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. Metal-organic frameworks 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 in chemical sensing owing to their suitable porosity, specific functional groups, higher quantum yield and tunable luminescent properties. This review summarizes some examples of the application of luminescent metal-organic frameworks for sensing of nitro explosives, metal ions, small molecules, pH value and temperature.

Keywords metal-organic frameworks, luminescent, sensing

Introduction

Nowadays, there has been 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.^[1] 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.^[2] 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.^[3] They have attracted great attention owing to their extensive applications in a wide areas such as light emitting,^[4] chemical sensing,^[5] gas storage and separation,^[6] heterogeneous catalysis,^[7] drug delivery,^[8] and magnetic properties.^[9] Among them, some luminescent MOFs are utilized for chemical sensing mostly based on the photoluminescence and tunable porous structure.^[10] 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 $\{[\text{Tb}(\text{Hbzptc})]_2 \cdot \text{bpp} \cdot 2\text{H}_2\text{O}\}_n$ (**1**) (H_4bzptc =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^{-5} M. The Stern-Volmer plots of the relative luminescent intensity (I_0/I) versus the nitrobenzene concentration, where I_0 and I are the luminescent intensities of compound **1** before and after adding nitrobenzene, respectively. Nonlinear Stern-Volmer curves can be well-fitted by the exponential equations of $I_0/I = 1.72e^{57700[\text{NB}]} - 0.72$ with quenching constant of 9.92×10^4 in the low concentration range.^[11] Wang *et al.* explored systematically the fluorescence sensing responses of $[\text{Cd}_2(\text{H}_2\text{L})_2(\text{H}_2\text{O})_5] \cdot 5\text{H}_2\text{O} \cdot 2\text{DMF}$ (**2**) [H_4L =2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide] to small organic molecules. Notably, complex **2** can act as a potential multifunctional fluorescence material for sensing of *p*-nitroaniline ion with high stability, selectivity and sensitivity (Figure 2).^[12] Zhou *et al.* reported a compound $[\text{Eu}_2\text{L}(\text{H}_2\text{L})(\text{NMP})_2] \cdot \text{H}_2\text{O}$ (**3**) (H_4L =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 (K_{sv}) of $2.084 \times 10^3 \text{ M}^{-1}$ (Figure 3).^[13] Zhu *et al.* reported a MOF $[\text{Cd}(\text{cis-chdc})(\text{anti-bpe})(\text{H}_2\text{O})]_n$ (**4**) [H_2chdc =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.^[14]

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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_0/I 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 Fe³⁺ ion

The first photoluminescent Cd(II)-organic framework {[Cd(5-asba)(bimb)]_n (**5**) based on a multi-functional ligand 2-amino-5-sulfobenzoic acid (H₂5-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 Fe³⁺ ions in environment and biological system at about one ppm level (Figure 5).^[15] Two stable MOFs, [Zr₆O₄(OH)₈(H₂O)₄(L¹)₂] (BUT-14) and [Zr₆O₄(OH)₈(H₂O)₄(L²)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'',1''':3''',1'''-quinquephenyl]-4,4'''-dicarboxylate (L¹) and 4,4',4'',4'''-(4,4'-(1,4-phenylene)bis(pyridine-6,4,2-triyl))tetrabenzoate (L²). Interestingly, they show intense fluorescence in water, which can be solely quenched by trace amounts of Fe³⁺ ions. The detection limits towards the Fe³⁺ ions were calculated to be 212 and 16 µg/L, respectively. The efficient fluorescent quenching effect is attributed to the photoinduced electron transfer between Fe³⁺ ions and the ligands in these MOFs (Figure 6).^[16] Ming *et al.* reported a Pb(II)-Na(I) coordination polymer, {[Pb₃NaL₃](Me₂NH₂)₂(C₂H₅OH)_{1.5}(H₂O)_{10.5}]_n (**6**) (H₃L=4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid). Luminescent investigations reveal that **6** can detect Fe³⁺ 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 Fe³⁺.^[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 Fe³⁺ ions in water.^[18] Otherwise, Cd(II)-MOFs,^[19] [H₂N(Me)₂][Eu₃(OH)(bpt)₃(H₂O)₃](DMF)₂·(H₂O)₄,^[20] [Eu(HL)(DMF)(H₂O)₂]·3H₂O, [Tb(HL)(DMF)(H₂O)₂]·3H₂O (H₄L=2,8,14,20-tetra-ethyl-6,12,18,24-tetra-methoxy-4,10,16,22-tetra-carboxy-methoxy-calix[4]arene)^[21] and [Eu₂(FDC)₃-DMA(H₂O)₃]·DMA·4.5H₂O (H₂FDC=9,9-dimethyl-2,7-fluorene-dicarboxylic acid, DMA=dimethylacetamide)^[22] also display high-sensitivity for Fe³⁺.

Figure 5 (a) Coordination environment of the Cd(II) ion in **5**, also showing the *trans-trans-trans* conformation of bimb. 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 ($\lambda_{\text{ex}}=300$ nm); (c) The maximum intensity (Bottom) of **5** dispersed in HEPES aqueous buffer solution (pH=7).

