Porosity tuning of carborane-based metal–organic frameworks (MOFs) via coordination chemistry and ligand design

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1. Introduction

Coordination chemistry provides a versatile pathway to construct a wide variety of supramolecular assemblies [1]. Metal–organic framework (MOF) materials (i.e. porous coordination polymers) are an emerging class of such structures that are promising for many applications, including small molecule storage, separations, and catalysis [2–4]. Over the past 10 years, there has been significant progress made towards building a library of MOF structures with favorable materials characteristics, including tailorable pore sizes and volumes, low molecular weights, and unsaturated metal coordination sites [5–7]. Control over these parameters is considered to be critical for realizing materials exhibiting high gravimetric uptake of small gas molecules, as well as selective gas separation capabilities [8,9]. However, achieving such control is extremely difficult. Specifically, thermal activation, which is required to generate unsaturated metal sites, often results in irreversible collapse of the porous structure [10,11]. Recently, we developed a series of robust microporous materials based upon icosahedral carboranes [11]. MOFs made from these materials have advantages compared to many aryl-based systems with regard to structural rigidity and thermal and chemical stability [12]. Prior studies have utilized dicarboxylated p-carboranyl ligands and Zn(II) and Co(II) salts to create MOFs and, more generally, infinite coordination polymer (ICP) materials [12,13]. In general, these materials exhibit unprecedented stability with respect to thermal degradation, allowing them to undergo activation by heating under vacuum. Such activation can lead to uncoordinated metal sites in the pores, which significantly enhance hydrogen gas uptake and influence selectivity in gas mixture separation experiments [14–16]. Herein, we report the synthesis of two ligands based on p-carborane and the MOF structures prepared from them. These MOFs exhibit significantly higher surface areas than their single carborane predecessors.

2. Results and discussion

We have selectively functionalized p-carborane 1 (Scheme 1) to form the rigid, linear precursors 2 and 4 via Cu(I) coupling chemistry, as reported by Michl et al. and Hawthorne et al. [17–19]. The chemical orthogonality of the BH and CH moieties in the carborane unit permits one to selectively derivatize it, which cannot be easily accomplished with polyaryl analogs. Specifically, the acidity of the carborane CH moieties allows them to be lithiated (1.6 M MeLi solution in diethyl ether) and further carboxylated through the addition of excess solid dry CO2 to the reaction mixture, as was demonstrated previously for p-carborane [12]. This carboxylation procedure allows one to prepare ligands 3 and 5 in 78% and 80% yields, respectively. Both 3 and 5 were characterized in solution by 1H, 11B{1H}, and 13C{1H} NMR spectroscopy, and all data are consistent with the proposed structural formulations.

Solvothermal reactions of 3 and 5 with Zn(II) nitrate salt in appropriate solvent mixtures yield crystalline MOFs 6 and 7, respectively. Both materials were characterized in the solid-state...
by single-crystal X-ray diffraction analyses (vide infra). MOF 6 was prepared by a solvothermal reaction between Zn(II) nitrate hexahydrate and ligand 3 in a 1:1:1 mixture of dimethylformamide (DMF), diethylformamide (DEF), and ethanol (EtOH). A single-crystal X-ray diffraction study of 6 revealed that it crystallizes in the monoclinic space group, P2₁/c. It is a 3D open framework with repeating secondary building units (SBU) comprised of Zn₄(OH)₂(DMF)₄ metal clusters (Fig. 1); ligand 3 serves as a connector between the Zn-based nodes, which binds in two distinct modes, η¹ and η² (Fig. 1A).

The asymmetric unit of 6 consists of four Zn(II) ions, three carborane-based ligands 3, two hydroxy groups, and four DMF moieties (in addition to the disordered solvent molecules trapped in the pores). Within the Zn₄(OH)₂(DMF)₄ clusters (Fig. 1A), two of the four independent Zn(II) ions are hexacoordinated with slightly distorted octahedral environments. Within the SBU, two oxygen atoms come from the η¹- and η²-bound ligands 3, two from two hydroxy groups, and two from two DMF molecules. The remaining two crystallographically independent metal centers are tetracoordinated in a slightly distorted tetrahedral environment of the ZnO₄ type [5]. One of the three ligands 3, bridges four Zn(II) ions and connects two adjacent Zn₄(OH)₂(DMF)₄ clusters. The remaining two independent 3 moieties bridge three metal centers from the two adjacent Zn₄(OH)₂(DMF)₄ nodes (in both cases, the non-coordinated oxygen atom is ~2.8 Å from the tetrahedral Zn(II) ion already coordinated by the ligand). The hydroxy groups bridge three metal centers within the same cluster, and DMF molecules complete the coordination sphere of the octahedral metal centers.

