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Colorimetric Detection of Water Vapor Using Thin Films of HKUST-1

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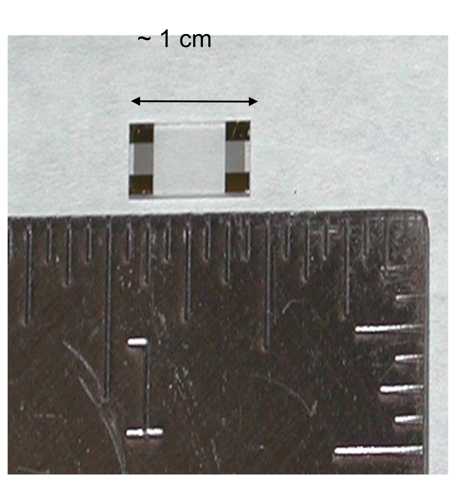
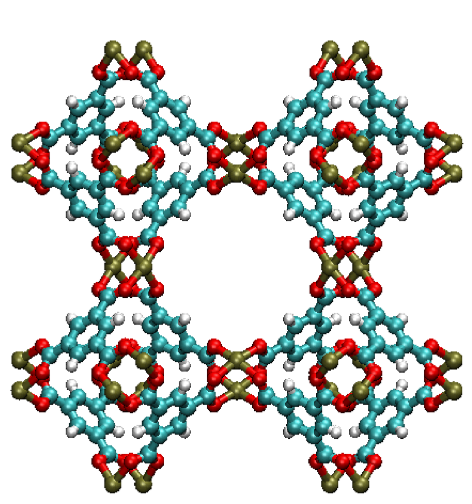
Background and Abstract

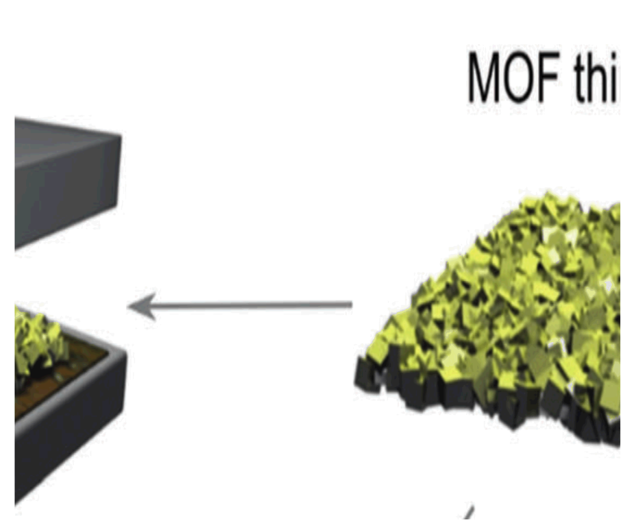
Due to their permanent porosity, metal-organic frameworks (MOFs) are showing great promise as materials for use in gas sensors. Sensors that rely on the detection of mass or electrical conductivity changes necessitate the use of costly electronic equipment that may needlessly complicate the detection system in cases when only a semi-quantitative indication of the amount of an analyte is required. An important example is water vapor; in many applications, simple qualitative knowledge of whether a material or container was exposed to atmospheric humidity is all that is required. Therefore, we sought to take advantage of the well-known color change associated with adsorption/desorption of H_2O from the open-metal sites of Cu in HKUST-1. We created a cheap, easily manufactured, humidity sensor that responds quickly in conjunction with optical detection by the human eye or, if desired, a miniature spectrometer comprised of an extremely inexpensive LED and photodiode.

