Application of Luminescent Metal-Organic Frameworks for Chemical Sensing

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Nowadays, there has been an enormous demand for chemical sensors to detect a variety of analytes for a range of applications, including homeland security guarding, exploration of mineral resources, meteorological observation and telemetry, industrial automation, agricultural fresh preservation, environment monitoring, and food quality controlling. Typically, chemical sensors can bind selectively and reversibly the experimental analytes of interest with a concomitant change in electrical, optical, or mechanical properties. Among all the chemosensors, luminescence-based ones make use of changes of a fluorescent probe material in the photoluminescence to detect the presence of an analyte or target condition, and they are within the most desirable transduction mechanisms due to its relative ease of use, technical simplicity, and broad adaptability. However, there still remain some challenges to realize better sensory performance including increased brightness, longer fluorescent life, higher quantum yield and multifunctional systems. Therefore, it is necessary to search for a particular class of materials as luminescent sensors to construct a robust platform to deal with these challenges.

Over the last two decades, metal-organic frameworks (MOFs) are a new class of porous materials, which are formed by the assembly of metal ions with functional organic ligands. They have attracted great attention owing to their extensive applications in a wide areas such as light emitting, chemical sensing, gas storage and separation, heterogeneous catalysis, drug delivery, and magnetic properties. Among them, some luminescent MOFs are utilized for chemical sensing mostly based on the photoluminescence and tunable porosity which has fluorescent quenching response towards the aromatic nitro compounds, especially for the 3,4-dinitrotoluene (3,4-DNT) with the presence of an analyte or target condition, and they are within the most desirable transduction mechanisms due to its relative ease of use, technical simplicity, and broad adaptability. However, there still remain some challenges to realize better sensory performance including increased brightness, longer fluorescent life, higher quantum yield and multifunctional systems. Therefore, it is necessary to search for a particular class of materials as luminescent sensors to construct a robust platform to deal with these challenges.

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The reason is as follows: Firstly, the functional sites in MOFs such as Lewis basic/acidic sites and unsaturated metal sites can be used for selective recognition of targeted molecules/ions; Secondly, the tunable porosity can enable the reversible storage of guest species, making MOFs both as detection and pre-concentrator medium. Clearly, MOFs are a great kind of materials in their development with respect to chemical sensing.

In this review, we will give a detailed introduction of the application of luminescent MOFs for sensing of nitro explosives, metal ions, small molecules, pH value and temperature.

Sensing applications

Sensing of nitro explosives

Nitro explosives, widely used in industrial processing on a large scale, are highly explosive molecules. During synthesis, processing and disposal, nitro explosives are released into the environment, especially to water streams, contaminating ground and surface water. Luminescent MOF materials have been utilized for effective detection of high nitro explosives. Zhang et al. reported a compound ([Tb(Hbzptc)]2·bpp·2H2O), (1) (Hbzptc=benzophenone-3,3’,4,4’-tetracarboxylic acid, bpp=1,2-di(4-pyridyl)ethane), as shown in Figure 1. Compound 1 has the sensitive detection for the trace content of nitrobenzene with 5.5×10−3 M. The Stern-Volmer plots of the relative luminescence intensity (I0/I) versus the nitrobenzene concentration, where I0 and I are the luminescence intensities of compound 1 before and after adding nitrobenzene, respectively. Nonlinear Stern-Volmer curves can be well-fitted by the exponential equations of I0/I=1.72e0.72[NOB]−0.72 with quenching constant of 9.92×104 in the low concentration range. Wang et al. explored systematically the fluorescence sensing responses of [Cd2(H2O)L]·5H2O·2DMF (2) [H2L=2,5-bis-(3,5-dicarboxyphenyl)thiophenumide] to small organic molecules. Notably, complex 2 can act as a potential multifunctional material for sensing of p-nitroaniline ion with high stability, selectivity and sensitivity (Figure 2). Zhou et al. reported a compound [Eu2L(H2O)2(NMP)2]·H2O (3) (H2L=1,1’:4’,1”-terphenyl-2’,4’,4”,5’-tetracarboxylic acid; NMP=N-methyl-2-pyrrolidone), which has fluorescent quenching response towards the aromatic nitro compounds, especially for the 3,4-dinitrotoluene (3,4-DNT) with the linear Stern-Volmer relationship in the concentration range of 0−1 mM and the quenching constant (Ksv) of 2.084×105 M−1 (Figure 3). Zhu et al. reported a MOF [Cd(cis-chdc)(anti-bpe)(H2O)2], (4) [H2chdc=1,4-cyclohexanedicarboxylic acid, bpe=1,2-bis-(4-pyridyl)ethane], the excellent ability of 4 for selective detection of 4-nitrotoluene from other nitroaromatic compounds has been demonstrated (Figure 4). The recyclability and reusability of 4 have also been tested based on consecutive detection reactions, in which 4 remains unchanged and detection efficiency retains.

