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Lithium-Based 3D Coordination Polymer with Hydrophilic Structure for Sensing of Solvent Molecules

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ABSTRACT: A lithium-based coordination polymer is synthesized from 1,3-benzene dicarboxylate acid with lithium perchlorate through a solvothermal way. The complex features a 3D hydrophilic structure. The adsorption of water and organic solvents on this coordination polymer was investigated in situ by quartz crystal microbalance (QCM), which indicated that this framework is highly sensitive to water and methanol.

Porous coordination polymers, the so-called metal-organic frameworks (MOFs), constructed by metal ions and polyfunctional organic linkers have attracted a great deal of interest in recent years.^{1–7} Their light weight, high porosity, low volumetric density give them great opportunity for the potential applications in ion exchange,^{3,8} chemical sensor,^{9–13} catalysis,^{14–17} gas storage,^{18–21} and separation.²² However, to the best of our knowledge, among these coordination polymers, most of them constructed from transitional metals and rare earth metals, but alkali-metal-based coordination polymers are scarcely investigated.^{23–26} Compared to the transitional metals, alkali metal units are lighter, which can offer a lower framework density and lead to an increase in gravimetric gas sorption capacity.²⁷ Recent studies have shown that lithium-modified coordination polymers have fantastic properties in improving hydrogen storage capacity.^{28–30} For their special coordination property, alkali-based coordination polymers open the possibility of designing new functional coordination polymers with special topology and interesting properties.

In the present paper, we report the first example of a lithium-based coordination polymer with hydrophilic structure, $\text{Li}_2(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_3\text{H}_7\text{NO})_{1/2} \cdot \text{H}_2\text{O}$ (**1**). We revealed that this coordination polymer with hydrophilic structure could allow only comparatively small and polar solvent molecules access into the channel or interact with the surface of the material. The performance of small solvent molecules adsorption and desorption on the polymer has been explored by in situ quartz crystal microbalance (QCM).

Materials and Methods. All starting materials were commercially available reagents of analytical grade and used without further purification. TGA data were obtained on a Setsys16/18 thermogravimetry analyzer (SETARAM, France) with a heating rate of 10 °C/min in air. X-ray powder diffraction (XRD), which was collected on a conventional PANalytical X-ray Diffractometer, X'Pert MPD PRO at 40 kv, 40 mA, with a scan speed of 0.2°/s and a step size of 0.0167 in 2 θ , using $\lambda\text{Cu K}\alpha 1$, $\text{K}\alpha 2$ radiation. Infrared spectroscopy was performed with a Bruker Equinox 55 FT-IR spectrometer at room temperature in the range 400–4000 cm^{-1} in KBr pellets. The program Mercury 1.4.2 was used for calculation of X-ray crystallographic powder patterns of **1**.

Synthesis of Compound 1. One one-hundredth of a mole of 1,3-benzene dicarboxylic acid (1.64 g) and 0.02 mol of

$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (4.00 g) were dissolved in 40 mL of *N,N*-dimethylformamide (DMF), then 20 mL of tetrahydrofuran (THF) were added to the solution under a vigorous stirring; the mixture was transferred into a 100 mL Teflon-lined stainless autoclave, and heated to 453 K at the rate of 1 K min^{-1} and held it for 3 days under autogenous pressure and afterward cooled naturally to room temperature. A colorless block-shaped crystal was filtered, washed thoroughly with DMF, and finally dried in a vacuum at 333 K for 12 h. The compound was obtained as a single phase of crystalline material without any traces of amorphous impurities (yield: 42%, based on Li). C, H, N elemental anal. Calcd for $\text{C}_{9.50}\text{H}_{9.50}\text{Li}_2\text{N}_{0.50}\text{O}_{5.50}$: C, 49.06; H, 4.12; N, 3.01. Found: C, 47.73; H, 3.95; N, 2.84.

