Methane Storage in Paddlewheel-Based Porous Coordination Cages


1Department of Chemistry and Biochemistry, 2Center for Neutron Science, and 8Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716 United States
2Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: Although gas adsorption properties of extended three-dimensional metal–organic materials have been widely studied, they remain relatively unexplored in porous molecular systems. This is particularly the case for porous coordination cages for which surface areas are typically not reported. Herein, we report the synthesis, characterization, activation, and gas adsorption properties of a family of carbazole-based cages. The chromium analog displays a coordination cage record BET (Brunauer–Emmett–Teller) surface area of 1235 m\(^2\)/g. With precise synthesis and activation procedures, two previously reported cages similarly display high surface areas. The materials exhibit high methane adsorption capacities at 65 bar with the chromium(I) cage displaying CH\(_4\) capacities of 194 cm\(^3\)/g and 148 cm\(^3\)/cm\(^3\). This high uptake is a result of optimal pore design, which was confirmed via powder neutron diffraction experiments.

As a result of continually increasing global reserves, natural gas has been touted as a cleaner alternative to gasoline and coal as a fuel in the transportation and power generation sectors, respectively. Because natural gas primarily consists of methane, which is the upper limit of H:C ratio, it is the most gravimetrically energy dense hydrocarbon fuel. Consequently, its combustion releases considerably less pollutants on a per energy basis. Indeed, U.S. CO\(_2\) emissions from power generation are near a 30 year low resulting from a transition to natural gas. In the transportation sector, however, the low volumetric energy density of methane at STP has limited its utility. Proposed solutions to this have included liquefaction or compression. Both of these have generally been viewed as not viable in passenger vehicles. Adsorbed natural gas systems have shown promise in this regard. The challenge here is the development of an adsorbent with appropriate methane capacity. Zeolites, activated carbons, metal–organic frameworks (MOFs), and a variety of other porous materials have been investigated for high pressure natural gas storage. MOFs currently display the most promising uptakes with reported CH\(_4\) adsorption capacities as high as 259 cm\(^3\)/cm\(^3\). Additionally, a number of interesting adsorption properties have been observed in these materials, including flexibility for thermal management and temperature-dependent negative gas adsorption. However, advancements in this area remain short of Department of Energy targets.

Porous molecular adsorbents may show promise in this regard as they can be thought of as soluble adsorbents with designer pores. This could potentially endow them with favorable properties such as tailored syntheses, flexibility upon adsorption, cooperative binding, and increased ease of processability. These molecules, which can be either all-organic or metal–organic, are discrete zero-dimensional materials that display permanent porosity in the solid state. Although the underlying chemistry of porous organic cages and porous coordination cages has been established for decades, permanent porosity in these materials is a relatively recent phenomena when compared to zeolites and MOFs. As a result, they have remained almost completely unexplored for high-pressure gas storage applications. This is somewhat surprising given their conceptually analogous nature to porous extended solid materials. In fact, many metal–organic frameworks contain cages as their building units. In an effort to expand the library of carbazole-based porous cages, we have thoroughly investigated the synthesis of novel isophthalic acid and carbazole-dicarboxylic acid materials. These latter molecules are particularly interesting for gas storage applications as the M\(_{12}\)(cdc)\(_{12}\) (cdc\(^2\) = carbazolidi-carboxylic acid) octahedral cage is present as one of three cages in DUT-49 and PCN-82, two MOFs with high methane and hydrogen storage capacities, respectively. Given the high surface area of recently reported cuboctahedral M\(_{12}\)(R-bdc)\(_{24}\) cages based on chromium(II), we sought to expand the synthesis of M\(_{12}\)(cdc)\(_{12}\) to this metal as a porous cage of this type is expected to show promising high-pressure adsorption properties.

Analogous to the synthesis of the Cu- and Mo-based M\(_{12}\)(cdc)\(_{12}\) materials, the air-free reaction of anhydrous Cr\(_2\)(OAc)\(_4\) with H\(_2\)cdc in a dimethylformamide (DMF)/methanol (MeOH) mixture affords Cr\(_{12}\)(cdc)\(_{12}\)·nDMF as large red/purple crystals. Single crystal X-ray diffraction confirms the material is isosstructural to the previously reported Cu\(^{2+}\) and Mo\(^{2+}\) cages. This structure is comprised of six bimetallic paddlewheel units in an octahedral arrangement coordinated to 12 cdc\(^2\) ligands (Figure 1). The cages consist of 8 triangular windows with corner–corner distances of approximately 12 Å. The molecules pack in the solid state with cage center to