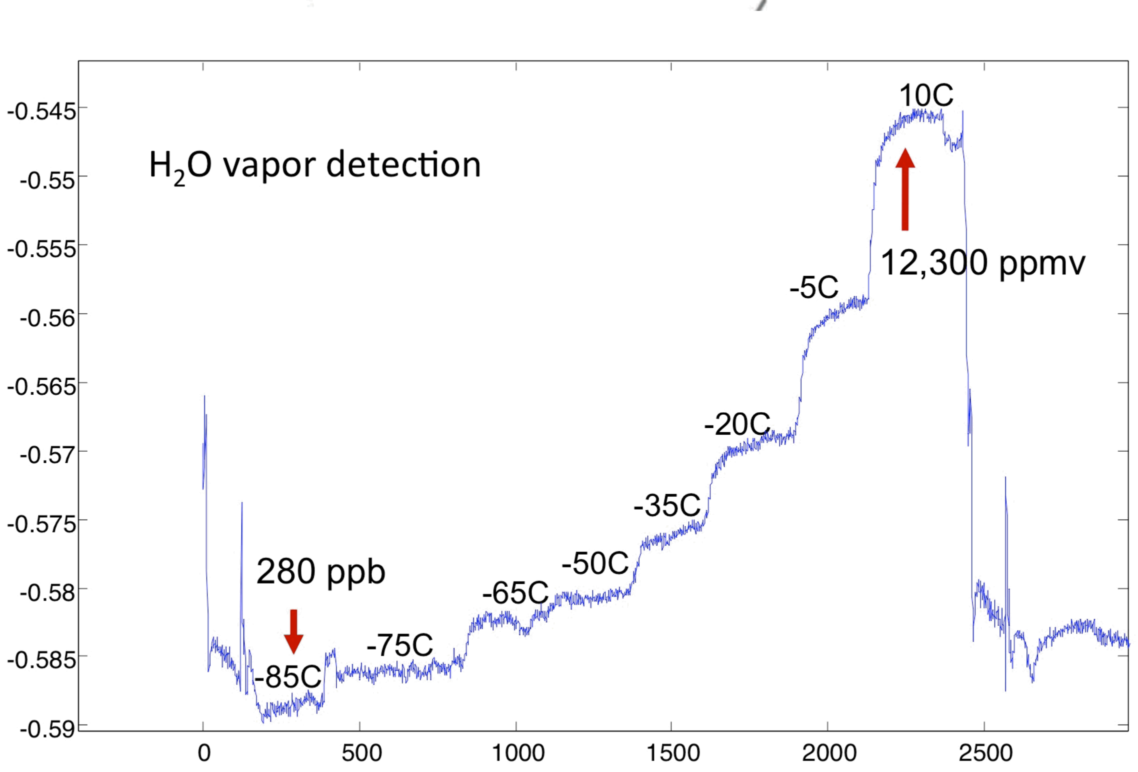
Prior results using a MOF-coated Surface-Accoustic Wave (SAW) Sensor

We deposited a 100 nm-thick film of HKUST-1 ($Cu_3(btc)_2$) on a SAW sensor. This device responds to water vapor over > 4 orders of magnitude in H_2O concentration.





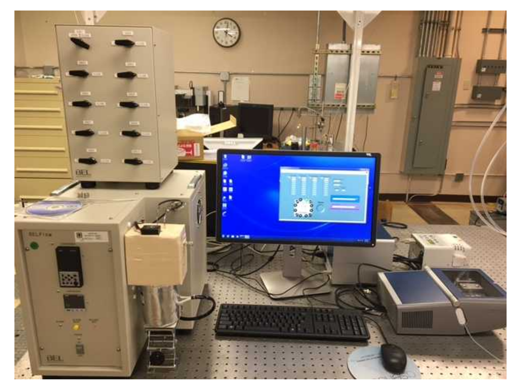


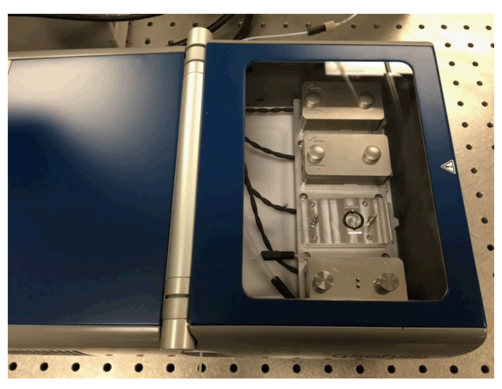


Surface accoustic wave (SAW) device
(~ 0.1 ng/cm^2 sensitivity)
A. Robinson et al. *Analyt. Chem.* **84** (2012), 7043

Experimental Methods

HKUST-1 thin films were deposited onto plastic foil or polystyrene-coated glass substrates by a spin-coating technique using HKUST-1 (**$Cu_3(BTC)_2$**) precursor ink. Activation by heating on a hot plate produced a deep purple film indicative of complete H_2O removal.



