

Pressure-Responsive Curvature Change of a “Rigid” Geodesic Ligand in a (3,24)-Connected Mesoporous Metal–Organic Framework

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Supporting Information

ABSTRACT: A (3,24)-connected mesoporous metal–organic framework, PCN-69, was synthesized by linking a hexatopic ligand btti with dicopper paddlewheel clusters. This material has rigid connectivity but a flexible framework, which has been attributed to a curvature change of the ligand.

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are newly emerging porous materials.¹ Their high surface area and tunable porosity make them good candidates in gas storage, separation, catalysis, and biomedical applications.² One of the characteristics that differentiates MOFs from other sorbents is their flexibility, which makes their porosity tunable under external stimuli.³ This framework flexibility often comes from weak interactions such as hydrogen-bonding, π – π -stacking, and van der Waals interactions. Framework interpenetration, coordination bond rotation, and terminal ligand exchange are frequently encountered in flexible MOFs. Theoretically, bond bending and stretching, which can be monitored by vibrational spectroscopy, are potential driving forces for framework flexibility as well. In fact, an existing example showed that MOFs with fixed geometry can accommodate either bent or stretched ligands.⁴ However, to the best of our knowledge, no framework isomerism originating from bond bending has been reported in MOFs yet, presumably because this effect is too trivial to be observed if it is given by a single bond bending. In other words, a larger ligand is needed to accumulate bond-bending effects from multiple bonds, thereby demonstrating an overall detectable change. Nevertheless, more extended ligands typically lead to unstable frameworks. The recently reported (3,24)-connected network (also known as an *rht*-type network), in which a ligand of 3-fold symmetry was linked by 24-connected cuboctahedral building blocks to form a robust network that can sustain larger ligands, offers a chance to test this hypothesis.⁵ Herein we report a new (3,24)-connected MOF, PCN-69 (PCN stands for porous coordination network), that maintains its mesoporosity after removal of the guest molecules. More importantly, we observed gate-opening gas-sorption isotherms, which is a strong indication of framework flexibility. This finding enriches the genesis of framework flexibility and may be used to design novel sorbent materials in the future.

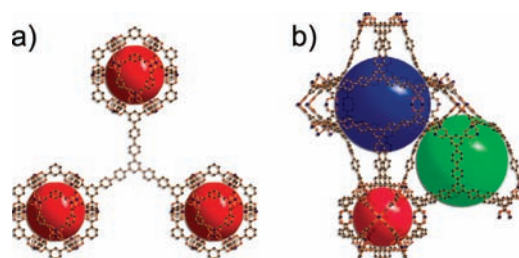


Figure 1. (a) 3-fold ligand btti and 24-connected cuboctahedral building blocks in PCN-69. (b) 3D polyhedra packing in PCN-69 (red, cuboctahedron; green, truncated tetrahedron; blue, truncated octahedron).

The ligand btti was designed to readily form the (3,24)-connected framework and is large enough to observe the overall bond-bending effect (Figure 1a). Solvothermal reaction between H_6btti and copper nitrate in *N,N*-dimethylformamide at 75 °C for 18 h afforded PCN-69 as green block crystals (see the Supporting Information for details). Single-crystal X-ray diffraction confirmed its (3,24)-connected structure. Like its (3,24)-connected predecessors, its structure can be viewed as the packing of three different polyhedra (Figure 1b).^{5c} In the truncated octahedra, the distance from the top to the bottom is 41.5 Å, clearly indicating its mesoporosity.⁶

As anticipated, the ligand btti is highly bent in PCN-69, leading to a geodesic conformation, which is even more obvious compared with PCN-68 and PCN-610 (Figure 2a).^{5g} The bending degree can be estimated by measuring the vertical distance between the center of the ligand and the plane defined by the six coordinated copper atoms. This distance in btti (3.821 Å) is significantly larger than that in ptei (1.652 Å) and ttei (2.527 Å), indicating that PCN-69 has the largest bending degree among the three. Evidently, the ligand size is not the sole factor determining the bending degree because the size of btti (defined by the distance between the center of the ligand and the center of a terminal benzene ring) is 13.024 Å, which lies between that of ptei (11.243 Å) and ttei (13.815 Å). It is probably because of the *p*-quaterphenyl structure in btti that a bent conformation would be preferred to alleviate the steric hindrance and to lower the overall system energy. Interestingly, this ligand curvature leads to shrunken truncated octahedra and expanded truncated tetrahedra, while the cuboctahedra remain intact (Figure 1b). Flipping the

