

Chemiresistive Sensor Arrays from Conductive 2D Metal–Organic Frameworks

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S Supporting Information

ABSTRACT: Applications of porous metal–organic frameworks (MOFs) in electronic devices are rare, owing in large part to a lack of MOFs that display electrical conductivity. Here, we describe the use of conductive two-dimensional (2D) MOFs as a new class of materials for chemiresistive sensing of volatile organic compounds (VOCs). We demonstrate that a family of structurally analogous 2D MOFs can be used to construct a cross-reactive sensor array that allows for clear discrimination between different categories of VOCs. Experimental data show that multiple sensing mechanisms are operative with high degrees of orthogonality, establishing that the 2D MOFs used here are mechanistically unique and offer advantages relative to other known chemiresistor materials.

Metal–organic frameworks (MOFs) that simultaneously display both porosity and electrical conductivity are an emerging family of materials¹ that display promise for a wide variety of applications such as electrocatalysis, fuel cells, supercapacitors, and chemical sensing.² The atomic-level control over molecular and supramolecular structure afforded by MOFs provides the opportunity for developing a new generation of designer materials for electronic and optoelectronic devices.^{1c} However, despite the recent surge in MOFs that display high charge mobility and/or conductivity,³ successful demonstrations of conductive MOFs as active components in the targeted applications remain rare. Here, we report that a family of conductive 2D MOFs can be used for selective chemiresistive detection of volatile organic compounds (VOCs) with different functional groups with greater than 90% accuracy.

Our team recently described the first example of chemiresistive sensing using a MOF, in which a Cu-based 2D MOF was shown to display a reversible “turn-on” response to sub-ppm levels of ammonia vapor.⁴ The change in response was linearly proportional to ammonia concentration in the measured concentration regime, allowing for quantitative detection, and a reliable response was observed even under ambient atmosphere and high humidity conditions. Most intriguingly, our initial results showed that an isostructural MOF featuring Ni centers in place of Cu did not display the same chemiresistive response toward ammonia, indicating that controlled chemical modifications to the MOF structure could be used to alter the sensing response toward a particular analyte. We therefore sought to explore the effect of MOF

chemical structure on chemiresistive response toward a variety of analytes, with the ultimate aim of developing a MOF-based sensory device that can distinguish between different types of molecules to provide selective detection.

In this work, we demonstrate that a sensor array constructed from three structurally analogous, but chemically distinct, conductive 2D MOFs (Figure 1) can reliably distinguish

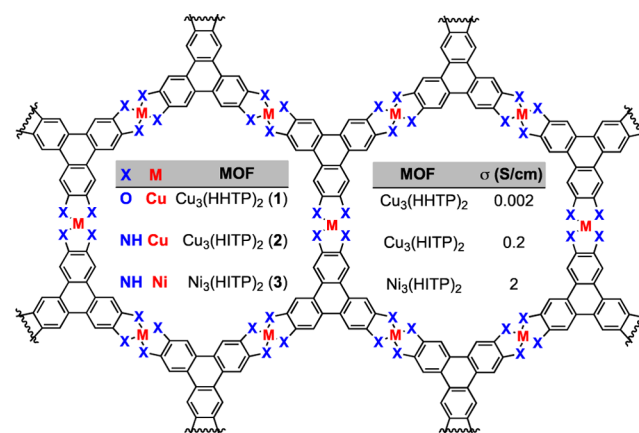


Figure 1. Chemical structures of the conductive 2D MOFs used here, and their electrical conductivities (two-point-probe, pressed pellet, room temperature).

between five categories of VOCs based on functional group. Changes to both metal center and ligand produce changes in chemiresistive response, which provides multiple dimensions of synthetic control. These results confirm that conductive MOFs, with well-defined and tunable chemical structures, are an excellent platform for the development of a new class of sensory devices. Additionally, we provide evidence that MOF-based chemiresistors can operate via multiple, orthogonal sensing mechanisms, and may therefore find complementary uses as compared to existing categories of chemiresistors.

