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# Metal-organic frameworks as materials for applications in sensors

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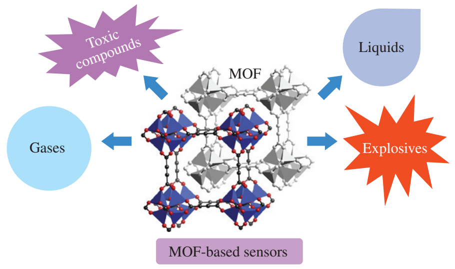
**The present review covers applications of metal organic frameworks (MOFs) in sensors. Particular attention is paid to gas sensors, since MOFs have demonstrated a good selectivity towards the adsorption of gas molecules. The applications of MOFs as pre-concentrators of the compounds to be analyzed are also outlined. Two modes of operation can be used in the considered sensors: photoluminescent and electrochemical ones.**



## Introduction

Metal-organic frameworks (MOFs) are crystalline coordination polymers comprising organic linkers and inorganic nodes. They represent a novel class of microporous polymer materials possessing tunable physical and chemical properties. About 8000–10000 of works related to MOFs and coordination polymers have been annually published since the first report in 1989.[1] Yaghi coined the term ‘MOF’.[2] A bit later, a new and special class of MOFs was prepared from imidazolate building blocks. This class exhibits similarities with zeolites, and therefore, such hybrid materials were consequently named ZIFs (zeolitic imidazolate frameworks).[3,4]

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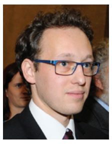

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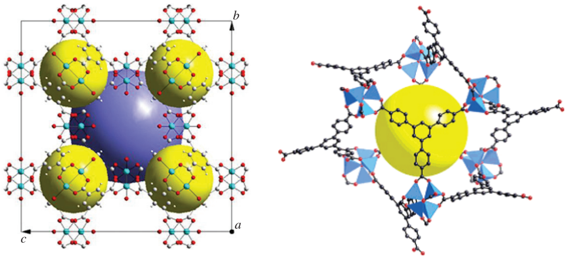
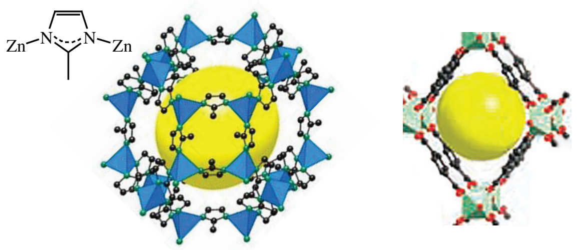
Dr. **Kamal Kumar Bisht** received his M.Sc. degree from the Government Post Graduate College at the Kumaun University (Pithoragarh) in 2006 and PhD from AcSIR in 2014 for the research undertaken under the supervision of Dr. E. Suresh at CSIR-CSMCRI. He started to work as Assistant Professor at the University of Petroleum & Energy Studies in Dehradun in 2014 and moved to the RCU Government Post Graduate College in Uttarkashi in 2016. His research interests include the areas of MOFs, chirality, molecular recognition, and alternate energy. He has published more than 30 research papers and book chapters to his credit.

The modular nature (a combination of inorganic and organic ingredients)[5–7] of these porous materials is ideal for tailoring the structures and functions of MOFs according to specific applications. The most remarkable feature of MOFs is their extremely high porosity. Depending on the sizes of ligands and inorganic building units, as well as the framework connectivity, the open channels and pores are sized from 4–5 Å to about 5 nm. The large pores (3.9 and 4.6 nm) in MIL-101(Cr) framework with naphthalene-2,6-dicarboxylate linkers can accommodate bulky molecules such as polysaccharides and proteins.[8] Figure 1 shows some illustrative examples of MOF structures that are of most interest in the context of sensing applications. Due to the tunable pore sizes, the molecular sieve effect can be successfully employed in MOF-based sensor materials.

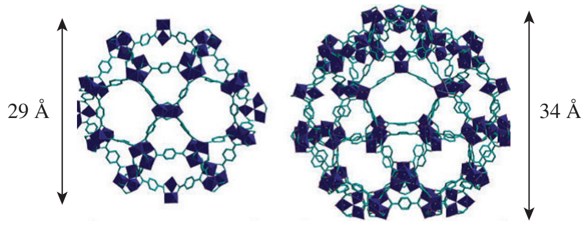
There are a few examples of MOFs possessing a high hydrothermal and thermal stability at temperatures of up to 400–450 °C. The specific surface areas of MOFs vary from a few to over 5500 $m^2 g^{-1}$ (5640 for MOF-177[9] and 5900 for MIL-101[10]), while theoretical predictions[11] have revealed the possible surface areas of up to 15000 $m^2 g^{-1}$.



