Detection of mercuric ion in water environment based on luminescent metal–organic frameworks

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Abstract: Luminescent metal-organic framework (LMOF), as a class of metal-organic framework (MOF), is a novel class of porous material formed from metal ion and bridging organic ligands. Its unique structural and chemical properties have enabled us to reliably detect mercury ions, one of the most toxic contaminants in the environment. Additionally, the luminescence of LMOFs has made the detection process ever more convenient. In this paper, we pay attention on the change of luminescent intensity of these materials in the presence of Hg2+.

We focus on several key publications in this area, including examples of LMOFs with excellent performance on Hg2+ detection, and we expect this review will provide new guidelines for Hg2+ sensor engineering.

1. Introduction

Mercury in the environment is generally considered one of the most toxic contaminants. It is widely distributed as a result of various kinds of human activities, such as fossil fuel consumption and gold mining.[1, 2] Its ionic form (Hg2+), a widespread pollutant, can be readily methylated by aquatic organisms.[3] When inhaled, Hg2+ can lead to extensive pulmonary fibrosis, necrosis of proximal convoluted tubules and the presence of metallothionein protein in the kidneys.[4] Nowadays, one of the most threatening issues is that Hg2+ was found in water resources. Therefore, it is imperative to develop efficient method for Hg2+ detection. Current methodologies for detecting Hg2+ mainly include chromatography, spectrohotometry, and so on.[5-7] However, these conventional methods proved to be inappropriate for routine analysis, because they require bulky instruments and usually time consuming. By contrast, fluorometry with advantages such as ease of abrica tion, high sensitivity as well as short response time has attracted more and more attention in detection analytes.[8, 9]

Metal–organic frameworks (MOF) materials, constructed by two parts: transition metal ions and bridging organic ligands, aroused great attentions.[10] MOFs usually have porous network structures, functional groups, and tailorabl e geometries. [11] These properties are attractive to a vast variety of usage, such as gas storage, catalysis and sensors.[12-14] In particular, luminescent MOFs (LMOFs) are a fascinating class that are both fundamentally important and technologically relevant.[15] They usually have luminescent behaviors from their special structure.[16] LMOFs is applicable in the detection of various different substances, such as nitro explosives, anions and DNA strands.[17-19] Detection of Hg2+ ions with LMOFs has recently been studied by researchers, and plenty improvement have been made in control over sensitivity, selectivity and even real-time conditions.

In this paper, we briefly review the recent advantages in LMOFs as luminescent sensors for Hg2+. Literature on the intensity-based detection of Hg2+ in water environments using LMOFs as sensors were reviewed. In our analysis we focus on the difference LMOF emission intensity changes with Hg2+ present.
in the water environment. This could be further divided into two key areas: luminescent quenching and luminescent enhancing.

2. **Mercuric ion detection**

Recently, many LMOFs have been used as mercuric ion sensors. Here, we have reviewed recent researches to discuss the sensing application of LMOFs on the mercuric ion detection. Based on the different change of the fluorescence intensity, including luminescent quench or enhance, respectively.

2.1 **Intensity-Based “Turn-off” detection**

Rachuri and coworkers designed a multi-responsive luminescent Zn(II) MOF for detection of Hg$^{2+}$.

\[20\] After dispersed the LCP [Zn(μ2-1Hade)(μ2-SO$_4$)] in the aqueous solution containing 1 × 10$^{-3}$ M MCl$_x$ (M = Zn$^{2+}$, Cd$^{2+}$, Cs$^+$, Ba$^{2+}$, Cu$^{2+}$, Na$^+$, K$^+$, Pb$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Cr$^{3+}$, Hg$^{2+}$), the intensity of the emission band of Hg$^{2+}$ at 395 nm decreased considerably. And the detection limit of this polymer to Hg$^{2+}$ is set to 70 nM. Moreover, as is shown in Fig. 1, with the addition of the polymer, the other ions remained unchanged, while the emission band of Hg$^{2+}$ was almost completely quenched. This shows the selective detection of this method.