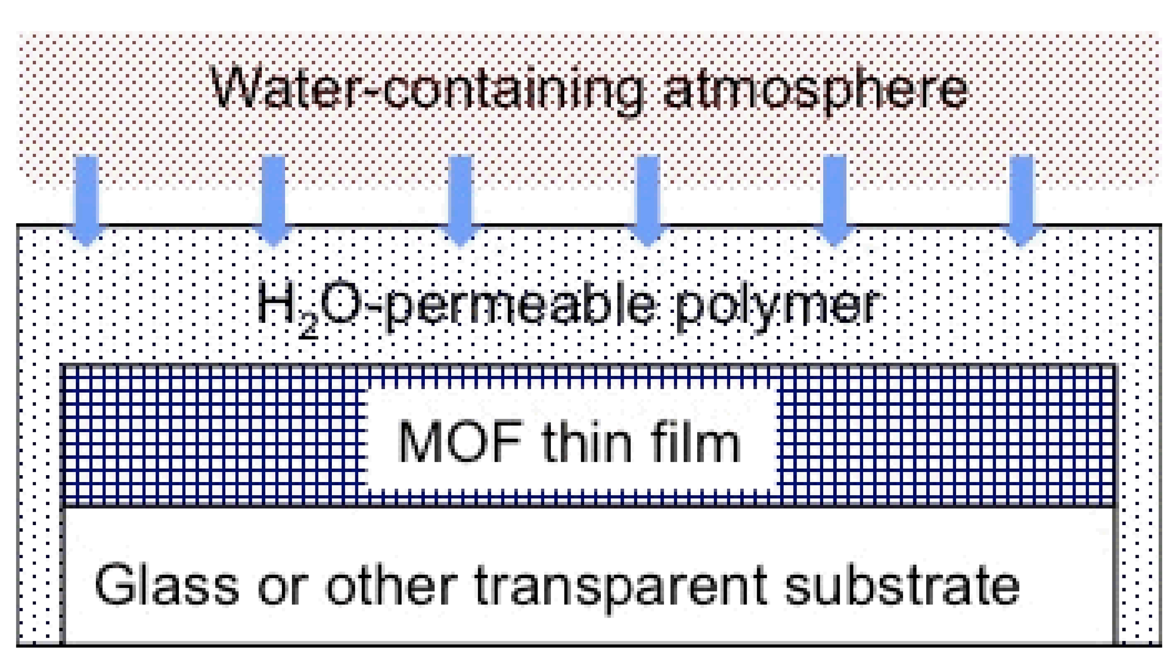


Quartz Crystal Microbalance (Biolin Scientific) interfaced to gas mixing and delivery system (Microtrac BELFlow) allows sensor and material testing with customized gas composition, including variable humidity

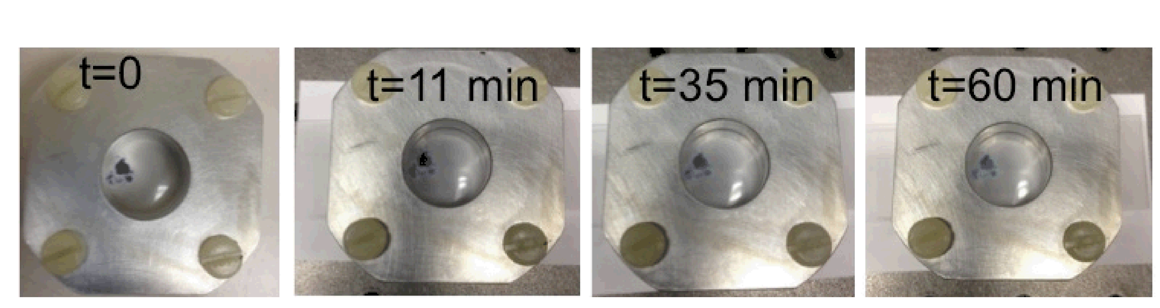
Results

We extended the MOF sensing concept to create MOF-polymer composites for colorimetric water vapor detection