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Figure 1  (a) Comparison the luminescence intensity of 1 dispersed into different solvents when excited at 355 nm; (b) Stern-Volmer plots of I/I₀ versus the nitrobenzene concentration.

Figure 2  (a) The 3D supramolecular network of 2; (b) Percentage of fluorescence quenching of 2 obtained for different analytes in isopropanol solution at room temperature.

Figure 3  (a) View of the asymmetric unit of 3 with the thermal ellipsoids drawn at the 30% probability level; (b) Luminescence quenching percentages when 3 was dispersed in eight different nitro compounds in DMF (excited and monitored at 340 nm and 617 nm, respectively).

Figure 4  (a) View of the two-dimensional helical structure of 4; (b) Fluorescence intensity ratio histograms of 4 upon exposure to 0.3 mM concentration of different analytes.
Sensing of metal ions

Sensing of Fe$^{3+}$ ion

The first photoluminescent Cd(II)-organic framework $\{[\text{Cd}(5\text{-asba})(\text{bim})]\}_n$ (5) based on a multi-functional ligand 2-amino-5-sulfobenzoic acid (H$_2$5-asba) has been successfully constructed. Photoluminescent properties of 5 indicated that 5 belongs to the rare category of MOFs that exhibits the multi-responsive photoluminescence sensing properties. It can be used as a rapid and efficient selective fluorescence sensor for Fe$^{3+}$ ions in environment and biological system at about one ppm level (Figure 5). Two stable MOFs, $[\text{Zr}_2\text{O}_2\text{(OH)}_2\text{H}_2\text{O}_2\text{L}_2]_2$ (BUT-14) and $[\text{Zr}_2\text{O}_2\text{(OH)}_2\text{H}_2\text{O}_2\text{L}_2]_2$ (BUT-15) were designed and synthesized for the detection of metal ions in water. Two new ligands utilized for construction of the MOFs, namely, 5',5''-bis(4-carboxyphenyl)-[1,1':3',1':4'',4':1''',3''',4''',1'''''-quenquephene]4,4'''-dicarboxylate (L$^1$) and 4,4',4''',4'''(4,4'-phenylene)bis(pyridine-6,4,2-triyl)tetrabenzocate (L$^2$). Interestingly, they show intense fluorescence in water, which can be solely quenched by trace amounts of Fe$^{3+}$ ions. The detection limits towards the Fe$^{3+}$ ions were calculated to be 212 and 16 ug/L, respectively. The efficient fluorescent quenching effect is attributed to the photoinduced electron transfer between Fe$^{3+}$ ions and the ligands in these MOFs (Figure 6).\textsuperscript{[13]} Ming et al. reported a Pb(II)-Na(I) coordination polymer, $[\{\text{Pb}_{10}\text{Na}_{10}\}[\text{Me}_2\text{NH}_{2}\text{C}_2\text{H}_4\text{OH}_{10}]_{16}]$ (6) (H$_2$L=4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid). Luminescent investigations reveal that 6 can detect Fe$^{3+}$ with relative high sensitivity and selectivity, and show broad linear range of 0–1000 μM, as well as low detection limits of 8.65 nM for Fe$^{3+}$.\textsuperscript{[17]} The sensing properties of Zr-based MOF structure UiO-66-BI towards different ions were studied, and the results demonstrated that UiO-66-BI showed excellent selective luminescent sensing of Fe$^{3+}$ ions in water.\textsuperscript{[15]} Otherwise, Cd(II)-MOFs,\textsuperscript{[19]} $[\text{Cd}_2\text{Na}(\text{Me})_6][\text{Eu}(\text{OH})(\text{bpt})(\text{H}_2\text{O})_2](\text{DMF})_2\cdot(\text{H}_2\text{O})_n$\textsuperscript{[20]} [Eu(2HL)(DMF)(H$_2$O)$_2$] 3H$_2$O, [Tb(2HL)(DMF)(H$_2$O)$_3$] 3H$_2$O (H$_2$L=2,8,14,20-tetra-ethyl-hexa-6,12,18,24-tetra-oxo-4,10,16,22-tetra-carboxy-methoxy-calix[4]aren)\textsuperscript{[21]} and [Eu(FDC)]-DMA(H$_2$O)$_2$]DMA·4·5H$_2$O (H$_2$FDC=9,9-dimethyl-2,7-fluorenedicarboxylic acid, DMA=dimethylacetamide)\textsuperscript{[22]} also display high-sensitivity for Fe$^{3+}$.

