Metal-Organic Frameworks for Mercury Sensing and Removal

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Removal of mercury contaminants from nature receives a global attention from a biological and environmental standpoint. Recently, metal-organic frameworks (MOFs) show much promises in the adsorptive removal of mercury species. This review summarizes the recent studies on the MOF-based materials for mercury sensing and removal. The design of those materials are listed in five categories—use of unfunctionalized MOFs, linker design of MOFs, modification of MOF system, post-synthetic modification of the frameworks, and development of MOF-based composites. Finally, several key learning points are discussed in the aim of a facilitating new design of MOF-based sensors and adsorbents for mercury.

Keywords metal-organic frameworks, Hg sensing and removal, linker design, post-synthetic modification, composites

Introduction

Mercury contamination in water and soil receives growing awareness due to its toxicity even at very low concentration. In nature, mercury mainly exists as inorganic (Hg\(^0\)), organic (CH\(_3\)Hg\(^+\), primarily), and elemental (Hg\(^2+\)) forms, as well as complexes. Mercury is in our daily life, from coal, paint, batteries, and any electronic equipment to name a few, which could be easily spread out to nature through human activities. One of the major toxicities is the accumulation of mercury in the human body through the food chain, which could ultimately lead to cardiovascular disease, heart disease, serious cognitive and motion disorders, and even renal failure. Additionally, the World Health Organization recommends the standard Hg level in drinking water should be less than 1 ppb. Therefore, designing facile, cheap, portable mercury sensors with fast response is an important task from the consideration of human health and environmental concerns. More importantly, high-performing and cost-efficient mercury adsorbents are in urgent needs to remove the mercury contaminants from the environment, especially the natural water.

Over the years, technologies, such as chemical precipitation\(^{[1]}\), membrane\(^{[2]}\), ion exchange\(^{[3]}\), liquid extraction\(^{[4]}\), and adsorption\(^{[5]}\), have been developed to remove and recovery the mercury species from nature. Among all the techniques, adsorption, the adsorption of atoms, molecules or ions to the surface of a material, stands out due to its simplicity. In general, the adsorption could be divided into the physical and chemical adsorption based on the interactions between adsorbate and adsorbent (usually porous). The adsorbate is typically trapped in the adsorbents by van der Waals forces, which is known as physisorption. The degree of physisorption depends highly on the interaction sites, which is based on the nature of both adsorbent and adsorbate. One of the advantages of physisorption is the ease of regeneration, which could be achieved by simple heat treatment or ion/solvent exchange. In this case, porous material with high surface area with suitable pore size will be an ideal adsorbent. On the other hand, increasing the chemisorption will theoretically increase the overall capacity of adsorbate, which enhances ultimately the removal efficiency in the case of mercury. In order to provide such chemisorption beyond physisorption, a good adsorbent for mercury should consist of mercury-favored groups. Herein, metal-organic frameworks (MOFs) offer both flexibility and accommodation to satisfy these two requirements. In many cases, the adsorption of guest species (mercury in this review) in the MOF-based material alters significantly the chemical and physical properties of the framework, which also promises MOFs as potential probes to sense various species.

MOFs, also known as porous coordination polymers, are superior porous materials because of their high surface area, huge porosity, and capability for functionalization. Tremendous efforts have been spent on the utilization of MOFs in the field of material science and biomedical technology\(^{[6-20]}\). Moreover, a significant amount of studies focus on the modification of MOFs to tune precisely the chemical and physical properties via topological guidance, linker design, post-synthetic modification, and construction of MOF-based composites\(^{[21-29]}\). Those successful cases are excellent references for designing the new mercury sensor/adsorbent.

This review will outline the use of MOF-related materials as Hg sensors and/or adsorbents. The special design of the MOF-based system will be pointed out. Those special design will be summarized into five categories—unfunctionalized MOFs, linker design of MOFs, modification of MOF system, post-synthetic modification (PSM) of MOFs, and MOF-based composite. Each category is further grouped based on the purpose of mercury sensing or mercury removal. The known examples of using MOF-related materials as Hg sensors/adsorbents are listed in Table S1 (see Supporting Information) in terms of design, mercury capacity, removal efficiency, degree of luminescence quenching, recovery from real samples for each MOF. Moreover, a couple of key learning points will be summarized in the Conclusion and Outlook as further reference to design new MOF-related sensors/adsorbents for mercury.
MOF-based adsorbents for mercury sensing and removal

Use of unfunctionalized MOFs

Mercury sensing

Wang and coworkers[39] developed a MOF Complex 1 with 5,5’-[(ethane-1,2-diylbis(oxo)]diisophosphonic acid (H$_2$EDDA) as the ligand. Compare to the solid-state UV-Vis spectra of free H$_2$EDDA ligand, the maximum emission at 350 nm based on the charge transfer between ligand and metal significantly decreased, while the ligand-based emission at 410 nm became conspicuous after immersing Complex 1 into the Hg$^{2+}$ solution. The detection limit (LOD) of Complex 1 was below 2 nM, and $K_{Q}$ was calculated to be 4.3×10$^4$ M$^{-1}$. The mechanism studies concluded from the FT-IR spectra and electrospray ionization MS measurements implied that introduction of Hg$^{2+}$ induced the collapse of Complex 1, regenerating free H$_2$EDDA to interact with Hg$^{2+}$. Besides, this study also demonstrated that Complex 1 was highly selective for Hg$^{2+}$ in presence of alkaline, alkaline-earth or other transition metals, such as Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Ag$^{+}$, Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$.[10]

Wen and coworkers[31] used 2-amino-1,4-benzene-dicarboxylic acid (2-NH$_2$H$_2$bdc) with coligands—4,4'-bis(imidazole-1-ylmethyl)-biphenyl (bipb) and 1,3,5-tris(1-imidazolyl)-benzene (tb)—to obtain two MOFs Complex 2 ([Zn(2-NH$_2$H$_2$bdc)(bipb)])$_2$, respectively. Complex 2 was a 5-fold interpenetrated MOF, while Complex 3 was a 2-fold interpenetrated MOF. Complex 2 displayed a diminishing blue emission when treated with an increasing concentration of Hg$^{2+}$. XPS study revealed the N atoms of 2-NH$_2$H$_2$bdc chelated to Hg$^{2+}$ ions, which enabled Complex 2 to have a quenching constant $K_{Q}$ of 4550 M$^{-1}$. Among all the ions of NH$_3^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ag$^{+}$, Zn$^{2+}$, Cd$^{2+}$, Cl$^-$, F$^-$, Br$^-$, I$^-$, ClO$_4^-$, HCO$_3^-$, NO$_3^-$, NO$_2^-$, H$_2$PO$_4^-$, OAc$^-$, SO$_4^{2-}$, CO$_3^{2-}$, PO$_4^{3-}$, and CrO$_4^{2-}$, only Hg$^{2+}$ and CrO$_4^{2-}$ gave the most significant emission suppression. In addition, the detection limit for Complex 3 reached 4.2×10$^{-6}$ M.

