Separation of Hydrocarbons with a Microporous Metal–Organic Framework**

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The past decade has witnessed a rapid growth of interest in the field of metal–organic frameworks (MOFs). Microporous metal–organic framework (MMOF) materials, a subset of the general family of MOFs, are of particular attraction owing to their potential application in gas separation, storage, molecular magnetism, and heterogeneous catalysis.[1] While many new structures are being discovered each year, the gas-adsorption properties of only a very small number of them have been investigated, which has prompted us to explore the scope of their unique sorption properties.

Unlike those of zeolites, the surfaces and voids of MMOF structures are typically composed of aromatic rings and other organic moieties,[2,3] and their pore structures are often quite complex and different from those of oxide-based materials.[2,3] The pore diameters of MMOFs generally fall in the region of micropores, often ultra-micropores.[2b] Their pore structures can be designed and modified to yield the desired shape, size, and surface characteristics. Among the reported sorption studies, the focus has been primarily on small gases such as Ar, N_2, H_2, O_2, CO_2, and C_2H_2.[2a,b,4] To date, there have been no reports of the separation of hydrocarbons with MOFs except for one simulation study.[5] Herein we report the first case in which the potential to separate hydrocarbons by using metal–organic-based sorbent material is observed.

We have recently designed and synthesized a group of MMOFs with a general formula $[M(hfipbb)L_x]$ (M is Co, Cu, or Zn; L can be pyriding, 3-picoline, or 4-picoline; $H_2hfipbb$ is 4,4′-(hexafluoroisopropylidene) bis(benzoic acid)). These are 3D[2a] or 2D[6] framework structures built upon paddle-wheel metal clusters (nodes) and a V-shaped dicarboxylate ligand, $H_2hfipbb$. These structures contain irregular-shaped micro-channels, with alternating large cages (or chambers) and small entrances (or necks) that connect these cages.

The crystal structure of 3D $[Cu(hfipbb)(H_2hfipbb)_{0.5}]$ (**1**) is shown in Figure 1a.[7] Each copper center has a square-pyramidal coordination environment. Two copper atoms share four carboxylate groups of the four hfipbb ligands, which are located in the equatorial plane, to form a paddle-

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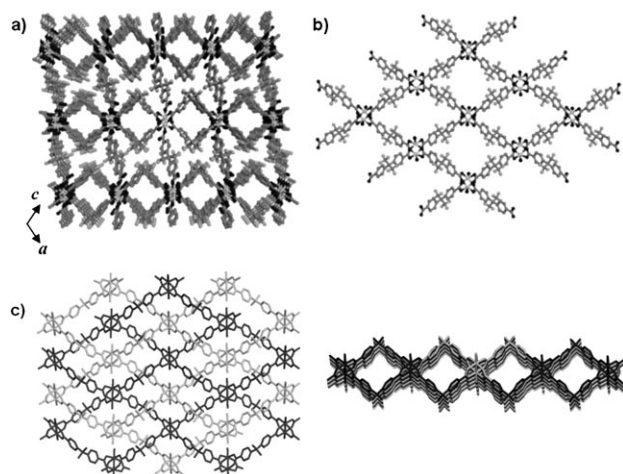
Figure 1. a) View of structure **1**. b) The core motif in **1**, in which each {Cu₂} paddle-wheel unit interconnects with four neighboring {Cu₂} units through four hfipbb ligands to form an undulating 4⁴ 2D net. c) Two such 2D nets, identical in structure (shown in dark and light gray), interpenetrate to form a layer composed of 1D tubular micro-channels. Left: top view; Right: side view.

wheel with a Cu–Cu interatomic distance of 2.645 Å as shown in Figure 2. Each paddle-wheel unit binds to four adjacent paddle-wheel units through the four remaining carboxylate


Figure 2. Representation of {Cu2} paddle wheel (light gray Cu, dark gray C, black O).

groups of hfipbb to form an undulating 2D network with 4⁴ topology (Figure 1b).[8] Two such identical networks inter-penetrate to form a layered structure consisting of micro-channels, as shown in Figure 1c. The adjacent layers are further interconnected by monodentate carboxylate groups of H₂hfipbb ligands that bind to the apical position of the metal centers to generate a 3D network (Figure 1a).