![Figure 5](image)

(a) Coordination environment of the Cd(II) ion in 5, also showing the trans-trans-trans conformation of bim. Symmetry codes: #2 = x-2, y-1, z+1; #3 = x-1, y, z; (b) The relative maximum emission intensity of 5 by introducing different metal ions with the same concentration of 0.075 mM in the final mixture ($\lambda_{ex}$=300 nm); (c) The maximum intensity (Bottom) of 5 dispersed in HEPES aqueous buffer solution (pH=7).

Sensing of Cu$^{2+}$ ion

The 2,2'-bipyridyl moieties lining the channels of two designer-metal-organic frameworks, UiO-bpydc and Eu-bpydc (bpydc is 2,2'-bipyridine 5,5'-dicarboxylic acid), recognize and preconcentrate metal ion analytes, and in the case of Eu-bpydc, transfer energy to the Eu$^{3+}$ centers, to provide highly sensitive luminescence sensors for transition metal ions (Figure 7). Comparing the sensitivities of the UiO-bpydc and Eu-bpydc towards the same metal ion, significant difference can also be identified. In particular, Cu$^{2+}$ gives a relatively high quenching response in the Eu-bpydc MOF, but not in UiO-bpydc.\textsuperscript{[23]} Photoluminescence measurement of a novel neodymium-organic framework (Nd-MOF) based on Nd(III) dinuclear nodes, with formula $[\text{Nd}_2\text{NH}(\text{BDC})_2\text{DMF})_2\cdot\text{H}_2\text{O}]$ (7) (NH$_2$BDC=aminoterephthalic acid) indicates that 7 exhibits excellent near infrared luminescence. In addition, 7 displays fast and selective sensing of Cu$^{2+}$ (Figure 8),\textsuperscript{[24]} which represents the first near infrared fluorescent probe of MOFs used for detection. [H$_2$N(Me)$_2$]-[Eu(1L$_2$)(HCO$_2$)(DMF)(H$_2$O)] (H$_2$L=2,6-di30,50-dicarboxyphenyl)glyridine) also reveals high luminescence selectivity and sensitivity for Cu$^{2+}$ ions as a result of weak contacts between pyridyl sites in L$^1$ and Cu$^{2+}$.\textsuperscript{[25]}

Sensing of Ag$^{+}$ ion

The Sm$^{3+}$-doped MOF has been used for highly sensitive sensing of Ag$^+$, and the weak fluorescence of Sm$^{3+}$-doped MOF was greatly enhanced by Ag$^+$.\textsuperscript{[26]} Besides, a robust gallium carboxylate Ga(OH)(btec)·0.5H$_2$O (MIL-61) is selected as parent MOF to prepare Ln-MIL-61 by PSMs. The weak fluorescence of Sm$^{3+}$ or Dy$^{3+}$ doped MIL-61 is effectively sensitized by Ag$^+$. Furthermore, the Sm-MIL-61 shows more highly sensitive and selective sensing towards Ag$^+$, which is a promising optical sensor for Ag$^+$ detection in several of daily water samples.\textsuperscript{[27]} Otherwise, a new approach inspired by fluorescent labeling technology to fluorescently functionalize MOFs via post-modification is reported. A fluorescein-containing MOF FITC@BTPY-NH$_2$ was synthesized for selective sensing and adsorption of Ag$^+$ in aqueous solution.\textsuperscript{[28]}

