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A zirconium metal-organic framework with exceptionally high volumetric surface area

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A zirconium metal-organic framework (MOF) PCN-111 has been synthesized by using an elongated ditopic carboxylate linker, 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate. Single crstal X-ray diffraction characterization indicates that the noninterpenetrated microporous structure of PCN-111 is isoreticular to UIO MOFs with 12 connected $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters and a fcu topology. It was successfully activated through solvent exchange with acetone followed by controlled evacuation, and its gas sorption was reported for the first time. By using 77 K nitrogen adsorption isotherm and strictly applying three consistency criteria, the BET surface area for PCN-111 was calculated to be 4825m²/g. Pore size distribution analysis suggests that the sizes of cavities contributing to nitrogen adsorption are predominately in the range of 15 to 20 Å, which are in good agreement with the two polyhedral cages (15.6 and 20.2 Å, respectively) in the single crystal X-ray solved structure. Owing to its relatively high crystal density (0.42 g/cm³), the volumetric surface area for PCN-111 was calculated to be 2026 m²/cm³. The value is among the highest of all reported ultrahigh surface area MOF materials. The exceptionally high microporosity of PCN-111 has also been validated by comparison with the simulated nitrogen derived MUSIC. adsorption isotherm from multipurpose simulation code

Introduction

For years, increasing number of metal-organic frameworks (MOFs) have received growing attention as an emerging class of highly ordered crystalline porous materials owing to their exceptional high porosity and framework tunabilty.¹⁻⁶ The numerous possibilities of combination through coordinate bonding between the metal clusters and organic linkers offers MOFs great flexibility to tune their properties in various aspects.⁷⁻¹¹ Among the large family of MOF materials, Zr-based MOFs stand out as one of the most promising group primarily due to their rich structure types and outstanding chemical stability.¹²⁻¹⁵ Many Zr-MOFs exhibit stability in water, some even under acidic and/or basic conditions, which is extremely important for the MOF materials to be considered for practical applications.¹⁶⁻²⁴ The high stability of Zr-based MOFs results from the strong bonding between the highly charged

zirconium(IV) ions of metal clusters and the carboxylates of organic linkers.^{25, 26} By using a simple dicarboxylate linker, terephthalate, the first Zr-based MOF (UIO-66, UiO stands for the University of Oslo) was synthesized by Lillerud and coworkers in 2008, its structure features 12-coordinated Zr6 clusters $[Zr_6O_4(OH)_4(O_2C)_{12}]$ and an **fcu** topology.²⁵ Since then, the use of carboxylate linkers with Zr6 clusters for the construction of MOFs has been well explored, particularly the so-called UiO-66 series with ditopic carboxylate linkers. Here we report the synthesis and characterization of a microporous Zr-MOF (PCN-111, PCN stands for porous coordination polymer), it is isostructural to UIO-66 with a much elongated dicarboxylate linker, 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate. As other UIO type MOFs, PCN-111 is stable in the presence of water. The activated PCN-111 exhibits high microporosity; its gravimetric surface area is estimated to be $4825m^2/g$ by using 77 K nitrogen gas adsorption isotherm and strictly applying three consistency criteria. More importantly, its volumetric surface area is calculated to be 2026 m²/cm³ by using its crystal density, the value is among the highest of all reported ultrahigh surface area porous materials.

Experimental

General Information

Commercially available reagents were used as received. 1 H NMR and 13 C NMR data were collected on a Mercury 300 MHz NMR spectrometer. TGA data were obtained on a DTG-60 (SHIMADZU) thermogravimetric analyzer with a heating rate of

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3 °C/min under a nitrogen atmosphere. SEM images were collected on JEOL JSM-6510LV Scanning Electron Microscope. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex 600 X-Ray Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å) and graphite monochromator at room temperature. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge *via* internet at http://www.iucr.org.

Synthesis of H₂BDDB

The synthetic procedure for H_2BDDB , 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoic acid, is shown in **Figure S1**.

