

RECOGNITION AND ENCAPSULATION OF GASES WITHIN SYNTHETIC SUPRAMOLECULAR HOSTS

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INTRODUCTION

Synthetic molecular containers are receptor molecules that possess rigid interior cavities. These containers mimic the binding pockets of enzymes, enabling the capture of smaller guest-species in a molecule-within-molecule fashion.^{1a} The encapsulation of guests in the solid and liquid phases is being extensively investigated due its potential in drug delivery, catalysis, and synthesis of materials. However, in contrast work on encapsulation of guests that are gases has been limited.

The ability to fix selectively gases, and to store them, using host guest chemistry, has many potential applications, and the significance has been recently acknowledged. Carbon oxides, nitrogen oxides, and sulfur oxides, are toxic pollutants that contribute to ground-level ozone, global warming, smog, acid rain, and other environmental problems. Also related is research on the use of methane and molecular hydrogen gases as alternative fuels and future energy sources.

In nature, molecular recognition of gases is crucial for multicellular organisms. Hemoglobins **1** and **2**, and other related blood cell components such as hemocyanin **3**, are able to distinguish between the blood gases CO₂/O₂ (**Figure 1**).² Some plant enzymes also possess iron-sulfur clusters (**4**) in their active site which are able to fix N₂ selectively.³ These recognition events take place in the hydrophobic pocket of the active sites of particular enzymes. From the examples of nature some interactions can be pointed out as key for making gas binding possible.

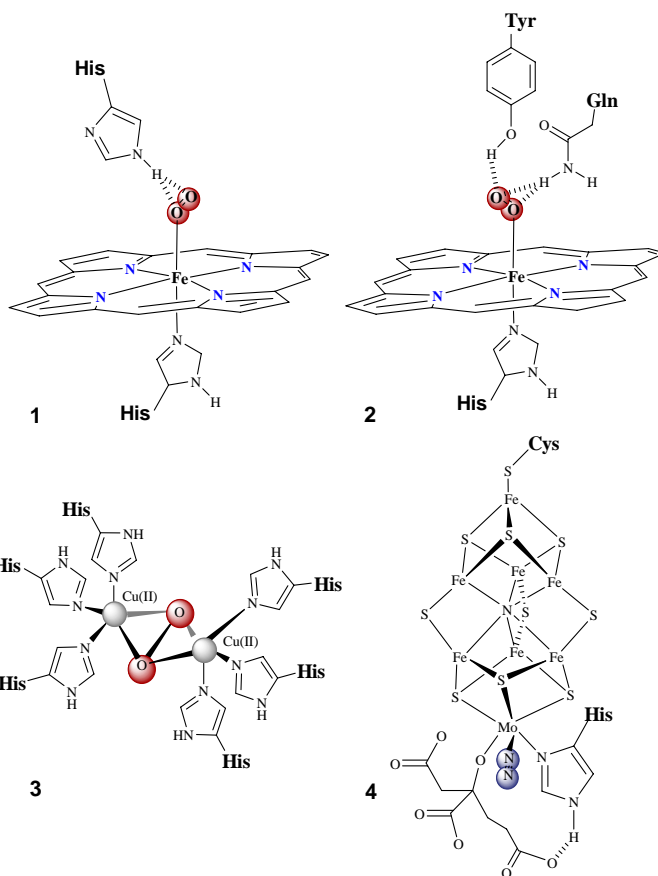


Figure 1. O₂ recognition sites in hemoglobins **1** and **2**, and hemocyanin **3**, and N₂ binding by nitrogenase **4**.^{2,3}

Metal-gas interactions, hydrogen bonding, and cavity effects are seen in many proteins that bind gases. The examples shown in **Figure 1** as well as their characteristic interactions serve as leads for the development of synthetic devices that selectively fix gases.