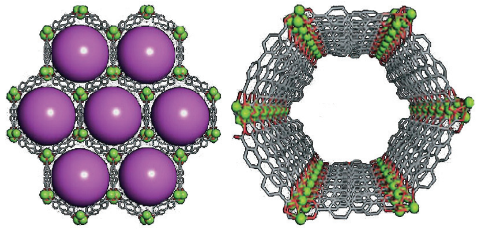
HKUST-1 (MOF-199) MOF-177



ZIF-8 MIL-53(Cr)



MIL-101 [$Cr_3OF(bdc)_3$]



JUC-48 [$Cd_3(BPDC)_3(DMF)$]·5DMF·18$H_2O$

**Figure 1** Structures of selected MOF materials. Figures from ref. 3 ©2006 National Academy of Sciences (USA), ref. 12 ©2004 Springer Nature Publishing AG, ref. 13 ©1999 American Association for the Advancement of Science, ref. 14 ©2002 Royal Society of Chemistry, ref. 15 ©2015 Elsevier B.V., and ref. 16 ©2007 John Wiley & Sons, Inc. Reproduced with permission.

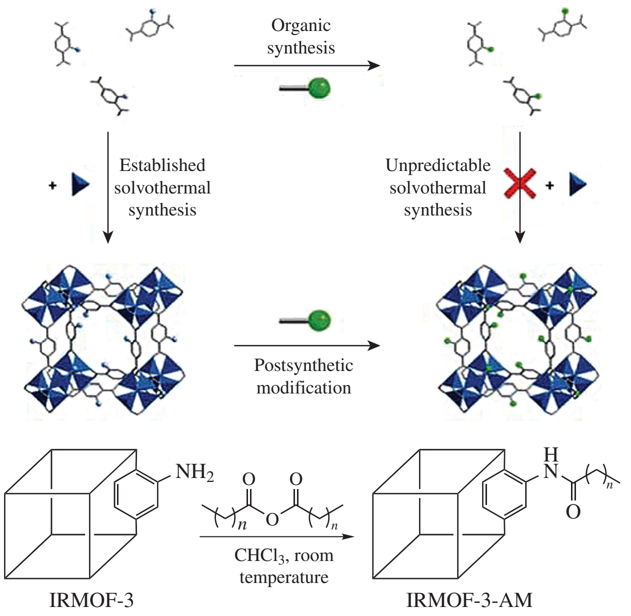


**Figure 2** The comparison of post-synthetic modification of MOF materials *via* a conventional incorporation of functional groups embedded in the ligand precursor and an example of post-synthetic modification reaction in IRMOF-3 matrix. IRMOF-3 is isoreticular metal-organic framework, which is a cubic lattice comprised of $NH_2$-bdc ligands (represented as the sticks) and $Zn_4O$ clusters (zinc ions are represented by the blue tetrahedra). Figure from ref. 22 ©2010 Royal Society of Chemistry. Reproduced with permission.

The chemistry and methodology of synthesis of MOFs are already summarized in a number of recent reviews.[17–20] Post-synthetic functionalization of MOFs, including the approaches of ‘click chemistry’, was rationalized by Cohen (Figure 2).[21,22] Various functional groups (amino, amido, mercapto ones, *etc.*) can be introduced in MOFs using the common methodology of organic syntheses. Some of them improve the stabilization of encapsulated metal nanoparticles or guest molecules, or increase the adsorption strength of adsorbates in the sensing materials. Of special interest are diverse composite MOF-based materials, including host–guest assemblies, membranes (both ceramic and mixed matrix membranes), core-shell structures, *etc.*[23]

The solid nature of a MOF determines not only its catalytic and adsorptive but also other physical properties, such as magnetic susceptibility, conductivity, and optical characteristics that are important for the sensor applications.

Approximately 20000 MOFs have been recently synthesized (Figure 3).[24–26] Among them, *ca.* 4000 and *ca.* 7000 compounds possess a three-dimensional and two-dimensional structure, respectively. The most commonly used metal ions are $Cu^{II}$, $Mn^{II}$, $Zn^{II}$, $Ni^{II}$, and lanthanides.

The percent of free volume inside MOFs with respect to the overall volume reaches 91.1% in the case of IRMOF-16 (organic linker is TPDC = 4,4′-terphenyldicarboxylate), while that of the majority of open zeolites is no more than 30–40%.[27] An important advantage of MOFs over traditional sorbents is the uniformity of pore size, while the shape of pores can be highly diverse.[28] While zeolites typically contain spherical, elliptical and slit pores, MOFs can also possess square, rectangular, and triangular ones.[29–31] This diversity of pore geometries is important for the selective adsorption and sensing.[32–35]

## Adsorption by MOFs

The capability of MOFs to selectively adsorb certain types of molecules is crucially important for their applications in sensors. Copper(II) benzene-1,3,5-tricarboxylate (MOF-177) is capable of adsorbing methane, *e.g.*, the capacity was 80 g $dm^{-3}$ at 38 bar. Some of covalent organic frameworks (COFs) turned out to be