To a solution of copper acetate (10.0 g, 55.1 mmol) in methanol/pyridine (50 mL/50 mL) was added methyl 4ethylnylbenzoate (5.0 g, 31.2 mmol). After stirred at 60 °C for 30 min, the reaction mixture was cooled to room temperature, then poured into 200 mL of ice water. The precipitate was isolated by filtration, washed with plenty of water. The crude product was dried, then triturated in 50 mL of hexanes to remove any unreacted starting material. The remaining solid was collected by filtration, then dried to produce an off-white product, dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate, (4.3 g, 13.5 mmol) with a yield of 87%. TLC (10 % ethyl acetate in hexanes as eluent) indicates no starting material left. NMR data (Figure S2-4) are in good agreement with literature.²⁷⁻²⁹ ¹H-NMR (300 MHz, CDCl₃): 8.01 (4H, d, *J* = 8.1 *Hz*), 7.59 (4H, d, J = 8.1 Hz), 3.93 (6H, s); ¹H-NMR (300 MHz, DMSO-d₆): 7.98 (4H, d, J = 8.7 Hz), 7.75 (4H, d, J = 8.7 Hz), 3.85 (6H, s); ¹³C-NMR (75 MHz, CDCl₃): 166.4 (2C), 132.4 (4CH), 130.8(2C), 129.5 (4CH), 126.1 (2C), 81.8 (2C), 76.2 (2C), 52.3 (2CH₃).

To a solution of sodium hydroxide (1.0 g, 25 mmol) in tetrahydrofuran/methanol/water (50 mL/50 mL/50 mL) was added dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate (1.0 g, 3.1 mmol), After stirred overnight, most of organic solvents in the clear solution was removed on a rotary evaporator. The precipitate was redissolved by adding ca. 100 mL of water. The clear aqueous solution was acidified with 1 M of HCl to ca. pH 2. The precipitate was collected by filtration and washed with plenty of water. The solid was dried in vacuum oven at 60 °C overnight to produce a yellowish product, 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoic acid, (H₂BDDB, 0.74 g, 2.6 mmol) with a yield of 84%. NMR data (Figure S5) are in good agreement with literature.^{27-29 1}H-NMR (300 MHz, DMSO-d₆): 13.28 (2H, brs), 7.96 (4H, d, J = 8.7 Hz), 7.73 (4H, d, J = 8.7 Hz); ¹³C-NMR was not collected because of its poor solubility in common organic solvents.

Synthesis of PCN-111

To a vial containing H₂BDDB (10 mg, 0.034 mmol) and ZrCl₄ (20 mg, 0.086 mmol) was added DMF (8.0 mL) and CF₃COOH (300 μ L). The above mixture was sonicated for 30 min before placed in an oven preheated to 120 °C. Colorless crystals appeared on the wall and at the bottom of the vial in three to five days. After cooled down to room temperature, the crystals were washed with DMF and collected for thermogravimetric analysis and powder X-ray diffraction analysis. For gas adsorption

measurement, the sample was activated as following: reaction solution was exchanged with fresh DMF twice in two days and then acetone three times in three days. After completion of solvent exchange, acetone was decanted, and the remaining solvent inside crystal cavity was carefully evacuated by an extremely slow vacuum, and full vacuum after it reached *ca*. 1.0 mbar.

Gas adsorption measurement

A Micromeritics ASAP 2020 surface area and pore size analyzer was used to measure nitrogen, argon, oxygen and hydrogen physisorption isotherms at different temperatures. *ca.* 100 mg of activated sample was used for each measurement. Highpurity gases were used (nitrogen: 99.999%, argon: 99.999%, oxygen: 99.999%, hydrogen: 99.999%). Pore size distribution was calculated from the nitrogen adsorption isotherm based on DFT model in the Micromeritics ASAP 2020 software package.

Single Crystal X-Ray Study

Single crystal X-ray structure determination of PCN-111 was performed at 173(2) K using the Advanced Photon Source on beamline 15ID-B at Argonne National Laboratory. Structures were solved by direct methods and refined by full-matrix leastsquares on F2 using SHELXTL.³⁰ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom. The solvent molecules of PCN-111 were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the SQUEEZE routine of PLATON, structures were then refined again using the data generated.³¹

Results and discussion

The diester of the carboxylate linker, H₂BDDB, were synthesized through a Cu(II)-catalyzed Eglinton homo-coupling reaction of methyl 4-ethylnylbenzoate. The NMR data are in good agreement with literature. It is worth pointing out that inexpensive metal was used as catalyst and column chromatography was avoided by judiciously selecting solvents for recrystallization. The diacid of the carboxylate linker, H₂BDDB, was then obtained by hydrolysis of the above diester in a NaOH solution of MeOH/THF/H₂O (1/1/1) mixture.

