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Effective Mercury Sorption by Thiol-Laced Metal–Organic Frameworks: in Strong Acid and the Vapor Phase

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S *Supporting Information*

ABSTRACT: Free-standing, accessible thiol (−SH) functions have been installed in robust, porous coordination networks to provide wide-ranging reactivities and properties in the solid state. The frameworks were assembled by reacting $ZrCl_4$ or $AlCl_3$ with 2,5-dimercapto-1,4-benzenedicarboxylic acid (H_2DMBD), which features the hard carboxyl and soft thiol functions. The resultant Zr-DMBD and Al-DMBD frameworks exhibit the UiO-66 and CAU-1 topologies, respectively, with the carboxyl bonded to the hard Zr(IV) or Al(III) center and the thiol groups decorating the pores. The thiol-laced Zr-DMBD crystals lower the Hg(II) concentration in water below 0.01 ppm and effectively take up Hg from the vapor phase. The Zr-DMBD solid also features a nearly white photoluminescence that is distinctly quenched after Hg uptake. The carboxyl/thiol combination thus illustrates the wider applicability of the hard-and-soft strategy for functional frameworks.

The combination of carboxylic and sulfur (e.g., thioether or thiol) functions (see Figure 1 for an example)[1] represents a potentially powerful strategy for the molecular design of coordination networks [or metal–organic frameworks (MOFs)].[2] One potential advantage is derived from the distinct hard-and-soft characters of the carboxyl and sulfur groups: the ionic, chemically hard carboxyl group tends to bind metal ions for network formation, while the softer thioether or thiol groups could remain as free-standing, secondary donor groups. In this context, the thioether function has been actively explored, generating a series of porous networks with free-standing thioether groups that have proved to be useful for metal uptake and other applications. By comparison, efforts to incorporate thiol functions into coordination networks have been very limited, and porous coordination networks appended with free-standing thiol functions have yet to be made.

The advantages of incorporating the very reactive thiol group are obvious. First, the stronger-binding thiol groups would enable the uptake of diverse metal ions into MOF pores for effective removal of heavy metal ions and the creation of electroactive or catalytic sites (e.g., mimicking the iron–sulfur and copper–sulfur proteins). Second, the versatile organic transformations of thiols would also allow for convenient postcrystallization (postsynthetic) modifications,[3] such as covalent cross-linking inside the pores to synergize studies of organic polymers and solid-state frameworks. Unfortunately, it is their reactive nature that also complicates the synthesis of thiol-laced MOFs. For example, metal ions that are commonly used to build MOFs (e.g., Zn^{2+}, Cu^{2+}) often interact strongly with the thiol groups and disrupt crystallization. To suppress the thiol–metal interaction, it is helpful to choose chemically very hard (i.e., oxophilic) metal ions that more selectively bind to the carboxyl groups, such as Al(III),[4] Cr(III),[5] Eu(III),[1b] Zr(IV).[6]

Among these, Zr(IV)-based MOFs (Zr-MOFs) are attractive because of their stability and versatile modifiability.[6] For example, Zr-MOFs are largely stable toward water and even under mild acid/base conditions,[7] and they can be formed persistently with extensive functional and geometric modifications[8] on the organic linkers.[7b,9] In this work, we studied the reaction between $ZrCl_4$ and the bifunctional building block 2,5-dimercapto-1,4-benzenedicarboxylic acid (H_2DMBD) (Figure 1, synthesis known[10]) in order to construct a thiol-laced coordination network, Zr-DMBD, and explore the synergism between the thiol function and well-ordered porosity in the solid state. We discovered that this thiol-laced Zr-MOF is capable of effective mercury uptake from both aqueous solutions and the gas phase. In addition, we examined frameworks based on Al(III) and the DMBD linker to demonstrate the wider applicability of

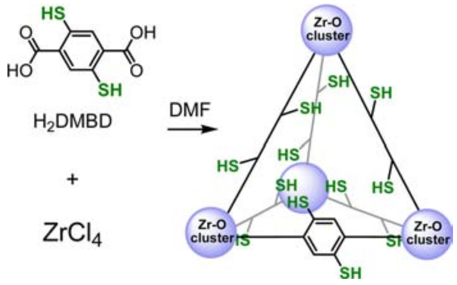

Figure 1. Synthetic scheme for the Zr-DMBD network. The topology is the same as for UiO-66 and is shown in simplified form as a tetrahedral cage.

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the hard-and-soft strategy in achieving thiol-functionalized porous networks.

