

# Unique gas and hydrocarbon adsorption in a highly porous metal-organic framework made of extended aliphatic ligands†

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Received (in Austin, TX, USA) 20th August 2008, Accepted 28th September 2008

First published as an Advance Article on the web 15th October 2008

DOI: 10.1039/b814498b

**High and unique gas and hydrocarbon adsorption in a highly stable guest-free microporous metal-organic framework constructed on rigid aliphatic ligands, H<sub>2</sub>bodc and ted, is reported in this work.**

Recent progress in the research of microporous metal-organic frameworks (MMOFs) has demonstrated the great potential of this new type of multifunctional materials in molecular storage, separation, catalysis, and sensing.<sup>1</sup> Design and synthesis of targeted MMOFs through rational selection and combination of organic ligands and single metal centers or metal clusters (often called secondary building units or SBUs) have been the main focus and driving force of this relatively new and fertile research field.<sup>2</sup> Aromatic carboxylic acids, such as benzene-1,4-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid and biphenyl-4,4'-dicarboxylic acid, are examples of the most common ligands of choice because their excellent chemical stability and structural rigidity help sustain the increasingly porous structures resulting from the progressively extended distances between the ligating carboxylate groups. In stark contrast, stable MMOFs that are solely built upon extended aliphatic ligands are rare. This is a direct result of the scarcity of rigid extended aliphatic carboxylic acids (or the corresponding carboxylates). Due to the aliphatic nature of these ligands, the gas and hydrocarbon adsorption behavior and mechanism are expected to be generally different from those of the MMOFs based on unsaturated aromatic carboxylates (and/or nitrogen-containing molecules, *e.g.* bipyridyl). Among the few MOF structures based on extended aliphatic carboxylate ligands,<sup>3</sup> no attempts have been made to study their gas and hydrocarbon adsorption properties. Therefore, this work on a new type of extended aliphatic ligand based, guest-free porous [Ni(bodc)(ted)<sub>0.5</sub>] (**1**) structure serves, to the best of our knowledge, as the first of its kind.

Bicyclo[2.2.2]octane-1,4-dicarboxylic acid (H<sub>2</sub>bodc, Scheme S1 in ESI†), a rod-like dicarboxylic acid, was synthesized *via* a 4-step synthetic route<sup>4</sup> in good overall yields, starting from the commercially available dimethyl 2,6-diketocyclohexane-1,4-dicarboxylate. Compared to the syntheses of the cubane<sup>5</sup>

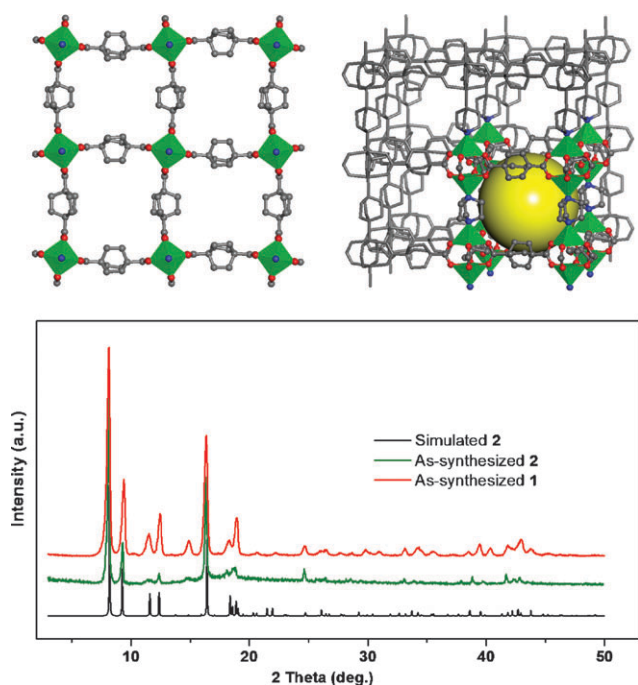
and adamantane<sup>6</sup> based carboxylic acids, the synthesis of H<sub>2</sub>bodc is quite straightforward and was successfully scaled up to afford over 5 g/batch of pure H<sub>2</sub>bodc, which greatly assisted the subsequent explorative and preparative studies on crystalline metal-organic framework materials. Other important factors, in addition to its rigidity, were also taken into consideration in the selection of H<sub>2</sub>bodc as the ligand of interest. For example, its bulky rod-like bicyclooctane fragment, a structural feature also found in triethylenediamine (ted), is likely to prevent interpenetration and thus to maximize pore space.