Solvothermal reaction of linker precursor, H₂BDDB, and ZrCl₄ in DMF solution in the presence of CF₃COOH afforded colorless octahedron-shaped crystals of PCN-111 with a formula of $Zr_6O_4(OH)_4(BDDB)_6$. It was harvested by solvent exchange with DMF and acetone. PCN-111 crystallizes in a cubic Fm-3m space group with a = 33.6644(6) Å. As an isoreticular structure to UIOs, it consists of 12 connected $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters, bridged by ditopic BDDB linkers (**Figure 1a**, **1d**). There are two types of polyhedral cages in the framework, one is octahedron and the other is tetrahedron. Space-filling model indicates that the sizes of these two cages are *ca*. 20.2 and 15.6 Å,

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respectively (Figure 1b, 1c). The potential solvent accessible volume of PCN-111 framework is estimated to be 81.7% by PLATON.



accountable and their intensities are strong, which suggests that the framework retains its crystallinity during all of these experiments.



c) d) **Figure 1**. a) Representation of the crystal structure of PCN-111 in a cubic unit cell. Zr, blue; O, red; C, black; all hydrogen atoms omitted for clarity. b) Octahedral cage (yellow ball) and tetrahedral cage (red ball) in PCN-111 structure. c) Packing of octahedral and tetrahedral cages. d) Topological representation of 12 connected structure in PCN-111. Zr6 cluster, blue ball; organic linker, yellow stick.

The powder X-ray diffraction (PXRD) patterns were collected at ambient atmosphere and temperature on a Rigaku MiniFlex 600 X-Ray Diffractometer. As shown in Figure 2a, the PXRD pattern of bulk sample of as-synthesized PCN-111 shows excellent agreement with the one simulated from its singlecrystal structure, which is noninterpenetrated and isostructural to UIOs. Although slight differences in peak strength were observed, all 2θ peaks were consistent. For comparison, an interpenetrated structure is constructed based on PIZOFs²⁶ and its PXRD pattern is also simulated. It turns out the PXRD pattern of interpenetrated structure is similar to that of noninterpenetrated one, except for the absence of two distinctive peaks at 5.2 and 9.1 degree (20). Although it is not possible to exclude entirely the presence of interpenetration based on PXRD solely, the resulting crystalline material is phase pure based on single-crystal X-ray data as well as comparison of experimental and simulated gas adsorption data.

PXRD was also utilized to confirm the framework's stability upon removal of guest-solvent molecules. As shown in **Figure 2b**, the PXRD patterns show the framework of PCN-111 remains intact after several rounds of gas adsorption measurements followed by exposed to air for a month, immersed in water for 48 hours, and resolvated in organic solvents such as DMF and acetone. All 2θ peaks are

Figure 2. a) PXRD patterns of as-synthesized PCN-111 in comparison with the simulated patterns from noninterpenetrated and interpenetrated structures. b) PXRD patterns of as-synthesized PCN-111 in comparison with after-gas-adsroption, soaked-in-water, and resovated-in-acetone PCN-111.

It is worth pointing out that Behrens et al. synthesized PEEP-UIO with a same crystal structure through a slightly different solvothermal reaction; however, the PXRD pattern of PEEP-UIO showed a low degree of crystallinity, as manifested by the broad reflections its PXRD pattern. Gas adsorption was not reported for PEEP-UIO.²⁷ Although the authors did not reveal that whether they used as-synthesized sample or activated one for the PXRD data collection, we believe our success might lie with the choice of solvent for exchange. DMF or other high boiling point solvents are often used for MOF synthesis, and these solvents need to be replaced by low boiling points solvents before vacuum is applied to expose the internal surface. Supercritical carbon dioxide activation is a mild activation technique, but it requires special set up. An extension of conventional solvents could be used instead, though might lead to loss of porosity during solvent evacuation, and surface tension is believed to be the cause of framework collapse.³² In our case, a list of organic solvents were tried for solvent exchange. Based on our numerous attempts, we found that using of low surface tension solvent such as acetone³³ and slow removal of solvent residue (evacuation rate at 1 mbar/sec) are two keys to warrant the intact of the framework during the activation process.

