Conductive Framework Materials for Chemiresistive Detection and Differentiation of Toxic Gases

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Abstract

Conspectus

Sensing complex gaseous mixtures and identifying their composition and concentration has the potential for achieving unprecedented improvements in environmental monitoring, medical diagnostics, industrial safety, and the food/agriculture industry. Electronically transduced chemical sensors capable of recognizing and differentiating specific target gases and transducing these chemical stimuli in a portable electronic device offer an opportunity for impact by bridging the utility of chemical information with global wireless connectivity. Among electronically transduced chemical sensors, chemiresistors stand out as particularly promising due to combined features of low-power requirements, room temperature operation, non-line-of-sight detection, high portability, and exceptional modularity. Relying on changes in resistance of a functional material triggered by variations in the surrounding chemical environment, these devices have achieved part-

per-billion sensitivities of analytes by relying on conductive polymers, graphene, carbon nanotubes (CNTs), metal oxides, metal nanoparticles, metal dichalcogenides, or MXenes as sensing materials. Despite these tremendous developments, the need for stable, selective, and sensitive chemiresistors demands continued innovation in material design in order to operate in complex mixtures with interferents, and variations in humidity, and temperature.

To fill existing gaps in sensing capabilities, conductive metal−organic frameworks (MOFs) and covalent organic frameworks (COFs) have recently emerged as a promising class of materials for chemiresistive sensing. In contrast to previously reported chemiresistors, these materials offer at least three unique features for gas sensing applications: i) bottom-up synthesis from molecularly precise precursors that allows for strategic control of material−analyte interactions, ii) intrinsic conductivity that simultaneously facilitates charge transport and signal transduction under low power requirements, and iii) high surface area that enables the accessibility of abundant active sites, and decontamination of gas streams by coordinating to and, sometimes, detoxifying harmful analytes. Through an emphasis on molecular engineering of structure−property relationships in conductive MOFs and COFs, combined with strategic innovations in device integration strategies and device form factor (i.e. the physical dimensions and design of the device components), our group has paved the way to demonstrating the multifunctional utility of these materials in the chemiresistive detection of gases and vapors. Backed by spectroscopic assessment of material−analyte interactions, we illustrated how molecular-level features lead to device performance in detection, filtration, and detoxification of gaseous analytes. By merging the bottom-up synthesis of these materials with their device integration, we show the versatility and scalability of using these materials in low power electronic sensing devices. Taken together, our achievements, combined with the progress spearheaded on this class of materials by other researchers, establishes conductive MOFs and COFs as promising multifunctional materials for applications in electronically transduced, portable, low-power sensing devices.

Key References

- Smith, M. K.; Mirica, K. A. Self-Organized Frameworks on Textiles (SOFT): Conductive Fabrics for Simultaneous Sensing, Capture, and Filtration of Gases. *J. Am. Chem. Soc.* **2017**, *139* (46), 16759-16767.[1] Our group reported the first example of solvothermal growth of conductive MOF on cotton to develop a functional electronic textile (e-textile). The resulting e-textile exhibited ppm-level sensitivity to NO and H_2S, with capability of analyte differentiation and possibility of filtration.
- Meng, Z.; Aykanat, A.; Mirica, K. A. Welding Metallophthalocyanines into Bimetallic Molecular Meshes for Ultrasensitive, Low-Power Chemiresistive Detection of Gases. *J. Am. Chem. Soc.* **2019**, *141* (5), 2046-2053.[2] We synthesized isoreticular MOFs from metallophthalocyanine and metallo-naphthalocyanine analogues to test the effect of different metal centers, linkers, and pore sizes on chemiresistive sensing. The sensors reached ppb-levels theoretical LODs for NH_3, H_2S, and NO, and differentiated analytes in humidity.
- Meng, Z.; Stolz, R. M.; Mirica, K. A. Two-Dimensional Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity. *J. Am. Chem. Soc.* **2019**, *141* (30), 11929-11937.[3] We synthesized a metallophthalocyanine-based COF with robust pyrazine linkages that exhibited intrinsic conductivity due to full aromatic annulation and layered stacking. Integration of this material into chemiresistive devices achieved ppb-level sensitivity of NO, NO_2, H_2S, and NH_3.

- Aykanat, A.; Meng, Z.; Stolz, R. M.; Morrell, C. T.; Mirica, K. A. Bimetallic Two-Dimensional Metal–Organic Frameworks for the Chemiresistive Detection of Carbon Monoxide. *Angew. Chem. Int. Ed.* **2022**, *61* (6), e202113665.[4] Our group designed the first MOF-based chemiresistive sensor for CO detection by linking metallophthalocyanine (metal= Co or Ni) ligands with copper (II) bisdioxoline linkages. The array achieved differentiation of NO, NO_2, and CO.

Introduction

Real-time, continuous monitoring of gaseous mixtures is crucial for pollutant protection,[5] non-invasive disease diagnosis,[6] and cost-saving measures through process optimization.[7] Reliable techniques are essential for detecting gases and volatile organic compounds (VOCs), determining analyte concentration, and discriminating analytes in mixtures. Chemiresistive detection offers simplicity, sensitivity, ease of miniaturization, versatility of material integration, high modularity, and low-power consumption. Chemiresistors, comprising two electrodes bridged by a material that changes resistance in response to the chemical environment (**Figure 1a–b**), rely on material−analyte interaction to modulate device resistance. Despite sensor advancement from partially-selective polymers[8] to tailored, analyte-specific, sensitive materials,[9] a single chemiresistor is unlikely to deconvolute a complex gas mixture alone.[10] Continued material development and optimal sensor combinations are needed for effective analyte detection and differentiation.

Chemiresistive arrays (**Figure 1c**), composed of cross-reactive sensors optimized for selectivity and sensitivity, offer a promising approach to detect and differentiate multiple analytes (**Figure 1d**).[10, 11] Established chemiresistive materials include semiconductive metal oxides (MOs),[10, 12-14] carbon nanotubes (CNTs),[15] CNT composites,[16-19] conductive polymers,[20-22] polymer composites,[23, 24] graphene-based materials,[25-27] metal nanoparticles,[28] and transition metal dichalcogenides (TMDCs).[29] Despite specific advantages, these materials have numerous limitations, such as the need for high temperature or driving voltage, post-synthetic modification

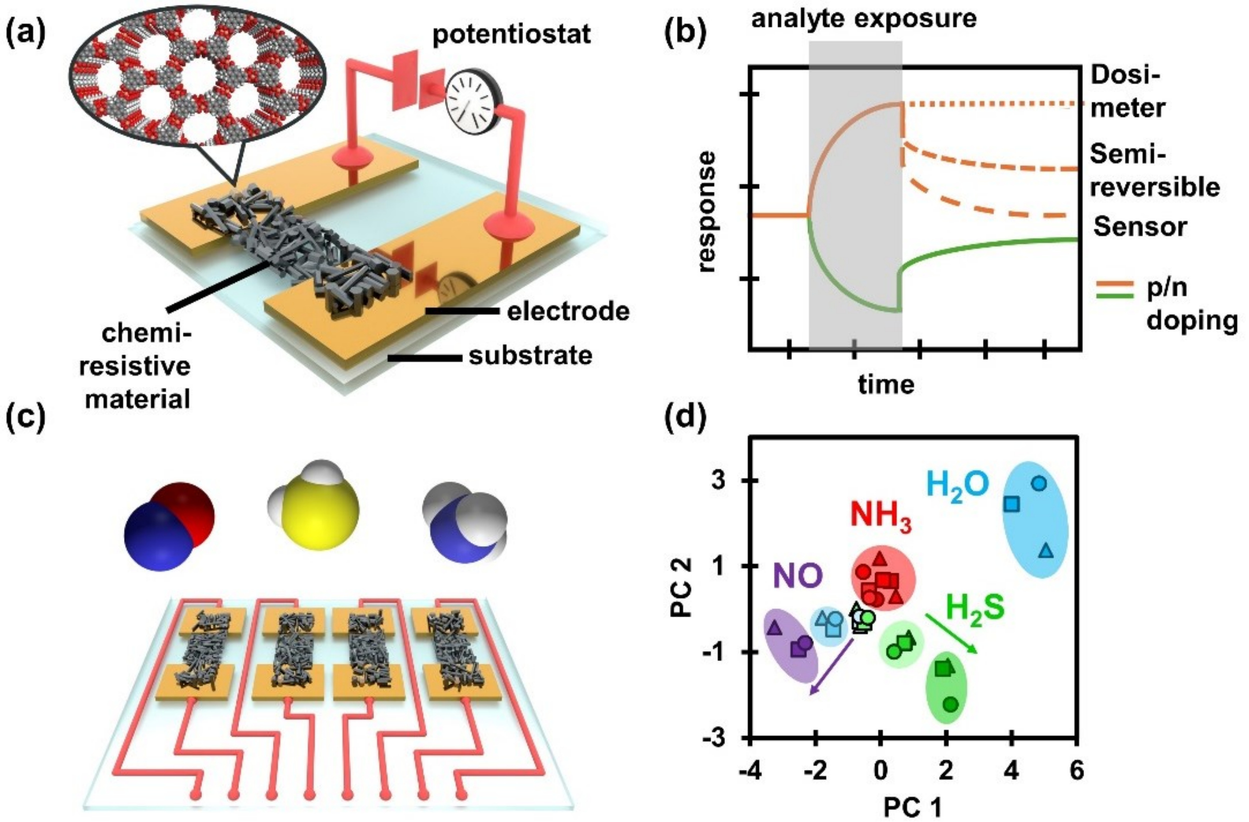


Figure 1: (a) Schematic of a MOF-based chemiresistive sensor (b) graph of chemiresistive response vs time (c) Schematic of a chemiresistive sensor array in the presence of different gases (d) Analyte differentiation via principal component analysis (PCA) using data from a MOF sensor array. Adapted from 30. Copyright 2016 American Chemical Society.

