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Thioether Side Chains Improve the Stability, Fluorescence, and Metal Uptake of a Metal–Organic Framework

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Supporting Information

ABSTRACT: This work builds on the recently developed hard—soft approach, as is embodied in the carboxyl-thioether combination, for functionalizing metal-organic frameworks (MOFs), and it aims to further demonstrate its efficacy and generality in connection with the prototypic MOF-5 system [i.e., $Zn_4O(bdc)_3$, where bdc is 1,4-benzene dicarboxylate]. Specifically, the thioether side chain $CH_3SCH_2CH_2S$ – (methylthioethylenethio, or MSES) is placed at the 2,5- positions of bdc, and the resultant molecule (L) was crystallized with Zn(II) ions into a porous, cubic network $[Zn_4O(L)_3]$ topologically equivalent to MOF-5. Compared with the previously used methylthio (CH_3S-) group, the MSES side chain is more flexible, has more S atoms as the binding sites (per chain), and extends further into the channel region; therefore, this side chain is predisposed for more-efficient binding to soft metal species when installed in a porous MOF matrix. Here, we report the significantly improved properties, with regard to stability to moisture, fluorescence intensity, and capability of metal uptake. For



example, activated solid samples of 1 feature long-term stability (more than 3 weeks) in air, have a notable sensing response to nitrobenzene (in the form of fluorescence quenching), and are capable of taking up HgCl₂ from an ethanol solution at a concentration as low as 84 mg/L.

KEYWORDS: sulfurated frameworks, metal-organic frameworks, fluorescent sensor, heavy metal removal, thioether donors

INTRODUCTION

In the fast growing field of porous coordination networks (aka metal-organic frameworks, MOFs),¹ it is of great interest to achieve systematic functionalization of the pores while maintaining the underlying topology of the main framework. Bifunctional molecules with primary groups for network construction and secondary groups for functionalization seem to be potentially versatile building blocks. Besides earlier systems of bifunctional building blocks from the groups of Lee (phenylacetylene-based nitriles),² Wuest (hydrogen-bonding nets),³ and Lin,⁴ notable recent efforts include 2-amino-1,4-benzene dicarboxylic acid,⁵ an azide-decorated MOF for click functionalization,⁶ zeolitic imidazolate framework (ZIF) post-synthetic modification,⁷ and ether/ thioether-tagged MOFs.8 In this regard, the combination of carboxylic and sulfur functions (see structure L in Chart 1, for example) provides appealing opportunities for functionalizing MOFs.^{8a,9} For example, the ionic, chemically hard carboxylate groups are predisposed, as the primary group, to interact with metal ions for network formation, while leaving the neutral, and generally weaker-binding, thioether groups as free-standing, secondary donors. In addition, thioethers are generally stable in air and can be attached to molecular building blocks with efficient organic synthetic procedures.¹⁰

We have recently reported a porous coordination network based on the Pb(II) ion and the bifunctional molecule 2,3,5,6tetrakis(methylthio)benzenedicarboxylic acid (TMBD), in which the reversible uptake of HgCl₂ into the channels was enabled by the methylthio (CH_3S-) functions.^{9c} That particular system, however, has several limitations. First, the Pb species poses an environmental concern in practical applications. Second, the effective uptake of the HgCl₂ species entails a rather stringent condition of heating in benzene. To further illustrate the usefulness of thioether groups for functionalizing MOF systems, here, we report a coordination network based on the molecule 2,5-bis(2-(methylthio)ethylthio)terephthalic acid (L) and Zn(II) ions [network composition: $Zn_4O \cdot (L)_{3}$, henceforth referred to as 1] that effectively overcomes these limitations. Besides the environmentally benign Zn species, the methylthioethylenethio side chains of L apparently provide stronger binding for the metal species (in comparison with the methylthio groups in TMBD)—for example, HgCl₂ can be effectively taken up from an ethanol solution at a concentration as low as 84 mg/L.

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Chart 1



Moreover, the 2,5-sulfur-substituted L brings about significantly enhanced photoluminescence in both the free ligand L and the network compound 1, enabling effective sensing for environmentally relevant guest species, such as $HgCl_2$ and nitrobenzene.

EXPERIMENTAL SECTION

General Procedure. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich, Merck, and Acros) and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. The ratios of the metal ions were determined using a Perkin-Elmer Model Optima 2100 DV ICP optical emission spectrometer. Solution ¹H and ¹³C NMR spectra were recorded on a 400 MHz Bruker superconducting magnetic high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric (TG) analyses were carried out in a nitrogen stream using Perkin-Elmer Thermal analysis equipment (Model STA 6000) with a heating rate of 10 °C/min. Single-crystal XRD data collection was conducted on a Bruker AXS SMART APEX CCD system, using Mo K α (λ = 0.71073 Å) radiation at 100(2) K. Data were collected, the unit cell determined and refined, and data were integrated and corrected for absorption using Apex2 (v2008.2-4, Bruker AXS Inc., Madison, WI, 2008). All absorption corrections were performed using the SADABS program. The structure was solved and refined by fullmatrix least-squares on F_{\circ}^2 , using SHELXL 6.14 (Bruker AXS, Inc., Madison, WI, 2003). X-ray diffraction (XRD) patterns for the bulk samples in Figures 3 and 5 (presented later in this work) were collected at room temperature on a Bruker Model D8 Advance diffractometer, using Cu K α radiation (λ = 1.5418 Å) with a power of 40 kV and 40 mA. Powder XRD patterns for the other samples were collected at room temperature on a Siemens D500 powder diffractometer (Cu Ka radiation, $\lambda = 1.5418$ Å). The power of the sealed X-ray tube was 40 kV and 30 mA. All powder samples were spread onto glass slides for data collection. The program Mercury (from the Cambridge Crystallographic Data Center) was used to calculate powder patterns from single-crystal structures.