The nitrogen sorption for the carefully activated PCN-111 at 77 K exhibited a reversible Type-I isotherm without noticeable hysteresis loop, as shown in **Figure 3a**, a characteristic of

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microporous materials.^{34, 35} PCN-111 exhibits a very high nitrogen capacity upon saturation (over 1200 cm³/g), which is among the highest of all microporous MOF materials reported so far. Microporosity of PCN-111 was confirmed by pore size distribution analysis of its nitrogen gas sorption isotherm at 77 K (**Figure 3b**), which indicates the sizes of cavities contributing to nitrogen adsorption are predominately in the range of 15 to 20 Å (1.5 to 2.0 nm). These values are in good agreement with the sizes of the observed octahedral and tetrahedral cages in the crystal structure discussed above.

As one of the most crucial properties for MOF materials, BET (Brunauer–Emmett–Teller) surface area³⁶ is normally estimated from the nitrogen or argon adsorption isotherm measured at cryogenic temperature (77 K for nitrogen and 87 K for argon). There are have been ambiguity in terms of which range of nitrogen adsorption isotherm is appropriate for BET surface area analysis. As emphasized by Kaskel and Snurr in several of their publications,^{29, 37} a set of consistency criteria should comply with: (1) The analysis should be limited to the range in which the term $V_{ads}(1-P/Po)$ increases continuously as a function of the relative pressure P/Po. (2) The value of the BET constant C resulting from the linear fit should be positive and the C constant should have a value of at least 10. (3) The BET monolayer capacity $n_{\rm m}$ calculated from the linear fit corresponds to a certain relative pressure, which must be located within the linear region chosen for the area calculation.



Figure 3. a) Nitrogen sorption isotherms for PCN-111 at 77 K, adsorption (•)/desorption (0). b) Amount of nitrogen adsorbed in PCN-111 at 77 K vs. log(P/Po); inset: pore size distribution, incremental surface area (cm³/g) vs pore width (Å). c) V(1-P/Po) vs. P/Po for PCN-111; inset: linear plot of the adsorption range for the estimation of the BET specific surface area.

We decided to apply all three criteria to the estimation of the BET surface area of PCN-111. As shown in **Figure 3c**, compliance of the first criterion limits the range of the BET plot to a relative pressure of 0.1. Next is to identify a linear range in the BET-plot. This is usually implemented in the software of gas adsorption equipment (ASAP2020 in this work). However, within this range of the BET plot of PCN-111 (relative pressure 0.0 to 0.1) one can find more than a few linear ranges with C constants higher than 10, thus more than one linear range comply with the second criterion. To narrow down the list by the third criterion, the relative pressure corresponding to a given monolayer capacity n_m calculated from the equation (1) should be located within the chosen relative pressure range of the linear region of BET plot.

$${\binom{P}{P_o}}_{n_m} = \frac{1}{(\sqrt{C}+1)}$$
 (1)

To apply the third criterion to here, only the linear fit in the pressure range $0.082 \le P/Po \le 0.10$ with a C constant of 95.64 (P/Po(n_m) = 0.093) meets all the requirements listed above (**Figure 3c inset**). By using this linear range, BET surface area

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for PCN-111 was calculated to be 4825m²/g (±105). As pointed out by Kaskel, many reported BET surface areas derived from adsorption isotherms were only in compliance with the first two consistency criteria, the third one was ignored, which likely led to certain errors in porosity estimation, especially for those contain both microporous and mesoporous cavities.



Figure 4. a) Comparison of simulated (•) and experimental (-) nitrogen adsorption isotherms for PCN-111 at 77 K. b) V(1-P/Po) vs. P/Po for simulated adsorption isotherm; inset: linear plot of the adsorption range for the estimation of the BET specific surface area.