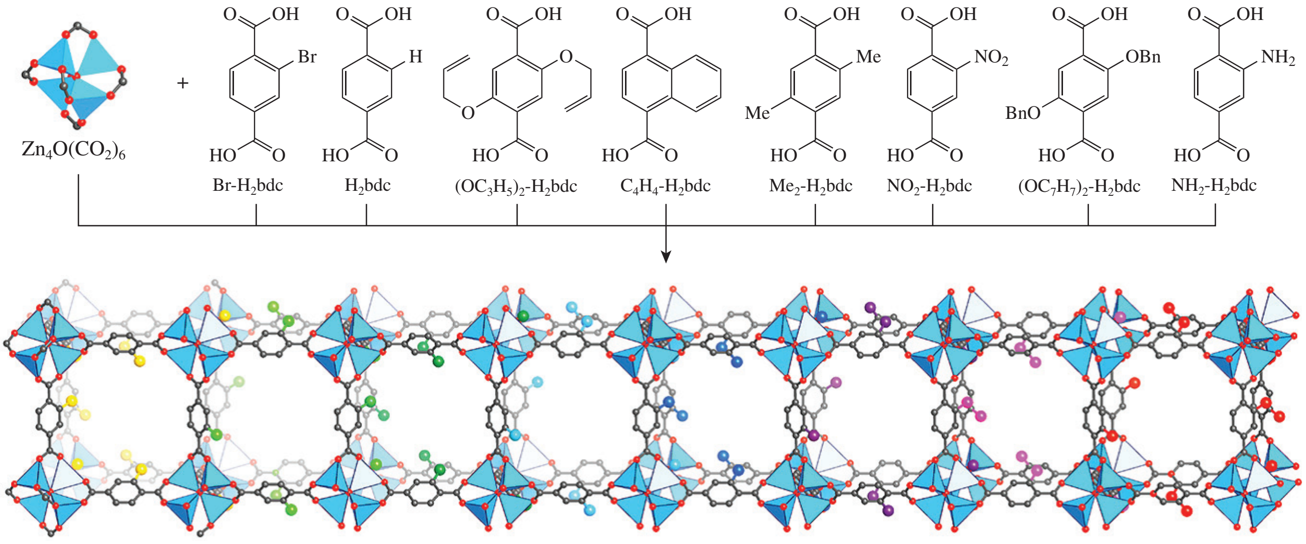


**Figure 3** An example of the synthesis of a wide range of MTV (multivariate) MOF materials *via* constructing the framework with multiple linkers of the same metrics but bearing various appended functionalities. Structure MTV-MOF-5 is composed of basic zinc carboxylate secondary building blocks and multiple differently functionalized bdc derivatives. Figure (with some modifications) from ref. 25 ©2018 American Chemical Society. Reproduced with permission.

even more efficient for the methane adsorption as compared to MOFs: COF-102 and COF-103 and post-synthetically modified COF-103-ETH-trans and COF-102-ANT exhibited the $CH_4$ uptake of 190 v/v (STP), which is significantly higher as compared to 112 v/v for MOF-177 and 137 v/v for COF-102.[36]

Copper(II) coordination polymers of the type $[Cu_2(pzdc)_2(L)]_n$ (pzdc = pyrazine-2,3-dicarboxylate and L = pillar ligand), so-called ‘CPL’ (coordination pillared layers), could selectively adsorb acetylene from its mixtures with $CO_2$ (CPL-1 containing 4,4′-bpy as the ligand).[37] At $P = 1.1$ kPa, the ratio of adsorbed amount of acetylene to that of $CO_2$ was about 26 at 270 K. Some MOFs demonstrated a unique selectivity towards alkenes *via* the formation of strong complexes with coordinatively unsaturated metal ions (they also act as Lewis acid sites). The $Fe_2$(dobdc) MOF (dobdc is 2,5-dioxido-1,4-benzenedicarboxylate) exhibited the selective adsorption of ethylene and propylene from their mixtures with ethane and propane at 318 K.[38]

Adsorption of NO is of particular interest for sensing since it is related to the problem of car exhaust control. Two coordination polymers, CPO-27–Co and CPO-27–Ni, demonstrated an excellent NO adsorption capacity (about 21 wt%).[39] Activated CPO-27 material can adsorb ~7.0 mmol $g^{-1}$ of NO, which is 3 orders of magnitude greater than the amount found for HKUST-1 and 7 times greater than that for zeolites. The $CO_2$ adsorption capacity as high as 25–30 wt% was found for several MOFs, *e.g.*, MOF-177 and MIL-53(Cr).[40,41]

Studies on the differences in adsorption of linear and branched hydrocarbons by a Cu-based MOF structure provided the evidence for definite preferences for the linear alkanes.[42] Quite a few examples of the so-called ‘molecular recognition’ by MOFs are known, *e.g.*, the predominant adsorption of certain isomers over the other, such as *p*-dichlorobenzene or *p*-xylene as compared to their *m*-isomers or linear alkanes as compared to the branched molecules.

Due to a short format of this mini-review, we will provide a sketch-wise survey of the most impressive sensing applications of MOFs for gases and liquids, however, the MOF-based biosensors (examples can be found in the recent review by Lei *et al.*[43]) will not be discussed.