The Zr-DMBD framework was first revealed by the distinct powder X-ray diffraction (PXRD) pattern (Figure 2) to be isostructural with the reported UiO-66, which contains linear 1,4-benzenedicarboxylate struts and $Zr_6O_4(OH)_4$ clusters as 12-connected nodes.[11] The structure features a face-centered-cubic arrangement of the Zr−O clusters and thus consists of tetrahedral and octahedral cages in 2:1 ratio. Scanning electron microscopy (SEM) indicated that the solid product uniformly consists of regular-shaped octahedral crystallites on the scale of 200 nm [see the Figure 3 inset and Figure S1 in the Supporting Information (SI)]. The observed crystalline morphology is consistent with those of other reported isoreticular Zr-MOF crystals.[9a,e]

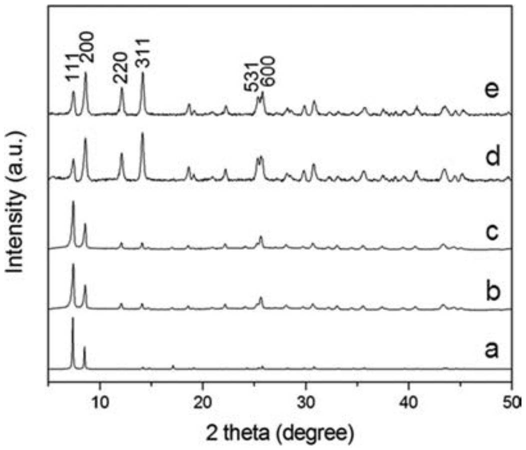

Figure 2. PXRD patterns (Cu Kα, $\lambda = 1.5418$ Å) for Zr-DMBD-related systems: (a) simulation from a structural model of Zr-DMBD (see the SI for the atomic coordinates); (b) as-made Zr-DMBD; (c) activated Zr-DMBD; (d) as-made Zr-DMBD after treatment with an aqueous solution of $HgCl_2$; (e) as-made Zr-DMBD after treatment with Hg(0) vapor.

The IR and Raman spectra of both as-made and activated (see the SI for the activation procedure) Zr-DMBD crystalline samples exhibit a peak at 2560 cm^{-1}, consistent with the S−H stretching frequency of free −SH groups (e.g., spectra a and b in Figures S2 and S3). The IR and Raman spectra also feature a distinct band at 501 cm^{-1} that can be assigned to the S−S stretch, indicating disulfide formation that is apparently due to air oxidation of the thiol groups (no measures were taken to exclude air in the crystallization and activation steps). The intensity of the S−S stretch at 501 cm^{-1} relative to that of the S−H stretch at 2560 cm^{-1} significantly increased in the activated sample (e.g., compare spectra a and b in Figure S3), suggesting that more of the −SH groups were oxidized to give disulfides under the heated conditions of the activation process. The elemental analysis and thermogravimetric analysis (TGA) data revealed the $[Zr_6O_4(OH)_4]$/DMBD linker ratio in the as-made Zr-DMBD sample to be 1:6 (see the SI).

The activated Zr-DMBD sample displayed typical type-I N_2 adsorption isotherms at 77.4 K with a BET surface area of 513 m^2/g and a micropore volume of 0.24 cm^3/g (Figure S5). The specific surface area is consistent with the results of CO_2 adsorption at 273 K (ca. 500 m^2/g; see the SI for details). Sorption tests at 273 and 283 K (Figure 3; also see the SI) indicated that the CO_2 adsorption could be fit to a dual-site Langmuir model, while the N_2 adsorption was fit using a single-site Langmuir approach. The calculated heat of adsorption for CO_2 was ca. 30 kJ/mol at low coverage and dropped to 25 kJ/mol at higher coverage. This finding agrees with calculations on other UiO-66 nets, in which functional groups giving rise to polar sites and pronounced interactions raised the low-coverage CO_2 heat of adsorption from 26 kJ/mol (for unmodified UiO-66) to 30−34 kJ/mol.[12] The interactions are also manifested in a distinct CO_2/N_2 selectivity of 187 at a gas composition of 0.15/0.85 (1 bar and 273 K), which is typical of microporous materials. Sorption of other gases (e.g., NH_3) would further unveil how the polar and acidic thiol groups impact the sorption behavior.