MOF 7 was prepared by a solvothermal reaction between ligand 5 and Zn(II) nitrate hexahydrate in a 1:1:1:1 mixture of DMF, DEF, EtOH, and water. Single-crystal X-ray analysis revealed that 7, unlike 6, is a 2D framework composed of 1D layers stacked in an ABAB arrangement, with a triclinic P₁ space group (Fig. 2). The framework for 7 consists of dinuclear Zn₂(H₂O)(EtOH) SBU clusters interconnected in a paddle wheel fashion, with four dianionic ligands 5 (η² fashion) to form a 2D infinite layer (Fig. 2A). The axial sites of the Zn₂-based paddle wheels are occupied by one EtOH molecule on one Zn(II) site (Zn–O distance: 1.977 Å) and one H₂O molecule on the other Zn(II) (Zn–O distance: 1.956 Å) in an alternating fashion. Consequently, both of the Zn(II) centers are penta-coordinated in distorted square pyramidal geometries within the Zn₂-based cluster. Importantly, solvents coordinated on the Zn(II) sites appear to act as pillars, which stabilize the structure via hydrogen bonding and van der Waals interactions (Fig. 2D).

The phase purity of 6 and 7 prepared in bulk was confirmed by comparing the powder diffraction pattern (PXRD) (Fig. 3). Both of these materials exhibit a strong diffraction pattern, which is characteristic of their high crystallinity. Importantly, the diffraction

**Scheme 1.** Syntheses of carborane-based MOFs: (i) nBuLi, CuCl₂, 45%, (ii) MeLi, CO₂, ether, 78%, (iii) nBuLi, CuCl, 1,4-diiodobenzene in THF, then Pd[PPh₃]₂Cl₂ in NMP, 55%, (iv) 1.6 M MeLi, CO₂, ether, 80%, (v) Zn(NO₃)₂ 6H₂O, DMF/DEF/EtOH, 80 °C, (vi) Zn(NO₃)₂ 6H₂O, DMF/DEF/EtOH/H₂O, 80 °C, (vii) heat, vacuum, (viii) heat, vacuum.
pattern generated from the bulk samples of 6 and 7 match the pattern of the samples generated from single-crystal diffraction data. As suggested by TGA analysis, both 6 and 7 can be activated in a manner that retains their crystallinity. PXRD patterns of the activated materials 60 and 70, respectively, fully supports this observation (see supporting information). Within 60, clathrated solvent molecules exit the framework between 100 and 170 °C, followed by coordinated DMF molecules in the 240–290 °C temperature range (Fig. 4).

Decomposition of 6 is observed only at 510 °C, which is significantly higher than most Zn(II) aryl-based MOFs (350–400 °C) [20]. A sample of 6 was thermally activated at 250 °C for 20 h under dynamic vacuum (0.01 m Torr), providing activated material 6'. This procedure results in complete solvent loss (both clathrated and coordinated at SBUs), as evidenced by CP-MAS 13C NMR spectroscopy. Indeed, resonances at 25 corresponding to DMF molecules are not observed in 6', in contrast with the parent material 6. Resonances corresponding to 13C-atoms in ligand 5 (5 165 and 75) in 6 and 6' do not change during activation, suggesting that the framework remains chemically intact. Volumetric gas-sorption measurements of 6' using N2 were used to verify its microporosity. Indeed, it exhibits a reversible Type 1 isotherm (Fig. 5A). Importantly, the calculated surface area (Brunauer, Emmett, Teller – BET = 1180 m²/g) is the largest for any studied carborane-based MOF thus
far, which is a direct consequence of the extended ligand design approach explored in this work. While it is yet unclear whether upon activation these structures result in a substantial number of open coordination sites being exposed, we are currently working towards probing this possibility spectroscopically via carbon monoxide (CO) binding studies.

Similar to 6, the TGA data indicate that 7 undergoes solvent-loss mass changes over the 100–160 °C (clathrated molecules) and 180–270 °C (coordinated solvent molecules-water/ethanol) temperature ranges (Fig. 4). The resulting porous framework begins to decompose only above 425 °C. PXRD studies reveal that 7 retains its crystallinity even after solvent molecules have been removed completely. Thermal treatment of 7 under vacuum (200 °C, 15 h, 0.01 mTorr) leads to 70, which has a microporosity of 800 m²/g as determined by CO₂ volumetric gas sorption and NLDFT (non-local density functional theory) modeling (Fig. 5B). The stability of material 7 is likely due to its unique stacking structure, which prevents the loss of porosity even when solvent molecules are removed and the layers shift closer to each other.