Dimethyl 2,5-dimercaptoterephthalate (S1). A round-bottomed flask (100 mL) was loaded with a magnetic stirring bar, powder of 2,5-dimercapto-1,4-benzenedicarboxylic acid (DMBD, 2.16 g, 9.39 mmol), methanol (30 mL), and concentrated H₂SO₄ (2.0 mL). The flask was then connected to a condenser and the mixture was refluxed at 80 °C for 48 h. After the reaction mixture was cooled to room temperature, water (200 mL) was added to the reaction mixture; the resulted yellowish precipitate was filtered off by suction, washed extensively with water, and dried in air (2.19 g, 90% based on the DMBD). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (s, 2H, CHAr), 4.66 (s, 2H, SHAr), 3.96 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 165.92, 133.57, 133.48, 129.12, 52.72. FT-IR (KBr pellet, $\bar{\nu}/cm^{-1}$): 3410(w), 3002(w), 2953(w), 2535(w), 1713(s), 1560(w), 1434(m), 1303(s), 1247(s), 1136(w), 1090(s), 954(m), 823(m), 777(m), 632(w). Chemical analysis of the product $C_{10}H_{10}O_4S_2$ yielded the following: Calcd [C (46.50%), H (3.90%)]; Found [C (46.30%), H (4.05%)].

Dimethyl 2,5-bis(2-bromoethylthio)terephthalate (S2). S1 (0.52 g, 2.01 mmol) and anhydrous acetone (40 mL) were loaded into a 100-mL two-neck flask that was charged with a magnetic stirring bar. The mixture was bubbled with N₂ for 10 min. Under N₂ protection, 1,2dibromoethane (10 mL, 116 mmol), K₂CO₃ (1.10 g, 7.96 mmol), and NaI (0.05 g, 0.334 mmol) were added, and N₂ was bubbled through the resulting reaction mixture for another 10 min. The reaction mixture was then stirred and refluxed (by means of an oil bath; bath temperature: 75 °C) under nitrogen protection for 24 h. After being cooled to room temperature, the solvents were removed with a rotary evaporator and the yellowish residue was purified via a silica gel plug (silica gel, with 1:3 hexane/dichloromethane as the eluent) to provide a bright yellow crystalline solid (0.51 g, 53% based on S1). ¹H NMR (400 MHz, CDCl₃): δ 7.844 (s, 2H, CHAr), 3.974 (s, 6H, CH₃), 3.4–3.6 (m, 8H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 165.76, 135.33, 132.46, 129.41, 52.84, 34.53, 28.48. FT-IR (KBr pellet, $\bar{\nu}/cm^{-1}$): 3415(w), 3036(w), 2987(w), 2943(w), 2843(w), 1713(s), 1473(m), 1435(m), 1298(m), 1232(m), 1196(m), 1132(w), 1086(s), 966(w), 899(w), 825(w), 775(s). Chemical analysis of the product $C_{14}H_{16}$ - $Br_2O_4S_2$ yielded the following: Calcd [C (35.61%), H (3.42%)]; Found [C (35.80%), H (3.25%)].

2,5-Bis(2-(methylthio)ethylthio)terephthalic Acid (L). In a nitrogen-filled glovebox, sodium thiomethoxide (0.44 g, 6.28 mmol) was loaded into a 50-mL two-neck flask equipped with a septum and a magnetic stirring bar. After the flask was taken out of the glovebox, DMEU (1,3-dimethyl-2-imidazolidinone, 10 mL) was injected via cannula under N2. When the sodium thiomethoxide was completely dissolved in DMEU, S2 (0.60 g, 1.27 mmol) was added. The reaction mixture was then stirred and heated at 90 °C under nitrogen protection. After 2 days, the reaction mixture was poured into 100 mL of water, and HCl (10%) was added slowly with vigorous stirring. After the pH was reduced to below 2, the resultant yellowish solid product was isolated by suction filtration [0.42 g, 87% based on S2]. The solid product thus obtained was pure, as indicated by NMR, and was used for crystal growth without further purification. ¹H NMR (400 MHz, DMSO-d₆): δ 7.80 (s, 2H, CHAr), 3.19 (m, 4H, CH₂), 2.71 (m, 4H, CH₂), 2.14 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 167.24, 135.25, 132.76, 128.49, 32.19, 31.44, 15.06. FT-IR (KBr pellet, $\overline{\nu}/cm^{-1}$): 3430(w), 2920(m), 2852(m), 2645(w), 2558(w), 1659(s), 1474(m), 1412(m), 1301(m), 1243(s), 1091(m), 895(w), 779(w), 633(w). Chemical analysis of the product $C_{14}H_{18}O_4S_4$ yielded the following: Calcd [C (44.42%), H (4.79%)]; Found [C (44.80%), H (4.52%)].

