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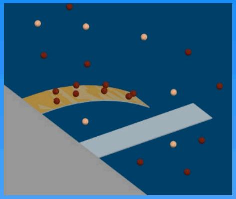
Time constants for adsorption and desorption $Cu\text{-}BTC@SiO_2$ on microcantilever

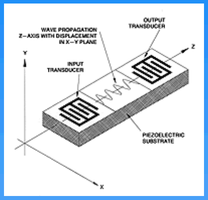


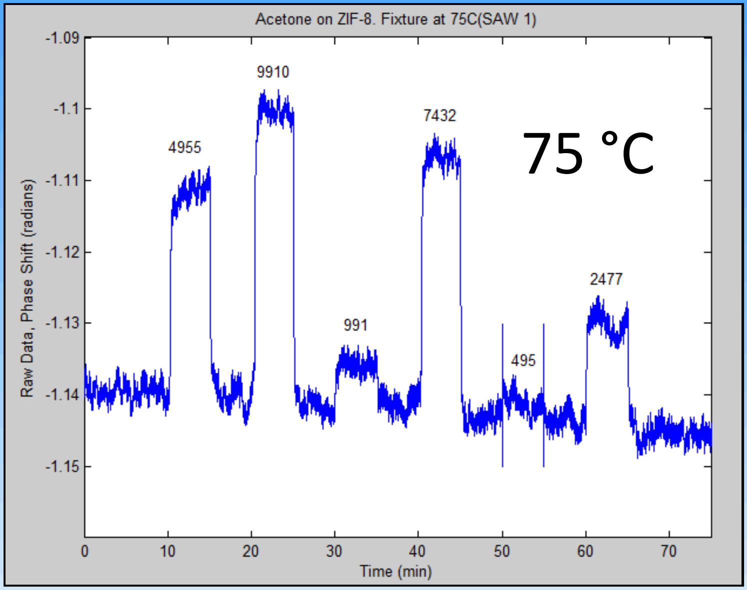
- τ is a complex function of:
  - Vapor pressure (thermodynamics)
  - Diffusion rate (kinetics)
  - Good correlation with b.p.

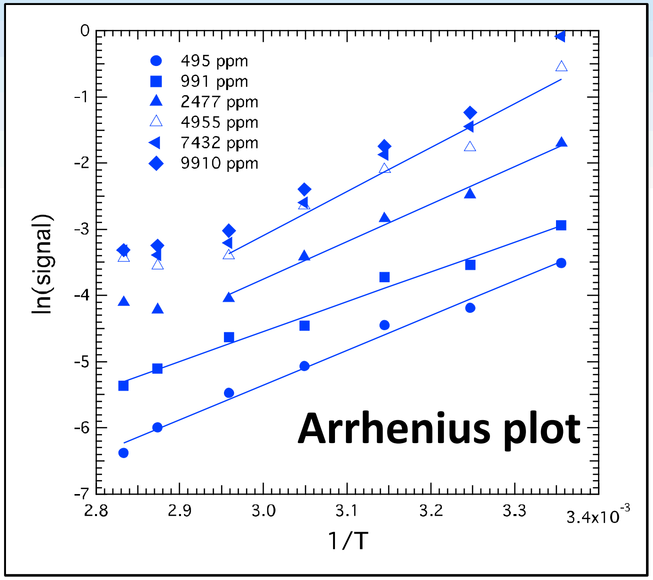
Analyte	b.p. (°C)	τ(s) (Adsorption)	τ(s) (Desorption)
Acetone	57	**52**	**59**
Methanol	65	**43**	**83**
Isopropanol	83	**14**	**22**
H_2O	100	**11**	**14**

- τ(desorption) > τ(adsorption); suggests:
  - ➡ Chemisorption
  - ➡ Molecular size plays a role

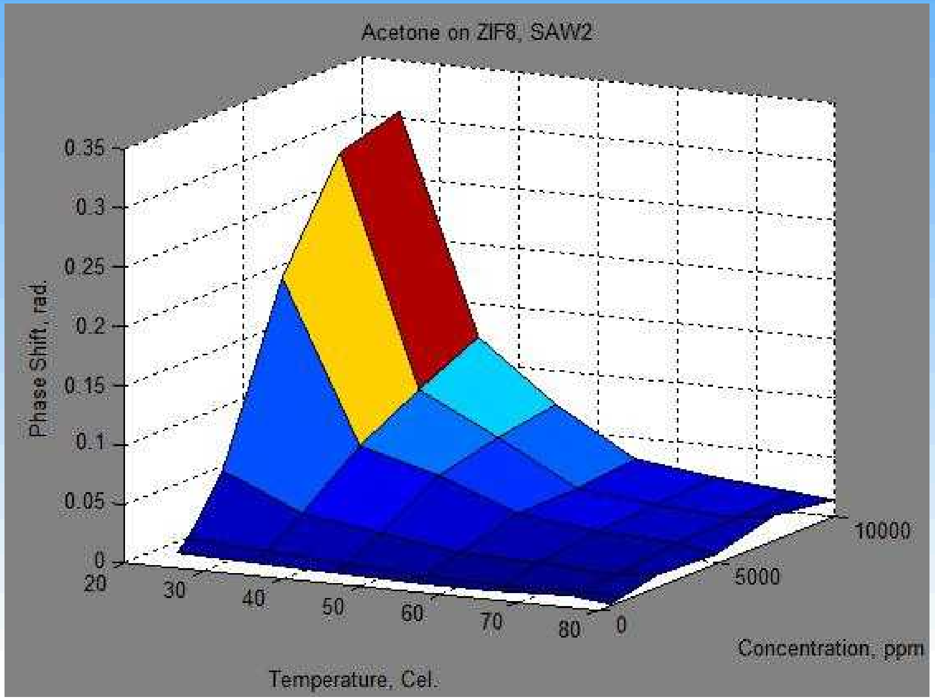
Response to acetone – temperature dependence ZIF-8 coated SAW device







SAW signal vs Concentration at various temperatures



Q_{st} from fit = 44.1 ± 7.7 kJ/mol

Q_{st} from GCMC calculation = 36.6 kJ/mol

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Summary

- **MOF coatings**
  - Ultra-high surface area (up to 7000 m^2/g) enhances sensitivity
  - Porous structure aids diffusion, decreases response time
  - Tailorable pore size, chemistry enable selectivity
- **MOF-functionalized MEMS sensors**
  - Sub-ppm sensitivity achievable (demonstrated for H_2O)
  - LOD for organics: 20 – 30 ppm; improvement strategies:
    - Should be possible to decrease based on Q_{st}
    - Increase SAW frequency to 500 MHz
    - Improve mechanical coupling and optimize thickness
  - Response time < 60 s feasible with microcantilevers
  - Discrimination against principal breath components possible

Acknowledgements

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