Single-Walled Polytetrazolate Metal−Organic Channels with High Density of Open Nitrogen-Donor Sites and Gas Uptake

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Ⓢ *Supporting Information*

ABSTRACT: The self-assembly between zinc dimer and 1,3,5-tris(2H-tetrazol-5-yl)benzene (H₃BTT), promoted by a urea derivative, leads to a highly porous 3D framework with a large percentage (67%) of N-donor sites unused for bonding with metals. The material exhibits high gas storage capacity (ca. 1.89 wt % H_2 at 77 K and 1 atm; 98 cm^3/g CO_2 at 273 K and 1 atm), even in the absence of open metal sites. The high percentage of open N-donor sites, coupled with the low framework density resulting from single-walled channels, is believed to contribute to the high uptake capacity.

Porous metal−organic frameworks (MOFs) are a promising class of sorbents for various applications such as on-board H_2 storage and CO_2 capture.[1] Continuing efforts are being devoted to the optimization of various chemical and structural factors such as surface area, pore geometry, and functional sites in MOFs, in hope of increasing storage capacity and separation efficiency, particularly under ambient conditions. Synthetic strategies employed include creation of unsaturated metal sites,[2] introduction of cross-linking ligands with additional functional groups such as −NH₂,[3] lowering of the connectivity of multidonor ligands (e.g., triazoles and tetrazoles) to leave behind unused donor sites,[4] and design of pore architecture to fit the size of the gas molecule (e.g., through catenation and cage-within-cage configurations).[5]

To increase gravimetric storage capacity, the use of lightweight elements such as Li, B, Mg, and Al has attracted wide attention.[6] However, the coordination chemistry of such lightweight elements is generally less diverse than that of 3d metals such as Zn. To take advantage of the rich coordination chemistry of 3d metals and to simultaneously achieve the low framework density, an alternative method is to construct porous frameworks that have the highest level of "atom economy" (a term which here denotes the percentage of framework atoms exposed toward the pore space and thus accessible for interactions with gas molecules). Recent studies have shown that gas molecules can interact with both metal sites and ligands of the porous frameworks.[7] Thus, having available the largest number of exposed framework atoms (both metals and nonmetals) would likely contribute to enhanced gravimetric storage capacity.

Clearly, the binding affinity between the framework atoms and gas molecules can vary significantly, depending on both framework compositions and the nature of gas molecules.[7] Of particular interest are functional groups such as aromatic −N(H)− donors found in metal azolate frameworks.[4] Despite the fact that the use of triazoles and tetrazoles has led to many MOF materials, it is still an ongoing challenge to create porous frameworks in which the largest possible number of N-donor sites are left uncoordinated to metals (called open donor sites, in analogy with open metal sites). To increase the percentage of open donor sites, individual triazole or tetrazole ligands are of limited utility, because at least two N-donor sites will be needed for the framework connectivity, and the maximum percentage of open donor sites would be 33% for a triazole and 50% for a tetrazole framework. For this reason, we are especially interested in ligands containing multiple triazole and tetrazole groups (i.e., polytriazole or polytetrazole such as 1,3,5-tris(2H-tetrazol-5-yl)benzene or H₃BTT in short), as such ligands can achieve high connectivity even if they only use one N-donor site (per triazole or tetrazole group) for bonding with metals. The highest percentage of open donor sites would be 67% for a triazole and 75% for a tetrazole, assuming each ligand uses just one N-donor site for the framework formation. Moreover, as in the case of H₃BTT, steric hindrance could reduce the likelihood for N1 and N4 sites to bind with metals.[8]

H₃BTT is one of the most interesting polytetrazole ligands and was successfully employed by Long et al. in their design of Cu-BTT or Mn-BTT MOFs with open metal sites and enhanced H_2 uptakes.[2a,b] However, despite this great potential for the MOF construction, relatively few BTT MOFs have been made since the initial success by Long's group.[9] The challenge with the synthesis of BTT-MOFs was highlighted by earlier work showing that many attempts with the 3d metals (Fe−Zn) and various solvents (or solvent mixtures) led to insoluble, amorphous solids.[2b]