Figure 6 Fluorescent spectra of (a) BUT-14 and (c) BUT-15 in water in the presence of different concentrations of Fe(NO₃)₃ under excitation at 330 and 320 nm, respectively (Inset: SV plots of Fe³⁺ 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-Fe³⁺ samples in water under UV light of 365 nm, and photographs of them as solid).

Sensing of Cu²⁺ 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 Eu³⁺ centers, to provide highly sensitive luminescent 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, Cu²⁺ gives a relatively high quenching response in the Eu-bpydc MOF, but not in UiO-bpydc.^[23] Photoluminescence measurement of a novel neodymium-organic framework (Nd-MOF) based on Nd(III) dinuclear nodes, with formula {[Nd₂(NH₂-BDC)₃(DMF)₄]_n (**7**) (NH₂-BDC=2-aminoterephthalic acid) indicates that **7** exhibits excellent near infrared luminescence. In addition, **7** displays rapid and selective sensing of Cu²⁺ (Figure 8),^[24] which represents the first near infrared fluorescent probe of MOFs used for detection. [H₂N(Me)₂]-[Eu₃(L)₂(HCOO)₂(DMF)₂(H₂O)] [H₄L=2,6-di(30,50-dicarboxyl-phenyl)pyridine] also reveals high luminescent selectivity and sensitivity for Cu²⁺ ions as a result of weak contacts between pyridyl sites in L⁴⁻ and Cu²⁺.^[25]

Sensing of Ag⁺ ion

The Sm³⁺-doped MOF has been used for highly sensitive sensing of Ag⁺, and the weak fluorescence of Sm³⁺-doped MOF was greatly enhanced by Ag⁺.^[26] Besides, a robust gallium carboxylate Ga(OH)(btec)·0.5H₂O (MIL-61) is selected as parent MOF to prepare Ln-MIL-61 by PSMs. The weak fluorescence of Sm³⁺ or Dy³⁺ 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.^[27] Otherwise, a new approach inspired by fluorescent labeling technology to fluorescentize functionalize MOFs via post-modification is reported. A fluorescein-containing MOF FITC@BTPY-NH₂ was synthesized for selective sensing and adsorption of Ag⁺ in aqueous solution.^[28]

Figure 7 The crystal structure of the two MOFs with free bpymoieties in the channel. (a) UiO-bpydc; (b) and (c) Eu-bpydc; scheme in the figures also showed how the metal chelation interrupts energy transfer and emission.

Figure 8 (a) The luminescence spectra of **7** dispersed into different metal ions M^{2+} DMF solution; (b) The NIR luminescence spectra of **7** immersed in DMF solutions with different concentrations of $CuCl_2$ (excited at 808 nm by laser).

Sensing of other metal ions

A novel 3D microporous compound $[Zn_3(Httca)_2(4,40\text{-bpy})-(H_2O)_2]_n(\text{MOF-COOH})$ containing uncoordinated carbonyl groups pointing to the pores was prepared. The uncoordinated carbonyl groups in the channels can act as postsynthetic modification sites for cation exchange. The MOF-COOH compound can serve effectively and selectively as an antenna for sensitizing the visible-emitting Tb^{3+} cation.^[29] $[Zn(p\text{-TIPhHIDC})]_n$, bearing two novel substituted imidazolidicarboxylate ligands, 2-(*p*-*N*-imidazol-1-yl)-phenyl-1*H*-imidazole-4,5-dicarboxylic acid (*p*-IPhH₃IDC) and 2-(*p*-(1*H*-1,2,4-triazol-1-yl)-phenyl-1*H*-imidazole-4,5-dicarboxylic acid (*p*-TIPhH₃IDC)) shows good luminescent sensing of K^+ .^[30] Two novel pillared MOFs $[Zn_2(\text{trz})_2(\text{tda})] \cdot \text{DMA} \cdot \text{CH}_3\text{OH}$ and $[Zn_2(\text{trz})_2(\text{bpdc})] \cdot \text{DMA}$ ($H_2\text{tda}$ =2,5-thiophenedicarboxylic acid, $H_2\text{bpdc}$ =4,4'-di-phenyldicarboxylic 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 Cd^{2+} ions.^[31] A new superstable, anionic terbium-metal-organic-

framework, $[H_2N(CH_3)_2][Tb(\text{cpa})_2(H_2O)_2]$, ($H_2\text{cpa}$ =5-(4-carboxyphenyl)picolinic acid), 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 limitation of 5×10^{-8} and 1×10^{-4} M in dimethyl formamide, respectively.^[32]