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curvature in the other direction, leading to expanded truncated octahedra and shrunken truncated tetrahedra, remains a possibility but may need additional energy. To facilitate the following discussion, we have built a crystal model, PCN-69', in which the composition and atom-to-atom connectivity are identical with those in PCN-69 but the ligand is completely flat. Compared with PCN-69, PCN-69' has an expanded unit cell with higher surface area and pore volume, according to the calculated results based on the crystal models (Table S1 in the Supporting Information). Powder X-ray diffraction (PXRD) patterns were also simulated based on the crystal models (Figure 2b). Compared with PCN-69, the peaks of PCN-69' shift to lower angles because of the expanded unit cell. Surprisingly, the PXRD pattern of a fresh PCN-69 sample measured directly using the bulk powder implies an intermediate unit cell. The diffraction peak from the $[5\ 1\ 1]$ lattice plane was chosen as a comparison because of its sensitivity toward unit cell change and

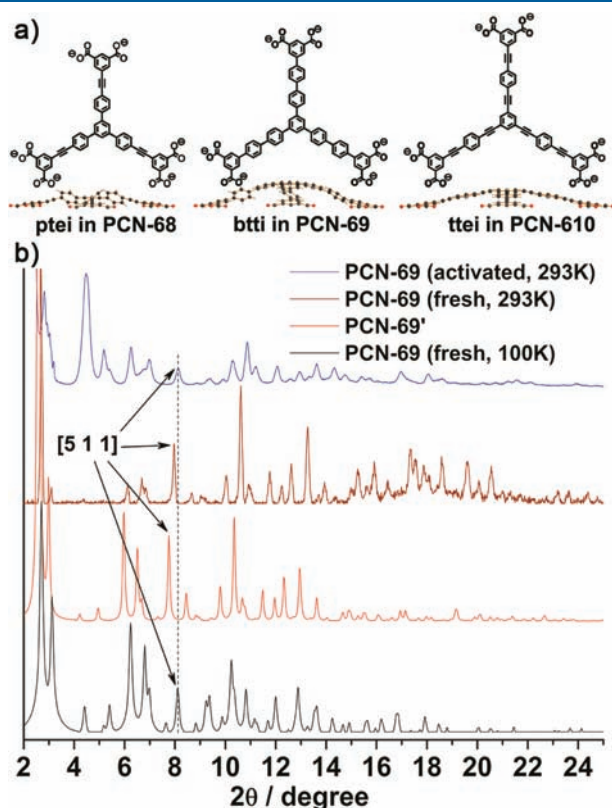


Figure 2. (a) Ligand structure and top-down-viewed conformation in crystals of the PCN-6X series. (b) PXRD patterns of PCN-69 and PCN-69' under various conditions.

the absence of interference (Figure S1 in the Supporting Information). This peak lies at 8.12° in PCN-69 simulated from the single-crystal model and is shifted to 7.76° in PCN-69'. In the bulk powdered sample, there is still some shift in this peak (7.96°), but not as much as in PCN-69', suggesting a less bent conformation of the btti ligand. This difference may come from the temperature at which the data were collected. The single-crystal X-ray diffraction experiment was carried out at 100 K, while the PXRD pattern of the bulk powdered sample was collected at 293 K. The crystals swell at higher temperature, leading to an expanded unit cell and somewhat stretched btti ligand. Besides the temperature, the pressure also affects the ligand's conformation. For the activated PCN-69, in which all of the guest molecules have been removed under vacuum, the PXRD pattern resembles that of the single-crystal model, with the diffraction peak from the $[5\ 1\ 1]$ lattice plane going back to 8.14° , indicating a shrunken unit cell. After activation, the old adage "nature abhors a vacuum" comes into play in this scenario. However, thanks to the robust (3,24)-connected network, the collapse of the framework was prevented, leading to a contracted unit cell with a highly curved ligand.

Low-pressure gas-sorption isotherms were taken on the activated PCN-69 to confirm its permanent porosity. The N_2 sorption at 77 K exhibits a pseudo type I isotherm, which is typical in MOFs with hybrid mesoporous structure (Figure 3a).^{5a,c,g,7} Because of the larger ligand used, the relative pressure at which the isotherm reaches its plateau is much higher in PCN-69 (0.26) than in PCN-66 (0.10) and PCN-68 (0.15). In addition, a noticeable hysteresis was observed, which is characteristic of mesoporous MOFs.⁸ Although PCN-69 has a similar amount of adsorbed N_2 compared with PCN-68, it has more pores distributing in the mesoporous range (Figure S2 in the Supporting Information), resulting a lower Brunauer–Emmett–Teller (BET) surface area ($3989\text{ m}^2\text{ g}^{-1}$ vs $5109\text{ m}^2\text{ g}^{-1}$). The H_2 adsorption capacity of PCN-69 was also evaluated (Figure S3 in the Supporting Information). PCN-69 has a surprisingly high heat of adsorption for H_2 (8.14 kJ mol^{-1} at low coverage; Figure S3b in the Supporting Information) presumably because of the bent ligands that create pockets and concaves with improved binding affinity toward H_2 , which is reminiscent of a similar case in corannulene.^{2a,9} The high-pressure H_2 uptake capacity in PCN-69 (5.22 wt %) is not as good as PCN-68 (7.21 wt %), indicating that a larger portion of mesoporosity is not good for high-pressure H_2 storage.¹⁰