When H<sub>2</sub>bodc was reacted with nickel(II) nitrate hexahydrate and ted under solvothermal conditions,<sup>7</sup> a highly crystalline light-green powder was obtained (**1**) in excellent yield (98%). While attempts of growing crystals of **1** with suitable quality for single-crystal X-ray diffraction were unsuccessful, single crystal data of the similarly grown [Co<sub>2</sub>(bodc)<sub>2</sub>(ted)]·3.5DMF (**2**) crystals were indeed obtained.† In spite of the difficulty encountered due to the highly disordered and twinned nature of the crystals of **2** (see ESI†), a three-dimensional framework structure was revealed, which features a pillared-layer topology similar to that of [Zn(bdc)(ted)<sub>0.5</sub>].<sup>8</sup> The bodc ligands are connected by the paddle-wheel like Co<sub>2</sub>(COO)<sub>4</sub> SBUs to form distorted square-grid like layers. The ted ligands coordinate to the paddle-wheels along the axial directions (coincident with *c* axis), pillaring the layers into the overall 3D structure (Fig. 1). The three-dimensionally interconnected pores, as calculated by PLATON,<sup>9</sup> occupy ~49% of the volume of the crystal. Powder X-ray diffraction study (Fig. 1) confirmed that **1** is iso-structural to **2**. Elemental microanalysis of a freshly made sample of **1**, in conformity with the thermogravimetric analysis results described below, not only established the proper composition but also uncovered its guest-free nature. A pore volume of 0.47 cm<sup>3</sup> g<sup>-1</sup>, a BET and Langmuir surface area of 958 and 1244 m<sup>2</sup> g<sup>-1</sup>, respectively, and a distribution of pore size around 7.0–7.3 Å (~7.8 Å for [Zn(bdc)(ted)<sub>0.5</sub>]<sup>10</sup>), were deduced from the argon adsorption isotherms of **1** (see ESI†).

Thermogravimetric analysis indicated that **1** is highly stable. No significant weight loss was observed until the compound began to decompose at around 450 °C, suggesting that no solvent molecules were encapsulated in the framework during the crystallization process (see ESI†). The high stability of **1** was also evidenced by the hundreds of the repeated hydrocarbon adsorption/desorption isotherm measurement cycles at elevated temperatures (typically, 30 to 150 °C) over an extended period of more than two months. The stability of **2**

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† Electronic supplementary information (ESI) available: Details of the synthesis of H<sub>2</sub>bodc, experimental procedures, PXRD patterns, TGA, gas and hydrocarbon adsorption/desorption results, selected crystallographic data. CCDC 698828. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814498b