In this work, by using a urea derivative as the cosolvent in a procedure reminiscent of urothermal synthesis method developed recently,[10] an interesting porous framework (denoted CPF-6, where CPF = crystalline porous frameworks) with 1D square single-atom-walled channel system has been prepared, further demonstrating the great synthetic utility of urea-derivative-containing solvent system.[2b]

Also of interest is that even though CPF-6 does not contain open metal sites, its H_2 uptake capacity comes very close to that

of the related Mn-BTT MOF that does contain a significant number of open metal sites. We attribute this property to the large number of open donor sites and the single-walled channels that maximize the "atom economy". CPF-6 is particularly unusual, because two-thirds of its tetrazolate groups use only one N-donor site (out of four N-donor sites per tetrazole group) for binding with metals, with an overall of 66.6% of N-donor sites left unbonded with metals. To our knowledge, this is the highest percentage of N-donor sites left uncoordinated to metals in azolate-based MOFs.[8,9]

Ligand H_3BTT was synthesized by following a modified literature procedure (see Supporting Information).[2a,11] Solvothermal reaction between H_3BTT and $Zn(NO_3)_2 \cdot 6H_2O$ in a dma:dmpu (3:2 v/v, dma = N,N-dimethylacetamide, dmpu = 1,3-dimethylpropyleneurea) mixed solvent with one drop of concentrated HCl afforded block-shaped crystals of Zn(HBTT) (**1**, CPF-6).[12]

Single-crystal X-ray diffraction studies reveal that CPF-6 crystallizes in the tetragonal space group $P4_2/mnm$ and consists of 1D square single-walled channels (Figure 1). The asymmetrical unit of the host framework includes one-fourth of the Zn^{2+} ion and one-fourth of the $HBTT^{2-}$ ligand. Two tetrahedrally coordinated Zn^{2+} centers are bridged by two tetrazole groups to form a dimer core. Each Zn^{2+} site is further connected to two N2 sites from two other tetrazolate rings. Thus, each zinc dimer is connected to a total of six $HBTT^{2-}$ ligands and serves as the 6-connected node. In turn, each $HBTT^{2-}$ spacer is bound to three zinc dimers and serves as the 3-connected node. The overall framework adopts a (3,6)-*rtl* (rutile) topology.

In comparison with Mn-BTT (or Cu-BTT) sodalite-type frameworks which exhibit one type of ligand−metal binding mode,[2a,b] three tetrazole groups in CPF-6 show two types of binding modes (one bidentate and two unidentate fashions). It is worth noting that in MOFs it is quite unusual for a tetrazole group to bind to metals using only one N-donor site, as shown in CPF-6. Such an unusual mode makes it possible to increase the density of uncoordinated N-donor sites. In addition, the coexistence of such two types of coordination modes by three tetrazole groups in the same tristetrazolate $HBTT^{2-}$ allows the synthesis of a rare 3D network based on single-walled channels with a diagonal separation of about 1.5 nm. Additionally, as depicted in Supporting Information, nanosized channels are interconnected to each other through triangular apertures, forming a continuous 3D pore system, which may contribute to the enhanced gas sorption properties. The anionic charge of the framework is balanced by a proton (corresponding to the N−H stretching peak at 3391 cm^{-1} in the infrared spectrum of CPF-6), whose position could not be located crystallographically.