## MOFs as sensing materials

Obviously, the sensing opportunities provided by this new class of hybrid inorganic-organic materials are unique since the choice of organic linker and inorganic nodes allows one to tune the textural parameters and design the structure (Figure 4).[43,44]

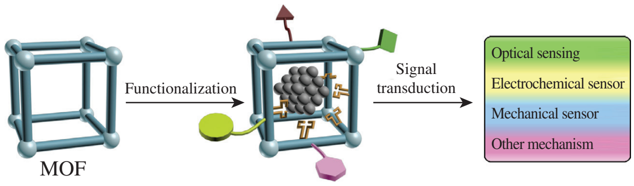


**Figure 4** Functionalization and signal transduction of MOF-based composites in the sensing applications. Figure from ref. 43 ©2014 Elsevier B.V. Reproduced with permission.

The nature of inorganic part in the MOF structure may be responsible for the sensing properties, whereas an interplay of the functional groups at the linkers, inorganic moieties, and introduced metal ions bring new opportunities for designing the unique single-site sensing centers. MOFs can be employed as both optical (luminescence)[45–47] and electrochemical sensor materials *via* the changes in the electroresistivity due to the adsorption and/or catalytic reaction occurring on the surface of electroconductive material (*e.g.*, $SnO_2$) modified with a MOF adsorbent.[48,49]

Some works were aimed at the detection of environmental contaminants.[50] There are also few reviews and a series of reports devoted to MOFs applied in gas sensing.[51] However, the studies on MOFs as the sensors are still remaining at the early stage, while the overall progress to explore the MOF applications in the sensors is not yet systematic.

## Luminescent MOF materials

The luminescent properties of MOFs, such as quenching of the nano-sheets of Zn(bdc) MOF upon interaction with ethylamine, were reported.[52,53] The emission at 446 nm was assigned to the fluorescence from excited states of intra-ligand emission. In general, $d^{10}$ elements (like $Zn^{2+}$ or $Cd^{2+}$) deserve a special attention in this concern, since they are known as exhibiting a strong fluorescence in the solid state.

A strong blue fluorescent emission at 499 nm with the satellite at 550 nm was observed for a new four-fold interpenetrated diamondoid MOF of $Zn^{II}$ urocanate (4/5-imidazoleacrylate) containing one-dimensional open channels.[54] A very similar MOF composition, $Zn^{II}$ imidazole-4,5-dicarboxylate, but having a helical structure, exhibits a strong luminescence at 420 nm.[55] MOF based

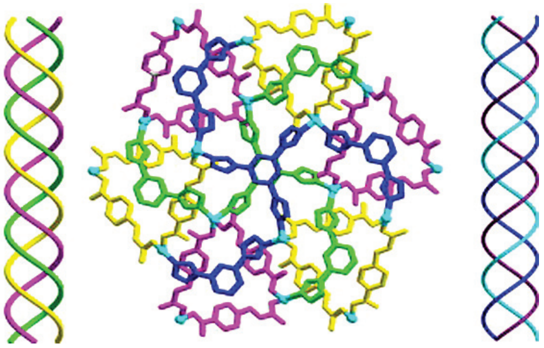


**Figure 5** Helical structure of $Zn_3(tib)_2(L)_3$. Figure from ref. 58 ©2013 Elsevier B.V. Reproduced with permission.

on Zn 2,2′-diimidazole-derived dicarboxylate[56] fluoresce at 414 nm. Optical properties of Zn-MOF materials have also been reviewed.[57]

Complex $Zn_3(tib)_2(L)_3$ synthesized from mixed ligands, 1,3,5-tris(1-imidazolyl)benzene (tib) and 4-carboxycinnamate ($L^{2-}$), exhibited interesting two-fold interpenetration, where triple-stranded homochiral left- and right-handed helical chains were formed by linear rigid ligand $L^{2-}$ and metal ions (Figure 5).[58] This complex demonstrated a strong photoluminescence in the solid state at room temperature.

The important feature of MOFs is their capability of changing the structure upon an adsorption of the specific molecules. Interpenetrated MOFs, *i.e.* materials consisting of two or more structures interpenetrated into each other, are especially sensitive to such interactions. For instance, two-fold interpenetrated material $[Zn_2(bdc)_2(dpNDI)]_n$ [bdc is 1,4-benzenedicarboxylate, dpNDI is *N*,*N*-di(4-pyridyl)-1,4,5,8-naphthalenediimide] can change its structure after adsorption of chemical compounds, adopting a conformation to maximize the overall binding interactions.[59] This material demonstrated a high selectivity towards larger methylated aromatic compounds, such as toluene and *p*-xylene, as compared to benzene. Unit dpNDI forms an exciplex with the aromatic compounds. The position of emission band depends on the strength of host–guest charge-transfer interaction.