![Figure 6](image)

Figure 6 Fluorescent spectra of (a) BUT-14 and (b) BUT-15 in water in the presence of different concentrations of Fe(NO$_3$)$_3$ under excitation at 330 and 320 nm, respectively (Inset: SV plots of Fe$^{3+}$ ions); Fluorescent quenching percentage of (b) BUT-14 and (d) BUT-15 in water by 1 mM different metal ions under excitation at 330 and 320 nm, respectively, at room temperature (Inset: photographs of BUT-15 and BUT-15-Fe$^{3+}$ samples in water under UV light of 365 nm, and photographs of them as solid).
Luminescent Metal-Organic Frameworks

Sensing of other metal ions

A novel 3D microporous compound \( \text{Zn}_2(\text{Htca})_2(4,40-\text{bpy})_2(\text{H}_2\text{O})_2 \) (MOF-COOH) containing uncoordinated carbonyl groups pointing to the pores was prepared. The uncoordinated carbonyl groups in the channels can act as postsynthetic modification sites for covalent exchange. The MOF-COOH compound can serve effectively and selectively as an antenna for sensitizing the visible-emitting Tb\(^{3+}\) cation.\(^{[20]}\) \( \text{Zn}^{2+}(\text{p-TipHdIC})_2 \), bearing two novel substituted imidazoledicarboxylate ligands, 2-(p-N-Imidazol-1-yl)-phenyl-1H-imidazole-4,5dicarboxylic acid (p-IPhHdIC) and 2-p-(1H-1,2,4-triazol-1-yl)-phenyl-1H-imidazole-4,5dicarboxylic acid (p-TipHdIC- DC) shows good luminescent sensing of \( \text{K}^{+} \).\(^{[20]}\) Two novel pillared MOFs \( \text{Zn}(\text{trz})(\text{tda}) \cdot \text{DMA CLHOH} \) and \( \text{Zn}(\text{trz})(\text{bpdc}) \cdot \text{DMA} (\text{H}_{3}\text{dta}=2,5-thiophenicarboxylic acid, \text{H}_2\text{bpdc}=4,4'-\text{di-phenylidicarboxylic acid}) \) were obtained under solvothermal condition and displayed a certain degree of framework stabilities in both acid/base solutions and water. The luminescence intensity of their activated phase are sensitive to metal ions, particularly \( \text{Cd}^{2+} \) ions.\(^{[20]}\) A new superstable, anionic terbium-metal-organic-framework, \( \text{H}_2\text{N(CH}_3)_2\cdot\text{[Tb}^{3+}\text{cpp}_3\text{][H}_2\text{O}_3] \), (H\(_2\)cpp=5-(4-carboxyphenyl)picolinicacid), is successfully prepared, which can be used as a turn-on, highly-sensitive fluorescent sensor to detect Eu\(^{3+}\) and Dy\(^{3+}\), with a detection limit of \( 5 \times 10^{-10} \) M in dimethyl formamide, respectively.\(^{[21]}\)

Sensing of gas molecules

Sensing of \( \text{H}_2\text{S} \)