X-ray Quality Single-Crystals of $Zn_4O \cdot (L)_3 \cdot (DMF)_4 \cdot (H_2O)_4$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (6.0 mg), L (3.8 mg) and *N*,*N*-dimethylformamide (DMF) (0.8 mL) was sealed in a Pyrex glass tube (outer diameter, OD = 10 mm; inner diameter, ID = 7.8 mm) and heated in an oven at 100 °C for 24 h and cooled to room temperature at a rate of 10 °C/h. Bright yellow block-like crystals were obtained (4.3 mg, 80%, based on L). Larger-scale preparations [e.g., with 36.0 mg of L, 60.0 mg of Zn(NO_3)_2 \cdot 6H_2O, and 8 mL of DMF in a 12-mL vial at 110 °C for 24 h], using a glass vial, provided the same product in similar yields and singlephase purity (as checked via powder XRD). Chemical analysis of the product $C_{54}H_{84}O_{21}N_4S_{12}Zn_4$, corresponding to $Zn_4O \cdot (L)_3 \cdot (DMF)_4$ - $(H_2O)_4$, yielded the following: Calcd [C (36.61%), H (4.78%), N (3.16%)]; Found [C (36.30%), H (4.41%), N (3.31%)].

Activation of Crystals of 1 and MOF-5. A bulk sample of brightyellow, cube-shaped crystals of 1 was prepared in a vial as described above [i.e., with 36.0 mg of L and 60.0 mg of $Zn(NO_3)_2 \cdot 6H_2O$]. After the mother liquid (of DMF) was decanted, the crystals were washed twice with anhydrous DMF (i.e., 2×8 mL)—each time, the crystals were allowed to soak for 6 h before the DMF was decanted. The crystals were then similarly washed three times with acetone $(3 \times 10 \text{ mL})$ again, the crystals were soaked for 8 h before the acetone was decanted, after which the solid was washed three times with chloroform $(3 \times 8 \text{ mL})$; the soaking time for each wash was 8 h). After the final chloroform wash, the solvent was decanted and the resultant crystals were evacuated with an oil pump at room temperature for 4 h to give 33 mg (75%, based on L) of $Zn_4O \cdot L_3 \cdot (CHCl_3)_{0.5}$ as yellowish cube-shaped crystals. Chemical analysis for C85H97Cl3O26S24Zn8 yielded the following: Calcd [C (34.80%), H (3.33%)]; Found [C (34.50%), H (3.62%)]. The powder XRD pattern of the bulk sample thus activated indicated a single crystalline phase, which was consistent with the single-crystal structure of as-made 1.

The preparation of single-crystal samples of MOF-5 and the subsequent activation were carried out according to the literature.¹¹ Zn-(NO₃)₂·6H₂O (180 mg, 0.610 mmol) and 1,4-benzenedicarboxylic acid (bdc, 33 mg, 0.198 mmol) were dissolved in diethylformamide (DEF, 5.0 mL) in a 12-mL glass vial with a septum. The reaction vessel was heated in an oven at 80 °C for 10 h and cooled to room temperature at a rate of 10 °C/h. After the mother liquid of DEF was decanted, the crystals were washed thrice with anhydrous DMF (i.e., $3 \times 8 \text{ mL}$)—each time, the crystals were allowed to soak for 8 h before the DMF was decanted. The crystals were then similarly washed six times with chloroform (6×8 mL; the soaking time for each wash was 8 h). After the final chloroform wash, the solvent was decanted and the included CHCl₃ was removed in vacuo to give 34 mg (67%, based on bdc) of activated MOF-5 product as colorless cube-shaped crystals. Chemical analysis of MOF-5 C24H15O14.5Zn4, corresponding to Zn4O · (1,4benzenedicarboxylate)₃ \cdot (H₂O)_{1.5}, yielded the following: Calcd [C (36.17%); H (1.90%)]; Found [C (36.04%); H (2.15%)]. The powder XRD pattern of the bulk sample thus activated indicated a single crystalline phase, which is consistent with the single-crystal structure of as-made MOF-5.

Sorption of Nitrobenzene (NB) for 1 and MOF-5. A small vial containing \sim 10 mg of the activated crystals of 1 (not ground) was placed into a larger vial containing ~ 10 mL of nitrobenzene (NB), with care being taken to avoid direct contact between the solid sample and the liquid. The larger vial was then sealed for the vapor sorption experiment for a period of 3 days. To remove solvent that was fortuitously located on the exterior of the solid sample, n-hexane was then used to wash the crystals repeatedly (e.g., 3×2 mL), and the washed crystals were left in the air, to allow the hexane to evaporate before characterizing the compound for the presence of NB molecules. Chemical analysis of the NB-treated crystals thus obtained, C48H59NO18S12Zn4, corresponding to $Zn_4O \cdot (L)_3 \cdot (NB)(H_2O)_3$, yielded the following: Calcd [C (36.39%), H (3.75%), N (0.88%)]; Found [C (36.18%), H (3.91%), N (0.97%)]. The NB-depleted sample was prepared by evacuating (by means of an oil pump) the NB-treated sample at 120 °C for 5 h (see Figure S6 in the Supporting Information for the IR spectrum).