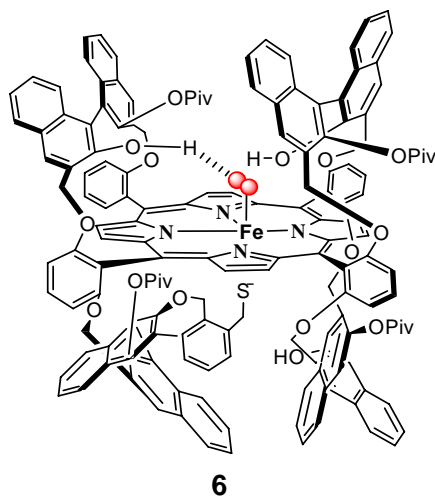
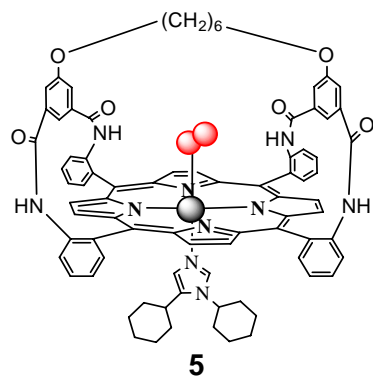


Figure 2. Gas binding in synthetic molecules.^{5,6}

Not surprisingly, early approaches to gas binding within organic molecules have structural and mechanistic similarities to the natural metalloporphyrins. Collman's "Picnic-Basket" porphyrin **5** was able to bind N_2 and O_2 reversibly.⁵ Naruta and co-workers synthesized functionalized binaphthyl porphyrin **6**, in an attempt to mimic the hydrophobic pocket of hemoglobin and to trap oxygen. They found that hydrogen-bond interactions in the complex are key factors for the positioning of the bound molecular O_2 .⁶

The modern design of organic hosts aims to create nanosized cavities capable of storing a guest within a space of 10-20 Å. Most approaches use supramolecular assemblies in order to form these nanosized cavities; however different designs have been proposed. The encapsulation of gases such as oxygen, nitrogen, noble gases, methane and others is currently being explored.^{1b} This seminar will discuss how supramolecular devices and synthetic organic structures can be used for fixation and selective storage of gases that are environmental and technologically relevant such as nitrogen oxides, carbon oxides,

and hydrogen.

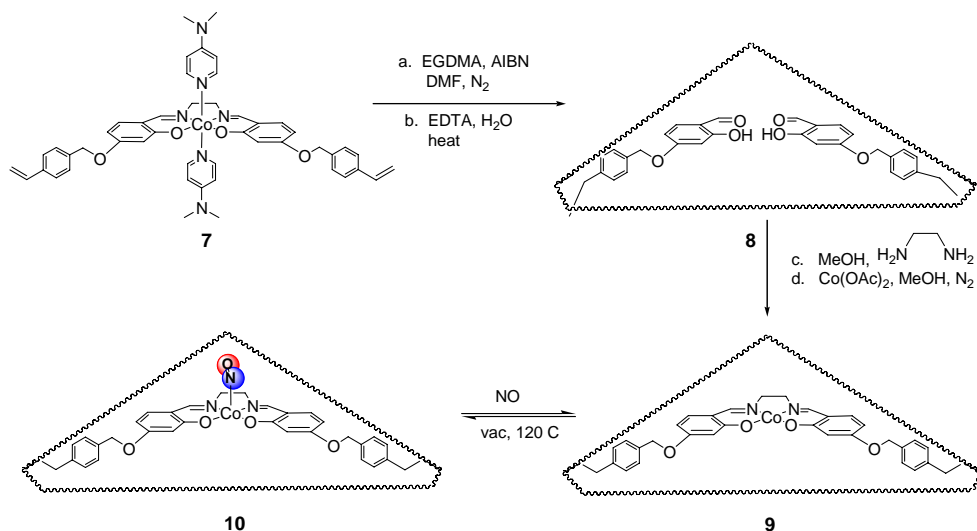
ENCAPSULATION OF COMMON ENVIRONMENTAL GASES

Advances in nitrogen oxides fixation

Nitrogen oxides (NO_x) can be both beneficial and damaging, and therefore much effort has been devoted to their storage and controlled release. Early encapsulation complexes with NO_x include inorganic clathrate hydrates and porous coordination polymers. Borovik and coworkers designed porous organic polymers such as **10** to bind to NO gas.⁷ These materials were synthesized from inert tetracoordinated metal complexes such as template **7** as shown in **Scheme 1**. The cobalt is coordinated

in a square-planar fashion to the nonpolymerizable 4-dimethylaminopyridine (DMAP) to form void spaces within the immobilized sites. The styrene-modified salen-cobalt ligand **7** was copolymerized with ethylene glycol dimethacrylate (EGDMA).