Suress group[32] utilized the nucleobase adenine to construct Complex 4 ([Zn(µ$_2$-1H-ade)(µ$_2$-SO$_4$)]) as a Hg$^{2+}$ sensor. Complex 4 exhibited a ligand-based photoluminescence at 413 nm (vs. 416 nm for adenine) with the excitation at 295 nm. Among the cationic mixture containing Zn$^{2+}$, Cd$^{2+}$, Cs$^+$, Ba$^{2+}$, Cu$^{2+}$, Na$^+$, K$^+$, Pb$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Cr$^{3+}$, Mg$^{2+}$, and Hg$^{2+}$ as well as AsO$_3^{2-}$, only Hg$^{2+}$ quenched almost completely the emission band, with quenching constant $K_{Q}$ of 7.7×10$^7$ M$^{-1}$. As the addition of Hg$^{2+}$ (0.05–1.0 mM) increased, the emission intensity of Complex 4 decreased linearly. The LOD of Hg$^{2+}$ reached 70 nM in water. It was believed that the coordination between the free N atoms from the adenine in Complex 4 and Hg$^{2+}$ led to the reduction of luminescence intensity.

The effects on the utilization of N-containing heterocyclic linkers also show enhanced performance for mercury sensing. Lang, Li, Brommer, and coworkers[33] constructed Complex 5 [Zn(ppypva)[1,4-NDC)], where ppypva abbreviated for di-pyridin-2-yl-[4-(2-pyridine-4-yl-vinyl)-phenyl]-amine and 1,4-H$_2$NDC was 1,4-naphthalenedicarboxylic acid. In this network, the basic unit Zn(ppypva)$_n$, where each Zn ion coordinated tetrahedrally to two O atoms from the NDC linkers and two N atoms from the ppypva linkers, was further interconnected by 1,4-NDC to produce a honeycomb network. As a result, the uncoordinated N atoms of the ppypva linkers, which was also observed in their previous nitroaromatic sensing work[34] promised the chelating with other metal ions (Hg$^{2+}$ and MeHg$^+$ in this case). The ppypva ligand demonstrated excellent colorimetric chemosensing ability evident by the diminishing fluorescence peak at 460 nm and the growing new peaks at 580 nm along with the addition of Hg$^{2+}$. The coordination between the N atoms of ppypva and Hg$^{2+}$ was further confirmed by $^1$H NMR titration. The quenching effects of Hg$^{2+}$ was much more significant than any other ions, such as Na$^+$, K$^+$, Zn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, and Pb$^{2+}$. Moreover, the researchers adopted Complex 5 for the mercury sensing. Only the coordination with Hg$^{2+}$ and MeHg$^+$ displayed not only a blue shift of one of the emission maximum peaks but also a decrease of the other emission peak, leading to a color change from pale orange to blue.

Another work from the same group later reported the synthesis of five different Zn-based MOFs using another pyridine-appended ligand 1,4-bis(2-pyridin-4-yl-vinyl)naphthalene (1,4-bpyna) with coligand of 1,3,5-benzene-tricarboxylic acid (1,3,5-H$_3$BTC) or 4,4'-H$_2$OBA.[35] The 1,4-bpyna ligand demonstrated itself excellent colorimetric probing ability evident by quenching the fluorescence band at 446 nm and the emission band at 471 nm along with a growth of a small peak at 510 nm along with the addition of Hg$^{2+}$. The $^1$H NMR titration results approved that Hg$^{2+}$ coordinated to the N atoms of 1,4-bpyna, inducing the intramolecular charge transfer and quenching the fluorescence. Moreover, the sensing ability of one of the five polymer Complex 6, [Zn$_2$(1,4-bpyna)(1,3,5-BTC)(OH)]$_n$, was also tested. No significant fluorescence change of Complex 6 was observed in the presence of Na$^+$, Ag$^+$, Ba$^{2+}$, Mn$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Cu$^{2+}$. However, the addition of Hg$^{2+}$ quenched the emission at 444 and 472 nm with a growth of new and broad peak at 520 nm, leading to a visible color change from blue to yellow. The quenching constant $K_{Q}$ was reported with a value of 3.23×10$^6$ M$^{-1}$ with the detection limit of 0.057 ppm. Additionally, Complex 6 demonstrated recyclability without loss of fluorescence intensity after six cycles.

Rossin group[36] used m-[2-thiозало]benzoic acid and Zn$^{2+}$ with different basic auxiliary ligands, such as 4,4′-dipyrlyl (bpy) and 1,2-bis(4-pyridyl)ethane (Py2EtP), to develop four Zn-based MOFs (Complex 7–10). In Complex 7 and 10, the dangling N atoms from the thiazole-based linkers coordinated to the Hg$^{2+}$ ions in aqueous solution and induced ultimate quenching of the thiazole-based luminescence along with a partial polymer aggregation.

Cui, Qian, and coworkers[37] utilized the ligand 4,4′,4″,4‴-tetrakis(1,3,5-triytri-p-aminobenzoic acid (H$_2$TATAB) and Ln$^{3+}$ (Ln = Eu, Tb, Sm, Dy, Gd) ions to synthesize a series of LnTATAB MOF. The series of MOFs were all constructed with 1D Ln-carboxylate chain with 1D rhombic channel with the dimensions of around 27×23 Å, which turned out to be beneficial for the diffusion and accumulation of Hg$^{2+}$ in the framework. Among all the Ln-TATAB MOFs, Complex 11 (Tb-TATAB) exhibited not only good water stability but also high quantum yield for its photoluminescence, which promised it as a potential mercury sensor. The detection limit of Hg$^{2+}$ for Complex 11 was estimated to 4.4 nM. Furthermore, only Hg$^{2+}$ caused a significant luminescence quenching ($K_{Q}$ was 4851 M$^{-1}$) for Complex 11 in the presence of other ions, such as Zn$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Na$^+$, Ca$^{2+}$, Cr$^{3+}$, Mn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, and Fe$^{3+}$. The high affinity of Hg$^{2+}$ towards the N atoms of TATAB disturbed the antenna effect of TATAB towards to Tb$^{3+}$. Thanks to the high selectivity of Hg$^{2+}$, Complex 11 was successfully applied to detect the concentration of Hg$^{2+}$ in samples of river water, drinking water, and tap water with more than 95% recovery with standard derivation (STD) smaller than 5%.