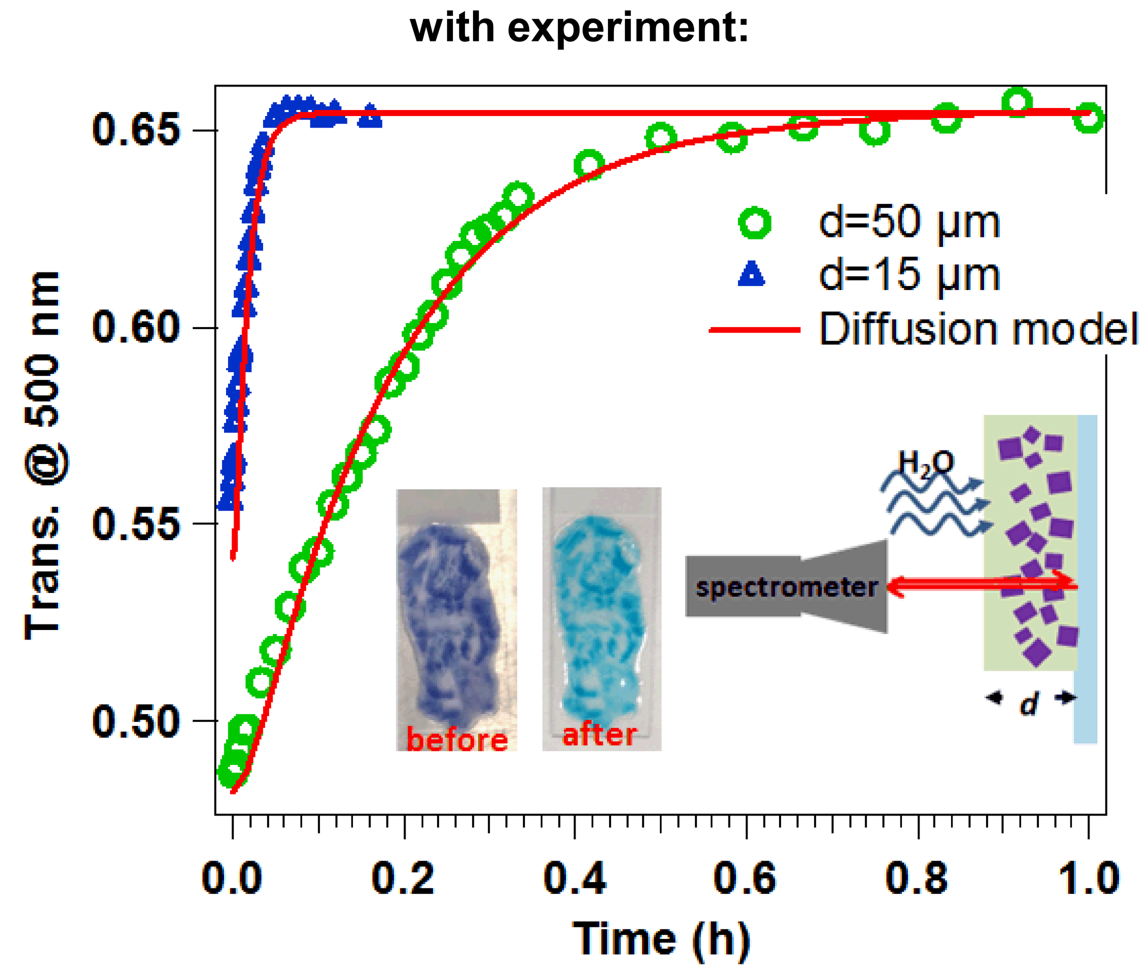
- Dispersion of the MOF powder in a water-permeable polymer controls response time
- Requires no power or electrical connections