Additionally, the nitrogen adsorption isotherm was simulated using multipurpose simulation code MUSIC.³⁸ The simulated nitrogen adsorption is slightly higher than the experimental one at lower relatively pressure region, but overall in good agreement (Figure 4a). Although theoretical does not usually cover all aspects of complex matter such as MOF and to some degree discrepancy is unavoidable. In our case, we suspected that limited equilibrium time during measurement could be one of the major reasons. To better understand the discrepancy between the simulated and experimental data, we decided to calculate the BET surface area for the simulated nitrogen adsorption isotherm. In compliance with all three consistency criteria, the relative pressure region (P/P_0 0.05 – 0.065) was identified with a C constant of 269.64 ($P/P_o(n_m)$ = 0.057) (Figure 4b), thus the surface area of $5199m^2/g$ (±84) was estimated from the simulated nitrogen adsorption isotherm. The value is slightly higher than the experimental one, which is understandable because simulation is based on perfect crystal structure; whereas sample used for gas adsorption measurement could carry a small amount of defect. It is interesting to point out that MOF materials with BET surface area over 5000 m²/g all have a considerable amount of mesoporous nature, which are evident from their cryogenic gas sorption isotherms and the calculated pore size distributions. Researchers in MOFs area nowadays are

particularly focusing on gravimetric capacity with an attempt to achieve higher and higher BET surface area in m²/g. However, volumetric capacity should also be well evaluated especially for applications in which spaces are limited. For example, on-board small vehicle hydrogen storage requires the tank neither too large nor too heavy. Maximizing MOF volumetric and gravimetric gas adsorption are incompatible, therefore, as Farha et al pointed out, an in-depth understanding of the trade-off between volumetric and gravimetric loadings is necessary.³⁹ A balance needs to be struck in order to achieve high volumetric and high gravimetric loadings simultaneously. Table 1 shows porosity data for PCN-111 in comparison with some selected high-surface-area MOFs both in volumetric and gravimetric units. It is worthy to note that although the gravimetric surface area of PCN-111 is much less than record high ones, its volumetric surface area is among the highest due to its relatively high crystal density. To date, most of ultrahigh surface area MOFs have been built from zinc oxide and copper paddlewheel clusters with carboxylate linkers, which unfortunately lose crystallinity and porosity when exposed to moisture. In this regard, PCN-111 clearly has the advantage for real world applications.

Table 1. Gravimetric and volumetric surface areas for PCN-111 and some selected MOEs

MOF Material	Density	BET surface area		
	g/cm ³	m²/g	m ² /cm ³	Metal cluster
MIL-101 ⁴⁰	0.44	4230	1861	Cr₃O(COO) ₆
PCN-82 ⁴¹	0.47	4488	2109	Cu ₂ (COO) ₄
MOF-177 ⁴²	0.43	4500	1935	Zn ₄ O(COO) ₆
DUT-2543	0.40	4670	2008	Zn ₄ O(COO) ₆
PCN-111 ^{this work}	0.42	4825	2026	Zr ₆ O ₄ (OH) ₄ (COO) ₁₂
PCN-68 ⁴⁴	0.38	5109	1941	Cu ₂ (COO) ₄
UMCM-2 ⁴⁵	0.40	5200	2080	Zn ₄ O(COO) ₆
NU-100 ⁴⁶	0.29	6143	1781	Cu ₂ (COO) ₄
MOF-210 ⁴⁷	0.25	6240	1560	Zn₄O(COO)₀
DUT-32 ⁴⁸	0.27	6411	1731	Zn ₄ O(COO) ₆
NU-1103 ⁴⁹	0.30	6550	1965	Zr ₆ O ₄ (OH) ₄ (COO) ₁₂
NU-110 ⁵⁰	0.22	7142	1571	Cu ₂ (COO) ₄

Conclusions

A zirconium metal-organic framework (PCN-111) with exceptionally high volumetric surface area has been synthesized and characterized. PCN-111 is isostructural to UIOs with 12 connected $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters bridged by much elongated ditopic BDDB linkers. By using low-surfacetension acetone for solvent exchange and slow evacuation, it was carefully activated and successfully measured gas adsorption for the first time. By using 77 K nitrogen adsorption isotherm and strictly applying three consistency criteria, the BET surface area for PCN-111 was calculated to be 4825m²/g. Owing to its relatively high crystal density (0.42 g/cm³), the volumetric surface area for PCN-111 was calculated to be 2026 m²/cm³. The value is among the highest of all reported ultrahigh surface area MOF materials. Its exceptionally high microporosity has been validated by simulated nitrogen

adsorption isotherm derived from multipurpose simulation code MUSIC. Unlike most of the published high-surface-area MOF materials, PCN-111 is neither air nor moisture sensitive, which is potentially useful in practical applications.

Conflicts of interest

There are no conflicts to declare.

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