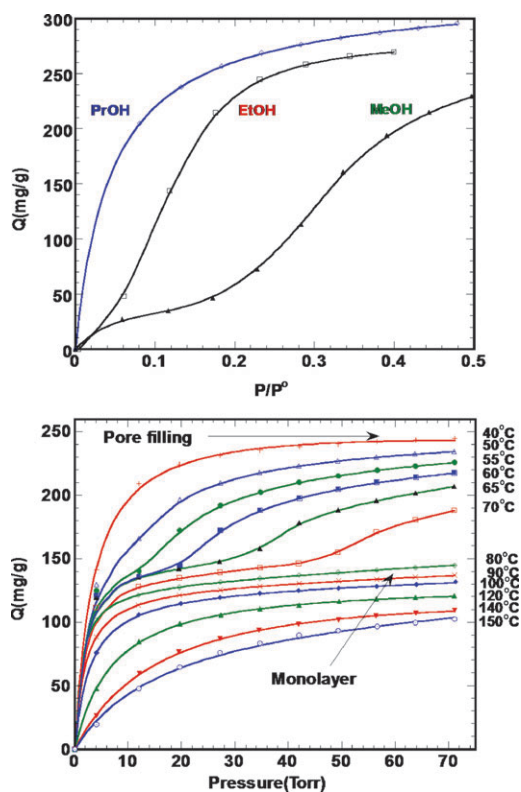


**Fig. 1** Top: the distorted square-grid like layer of [Co(bodc)] viewed along the *c* axis (left) and the overall 3D structure of **2** with one cage shown in ball-and-stick model and the remainder of the framework in gray stick model (right). The space inside one cage is highlighted by the yellow sphere (Co: green square pyramids; C: gray; N: blue; O: red; only one set of disordered carbon atoms of bodc and ted are shown; hydrogens were omitted for clarity). Bottom: a comparison of the calculated pattern of **2** (black), and the observed patterns of as-synthesized **2** (green) and **1**.

(decomposing quickly in air), however, is significantly inferior; therefore the gas and hydrocarbon sorption properties are attainable only for **1**.

**1** exhibits very interesting and unique gas adsorption properties. It takes up significant amounts of hydrogen at 77 K (1.29 wt%) and 87 K (0.78 wt%) at 1 atmosphere. At 77 K and 60 bar, the hydrogen amount reaches  $\sim 2.76$  wt% (see ESI†). This behavior is comparable with MMOFs based on aromatic ligands. If the differences of their BET surface areas and pore volumes are taken into consideration ( $958 \text{ m}^2 \text{ g}^{-1}$  and  $0.47 \text{ cm}^3 \text{ g}^{-1}$  vs.  $1450 \text{ m}^2 \text{ g}^{-1}$  and  $0.75 \text{ cm}^3 \text{ g}^{-1}$ ), **1** actually adsorbs comparable amount of hydrogen per unit surface area (or per unit pore volume) as [Zn(bdc)(ted)<sub>0.5</sub>] does,<sup>10</sup> suggesting that the aliphatic nature of **1** does not diminish its capability of taking up hydrogen. It is also of interest to note that the calculated isosteric heats of hydrogen adsorption ( $Q_{st}$ , based on the isotherms at 77 and 87 K, see ESI†) are between 5.7 to 6.5  $\text{kJ mol}^{-1}$ , somewhat ( $\sim 1 \text{ kJ mol}^{-1}$ ) higher than those observed in [Zn(bdc)(ted)<sub>0.5</sub>] (5.0–5.3  $\text{kJ mol}^{-1}$ ).<sup>10</sup> This stronger adsorbent–adsorbate interaction could be attributed to the smaller pores found in **1**, consistent with similar  $Q_{st}$  values found in other small-pore metal-organic frameworks.<sup>11</sup>

**1** also adsorbs significant amounts of selected aromatic and aliphatic hydrocarbons (Table 1). This capacity, as exemplified by the *n*-hexane adsorption at 30 °C ( $0.41 \text{ cm}^3 \text{ g}^{-1}$ ), is substantially higher than the  $0.26 \text{ cm}^3 \text{ g}^{-1}$  of the widely used zeolite Y. A comparison of the sorption isotherms for



**Fig. 2** Top: comparison of methanol, ethanol and propanol adsorption isotherms at 30 °C. Bottom: cyclohexane adsorption isotherms.

methanol, ethanol and propanol at 30 °C (Fig. 2, top) clearly shows that with each added  $\text{CH}_2$  group, the increased organophilic attraction results in higher adsorption at lower pressure. The isosteric heats of adsorption,  $Q_{st}$ , for this series are 52–52, 49–57 and 64–64  $\text{kJ mol}^{-1}$  (from low to high loading), respectively, increasing as each additional  $\text{CH}_2$  group is added (see ESI†). The results also indicate that these alcohols could be separated (methanol from ethanol and propanol) by **1** in an equilibrium-based process such as Pressure Swing Adsorption.<sup>12</sup>