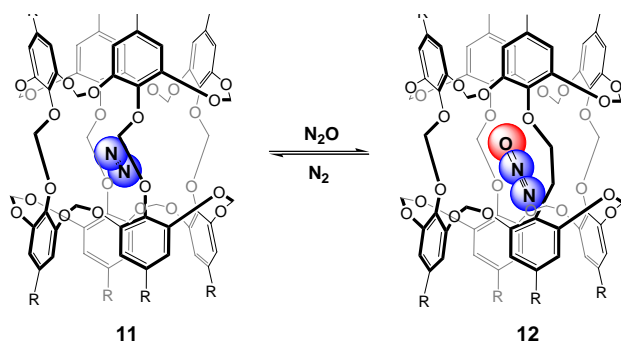
Scheme 1. Synthesis of an imprinted site for NO selective binding, EGDMA = ethylene glycol dimethacrylate, EDTA = ethylenediaminetetraacetic acid.



After the addition of azobis (isobutyronitrile) (AIBN) as the radical initiator, a polymethacrylate host containing 25 Å pores with the immobilized ligand **7** was formed. Removal of the Co (III) ions and the DMAP ligands under acidic conditions produced the immobilized uniform salicylaldehyde template **8**. Reaction of template **8** with ethylenediamine produced a tetradentate salen ligand complex that bound Co (II) ions to form the tetracoordinate Co (II) immobilized sites **9**. Exposure of the polymer-containing sites **9** to NO, resulted in absorption of the gas and produced the complex **10** in which 70% of the sites were loaded with the gas. A dramatic color change from orange to brown-green confirmed the presence of NO in the polymer. Polymer **9** showed significant affinity for NO over other gases similar in size and polarity such as O₂, CO₂ and CO. Heating at 120°C under vacuum released the gas in one hour. However, at standard conditions of pressure and temperature, the material remained in its NO-encapsulated form. After 14 days, decomposition started, and after 30 days 80% of the NO was released from the polymer. The spatial arrangement of the cavities and their affinity for binding NO was retained after the gas was released.⁸

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Scheme 2. Reversible encapsulation of N₂O in hemicarcerands



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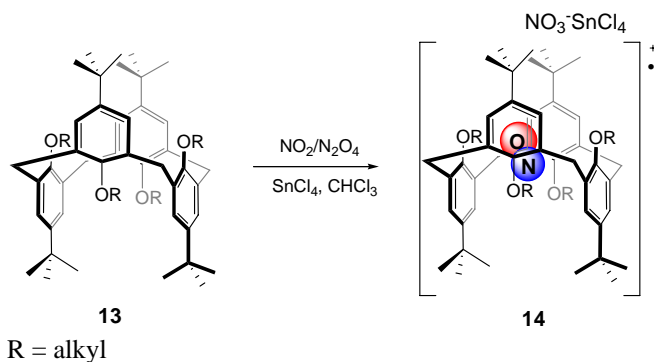
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cavity volume of $\sim 110 \text{ \AA}$. These cavities absorbed N_2 from the atmosphere in the solid state to form the hemicarcerand **11**. Displacement of N_2 from the cavity by bubbling N_2O through **11** in chloroform until dryness resulted in the formation of the hemicarcerand **12** in a 1:1 stoichiometry (**Scheme 2**).⁹ However after exposure to air, the N_2O gas was released after 1 hour. These experiments proved that N_2O can be trapped in molecular organic containers and modifications of the structure could lead to improved selectivity and storage.