The band gap of MOFs can be tuned *via* the replacement of oxygen in IRMOF-1 with sulfur and selenium to allow these materials to absorb visible light.[60]

Another approach is based on the application of porous coordination polymer capable of demonstrating a breathing effect of the framework [in particular, $Zn_2$(terephthalate)$_2$(triethylenediamine)$_n$ with the channel sizes of 7.5×7.5 Å] and fluorescent agents that can change their conformation upon the adsorption of certain molecules. Distyrylbenzene was chosen as such fluorescent molecule resulting in the composite system that can selectively adsorb $CO_2$ from other atmospheric gases.[61] The adsorption induces a transformation of the encapsulated distyrylbenzene molecules accompanied by a significant variation in the fluorescence at a specific threshold pressure. The developed composite demonstrated different fluorescence responses to $CO_2$ and acetylene, which are known as the compounds with similar physicochemical properties. This is the first report claiming that fluorescent molecules can detect gases without any chemical interaction or energy transfer. The host–guest coupled transformations are crucial for the generation of detectable output signals.

The luminescent properties of $Cd^{II}$ are very similar to those of $Zn^{II}$ in the MOF materials. A series of MOFs based on rigid $Cd^{II}$ and $Zn^{II}$ tricarboxylates and flexible imidazolates[62] fluoresce at 425 nm (the same band for all the three materials), which was assigned to the $\pi^*$–$\pi$ transitions in the ligands. The luminescent properties of binuclear and pentanuclear (adipic acid and triazole derivatives) $Cd^{II}$-based MOFs were also explored.[63,64] A ligand-to-metal charge-transfer emission at 364 and 460–495 nm was observed for a Cd-based MOF prepared from cyclohexanetricarboxylate and pyrazinedicarboxylate.[65,66] The band position depended on the presence of a bipyridyl moiety in the structure.

A highly sensitive sensing of nitroaromatic compounds in ethanol solution was performed with nanocrystal MOF of $[Cd(atc)(H_2O)_2]_n$ (atc is 2-aminoterephthalic acid) *via* the fluorescence quenching and fluorescence titration.[67]

Lanthanides represent another group of luminescent materials suitable for sensors. Dysprosium and samarium pyridinedicarboxylates[68] exhibited a set of 3–4 emission bands assigned to different transitions of Dy and Sm with maxima ranging from 480 to 623 nm for Dy and from 560 to 710 nm for Sm. The energy transfer from the organic ligand to the lanthanide ion was concluded to be an efficient one.

Investigations of Eu- and Tb-based MOFs revealed their strong photoluminescence peaks at 580–695 nm for Eu and 490–620 nm for Tb due to $f^*$–$f$ transitions.[69] The luminescent properties of Tb-, Yb- and Eu-MOFs were also proved as sensitive to the molecules trapped in the MOF pores.[70]

The luminescence of Pb pyridineacrylate MOFs is represented by two emission bands at 418 and 438 nm appearing due to the charge-transfer interactions.[71] Phosphorescence properties of MOF materials based on $Pb^{II}$, $Co^{II}$, $Ni^{II}$ pyridinedicarboxylates were also revealed, *e.g.*, the red-shifted band at 475 nm for the Pb sample.[72]

Although the solid-state luminescence of silver complexes is typically observed only at low temperatures due to the intense spin-orbital coupling of $Ag^I$, several Ag-MOF materials containing various organic pyrimidine linkers were explored.[73] Their luminescence and emission bands at 327–360 nm were observed at room temperature, however these bands were assigned to the organic moieties.

Metal organic framework $[Zn_2(bpdc)_2(bpee)]\cdot 2DMF$ (bpdc is 4,4-*o*-biphenyldicarboxylate and bpee is 1,2-bipyridylethylene) was post-functionalized with $AgNO_3$ in order to detect olefins, such as ethylene and 1-hexene, by luminescence of the silver ions.[74]

The JUC-48 material, $[Cd_3(bpdc)_3(DMF)]\cdot 5DMF\cdot 18H_2O$ (see Figure 1), has also demonstrated quite good luminescent properties.[75] Moreover, JUC-48 was assembled with a nanosized dye Rh6G (a xanthene derivative) and showed a strong luminescence at 563 nm, while the peak position remained unchanged upon decreasing the temperature.[76] Such materials can be employed in temperature-sensing devices.

In a comprehensive review on the luminescent properties of MOFs by Cui *et al.*,[77] the outlook goes beyond the sensor materials and covers the fields of lighting (MOF-based OLEDs), display materials, and optical devices. In most cases, composite materials based on MOFs as the matrices or hosts were considered. A nanocomposite of luminescent europium organic framework and CdSe quantum dots has been for the first time investigated for the photoluminescence to develop a highly sensitive detection of trinitrotoluene.[78] The linear range of photoluminescence quenching based detection of trinitrotoluene with the nanocomposite was 5–1000 ppb with the detection limit of 3 ppb. The trinitrotoluene detection was selective with respect to some other explored aromatic compounds, such as phenol, *o*-cresol, toluene, benzene, nitrobenzene, and nitrophenol. In general, the detection of explosives is a crucial problem, and MOFs can thus serve as preconcentrators of vapors of explosives. This was proved using hexahydro-1,3,5-trinitro-1,3,5-triazine as another example of explosive compound.[79] MOFs were able to concentrate this substance up to 3000 times (by volume) as compared to the gas phase. The selectivity to hexahydro-1,3,5-trinitro-1,3,5-triazine over butane was up to 5000.