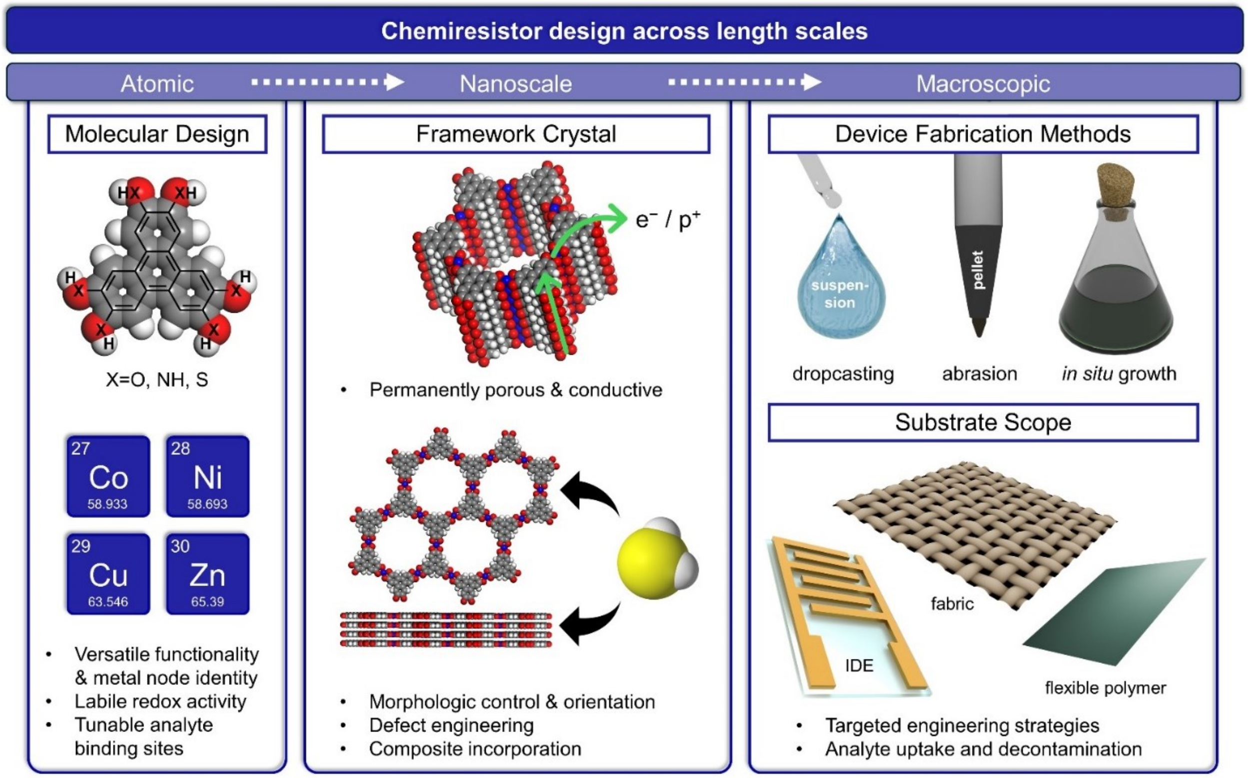


Figure 2: Summary of advantages afforded to conductive frameworks and strategies for tuning framework structure and deposition to result in optimal device function across multiple dimensions.

producing heterogeneous materials with limited stability at interfaces, and challenges in synthetic accessibility. Achieving comprehensive analyte differentiation remains difficult due to selectivity, stability, and performance variations across diverse sensing environments and device batches.[31] Thus, stable, modular chemiresistive materials with tunable structural and electronic properties are needed for low-power analyte detection and differentiation in complex milieu.

Conductive framework materials, metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), can address the need for sensitive and selective gas chemiresistors by virtue of unique advantages. (**Figure 2**) First, judicious selection of metal nodes and ligands, including functionalized benzene, triphenylene (TP), and metallophthalocyanine (MPc), yields structurally tunable frameworks with accessible surface sites and pore area, enhancing analyte interaction (**Figure 3**). Second, bottom-up synthesis enables strategic investigation of structural effects on analyte interaction and sensing performance. Third, structural

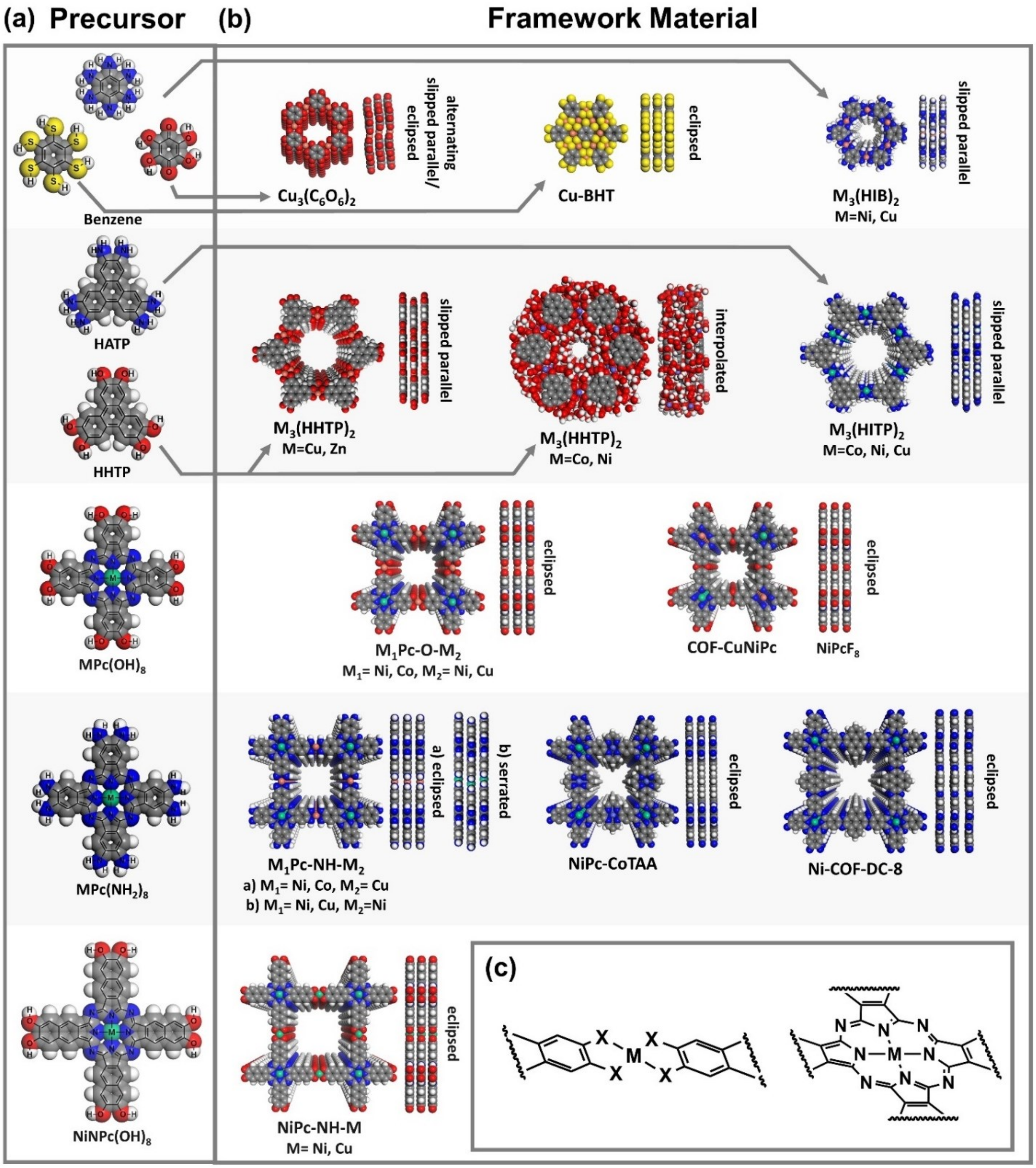


Figure 3: Depiction of (a) ligands and precursors, respectively, utilized to synthesize (b) MOFs and COFs of various crystal packing and chemical compositions. (Note: in each respective row without arrows, the ligand/precursor was used to synthesize all the frameworks to the right) (c) Structural features proposed to be key active sites for labile interactions.

elements such as conjugated organic linkers or metal nodes enable through-space and through-bond charge transport resulting in optimal electrical conductivity. Conductive frameworks enable

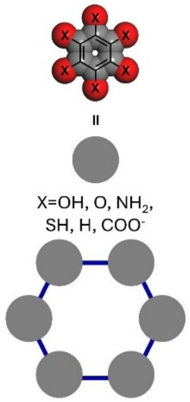
i) efficient charge transport upon chemical stimuli for analyte detection and ii) good electrical contacts with device electrodes. Probing material−analyte interactions of these unique materials, which serve as simultaneous analyte recognition site and signal transducer, demonstrates how precise tuning at atomic, nanoscale, and macroscopic levels can control sensitivity and selectivity for gas detection.