Yang group[38] obtained a luminescent MOF Complex 12 (Tb$	ext{L}_{3}$+2(H$_2$O)$_2$H$_2$O), which was prepared using 5-(3′-carboxylphenyl)nicotinic acid (H$_2$L) and Tb$^{3+}$. It was found that Hg$^{2+}$ ions showed better affinity to the free pyridyl N atoms and the Hg–N coordination consequently quenched significantly the lumines-
cent intensity of Complex 12 at 545 nm. At the same time, other ions, such as Ba\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\), Co\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Pb\(^{2+}\), displayed much less influence on the intensity. To describe the question quantitatively, \(K_{d}\) was measured with a value of 7465 M\(^{-1}\). In addition, Complex 12 exhibited reusability up to five times with only 12.2% decrease of luminescent intensity along the way.

Wang, Long and coworkers\(^{59}\) used Complex 13 (ZIF-7) and Complex 14 (ZIF-60) to probe Hg\(^{2+}\) and CH\(_3\)Hg\(^+\) species, respectively. Interestingly, the fluorescence intensity decayed with an increasing concentration of Hg\(^{2+}\) for Complex 13 while enhanced with an increasing concentration of CH\(_3\)Hg\(^+\) for Complex 14, even in the presence of other ions. The authors attributed the different influences to the facts that Hg interacted with the N atoms of Complex 13 prevented the electron transfer, while the CH\(_3\)Hg\(^+\) inhibited the linker motion, slowed down the nonradioactive decay process, and increased the decaying of excited species. The detection limit of Hg\(^{2+}\) was 3 ng/mL for Complex 13, and that of CH\(_3\)Hg\(^+\) was 6 ng/mL for Complex 14. The researchers further used Complex 13 and Complex 14 in the local drinking water samples to preconcentrate Hg\(^{2+}\) and CH\(_3\)Hg\(^+\), respectively. It turned out that the recoveries were 102% and 96.2%, respectively.

Using another porotype MOFs Complex 15 (Cr-MIL-101), Guo group\(^{40}\) found the detection limit was 8.8 nm.

In the study of using Complex 16 (PCN-222/MOF-454), the researchers found the maximum capacity with the value of 35 mg/g and the detection limit was 0.02 µg/L. Most of the Hg\(^{2+}\) recovery percentage of Complex 16 was more than 98% from three real fish samples under the optimal conditions. Significantly, Complex 16 can be reused for 15 times without decrease of extraction recoveries.

As the PCN-2XX series show good stability, Gu group\(^{42}\) utilized Complex 17 (PCN-224), constructed with meso-tetra(4-carboxyphenyl)porphyrin as the bridging structs, as a Hg\(^{2+}\) sensor. The ligand-based florescence of Complex 17 showed a strong emission peak at 651 nm with a weak shoulder at 705 nm. The addition of Hg\(^{2+}\) introduced a reverse photoinduced electron transfer by coordinating to the N atoms of porphyrin in an out-of-plane mode and quenched the red emission within 2 min. The \(K_{d}\) constant for Complex 17 was calculated to be 6.4 x 10\(^{17}\) M\(^{-1}\) and the detection limit was 6 nM. The variation of Hg\(^{2+}\) concentration changed the color of Complex 17 gradually from purple to light green due to the charge transfer in the porphyrin-Hg complex, which could be easily distinguished by naked eye. Moreover, no obvious perturbation was overserved when other ions, such as Al\(^{3+}\), Ca\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\), Mg\(^{2+}\), Ni\(^{2+}\), K\(^+\), Na\(^+\), and Zn\(^{2+}\), were further introduced in the system. Furthermore, the Hg\(^{2+}\) species in Complex 17 could be easily recovered by adding I\(^{-}\), which had a high binding affinity towards Hg\(^{2+}\). Due to the ease synthesis, excellent stability, and facile regeneration, the researchers also applied Complex 17 as the probe in tap, distilled, and river water samples. The resultant recoveries maintained in the high range from 96%–104%.

**Mercury removal**

Roy and coworkers\(^{43}\) synthesized Complex 18 ([Ni(3-bpdp)(NCS)\(_2\)]\(_n\)), where the Ni ion coordinated octahedrally with four nitrogen atoms of the pyridine-based linkers in the equatorial position and two nitrogen atoms of the thiocyanate moieties in the apical position. Notably, the sulfur atoms of thiocyanate remained uncoordinated. After immersing Complex 18 into the Hg\(^{2+}\) solution, the sulfur coordinated to Hg atom with the evidence of increasing wavenumber of IR peaks (2138 cm\(^{-1}\) vs. 2069 cm\(^{-1}\) for thiocyanate groups in Complex 18) due to the decreasing electron density on sulfur. As a result, Complex 18 turned from green to grey (Ni:Hg = 1:2) with the naked eye. Complex 18 also demonstrated 94.3% removal efficiency with initial Hg concentration of 10 µg·L\(^{-1}\) and a maximum mercury capacity of 713 mg/g.

Zhou group\(^{44}\) developed two nitrogen-rich MOFs, Complex 19 (PCN-100) and Complex 20 (PCN-101), which were built on zinc paddle-wheels with 4,4'4''-s-triazine-1,3,5-triytr(o-aminobenzoate (TATAB), and benzene-1,3,5-triytris(azanediyl)-tri-benzoate (BTABT), respectively. They found that Complex 20 captured 0.61 Hg per formula unit, while Complex 19 increased the capacity to 1.38 Hg\(^{2+}\) per formula unit due to the coordination of aminopyridinato to Hg\(^{2+}\). Hu's group\(^{45}\) utilized Complex 21 (JUC-62) constructed from 3,3',5,5'-azobenzene-tetracarboxylate and copper paddle-wheel to preconcentrate Hg\(^{2+}\) in agricultural products. The nitrogen-richness and mesoporous nature endowed Complex 21 with the maximum adsorption capacity for Hg\(^{2+}\) of 836.7 mg/g. The removal efficiency of Hg\(^{2+}\) was ~80%, which was much higher compared to those of Pb\(^{2+}\), Cr\(^{3+}\), Cd\(^{2+}\), Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{3+}\), Zn\(^{2+}\), Na\(^+\), and K\(^+\). In the preconcentration of the black tea and mushroom samples, Complex 21 recovered successfully ~94.0% and 90.0% Hg\(^{2+}\), respectively.

Zhang group\(^{46}\) investigated the adsorption ability of Complex 22 (MOF-74-Zn). They found the maximum Hg\(^{2+}\) uptake reached to 63 mg/g at pH = 6 via both physisorption and chemisorption (the hydroxyl sites). Complex 22 showed the removal efficiencies of 54.48%, 69.71%, and 72.26% at the Hg concentrations of 20, 40, 50 ppb, respectively. They also found increasing the adsorption temperature increased the overall mercury uptake of Complex 22, since the adsorption of mercury was an endothermic monolayer reaction. In the last few years, the exploration of Zr-based MOFs becomes a hot topic in the field due to the strong coordination between Zr\(^{4+}\) and carboxylate produces multiple hydrophobic Zr-O units and endorses the corresponding MOFs with great stability. Shen and coworkers\(^{47}\) constructed the bromine-based analogues of Complex 23 (Uio-66), namely Complex 24 (Uio-66-Br) and Complex 25 (Uio-66-2Br), using bromine derivatives of 1,4-benzedicarboxylic acid as the ligands. During a five-hour period, the removal efficiencies of Hg\(^{2+}\) from the flue gas at 200 °C dropped from 96.0% to 52.2% and from 100% to 80% for Complex 23 and Complex 24, respectively. However, Complex 25 retained its removal efficiency as 100% for 48 h. It was clear that the two bromine atoms on the phenyl ring contributed predominantly to the steady removal efficiency during a long period of time. The highest accumulative adsorption amount of Complex 25 was 302 µg/g. Notably, the exposure of the MOF sorbents to SO\(_4\) enhanced the Hg\(^{2+}\) adsorption, while the presence of H\(_2\)O destroyed the crystalline structure and prohibited the adsorption.