In order to test our hypothesis that controlled chemical modifications could be used to produce conductive MOFs with divergent sensing responses toward different types of molecules, we targeted materials that were chemically diverse but structurally analogous. Therefore, we selected a family of conductive 2D MOFs based on triphenylene-derived ligands with square planar metal centers. The three materials used in

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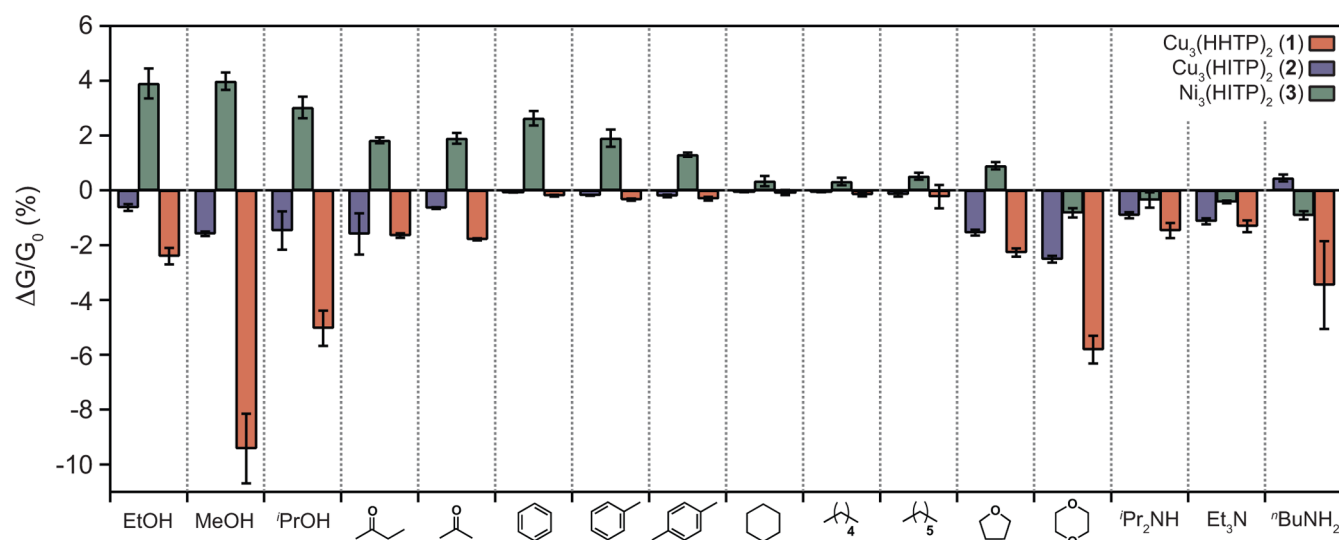


Figure 2. Sensing responses of the MOF array to representative examples from different categories of VOCs, where $\Delta G/G_0$ is the relative response (change in conductance) upon a 30 s exposure to 200 ppm of the VOC vapor; each response is averaged from 12 measurements (4 exposures to 3 separate devices for each MOF); error bars show one standard deviation.

this study feature the ligands HHTP and HITP (2,3,6,7,10,11-hexahydroxytriphenylene and 2,3,6,7,10,11-hexaiminotriphenylene, respectively), and Cu or Ni metal centers. The chemical structures of $\text{Cu}_3(\text{HHTP})_2$ (1), $\text{Cu}_3(\text{HITP})_2$ (2), and $\text{Ni}_3(\text{HITP})_2$ (3) are shown in Figure 1 and consist of hexagonal 2D sheets. The synthesis and characterization of 2⁴ and 3^{3f} have been previously reported by part of our team, and 1 has been described by the Yaghi group.⁵ Powder X-ray diffraction (PXRD) analysis shows that 1–3 adopt analogous hexagonal structures, in which the 2D sheets stack in an eclipsed or slipped-parallel conformation (Figure S1). These stacking modes result in the formation of extended 1D pores with diameters of ~ 1.5 nm. Pressed pellets of 1–3 display room temperature conductivities in the range of 0.002–2 S/cm as measured by the two-point-probe method.