While reviews have highlighted the chemiresistive ability of porous frameworks,[9, 32] this Account summarizes diverse chemistries and techniques used to tailor conductive MOFs and COFs, and framework composites for exceptionally sensitive, low-power analyte detection, and differentiation. Sections are organized by molecular building blocks (benzene, TP, and metallo-containing ligands) that comprise the framework materials to illustrate how molecular design and structure determines device sensitivity and selectivity. We highlight spectroscopic techniques probing key material−analyte interactions and controlled framework placement on surfaces to enhance sensing performance in terms of sensitivity and multifunctionality. Key framework-based composites that excel in enhancing ease of fabrication, sensitivity, or selectivity are featured. This Account showcases the promise of conductive frameworks in chemiresistive detection and differentiation, highlighting future research opportunities.

Frameworks based on Benzene Ligands and Precursors.

Benzene-based conductive frameworks are promising for gas detection due to synthetic accessibility, cost efficiency amenable to scalable synthesis, densely packed active sites due to the small linker size, and good bulk conductivity promoted by d-π orbital overlap and layered stacking. These frameworks are constructed by reacting hexa-substituted ligands functionalized with $-NH_2$, $-OH$, and $-SH$ groups with divalent metal ions or different organic linkers to sense a variety of gases (**Table 1**).

Table 1: Benzene-based Framework and Framework Composite Chemiresistors for Sensing Analytes with Respective LODs

Building Block/ Framework Structure	**Framework-Based Active Material**	**Analyte**	**LOD (ppm)**	**Ref.**
	Ni-HIB	Humidity	N/A	33
	$Cu_3(C_6O_6)_2$	NH_3	0.014[a]	34
		H_2S	0.025[a]	
		NO	0.013[a]	
	$Cu_3(THQ)_2$	NH_3	0.45[a]	35
	$Cu_3(HIB)_2$	CO_2	400	36
	Cu-BHT	NH_3	0.23	37
	$Ni_3(BTC)_2$/ SWCNT	NH_3	0.5	38
		NO_2	0.5	
		CO	0.5	
	TpPa-SO_3H COF/Pd nanoparticles	H_2	2,000	39

[a] Calculated LOD

[b] For more details including analyte concentration range, sensing environment, and device fabrication, see the SI.

Pristine Devices:

Dincă and coworkers utilized Cu_3(hexaiminobenezene)$_2$ ($Cu_3(HIB)_2$) for CO_2 detection under humid, ambient conditions.[36] The researchers attributed the high CO_2 sensitivity to autogenous hydration and density of imino-semiquinonate active sites. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), coupled with chemiresistive response, suggested a charge trapping mechanism driven by CO_2 adsorption. In another study, Liu *et. al.* demonstrated the effect of defect sites in amorphous Ni-HIB on humidity sensing.[33] The resulting amorphous framework contained more hydroxyl and amino groups compared to the crystalline Ni-HIB, resulting in a more sensitive and selective humidity sensor, likely due to increased hydrogen bonds facilitating surface adsorption.

Other benzene-based MOFs facilitate detection of NH_3, H_2S, and NO. Chen *et. al.* integrated a film of Cu-benzenehexathiol (Cu-BHT), a nonporous, 2D conductive material, onto a flexible substrate for NH_3 detection, achieving a limit of detection (LOD) of 0.23 ppm.[37] Shorter synthesis times resulted in smaller crystal particles with more grain boundaries and higher NH_3 sensitivity compared to crystals synthesized via longer reaction times. As found via x-ray photoelectron spectroscopy (XPS), computational studies, and *in situ* FTIR, smaller crystallites led to a greater density of Cu sites and sites for NH_3 interaction compared to larger crystals. Recently, our group modulated the electronic and magnetic properties of Cu_3(hexahydroxybenzene)$_2$ ($Cu_3(C_6O_6)_2$) via exposure to NH_3, H_2S, and NO, demonstrating theoretical LODs of 14, 25, and 13 ppb, respectively.[34] Spectroscopic analyses (DRIFTS, XPS, and electron paramagnetic resonance (EPR) spectroscopy) revealed NH_3 interaction with Bronsted and Lewis acidic sites, H_2S-induced formation of Cu_2S, polysulfides, and CuSH species, and NO binding to C atoms via a radical combination mechanism. The multifaceted approach to benzene-based MOFs as chemiresistors highlights structural versatility of these materials.

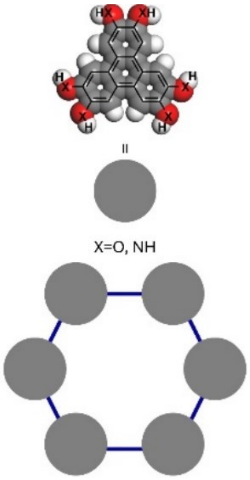
Composite Devices:

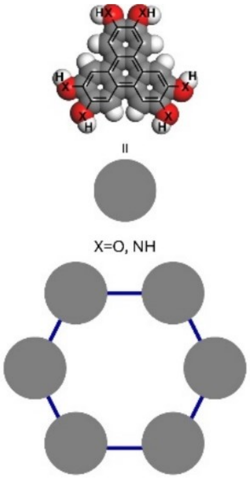
Using benzene-based COFs as chemiresistors in framework composite devices, Kalidindi and coworkers hybridized a COF synthesized from triformylphloroglucinol and diaminobenzenesulfonic acid (TpPa-SO_3H COF) with palladium (Pd) nanoparticles to result in Pd@TpPa-SO_3H.[39] Pd provided rapid H_2 interactions resulting in device response and recovery times as low as 3.6 and 3.7 s, respectively, showcasing the importance of functionalizing crystalline, non-metallo containing frameworks with abundant active sites for analyte recognition.

Frameworks based on Triphenylene Ligands and Precursors.

Although benzene-based frameworks offer cost-effective, straightforward synthesis, TP-based MOF chemiresistors excel in low-power, portable gas and VOC detection (**Table 2**). TP-based frameworks feature extended π-conjugation from large, conjugated linkers, enhanced porosity for improved gas sorption and interaction, and versatile modularity via diverse organic linker. These materials offer excellent structural diversity via the choice of metal and crosslinker thereby exerting precise control over material−analyte interactions, enhancing sensing performance.

Table 2: TP-based Framework- and Framework Composite-Based Chemiresistors for Sensing Analytes with Respective LODs

Building Block/ Framework Structure	**Framework-Based Active Material**	**Analyte**	**LOD (ppm)**	**Ref.**
	$Ni_3(HHTP)_2$ $Cu_3(HHTP)_2$	NH_3	2.5	30
		H_2S	5[a]	
		NO	20	
	$Cu_3(HITP)_2$	NH_3	0.5	40
	$Ni_3(HITP)_2$	VOCs	N/A	41
	$Cu_3(HHTP)_2$			
	$Cu_3(HITP)_2$			
	$Cu_3(HHTP)_2$	NH_3	0.000087[a]	42
		CO	N/A	
		CO_2	N/A	
		MeOH	N/A	
		EtOH	N/A	
		acetone	N/A	
	$Cu_3(HHTP)_2$	NH_3	0.5[a]	43
	$Cu_3(HHTP)_2$	CO	N/A	4
	$Cu_3(HHTP)(THQ)$	NH_3	1	35
	$Cu_3(HHTP)_2$	NH_3	N/A	
		NO_2	N/A	
	$Cu_3(HITP)_2$	NH_3	N/A	
		NO_2	N/A	
		acetone	N/A	
		toluene	N/A	
	$Zn_3(HHTP)_2$	NH_3	10	44
		CO	3.96	

		SO_2	10	
	Bi(HHTP)	NH_3	0.29^a	45
		NO	0.15^a	
		MeOH	278^a	
		EtOH	185^a	
		isopropanol	50.2^a	
		acetone	41.2^a	
	$Ni_3(HHTP)_2$	H_2S	0.23^a	1
		NO	1.4^a	
	$Ni_3(HITP)_2$	H_2S	0.5^a	
		NO	0.16^a	
	$Cu_3(HHTP)_2$	H_2S	1	46
		NO	1	
	Graphite/$M_3(HHTP)_2$ (M=Fe, Co, Ni, Cu)	NH_3	19	47
		H_2S	35	
		NO	17	
		MeOH	N/A	
		EtOH	N/A	
		acetone	N/A	
	Nanoparticle-functionalized $Co_3(HITP)_2$	NH_3	N/A	48
		H_2S	0.0007^a	
		CO	N/A	
		H_2	N/A	
		methane	N/A	
	$Co_3(HITP)_2$/rGO/polymer	NO	0.0112^a	49
		NO_2	0.0068^a	
	$Ni_3(HHTP)_2$@UiO-66NH_2	H_2S	0.0014^a	50
	$Ni_xCu_{3-x}(HHTP)_2$/ poly-pyrrole	H_2S	0.5	51
	HITP doped $Cu_3(HHTP)_2$	NH_3	N/A	52
		benzene	$0.24–0.096^a$	
	Cu-TCPP on $Cu_3(HHTP)_2$	NH_3	1	53
		acetone	N/A	
		hexane	N/A	
		benzene	0.12^a	
	$Cu_3(HITP)_2$/polymer/ metal	MeOH	N/A	54
		EtOH	0.5^a	
		acetone	N/A	
		butanone	N/A	
		toluene	N/A	
		xylene	N/A	
		Cyclo-hexane	N/A	

	TiO_2@COF-316	NO_2	1.41[a]	55

[a] Calculated LOD

[b] For more details including analyte concentration range, sensing environment, and device fabrication, see the SI.

Pristine Devices:

Dincă and coworkers reported the first chemiresistive sensors using 2D conductive MOFs $Cu_3(HITP)_2$ and $Ni_3(HITP)_2$, synthesized solvothermally from hexaaminotriphenylene complexed with copper (II) and nickel (II), respectively.[40] Devices were fabricated via dropcasting MOF suspensions onto gold interdigitated electrodes (IDE). $Cu_3(HITP)_2$ responded to NH_3, whereas $Ni_3(HITP)_2$ did not. The authors hypothesized that the theoretically higher Fermi level of $Cu_3(HITP)_2$ resulted in a more optimal electronic structure for NH_3 interaction compared to $Ni_3(HITP)_2$. This seminal contribution established that the metal identity in conductive MOFs profoundly influences their sensing performance.