The total solvent-accessible volume of CPF-6 was estimated to be 69.7% by PLATON. Thermogravimetric analysis (TGA) of solvated CPF-6 under N_2 atmosphere showed a sharp weight loss of 22% below 160 °C, suggesting that dma and/or dmpu molecules were evacuated at this temperature. No steep weight loss between 160 and 210 °C (see Supporting Information) were observed. Thermal powder X-ray diffraction (PXRD) analysis indicated the sample CPF-6 retains its crystallinity after being heated to ca. 180 °C. To evaluate the porosity, N_2, H_2, and CO_2 isotherms on the guest-free sample were measured. Prior to the measurement, as-synthesized sample of CPF-6 was immersed in low-boiling-point acetone. During the exchange, the solvent was refreshed multiple times. The resulting
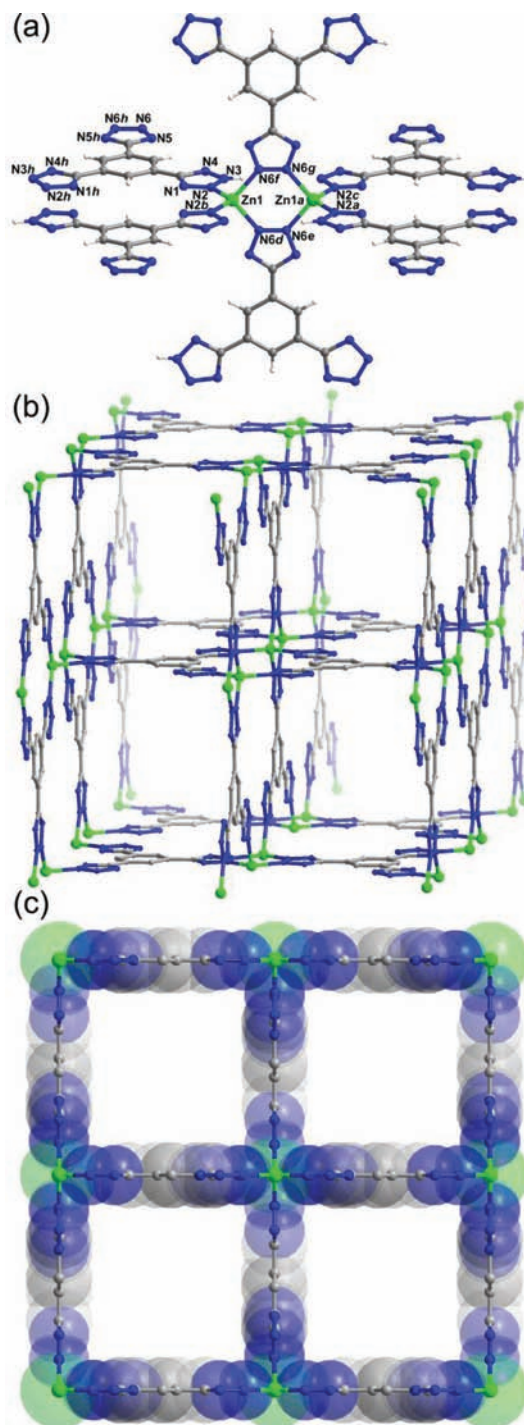

Figure 1. (a) View of the zinc dimer bridged by two tetrazolate groups (in bidentate fashion) and completed by four other tetrazolate groups (in unidentate fashion) (symmetry codes: a = y, x, −z; b = 1 − x, 1 − y, z; c = 1 − y, 1 − x, −z; d = 0.5 − x, −0.5 + y, 0.5 − z; e = −0.5 + y, 0.5 − x, −0.5 + z; f = 0.5 + x, 1.5 − y, 0.5 − z; g = 1.5 − y, 0.5 + x, −0.5 + z; h = 1 − y, 1 − x, 1 − z). (b) Ball-and-stick and (c) space-filling representations of the extended network with single-atomic-walled channels.

exchanged sample was then evacuated (10^{-3} Torr) successively at room temperature and 80 °C.

CPF-6 exhibits typical type I reversible sorption isotherms and takes up N_2 to 220 cm^3/g at 77 K and 1 atm, corresponding to a Langmuir and BET surface areas of 883