An interesting gate-opening sorption isotherm was observed when O_2 was used as the adsorbate (Figure 3b). The adsorption isotherm reaches its first plateau at $P/P_0 = 0.22$ and a second plateau at $P/P_0 = 0.54$, leading to a 17.3% increase in the pore volume ($1.97\text{ cm}^3\text{ g}^{-1}$ vs $2.31\text{ cm}^3\text{ g}^{-1}$). More importantly, an oscillatory pressure decrease was also observed at $P/P_0 = 0.41$.

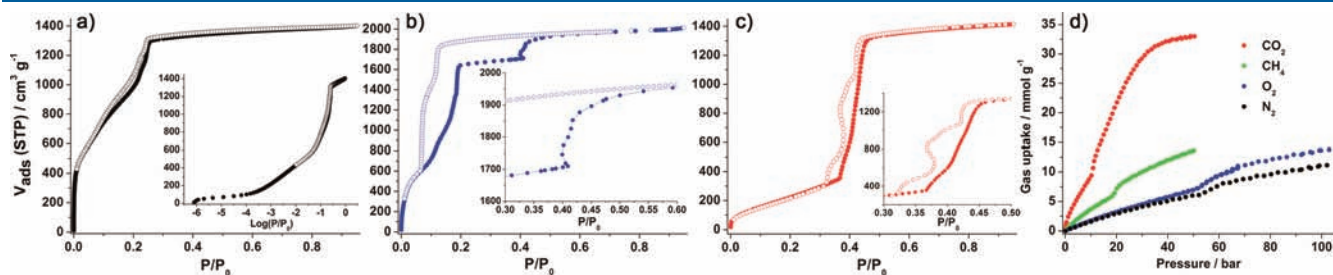


Figure 3. Gas-sorption isotherms of PCN-69 (filled, adsorption; open, desorption): (a) N_2 at 77 K; (b) O_2 at 77 K; (c) CO_2 at 195 K; (d) excess-adsorption isotherms of N_2 , O_2 , CH_4 , and CO_2 in PCN-69 at 298 K.

The abrupt adsorption increase and pressure decrease are very typical in flexible MOFs, where an expanded structure can be achieved under pressurization.¹¹ Because there are no flexible motifs in PCN-69 and the increase of the pore volume after the gate-opening pressure is close to that between PCN-69 and PCN-69' (24.3%), we attribute this flexibility to the stretch of the bent ligand btti. Namely, adsorbing O₂ triggers the conformation change of btti from a bent ligand to a stretched one. The reason why this phenomenon was not observed in the N₂ isotherm is because O₂ has a higher heat of adsorption, which is sufficient to provide the energy penalty needed for this framework expansion. Thanks to this conformation change, the O₂ uptake in PCN-69 is as high as 2012 cm³ g⁻¹ (77 K, 150 mmHg), which is the highest yet observed for MOFs.¹² Because the heat of adsorption of CO₂ is higher than that of O₂, we expect the same gate-opening isotherm for CO₂. However, a type IV isotherm was observed instead, with a sharp increase of adsorption starting at $P/P_0 = 0.36$ that conceals any contribution brought by framework expansion (Figure 3c). A closer look at the desorption branch, however, reveals a similar oscillatory pressure increase at $P/P_0 = 0.36$. This pressure increase is due to the shrinkage of the crystal when the pressure drops to certain point and is also a strong indication for framework flexibility.

It has been reported that the gate-opening pressure in flexible MOFs can be unveiled by pressurization with supercritical gases.¹³ The high-pressure excess-adsorption isotherms of supercritical N₂, O₂, CH₄, and CO₂ were collected in PCN-69 (Figure 3d). A step was clearly observed in all of the isotherms, which is very rare in high-pressure gas-sorption isotherms and is a strong indication of framework flexibility. The gate-opening pressure follows the sequence of N₂ > O₂ > CH₄ > CO₂, which is opposite to the heat of adsorption and reflects a certain amount of energy needed to expand the framework. Compared with the previously published results, where the framework flexibility originates from $\pi-\pi$ stacking,¹³ the gate-opening pressures in PCN-69 are higher, revealing a higher energy needed to trigger the curvature change.

In this work, we report a mesoporous MOF, PCN-69. It has rigid network connectivity with an expandable scaffold under pressurization. This flexibility comes from the pressure-responsive curvature change of the geodesic ligand btti adopted, which is confirmed by model simulation, PXRD, and gas-sorption experiments. To the best of our knowledge, this is the first example of a flexible MOF induced by covalent bond bending and curvature change.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data for PCN-69 and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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