

Oriented design and synthesis of water-stable heterometallic metal–organic frameworks by bridging ligands containing hydrophobic ($-\text{CH}_3$) substituents



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ABSTRACT

Two new 3D metal–organic frameworks (MOFs), $[\text{NH}_2(\text{CH}_3)_2][\text{KZn}(\text{DMTDC})_2]$ (**1**) and $[\text{NH}_2(\text{CH}_3)_2][\text{NaZn}(\text{DMTDC})_2]$ (**2**), have been solvothermally synthesized and structurally characterized. Both **1** and **2** exhibit 3D structures with 1D infinite helical K–O–Zn and Na–O–Zn metallic chains. Meanwhile, stability studies indicate that **1** was robust even after immersed in various solvents and heated in the air. Furthermore, the N_2 and CO_2 adsorption isotherms of **1** and **2** were also measured.

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Due to the striking physical and chemical properties such as pore size distribution, surface properties and chemical functionality, metal–organic frameworks (MOFs) have established themselves as highly promising materials for a host of applications [1–6], including molecular separations [7–9], gas storage [10–18] and heterogeneous catalysis [19, 20], as well as drug delivery [21,22]. With the research going deeply, some relations between structures and properties have been established, which promotes the object-oriented design and synthesis of functional materials. As the critical factor for application, structural stability of MOFs is widely studied. The stability of the framework is mainly controlled by the inorganic brick and the strength of the chemical bonds between the inorganic brick and the linker. Some inorganic building units, such as $\text{Zn}_4\text{O}(\text{CO}_2)_6$ [23], $\text{Cu}_2(\text{OH})_2(\text{CO}_2)_4$ [24], and $\text{Cr}_3\text{O}(\text{OH})_3(\text{CO}_2)_6$ [25] exhibit high thermal stability, however, they are moisture-sensitive because the relative weak metal–oxygen coordination allows for attack by water molecules, resulting in the phase transformation and decomposition of the frameworks. Thus, the design and synthesis of MOFs with high structural stability is still one of the most challenging issues.

The main factors determining the stability of frameworks are derived from the basic structural unit. To enhance the stability, some units were brought in that were stable to water, air and solvent. Some building blocks that conducted to strengthen the stability of frames have been found in theory and experiment [26], such as Cu_2 , azoles [27] and Zr_6 [28]. Otherwise, metal organic-rod chain has revealed highly hydrothermal stability in some reports. However high percentage of

metal ions would contribute to higher skeletal density and it goes against to enhance the gas absorption of the frameworks. It is a key work that how to balance stability and skeletal density. We conceive that replacing some metal ions with alkali ions in the known or unknown neutral rod-chains would get a nearly stable mixed-metal rod chain. This chain can well maintain the thermo-stability in a lower skeletal density. Some frameworks that have analogous features were reported, but research in this field was still very lacking [29–31].

In addition, it is conducive to enhance the stability of the frameworks by importing hydrophobic substituents such as $-\text{CH}_3$ and $-\text{OCH}_3$. The steric-hindrance effect and hydrophobicity of the substituents can insulate the unsaturated coordinated metal ions, and improve the stability of the building-blocks, thereby enhancing the stability of the whole frameworks. For example, MOF-5 can absorb water in the air and switch to lower porous framework, resulting in the reduction of hydrogen storage capacity. But the synthesized MOF-5 with the double methyl substituent stayed the same after placing in the air for 4 days. And the hydrogen storage capacity was maintained effectively at the same time.

On account of the factors above, we have succeeded in synthesizing a negative charged skeleton with lower density, by replacing heavy metal ions with alkali metal ions. In this work, $[\text{NH}_2(\text{CH}_3)_2][\text{KZn}(\text{DMTDC})_2]$ (**1**) and $[\text{NH}_2(\text{CH}_3)_2][\text{NaZn}(\text{DMTDC})_2]$ (**2**) (3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylic acid abbreviated for H_2DMTDC) possess screwed rod chain, which consists of Zn and K (or Zn and Na) linked by carboxylate ligands with hydrophobic methyl groups. Furthermore, the thermo-stability, solvent stability and the adsorption properties of the two synthesized ionic MOFs were investigated. We researched the framework systematically and preliminary about the porosity.