In contrast to the classical Langmuir adsorption/desorption behavior for benzene, *p*-xylene and *n*-hexane (see ESI†), the isotherms of cyclohexane (*c*-hexane) sorption shows particularly interesting features between 50 and 80 °C (Fig. 2, bottom). We propose that the *c*-hexane isotherms may be considered as having two regions, pore filling, occurring at lower temperatures (below 50 °C) and a monolayer region (above 80 °C). The “abnormal” features observed between these two temperatures are due to the transition from monolayer adsorption to pore filling. The calculated isosteric heats of adsorption support this description, with  $Q_{st}$  linear up to about  $130 \text{ mg g}^{-1}$  with a value of 52  $\text{kJ mol}^{-1}$  and then 66 to 73  $\text{kJ mol}^{-1}$  in the pore filling region, 145 to 230  $\text{mg g}^{-1}$  (see ESI†). In the latter region,  $Q_{st}$  gradually increases as adsorbate–adsorbate interactions increase.

In summary, a highly stable guest-free microporous metal-organic framework constructed on rigid aliphatic ligands,  $\text{H}_2\text{bodc}$  and ted, is reported in this work. The use of rigid, bulky aliphatic ligands effectively prevented the structure from interpenetration, thus, resulting in a highly porous framework with three-dimensional pores. [Ni(bodc)(ted)<sub>0.5</sub>] (**1**) exhibits

**Table 1** A summary of the hydrocarbon adsorption properties of **1**

Adsorbate	Weight adsorbed/mg g <sup>-1</sup>	Volume adsorbed/cm <sup>3</sup> g <sup>-1</sup>	Q <sub>st</sub> /kJ mol <sup>-1</sup>
<i>n</i> -Hexane	268	0.41	54–73
<i>c</i> -Hexane	254	0.33	52–73
Benzene	268	0.31	44–58
<i>p</i> -Xylene	319	0.37	64–88
Methanol	260	0.33	52–52
Ethanol	300	0.38	49–57
Propanol	296	0.37	64–64

increasingly stronger affinity towards hydrocarbons with decreasing polarity. As a consequence, **1** can take up significant amounts of selected aromatic and aliphatic hydrocarbons, ~50% higher than those observed for the large-pore zeolite Y. Unique features in the adsorption isotherms of *c*-hexane were observed, which indicate a transition from monolayer adsorption to pore filling. This is the first time, to the best of our knowledge, that such phenomenon is observed in metal-organic frameworks. It appears that this kind of behavior is closely related to the pore size, shape and nature (aliphatic or aromatic). In depth study and understanding of similarly unique hydrocarbon adsorption behavior in a few MMOFs are currently under way and will be reported in the near future.

The authors are grateful to the Department of Energy (DOE) for the financial support through Grant No. DE-FG02-08ER46491. J. L. would like to thank Rutgers University for an Academic Excellence Fund (AEF) award for the purchase of a high pressure gas analyzer.

## Notes and references

† Crystal data for **2**: Co<sub>2</sub>C<sub>36.5</sub>H<sub>60.5</sub>N<sub>5.5</sub>O<sub>11.5</sub>, *M<sub>r</sub>* = 878.26, tetragonal, space group *P*4<sub>2</sub>2<sub>1</sub>2 (no. 94): *a* = 15.2597(6), *c* = 19.092(1) Å, *V* = 4445.7(4) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.312 g cm<sup>-3</sup>, μ(Mo-Kα) = 0.806. All measurements were made on a SMART CCD area detector at 296(2) K with graphite-monochromated Mo-Kα radiation. A total of 47325 reflections were collected (5522 unique, *R*(int) = 0.0368) between a θ of 1.71° to 28.28° (99.5% completeness). *R*<sub>1</sub> = 0.053 (*I* > 2σ(*I*)), *wR*<sub>2</sub> = 0.185 (all data) and GOF = 1.002 (all data). Largest diff. peak and hole 1.050 and -1.202 e Å<sup>-3</sup> (see ESI† for details on the handling of pseudosymmetry).

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