Received: June 1, 2018
Published: August 18, 2018
The structure of Cr$_{12}$(cdc)$_{12}$ contains solvent accessible voids in excess of 60%, which rivals the values displayed by many MOFs. Accordingly, thermogravimetric analysis (TGA) of a DMF-exchanged sample reveals a mass loss of 40% at 250 °C (Figure S4). Precise solvent exchange protocols must be implemented to achieve high surface areas for molecular materials as cages are potentially soluble in a variety of solvents. For Cr$_{12}$(cdc)$_{12}$, room temperature solvent exchanges with DMF and methanol were used. Powder X-ray diffraction confirms the as-synthesized material retains high crystallinity upon exchange with DMF and methanol (Figure 2). However, given the lack of three-dimensional connectivity and in contrast to most MOFs, there is significant structural rearrangement upon initial solvent exchange. Activation at 70 °C affords a BET surface area of 1235 m$^2$/g. To the best of our knowledge, this is the highest surface area reported for a molecular metal–organic material.

In order to achieve comparable surface areas for Cu$_{12}$(cdc)$_{12}$ and Mo$_{12}$(cdc)$_{12}$, we surveyed a range of synthesis, solvent exchange, and activation procedures. In contrast to metal–organic frameworks where identical surface areas for a material should be obtained regardless of synthesis conditions (assuming phase purity and full activation), a porous coordination cage can deposit in different crystalline phases depending on synthetic conditions. Although the individual cage structures remain in these various analogs, their three-dimensional packing, stability, and porosity can potentially vary. For Mo$_{12}$(cdc)$_{12}$, a DMPU-based synthesis was reported affording a solid that crystallizes in R$3$. Despite our best efforts, we were only able to obtain an activated material with a surface area of approximately 550 m$^2$/g. Synthesis of the cage in DEF affords the same cage that instead crystallizes in P2$_1$/n. Methanol exchange of this material followed by activation at 50 °C affords a solid with a BET surface area of 1108 m$^2$/g. In an analogous manner, Cu$_{12}$(cdc)$_{12}$ can be synthesized and crystallized from a variety of amide-based solvents. The highest surface area that was observed (657 m$^2$/g) was for a material synthesized in DMF/MeOH, washed in MeOH, and activated at 50 °C.

To evaluate the methane storage potential of the three porous cages, high-pressure adsorption isotherms were collected from 0 to 65 bar at 298 K. At 35 bar the total gravimetric uptakes follow the surface area trends with capacities of 148, 135, and 81 cm$^3$/g for Cr$_{12}$(cdc)$_{12}$, Mo$_{12}$(cdc)$_{12}$, and Cu$_{12}$(cdc)$_{12}$, respectively (Figure 3). These values are not only significantly higher than those for previously reported coordination cages, they are consistent with the capacities displayed by metal–organic frameworks with similar surface areas. Methane uptake increases up to at least 65 bar with the Cr$_{12}$(cdc)$_{12}$ displaying the highest gravimetric capacity of 194 cm$^3$/g while Mo$_{12}$(cdc)$_{12}$ has the highest volumetric capacity (150 cm$^3$/cm$^3$) (Table 1) (Figures S30, S31). To the best of our knowledge, both the gravimetric and volumetric capacities are the highest observed for a porous
molecular assembly. For all three materials, moderate hysteresis is seen upon desorption, likely a result of the lack of three-dimensional connectivity between the cages.

To directly compare the CH₄ storage capacities of M₁₂(cdc)₁₂ cages with MOFs containing similar methane binding environments, we targeted previously reported materials with M₁₂(cdc)₁₂ as their building units. DUT-49 has been thoroughly investigated for its high CH₄ uptake at high pressure, however the flexibility of the material complicates adsorption studies. Two analogous materials, PCN-81 and PCN-82, are similarly based on M₁₂(cdc)₁₂ cages, although the former was shown to lack permanent porosity. However, synthesis of PCN-81 via the reported route followed by thorough room temperature DMF and MeOH exchanges and activation at 100 °C afforded a highly crystalline material with a BET surface area of 4050 m²/g. Consistent with its high gravimetric surface area, PCN-81 displays an incredibly high CH₄ uptake of 305 cm³/g at 35 bar and 298 K. At 65 bar this value reaches 449 cm³/g. Given the low density of the material, its volumetric capacity at 35 bar is significantly lower at 147 cm³/cm³. As a result of the shallow nature of its adsorption isotherm (Figure 3), PCN-81 has a deliverable CH₄ capacity of 190 cm³/cm³ for a pressure swing of 65 to 5 bar, which is on par with the highest value reported for a porous material. Low temperature isotherms collected over a range of temperatures indicate methane adsorption enthalpies of −16 to −18.5 kJ/mol for all four materials.