HgCl₂ Sorption of 1. Inside a capped 5-mL vial, activated crystals of 1 (10 mg, equivalent to 0.0071 mmol of $Zn_4O(L)_3$) were allowed to soak undisturbed in an ethanol (ABS, 2.0 mL) solution of HgCl₂ (10.0 mg, 0.036 mmol) at room temperature for 2 weeks. The mixture was then suction-filtered, and the solid that was isolated was then washed with

10 mL of ethanol to give a final product (11.6 mg). This solid product was then examined via powder XRD to reveal that the main framework remained intact (see below). Part of this solid product was also dissolved in concentrated HNO₃ for inductively coupled plasma (ICP) elemental analysis, which indicated a Zn/Hg molar ratio of 5.56:1. Chemical analysis of the product $C_{45}H_{57}Cl_{1.44}Hg_{0.72}O_{14.5}S_{12}Zn_4$, corresponding to Zn₄O·(L)₃·(HgCl₂)_{0.72}·(EtOH)_{1.5}, yielded the following: Calcd [C (32.33%), H (3.44%)]; Found [C (32.58%), H (3.06%)].

In another test (to probe the ability of the activated sample of 1 to take up $HgCl_2$ from dilute solutions), activated crystals of 1 (10.0 mg) were added into a 5-mL clear vial containing a (weaker) ethanol solution of $HgCl_2$ (2.0 mL, 84 mg/L). The mixture was then left to stand undisturbed for six days at room temperature, and ICP was used to detect how much $HgCl_2$ was left in the solution (see Results and Discussion section below).

The HgCl₂ was depleted from the host framework via the following procedure: a mixture of $Zn_4O \cdot (L)_3 \cdot (HgCl_2)_{0.72} \cdot (EtOH)_{1.5}$ (5.0 mg) (the ratio of Zn/Hg was predetermined by ICP) and freshly distilled anhydrous acetonitrile (2.5 mL) in a sealed Pyrex glass tube was heated at 100 °C for 2 days and cooled to room temperature. The product was filtered and washed with freshly distilled acetonitrile and then dried in vacuo overnight (yield = 4.5 mg). The sample then was dissolved in concentrated HNO₃, and the ensuing ICP elemental analysis yielded a Zn/Hg ratio of 36.4:1, which indicates that ~85% of the HgCl₂ component had been removed from the solid sample. Chemical analysis of the product $C_{44.4}H_{51.6}Cl_{0.22}Hg_{0.11}N_{1.2}O_{13}S_{12}Zn_4$, corresponding to Zn₄O · (L)₃ · (HgCl₂)_{0.11} · (CH₃CN)_{1.2}, yielded the following: Calcd [C (35.88%), H (3.50%), N (1.13%)]; Found [C (35.62%), H (3.15%), N (1.48%)].

RESULTS AND DISCUSSION

Syntheses and Stability Tests. As shown in Chart 1, molecule L was conveniently synthesized from the methyl ester of 2,5-dimercaptobenzenedicarboxylic acid (DMBD, which we recently introduced as a bifunctional building block for coordination networks^{9b}). In this connection, it is also our intention to further highlight DMBD as an especially versatile entry point to a large class of functionalized building blocks for the field of coordination networks, because a wider array of organic groups can be conveniently anchored to the highly nucleophilic sulfur atoms in DMBD to structurally and functionally impact the prospective MOFs.

Compound 1 was obtained by reacting L with $Zn(NO_3)_2$ in N, N-dimethylformamide (DMF) under solvothermal conditions (see Experimental Section). Table 1 gives X-ray data regarding 1. X-ray single-crystal analysis reveals that the network of 1 (see Figure 1) features the α -Po topology (i.e., a simple cubic net) and is isoreticular with the reported MOF-5 that builds on 1,4benzenedicarboxylate (bdc) linear struts and the Zn₄O cluster octahedral nodes.¹² Notice that, in 1, the 2-methylthioethylthio side chains (-SCH₂CH₂SCH₃) of L are not bonded to the Zn(II) centers and thus extensively decorate the channels as freestanding donors for metal guests. These floppy side chains are highly disordered, and only the S atom on the benzene core was located, using XRD data (see the Supporting Information for details). The presence of the $-SCH_2CH_2SCH_3$ side chains in the crystals of 1 was verified by solution ¹H NMR and IR measurements (i.e., by dissolving crystals of 1 in 1:8 DCl (38% in D_2O /DMSO- d_6 , see also Figure S1 in the Supporting Information for the NMR spectrum and Figure S2 in the Supporting Information for the IR spectrum).

