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Unique Coordination-Based Heterometallic Approach for the Stoichiometric Inclusion of High-Valent Metal Ions in a Porous Metal−Organic Framework

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Supporting Information

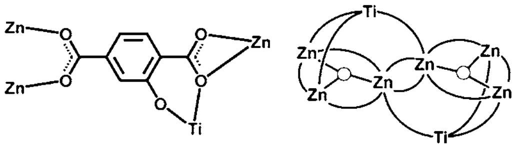
ABSTRACT: A heterometallic metal−organic framework incorporating Zn^{2+} and Ti^{4+} is successfully synthesized. The unique coordination mode of each metal ion to 2-oxido-1,4-benzenedicarboxylate leads to Zn_6Ti_2 building blocks, which extend to form a double-walled primitive cubic net. This material possesses a permanent porosity and long-term stability.

Research on the discovery and synthesis of porous coordination polymers (CPs) or metal−organic frameworks (MOFs) has greatly been promoted by the possibility of using these materials for industrially important applications, such as storage, separation, catalysis, electronics, drug delivery, and others.[1] Therefore, the utility of the new type of crystalline porous materials depends critically on their ability to maintain the porosity under practical conditions. This is especially true considering that the majority of highly porous MOFs are based on coordination bonds between divalent metal ions and carboxylate ligands, which are prone to hydrolytic cleavage. Recently, some high-valent metal ions, such as Ti^{4+} and Zr^{4+}, have been reported to form water-stable and highly porous MOFs.[2] Those MOFs, however, are limited in diversity, and in general it is more difficult to obtain new materials in a single-crystalline phase, which promises high purity and facile structure determination.

Therefore, we initiated a systematic investigation toward new MOFs based on high-valent metal ions that can easily be obtained in a single-crystalline form. Our initial efforts focused on synthesizing heterometallic MOFs that contain M^{II} and M^{IV} within the same secondary building unit (SBU). This is because the mixed-metal system should cause fewer complications during synthesis, such as the formation of insoluble oxides, than M^{IV}-only systems, while the presence of high-valent metal ions may provide an extra source of stability originating from the increased covalent character of metal−oxygen bonds.

In order to host the two distinct types of metal ions within the same framework, a simple, asymmetrically substituted dicarboxylate ligand was selected as the linker. As shown in Scheme 1, the trianion of 2-hydroxyterephthalic acid can function as a terephthalate-like linker and salicylate-like chelate at the same time. Thus, we reacted a mixture of zinc(II) nitrate, titanium(IV) isopropoxide, and 2-hydroxyterephthalic acid (H_3obdc) under solvothermal conditions to obtain orange-colored crystals in which the two metal ions are stoichiometrically included. This material is formulated as $[H_2N(CH_3)_2][Zn_3(OH)Ti(obdc)_3(HCO_2)]$ based on X-ray crystallographic analysis on single crystals and referred to as ZTOF-1 (zinc−titanium−organic framework).

Scheme 1. (Left) Coordination Mode of 2-Oxido-1,4-benzenedicarboxylate and (Right) Connectivity within the SBU of ZTOF-1[a]



[a]Open circles represent μ_3-hydoxo groups.

The results of elemental analysis including inductively coupled plasma atomic emission spectrometry for Zn and Ti support this assignment (see the Supporting Information, SI). The purity of the bulk crystalline phase has been further confirmed by comparing the powder X-ray diffraction (PXRD) patterns with the simulation based on single-crystal analysis (see below).

The SBU for ZTOF-1 is composed of a Zn_6Ti_2 cluster with an internal center of inversion symmetry (Scheme 1 and Figure 1a). The crystallographically asymmetric Zn_3Ti unit is formed by titanium capping of the $Zn_3(\mu_3\text{-OH})(CO_2)_6$ moiety. The triply bridging oxygen atom of the μ_3-hydroxo group is located 0.6 Å above the least-squares plane defined by the three Zn^{2+} ions. The asymmetric unit is then joined to its inversed half by bridging formate ligands generated from thermal decomposition of the solvent *N*,*N*-dimethylformamide (DMF). The dimeric $M_6(\mu_3\text{-OH})_2(CO_2)n$ ($n = 10-14$) cluster, which has the same geometry as the SBU of ZTOF-1 except for the titanium capping, is well-known, and the complexes of manganese, cobalt, and nickel have been reported.[3] The coordination geometries around Zn^{2+} ions are either distorted octahedral or trigonal bipyramidal with the Zn−O distances in the range 1.951(2)−2.452(2) Å. The triply chelated Ti^{4+} ion is bonded to six oxygen atoms from oxido and carboxylate groups, and the geometric details closely resemble the structure of the $[Ti(salicylate)_3]^{2-}$ ion.[4] The very short distances between titanium and oxido oxygen atoms [1.868(2), 1.870(2), and 1.885(2) Å], as well as the behavior of the chelated metal during structure refinements, clearly indicate that the site is