The microchannels of these frameworks typically have strong interactions with hydrocarbons, which results in large values for the heat of adsorption; they are also hydrophobic, thus allowing the separation of nonpolar molecules from water. We have investigated the sorption properties of **1**, one of the most thermally stable [M(hfipbb)Lₓ]-type structures,[6] by using several organic hydrocarbons of different shapes, sizes, and polarities. Both experimental and simulated adsorption measurements have been conducted. The pore

volume of structure **1** is modest, about 0.070 cm³ g⁻¹. How-ever, **1** exhibits unique adsorption properties as it adsorbs propane and butane rapidly (Figure 3) but does not adsorb pentane or higher normal or branched hydrocarbons
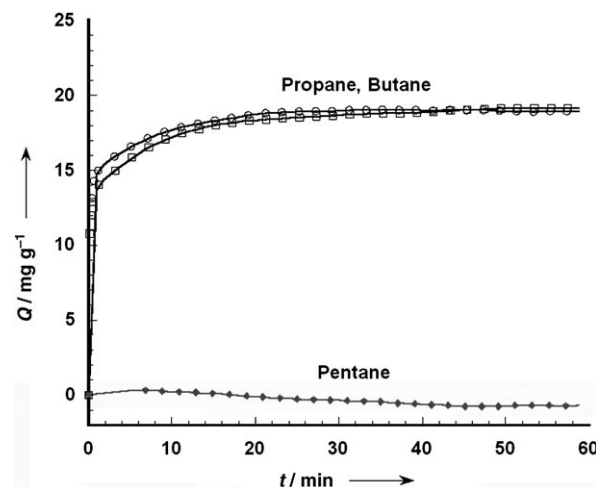
Figure 3. Adsorption of propane (○), butane (□), and pentane (◆) at 90°C and 650 torr in **1** as a function of time. Q is the weight of hydrocarbon molecules adsorbed in the adsorbent.

(Table 1). It is worth noting that all zeolites that adsorb butane also adsorb higher alkanes and do not have a fixed

Table 1: Sorption properties of **1** at 25°C.

| Hydrocarbon	P/P^{o} [a]	Sorption (wt%)
methanol	0.60	2.0
propane	0.062	2.6
propene	0.019	2.0
n-butane	0.33	4.0
2-methylpropane	≈0.1	0.0
n-pentane	0.100	0.0
3-methylbutane	≈0.1	0.0
n-hexane	0.071	0.0
3-methylpentane	0.078	0.0

[a] P is the partial pressure of the adsorbate and P^{o} is the vapor pressure of the adsorbate at the sorption temperature.

carbon-number cutoff for adsorption. Thus, the microchan-nels in **1** are unique in being able to separate normal C₂, C₃, and *n*-C₄ olefins and alkanes from all branched alkanes and all normal hydrocarbons above C₄. To the best of our knowledge, there are no existing adsorbents capable of separating normal C₄ from higher normal alkanes and olefins. Compound **1** is the first material found to have such capability. This unusual property is attributed to a narrowing of the channels at intervals of 7.3 Å (the length of the large chamber or cage), which is just greater than the length of *n*-C₄, approximately 6.9 Å, and just less than the length of *n*-C₅, about 8.1 Å. The diameter of the neck is approximately 3.2 Å (2 Å is allowed for the size of the two hydrogen atoms on the surface of the neck). Thus, the neck is too small for this region to be an equilibrium position for alkanes with diameters of around

3.9 Å but large enough to allow the passage of normal alkanes while excluding branched alkanes.