The crystal samples thus prepared show remarkably enhanced stability toward moisture, in comparison to MOF-5. For example,

parameter	value
chemical formula	$C_{42}H_{48}O_{13}S_{12}Zn_4$
formula weight, fw	1407.00
temperature	100(2) K
wavelength	0.71073 Å
crystal system	cubic
space group	Fm 3 m
lattice parameter, <i>a</i>	25.559(6) Å
unit-cell volume, V	16696(4) Å ³
Z	8
density, $ ho_{ m calcd}$	1.119 g/cm ³
absorption coefficient	1.474
F(000)	5728
goodness-of-fit on F ²	0.834
$R_1^{b} \left[I > 2\sigma(I) \right]$	0.0948
$wR_2^c [I > 2\sigma(I)]$	0.2878
Partial model; disordered $-CH_2CH_2SCH_3$ signals of the set of	de chains were unre- tails ${}^{b}R_{1} = \Sigma F_{1} - $

solved; see Supporting Information for more details. ${}^{\circ}R_1 = \Sigma ||F_o| - F_c ||/\Sigma(|F_o|)$. ${}^{\circ}wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$.

the activated solid samples (see the Experimental Section for the preparation of the activated sample) of 1 are stable in air for more than 3 weeks, as is shown by the powder XRD patterns in Figure S3 in the Supporting Information. However, the prototypical MOF-5 is well-known to degrade steadily within a couple of hours when placed in air.^{11a,13} In another experiment, the activated crystals of 1 were immersed in water at room temperature to further test their stability. As seen in Figure S4 in the Supporting Information, although the major diffraction peaks of the solid sample of 1 were substantially retained after 3 h of immersion in water, longer exposure (e.g., 6 h) led to significant degradation of the crystalline samples of 1 (apparently due to the inherent water-sensitive nature of the Zn₄O cluster). Overall, the enhanced stability of 1 toward water can be attributed to the hydrophobic nature of the thioether side chains of L, as well as to the proximity of such hydrophobic groups to the Zn₄O clusters.

Fluorescence Properties and Sorption of Nitrobenzene. Photoluminescent data on benzene 1,4-dicarboxylate ions and its network compound MOF-5 were reported.¹⁴ It was found that the emission maximum occurs at \sim 410 nm for the free ligand in the anionic form, while the network compound MOF-5 emits at 525 nm, which was attributed to ligand-metal charge transfer (LMCT).¹⁵ Notice, however, that the documented data of MOF-5 were measured on nanosized samples that were obtained as a precipitate from a "direct mixing" procedure.¹⁶ When using the larger single crystals of the MOF-5 samples ($\sim 0.2 \times 0.2 \times 0.2 \text{ mm}^3$, see the Experimental Section for details) for photoluminescence measurements (e.g., at the various excitation wavelengths of 280, 320, and 350 nm), we obtained spectra that differ from the data reported on the nanosized samples,¹⁴ with a blue-shifted, broad emission that peaks at \sim 420 nm (curve (b) of Figure S5 in the Supporting Information). Because of its similarity to the dominant features among the emission spectra of free bdc (1,4benzene dicarboxylic acid)-as in spectrum a of Figure S5 in the Supporting Information, the reported data of its disodium salts^{14b}—the emission of the MOF-5 single-crystal samples observed herein seems to be largely arising from ligand-centered transitions, with the LMCT mechanism reported elsewhere on



Figure 1. Crystal structure of 1: (a) $Zn_4O(COO)_6$ cluster shown as a ball-and-stick model (Zn1-O1, 1.934 Å; Zn1-O2, 1.885 Å; Zn···Zn 3.158 Å); (b) the same cluster with ZnO₄ shown as tetrahedra; (c) one of the cavities. The side chain atoms beyond the first S atom (e.g., $-CH_2CH_2SCH_3$) and guest molecules (e.g., DMF and H_2O) are disordered and omitted. The two S atoms on the phenylene core of L are shown here as disordered over all four (e.g., the 2, 3, 5, and 6) positions. The large central yellow sphere highlights the void feature.

nanoparticles of MOF being less significant. Further studies are apparently needed to explain the difference between the luminescence data observed herein of the MOF-5 single crystals and those of the nanoparticle samples.¹⁷

Compared to the emission maximum (λ_{max}) of ~390 nm for the powder sample of the dbc molecule (curve (a) of Figure S5 in the Supporting Information), the sulfur functions in molecule L significantly red-shift the emission maximum of its solid sample to a longer wavelength of 500 nm (with a weaker side peak at 410 nm; see Figure 2), which is consistent with the $n-\pi$ conjugation between the sulfur groups and the aromatic core in molecule L. Similarly, for the framework compound 1, a broad and intense emission was observed with $\lambda_{max} = 475$ nm, together with a weaker sideband with $\lambda_{
m max}$ at 410 nm (e.g., compare curve (b) of Figure S5 in the Supporting Information and spectrum a of Figure 2). As seen in Figure 2 (inset), the powder of 1 emits bright cyan (blue-green) light under UV radiation (365 nm). Overall, the major features of the emission spectra for L and 1 are similar, thus indicating a largely ligand-based luminescent process. Ligand-based photoluminescent phenomena were also observed in the isoreticular systems of IRMOF-11 ($Zn_4O(4,5,9,10$ tetrahydropyrene-2,7-dicarboxylate)₃), IRMOF-13 (Zn₄O(2,7pyrene dicarboxylate)₃), and $Zn_4O(stilbene dicarboxylate)_3$), in which the greater degree of π -conjugation in the organic linkers was presented as being responsible for the ligand-based luminescence.¹⁵ In this line of argument, the ligand-based luminescence



Figure 2. Room-temperature solid-state emission spectra from (a) a desolvated sample of 1, (b) an NB-loaded sample of 1, (c) an NB-depleted sample, and (d) a powder sample of molecule L (excitation wavelength λ_{ex} = 360 nm). The inset shows photographs of the samples that generated spectra a, b, and c.

of 1 is in accord with the conjugation between the terephthalate π -system with the electron-donating thioether sulfur substituents in molecule L.