To achieve selective detection of VOCs, we constructed a cross-reactive chemiresistive sensor array using MOFs 1–3 in a fashion similar to what has been performed for carbon nanotube (CNT) composites.⁶ The precise atomic-level control over structure afforded by MOFs, as compared to CNT composites, may ultimately allow for improved access to sensor materials tailored for a particular application. Additionally, the MOFs used here have the advantage of more narrowly defined composition and structure, which is beneficial in terms of reproducibility and long-term device stability. In the array sensing process, a set of chemiresistors fabricated from MOFs 1–3 is exposed to vapors of VOCs while their responses are recorded; these conductance responses are then subjected to statistical analyses that allow for VOC classification by functional group (Figure S2).⁶

The sensor array was fabricated by drop-casting a dispersion of each MOF in acetone onto interdigitated gold electrodes, or by using a solvent-free mechanical “drawing” method onto gold electrodes on paper (Figures S3 and S4).⁷ Figure 2 shows the average responses ($\Delta G/G_0$) of the chemiresistive array’s MOF-based devices to five classes of VOCs (aliphatic hydrocarbons, alcohols, ketones/ethers, aromatic hydrocarbons, and amines; Figure S5), each represented by three or four distinct molecules. Even from a qualitative inspection of the data, it is clear that each MOF displays a response that varies with the

type of analyte. Additionally, for a given analyte, each MOF often displays a difference in the direction and/or the magnitude of response. In particular, $\text{Ni}_3(\text{HITP})_2$ (3) often displays a direction of response opposite to Cu-based MOFs 1 and 2, with 1 and 2 themselves frequently showing a significantly different magnitude of response with respect to each other. MOFs 1–3 are generally responsive to VOCs with polar character, while (perhaps unsurprisingly) all three materials show no appreciable response to aliphatic hydrocarbons. As shown below, these distinct variations in chemiresistive response between 1–3 can be exploited to allow for discrimination between different types of VOCs.

We treated the sensing data from the chemiresistive MOF array in Figure 2 to two types of statistical analyses: principal component analysis (PCA) and linear discriminant analysis (LDA).⁸ PCA is a commonly used tool in unsupervised exploratory data analysis, which can result in grouping of data points based on their similarity without any prior knowledge of their classification. Figure 3 shows the results of applying PCA to our data, which yields clear groupings of the data by functional group class, as indicated by the colored ovals superimposed onto the data.

LDA offers a more quantitative indication of the ability of the MOF-based chemiresistor array to distinguish among the five groups of chosen VOCs. LDA is a supervised statistical analysis technique that aims to use the data associated with members of predetermined groups in order to classify new cases into those groups. The results of our LDA are shown in the jackknifed classification matrix in Table 1, demonstrating 92% accuracy in classifying 64 trials with only one amine mistaken for an alkane and four out of the 16 ketones/ethers mistaken for aromatic hydrocarbons. This analysis shows that the MOF-based sensor array can distinguish among these classes of VOCs with a high degree of confidence. This result is remarkable considering that our sensory array device is comprised of only three different MOF materials that were not explicitly designed to have specific interactions with particular types of functional groups. In comparison, previously reported CNT-based sensor arrays that can accomplish a similar VOC discrimination are typically

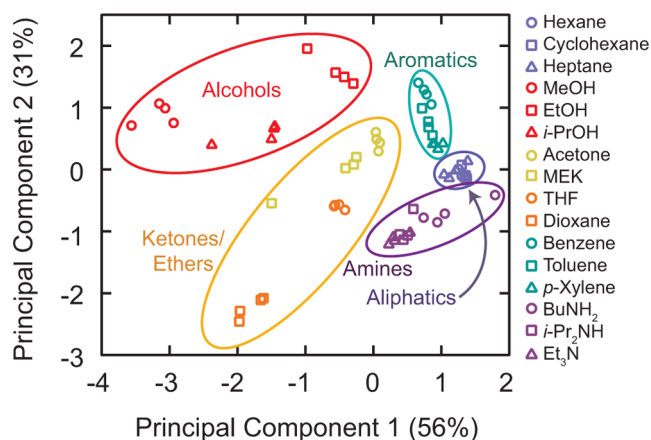


Figure 3. Principal component analysis of the MOF sensor array's responses to VOCs.