In general, the prospects for the detection of explosives by MOFs are quite optimistic,[80] so new reports on such applications of MOFs appear.[81] For example, a very selective system for detecting 2,4,6-trinitrophenol in the presence of other aromatic and nitro compounds has been reported.[82] The used material was $[\mathrm{Me_2NH_2}]^+[\mathrm{Zn_4}(m_4\text{-O})(\mathrm{NTB})_2(\mathrm{NO_2}\text{–bdc})_{0.5}]\cdot 3\mathrm{DMA}$ (NTB is 4,4′,4″-nitrilotrisbenzoic acid, $\mathrm{NO_2}$–bdc is 2-nitro-4-benzenedicarboxylic acid), demonstrating the luminescence quenching at a quite low concentration (4 mmol dm$^{-3}$) of the explosive in an acetonitrile solution.

### Electrochemical sensing materials based on MOFs

The luminescence MOF-based sensors are just one among the groups of sensors. Another group employ semiconducting MOFs, whose semiconducting properties provided by Zn, In, W, Sn and Ti oxides, using electroresistivity or electroconductivity as the detection parameter. Unfortunately, in contrast to a number of works related to such sensors based on bulk oxides (ZnO, $\mathrm{SnO_2}$, $\mathrm{In_2O_3}$),[83,84] there are not much data reported on MOF-based electrochemical sensors. Most of MOFs are insulating materials, which is a limiting factor in the design of electrochemical MOF-based sensors. One of the first reports[85] described the semiconductor properties of conventional Zn-MOF-5 (terephthalate). Nevertheless, some recent works revealed MOF candidates possessing a sufficient electroconductivity.[86–89] Figure 6 shows another example of MOF material with the enhanced electroconductivity, $\mathrm{Cu_3(btc)_2}$ (HKUST-1), containing adsorbed molecules of TCNQ (7,7,8,8-tetracyanoquinodimethane).

Amino-functionalized metal-organic framework, $\mathrm{NH_2}$–$\mathrm{Cu_3(btc)_2}$ was reported as an electrode modifier for the determination of lead traces at the detection limit of $5.0\times10^{-9}$ mol dm$^{-3}$.[90]

Electrocatalysts consisting of metal nanoparticles supported on MOFs are also promising for the sensing applications. For example, electrocatalyst immobilized onto the surface of glassy carbon electrode Au–SH–$\mathrm{SiO_2}$@Cu–MOF/GCE demonstrated a good electrocatalytic activity towards the oxidation of hydrazine in a neutral phosphate solution.[91] This sensor exhibited the low detection limit, high sensitivity, and good stability. The same authors proposed a novel electrochemical sensor based on Au–SH–$\mathrm{SiO_2}$ nanoparticles supported on MOF for the electrocatalytic oxidation and determination of L-cysteine.[92] The detection limits were estimated as 8–10 μM for both the analytes.

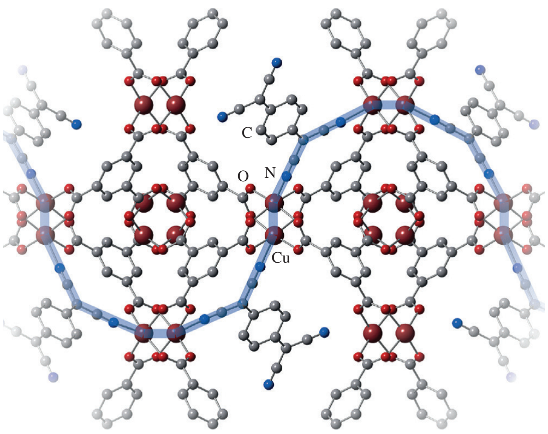


**Figure 6** Structure of TCNQ-adsorbed $\mathrm{Cu_3(btc)_2}$ (HKUST-1) MOF material. The blue line highlights the covalent charge-transport pathway *via* Cu–TCNQ. Figure from ref. 89 ©2016 John Wiley & Sons, Inc. Reproduced with permission.

MOF-5 $[\mathrm{Zn_4O(bdc)_3}]$ supported on a carbon paste electrode was proposed for a lead detection by the differential pulse stripping voltammetry.[93] The achieved detection limit was $4.9\times10^{-9}$ mol dm$^{-3}$. MOF-5 doped with Y was applied as the sensing material for cataluminescence detection[94] of isobutanol at the detection limit of 3.7 mg dm$^{-3}$.