X-ray Crystallography. $\text{C}_{9.50}\text{H}_{9.50}\text{Li}_2\text{N}_{0.50}\text{O}_{5.50}$, $M = 393.29$, crystal dimensions 0.30 \times 0.10 \times 0.10 mm^3 , orthorhombic, $T = 273$ (2) K, space group $C222_1$, $a = 13.359(5)$, $b = 13.845(5)$, $c = 12.817(3)$ Å, $\beta = 90.00^\circ$, $V = 2370.6(16)$ Å³, $Z = 8$, $\mu(\text{Mo K}\alpha) = 0.104$ mm^{-1} , $D_c = 1.303$ g cm^{-3} . Final residuals were $R_1 = 0.0761$ for 1966 reflections with $I > 2\sigma(I)$, $wR_2 = 0.2266$, GOF = 1.137, max/min. Residual electron densities $-0.30/0.60$ eÅ⁻³, Flack parameter = $-1(2)$, CCDC-656897. Data for **1** was performed using a SMART APEX II-CCD single-crystal X-ray diffractometer equipped with a fine-focus sealed tube with graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation source at 273 K. The structures were solved by direct methods and refined by full-matrix least-squares method implemented in SHELXTL³¹ program package. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the aromatic rings were added theoretically. The position and composition of the guest water molecules could not be accurately determined because of their structural disorder, which were confirmed by EA and TG analysis.

Results and Discussion. Single-crystal X-ray diffraction studies revealed that **1** is a three-dimensional (3D) network in orthorhombic chiral space group $C222_1$. This crystalline material composed of Li (I) ions and 1,3-benzene dicarboxylate anions in 2:1 ratio. Figure 1 illustrates the structure of **1** consists of Li centers and 1,3-benzene dicarboxylic ligand (1,3BDC). Each Li^+ ion, located at an inversion center i , is connected to its four nearest neighbors by four bridging 1,3BDC ligands through their oxygen atoms. It should be mentioned that the coordination mode of 1,3BDC with Li in **1** is quite interesting; the carboxylic ligand in 1,3BDC acts as a μ_3 -carboxyl bridge (see the Supporting Information, Figure S1). As shown in Figure 1, there are three crystallographically independent Li (I) centers in this framework. Both Li1 and Li2 coordinated by four carboxyl oxygen atoms from different 1,3BDC, whereas the Li3

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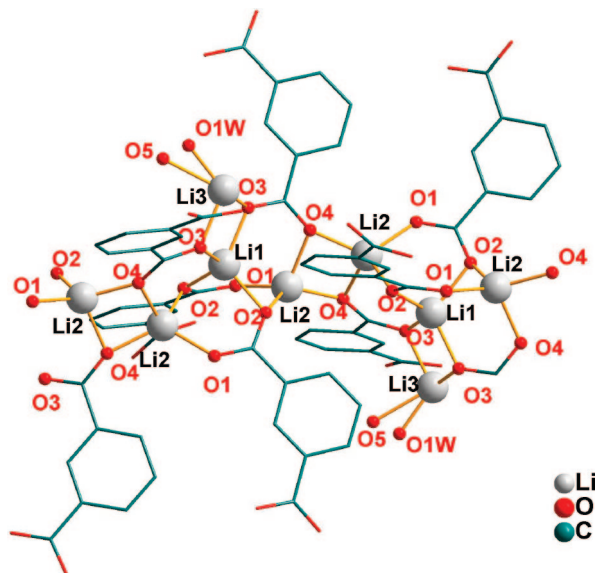


Figure 1. View of the coordination mode of 1,3BDC with Li atoms.

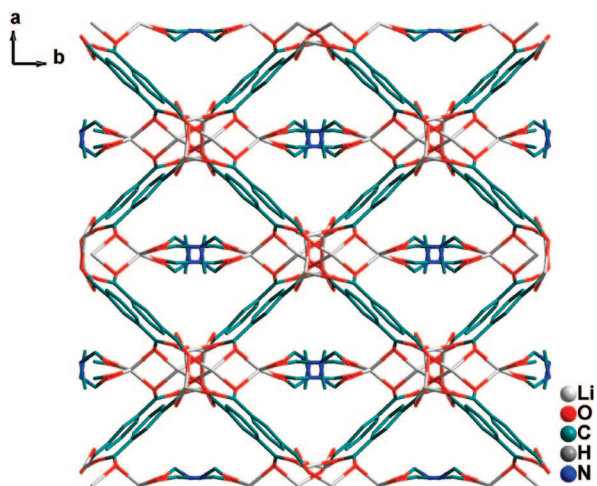


Figure 2. X-ray crystal structure of **1** along the *c* axis.