**Linker design to construct MOFs**

**Mercury sensing**

Mercury sensing design has been approved to be one of the most efficient ways to improve the sensitivity and selectivity of a MOF-based sensor.\(^{48}\) Following this thought, Lai et al.\(^{49}\) found the fluorescent 2, 9-dimethyl-1,10-phenathroline (2,9-DMP) was an excellent probe to sense Hg\(^{2+}\) in water samples. As a result, they achieved Hg\(^{2+}\)-based MOFs Complex 26. Among 19 ions, only the coordination between Hg\(^{2+}\) and DMP almost quenched the fluorescence of DMP. Besides, the DMP linker exhibited high Hg\(^{2+}\)-sensitivity in a fast rate within 20 s.

**Mercury removal**

Later, more studies were focused on the incorporation of sulfur-containing groups, thiol and thioether in particular, on the framework. Since sulfur shows a high affinity towards mercury, an inclusion of sulfur-containing groups could increase the mercury capacity as well as the removal efficiency. Xu group\(^{50}\)
reported the free-standing thioether groups in Complex 27 constructed from tetrakis(methylthiol)-1,4-benzenedicarboxylic acid (TMDB) and Pb$^{2+}$. Complex 27 could adsorb Hg$^{2+}$ with the maximum ratio of Pb:Hg = 1:1. Majority of adsorbed Hg$^{2+}$ in Complex 27 could be easily removed using acetonitrile.

Similarly, exposed 2-methylthioethylthio side chain (SCH$_2$-CH$_3$SCH$_3$) was introduced into the cavity of MOF-5 to achieve Complex 28 (MOF-5-SCH$_2$CH$_3$SCH$_3$). The extended thioether chain significantly red-shifted the emission wavelength to 500 nm with a weaker side peak at 410 nm (vs. 390 nm for unfunctionalized ligand). At the same time, Complex 28 displayed the emission wavelength at 475 nm with a side peak at 410 nm. The flexible thioether chain enhanced the accessibility for the incoming Hg$^{2+}$ ions. However, the mercury capture of Complex 28 suppressed 90% of the original emission, which made it barely visible. The mercury uptake reached the Zn:Hg ratio of 5.56:1. Immersing 10 mg Complex 28 in 2.0 mL HgCl$_2$ in ethanol solution (84 mg/L), the removal efficiency was over 94% after six days.

Another similar study was based on Complex 29 (FJ-H12-Co), which consisted of 2,4,6-tri(1-imidazolyl)-1,3,5-triazine (Tmt), NCS$^-$, and Co$^{2+}$. In Complex 29, the exposed sulfur was pointing to the cavity, which promised Complex 29 a good selectivity of Hg$^{2+}$ over other common metal ions (except Cd$^{2+}$) with a maximum mercury capacity of 439.8 mg/g. The IR shift at 2072–2125 cm$^{-1}$ revealed that chemisorption from the exposed sulfur sites of NCS$^-$ to Hg$^{2+}$ contributed to the overall mercury capacity. Interestingly, the researched also packed 2 g Complex 29 into a 10 mL syringe, and this MOF-filled column was capable to purify a 50 mL solution with the concentration of 20 ppm.

Thanks to the stability of Zr-O clusters, Zr-based MOFs are an attractive class of MOF as platforms for most types of modifications. As an example, thiol groups were introduced to UiO-66 to produce Complex 30 (UiO-66-SH), shown in Figure 1. After immersing 10 mg Complex 30 in 10 mL 10 ppb Hg(NO$_3$)$_2$ solution for 12 hrs, the removal efficiency was over 99.9%. The maximum mercury capacity reached Zr:Hg = 6:1.82. Further studies of the adsorption showed that IR peaks at 2560 cm$^{-1}$, indicating S–H stretching, disappeared with the appearance of peaks at 355 cm$^{-1}$ for the Hg–S stretching. In the Hg vapor test, the adsorption of Hg vapor suppressed significantly the photoluminescence of Complex 30, which could hardly be seen by eye (vs. a near-white emission for Complex 30 itself).

Later, Liu and coworkers fabricated a stable MOF Complex 31 (Zr-DTDC) using 3,3-dimethylthioglycolic acid (HDTC) as the ligand. Complex 31 was successfully used to capture the Hg$^2+$ vapor with a distinct color change from white to yellow. The Hg$^2+$ vapor was believed to coordinate to the thiophene part of the linkers and suppressed ~70% of the photoluminescence emission of Complex 31. Interestingly, the binding energy of Hg 4f 7/2 shifted to 101.3 eV (vs. 99.9 eV for Hg$^0$), indicating a chemisorption of Hg$^2+$.

Beside of the sulfur-containing groups, researchers also utilized acylamide and hydroxyl groups in MOFs to adsorb Hg$^{2+}$ species. Luo and coworkers developed Complex 32 (Zn(nip)(L)-(DMF))$_n$, where H$_2$DPA=5-hydroxysalicilic acid and L=N$^+$N$^-$-(di(pyridine-4-yl)biphenyl)-4,4’-dicarboxamide. The hydroxyl and acylamide group attracted strongly Hg$^{2+}$ through chemisorption, leading to a maximum capacity of 278 mg·g$^{-1}$ and maximum removal efficiency to 84.76% when the initial concentration was 20 ppb.

In addition, Li group developed three ligand-based luminescent MOFs, namely LMOF-261-263. Among the series of MOFs, Complex 33 (LMOF-263) exhibited the best chemical and water stability and highest fluorescence quantum yield. Upon the addition of Hg$^{2+}$, ~84% of the emission intensity was quenched. $K_{	ext{qe}}$ of Complex 33 for Hg$^{2+}$ was 459,446 M$^{-1}$ with the detection limit of 3.3 ppb. Moreover, the removal efficiency of Complex 33 could reach to ~99.6%, and the maximum Hg$^{2+}$ adsorption capacity of Complex 33 was 380 mg/g. Additionally, the distribution coefficient of Complex 33 was determined to be 6.45×10$^3$ mL/g, which was high among all the reported values. In Complex 33, the electron density on the surrounding oxygen atoms elevated from the π bonding with the S atoms from sulfone group and showed a higher affinity to Hg$^{2+}$ via soft acid–soft base attractions, which led ultimately to the high distribution coefficient.