Sensing of gas molecules

Sensing of H_2S

The azide (**1-N₃**) and nitro (**2-NO₂**) functionalized Ce MOFs have been synthesized under similar solvothermal conditions using ammonium cerium(IV) nitrate and $H_2\text{BDC-X}$ (BDC =1,4-benzenedicarboxylate; $X=-N_3$ for **1-N₃** and $-NO_2$ for **2-NO₂**). The thermally activated forms of both compounds (**1'-N₃** and **2'-NO₂**) show fast response time, excellent selectivity and sensitivity for the detection of H_2S under physiological conditions (HEPES buffer, pH 7.4) through fluorescence 'turn-on' mechanism. The detection limits (12.2 μM for **1'-N₃** and 34.8 μM for **2'-NO₂**) of both materials lie within the range of H_2S concentration observed in the biological systems. The materials can selectively detect H_2S even in the presence of other competing biomolecules.^[33] Chen reported a coordination polymer nanoparticle composing of Tb^{3+} ions, Ag^+ ions, and adenosine monophosphate, where the fluorescence of Tb^{3+} ions was sensitized by Ag^+ ions.^[34] When H_2S was introduced, a fluorescence quenching would be observed because of strong affinity of H_2S to Ag^+ ions. In addition, Ma *et al.* also reported a heterogeneous nano MOF fluorescence probe for highly selective and sensitive detection of H_2S in living cells. Legrand *et al.* reported the designed MOF-based system achieving *in vitro* H_2S 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 H_2S fluorescent detection.^[35]

Sensing of CO_2

Pentyala investigated the gas sensing behavior of Mg- and Co-MOF-74 towards CO_2 by means of work function based readout with Kelvin Probe.^[36] 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 O_2

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 O_2 -sensing, by using bridging ligands derived from classic phosphorescent precious metal complexes. By connecting Zn(II) with two metalloligands derived from a common O_2 sensitive complex $Ir(\text{ppy})_3$ (ppy =2-phenylpyridine), three phosphorescent MOFs were synthesized.^[37] At 1 bar O_2 , 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 showing the highest efficiency of 59%. Moreover, Chen synthesized a Cu(I)-triazolate $[Cu(\text{detz})]$ ($H\text{detz}$ =3,5-diethyl-1,2,4-triazole) NMOF, which was not luminescent in air due to the quenching effect by oxygen.^[38]

Sensing of other gas molecules

A classic anionic metal-organic framework [bio-MOF-1, $Zn_8(\text{ad})_4(\text{BPDC})_6\text{O} \cdot 2\text{Me}_2\text{NH}_2$ (BPDC =biphenyl-4,4'-dicarboxylate, Ad =adeninate)] encapsulated by Eu^{3+} - β -diketonate complex *via* cation exchange can be used for sensing volatile amines, which is of great significance in environment and industrial monitor.^[39] MIL-101(Cr) nanoparticles were successfully HF-free synthesized *via* hydrothermal method. Then resistive humidity sensor was fabricated to investigate humidity sensing properties.^[40] 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 Tb^{3+} 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 H^+ is highly specific and sensitive and could be used to indicate fluorescently pH value of strong acidic solution via preset mechanism through luminescence of Tb^{3+} . 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 $Eu_xTb_{1-x}Hdpda$ [$x=0.097, 0.205, 0.303$, $Hdpda=4-(3,5\text{-dicarboxyphenyl})pyridine-2,6\text{-dicarboxylic acid}$] exhibit excellent stability in phosphate buffer solution with pH values varying from 3.90 to 7.50.^[42] Aguilera-Sigalat *et al.* reported firstly the pH-dependent fluorescence of $UiO\text{-}66\text{-}NH_2$ across the wide range from 1 to 9.^[43] By application of a postsynthetic modification (PSM) diazotisation strategy, they synthesized a new material, $UiO\text{-}66\text{-}N=N\text{-ind}$, which shows increased chemical stability and enhanced sensing up to pH 12.

Sensing of temperature

A luminescent lanthanide metal-organic framework (MOF) based on Eu^{3+} and Tb^{3+} ions with 2-phenylsuccinate ($EuTb\text{-}psa$) 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 ($Me_2NH_2)_3[Eu_3(FDC)_4(NO_3)_4]\cdot 4H_2O$ has been prepared.^[45] Due to the suitable triplet excited state energy of the ligand (the difference between the T_1 and 5D_0 levels of Eu^{3+} is lower than 1500 cm^{-1}), the Eu^{3+} 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, $Eu_{0.0066}Tb_{0.9934}L$ and $Eu_{0.0089}Tb_{0.9911}L$ ($H_4L=2,6\text{-di}(2',4'\text{-dicarboxyphenyl})pyridine$) show good linear responses to temperature with high sensitivities over a very wide range (from 77 K to 450 K) (Figure 9), of which $Eu_{0.0066}Tb_{0.9934}L$ exhibits a maximum relative sensitivity (S_m) 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 (a) Solid-state emission spectra of $Eu_{0.0066}Tb_{0.9934}L$ recorded between 77 K and 450 K excited at 335 nm; (b) Temperature-dependent normalized emission intensity of the $^5D_4 \rightarrow ^7F_5$ and $^5D_0 \rightarrow ^7F_2$ transitions of $Eu_{0.0066}Tb_{0.9934}L$.

Conclusions

Luminescent MOFs are an exactly fascinating class of multifunctional chemosensors through the unique performance of MOF mate-

rials 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. Fourthly, 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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