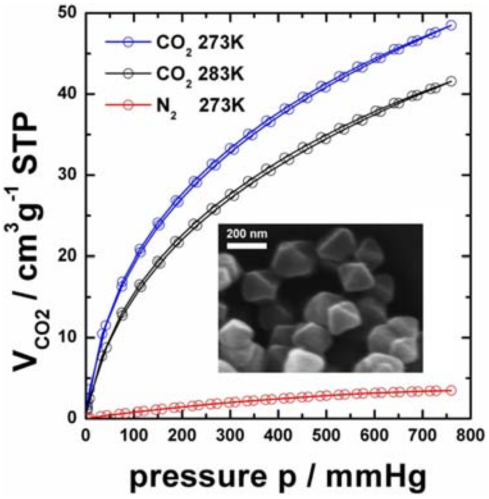

Figure 3. CO_2 (273 and 283 K) and N_2 (273 K) adsorption/desorption isotherms for activated Zr-DMBD. Inset: SEM image of an as-made sample of Zr-DMBD (grown with 160 equiv of acetic acid added as a modulator).

Sulfur-functionalized materials are often studied for mercury removal applications. Such materials include chalcogenide frameworks/aerogels,[13,14] thiol-functionalized mesoporous silica,[15] polymers appended with sulfur crown ethers,[16] and sulfurated mesoporous carbon.[17] Interestingly, MOFs, as a growing class of porous materials, have remained largely untapped in the important application of mercury removal, even though increasing efforts are being made to load metal species into the pores of MOFs.[3d,18]

To demonstrate the effective capture of mercury from water, an as-made Zr-DMBD sample (~10 mg) was placed in a dilute aqueous solution (10 mL) of $Hg(NO_3)_2$ containing 5% HNO_3 (concentration of Hg^{2+} ions, 10 ppm; total amount of Hg^{2+} ions, 0.1 mg). After the mixture wa stirred at room temperature for 12 h, the residual mercury concentration in the solution was smaller than 0.01 ppm, that is, over 99.9% of the mercury was removed by Zr-DMBD even when the initial Hg^{2+} concentration was as low as 10 ppm. Compared with an earlier MOF with a thioether function,[18] which lowered the Hg^{2+} concentration in an ethanol solution to 84 ppm, the improvement enabled by the stronger-binding thiol function in Zr-DMBD is dramatic. Also, Zr-DMBD is stable toward water, adding to the practical advantages.

To assess the mercury uptake capacity, an as-made sample of Zr-DMBD (20 mg) and 4.0 mL of a 3.5% w/w aqueous solution of $HgCl_2$ (140 mg total) were stirred at room temperature for 12 h. The solid was then isolated by centrifugation and further washed with methanol to remove residual $HgCl_2$ on the exterior of the Zr-DMBD powder. The solid sample thus obtained (denoted as Zr-DMBD-$HgCl_2$) was subjected to regular CHN and inductively coupled plasma (ICP) elemental analyses; ICP analysis determined the Zr/Hg ratio to be 6:1.82, leading to a composition of $Zr_6O_4(OH)_4\cdot(C_8H_2O_4S_2)_6\cdot(DMF)_{0.5}\cdot(H_2O)_{29}\cdot(HgCl_2)_{1.82}$. More notably, similar Hg uptake capacities (i.e., DMBD/Hg ratios of ca. 3:1) were observed over a wide range of Hg^{2+} concentrations (e.g., 100 ppm) and pH conditions (e.g., even in 2 M HNO_3), with the crystallinity of the Zr-DMBD host network being well-preserved (Figure S8). The Hg uptake capability was thus found to be substantial and robust. If measures are taken to minimize the formation of the weaker-binding S−S units (e.g., crystallizing Zr-DMBD under O_2-free conditions), one might access even higher uptake capacities that are closer to the stoichiometric DMBD/Hg ratio of 1:1 (each DMBD has two −SH groups, and we assume that each Hg^{2+} ion binds two thiolate S atoms).

The IR and Raman spectra and the PXRD pattern of the Zr-DMBD-$HgCl_2$ sample also indicate mercury uptake into the porous solid. In the IR and Raman spectra, the characteristic S−H stretch mode at 2560 cm^{-1} is absent in the Zr-DMBD-$HgCl_2$ sample (compare spectra a and b to spectrum c in Figures S2 and S3); moreover, a strong band at 355 cm^{-1} consistent with Hg−S stretching emerged for the $HgCl_2$-loaded sample. As shown in Figure 2, the lowest-angle peak (111) was greatly diminished after $HgCl_2$ treatment (pattern d), whereas the higher-angle peaks (e.g., 200, 220, 331, 600) generally became stronger. Such significant changes in diffraction intensity reflect the large increase in electron density in the channel region (i.e., the system becomes less porous) as a result of $HgCl_2$ uptake while indicating that the original crystal lattice remains intact in the process.