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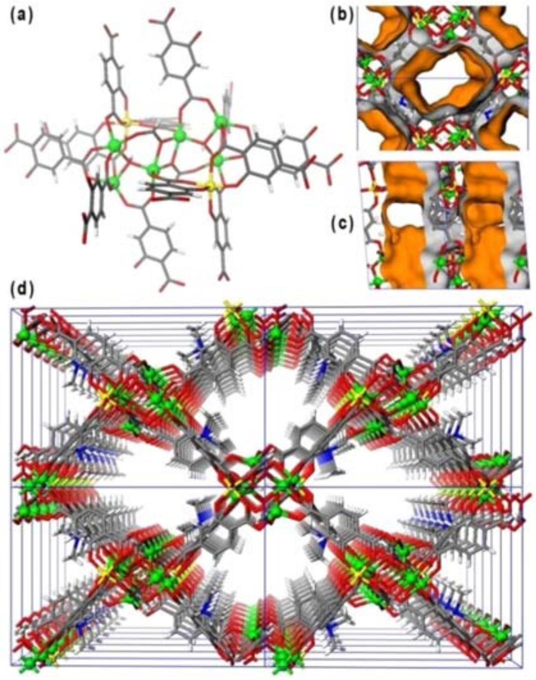

Figure 1. X-ray crystal structure of ZTOF-1: (a) Zn_6Ti_2 SBU; (b and c) Connolly surface (1.4 Å) showing the accessible void; (d) perspective view of the net along the *a* axis.

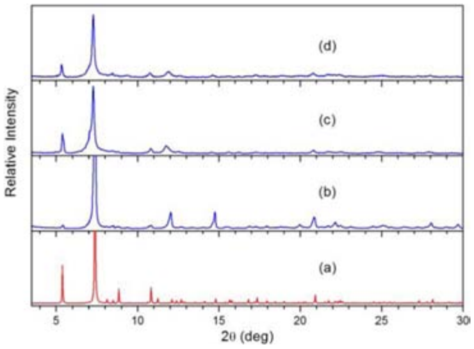

Figure 2. PXRD patterns of ZTOF-1: (a) simulated; (b) as-synthesized; (c) evacuated; (d) 2 months after evacuation and gas-sorption measurements.

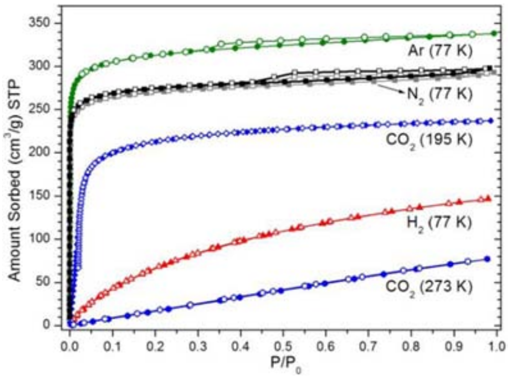

Figure 3. Gas-sorption isotherms of ZTOF-1. The overlaid data for N_2 were measured after storage of the activated sample for 97 days. For H_2 and CO_2 (273 K), the maximum pressure is 100 kPa.

occupied exclusively by titanium. Overall, the Zn_6Ti_2 SBU is supported by 12 obdc ligands, and the linkers are paired by either $\pi-\pi$ or CH$-\pi$ interactions to extend the connectivity along six mutually perpendicular directions. Therefore, the network structure of ZTOF-1 is best described as a double-walled primitive cubic (pcu) net (Figure 1d).

The framework is anionic, and the charge is balanced by dimethylammonium cations derived from the solvent DMF. The counterions partially block the window between straight, open channels (6 × 12 Å^2), which propagate along the crystallographic *a* axis (Figure 1d). Thus, the pore structure of ZTOF-1 can be illustrated as one-dimensional channels interconnected through limited openings (3 × 4.5 Å^2; Figure 1b,c). The solvent-accessible void in ZTOF-1 after consideration of the cations is estimated to be about 49% of the total crystal volume.