Gas sensing properties of MOFs with different metal sites (Co, Ni, Cd, and Al) towards linear alkanes and alcohols utilize a work function.[95] The work function read-out requires changes in electronic properties of the sensing materials to make the adsorption of target molecules ‘visible’ for the detection. Another example of the work function approach used in MOF-based sensors was presented by Pohle *et al.*[96]

Enhanced electrocatalytic activity towards oxidation of dopamine and uric acid was observed at the oxidative potentials of 218 and 336 mV, respectively, using a MIL-101-carbon paste electrode.[97] The MOF (Fe-BTC) capability of detecting humidity in air was revealed by impedance measurements.[98] Ethanol and methanol can also be detected *via* the same approach. The efficacy of the electrochemical impedance spectroscopy was demonstrated for the $\mathrm{CO_2}$ detection[99] and humidity determination.[100]

Efficiency of electrochemical MOF sensors can be enhanced when their composites with conducting materials (indium or tin oxides, carbon nanotubes, *etc.*) are used.[101] The nanocomposites of multi-walled carbon nanotubes with MOFs $[\mathrm{Cu_3(btc)_2}]$ were applied for sensing traces of lead in water by differential pulse anodic stripping voltammetry in a lab-on-valve mode of operation using the composite supported onto an electrode. The detection limit was reported to be very low (0.79 nM).

The high capacitance of some MOF materials can be successfully employed for the sensing of molecules affecting this parameter, such as alcohols. The Cu-btc MOF-199 material has shown promising results in the detection of such volatile organic compounds.[102,103] The similar approach was revealed as a robust method for controlling $\mathrm{H_2S}$[104] and ammonia.[105]

### Other types of sensing

Another method of sensing is based on monitoring the magnetic properties of MOFs. Some of these materials exhibit unique magnetic features that are sensitive to the host–guest interactions, temperature, and presence of adsorbed molecules. For instance, $\mathrm{Cu_3(PTMTC)_2(py)_6(EtOH)_2(H_2O)}$ (MOROF-1) containing very large pores (2.8–3.1 nm) in combination with bulk magnetic ordering demonstrated a reversible and highly selective solvent-induced ‘shrinking–breathing’ effect that strongly influences its magnetic properties, which makes this magnetic sponge-like behavior a promising route towards the magnetic solvent sensors.[106]

A layer of MOF nanoporous material was deposited by electrospraying on the surface of a quartz resonator (piezoresistive cantilevers) to prepare a gravimetric sensor for volatile organic compounds (acetone, tetrahydrofurane, and isopropanol).[107] Significantly higher sensitivity, resolution, and stability of the developed sensors were reported. The minimum detectable concentrations of chosen organic compounds were 50, 10 and 2 ppm, respectively.

The HKUST-1 material was used on a microcantilever to detect water, methanol and ethanol vapors (detection level of about 0.5%),[108] whereas piezoresistive cantilevers with MOF layers were used for sensing carbon dioxide.[109]

In addition to the microcantilever method of sensing, other mechanical methods are available, such as quartz crystal microbalance, microresonator, and surface acoustic wave sensors coated with thin MOF layers capable of enhancing the adsorption of analyzed gas.[110,111]

**Table 1** Chemical analytes detectable by MOF sensors.

| Type of target chemicals | Documented examples |
|---|---|
| Cations | $Fe^{3+}$, $Al^{3+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Ag^{+}$, $Pb^{2+}$, $Ca^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Mg^{2+}$, $Mn^{2+}$, $Bi^{3+}$, $Pb^{2+}$, $Cd^{2+}$, $Ln^{3+}$ ($Eu^{3+}$, $Tb^{3+}$), $Pd^{2+}$, $K^{+}$ |
| Anions | $F^-$, $Cl^-$, $Br^-$, $I^-$, $CN^-$, $SCN^-$, $N_3^-$, $NO_2^-$, $NO_3^-$, $N(CN)_2^-$, $CO_3^{2-}$, $PO_4^{3-}$, $ClO_4^-$, $BF_4^-$, $MnO_4^{2-}$, $CrO_4^{2-}$, $Cr_2O_7^{2-}$ |
| Inorganic molecules | $O_2$, $H_2$, $NH_3$, NO, $NO_2$, HCl, $H_2O$, $H_2S$, $I_2$, CO, $CO_2$, $N_2H_4$ |
| Organic molecules | Alkanes, alkenes, alcohols, amines, amino alcohols, amino acids, nitro aromatic hydrocarbons, aldehydes, formaldehyde, dimethyl ether, ketones, phenol, chloroform, DMF, explosives, organophosphorus compounds, antibiotics, mycotoxins |

Some metal nanoparticles (Au, Ag) supported on MOFs and other materials can manifest specific features in the UV-visible region due to the surface plasmon resonance, and these features are fairly responsive to the interaction with specific molecules capable of being strongly adsorbed on the surface of such metal nanoparticles.[112]

And last but not least method of sensing is based on the changes in the refractive index of MOF upon adsorption of molecules.[113]

Table 1 summarizes presumably all types of chemical analytes, including cations, anions, inorganic molecules, and organic molecules, which have been studied using MOF materials as sensors. Among the organic compounds, there are, in particular, explosives and organophosphorus chemicals.

We have also tried to summarize the most sensitive MOF materials demonstrating the records in low detection limits towards the essential analytes (Table 2). To the best of our knowledge, the values of detection limits presented in Table 2 exceed the corresponding parameters achievable in the case of conventional sensor materials.