In addition to the experimental adsorption measurements, the Sorption module of the Cerius2 program was used to perform gas-sorption simulations. These calculations indicate that if pentane were to locate in the large chamber area of the microchannel, the closest H–H interatomic distance between the molecule and the wall would be 1.86 Å, which is too small to be reasonable. The calculations predict that a maximum of one propane or butane molecule is adsorbed per cage, as illustrated in Figure 4. The calculations also indicate that
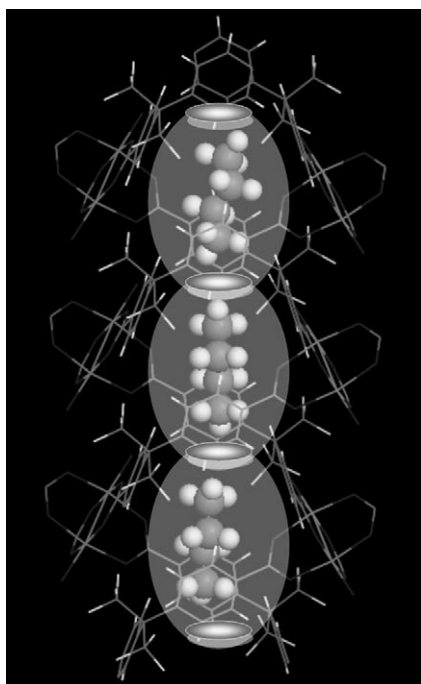
Figure 4. Arrangement of butane molecules in the microchannel of **1**, with one molecule per cage.

essentially no pentane is adsorbed, which is in agreement with the experimental results. Helium-adsorption simulation reveals the pore-filling pattern shown in Figure 5. A view along [100] indicates clearly the formation of a microchannel as a result of the repetition of an oval-shaped cage with a narrow neck region. The substantial amount of 2,2-dimethyl-propane accommodated, 0.89 molecules per cage, but no 2,2,3-trimethylbutane is also consistent with the oval-shaped description of the cages (see Table 2). The sorption simulations also indicate that 2,2-dimethylbutane does not adsorb, that is, it does not fit in the chamber area. Thus, the shape of the molecules is critical.

Adsorption isotherms for propane and butane in **1** are shown in Figure 6. Values for zero-loading heat of adsorption, calculated from these data from the Clausius–Clapeyron equation, are 47 kJ mol^{-1} for propane and 50 kJ mol^{-1} for butane. The value of 47 kJ mol^{-1} for propane is higher than the values of 41 and 34 kJ mol^{-1}, which were reported for propene adsorbed by the pure-silica 8-ring zeolites, ITQ-12 and Si-CHA, respectively.[9] The higher value of 41 kJ mol^{-1}
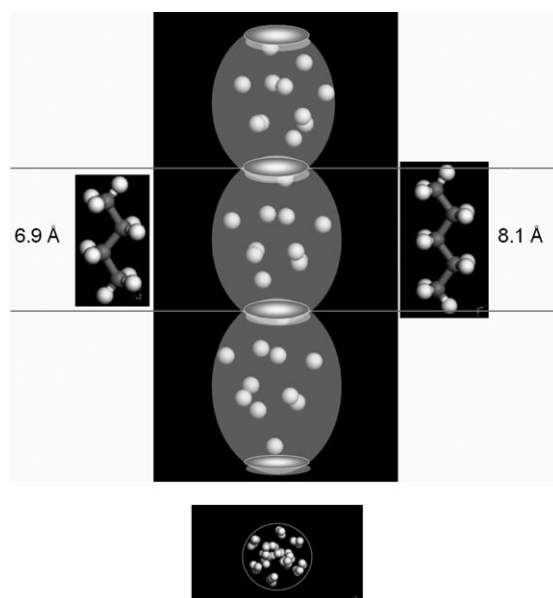
Figure 5. Top: The shape of a microchannel outlined by fitting He sorption at 298°C and 10 atm by Cerius2 simulation. Butane and pentane are shown in real scale. Clearly, pentane (C$_5$) is longer than the chamber. Bottom: Top view of the adsorbed He atoms in the microchannel.

Table 2: Sorption capacities simulated by using Cerius2/Sorption.[a]

Hydrocarbon	T [K]	P [kPa]	Q [mol/cage]
propane	303	80	0.98
butane	298	243	0.81
trans-butene	303	80	0.62
cis-butene	303	80	0.87
2-methylbutane	303	80	0.68
2,2-dimethylpropane	303	80	0.89
2,2-dimethylbutane	303	80	0.04
pentane	303	9	0.06
2,2,3-trimethylbutane	303	80	0.00
2,2-dimethylpentane	303	80	0.00

[a] Calculated by using Monte Carlo placement of molecules. Thus, the results reflect cage size and shape but not the ability of the molecules to pass through the narrow neck region.

for ITQ-12 is attributed to its smaller adsorption cavity size and consequently greater adsorbate–adsorbent interaction. Compound **1** also adsorbs 2.0 wt% of methanol at $P/P° = 0.6$ (80 torr) and 25°C, which shows that it is capable of gas-phase separation of methanol from water (Table 1).