The facile mercury uptake from solutions prompted us to probe mercury vapor sorption, a property that bears closely on the industrial processes of flue gas detoxification.[14] On the basis of the setup for mercury vapor sorption recently reported by the Kanatzidis group,[14] an as-made crystalline sample of Zr-DMBD (20 mg) and elemental mercury (liquid, 300 mg) were placed in a sealed vial with spatial separation maintained to prevent the two from directly contacting each other. The vial was then immersed in a sand bath and heated at 140 °C for 24 h. The Zr-DMBD thus treated (i.e., Zr-DMBD-Hg) was found to have the composition $Zr_6O_4(OH)_4\cdot(C_8H_2O_4S_2)_6\cdot(DMF)_{0.25}\cdot(H_2O)_{34}\cdot(Hg)_{1.2}$ as jointly determined by ICP (indicating a Zr/Hg molar ratio of 6:1.2) and regular CHN elemental analyses (see the SI). The DMBD/Hg ratio of 4.6:1 indicates that the mercury vapor uptake was slightly lower than in the solution-treated sample (Zr-DMBD-$HgCl_2$) but still significant. In parallel to the solution treatment, the IR and Raman spectra and PXRD data for the vapor-treated sample also pointed to significant Hg uptake, as indicated by the absence of the S−H stretch mode at 2560 cm^{-1} (spectra d in Figures S2 and S3), the emergence of the Hg−S stretch at 355 cm^{-1} (spectrum d in Figure S3), and the weakening of the 111 peak in the PXRD pattern (Figure 2e).

The photoluminescence (PL) of the Zr-DMBD host network was also greatly impacted by the mercury uptake, be it from solution (e.g., $HgCl_2$/water) or Hg(0) vapor. As shown in Figure 4, the as-made sample features a broad emission centered around 500 nm (spectrum a), generating a distinct near-white emission. In the $HgCl_2$- and the Hg(0)-treated samples (Zr-DMBD-$HgCl_2$ and Zr-DMBD-Hg, respectively), the PL was largely suppressed, being less than $^{1}/_{10}$ of the intensity for the as-made sample (spectra b and c) and hardly visible to the eye (Figure 4 inset). Fluorescence quenching by heavy metal ions is well-documented and occurs via many intramolecular/intermolecular pathways, including spin−orbit coupling, energy transfer, and electron transfer.[19] Further studies of MOFs with combined PL, porosity, and thiol functions should better uncover the applicability in the uptake and monitoring of Hg^{2+} and other metal species.

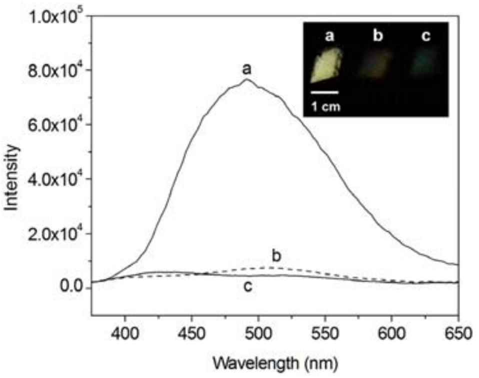

Figure 4. Room-temperature solid-state emission spectra (λ_{ex} = 355 nm) of Zr-DMBD samples: (a) as-made sample; (b) after treatment with an aqueous solution of $HgCl_2$; (c) after treatment with Hg(0) vapor. The inset shows photographs of samples a−c under 365 nm UV radiation.

The synthesis of thiol-functionalized MOFs is not limited to Zr(IV)-based systems. Our tests with Al(III) and H_2DMBD yielded a crystalline framework exhibiting the reported CAU-1 topology (discovered by Stock and co-workers[4b]). This thiol-laced Al-MOF (designated as CAU-1-SH; see Figures S9−S14 for the characterization and property studies) was made using very inexpensive starting material ($AlCl_3\cdot6H_2O$) and solvents (water or methanol), and the solid sample can be readily activated for porosity studies (e.g., the specific surface area for activated CAU-1-SH was 750 m^2/g; see Figure S12). The CAU-1-SH system thus offers significant advantages for large-scale production and applications. Further studies on these and other thiol-functionalized MOF systems are ongoing and will be published in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; network synthesis and activation; SEM images; and elemental analysis, N_2/CO_2 sorption, TGA, IR/Raman, and PXRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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