and 599 m^2/g, respectively. The H$_2$ isotherm collected at 77 K was completely reversible, and the material adsorbs a maximum of 1.85 wt % at 77 K and 1 atm (Figure 2a), which is close to
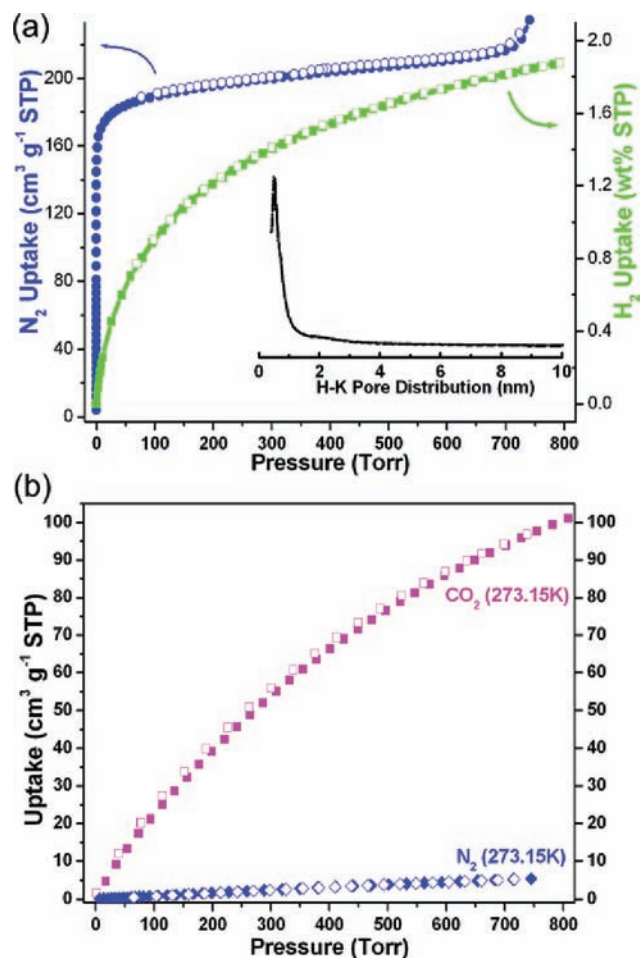

Figure 2. (a) N$_2$ (blue circles) and H$_2$ (green squares) sorption isotherms and Horvath−Kawazoe pore distribution at a highest pore width of 4.7 Å (inset) at 77 K. (b) CO$_2$ (magenta squares) and N$_2$ (blue diamonds) sorption isotherms at 273 K, showing selective adsorption of CO$_2$ over N$_2$. STP = standard temperature and pressure (solid symbols, adsorption; open symbols, desorption).

the observation for Mn-BTT.[2a] A recent theoretical study suggests that nitrogen atoms on aromatic rings can enhance the adsorption energy of H$_2$.[13] Since such a structural feature is also expected to enhance interactions with CO$_2$, the CO$_2$ isotherm at 273 K was also measured, which shows an uptake of 98 cm^3/g at 1 atm (Figure 2b). For comparison, the N$_2$ uptake at 273 K is only 4.7 cm^3/g at 1 atm, which leads to the calculated CO$_2$/N$_2$ selectivity of 20.8:1 at 273 K. The H$_2$ and CO$_2$ uptake capacity of CPF-6 ranks among the high end for MOF materials. So far, the number of materials and structure types with the CO$_2$ uptake of more than 100 cm^3/g (273 K and 1 atm) and H$_2$ uptake of 2.0 wt % is still very limited.[14]

In conclusion, a single-walled 3D framework CPF-6, containing a high concentration of tetrazolate nitrogen sites uncoordinated to metal sites, has been synthesized. The high percentage of open N-donor sites, together with low framework density (due to the single wall) leads to the high uptake capacity for H$_2$ and CO$_2$, even in the absence of any open metal sites. This work points to an intriguing possibility for the

dramatic enhancement of gas sorption if it is possible to integrate high concentrations of open metal sites together with open donor sites and single walls.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional structural figures, powder X-ray diffraction, thermal analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for [Zn(HBTT)]·*x*(solv) (**1**, CPF-6), $C_9H_4N_{12}Zn$, $M = 345.63$, tetragonal, $P4_2/mnm$ (No. 136), $a = 15.4962(7)$ Å, $c = 13.7523(12)$ Å, $V = 3302.4(4)$ Å^3, $Z = 4$, Bruker APEX II, Mo Kα radiation, $\lambda = 0.71073$, $T = 150(2)$ K, 10 126 reflections collected, 2137 unique ($R_{int} = 0.0394$). $R_1 = 0.0372$ ($I > 2\sigma(I)$). wR (F^2) = 0.0816 ($I > 2\sigma(I)$). GOF = 1.062.

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