Table 1. Jack-knifed Classification Matrix of the MOF Sensor Array's Responses to Different Classes of VOCs

	-ane	ROH	-one/ether	Ar	amine	correct (%)
alkane	12	0	0	0	0	100
alcohol	0	12	0	0	0	100
ketone/ether	0	0	12	4	0	75
aromatic	0	0	0	12	0	100
amine	1	0	0	0	11	92
<i>total</i>	<i>13</i>	<i>12</i>	<i>12</i>	<i>16</i>	<i>11</i>	<i>92</i>

composed of ~ 10 different CNT composites that are often designed to interact with specific types of functional groups.⁶

A key question for the future development of MOF-based sensory devices is how changes in MOF structure cause the variations in chemiresistive responses observed here. Several common sensing mechanisms predominate in chemiresistive devices, including charge transfer,⁹ swelling/solvation,^{6c,10} and Schottky barrier modulation.¹¹ In the case of our MOF-based chemiresistors, several of these possibilities can be excluded: The rigid crystalline structures of the 2D MOFs used here are not susceptible to swelling effects; additionally, we observed ohmic contacts for all of our MOF devices, ruling out Schottky barrier modulation (Figure S6). The data in Figure 2 show that the identity of the metal center (Ni vs Cu) has the largest impact on sensing response. Indeed, for most analytes, Ni-based MOF 3 has an opposite direction of response to Cu-based MOFs 1 and 2. These data seem most consistent with a charge transfer mechanism for sensing, in which the inherent charge density of the MOF (affected by d^8 Ni^{II} versus d^9 Cu^{II}) would play a key role.

A charge transfer mechanism alone is not sufficient to account for all observations, however, and our data show that multiple mechanisms are operative. For example, devices fabricated from $\text{Cu}_3(\text{HITP})_2$ (2) display an unusual concentration dependence for amine analytes such as $n\text{BuNH}_2$: at lower concentrations (e.g., 200 ppm) a "turn-on" response is observed, with a sluggish recovery time, whereas increasing the concentration to 2500 ppm produces an opposite "turn-off" response of similar magnitude, which recovers quickly (Figure 4). To the best of our knowledge, such a concentration-dependent switch in response has not been observed for other chemiresistor materials. Furthermore, chemiresistors fabricated from 2 display an opposite direction of response between

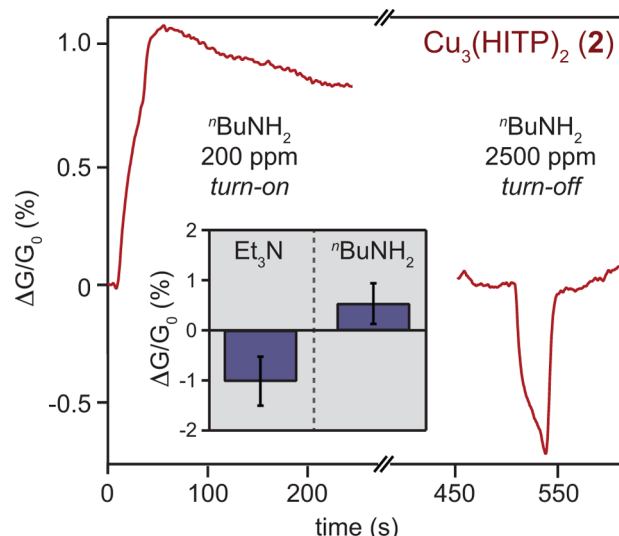


Figure 4. Evidence for simultaneous operation of multiple sensing mechanisms: the direction of sensing response for $\text{Cu}_3(\text{HITP})_2$ (2) with $n\text{BuNH}_2$ displays unusual concentration dependence. Inset: opposite directions of response are also observed for 2 with primary vs tertiary amines at the same concentration (200 ppm).

amines with different degrees of substitution at the same concentration (e.g., Et_3N and $n\text{BuNH}_2$, Figure 4 inset). Taken together, these data indicate that multiple competitive sensing mechanisms are operating simultaneously (see the Supporting Information for additional discussion). We postulate that, in addition to charge transfer, hydrogen bonding is a likely contributor to the observed sensing response. Overall, the behavior of the 2D MOFs used here is unique as compared to other known categories of chemiresistors.

In summary, we have described the first MOF-based chemiresistive sensor array, which is able to reliably distinguish between different categories of VOCs. The high degree of analyte discrimination observed, with relatively small chemical perturbations, suggests this approach to be attractive relative to existing technologies such as CNT and metal oxide composites. Our results establish conductive MOFs as a distinct new category of chemiresistor materials. Rational tuning of the MOF's chemical and electronic structure may allow for future development of improved sensor materials that can exhibit selective detection and identification. Conductive MOFs will thus provide an exciting and powerful platform for the development of new sensing technologies.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and supplementary figures (PDF)

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Notes

The authors declare no competing financial interest.

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