Since nitrogen oxides are neutral and relatively non-polar, an alternative approach to bind these gases involves transformation into more reactive forms prior to binding. This reactive species may have more binding interactions and higher affinity for the host. Rathore and coworkers found that

Scheme 3. Formation encapsulated nitrosonium complexes with calix[4]arene



calix[4]arene cation-radicals, bind NO strongly, forming a cationic calixarene-nitrosonium species in which the NO gas had been oxidized to the cation radical NO^+ .¹⁰ Later Rudkevich complexed $\text{NO}_2/\text{N}_2\text{O}_4$ using the π -electron-rich calix[4]arene **13** and isolated the stable complex **14** by adding Lewis acids SnCl_4 and $\text{BF}_3 \cdot \text{Et}_2\text{O}$.¹⁰ The resulting nitrosonium complexes showed a broad charge-transfer band at $\lambda = 560 \text{ nm}$ and

($\epsilon = 8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). In the UV spectrum, neither the calixarene nor the NO_2 absorb in this region. Another approach for efficient storage of NO_2 makes use of calixarene nanotubes. Different research groups found that gases including NO_x can be absorbed inside single-walled carbon nanotubes.¹¹ Rudkevich and coworkers are working on the development of a nanotube based on polycalixarenes connected by diethylene glycol linkers. These calixarene tubes have a 6 \AA cavity with a maximum capacity of three nitrosonium-calixarene complexes.

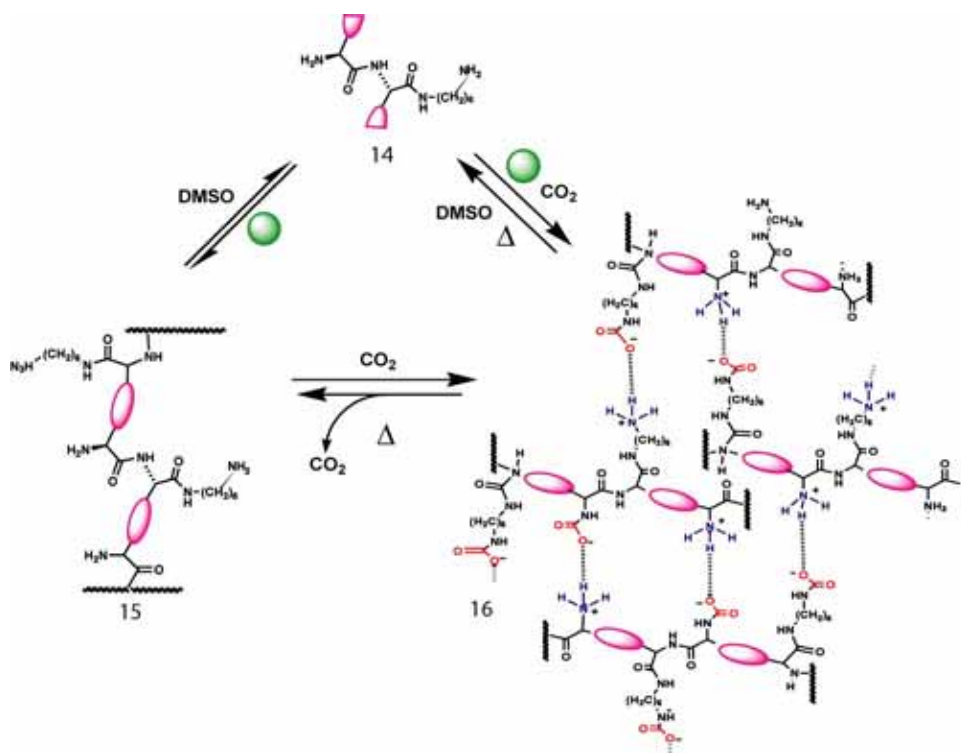
Supramolecular assemblies that bind CO_2

The reaction of CO_2 with amines to produce carbamates has been known for centuries. Polymers that display multiple primary amines are widely used in industry to remove CO_2 from exhaust streams. Absorption of CO_2 into immobilized amines has also been employed for gas sensing.