Dincă and coworkers expanded MOF chemiresistors from single analyte detection to multi-analyte differentiation using an array comprising $Cu_3(HHTP)_2$, $Ni_3(HITP)_2$, and $Cu_3(HITP)_2$.[41] The array, made via dropcasting or mechanical abrasion, effectively distinguished 200 ppm concentration VOCs with different functional groups. Through principal component analysis (PCA), the cross-reactive array accurately differentiated gases with alcohol, ketone, aromatic, amine, and aliphatic-containing groups. This study demonstrated the effectiveness of using conductive, structurally analogous, but chemically distinct, MOFs arrays for analyte detection and differentiation.

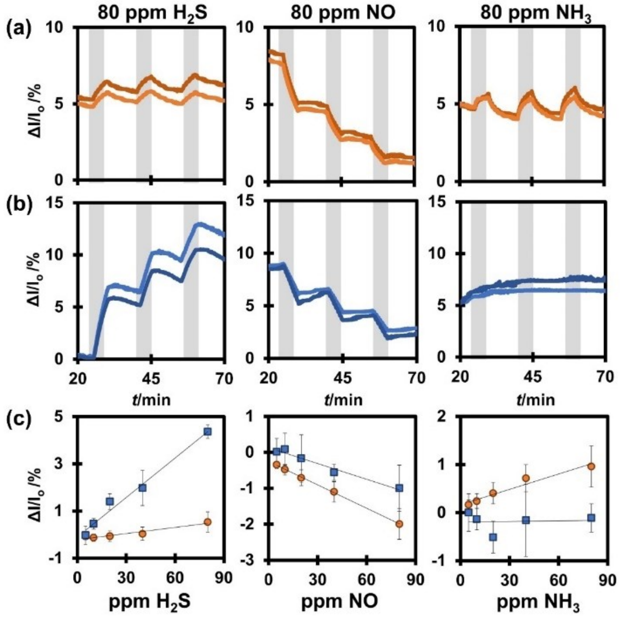


Figure 4: Change in normalized conductance over time of (a) $Cu_3(HHTP)_2$ (orange) and (b) $Ni_3(HHTP)_2$ (blue) exposed to H_2S, NO, and NH_3 in 3 x 80 ppm exposure-recovery with a carrier gas of dry N_2. (Note: analyte exposure is indicated by shaded area.) (c) concentration-dependent sensing responses of devices to 80, 40, 20, 10, and 5 ppm of H_2S, NO, and NH_3 (left−right). Adapted from 30. Copyright 2016 American Chemical Society.

Building upon the work of the Dincă group, our lab expanded the development of TP-based MOFs as chemiresistors for the detection and differentiation to other toxic gases. Using an array of $Cu_3(HHTP)_2$ and $Ni_3(HHTP)_2$ we detected and differentiated NO, H_2S, and NH_3 **(Figure 4)**.[30] Each MOF-analyte pairings exhibited unique magnitudes of responses, initial rates of response, and device reversibility. PCA efficiently differentiated ppm-concentrations of NO, H_2S, NH_3, and H_2O (1000 ppm). $Cu_3(HHTP)_2$ responded to NH_3, whereas $Ni_3(HHTP)_2$ did not, further confirming the importance of the metal in analyte interaction. This study broadened MOF-based sensing to NO and H_2S, gases vital in environmental and biological contexts.

The efficacy of TP-based MOF sensors, particularly $Cu_3(HHTP)_2$, was further improved by Xu and coworkers in 2021 to achieve high NH_3 sensitivity, landmark LOD, and fast response by growing highly oriented 3D thin films of $Cu_3(HHTP)_2$.[42] The group utilized a corrugated TiO_2 nanowire array, which was inert to NH_3, to grow thin films of $Cu_3(HHTP)_3$ layer-by-layer. The 3D oriented film facilitated fast mass and charge transport, as well as increased the surface area for NH_3 interaction, resulting in a theoretical LOD of 87 part-per-trillion (ppt). The device achieved selectivity for NH_3 over various other analytes, such as CO_2, CO, acetone, ethanol (EtOH), and methanol (MeOH), despite the presence of interferent gases in air. The innovation in both material growth and device form factor was key to achieving outstanding performance metrics.

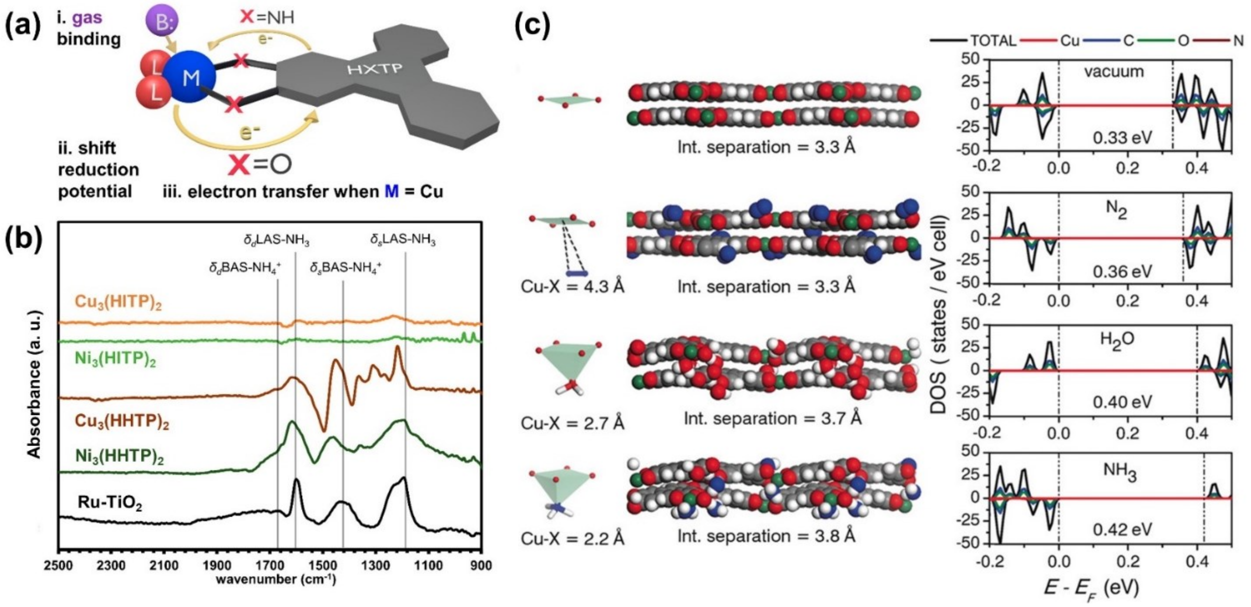


Figure 5: (a) Sites of analyte interactions (Bronsted and Lewis acids sites) on $Ni_3(HHTP)_2$, $Ni_3(HITP)_2$, $Cu_3(HHTP)_2$, and $Cu_3(HITP)_2$ (b) DRIFTS difference spectra of aforementioned MOFs after exposure to 10% NH_3 in He for 6 min. Adapted from 56. Copyright 2020 American Chemical Society. (c) effect of N_2, H_2O, and NH_3 binding on $Cu_3(HHTP)_2$ crystal structure, particularly interlayer distances and calculated electronic density of states. Reproduced with permission from ref 57. Copyright 2018 Wiley-VCH.

Understanding structure−property−performance relationships governing gas sensing mechanisms is critical to advancing fundamental knowledge and improving performance of chemical sensors. Our group utilized DRIFTS, XPS, EPR, and PXRD to investigate material−analyte interaction between NH_3 and Ni- and Cu-linked TP-based MOFs.[56] The organic ligand identity determined surface acidic sites (weak or strong Lewis acid site (LAS) or Bronsted acid site (BAS)) in each MOF, whereas metal identity determined redox lability and NH_3 binding (**Figure 5a−b**). XPS and EPR methods revealed that Cu(II) centers in $Cu_3(HHTP)_2$ and $Cu_3(HHTP)_2$ underwent oxidation and reduction, respectively, to balance the opposite ligand redox reactions triggered by NH_3 binding. Our work supported Martí Gastaldo and coworkers findings that NH_3 bound to ultrathin $Cu_3(HHTP)_2$ at open metal sites and subsequently disrupted Cu(II) geometry (**Figure 5c**).[57] In their study, $Cu_3(HHTP)_2$ films exposed to NH_3 increased in resistance, consistent with the response of a p-type semiconductor interacting with a reducing gas. Taken together, these studies provide insight into structural and electronic changes responsible for chemical sensing in TP-based MOFs.

Composite Devices:

To generalize MOF deposition and eliminate solvent in device fabrication, our group employed mechanical abrasion for TP-based MOF device fabrication.[47] By blending MOF and graphite, we detected NO, H_2S, NH_3, MeOH, EtOH, and acetone. Integrating graphite in a 1:9 ratio with $M_3(HHTP)_2$ (M= Fe, Co, Ni, Cu) increased the bulk material conductivity of pristine MOF (10^{-6}–10^{-2} S/cm) to 10^{-2}–10^{-1} S/cm, enabling low device driving voltages. The array differentiated NO, H_2S, NH_3, but exhibited relatively high LODs (17, 19, and 35 ppm, respectively) compared to pristine MOF chemiresistors. Incorporating conductive additives through ball milling, compression, and abrasion-based deposition can result in inconsistent distribution of active sites and, therefore, challenges in device uniformity and sensitivity, demonstrating the need for more refined material-on-electrode deposition and device form factor.