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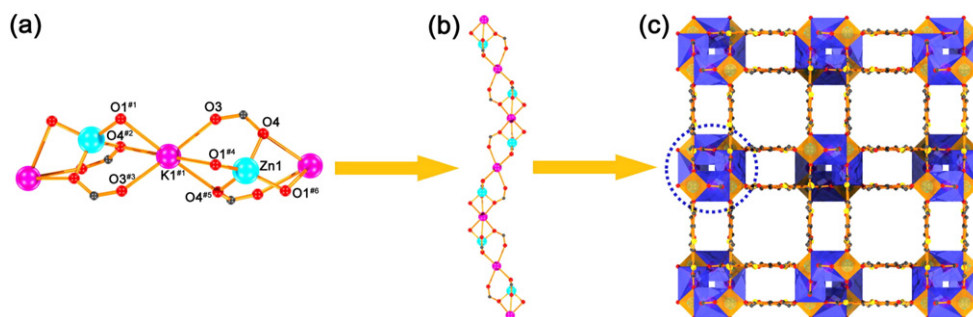


Fig. 1. The structure of **1**: (a) the coordination environments of Zn(II) and K(I) atoms in **1**. Symmetry codes: #1 $0.25 + y, 0.75 - x, 0.25 - z$; #2 $0.25 + y, 0.25 - x, -0.25 + z$; #3 $0.5 - x, y, -z$; #4 $0.25 - y, 0.75 - x, -0.25 + z$; #5 $0.25 - y, 0.25 - x, 0.25 - z$; and #6 $-0.5 + x, y, 0.5 - z$. Hydrogen atoms are omitted for clarity. (b) The 1D rod chain in **1** viewed along *b* axis and (c) polyhedron representation of the 3D structure of **1** along the *c* axis.

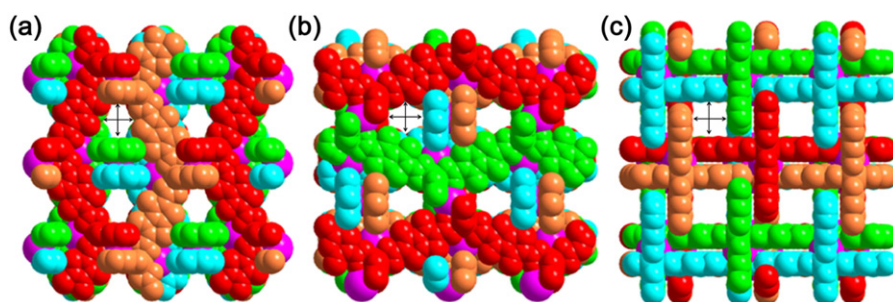


Fig. 2. The spacefilling representation of the 3D framework in **1** viewed along *a* axis (a), *b* axis (b) and *c* axis (c).