In conclusion, MMOFs built upon bimetallic paddle wheels contain 1D microchannels with hydrophobic internal surfaces. These channels consist of alternating oval-shaped large chambers and narrow windows. The most striking feature of these microchannels is their unique sorption properties, including shape and size selectivity for hydro-carbons. Compound **1** is the first adsorbent capable of separating normal C$_4$ from higher normal alkanes and olefins. This work reveals the potential of microporous metal–organic framework materials for applications in various hydrocarbon separations.
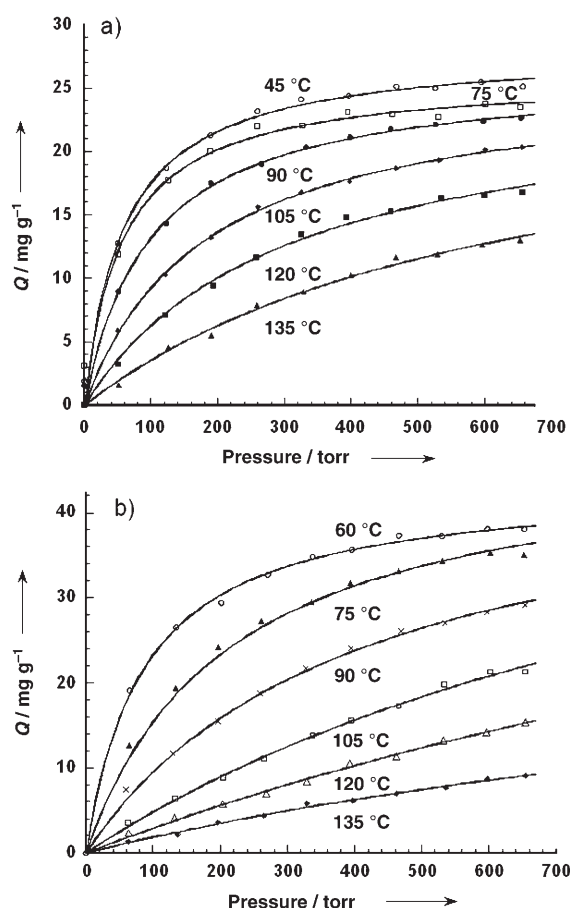
Figure 6. a) Propane adsorption isotherms for **1** at several temperatures (45, 75, 90, 105, 120, and 135 °C). b) Butane adsorption isotherms for **1** at 60, 75, 90, 105, 120, and 135 °C.

Experimental Section

Synthesis of **1**: Hydrothermal reactions of $Cu(NO_3)_2 \cdot 3H_2O$ (0.029 g, 0.12 mmol) with excess H_2hfipbb (0.195 g, 0.5 mmol) in deionized water (5 mL; mole ratio 1.2:5:2278) at 125 °C for 3 days produced blue columnlike crystals of **1** in quantitative yield. The product was washed with *N,N*-dimethylformamide (DMF; 10 mL) three times to remove excess H_2hfipbb.[2a]

Adsorption measurements were carried out on a computer-controlled thermogravimetric balance consisting of a TA51 electro-balance with associated TA-2000/PC control system, and a series of mass flow controllers and a Eurotherm temperature controller. This flow-through, one-atmosphere electrobalance system was controlled by the LabView program through Kinetic Systems Interface. In addition to the experimental adsorption measurements, the Sorption function of the Cerius2 program was used to simulate gas-sorption processes.

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[7] Crystal data for **1**: space group $P2/n$, $a = 18.723(4)$, $b = 7.271(1)$, $c = 20.481(4)$ Å, $\beta = 107.02(3)°$, $V = 2666.1(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.619$ Mg m^{-3}.

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