The supramolecular polymer shown in **Scheme 4** designed by Rudkevich and coworkers takes advantage of dynamic and reversible processes.¹² This new supramolecular approach uses the reaction of amines with CO_2 , and the strong hydrogen bonding of calixarenes to produce a responsive

polycarbamate network. Calixarene monomers **15** with amino groups on their periphery were used as building blocks for this network through their ability to self-assemble in the presence of an apolar solvent to form the dimer capsule **16**. The amino groups reacted with CO₂ gas to form carbamate salts yielding the three-dimensional supramolecular gel **16** that quickly precipitated. Formation of these carbamate salt bridges was confirmed by the appearance of two singlets at $\delta = 163$ and 164 ppm in the ¹³C NMR spectrum.

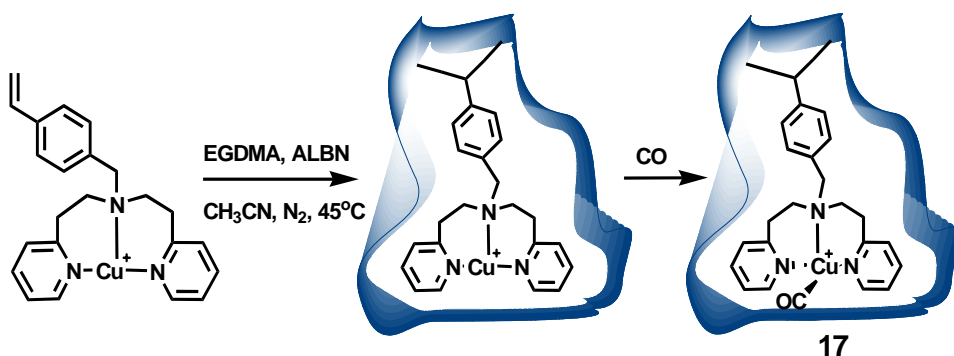
Scheme 4. Formation of polycarbamate networks using CO₂ a crosslinker



While carbamates are highly unstable and release CO₂ easily, this network was stable at ambient temperature. This unique material assembles and dissociates reversibly upon changes of the temperature and solvent polarity.¹³ This supramolecular polymer released CO₂ thermally without disrupting the hydrogen bonding of the calixarene capsules.

Also the hydrogen bonds could be broken without destroying the crosslinking carbamate bridges that hold CO₂ (**Scheme 4**). Heating the polymer solution for 1 hour at 100° C released the gas as evidenced by the disappearance of the characteristic carbamate peaks in the ¹³C NMR spectrum.

Borovik and coworkers explored the selective binding of CO in the copper-containing cavity **17** within an imprinted polymer using the same synthetic approach previously shown in **Scheme 1**.¹⁴ Introduction



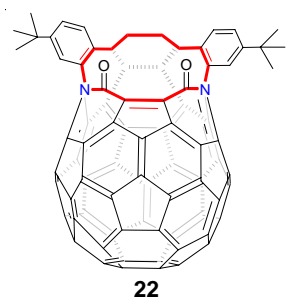
Scheme 5. CO binding inside porous polymer networks, EGDMA = ethylene glycol dimethacrylate, EDTA = ethylenediaminetetraacetic acid.

of CO into the porous solid, lead to the appearance of a new band at $\nu = 2085$ cm⁻¹ in the FTIR spectrum. Up to 95% of the gas was bound to this polymer network. This process was

reversible, and the CO was liberated by flushing the polymer with N₂ for 15 minutes without any alteration of the shape of the cavity for subsequent binding.

Additional studies by Yaghi and coworkers led to the development of a porous organic framework having the capacity to store up to 140 wt% of CO₂.¹⁵ The gas uptake by this material exceeds that of any other known material.