The strong fluorescence, as well as enhanced air stability of the network of 1, facilitate the testing of its potential use as a fluorescent sensor. In our preliminary tests (conducted in air, with no measures to exclude moisture taken), we discovered that immersing an activated sample of 1 in nitrobenzene (NB) vapor for 2-3 days results in significant inclusion of NB molecules in the pores of 1 (see Figure S6 in the Supporting Information for the IR evidence for the uptake of NB), and effectively suppresses the luminescence, whereas molecules such as benzene and toluene, under similar conditions, do not significantly alter the fluorescence intensity or appearance of the solid sample of 1. Moreover, as shown in Figure 2, the fluorescence intensity of the host net in 1 can be substantially recovered upon removal of the NB guests (e.g., by evacuating at 120 °C for 5 h; removal of NB molecules checked by IR; see Figure S6 in the Supporting Information). The structural integrity of the host net was maintained in this guest exchange process, as seen in the powder XRD patterns of Figure 3-the positions of the peaks for the NBloaded sample and NB-free samples are slightly shifted, while the relative intensity changes (e.g., in the 111 and 400 peaks) are apparently due to the electron densities from the NB molecules. The fluorescent quenching of nitrobenzene on aromatic fluorophores is well-documented, and it is generally considered to involve a charge transfer from the fluorophore excited state to the low-lying molecular orbital associated with the strongly electronwithdrawing nitro group.¹⁸

In a comparative study, we also tested the fluorescent responses of the prototypical MOF-5 system (in an N₂-filled glovebox) and found that the MOF-5 samples in their activated form also feature a similar response to NB (see Figure S5 in the Supporting Information for the emission spectra, Figure S7 in the Supporting Information for the IR spectra regarding the uptake of NB, and Figure S8 in the Supporting Information for the support and Figure S8 in the Support of the powder XRD patterns), although better calibrated tests are still needed to compare 1 and MOF-5, with regard to the sensitivity to NB. The use of MOF materials as fluorescent sensors for organic nitro compounds¹⁹ and other analytes²⁰ is starting to attract interest and further studies on the properties of



Figure 3. Powder X-ray diffraction (XRD) patterns (Cu K α , $\lambda = 1.5418$ Å) from (a) a simulation from the single-crystal structure of 1, (b) an activated sample of 1 [Zn₄O·(L)₃], (c) a nitrobenzene (NB)-loaded sample [Zn₄O·L₃·(NB)(H₂O)₃] prepared from treating the sample that generated spectrum b with NB vapor, and (d) an NB-depleted sample prepared from evacuating the sample that generated spectrum c at 120 °C for 5 h.



Figure 4. Conformations of the TMBD molecule in the crystal structure of PbTMBD (A) before and (B) after the uptake of HgCl₂. The Hg–S distance in panel B is 2.692 Å.

1 and related systems might shed more light on its suitability for practical applications in this direction.

Sorption of HgCl₂. As demonstrated in the previously reported network PbTMBD,^{9c} the presence of the methylthio groups (from the molecule TMBD) in the pores of the network solid allowed for the uptake of HgCl₂. However, that particular test entailed a stringent condition of heating at 100 °C for 48 h in a sealed tube with HgCl₂ powder, crystals of PbTMBD, and benzene, while placing the PbTMBD crystals in an HgCl₂ solution (e.g., in THF or ethanol) at room temperature did not lead to significant uptake of HgCl₂. We suspect that the sluggish binding of HgCl₂ therein might be due to the steric factors around the sulfur functions, e.g., the methylthio groups are directly attached to the rigid and crowded hexasubstituted benzene cores, and they are installed in a compact microporous milieu.

Specifically, the pristine crystal of PbTMBD features the space group C2/c, with the 1,2-bis(methylthio) groups all adopting the *ab* (or up/down) configuration—i.e., one methyl group being above and the other below the benzene plane (see Figure 4). After taking up HgCl₂, the space group changed to C2/m, with the reflection symmetry imposed on one of the TMBD molecules (i.e., one out of three) to enforce an *aa* conformation (with both methyl groups on the same side of the benzene plane; see Figure 4). With both methyl groups on the same side of the benzene plane, the Hg(II) atom can approach the S atoms from



Figure 5. Powder XRD patterns (Cu K α , $\lambda = 1.5418$ Å) of (a) calculated pattern from single crystal structure; (b) a desolvated sample of 1 [Zn₄O·(L)₃]; (c) a HgCl₂-loaded sample of 1 [Zn₄O·(L)₃. (HgCl₂)_{0.72}]; and (d) a HgCl₂-depleted sample obtained from washing the sample that generated spectrum c with acetonitrile.

the other side, without being hampered by the methyl groups. Since such an open and accessible geometry is more difficult with the *ab* conformation in the pristine structure (C2/c), the conversion into the *aa* conformation becomes especially helpful for effecting the HgCl₂ uptake. Such a conformational change is apparently difficult with the hexasubstituted configuration, as well as its being part of a solid state matrix; therefore, prolonged heating (or other activating measures) is necessary.