A sensor for selective detection Hg$^{2+}$ ions based on a 3D porous layer MOF, [Cd$_x$BPDC)$_{0.5}$(L$_1$)(NO$_3$)].3.4DMF (1), was discovered by Liu and coworkers.

\[21\] After immersed 1 in a Hg$^{2+}$ solution (1.0 × 10$^{-2}$ M) for 5h, the quenching of luminescence intensities can be observed of Hg$^{2+}$ at 330 nm. Additional testing of Ba$^{2+}$ and Mg$^{2+}$ showed that there were little effects in the luminescent intensity, which indicates the selectivity of this method.

**Fig.1.** (a) Fluorescent spectra of LMOF in different solvents. (b) emission intensities of LMOF in different solvents.[20]

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Fu and coworkers reported a sensor for the detecting Hg\(^{2+}\) based on an anionic MOF, 
\[ [(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{TNB})_4/3](2\text{DMF})(3\text{H}_2\text{O}) \] (1, H\(_3\text{TNB}\) = 4, 40, 400-nitritotribenzoicacid).[22] In the presence of Hg\(^{2+}\), an 1×10\(^{-3}\) M aqueous solution of 1*DSM powder produced a quenching of fluorescence at 478nm. The detection limit was 1.75 ppb. Furthermore, the florescence properties of other ions, shown in Fig.2, was also studied, which showed the fluorescence intensity quenched by Hg\(^{2+}\) was hardly interfered by these cations. This goes to show the selectivity of this method.

![Fig.2](image_url)

**Fig.2** (a) Luminescence intensity change of 1⊃DSPM in 1 × 10\(^{-3}\) mol L\(^{-1}\) aqueous solution with different anions; (b) emission spectra change of 1⊃DSPM with addition of Cr\(_2\text{O}_7\)^{2-} ions (150 \(\mu\)L).[22]

Another sensor, [[Cd(BIPA)(tfbdc)(H\(_2\text{O}\))]-DMF]\(_n\) (1), was discovered by Wang and coworkers as a sensor for Hg\(^{2+}\) detection.[23] Different fresh DMF solutions containing 5 × 10\(^{-3}\) M M(NO\(_3\))\(_x\) (M\(_{z+}\) = Na\(^+\), Mg\(^{2+}\), Al\(^{3+}\), K\(^+\), Ca\(^{2+}\), Cr\(^{3+}\), Fe\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\)) were added into suspensions of MOF 1. Upon addition of 50 \(\mu\)L Hg\(^{2+}\) solution, the photoluminescence intensity of MOF 1 decreased to 11.00 % at 315 nm. The detection limit was 1.2 × 10\(^{-7}\) M. Additionally, further investigation into the fluorescence emission changes of MOF 1 with other metal cations shows minimal fluorescence intensity quenching, which indicates the selective detection of this method.

A Zr-MOF with high sensitivity and selectivity was designed for Hg\(^{2+}\) detection by Zhang and coworkers.[24] UiO-66-PSM (1 mg) was immersed into aqueous solutions (1 mL, 10\(^{-2}\) M) of M(NO\(_3\))\(_x\), (M\(^{z+}\) = Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Al\(^{3+}\), Cr\(^{3+}\), Fe\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Ag\(^+\), Zn\(^{2+}\), Hg\(^{2+}\), and Pb\(^{2+}\)). After the introduction of Hg\(^{2+}\), an obvious quenching on the cetonitril intensity of UiO-66-PSM was shown at
544 nm. Moreover, the metal ions tests showed that only Hg$^{2+}$ can give a obvious fluorescence signal change. This goes to show the selectivity of this method.