Modification of MOF system

Mercury sensing

Considering the fact that MOFs are 3D crystalline materials, the diffusion of mercury species through the network slows down the sensing or adsorption process. Therefore, changing the morphology of the adsorbent MOFs could be one strategy to address this issue. Chen group utilized adenosine, dipicolinic acid (H$_2$DPA) with Tb$^{3+}$ to form coordination polymer nanoparticle (CPNP), namely Complex 34 (Ad/Tb/DPA CPNP). The fluorescence of Complex 34 was very weak due to the prevented energy transfer from DPA to Tb$^{3+}$ by the photoinduced electron transfer from adenosine to DPA. However, Hg$^{2+}$ ions suppressed the energy transfer by coordinating to the N atoms of the adenosine linkers, consequently, enhancing the fluorescence of Complex 34 by ~5 fold. In a mixed solution with Cr$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, Cd$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Ag$^{+}$, Cu$^{2+}$, Pb$^{2+}$, Mg$^{2+}$, and Hg$^{2+}$, the interference of other cations was significantly weaker than that of Hg$^{2+}$. Moreover, Complex 32 exhibited a detection limit of 0.2 nM.

In Yang’s study, Complex 35 (Eu$_2$(bqdc)$_2$(H$_2$O)(DMF))$_n$ was developed in the form of film to sense Hg$^{2+}$. They used electrodiposition in combination with subsequent solvothermal synthesis to fabricate Complex 35 consisting of Eu$^{3+}$ and 2,2-biquinoline-4,4’-dicarboxylate with uncoordinated pyridyl N atoms. Upon the addition of Hg$^{2+}$, the chelating of Hg$^{2+}$ to the pyridyl N atoms of the linkers quenched the luminescence. Meanwhile, ions, such as Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Hg$^{2+}$, the interference of other cations was significantly weaker than that of Hg$^{2+}$. Moreover, Complex 35 exhibited a detection limit of 1×10$^{-6}$ M.

In spite of fine tuning the morphology, efforts were also spent on utilizing different solvents in the sensing system. For example, Long, Hou, Sepaniak, and coworkers adopted Complex 36 (MIL-53-Fe) and CCl$_4$ (the dispersant) as the platform to determine CH$_3$Hg$^+$. Complex 36 displayed fluorescence emission at 455 nm with excitation at 292 nm. Among the treatments of Hg$^{2+}$, CH$_3$Hg$^+$, EtHg$^+$, and PhHg$^+$ to Complex 36 with CCl$_4$, only CH$_3$Hg$^+$ increased the fluorescence signal with a
The detection limit of 0.36 ppb. No significant change of fluorescence intensity of Complex 36 was observed when Ag\(^{2+}\), Al\(^{3+}\), Ca\(^{2+}\), Cd\(^{2+}\), Cr\(^{3+}\), Cu\(^{2+}\), Fe\(^{3+}\), K\(^{+}\), Mg\(^{2+}\), Mn\(^{2+}\), Na\(^{+}\), Ni\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), Cl\(^{-}\), SO\(_4^{2-}\), or NO\(_3^{-}\) was introduced individually.

In another example, a dual-solvent sensing system with fast response was developed for Complex 37 (TMU-34), which consisted of zinc paddle-wheel Zn\(_2\)(COO)\(_4\), 4,4’-oxybis(benzoate OBA\(^-\)) and 3,6-di(pyrindin-4-yl)-1,4,5-tetrazine (DPT) linkers.\[^{29}\] Taking advantage of the feasibility of tetrazine in the field of sensing, the researchers found the emission peaks of Complex 37 (618 nm) enhanced with the increasing polarity of solvent. However, a red shift of photoluminescence emission was observed for Complex 37 in water compared to that in acetonitrile, which might be caused by the hydrogen bonding between water and nitrogen of tetrazine moieties. This shift promoted Complex 37 for cation sensing. In particular, the photoluminescence emission spectra of Complex 37 in presence of Hg\(^{2+}\) displayed 90% quenching in acetonitrile but 243% enhancement in water, respectively (Figure 2). Due to the distinct influence on the emission peaks in two different solvents, the author proposed to use 2D transduction to eliminate the interference of other cations and improve ultimately the sensitivity of Hg\(^{2+}\). As a result, the response time for Complex 37 for Hg\(^{2+}\) sensing was 15 s.

Chi group\[^{30}\] demonstrated another strategy to functionalize bio-MOF-1 with Ru(bpy)\(_{3}\)^{2+} in situ to obtain Complex 38. In Complex 38, the Ru(bpy)\(_{3}\)^{2+} was well-dispersed in the framework and led to a strong red fluorescence under the UV or blue light. Interestingly, only Hg\(^{2+}\) ions triggered the release of Ru(bpy)\(_{3}\)^{2+} in the presence of H\(^{+}\), causing other aqueous mixtures of Li\(^{+}\), Na\(^{+}\), K\(^{+}\), NH\(_4^{+}\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), and CH\(_3\)CH\(_2\)Hg\(^{-}\). The increasing concentration of Hg\(^{2+}\) accelerated significantly the release of Ru(bpy)\(_{3}\)^{2+} with the molar ratio of Ru(bpy)\(_{3}\)^{2+} to Hg\(^{2+}\) range from 103 to 106. This fast release was suspected to occur mainly based on the disassembly of Complex 38 resulted from the higher affinity of adenine towards Hg\(^{2+}\). This ion-responsive release made Complex 38 an excellent ultrasensitive sensor of Hg\(^{2+}\) with the LOD of 5.3×10\(^{-13}\) M. The preconcentration of Hg\(^{2+}\) from the water sample of Min River using Complex 38 was consistent with the results obtained using ICP-MS.

**Mercury removal**

Additionally, Wang and coworkers\[^{31}\] took advantage of the strategy of in situ ligand formation to embed an anionic framework Complex 39 (BUT-52) with Cu\(_2\)S\(_6\) cluster (Figure 3). The Cu atom was trigonal coordinated to one pyridyl N atom and two S atoms from three independent linkers to produce a Cu\(_2\)S\(_6\) unit. Furthermore, the indium atoms in Complex 39 were coordinated with four carboxylate oxygens in a distorted tetrahedral geometry to make the classic In(COO)\(_4\) units, leading to an anionic framework. The richness of sulfur enabled Complex 39 with strong affinity toward mercury, and more than 92% mercury in methanol could be removed.