3. Experimental

3.1. Materials and methods

Solvents and all other chemicals were obtained from Aldrich Chemical Co. (Milwaukee, USA) and used as received unless otherwise noted. 1,12-Dicarba-closo-dodecaborane (p-carborane) was purchased from Katchem (Czech Republic) and used as received. Compounds 2 and 3 were prepared according to previously published procedures [17–19]. Compound 4 was prepared according to the same procedure reported by Michl et al., where instead of 1,3-diiodobenzene, 1,4-diiodobenzene was used (NMR data for 4: ¹H NMR (CDCl₃, 400 MHz): δ 6.9 (s, 4H, CH), δ 3.4–1.4 (bm, 20H, BH); ¹³C NMR (CDCl₃, 100 MHz): δ 137.1 (s, aromatic-C), δ 126.9 (s, aromatic-CH), δ 60.2 (s, BCH), ¹¹B{¹H} NMR (CDCl₃, 128.5 MHz, BF₃-ether): δ −12.5 (s), −14.7 (s)) [18]. Solution NMR data was acquired on a Varian Inova 400 instrument equipped with a broadband probe. CP-MAS ¹³C NMR spectroscopy was done on a Varian Inova 400 Widebore instrument. CHN Elemental Analyses data were obtained from Quantitative Technologies Inc. (Intertek), Whitehouse, NJ. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA851e. Adsorption isotherms were measured with an Autosorb 1-MP from Quantachrome Instruments.

3.2. Synthetic procedures

Compound 5. To 610 mg (1.8 mmol) of 4 dissolved in 16 mL of dry diethyl ether and stirred at 0 °C, 1.6 M (4 mL, 6.4 mmol) n-HeLi was added via syringe under nitrogen. The reaction mixture was slowly brought up to room temperature and then refluxed for 1.5 h. The reaction was subsequently cooled to −78 °C on a dry-ice/acetone bath. Carbon dioxide gas was bubbled into the reaction mixture for an hour while stirring. The reaction mixture was then quenched with 25 mL of 6 M hydrochloric acid and extracted with diethyl ether (2 ×, 50 mL). The combined organic layers were con-
centrated in vacuo to yield a crude solid product, which was then washed with excess water and hexanes on a fritted glass filter to yield an off-white solid 5 (600 mg, 78%). 1H NMR (d6-THF, 400 MHz): δ 7.6 (bs, 2H, COOH), δ 7.0 (s, 4H, CH), δ 3.4–1.4 (bm, 2OH, BH); 13C NMR (d6-THF, 100 MHz): δ 162.7 (s, COOH), δ 136.8 (s, aromatic-C), δ 127.0 (s, aromatic-CH), δ 83.8 (s, BC), δ 78.0 (s, BC); 12C NMR (d6-THF, 100 MHz, DEPT), δ 127.0 (s, aromatic-CH).

Compound 6. Zinc (II) nitrate hydrate (Zn(NO3)2·6H2O) (30 mg) and 3 (40 mg) were dissolved in DEF/DMF/water (1:1:1:1 by volume) in a glass vial and then allowed to react at 80 °C for 24 h. Crystals of 6 were washed with excess water and hexanes on a fritted glass filter to afford a white material (60% yield). Elemental analysis: Anal (1:1:1:1 by volume) in a glass vial and then allowed to react at 70 °C under vacuum to afford a white material (60% yield). Elemental analysis: Anal. Calc. for (C18H62B60O14)·(4DMF): C, 31.31; H, 5.76; N, 2.51. Found: C, 32.62; H, 5.73; N, 2.45%. For gas-sorption studies, a sample was evacuated at 250 °C for 20 h under dynamic vacuum at 10−5 Torr.

Table 1

<table>
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<tr>
<th>Structure</th>
<th>6</th>
<th>7</th>
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<tr>
<td>Empirical formula</td>
<td>C60H36B60O36Zn2</td>
<td>C26H56B40O10.Zn2</td>
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<td>16.930(4)</td>
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<td>c (Å)</td>
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<tr>
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<td>R1 = 0.0504, wR2 = 0.1268</td>
<td>R1 = 0.1016, wR2 = 0.2465</td>
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<td>5.688 and −1.178</td>
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</table>

3.3. Crystallographic studies

Single crystals were mounted on a Bruker APEX2 V2.1.0 diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source in a cold nitrogen stream. All crystallographic data were corrected for Lorentz and polarization effects (SAINTE), and face-index absorption corrections. The structures were solved by direct methods and refined by the full-matrix least-squares method on F2 with appropriate software implemented in the SHELXTL program package [21]. All the non-hydrogen atoms were refined anisotropically and added at their geometrically ideal positions (see Table 1 for refinement summary).

In the solid-state structure of 7, most of the guest solvent molecules were severely disordered, which hindered their satisfactory refinement; therefore, the SQUEEZE routine (PLATON) was applied to remove the contributions of electron density from disordered solvent molecules [22]. The outputs from the SQUEEZE calculations are attached to the CIF file.

4. Conclusions

In summary, we have designed and synthesized new MOF materials using extended boron-rich ligands comprised of p-carborane building blocks. These materials are robust and can be activated thermally, resulting in highly porous structures. Indeed, these are the most porous carborane-based MOFs realized, and their properties point to potential use in gas separations.

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Appendix A. Supplementary material

CCDC 773979 and 773980 contain the supplementary crystallographic data for 6 and 7. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.08.007.

References