Wu and coworkers explored another MOF composite by combining $Co_3(HITP)_2$ with reduced graphene oxide (rGO) and polymer to selectively sense NO and NO_2, biomarkers for lung disease.[49] Achieving low LODs of 11.2 and 6.8 ppb for NO and NO_2, respectively, the device showed high fidelity response despite humidity and long term use. The device successfully differentiated between breath samples from healthy and respiratory-inflamed patients, demonstrating selective and sensitive NO_x detection and potential for non-invasive respiratory disease diagnosis.

Xu and coworkers advanced MOF composites by layering two MOFs, a metal-free porphyrin-based MOF (Cu-TCPP) on $Cu_3(HHTP)_2$, enhancing analyte differentiation through gas adsorption and separation.[53] Their MOF-on-MOF device utilized a stamping method to transfer Cu-TCPP thin films onto substrates with pre-grown $Cu_3(HHTP)_2$ thin films. The Cu-TCPP layer enabled selective benzene detection over NH_3 with a theoretical LOD of 0.12 ppm, whereas pristine $Cu_3(HHTP)_2$ showed reverse selectivity. This tunable selectivity is attributed to strong interactions between Cu^{2+} ions in Cu-TCPP and NH_3, enabling the top MOF to act as a molecular sieve. A sensor array of pristine $Cu_3(HHTP)_2$, and two MOF-on-MOF devices of varying layer thicknesses successfully differentiated benzene, NH_3, CO, hexane, and acetone. This approach differentiated gases of biological importance, and tuned analyte selectivity based on MOF adsorption.

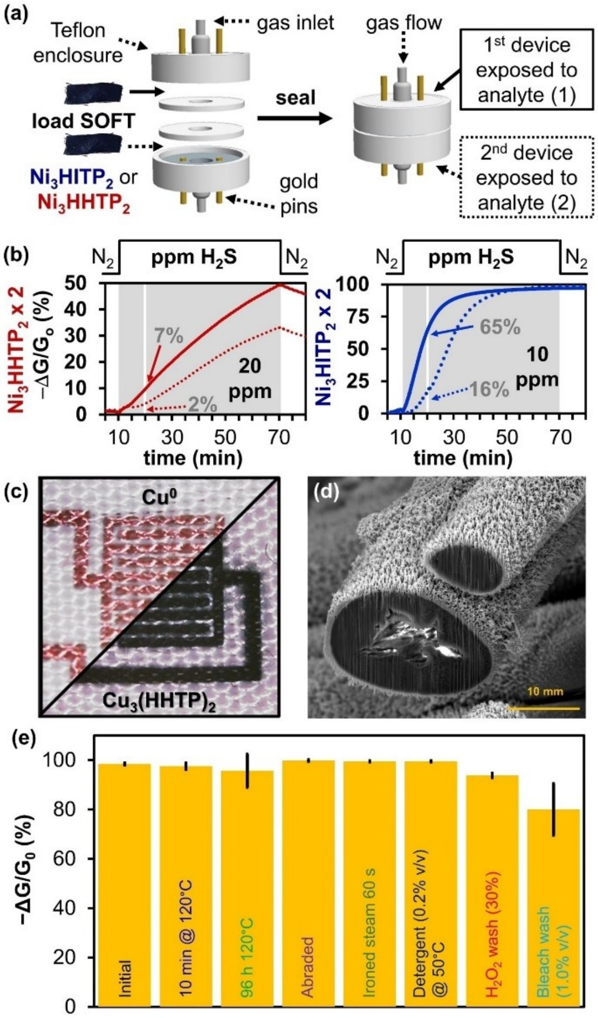


Figure 6: (a) Device configuration for loading two MOF on textile composites in series (b) Response measured in negative normalized conductance ($-\Delta G/G_o$) of $Ni_3(HHTP)_2$ and $Ni_3(HITP)_2$ on textiles using the device configuration described above. Diminished sensing of the second device suggests potential H_2S uptake and filtration via the first device. Reproduced from 1. Copyright 2017 American Chemical Society. (c) patterning of MOF on cotton textile via growth of $Cu_3(HHTP)_2$ on templated Cu^0 (d) SEM of a cotton thread cross section showing MOF growth on the textile substrate. (e) sensing response of $Cu_3(HHTP)_2$ on cotton to 80 ppm of H_2S after the MOF composite was subjected to a range of physical and chemical tests. Adapted with permission from ref 46. Available under a CC-BY-NC-ND 4.0 license. Copyright 2022 Eagleton, A.M.; *et. al.* Future permissions related to the material excerpted should be directed to ACS.

To leverage MOFs' porosity for sensing applications, our group combined the microporous structure of MOFs with macroporous features of woven substrates by growing MOFs on textile to form composites.[1] These electronic textiles (e-textiles) enable facile device integration as a wearable electronic, increased flexibility coupled with mechanical stability, and improved MOF processability, hereby overcoming challenges associated with deposition of microcrystalline, powdered MOFs and offering a route to scalable device production.[58] $Ni_3(HHTP)_2$ and $Ni_3(HITP)_2$ integrated onto cotton and polyester substrates via self-assembly enabled the detection, capture, and filtration of ppm-level NO and H_2S. The e-textiles exhibited enhanced porosity (>1 order of magnitude increase in BET surface area compared to bare textile), flexibility, and retention of electronic properties during physical manipulation and post-washing. Difference directional response of $Ni_3(HHTP)_2$ or $Ni_3(HITP)_2$ to NO suggested a ligand-specific mechanism enhancing toxic gas differentiation using MOF arrays. Breakthrough studies and sensing traces using the device architecture seen in **Figure 6a-b** indicated the potential for H_2S uptake and filtration by the e-textile. This study demonstrated MOF-textile composites as promising materials for dual detection and possible filtration of toxic gases.

Our group further demonstrated the multifunctionality of e-textiles for sensing, filtration, and detoxification of H_2S and NO in a study by Eagleton *et. al*. Oxidative restructuring of copper pre-deposited on textile into $Cu_3(HHTP)_2$ enabled precise MOF patterning (**Figure 6c**) and strong MOF adhesion (**Figure 6d**).[46] The device showed robust sensing response to H_2S, enduring harsh conditions, such as heating, abrasion, and bleach treatment (see **Figure 6e**), and analyte filtration, with $Cu_3(HHTP)_2$ achieving H_2S uptake capacities of 4.6 mol/kg_{MOF}. Spectroscopic investigations (**Figure 7**) suggested H_2S oxidation to elemental sulfur and copper sulfides, facilitating gas detoxification. MOF−NO interactions revealed irreversible binding of N-containing species to the MOF material, formation of NO_x species, and oxidation of MOF copper nodes. This work highlighted the precise control over MOF deposition, and robust nature of e-textiles as multifunctional materials for analyte detection, filtration, and detoxification.

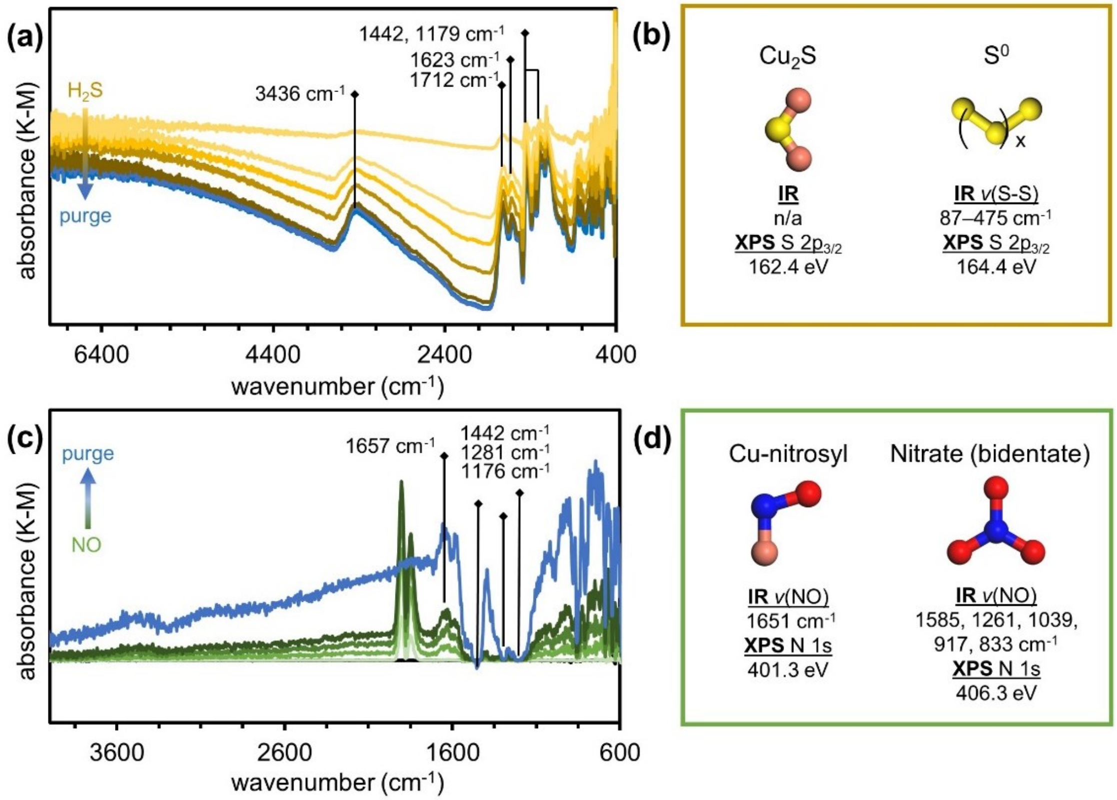


Figure 7: DRIFTS difference spectra of Cu$_3$(HHTP)$_2$ powder after exposure to (a) 1% H$_2$S and (c) 1% NO in N$_2$. Proposed binding of transformed species from (b) H$_2$S and (d) NO exposure based on IR and XPS data. Adapted with permission from ref 46. Available under a CC-BY-NC-ND 4.0 license. Copyright 2022 Eagleton, A.M.; *et. al.* Future permissions related to the material excerpted should be directed to ACS.