The azide \((1-\text{N}_3)\) and nitro \((2-\text{NO}_2)\) functionalized \( \text{Ce MOFs} \) have been synthesized under similar solvothermal conditions using ammonium cerium(IV) nitrate and \( \text{H}_3\text{BDC-X} \) (BDC=1,4-benzenedicarboxylate; X=-\text{N}_3 \) for \( 1-\text{N}_3 \) and -\text{NO}_2 for \( 2-\text{NO}_2 \). The thermally activated forms of both compounds \((1-\text{N}_3 \) and \( 2-\text{NO}_2 \)) show fast response time, excellent selectivity and sensitivity for the detection of \( \text{H}_2\text{S} \) under physiological conditions (HEPES buffer, pH 7.4) through fluorescence ‘turn-on’ mechanism. The detection limits (12.2 µM for \( 1-\text{N}_3 \) and 34.8 µM for \( 2-\text{NO}_2 \)) of both materials lie within the range of \( \text{H}_2\text{S} \) concentration observed in the biological systems. The materials can selectively detect \( \text{H}_2\text{S} \) even in the presence of other competing biomolecules.\(^{[22]}\) Chen reported a coordination polymer nanoparticle composed of \( \text{B}^{3+} \) ions, \( \text{Ag}^+ \) ions, and adenosine monophosphate, where the fluorescence of \( \text{B}^{3+} \) ions was sensitized by \( \text{Ag}^+ \) ions.\(^{[23]}\) When \( \text{H}_2\text{S} \) was introduced, a fluorescence quenching would be observed because of strong affinity of \( \text{H}_2\text{S} \) to \( \text{Ag}^+ \) ions. In addition, Ma et al. also reported a heterogeneous nano MOF fluorescence probe for highly selective and sensitive detection of \( \text{H}_2\text{S} \) in living cells. Legrand et al. reported the designed MOF-based system achieving \( \text{in vitro} \) \( \text{H}_2\text{S} \) dosing by turn-on fluorescence with unprecedented sensitivity, and Li et al. have designed and synthesized a novel porous polymeric fluorescence probe, MN-ZIF-90, for quantitative \( \text{H}_2\text{S} \) fluorescence detection.\(^{[23]}\)

Sensing of \( \text{CO}_2 \)

Pentyala investigated the gas sensing behavior of Mg- and Co-MOF-74 towards \( \text{CO}_2 \) by means of work function based readout with Kelvin Probe.\(^{[24]}\) The observed changes in work function were explained in field of interactions between open metal sites of Mg-MOF-74 coordinated with water and gas molecules.

Sensing of \( \text{O}_3 \)

Highly-sensitive sensors for trace oxygen analytes are demanded in many oxygen-free environments, such as medical environment, chemical industry, and so on. Lin et al. reported the first luminescent MOFs for \( \text{O}_3 \)-sensing, by using bridging ligands derived from classic phosphorescent precious metal complexes. By connecting \( \text{Zn}(\text{II}) \) with two metalloligands derived from a common \( \text{O}_3 \) sensitive complex \( \text{Ir}(\text{ppy}) \) (ppy=2-phenylpyridine), three phosphorescent MOFs were synthesized.\(^{[22]}\) At 1 bar \( \text{O}_3 \), the luminescence quenching efficiencies for the three MOFs and the two ligands are in the range of 32%–59% and 8%–16%, respectively, in which the tetranuclear-based structure of \( \text{H}_2\text{MOF-74} \) coordinated with water and gas molecules.

Sensing of other gas molecules

A classic anionic metal-organic framework \([\text{bio-MOF-1}, \text{Zn}(\text{ad})_4(\text{BPDC})_3\text{O}2\text{MeCNH}_3] \) (BPDC=2-hydroxy-1,4-‘dicarboxylate, \text{Ad}=adeninate) encapsulated by \( \text{Eu}^{3+}-\text{diketonate complex} \) via covalent exchange can be used for sensing volatile amines, which is of great significance in environment and industrial monitor.\(^{[25]}\) MIL-101(Cr) nanoparticles were successfully HF-free synthesized via hydrothermal method. Then resistive metal sensor was fabricated to investigate humidity sensing properties.\(^{[26]}\) The response time...
and recovery time are 17 s and 90 s, respectively, which illustrates that porous MIL-101(Cr) nanoparticles have great potential to be used as humidity sensing materials.