Proof of Concept: HKUST-1 powder dispersed in polystyrene

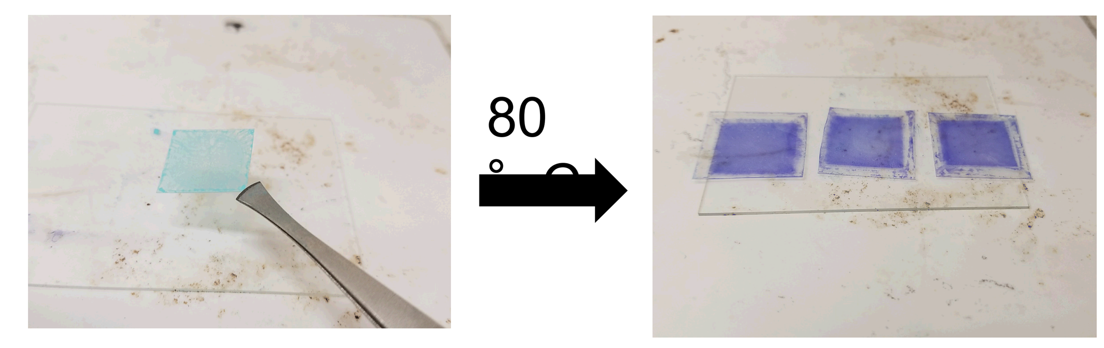


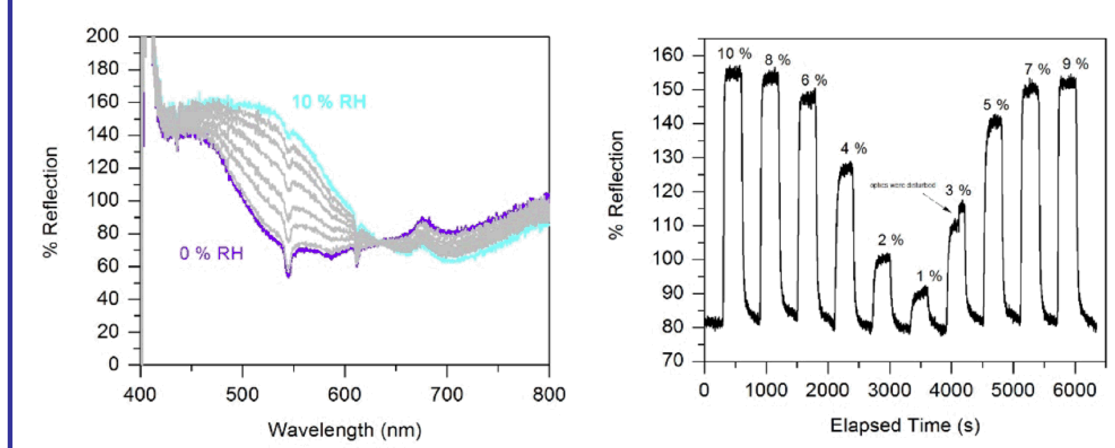
Sensor performance was predicted using a diffusion model, obtaining excellent agreement with experiment:



MOF-polymer composites

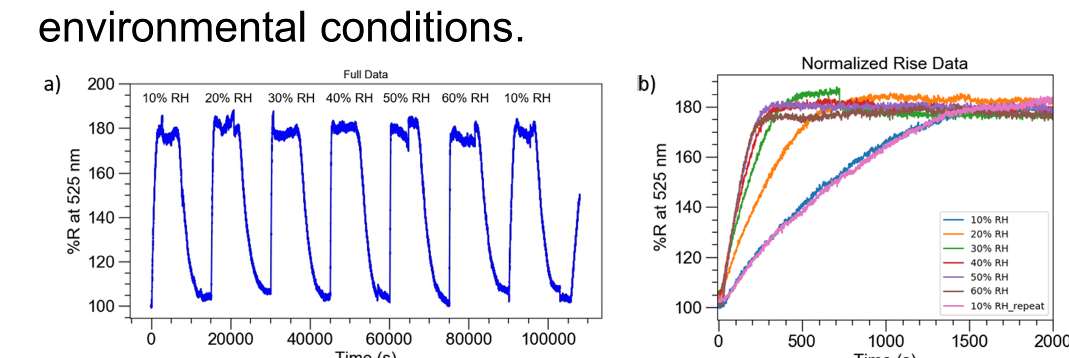
Water vapor can be detected by monitoring the reflectance of the MOF thin film, which changes color upon exposure to water vapor



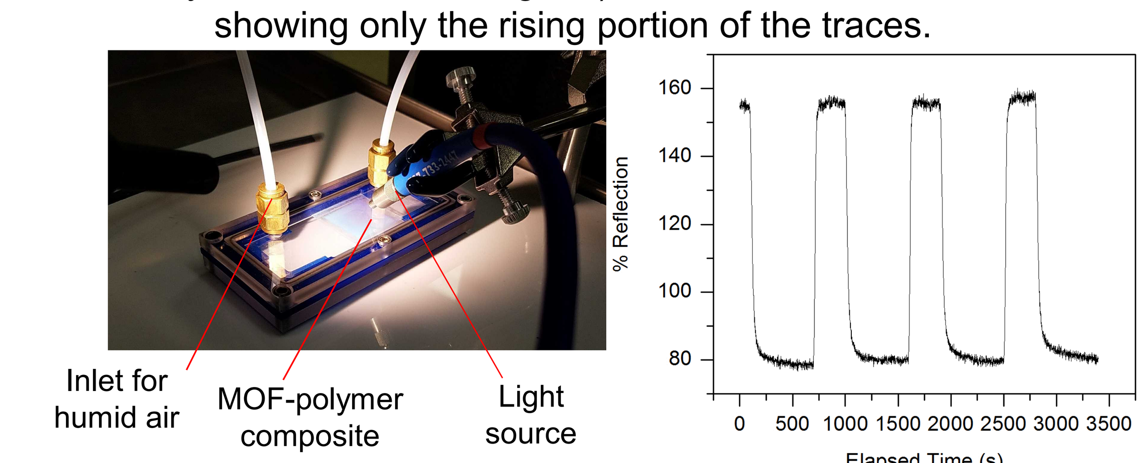


Following exposure to humid gas, a reversible color change from purple to teal blue was measured using reflection spectroscopy (Figure above, left). The greatest change in reflection intensity occurs at 525 nm, with an isosbestic point at 642 nm. In the limit of low humidity (<6%), the magnitude of the change at 525 nm is a function of the relative humidity (Figure above, right). However, above this limit the MOF film is saturated and the dynamic range of the sensor is lost.

To discriminate between higher relative humidities (10% - 60%), hydrophobic polymers were used to coat the MOF films. The rate at which the MOF becomes saturated with H_2O depends on the chemical makeup and thickness of the polymer layer. The thicker the layer the slower the permeation of H_2O to the MOF film. Together these results provide a framework for the production of a MOF-based water vapor sensor that can find broad use rapid detection of relative humidities within a range of environmental conditions.



Left: Percent reflection changes at 525 nm associated with relative humidity in the 10-60 % range. b) Normalized reflectance data showing only the rising portion of the traces.



Left: Benchtop detection setup using white-light source. Right: Switching between 10 % and 0 % relative humidity (RH)

Summary and Conclusions

- Colorimetric sensing using HKUST-1 powders is an effective way to visually detect the presence of water vapor.
- The speed of the color change can be modulated using composites of MOF powder with polymers, deposited using spin coating. This approach can be used to design MOF-polymer tapes that respond at varying rates, depending on either the relative humidity or the duration of exposure.
- Detection can be made quantitative using UV-visible light reflectance.

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