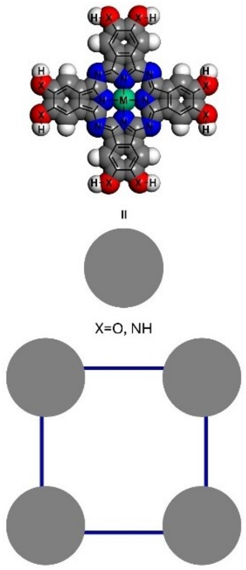
Composite chemiresistors leverage COFs for reversible sensing selectivity.[55] Xu and coworkers grew COF-316 on TiO$_2$ via combination of HHTP and tetrafluorophthalonitrile, forming a core−sheath nanowire array. Adding stable, conductive COF-316 to TiO$_2$ altered the composite's redox properties, increasing reductive sites. This change shifted chemiresistive selectivity from reducing ethanol to oxidizing NO$_2$. TiO$_2$@COF-316 exhibited improved sensitivity, selectivity, and anti-humidity performance, demonstrating COFs' potential as a selective signal amplifier in composite chemiresistors.

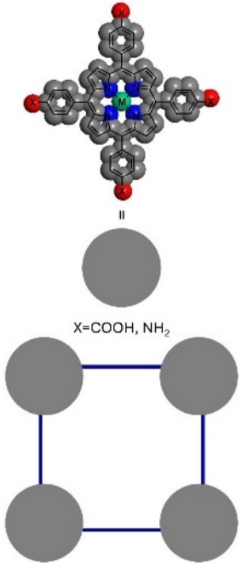
Using various methods to study TP-based material−analyte interactions provides atomic-level insights into device performance. Factors like metal center, heteroatomic ligand, material morphology and topology, and device configuration combine to enable synergistic control over sensing performance. The broad utility of TP-based MOF materials is poised to accelerate targeted sensor development by harnessing the precise active site tuning, and multifunctional properties of these materials.

Frameworks based on Metallo-containing Ligands and Precursors.

Metallo-containing ligands like MPys and MPcs feature unique optical properties and afford variable framework topologies and pore geometries. Additionally, they feature an embedded metal center in the organic precursor itself, ergo, endowing the resultant framework with a level of control over gas interaction unachievable in benzene- and triphenylene-bases systems. That is to say, MOFs based on metallo-containing ligands feature bimetallic sites capable of tuning charge transport and leveraging synergistic material–analyte interactions at two structurally distinct sites. Further, COFs based on metallo-containing ligands feature more chemically and thermally stable structures than MOFs due to covalent linkages while retaining a labile, embedded metal center for gas interaction without the need for post-synthetic functionalization. These frameworks have proven effective chemiresistive sensors, capitalizing on the versatility and functionality of metallo-containing ligands (**Table 3**).

Table 3: Metallo-containing Ligand-based Framework- and Framework Composite-Based Chemiresistors for Sensing Analytes with Respective LODs

Building Block/ Framework Structure	**Framework-Based Active Material**	**Analyte**	**LOD (ppm)**	**Ref.**
	CoPc-Cu-O	NO	10	4
		NO_2	10	
		CO	0.53^a	
	CoPc-Cu-NH	NO	N/A	
		CO	10	
	NiPc-Cu-O	NO	10	
		NO_2	10	
		CO	3.0^a	
	NiPc-Cu-NH	NO	N/A	
		CO	10	
	NiPc-Ni-O	NH_3	0.31^a	2
		H_2S	0.032^a	
		NO	0.0011^a	
	NiPc-Cu-O	NH_3	0.33^a	
		H_2S	0.019^a	
		NO	0.0010^a	
	NiNPc-Ni-O	NH_3	N/A	
		H_2S	N/A	
		NO	N/A	
	NiNPc-Cu-O	NH_3	N/A	
		H_2S	N/A	
		NO	N/A	
	$Ni_2[CuPc(NH_2)_8]$	Chloroform	N/A	59
		MeOH	10	
		EtOH	10	
		isopropanol	50	
		acetone	100	
	$Ni_2[NiPc(NH_2)_8]$	MeOH	10	
		EtOH	10	
		isopropanol	50	
		acetone	200	
	Ni-COF-DC-8	NH_3	0.07^a	3
		H_2S	0.204^a	
		NO	0.005^a	

		NO_2	0.016[a]	
	NiPc-CoTAA	NH_3	1	60
		H_2S	1	
		NO	1	
		NO_2	1	
		H_2	N/A	
	COF-CuNiPc	NO_2	0.0054[a]	61
	PCN-222-M (M=Fe, Co, Ni, Cu)	NH_3	N/A	62
		H_2S	N/A	
		NO_2	0.00093[a]	
		SO_2	N/A	
	Co-TPCOF Cu-TPCOF	NO_2	0.0068[a]	63
	Zn-TDCOF-12	NO_2	0.0079[a]	64
	Co-TCPP(Fe)/MXene	NH_3	N/A	65
		H_2S	N/A	
		NO	0.2	
		CO_2	N/A	
		MeOH	N/A	
		EtOH	N/A	
		acetone	N/A	
		AcOH	N/A	
		benzene,	N/A	
		toluene	N/A	
		ethylbenzene	N/A	
		o-xylene	N/A	

[a] Calculated LOD

[b] For more details including analyte concentration range, sensing environment, and device fabrication, see the SI.

Pristine Devices:

Our group pioneered MPc-based framework materials for chemiresistive gas sensors, advancing the field by investigating the effects of linker identity, metal node, and framework topology on device performance (Figure 8). In 2019, Meng *et. al.* linked Ni(II)phthalocyanine (NiPc) or Ni(II)naphthalocyanine (NiNPc) via Ni or Cu bis-dioxolene linkages to produce conductive MOFs with tunable pore apertures.[2] These materials achieved exceptional sensitivities for H2S and NO (LODs of 19−32 ppb, and 1.0−1.1 ppb, respectively) and differentiated these analytes based on metal identity, with Cu-linked MOFs giving higher response to H2S, and Ni-linked MOFs favoring detection of NO. Different chemiresistive responses across the material−analyte pairings underscore the ability to modulate sensing through the choice of molecular building blocks.