atom is coordinated by two adjacent μ_2 -O3 atoms, one O5 atom from the DMF guest molecule, and one O1W atom from the guest water molecule. Li1 atom is coordinated by two adjacent μ_2 -O3 atoms, one μ_2 -O2 atom and one μ_1 -O1 atom, and Li2 atom is coordinated by two μ_2 -O4 atoms, one μ_2 -O2 atom, and one μ_1 -O1 atom. The two adjacent Li2 atoms share two μ_2 -O4 atoms from the carboxylic ligand, Li1 and Li3 are connected by μ_2 -O3 atom, and Li1 and Li2 are linked together by the μ_2 -O2 atom. The O–Li–O bond angles range from 102.28 to 123.37°, and thus the Li⁺ ion has a distorted tetrahedral coordination geometry. It is common that Li⁺ ions are in a coordination number of 4;^{23,24} however, five-coordinated lithium complexes in a tetragonal pyramid geometry³¹ or even six-coordinated in an octahedral geometry²⁵ have also been reported. Despite the high distortion of the coordination tetrahedron around Li(I) atom, the bond lengths of the four Li–O bonds also vary. The interatomic distances are close to those usually reported for lithium solids;^{24,31} Li–O distances are in the range of 1.94–2.01 Å at room temperature. In the lattice, the Li–O–C linkages are along the *c* axis.

The key feature of the structure is the framework has ordered channels running along the *c*-axis. As shown in Figure 2, the channel is a one-dimensional (1D) channel with internal van der Waals dimensions of ca. 4.94×6.22 Å². the coordinated DMF

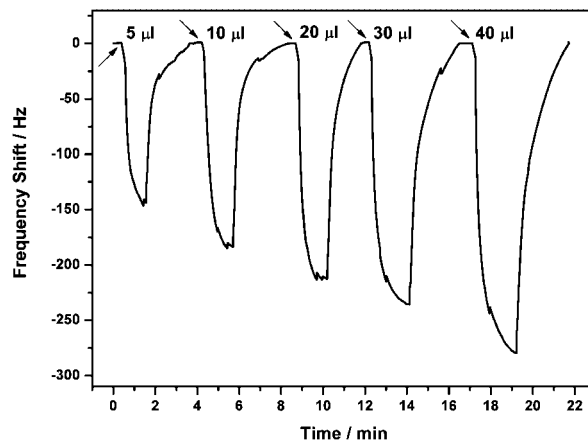


Figure 3. Frequency shift for dehydrated **1** coated QCM response to methanol of 5, 10, 20, 30, and 40 μ L; the corresponding concentrations of methanol in the chamber are 8, 16, 32, 48, and 64 ppm.

atoms and water molecules occupy the channel, and thus in the *ac* plane the lattice showed a paddle-wheel motif.

To examine the thermal stability of this porous framework, thermogravimetric analysis (TG/DTA) and X-ray powder diffraction (XRPD) studies are carried out. The TG/DTA curves of **1** (see the Supporting Information, Figure S2) reveals a weight loss of 11.2% in the temperature range of about 150–310 °C, corresponding to the liberation of all guest water molecules trapped inside the channels (cal. 13.9%). The DTA curve exhibits endothermic peaks during this temperature range, confirming the release of guest molecules. The release of the guest water molecules upon such a high temperature is ascribed to the strong hydrogen-bonding interaction between the main structure and coordinated water molecules, which, together with the COO[−] polar groups in the structure, indicates that this coordination polymer is hydrophilic. The decomposition of the framework starts at about 410 °C; correspondingly, the DTA curve exhibits a series of exothermic peaks that are attributed to the decomposition of the organic ligand. No weight loss is observed between the dehydration and ligand-release temperatures from 310 to 410 °C, indicating the presence of a stable dehydrated framework over a wide range of temperatures. XRPD patterns of as-synthesized **1**, dehydrated **1**³² together with the simulated XRPD pattern from single X-ray diffraction (see the Supporting Information, Figure S3) show that the dehydrated framework retains its structural integrity as confirmed by the preservation of the majority of the X-ray powder diffraction peaks initially observed for **1**. Some differences in reflection intensities between the simulated and experimental patterns are due to the variation in crystal orientation of the microcrystals, and the solvent water molecules can also cause minor differences. When exposed to air at room temperature, the dehydrated sample would quickly soak water. It illuminates that this dehydrated 3D framework with cubic cavities is a suitable host for researching the inclusion of water molecules. It should be mentioned that we have synthesized a series of samples with the same way; the XRPD characterization indicates that the samples are of the same structural integrity.