A simultaneous analysis using differential scanning calorimetry/thermogravimetric analysis (TGA) on as-synthesized and solvent-exchanged crystals of ZTOF-1 shows a similar pattern in which an exothermic weight loss step at around 100 °C is followed by a series of endothermic processes starting at 250–300 °C (Figure S1 in the SI). This suggests that the included solvents can be safely removed by mild heating before the evacuated solid starts to decompose at around 250 °C. A more direct evidence for the stability of the framework of ZTOF-1 is provided by PXRD measured in air after heating of a solvent-exchanged sample to 100 °C for 12 h under vacuum (Figure 2c).

ZTOF-1 thus activated exhibits reversible sorptions for nitrogen and argon at 77 K and carbon dioxide (CO_2) at 195 K. The observed isotherms are of type I typical for microporous materials (Figure 3). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas obtained from the three different isotherms are similar with an average of 1045(22) m^2/g by BET and 1245(11) m^2/g by Langmuir. The total pore volume of ZTOF-1 estimated from dinitrogen (N_2) sorption is 0.45 cm^3/g. Taking the crystallographic density of the void framework (1.175 g/cm^3) into account, this is equivalent to a porosity of 53%. The weak hysteresis between the adsorption and desorption isotherms of N_2 is type H4 according to the IUPAC classification[5] and suggests the presence of kinetically hindered regions or narrow slit-type pores.[6] We believe that this is due to the presence of cations in the passage between one-dimensional channels (see above). If that is the case, then the hysteresis should become less pronounced when the adsorptive molecule has a smaller kinetic diameter or when the adsorptive molecule carries higher kinetic energy. Indeed, that is the result observed in the sorptions of argon at 77 K and CO_2 at 195 K.

The uptake capacities for dihydrogen (H_2) and CO_2 at 1 atm are moderate with 150 cm^3/g of H_2 at 77 K and 80 cm^3/g of CO_2 at 273 K. The isosteric heat (Q_{st}) of CO_2 adsorption obtained by applying virial-type equations is 22 kJ/mol.[7] The Q_{st} value is comparable to well-known M^{IV}-based MOFs, such as UiO-66 (26 kJ/mol) or MIL-125 (21 kJ/mol),[8] but much lower than one of the best-performing MOFs, Mg_2(dobdc) (44 kJ/mol)[9] or industrial sorbent zeolite 13X (40 kJ/mol).[10]

As mentioned above, one of the motivations for this work was to learn whether a partial inclusion of high-valent metal ions can improve the stability of the material. When soaked and stirred in distilled water, a pristine sample of ZTOF-1 turns to an X-ray-amorphous yellow powder, although Fourier transform infrared spectroscopy does not show a marked difference in the fingerprint region and $\nu(CO_2)$ bands (Figure S2 in the SI). The material is, however, permanently stable in common organic solvents including methanol. In the solid state, the crystalline phase is not significantly altered upon prolonged standing in air.

This is shown by the PXRD pattern (Figure 2d) and N_2-sorption data (Figure 3) measured for an activated sample that has been stored under ambient conditions for 2−3 months.

MOFs based on heterometallic building blocks have advantages over conventional systems in introducing functional sites for catalysis or gas sorption.[11] Typically, preformed metalloligands or oxometallates are used as linkers in the synthesis.[12] In other cases, a mixed-metal approach has been adopted without a specific binding selectivity.[13]

The method we used here is based on the unique coordination of two different metal ions, labile Zn^{2+} and hard acid Ti^{4+}, to a ligand having dissimilar binding sites. This is simple, straightforward, and applicable to other ligands that can be readily obtained. The presence of two distinct metal ions may even lead to the formation of two different SBUs resulting in novel frameworks with interesting topologies. Considering the vast diversity of carboxylate building blocks, the unique approach adopted for ZTOF-1 is believed to significantly enrich the synthetic chemistry of MOFs.

In summary, we used an asymmetrically substituted dicarboxylate to synthesize the first heterometallic MOF that contains Zn^{2+} and Ti^{4+} as an essential part of the framework. The two different metal ions in ZTOF-1 are crystallographically discernible, and their geometry and stoichiometry are unambiguously defined. This material possesses s high surface area (>1000 m^2/g) and porosity (∼50%), as well as long-term stability under ambient conditions. The synthetic approach described here may be useful for the discovery of new heterometallic MOFs with interesting properties.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, details of the synthesis and X-ray crystal structure analysis, IR, TGA, and gas-sorption 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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