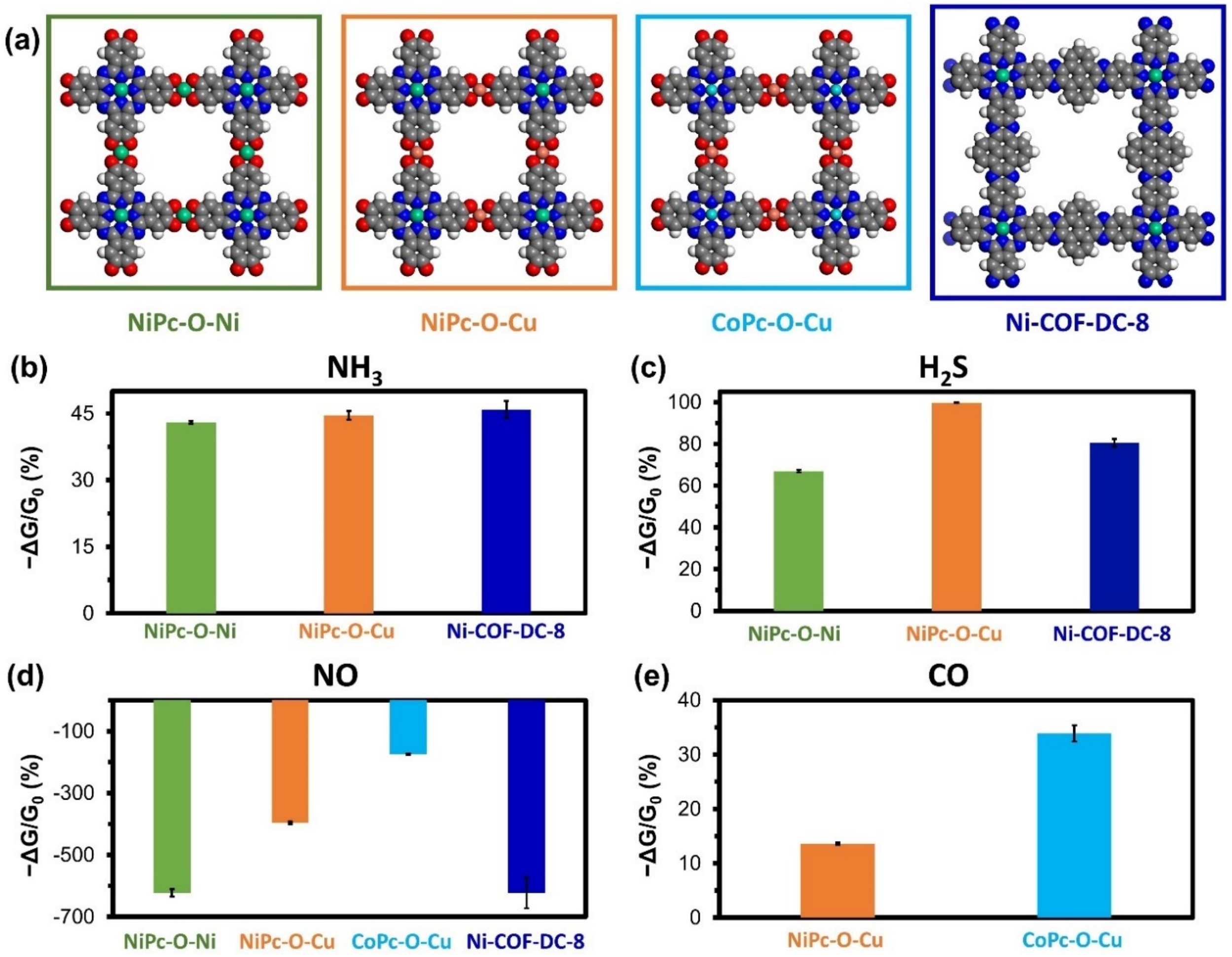


Figure 8: (a) Structure of MPc-based MOFs, NiPc-Ni-O, NiPc-Cu-O, and CoPc-Cu-O, and COF, Ni-COF-DC-8. Sensing responses recorded in change in negative normalized conductance of devices exposed to (b) 80 ppm NH_3, (c) 80 ppm H_2S, (d) 1 ppm NO, and (e) 80 ppm CO. (Note: data for CoPc-O-Cu sensing NO was performed at 80 ppm.) Adapted with permission from 2, 4, and 3. Copyright 2019 American Chemical Society. Copyright 2022 Wiley-VCH. Copyright 2019 American Chemical Society.

Encouraged by the success of MPc-based sensors, our group targeted CO, which is notoriously difficult to detect and differentiate due to its stability. Aykanat *et. al.* sensed CO in dry

N_2 environments using CoPc-O-Cu and NiPc-O-Cu with calculated LODs of 0.53 and 3.0 ppm, respectively.[4] Despite retaining responsivity to 80 ppm CO in air, sensors showed reduced response in humidified air. DRIFTS and computational studies (**Figure 9a−c**) suggested that improved sensing performance of CoPc-O-Cu compared to NiPc-O-Cu resulted from energetically favorable CO interactions at the Cu(II)bis-dioxolene linkages, tuned by the CoPc constituent. In addition to CO, the chemiresistive array successfully differentiated NO_2, NO, and CO. This study enhanced chemiresistive CO detection, and discriminated multiple toxic gases, facilitating differentiation of both strong and weakly binding analytes.

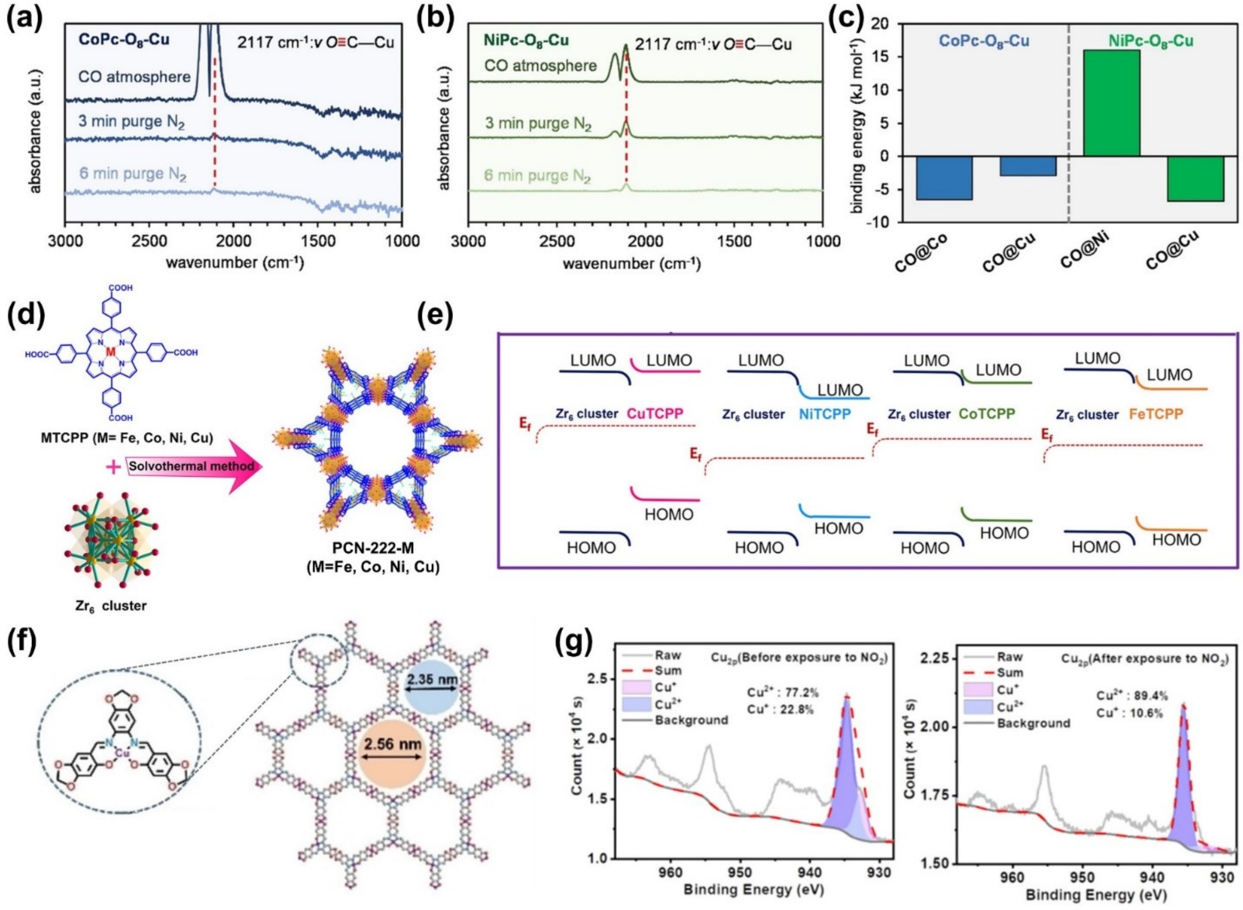


Figure 9: DRIFTS spectra of (a) CoPc-O-Cu and (b) NiPc-O-Cu after exposure to 1 % CO for 6 min. (c) Computational binding free energies of CO at different sites of the MPc-O-Cu (M=Co, Ni) MOFs. Reproduced with permission from 4. Copyright 2022 Wiley-VCH. (d) Schematic of PCN-222-M (M=Fe, Co, Ni, Cu) synthesis (e) Side-by-side comparisons of the energy level structures and Fermi levels of the PCN-222-M. Reproduced from 62. Copyright 2023 American Chemical Society. (f) Schematic of Cu-

salphen-MOF synthesis. (g) XPS of Cu-salphen-MOF before and after NO_2 exposure. Reproduced with permission from ref 66. Copyright 2023 Wiley-VCH.

Our work utilizing pristine MOF chemiresistors transitioned to innovative approaches using metal-containing linkers to form bimetallic frameworks. Zheng *et. al.* utilized films of PCN-222-M (M=Fe, Co, Ni, Cu), a conductive MOF formed from MPys and Zr nodes, achieving an ultra-low NO_2 LOD of 0.93 ppb.[62] Enhanced sensitivity was linked to Cu's high Fermi level compared to other metals, facilitating electron transfer to NO_2 (**Figures 9d−e**). Su *et. al.* utilized a copper-salphen MOF (see **Figure 9f**) for selective NO_2 sensing, showcasing enhanced response in humidity.[66] XPS demonstrated the importance of Cu sites as electron donors for NO_2 interaction. (**Figure 9g**) These MOF chemiresistors diversified metal-containing structures and topologies for NO_2 sensing, investigating the effects of different Cu environments on sensing.

Encouraged by our lab's success with MPc analogs in conductive MOFs, we developed the first conductive MPc-based COF chemiresistor. Meng *et. al.* synthesized Ni-COF-DC-8, a porous, conductive from the polycondensation of Ni(II) octaaminophthalocyanine and pyrene tetraone to obtain a robust phenazine-linked material.[3] Ni-COF-DC-8 exhibited low theoretical LODs for NH_3, H_2S, NO, and NO_2 (70, 204, 5, and 16 ppb, respectively). The material's fully annulated structure ensured chemical and thermal stability. Analyte re-exposure studies demonstrated comparable device performances to freshly prepared devices after solvent treatment, highlighting the robust COF's advantage for device regeneration. Following exposure to H_2S, NO, and NO_2, XPS (Figure **10b−c**) revealed formation of sulfphite, NO, and NO_2 species bound to the Ni metal center, respectively, underlining the NiPc's importance in chemiresistive activity.[3] Ni-COF-DC-8 rivaled conductive MOFs in sensing performance, boasting a chemical structure conducive to long-term stability, harsh environmental treatment, and device reusability.