As this porous material is highly sensitive to water, we use quartz crystal microbalance (QCM) (see the Supporting Information) to study the polymers' sensor performance for potential analysis of small solvents molecules such as methanol, water, tetrahydrofuran, and acetone. The result shows an interesting reaction of this coordination polymer, indicating that **1** has a reversible response to water and methanol, whereas the sensor shows no response to tetrahydrofuran and acetone. Figure 3 shows an illustrative set of results for **1** coated QCM frequency changes, with the injection of methanol varying from 5 to 40 μ L in a 0.5 L chamber. The frequency shift gets a positive change with the increase in the content of methanol in the chamber. The increase in film mass is

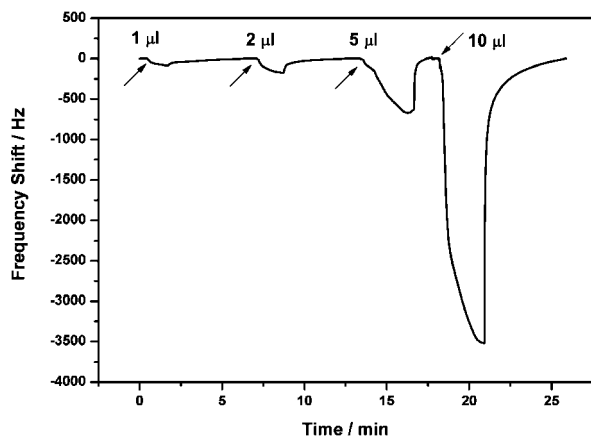


Figure 4. Frequency shift for dehydrated **1** coated QCM response to water of 1, 2, 5, and 10 μL ; the corresponding concentrations of water in the chamber are 2, 4, 10, and 20 ppm.

signaled by the decrease in the crystal's resonance frequency. When the crystal is exposed to different injections of water from 1 to 10 μL in the same chamber, the variety of the frequency shift is shown in Figure 4. It is worth noting that dehydrated **1** coated QCM disk shows higher sensitivity to water than methanol, which results in a higher frequency shift to water, especially when 10 μL of water is injected into the chamber, and dehydrated **1** coated QCM disk shows a stable performance with good reappearance. The sorption/desorption processes of both water and methanol are totally reversible. This dehydrated compound is sensitive only to water and methanol; it may be because the complex structure is hydrophilic, which makes the coordination polymer more easily form a hydrogen bond with polarized solvents. As for water and methanol, the polarity is much higher than tetrahydrofuran and acetone; therefore, the compound only shows a selective adsorption to water and methanol. In the present study, it is demonstrated that dehydrated **1** coated QCM can be used as an extremely sensitive method for the study of interaction between this coordination polymer and solvent molecules, and the results show potential application of this coordination polymer to be utilized to monitor water and methanol in direct methanol fuel cells.

Conclusions. In summary, we have synthesized a 3D lithium benzene dicarboxylate coordination polymer with 1D channels. The hydrophilic framework is highly sensitive and can detect small and polar molecules such as water and methanol; this character makes the coordination polymer have a potential use as chemical sensors for direct methanol fuel cells, gas storage and separation, etc. Further investigation based on lithium-based coordination polymer is still in progress.

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Supporting Information Available: Crystallographic data in CIF format; details of quartz crystal microbalance test, FT-IR spectrum, X-ray powder patterns, and TG/DTA measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (32) The dehydrated **1** was prepared by heating complex **1** to 603 K at a rate of 5 K min⁻¹ and holding it for 1 h; it was then cooled naturally to room temperature and kept under a sealed dry area.

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