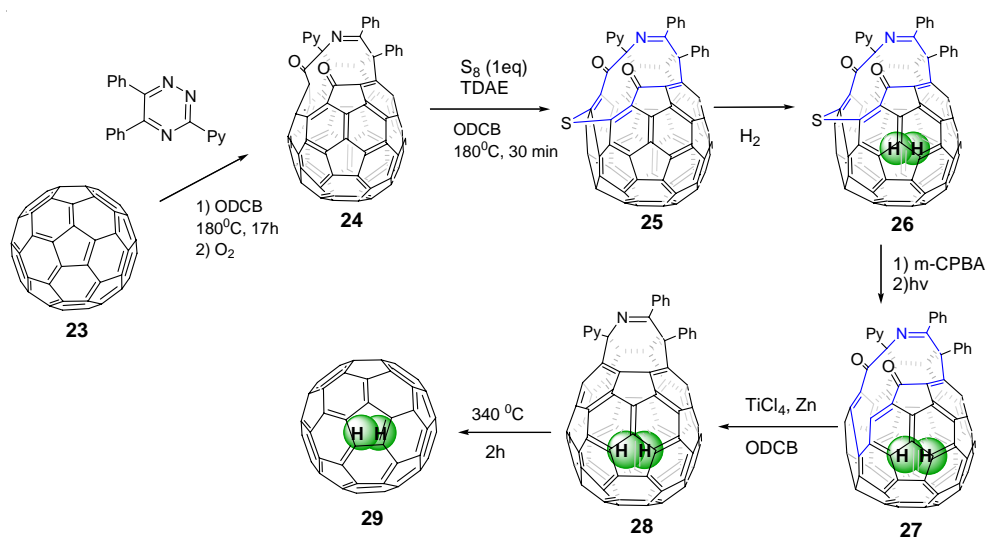
FIXATION AND STORAGE OF HYDROGEN



Efforts are being focused on storing H₂ in solids and solid matrices. By these means, it is possible to exceed the density of liquid H₂. Numerous metal hydrides including MgH₂, NaAlH₄, LiNH₂, AlH₃, and others have been proposed as vehicles to store H₂.¹⁹ However, most of these metal hydrides are formed irreversibly under extreme conditions such as low pressure and high temperature. Because of their low density, high surface area, and chemical stability, carbon-based materials have recently received attention as potential H₂ storage devices.

Attempts to incorporate gases inside fullerenes have been reported. After exposure of C₆₀ to the extreme conditions of 600°C and 3000 atm, Cross and coworkers obtained fullerenes that contained He molecules within their cavity, albeit in only 0.1% yield.²⁰ Rubin and coworkers found that the gas-uptake properties were enhanced by using a partially-cleaved fullerene. Bridged bislactam fullerene **22** having a 14-membered-ring opening trapped H₂ in 5% yield under the conditions of 300°C and 475 atm.²¹ Two years later, Komatsu and coworkers improved this approach by opening the fullerene **24** and including a sulfur atom in the opening as shown in

Scheme 6.²² Exposure of **25** to 800 atm of H₂ and 200°C in an autoclave, afforded the H₂ adduct **26** and the yield of H₂ uptake was 100%.²³ Thermal closure of the fullerene at 340°C occurred without loss of



Scheme 6. Encapsulation of H₂ inside a fullerene. ODCB = ortho-dichloro benzene, TDAE = tetrakis-dimethylaminoethylene

H₂ to give fullerene **29** containing the H₂. Although this method is not economically viable, it is an excellent example of a synthetic approach for the encapsulation of hydrogen for storage applications.

Some of the most promising materials for hydrogen storage are the metallo-organic frameworks (MOF) developed by Yaghi and coworkers.²⁵ This group has synthesized about 500 different MOFs with different porous properties and metals. New techniques still need to be developed to improve the gas uptake properties of the materials. An increase in the percent of hydrogen storage from the current maximum of 3% to 10% is needed in order for commercial applications.

CONCLUSION

It took about 300 years after the first discovery of gases to explore their binding properties and recognition. The major drawback of reversible encapsulation complexes with gases is their low thermodynamic stability. Various container molecules are being developed as potential candidates for selective binding of gases. Despite the tiny dimensions and simple atomic composition, each gas is different in its physical and chemical properties and requires an individual approach. Most of these designs rely on hydrogen bonding, metal-gas interactions, and cavity effects to bind gases. Receptors for the recognition of methane, sulfoxides, molecular oxygen, nitrogen and other important gases are also being studied and many other structures have been proposed for their selective binding.^{1b} The techniques for molecular recognition can be used for efficient gas sensing, and gas delivery in medicine. Additional efforts are aimed at transforming the trapped gases into synthetically useful reagents.

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