Figure 2  (a) Effects of cations on the photoluminescence peak of Complex 37 at 618 nm upon excitation at 458 nm in acetonitrile. (b) Effects of cations on the photoluminescence peak at 648 nm of Complex 37 upon excitation at 504 nm in water.\[^{39}\]

**Figure 3** Synthetic scheme for the rational design of Complex 39 on the basis of In\(^{3+}\), Cu\(^{2+}\), and the in situ synthesized ligand involving carboxylate, pyridyl, and thiol groups.\[^{81}\]

**Post-synthetic Modification solely on MOFs**

**Mercury sensing**

Lang and Li groups\[^{32}\] demonstrated that the photochemical [2+2] addition of olefinic bonds in MOFs could help improve the sensing ability for Hg\(^{2+}\). In this work, the previously reported Complex 40, ([Cd(ppene)]\(_2\)(1,4-BDC)\(_2\))·MeCN, (ppene = 4-ppy-poly-2-ene), was exposed under the UV light radiation and turned to the cyclobutane-appended MOF [Cd\(_2\)(4-tp-3-lad)-(1,4-BDC)\(_2\))·MeCN], where 4-tp-3-lad was 2,3,5,6-tetra(pyrindin-4-yl)-bicyc[2.2.0]hexane, in a single-crystal-to-single-crystal transformation. The olefinic Complex 40 was not capable to be used to probe Hg\(^{2+}\) in aqueous solution. However, the change from the olefinic bonds to the cyclobutane rings upon radiation made the sensing of Hg\(^{2+}\) possible. The emission peak not only blue-shifted but also displayed an enhancement of the intensity.

**Mercury removal**

Zhu and coworkers\[^{33}\] grafted rationally thiol groups into the unsaturated Cu sites of HKUST-1. Different amounts of thiol groups could be predictably controlled by the variation of thiol source dithioglycol. Among all the thiol-functionalized HKUST-1 materials, Complex 41 (MOF with S:Cu = 0.92) displayed not only a remarkably distribution constant of 4.73×10\(^4\) mL·g\(^{-1}\) but also the best Hg\(^{2+}\) adsorption with the maximum capacity of 714.29 mg/g and the removal efficiency of 99.79%.

As mentioned previously, harsh post-synthetic modifications are likely to be done on stable MOFs for the sake of retaining the framework. Davis and coworkers\[^{34}\] post-synthetically introduced thiourea, isothiocyanate and isocyanate functional groups to UiO-66-NH\(_2\) and constructed six different UiO-66 derivatives (UiO-66-NCO, UiO-66-NHC(S)NHPh, UiO-66-NHC(S)NHMe, UiO-66-NC, UiO-66-NH(S)NHBu\(_2\), and UiO-66-NHC(S)NH(Cy)). Among all those functionalized MOFs, Complex 42 (UiO-66-NHC(S)NHMe) removed markedly 99.4% of mercury (vs. ~8% for UiO-66 and ~32% for UiO-66-NH\(_2\)). The maximum Hg\(^{2+}\) adsorption capacity of Complex 42 was 769 mg/g.

Tandem post-synthetic modifications has also been demonstrated in another stable MOF Cr-MIL-101. Dong, Liu and coworkers\[^{35}\] explored the utilization of post-synthetically modified Cr-MIL-101-N\(_2\)BF\(_4\), which was prepared by mixing Cr-MIL-101-NH\(_2\) in an acidic solution followed by an addition of NaNO\(_2\) to enhance the adsorption of Hg\(^{2+}\). Then they converted the diazonium salt to alkényl-derived MOF, Cr-MIL-101-A1-6, by means of a carbon-carbon bond-forming reaction with Pd (OAc)\(_2\) as the catalyst. They further converted Cr-MIL-101-A4 (the alkényl and benzyl alcohol-derived MOF) to
Complex 43 (Cr-MIL-101-AS), Notably, Complex 43 displayed a remarkable Hg$^{2+}$ removal efficiency of 99.3% under 6 h for at least two times without losing any activity.

**Construction of MOF-based composites**

**Mercury sensing**

Chen group$^{[38]}$ utilized the inner filter effect in the design of an Eu/IPA MOF nanoparticle (NP) system using Eu$^{3+}$ as the fluorophore, and isopthalic acid (IPA) as the bridging ligand. Post-synthetically, they introduced dicarbolic acid (Im) to construct Complex 44. Im had a strong absorption band overlapping with the excitation spectrum of the MOF NP and would filter out the energy transfer from ligand to Eu$^{3+}$ and decrease significantly the strong red fluorescence of the NP. Interestingly, the further addition of Hg$^{2+}$ into Complex 44 resulted in a stable Hg/Im complex, which led to the complete fluorescence recovery within 2 min without any structural change of the NP. At pH = 7, the detection limit of Complex 44 was estimated to ~2 nM. Under the similar experimental measurements, none of those common ions (Ag$^{+}$, K$^+$, Na$^+$, Mg$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Ca$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Ce$^{3+}$, Fe$^{3+}$, Cr$^{3+}$ and Al$^{3+}$), amino acid, glucose, and ascorbic acids, enhanced significantly the fluorescence. The following application of Complex 44 as the turn-on sensors in the urine samples exhibited more than 95% recovery. 

Yan and coworkers$^{[67]}$ constructed a dual emissive MOF composite by utilizing the optical active carbon dots (CDs) in MOF-253 in one-pot synthesis, which consisted of 1% Al metal chain with 2,2’-bipyridine-5,5’-dicarboxylic forming 1D rhombic channels. They post-synthetically introduced Eu$^{3+}$ to produce Complex 45 (Eu$^{3+}$/CD@MOF-253). The *in situ* encapsulation of CDs in MOF-253 enabled blue florescent framework with an emission peak at 453 nm and excitation of 360 nm. Upon the introduction of Eu$^{3+}$, a second characteristic of Eu$^{3+}$ (D$_{2s}$→F$_{2p}$) at 614 nm was monitored with excitation of 340 nm. Complex 45 displayed both photostability at room temperature for 9 d and pH stability in aqueous solution between pH 4–9, which promised Complex 45 a good candidate for fluorescence sensing. When Hg$^{2+}$ ions were introduced to the composite, the mercury coordinated to the functional group of CDs and thus changed the surface traps or electron-hole recombination annihilation via electron/energy transfer. Ultimately, the fluorescence of CDs was quenched efficiently with the evidence of decreasing intensity of blue fluorescence at 453 nm, wherein the solution turned from blue to red under UV light. When Complex 45 was immersed in the aqueous solution with different concentrations of Hg$^{2+}$, the fluorescent color changed visibly from blue to faint blue, dark red and finally red with an increasing amount of Hg$^{2+}$ under UV radiation (3 mg/g composite). Among all the potential interference ions (Zn$^{2+}$, Ni$^{2+}$, Na$^+$, Mn$^{2+}$, Mg$^{2+}$, K$^+$, Pb$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, Fe$^{2+}$, Al$^{3+}$, Cr$^{3+}$, Co$^{3+}$, and Hg$^{2+}$), significant quenching effect was only observed in the presence of Hg$^{2+}$ and led to a red-colored fluorescence emission. The researcher also reported the use of Complex 45 to remove the mercury in environmental water samples (river water, fountain water, and tap water), and the removal efficiencies were all above 90.0%.