We turned to powder neutron diffraction to gain insight into the nature of CH₄ adsorption in these materials. Although the porous coordination cages retain crystallinity upon solvent removal, it is decreased during activation to the point of precluding the use of diffraction studies to interrogate binding sites. PCN-81, however, remains highly crystalline upon degassing. Refinement of data collected on an activated sample reveals it is significantly less distorted upon evacuation (Figure 4) compared to its solvated state. At a CD₄:Cu loading of 1:1, three main adsorption sites are apparent. Although the framework is composed of three types of pores, the methane is exclusively adsorbed in the M₁₂(cdc)₁₂ cage. A primary adsorption site is the open copper(II) center with a Cu–C distance of 2.777(5) Å and an occupancy of 0.63(3). A site with similar occupancy (0.64(3)) is at the edge of a carbazole ligand with C₆H₄–C₆H₄ distances of 3.27 and 3.69 Å. This methane molecule is only present in six of the eight triangular windows of the Cu₁₂(cdc)₁₂ building unit. Together, these two adsorption sites form the basis for the lowest occupancy site (0.28(3)) in a triangular pocket between two of the metal-bound CD₄ and a carbazole-bound CD₄ with methane–methane distances of 2.79–4.13 Å (Figure 4). At double the methane loading, a number of additional sites are populated.

### Table 1. Methane Storage Properties of M₁₂(cdc)₁₂ Cages in Comparison to PCN-81, HKUST-1, and IRMOP-51

<table>
<thead>
<tr>
<th>Material</th>
<th>BET Surface Area m²/g</th>
<th>35 bar Capacity cm³/g [cm³/cm³]</th>
<th>65 bar Capacity cm³/g [cm³/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOP 51</td>
<td>480</td>
<td>48.4 [25]</td>
<td>–</td>
</tr>
<tr>
<td>Cu₁₂(cdc)₁₂</td>
<td>657</td>
<td>81.3 [69.4]</td>
<td>111.8 [95.4]</td>
</tr>
<tr>
<td>Cr₁₂(cdc)₁₂</td>
<td>1235</td>
<td>147.5 [112.1]</td>
<td>193.9 [147.8]</td>
</tr>
<tr>
<td>Mo₁₂(cdc)₁₂</td>
<td>1108</td>
<td>135.0 [111.5]</td>
<td>181.1 [150.0]</td>
</tr>
<tr>
<td>PCN-81</td>
<td>4050</td>
<td>305.3 [146.8]</td>
<td>448.7 [215.8]</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1850</td>
<td>255.24 [224.9]</td>
<td>298.5 [263.0]</td>
</tr>
</tbody>
</table>

“All values are total uptake.
are attainable for porous coordination assemblies. Although the surface areas displayed by these materials currently fall short of the record values displayed by metal–organic frameworks, the materials discussed here show the potential utility of porous coordination cages for high-pressure gas storage. Neutron diffraction experiments suggest the M12(cdc)12 cage that is also present in PCN-81 and a number of related MOFs may be the optimal pore environment for high-pressure methane storage. An ideal methane storage material may consist nearly entirely of M12(cdc)12 cages, whether it is molecular or an extended solid. Future work along these lines will involve tailoring cage stability, solubility, and gas uptake via ligand functionalization.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05780.

Detailed experimental procedures, powder X-ray and neutron diffraction data, gas adsorption isotherms and fits, and spectroscopic data (PDF)
Single-crystal data for C204H176Cu12N24O66 (CIF)
Single-crystal data for C18.89H8.00CuD7.56NO4 (CIF)
Single-crystal data for C168H84Mo12N12O68 (CIF)
Single-crystal data for C17.75H20Cu8O40 (CIF)
Single-crystal data for C17.75H20Cu8O40 (CIF)

■ AUTHOR INFORMATION

Corresponding Author
*edb@udel.edu

ORCID
Eric D. Bloch: 0000-0003-4507-6247

Author Contributions
These authors contributed equally.

Funding
We are grateful to the University of Delaware for start-up funds. This paper was prepared under cooperative agreement no. 70NANB17H302 from NIST, U.S. Department of Commerce. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron facilities used in this work. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We thank the staff of 17-BM for help with synchrotron X-ray data collection. B.A.T. recognizes the National Academies/National Research Council for his Postdoctoral Fellowship. A portion of this work was supported by the National Institutes of Health under award number P20GM104316. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Xu, C.; Bell, L. Oil 2017, 115, 18–19.