## Conclusions

The state of the art shows that the area of the use of MOFs in sensing materials is a promising alley for the future research. This field shall start from the scratch and accumulation of facts and will be definitely developed into a bunch of interesting applications due to the unique properties of MOFs, such as an extremely high specific surface area and pore volume, molecular sizes of the pores, flexibility of the framework that is responsive (adaptive) towards the adsorbate, as well as *via* a 'molecular recognition' approach.[128] The further improvements may be spurred by the development of more efficient methods of layer-by-layer deposition of MOFs onto a surface[129,130] and the inventive synthesis of nanocomposites with the aim to find a synergy between the MOF and support and/or another component of the nanocomposite.[131–136] Among the new methodologies in sensing by MOF materials, one should also focus on photoelectrochemical sensors.

Another broad alley is the application of MOFs as sacrificing precursors of oxide (typically mixed oxides) nanoparticles of different morphology (nanocubes, nanocages, hierarchical structures, core-shell materials, *etc*.). Many of such novel materials preserving the structure or at least developed porosity of the starting MOF materials exhibit a great potential in sensor applications, and some examples have been already reported.[137,138] Another developing class of materials exhibiting MOF features are metal organic gels, which do not have a regular crystalline structure but do have a rather high specific surface area and pore volume with tunable pore size distribution. Such materials have already shown an excellent performance in detecting aromatic and nitro compounds with enhancement (turn-on) or quenching (turn-off)

**Table 2** The most illustrative examples of sensitive MOF materials demonstrating the records in low detection limits towards the essential analytes.

| MOF | Sensor type/ sensing mechanism | Target chemical | Detection limit | Reference |
|---|---|---|---|---|
| | | *Cations* | | |
| $Tb(BTB)(DMF)\cdot 1.5DMF\cdot 2.5H_2O$ | Luminescence | $Fe^{3+}$ | $10^{-2}$ mmol $dm^{-3}$ | 114 |
| $Eu^{3+}$@UiO-66(Zr)–COOH | Luminescence | $Cd^{2+}$ | $6\times10^{-2}$ mmol $dm^{-3}$ | 115 |
| Adenine–La-MOF | Luminescence | $Hg^{2+}$ | 0.2 nmol | 116 |
| $Eu^{3+}$@MIL-121 | Luminescence | $Ag^{+}$ | 0.1 mmol | 117 |
| DNA-functionalized Fe(porphyrin)-MOF | Luminescence | $Pb^{2+}$ | 0.034 nmol | 118 |
| Branched poly(ethylenimine)-capped CQDs/ZIF-8 | Luminescence | $Cu^{2+}$ | 90 pmol | 90 |
| | | *Anions* | | |
| $\{[Ln_2ZnL_3(H_2O)_4](NO_3)_2\cdot 12H_2O\}_n$ (Ln = Eu, Tb; L = 4,4′-dicarboxylate-2,2′-dipyridine anion) | Luminescence | $I^-$ | 1 ppb | 119 |
| $\{Ru^{II}(Bu^tbpy)(CN)_4[Cu^{II}(dien)]_2\}(ClO_4)_2$ | Luminescence | $CN^-$ | 30 ppb | 120 |
| $NH_2$-MIL-53(Al) | Luminescence | $ClO^-$ | 40 nmol | 84 |
| (ZnO QDs)–MOF-5 nanocomposite | Luminescence | $PO_4^{3-}$ | 53 nmol | 82 |
| | | *Inorganic molecules* | | |
| Layers of Cu–btc | Surface acoustic waves | $H_2O$ | $<1$ ppm | 121 |
| $Cu_3(HITP)_2$ | Chemiresistive | $NH_3$ | 0.5 ppm | 122 |
| $Ni_3(HHTP)$ | Chemiresistive | NO, $H_2S$ | 0.1 ppm (NO), 1 ppm $H_2S$ | 123 |
| MFM-300 (In-MOF) | Capacitive | $SO_2$ | 5 ppb | 123 |
| Au–SH–$SiO_2$ nanoparticles on Cu-MOF | Electrochemical | $N_2H_4$ | 10 nmol | 90 |
| | | *Organic molecules* | | |
| ZIF-67 | Chemiresistive | $CH_2O$ | 5 ppm | 124 |
| $Co(Im)_2$ | Chemiresistive | $Me_3N$ | 2 ppm | 125 |
| UiO-66-$NH_2$ | Work function | Dimethyl methylphosphonate | 3 ppb | 126 |
| HKUST-1 | Work function | Alcohols | 2 ppm | 127 |
| Au–SH–$SiO_2$ nanoparticles on Cu-MOF | Electrochemical | L-cysteine | 8 nmol | 91 |
| IRMOF-3 | Luminescence | Trinitrophenol | 0.1 ppm | 96 |

of luminescence, *e.g.*, a dramatic enhancement of the luminescence intensity of host framework Fe–ndc in the presence of toluene (862%) has been revealed .[139]

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