By comparison, molecule L is equipped with flexible and extended sulfur functions, in order to enhance the accessibility to the incoming HgCl₂ species. Therefore, we expected that the resultant network 1, with its larger porosity and 3D-connected channels (in comparison to the above PbTMBD), would provide for better efficiency of HgCl₂ uptake. Indeed, even with ethanol (absolute) as the solvent for HgCl₂ and at a concentration of 0.5% (w:w), significant HgCl₂ uptake can be achieved by simply mixing in the activated crystals of 1 at room temperature (see the Experimental Section for details). A new composite with the formula Zn₄O·L₃·(HgCl₂)_{0.72}·(EtOH)_{1.5} (i.e., a molar ratio of Zn/Hg = 5.56:1, determined from ICP elemental analyses; the formula also fits with results of CHN elemental analyses, see the Experimental Section), for example, can be achieved after immersing the crystals in the HgCl₂ ethanol solution for 14 days.

The uptake of $HgCl_2$ into the host net of 1 was also monitored by powder XRD studies. As shown in Figure 5, the lower angle peaks of 111 and 200 greatly diminished for the $HgCl_2$ -loaded sample (pattern c), whereas the higher-angle peaks (e.g., 220, 400) become relatively strong. Such a drastic change in diffraction peak intensities reflects the significant increase of electron density in the channel region (i.e., the system becomes less porous), as a result of the uptake of $HgCl_2$, while indicating that the original crystal lattice of 1 remains intact in the process.

Moreover, the majority of the $HgCl_2$ component in the $HgCl_2$ -loaded sample of 1 can be removed by a polar solvent such as acetonitrile, while maintaining the structural integrity of the host net of 1. For example, a mixture of the above $Zn_4O \cdot L_3 \cdot (HgCl_2)_{0.72} \cdot (EtOH)_{1.5}$ (5.0 mg) and freshly distilled anhydrous acetonitrile (2.5 mL) in a sealed Pyrex glass tube was heated at



Figure 6. Room-temperature solid-state emission spectra from (a) a desolvated sample of 1 [Zn₄O·(L)₃]; (b) a HgCl₂-loaded sample of 1 [Zn₄O·(L)₃·(HgCl₂)_{0.72}]; and (c) a HgCl₂-depleted sample from washing the sample that gave spectrum b with acetonitrile (excitation wavelength λ_{ex} = 360 nm). The inset shows photographs of the samples that yielded spectra a, b, and c.

100 °C for 2 days and then cooled to room temperature. The product was filtered and washed with freshly distilled acetonitrile and then dried in vacuo overnight (yield = 4.5 mg). ICP elemental analysis yields a Zn/Hg ratio of 36.4:1, indicating that ~85% of the HgCl₂ component has been removed from the HgCl₂-loaded sample (see the Experimental Section for the details). Powder XRD studies on the HgCl₂-depleted sample thus recovered revealed that the relative intensity of the peaks was largely restored to resemble that of the pristine samples of 1, consistent with the recovering of the porous features of the host net (pattern d in Figure 5).

To probe the lower limit of the HgCl₂ concentration achievable by 1 as an absorbent, a relatively large amount of activated sample of 1 (e.g., 10.0 mg) was added to an ethanol solution (2.0 mL) of HgCl₂ with the initial concentration of 84 mg/L. After standing undisturbed at room temperature for six days, the concentration of HgCl₂ in the solution was decreased to 5.0 mg/L (equivalent to 5.0 ppm), as determined by the ICP method, indicating that >94% of the HgCl₂ was thus removed in this test.

The uptake of HgCl₂ also impacts significantly the photoluminescence of the host net of 1. As seen in Figure 6, \sim 90% of the original emission of the activated sample of 1 (spectrum a) was suppressed after the HgCl₂ uptake (to form $Zn_4O \cdot L_3 \cdot$ $(HgCl_2)_{0.72}$, spectrum b). Correspondingly, the powder of the loaded sample features a dim emission that is barely visible. The fluorescence substantially recovers upon removing the HgCl₂ component (by a polar solvent such as acetonitrile, same as that previously mentioned). Fluorescence quenching by heavy-metal ions is a well-documented phenomenon and occurs via many intramolecular/intermolecular pathways, which include spinorbit coupling, energy transfer, and electron transfer.²¹ In parallel to the solid-state behaviors observed herein, fluorophors equipped with thioether side chains also exhibit effective quenching by Hg(II) ions in organic solution.²² Further studies on MOF systems with the combined features of photoluminescence, porosity, and thioether donor function should lead to a better understanding of the potential applicability in the uptake and monitoring of Hg(II) ions and other metal species.