After the reaction of H_2MTDC , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KOH in a mixture of DMA/EtOH , colorless crystals (**1**) were isolated [32]. **1** was formulated as $[\text{NH}_2(\text{CH}_3)_2][\text{KZn}(\text{DMTDC})_2]$ based on thermal gravimetric analysis (TGA), single-crystal X-ray diffraction, and element analysis. In a similar process to that used for **1**, but with NaOH replacing KOH , compound **2** was synthesized. Phase purity of the bulk materials was independently confirmed by powder X-ray diffraction (PXRD, Figs. S1 and S2). The TGA measurements were performed under N_2 atmosphere and the results are shown in Fig. S3. TGA studies indicate that the dimethylamine guest molecules can be readily released in the temperature range from room temperature to 300°C , followed by a weight loss of 7%. The rest of the frameworks can be stable up to 300°C (Fig. S3), demonstrating that **1** has high thermal stability.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the tetragonal system, space group $I4_1/acd$. As shown in Fig. 1a, each Zn1 ion adopts tetrahedron coordination mode surrounded by four carboxylate oxygen atoms from three H_2MTDC . The K1 cation is six-coordinated by six oxygen atoms, showing a distorted octahedron geometry. The Zn–O bond lengths are in the range of $1.995(2)$ – $2.000(1)$ Å. The K–O bond distances are in the $2.7179(7)$ – $2.8603(7)$ Å range. The adjacent Zn1 and K1 are linked with each other in a corner-sharing (O1 and O4) mode, generating an infinite spiral chain, which is perpendicular to the *ac* crystallographic plane (Fig. 1b). The rod chains are interlinked through H_2DMTDC , leading to an extended anionic 3D framework (Fig. 1c). As shown in Fig. 2, **1** possesses hexagonal channels with window dimensions of about 4.3×4.3 Å², as viewed along *a*- and *b*-axis. When viewed along *c*-axis, the square channel is about 3.0×4.0 Å². **1** contains 33.9% solvent void accessible based on a PLATON calculation.

As shown in Fig. 3, the structure of **2** is isostructural to **1**, with only slight differences in coordination modes of Zn^{2+} . In **2**, each Zn ion was coordinated to six carboxylate oxygen atoms from four H_2DMTDC , generating a distorted octahedron. The Na cation is six-coordinated with a distorted octahedron from six oxygen atoms. The Zn–O and Na–O bond lengths are in the ranges of $2.0092(3)$ – $2.4100(4)$ Å and $2.237(5)$ – $2.299(4)$ Å, respectively.

Stability is essential for the applications of MOFs as materials. For long-term usage, they should stand the trials of moisture and other experimental environments. Thus, we examined the stabilities of **2** for future practical applications. **2** was immersed in organic solvents (such as ethyl acetate, aether, cyclohexane, benzene, CH_3CN , CH_3OH , CH_2Cl_2 and DMF) for 24 h, no significant changes in the XRPD patterns were found for the samples. Even after exposure to water for three days, the framework of **2** was maintained because the broadened peak positions remained, revealing its good stability. As hydrophobic groups, $-\text{CH}_3$ effectively enhances the stability in water and organic solvents. The thermal stability of **2** was also investigated. **2** was heated in the air for 24 h under $50, 90, 120, 150,$ and 180°C , followed by measurement of powder X-ray diffraction (Fig. 4). The powder X-ray diffraction patterns of the heated samples were in good agreement with that of the original structural characteristics. TGA curve illustrates that the framework can be stable up to 300°C (Fig. S3). The excellent solvent and thermal

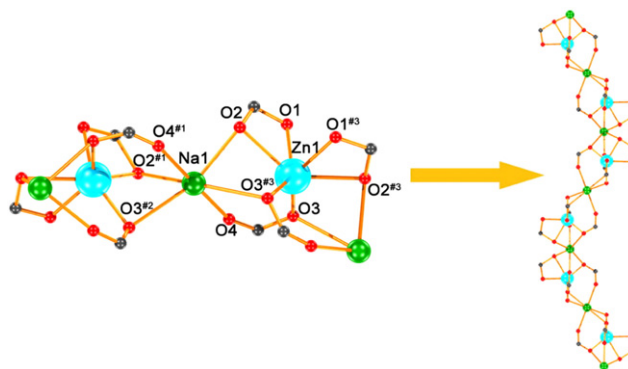


Fig. 3. The structure of **2**: (a) the coordination environments of Zn(II) and Na(I) atoms in **2**. Symmetry codes: #1: $x, -y, -0.5 - z$; #2: $x, -y, -0.5 - z$; and #3: $0.25 + y, -0.25 + x, -0.25 - z$. Hydrogen atoms are omitted for clarity. (b) The 1D rod chain in **2** viewed along *b* axis.

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