Razavi and coworkers reported another detection method of Hg$^{2+}$ based on the π-conjugated tetrazine motif of TMU-34(-2H) and the double solvent sensing method. [25] In the presence of Hg$^{2+}$ in acetonitrile and water, the PL spectra of TMU-34(-2H) showed 90% quenching and 243% enhancement respectively. In addition, as shown in Fig.3, when extra cations were added, none of them had obvious effect on the fluorescence intensity of TMU-34(-2H), which shows the selective detection of this method.

Another sensor for Hg$^{2+}$ detection based on the UiO-66@Butyne was reported by Samanta and coworkers. [26] After excited at 340 nm, UiO-66@Butyne showed a maximum emission peak at 537 nm, and the intensity was quenched with the addition of Hg$^{2+}$ ion. The limit of detection was 200 μL. Moreover, no response on the fluorescence intensity was observed with the addition of other cations, which shows the selectivity of this method.

Zhu reported a detection method for Hg$^{2+}$ based on LnMOFs.[27] In the presence of Hg$^{2+}$, the new highly luminescent porous LnMOF n coordinates with Hg$^{2+}$ to produce a maximal excitation wavelength of 368nm. Moreover, the LnMOF film immersed in Hg$^{2+}$ for 4h shows no luminescence with excitation in daylight. In a blank solution or in a 0.001 M Na$^+$, K$^+$, Mg$^{2+}$,Ca$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ solution, the red luminescence was shown. This goes to show the selective detection of this method.

2.2 Intensity-Based “Turn-on” detection

Another method of luminescent sensing is “turn on” detection, where the detection of Hg$^{2+}$ cause the increase of the fluorescence intensity. For example, a method of successive and specific detection of Hg$^{2+}$ based on a 2D MOF of \([\text{Cu}(\text{Dcbb})(\text{Bpe})\cdot\text{Cl}]_n\) (1) was reported by Hu and coworkers.[28] Addition P-DNA in different concentrations of MOF 1, and stirred for a certain time. After the addition of Hg$^{2+}$, the fluorescence intensity was enhanced at 518 nm, and the detection limit was 3.2 nM. Moreover, additional investigation into the fluorescence emission changes of MOF 1 with other metal cations showed minimal intensity enhancement, which indicates the selective detection of this method.
Wang and coworkers designed a novel method of Hg\textsuperscript{2+} detection based on Zr-Based MOFs (RuUiO-67).[29] With the addition of different concentration of Hg\textsuperscript{2+} into the RuUiO-67 suspension, as shown in Fig.4 the absorbance at $\lambda = 435$ nm increased quickly at initial 100 s and then reached to the maximum absorption level about 150 s later. The detection limit is determined to be 0.5 μM. Influences of other cationic species was also tested. Various possibly coexisting cations (Cr\textsuperscript{3+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, NH\textsubscript{4}\textsuperscript{+}, Mg\textsuperscript{2+}, Pb\textsuperscript{2+}, Fe\textsuperscript{3+}) were added in the solutions. There is no obvious color changes with other cationic species, which indicates RuUiO-67 can selective detecting Hg\textsuperscript{2+}.}

3. Conclusion
MOFs has gathered the attention of multiple research teams. As a class of MOFs, LMOFs with luminescent properties, was frequently used as sensors for the selective identification of target analytes. This review summarizes sensors based on luminescent MOFs for Hg\textsuperscript{2+} detection in recent years. Based on the optical signal changes in emission intensity, we divided the type of detection process into two categories: fluorescence quenching and fluorescence enhancing. Additionally, it is concluded that such sensors possess excellent sensitivity, selectivity and recyclability in the detection process.

Although LMOFs have proved to possess huge potential with impressive advantages in the detection of Hg\textsuperscript{2+}, there still need more efforts for their application in the real waters samples. LMOFs are mostly limited in organic solvents, and some fluorescent sensors are excessively expensive to fabricate. Moreover, most researchers are focused on the performance of detection, instead of exploring the mechanism, while deep analysis of the mechanism is the basis for the application of LMOFs in the future. Therefore, great strides must be made for LMOF-based sensors to be commercially applicable.
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