Thermogravimetric Analyses. As shown in curve (a) of Figure S9 in the Supporting Information, no significant weight

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loss below 240 °C was observed for the solid sample of free ligand (L). Subsequently, a sharp weight loss (67.6%) between $250 \,^{\circ}\text{C}$ and 354 °C occurred, which possibly involves the departure of the ethylenethioether side chain and the carboxylic groups (c.f., the CH₂CH₂SCH₃ and COO components together account for 63.5% of the total weight of L). As shown in the TGA plot (curve (b)) of the as-made sample of 1, the weight loss proceeds rather smoothly (gradual and continuous weight loss) from room temperature up to 470 °C. However, two stages of weight losses can be roughly identified. The first stage (from room temperature up to 170 °C) registers a weight loss of 21.8%, closely corresponding to the weight fraction of the DMF and water guests calculated from the formula determined from the crystallography and elemental analysis [i.e., DMF and water weight proportion in $Zn_4O \cdot L_3 \cdot (DMF)_4(H_2O)_4$: 20.6%], whereas the second-stage weight loss (31.2%, from 170 °C to 470 °C) likely involves the decomposition of the host framework. Notice that the onset decomposition temperature for the host net in the asmade sample of 1 (i.e., $170 \,^{\circ}$ C) is substantially lower than that of the free ligand L (ca. 240 °C), which could be due to the especially strong collision between the floppy side chains of L and the nearby Zn_4O nodes (e.g., the S atoms on the side chains could even attack the Zn^{2+} centers at higher temperatures).

For the activated sample (i.e., prepared from subjecting the asmade sample to solvent exchange with CHCl₃), only a minimal weight loss (i.e., <2.0%; see curve (c) in Figure S9 in the Supporting Information) observed below 200 °C, which is probably due to residual CHCl₃ molecules. From 200 °C up to 470 °C, a sharper decrease of 39.5% involving the decomposition of the host net occurred, which, notably, largely parallels that of the corresponding stage of plot 2 (for the as-made sample).

Unlike curves (b) and (c) in Figure S9 in the Supporting Information, the TGA plot (curve (d) in Figure S9 in the Supporting Information) for the nitrobenzene-filled sample of 1 features a more monotonic weight loss below 450 °C, with no distinct stages of weight losses observed. The monotonic process of weight loss is presumably related to the less-volatile nature of the nitrobenzene molecules (compared with the guests of DMF, water, and CHCl₃ for the samples that yielded curves (b) and (c) in Figure S9 in the Supporting Information). The weight loss (up to 180 °C) is 11.7%, corresponding to the removal of one nitrobenzene molecule and three water molecules from the formula $Zn_4O \cdot L_3 \cdot (NB)(H_2O)_3$ (calculated: 11.2%). The ensuing weight loss beyond 180 °C very likely involves the collapse of the host net and decomposition of the organic components.

CONCLUSION

This work serves to further highlight the multiple advantages of the thioether units for functionalizing metal—organic frameworks (MOFs) and serves to stir our imagination in several directions. The advantages include the following:

(1) In general, thioethers are moderate donors (e.g., compared with the stronger-binding phosphines), with a distinct chemical softness that contrasts with the hard and ionic carboxylate units. As a result, the MSES (CH₃-SCH₂CH₂S-) side chain, despite the chelating disposition of the two S atoms, refrains from bonding to the chemically hard Zn(II) centers, and thereby minimizes interference on the formation of the Zn₄O-carboxylate host net. The chemical softness also implies significant hydrophobicity of the thioether side chains, which proves

to be especially effective in suppressing the moisture sensitivity that is symptomatic of the prototypal network of MOF-5.

- (2) Thioether groups are generally stable in air and, in the hands of a trained synthetic chemist, can be readily modified in variable lengths and arrangements—for example, thioether groups have even been used as mainstays for the assembly of dendritic scaffolds.²³
- (3) Thioether groups are generally compatible with the Sonogashira and Suzuki C-C coupling reactions and other well-established synthetic protocols, thus allowing for the thioether groups to be efficiently integrated into diverse arrays of organic molecular scaffolds.

The functional advantages of the thioether groups become especially attractive in light of the recent development of solid state network materials: ever larger pores (e.g., over 20 Å) are being achieved in increasing numbers of MOFs,²⁴ and in the related boroxine or boronate ester-based covalent organic frameworks²⁵ (COFs). In fact, one does not have to be limited to crystalline systems: microporous polymer systems, for example, are also have been the subjects of intense investigation.²⁶ Conjoining the rich and rapid developments in framework materials with the functional/synthetic advantages of the thioether groups, we foresee a wide growth area in which pore features and functions can be systematically tuned by thioether side chains, to optimize the characteristic solid-state properties such as guest absorption/separation, metal uptake, and the consequential developments with regard to catalysis and advanced electronic properties within the matrices of framework materials.

ASSOCIATED CONTENT

Supporting Information. Additional experimental procedures, full crystallographic data in CIF format for 1, powder diffraction patterns for bulk samples of 1, and solution NMR spectra, IR spectra, and TGA plots of 1 and related compounds. This material is available free of charge via the Internet at http:// pubs.acs.org.

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(17) In private communications with Dr. Christina A. Bauer, we were told that the MOF-5 single crystals in her hands emit at 525 nm, like the nanosized samples. We have repeated our experiments a few more times, and yet we continued to observe the same 420-nm emission.

At this stage, we are unable to explain the discrepancy between our emission data on MOF-5 and those of others.

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