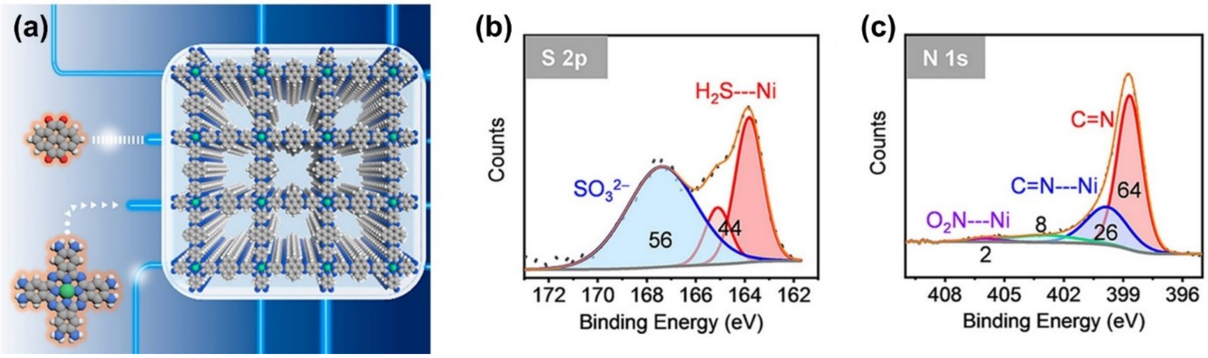


Figure 10: (a) Schematic of Ni-COF-DC-8 synthesis. (b) XPS of Ni-COF-DC-8 after H_2S exposure in the S 2p region. (c) XPS of Ni-COF-DC-8 after NO_2 exposure in the N 1s region. Reproduced from 3. Copyright 2019 American Chemical Society.

Subsequently, multiple studies investigated chemiresistive NO_2 detection using bimetallic MPc-based COFs.[60, 61] These included NiPc-CoTAA, featuring NiPc linked via Co(II)tetraaza[14]annulene moieties (CoTAA),[60] and COF-CuNiPc, featuring CuPc linked to NiPc moieties via dioxane linkages.[61] NiPc-CoTAA thin films demonstrated sensitive NO_2 detection and moderate response to NO, H_2S, and NH_3. COF-CuNiPc achieved selective NO_2 detection, fast response, and UV-light-reversible signals, sustaining performance over weeks under varying humidities. Dual metal centers optimized the materials band gap, enhancing NO_2 response speed and reversibility. Besides MPc-based COFs, MPy-based COFs have also detected NO_2.[63, 64] In recent years, COF-based NO_2 detection gained momentum, owing to improvements in synthetic control and tunability of structurally precise metallo-containing materials.

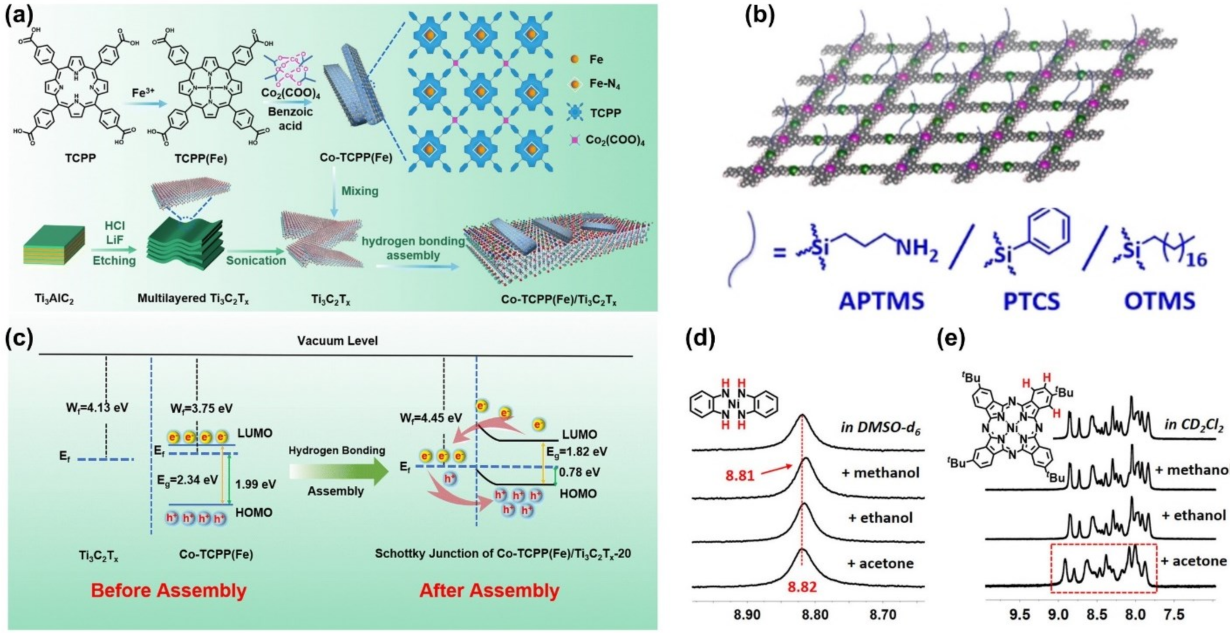


Figure 11: (a) Schematic of Co-TCPP(Fe)/$Ti_3C_2T_x$ composite formation. (b) Schematic of MPc-NH-Ni (M=Ni, Cu) 2D films with different appended alkyl groups. (c) comparisons of energy level structures and Fermi levels of CoTCPP(Fe) and the Mxene before and after formation of composite. ^{1}H NMR spectrum of (d) $Ni[C_6H_4(NH)_2]_2$ in $[D_6]$DMSO and (e) ^{t}Bu$_4$NiPc in CD_2CCl_2 in the presence of methanol, ethanol, or acetone. Reproduced with permission from 65. Copyright 2023 Royal Society of Chemistry. Reproduced with permission from 59. Copyright 2021 Wiley-VCH.

Composite Devices:

Other groups utilized MPy- or MPc-based MOF composite devices for chemiresistive sensing, investigating novel sensing motifs and mechanisms. Chang *et. al.* combined a metalloporphyrin MOF (Co-TCPP(Fe)), a wide bandgap semiconductor,[67] with a MXene, $Ti_3C_2T_x$, to build a conductive device (**Figure 11a**) with a sensing mechanism modulated by the Schottky junction (**Figure 11c**).[65] The device exhibited selectivity towards NO, with device recovery achieved by simple air purging. Wang *et. al.* affixed aliphatic alkyl chains on bimetallic MPc-NH-M (M=Ni, Cu) to modify surface hydrophobicity (**Figure 11b**),[59] enhancing device recovery in humid environments. The alkyl chains on the MOF tuned selectivity towards MeOH vs EtOH (**Figure 11d−e**). The use of composite materials holds promise for enhancing performance metrics, such as the rate of recovery and response.

Conclusion and Outlook

This Account features conductive framework materials as chemiresistors for sensitive, selective detection of small gaseous molecules, fundamental research on material−analyte interactions, and development of streamlined, uniform, low-power sensors. We highlight contribution to material design, synthesis, device fabrication techniques, and chemiresistive sensing capabilities. Despite the progress, unresolved challenges necessitate collective efforts to optimize the utility of conductive framework materials as chemiresistors.

First, achieving selective and sensitive analyte detection in complex mixtures remains a challenge due to competing interactions that can obfuscate differentiation. Sensitive sensors depend on synthesizing novel conductive frameworks with tailored functionalities and structures for specific analyte interaction. Alongside synthetic trials, computational techniques, including density functional theory and machine learning, are essential for accelerating material development through *silico* survey to guide experimental design, synthesis and device testing.

Second, the lack of mechanistic understanding of conductive framework−analyte interactions impedes chemiresistor development, as the underlying principles governing device function remain unknown. Improvements depend on controlled growth of MOF and COF single crystals, thin films, and emergent morphology. Structurally resolved materials enable precise binding studies using *in situ* spectroscopic and diffraction techniques to investigate material structure, as well as the effect of dopants, and defects on device function. Achieving atomistic understanding requires control and expansion of techniques to probe framework crystallization and analyte interactions.

Third, the field has yet to fully exploit reticular synthesis to precisely deposit conductive frameworks on substrates to engineer robust, processable devices. Enhancing framework processibility and device integration requires utilizing and innovating techniques for *in situ* growth and deposition on various substrate through refined solvothermal approaches, microfluidics, layer-by-layer assembly, sol-gel processing, and spin coating.

Finally, real-world applications demand versatile, robust chemiresistors capable of detecting and differentiating analytes beyond controlled settings. Sensors must be low-powered, wireless, and resistant to humidity and temperature changes. Conductive frameworks can meet these demands with i) stable framework designs, ii) selective layers and functionalization to prevent interference, and iii) inherent hydrophobicity and low oxygen affinity through judicious linker selection. Additionally, conductive framework array combinations will enable differentiation of multiple concomitant analytes, presenting opportunities for computational investigations and AI to expedite sensor discovery. Targeted materials synthesis, computational chemistry, and data analysis promise advancement in framework-based chemiresistors for real-world sensing.

Continued focus on these challenges is crucial to enhance materials discovery and sensor functionality for real-world conditions. Conductive frameworks offer modularity, diverse functionality, optimal electronics, porosity, and versatile device integration. These materials and their composites are poised to usher in an era of low-power, cost-effective chemical sensors for healthcare, personal protection, environmental monitoring, and pollution remediation.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Full length table of framework- and framework composite-based chemiresistors detailing analytes, active sensing material, device fabrication, LOD, and analyte concentration range. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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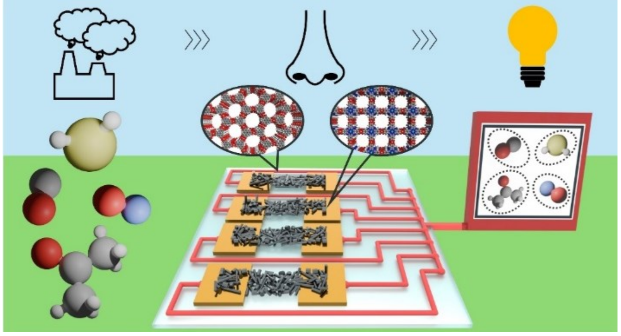

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