Additionally, Azzazy group$^{[68]}$ loaded dithizone (DZ) into UiO-66 to fabricate an efficient Hg$^{2+}$ sensor—Complex 46. In the inclusion of DZ decreased the BET surface to 421 m$^2$·g$^{-1}$ (vs. UiO-66 839 m$^2$·g$^{-1}$). The detection limit of Complex 46 reached 0.52 nM at pH = 9.5.

Due to the fact that Hg$^{2+}$ binds specifically to thymine-thymine (T-T) mismatched base pair, the hybridization of T-rich fluorophore (FAM) single stranded DNA and UiO-66, leading to Complex 47, was demonstrated as an excellent mercury sensor (Figure 4).$^{[69]}$ The FAM had fluorescence at 518 nm under excitation at 480 nm, in which no shift was observed by either Hg$^{2+}$ or UiO-66-NH$_2$. In Complex 47, FAM bonded to UiO-66-NH$_2$ through π-π stacking and hydrogen-bonding between the nucleotide bases of DNA and the aromatic ring in UiO-66-NH$_2$, consequently quenching the fluorescence (~75%). The introduction of Hg$^{2+}$ (10.0 μM) had better affinity to coordinate to FAM, inducing the formation of helical structure and blocking the photoinduced electron transfer, and enhanced eventually the fluorescence by more than two fold. Therefore, the monitoring of the fluorescence of Complex 47 indicated the presence of Hg$^{2+}$. In the range of 0.1–100 μM of Hg$^{2+}$, the enhancement improved along with the increasing concentration of Hg$^{2+}$. In addition, Complex 47 showed not only a detection limit of 17.6 nM but also a high selectivity of Hg$^{2+}$ over other metal ions (Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$).
initially adsorbed at an extreme fast rate and then a slow loading until five molecules were adsorbed. Due to the poor solubility and weak affinity of CH$_2$HgCl in the solvent of water/methanol, the adsorption of CH$_2$HgCl was relatively slow and ended up with one molecule per formula unit. In Complex 50, the sulfur atoms of the methionine units showed a good affinity to the mercury species. As a result, Complex 50 demonstrated a good selectivity of Hg$^{2+}$ over other common ions in water, such as Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, Cl$^-$, and NO$_3^-$.

A MOF-polymer wetted was made by mixing Complex 50 with a commercial polymer for the sake of better stability. Remarkably, this pellet adsorbed 99.95% HgCl$_2$ and ~90.0% CH$_2$HgCl in the aqueous solution in a reversible manner over 2.8 d and decreased the level of Hg$^{2+}$ and CH$_2$Hg$^+$ from 10 ppm to 5 ppb and 27 ppb, respectively. The maximum mercury adsorption was calculated to be 5 mg/g pellet.

In the light of Mn-Ce catalysts facilitate the Hg$^+$ oxidation and the selective catalytic reduction of NO from the flue gas, Shen group$^{[2]}$ designed a Mn-Ce loaded complex Composite 51 (MnCe@UiO-67). Interestingly, the researchers also found either the introduction of NO or a small amount of O$_2$ in the simulated flue gas promoted the Hg$^+$ removal of Complex 51, while the presence of NH$_3$ inhibited the removal. Under an optimal condition of 300 °C in the presence of 500 ppm NO in the flue gas, the Hg$^+$ removal efficiency of Complex 51 reached above 95%. In addition, the gradually decreasing of Ce$^{3+}$/Ce$^{4+}$ ratio during extended reaction time implied the consumption of adsorption oxygen in the composite. As a result, the removal efficiency decreased over the reaction time, since the oxygen, serving as the oxidant for Hg$^+$, was consumed.

Conclusion and Outlook

Overall, all those studies approve that MOF-based materials promise greatly the mercury sensing and removal. However, there are still some concerns remaining unaddressed. (1) Some of the aforementioned examples reveal the importance of temperature in mercury adsorption. Therefore, it is important to standardize the adsorption condition (25 °C and 1 atm as an example) for mercury species from the consideration of practical uses. (2) Many of those MOF-based materials are capable for one-time use, and only a few show capability for multiple uses. In this case, the reusability should be considered in order to minimize the cost when commercializing the MOF-based adsorbents. To address this concern, water-stable MOFs (usually constructed from high-valent metal ions) are good candidates to expand the working span of those materials for the sake of good recyclability. (3) Among all the reported MOF-based materials for mercury removal, less than ten materials were applied to extract/preconcentrate mercury from real samples. In the future, it will be straightforward if the reports could include the application of new materials for the mercury removal from real samples, biomass, water and soil samples to name a few. (4) The presence of sulfur- or nitrogen-containing groups with exposed sulfur or nitrogen atoms in the MOF-based materials truly enhance the overall mercury capacity in most cases. Continuous efforts on incorporation of more adsorption sites with exposed sulfur and nitrogen atoms (polyamines, cyclam and its carboxylate derivatives, thiophene, thiol chains, acylamide for example) on the framework should also be spent to maximize the overall capacity and removal efficiency. (5) In the application of methane, hydrogen, and carbon dioxide storages, significant amount of analysis on adsorption enthalpy, interaction sites and binding energy obtained from computation calculation provide meaningful guidance in the design of high-performance adsorbents. So far, only a handful of computational calculations have focused on the application of MOF for mercury sensing and adsorption.$^{[53,74]}$ Similar computational support should be provided in designing new MOF-based materials with specific targets, incorporation of more adsorption sites, and the framework for example, of mercury sensing and adsorption. Additionally, many reports assessed the quenching or enhancing effect for mercury sensing to the ligand-metal and/or metal-ligand electron transfer. No systematic investigation demonstrated detailed insights about the sensing mechanism. In this case, computational simulation may provide such aids to help understand the sensing and/or adsorption mechanism. (6) In one of the previous study, the researchers packed a MOF-filled column to test the removal ability from real samples.$^{[5]}$ Similar endeavors should be encouraged from the scaling-up point of view. As some of the aforementioned MOF-based materials displayed fast response to the mercury species, it will be significant to adopt such a MOF-filled column in a real flow line, where MOFs are used to sense the mercury species. (7) Currently, a booming area of MOFs focuses on the use of MOF-based materials for cancer treatment or drug carrier. As the mercury species accumulate in the food chain, similar biomedical studies could also be introduced on applying MOFs as “nanocustodian” to selectively extract mercury from blood or proteins and then take the mercury trash out. Mercury pollution is everywhere and harming our life in every second. Thereby, there is an urgent need to remove those stable mercury species from nature in an affordable way. As the exploration of MOF booms up, such a useful MOF-based mercury remover will be developed in the near further.

