Porous Organic Molecular Materials for CO_2 Capture Applications

Jian Tian and Praveen K. Thallapally
Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

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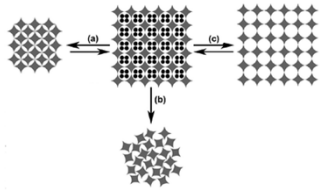
Background

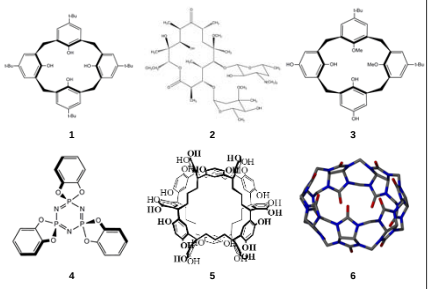
Discrete organic molecules tend to pack efficiently in the solid state to maximize intermolecular interactions, leaving as little empty space as possible, which generally leads to non-porous materials. We demonstrate recent developments in our group on porous organic molecules and their applications for CO_2 storage and separation. Organic molecular porous materials assembled from cheap, robust, and readily available organic molecules may be good candidates for CO_2 adsorbents.

Concept



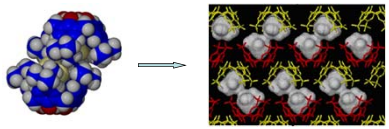
Possible processes involving removal of included solvent within an organic crystal: (a) transformation to a non-porous, denser crystal; (b) collapse of crystal structure to a non-porous or porous amorphous solid; (c) formation of a nanoporous molecular crystal without collapse of the host lattice.

Porous Organic Molecules



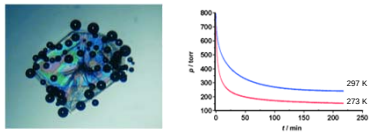
Porous molecular crystals with isolated voids (0-D)

p-tert-butylcalix[4]arene (1)



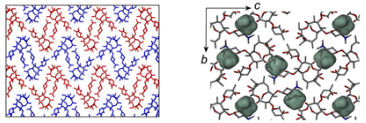
- Highly crystalline crystals obtained by sublimation of **1**
- Molecular packing: two facing **1** molecules shape an offset dimeric capsule with an enclosed cavity (V= 230 Å^3) suitable for trapping guests. Voids are isolated from each other in the host lattice and cannot merge into channels.

CO_2 uptake at 1 atm



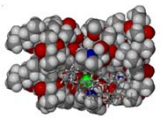
- Gas molecules diffuse into molecular capsules through non-porous host lattice
- Highly selective to CO_2 over H_2
- Fast reversible uptake and release of gases

Clarithromycin (2)

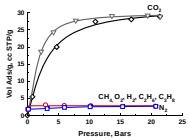


- Highly crystalline crystals obtained by sublimation of **2**
- A zigzag arrangement of **2** molecules in the host lattice with embedded lattice voids (V= 87 Å^3)

Selective CO_2 uptake over N_2, H_2, CH_4 and hydrocarbons

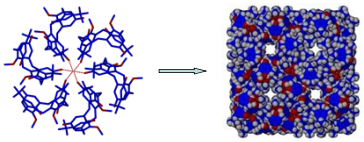


one single isolated lattice void



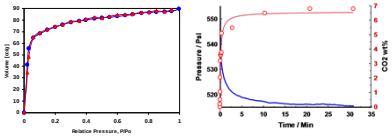
Porous molecular crystals with 1-D nanochannels

Calix[4]dihydroquinone (3)



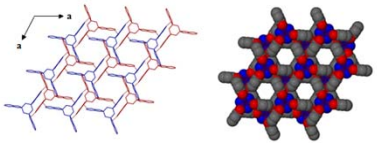
- Molecules of **3** are self-assembled in a tubular fashion *via* strong hydrogen bonds
- Polar open nanochannels with different diameters exist in the host lattice

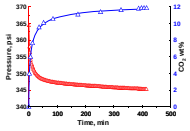
BET measurement and CO_2 uptake studies



- BET surface area (230 m^2g^{-1}) comparable to those of zeolite
- 7 wt% uptake of CO_2 at 30 bar corresponding to one CO_2 molecule per calixarene

Tris-*o*-phenylenedioxycyclotriphosphazene (4)

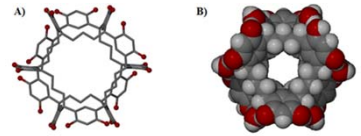


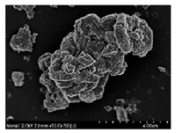


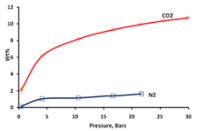
- Alternating layers of **4** molecules (depicted in blue and red) consolidated by strong hydrogen bonding pack into a hexagonal system with 1-D channels of ~4.6 Å in diameter
- 25% of the crystal volume is available to guests in the noncovalent architecture stable up to 150 ºC
- 12 wt% CO_2 uptake at 25 bar and room temperature corresponding to 1.4 mol CO_2 per mol host.

Porous amorphous molecular solids

Noria (5)

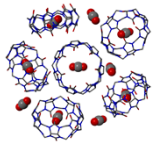


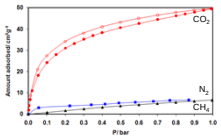




- Obtained from one-pot synthesis and precipitated as an amorphous solid from the reaction system. The molecular shape of **5** resembles a water wheel ('noria' in *greek*) with an intrinsic cavity (molecular cage) of ~160 Å^3.
- The amorphous **5** solid shows permanent porosity as evidenced by gas sorption studies
- Highly selective CO_2 uptake over N_2 and H_2. CO_2 molecules are stored in the internal cavities of host molecules, as well as disordered interstitial voids

Cucurbit[7]uril (6)





- Amorphous solids of **6** are readily available by one pot synthesis form cheap starting materials
- Molecule **6** has a "hollow-out" structure with a larger internal cavity (279 Å^3) compared to that of 'Noria'
- Highly selective CO_2 uptake with a capacity of 10 wt% at 1 bar and 297 K which is the highest value of any known porous organic molecular materials.
- CO_2 molecules are stored in molecular cages and disordered interstitial voids with a strong interaction with molecules of **6**.

Summary and future work

Porous organic molecular materials are still rare compared to those network materials, such as organic network polymers and metal-organic frameworks (MOFs). Assembly of organic host molecules into channel-forming structures is intriguing not only from the perspective of crystal engineering but also for its great potential in CO_2 capture and separation applications. We have demonstrated that certain organic molecules could be engineered into porous crystalline solids with 0-D voids or 1-D nanochannels by means of crystal engineering, which have shown highly selective CO_2 uptake. We also reveal that amorphous solids of organic cage molecules are inherently porous. Future work will be focused on developing porous organic molecular materials with very high BET surface area and CO_2 storage capacities.

Acknowledgements

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References:

1. Thallapally, P. K. *et. al., Angew. Chem., Int. Ed.*, **2006**, 39, 6506.
2. Thallapally, P. K. *et. al., Chem. Mater.*, **2007**, 19, 3355.
3. Tian, J. *et. al., J. Am. Chem. Soc.*, **2009**, 131, 13216.
4. Tian, J. *et. al., Angew. Chem., Int. Ed.*, **2009,** 48, 5492.
5. Tian, J. *et. al., Chem. Commun.* **2011**, 47, 701.
6. Tian, J. *et. al., J. Am. Chem. Soc.* **2011**, 133, 1399.
7. Tian, J. *et. al., Chem. Commun.* **2011**, 47, 7626.