**Sensing of pH value**

One of the significant subjects in MOF-based chemical sensors is the detection of pH values in aqueous solution, especially for monitoring subtle pH changes in biological environments and living cells. Qi et al. used lanthanide Tb³⁺ ions and small molecular ligands to design and assemble a kind of pH-sensitive MOF nanoparticle based on intramolecular-charge-transfer effect.[41] This kind of made-to-order MOF nanoparticle for pH is highly specific and sensitive and could be used to indicate fluorescently pH value of strong acidic solution via preset mechanism through luminescence of Tb³⁺. Otherwise, a strategy utilizing mixed-lanthanide metal-organic frameworks (MOFs) for self-referencing and colorimetric luminescent pH sensing has been developed. The mixed-lanthanide MOFs Eu₂Tb₃H₂dpda [s=0.097, 0.205, 0.303, H₂dpda=4-(3,5-dicarboxyphenyl)pyridine-2,6-dicarboxylic acid] exhibit excellent stability in phosphate buffer solution with pH values varying from 3.90 to 7.50.[42] Aguilleras-Sigal et al. reported firstly the pH-dependent fluorescence of UiO-66-NH₂ across the wide range from 1 to 9.[43] By application of a postsynthetic modification (PSM) diazotisation strategy, they synthesized new material, UiO-66-N=N-Ind, which shows increased chemical stability and enhanced sensing up to pH 12.

**Sensing of temperature**

A luminescent lanthanide metal-organic framework (MOF) based on Eu²⁺ and Tb³⁺ ions with 2-phenylbuccinato (EuTb-psa) was obtained solvothermally to explore its behavior as a temperature sensor in an unconventional temperature range from 13.5 to 313.5 K.[44] The first single-lanthanide MOFs ratiometric luminescent thermometer(Me₂N)₃[Eu₂(FDC)₄(NO₂)]·4H₂O has been prepared.[45] Due to the suitable triplet excited state energy of the ligand (the difference between the T₁ and D₀ levels of Eu³⁺ is lower than 1500 cm⁻¹), the Eu³⁺ to the ligand triplet emission intensity ratio allows measuring the temperature in the 12–320 K range, with a relative thermal sensitivity up to 2.7% K⁻¹ at 170 K (0.33% K⁻¹ at 300 K) and a repeatability up to 96%. In binary co-doped system, Eu₃₀₀₆₀Tb₉₀₃L and Eu₃₀₀₆₀Tb₉₀₃L (H₂L=2,6-di(2',4'-dicarboxylphenyl)pyridine) show good linear responses to temperature with high sensitivities over a wide range (from 77 K to 450 K) (Figure 9), of which Eu₃₀₀₆₀Tb₉₀₃L exhibits a maximum relative sensitivity (Sₐ) of 3.76% K⁻¹ at 450 K.[46] The value is comparable to those of other excellent LnMOF thermometers reported recently whereas the response temperature range is greatly enlarged.

![Figure 9](image-url) (a) Solid-state emission spectra of Eu₃₀₀₆₀Tb₉₀₃L recorded between 77 K and 450 K excited at 355 nm; (b) Temperature-dependent normalized emission intensity of the D₀→F₁ and D₀→F₂ transitions of Eu₃₀₀₆₀Tb₉₀₃L.

**Conclusions**

Luminescent MOFs are an exactly fascinating class of multifunctional chemosensors through the unique performance of MOF materials with suitable porosity, specific functional groups, higher quantum yield, and tunable luminescent properties. Although at the early stage of their development, luminescent MOFs have been a versatile and remarkable type of chemical sensors for the detection of ions, nitro explosives, gas molecules, pH value, and temperature. While luminescent MOFs hold great promises for chemical sensing, there are important issues that should be addressed in the area of chemical sensing. First of all, a major challenge is to pre-design novel MOF materials with desired properties. Any specific application can theoretically be realized through the rational design of MOF materials in the terms of compositions, shapes, porosity, and luminescent properties. Secondly, the majority of MOF sensors are based on the monitoring of emission intensity changes in a single emission peak by a fluorometer. The accuracy can be heavily affected by the optoelectronic drifts of excitation power and detectors. Thirdly, most of them can only be used in organic solvents due to their poor stability in aqueous solution. Forthly, these materials often sense more than two targeted analytes simultaneously. An improved approach is to couple luminescent MOFs with other methods of signal transduction, such as interferometry, localized surface plasmon resonance (LSPR), and electrical/electrochemical/mechanical schemes, developing multifunctional MOFs for the diverse chemosensory applications.[1] Briefly, luminescent MOFs will be extensively pursued for their practical applications in chemical sensing.

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