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Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc20180003.

References

[1] Wan Ngah, W. S.; Hanafiiah, M. A. K. M. Bioresource Technol. 2008, 99, 3935.
[2] Kumar, P.; Guliants, V. V. Micropor. Mesopor. Mater. 2010, 132, 1.
[3] Dębrowski, A.; Hubicki, Z.; Podkóscielný, P.; Robens, E. Chem. Soc. Rev. 2004, 56, 91.
[4] Huebra, M.; Elizalde, M. P.; Almeida, A. Hydrometallurgy 2003, 68, 33.
[5] Gupta, V. K.; Carroll, P. J. M.; Ribeiro-Carrott, M. M. L.; Suhas, P. K. J. Environ. Sci. Technol. 2009, 39, 783.
[6] Adil, K.; Blemelkhouyt, Y.; Pillai, R. S.; Cadiacu, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Chem. Soc. Rev. 2017, 46, 3402.
[7] Bobbitt, N. S.; Mendonca, M. L.; Howarth, A. J.; Islamoglu, T.; Hupp, J. T.; Farha, O. K.; Snurr, R. Q. Chem. Soc. Rev. 2017, 46, 3357.
[8] DeCote, J. B.; Peterson, G. W. Chem. Rev. 2014, 114, 5695.
[9] Evans, J. D.; Jelfs, K. E.; Day, G. M.; Doonan, C. J. Chem. Soc. Rev. 2017, 46, 3286.
[10] Huxford, R. C.; Rocca, J. D.; Lin, W. Curr. Opin. Chem. Biol. 2010, 14, 262.
[11] Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Chem. Soc. Rev. 2009, 38, 1450.
[12] Li, J.-R.; Sculley, J.; Zhou, H.-C. Chem. Rev. 2012, 112, 869.

[13] Liu, J.; Thalapally, P. K.; McGraith, B. P.; Brown, D. R.; Liu, J. Chem. Soc. Rev. 2012, 41, 2306.

[14] Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Chem. Soc. Rev. 2017, 46, 3242.

[15] Murray, L. J.; Dinca, M.; Long, J. R. Chem. Soc. Rev. 2009, 38, 1294.

[16] Rogge, S. M. J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivos-Suarez, A. I.; Sepulveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kajtzej, F.; Daturi, M.; Ramos-Fernandez, E. V.; Llabres i Xamena, F. X.; Van Speybroeck, V.; Gascon, J. Chem. Soc. Rev. 2017, 46, 3134.

[17] Stassen, I.; Burtch, N.; Talin, A.; Falcaro, P.; Allendorf, M.; Ameloot, W.; Wang, C.-C.; Li, J.-R.; Lv, X.-L.; Zhang, Y.-Q.; Guo, G.; Zhang, T.; Lin, W.; Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Lalonde, M.; Bury, W.; Karagiaridi, O.; Brown, Z.; Hupp, J. T.; Zhu, Q.-L.; Xu, Q.; Lian, X.; Fang, Y.; Joseph, E.; Wang, Q.; Li, J.; Banerjee, S.; Lollar, D.; Doherty, C. M.; Buso, D.; Hill, A. J.; Furukawa, S.; Kitagawa, S.; Kitao, T.; Zhang, Y.; Kitagawa, S.; Wang, B.; Uemura, T.; Corma, A.; García, H.; Llabrés i Xamena, F. X.; Van Speybroeck, V.; Gascon, J. Chem. Soc. Rev. 2017, 46, 3134.

[18] Ghosh, S. K. Chem. Soc. Rev. 2009, 38, 5439.

[19] Chen, F.; Hall, G.; Chabal, Y. J.; Li, J. ACS Appl. Mater. Inter. 2016, 8, 30294.

[20] Tan, H.; Liu, B.; Chen, Y. ACS Nano 2012, 6, 10505.

[21] Zhu, Y.-M.; Zeng, C.-H.; Chu, T.-S.; Wang, H.-M.; Yang, Y.-Y.; Tong, Y.-X.; Su, C.-Y.; Wang, W.-T. J. Mater. Chem. A 2013, 1, 11312.

[22] Jia, J.; Xu, F.; Long, Z.; Hou, X.; Sepaniak, M. J. Chem. Commun. 2013, 49, 4670.

[23] Razavi, S. A. A.; Masoomi, M. Y.; Morsali, A. Inorg. Chem. 2017, 56, 9664.

[24] Lin, L.; Luo, F.; Zheng, L.; Gao, G.; Chi, Y. Anal. Chem. 2015, 87, 4864.

[25] Han, Y.; Zheng, H.; Liu, K.; Wang, H.; Huang, H.; Xie, L.-H.; Wang, L.; Li, J.-R. ACS Appl. Mater. Inter. 2016, 8, 23331.

[26] Gong, W.-J.; Ren, Z.-G.; Li, H.-X.; Zhang, J.-G.; Lang, J.-P. Cryst. Growth Des. 2017, 17, 870.

[27] Ke, F.; Qiu, L.-G.; Yuan, P.-F.; Peng, F.-M.; Jiang, X.; Xie, A.-J.; Shen, Y.-H.; Zhu, J.-F. J. Hazard. Mater. 2011, 196, 38.

[28] Saleem, H.; Rafique, U.; Davies, R. P. Angew. Chem. Int. Ed 2012, 51, 4961.

[29] Liu, T.; Che, J.-X.; Hu, Y.-Z.; Dong, X.-W.; Liu, X.-Y.; Che, C.-M. Chem. Eur. J. 2014, 20, 14090.

[30] Li, Q.; Wang, C.; Tan, H.; Tang, G.; Gao, J.; Chen, C.-H. RSC Adv. 2016, 6, 17811.

[31] Xu, X.-Y.; Yan, B. Journal of Materials Chemistry C 2016, 4, 1543.

[32] Shihahat, A.; Hassan, H. M. A.; Azzazy, H. M. E. Anal. Chim. Acta 2013, 793, 90.

[33] Wu, L.-L.; Wang, Z.; Zhao, S.-N.; Meng, X.; Song, X.-Z.; Feng, J.; Song, S.-Y.; Zhang, H.-J. Chem. Eur. J. 2016, 22, 342.

[34] Sobjari, M. Microchim. Acta 2014, 181, 435.

[35] Huang, L.; He, M.; Chen, B.; Hu, B. J. Mater. Chem. A 2015, 3, 11587.

[36] Mor, M.; Lloret, F.; Ferrando-Soria, J.; Martí-Gastaldo, C.; Armentano, D.; Pardo, E. Angew. Chem. Int. Ed. 2016, 55, 11167.

[37] Zhang, X.; Shen, B.; Shen, F.; Zhang, X.; Si, M.; Yuan, P. Chem. Eng. J. 2017, 326, 551.

[38] Liu, Y.; Li, H.; Liu, J. Fuel 2016, 184, 474.