

# Porous organic cages: modular, soluble and molecular pores

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**Keywords:** porous organic cages, molecular crystals, pollutants capture

Porous molecular cages are an alternative to porous extended frameworks such as zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and microporous polymer networks. One distinguishing property of molecular materials is their solubility: unlike extended frameworks, molecular crystals can be processed in solution into a variety of formats, or even as “porous liquid”. They can also show unique physical properties, such as perfect shape selectivity for rare gases or organic isomers and protonic conductivity. However, molecular crystals also raise challenges in terms of stability and the purposeful design of solid-state function <sup>[1]</sup>. This is because the energy landscape for molecular crystals is often not dominated by a single intermolecular interaction, unlike bonded crystalline frameworks such as MOFs and covalent organic frameworks. This talk will discuss strategies for the design and synthesis of new functional organic crystals by using a mixture of intuitive design and computation. The talk will exemplify this with recent examples of post-synthetic modification of porous organic cages, in which their stability or function can be tuned <sup>[2]</sup>. Some most recent progress of using cages in real-life applications, such as for pollutants capture, will also be introduced <sup>[3]</sup>.

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# De novo design of nanopores reconstituted in bilayer lipid membrane

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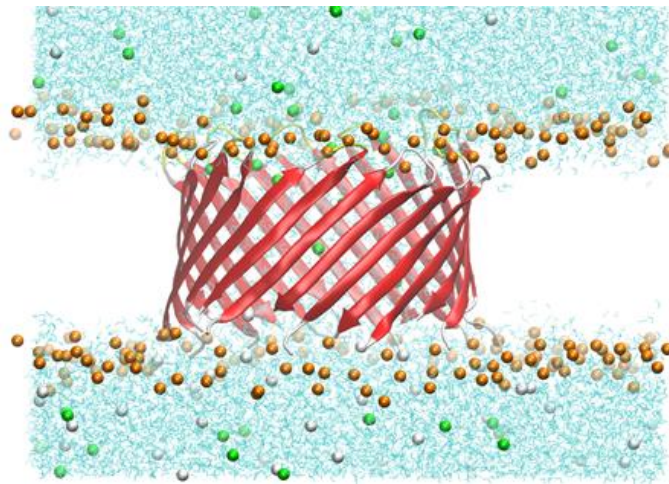
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**Keywords:** Nanopores, Lipid bilayers, Peptides, *De novo* design

Nanopore sensing/sequencing are emerging technologies for rapid and low-cost single-molecule detection. Pore-forming proteins are used as the sensor component and their size and geometry compatibility for the target molecule are essential for detectability. A bottom-up approach, *de novo* design of the amino acids sequence, is a potent tool for constructing target-specific nanopores. We have recently reported *de novo* peptide nanopores and they have several advantages such as low-cost synthesis, chemical stability, and the ability to readily reconstitute in a lipid membrane.

The pore-forming peptide, named SV28, that has a  $\beta$ -hairpin structure and assembles to form a stable nanopore in a bilayer lipid membrane. The peptide forms multidispersely sized nanopore structures ranging from 1.7 to 6.3 nm in diameter and can detect DNAs. To form a monodispersely sized nanopore, we redesigned the SV28 by introducing a glycine-kink mutation. The resulting redesigned peptide forms a monodisperse pore with a diameter of 1.7 nm leading to detection of a single polypeptide chain.[1] In this seminar, I will give the detailed results on a construction of *de novo* designed nanopore with a lipid bilayer system based on a microfabrication technology.



**Figure 1.** MD simulation of the *de novo* designed peptides that form a nanopore structure in lipid bilayer.

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# Biological pores found in membrane proteins

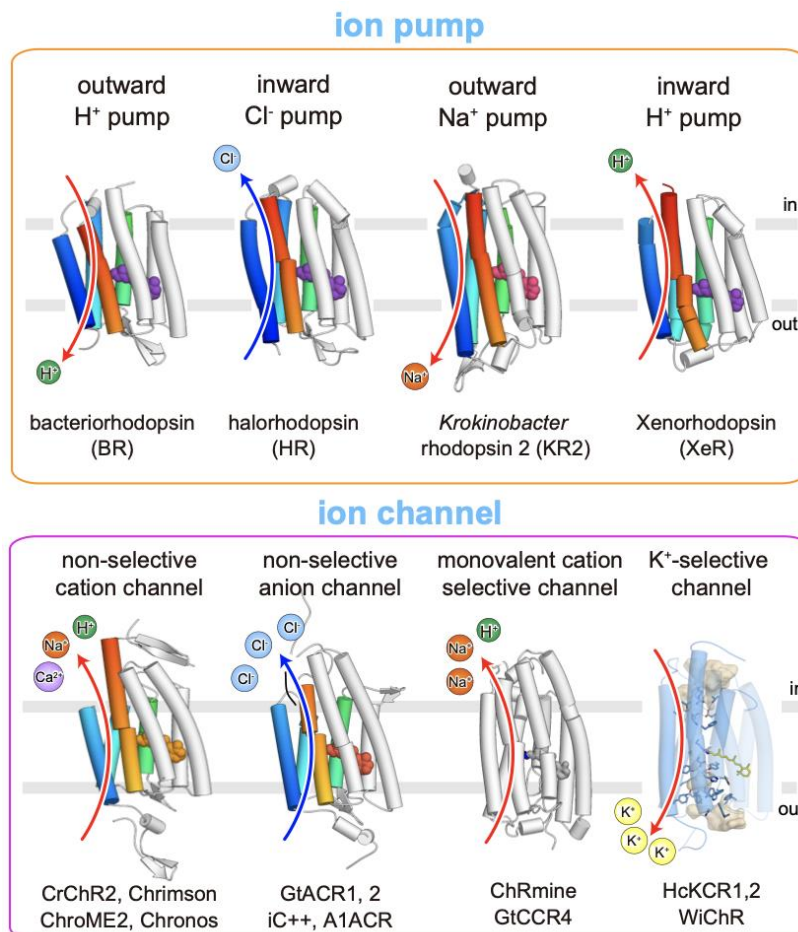
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**Keywords:** ion pumps, ion channels, rhodopsins

The cell is the basic unit of life, and the plasma membrane defines its boundaries and maintains the differences between the intracellular and the extracellular environment. The plasma membrane is impermeable to water-soluble molecules, including ions and most biological molecules, so these molecules enter or leave cells mainly via membrane transporters (pumps) or channels. Pumps and channels specifically recognize their substrates and regulate the timing and direction of the substrate transport by dynamically changing the shape and property of “pores”. In this talk, first I will introduce the basic concept and classic examples of membrane pumps and channels and later focus on the specific family of membrane proteins called rhodopsins. Rhodopsins are a large family of photoreceptive membrane proteins found in archaea, bacteria, eukaryotes, and viruses. They are seven-helix transmembrane proteins that are covalently bound to a retinal chromophore, and their diverse molecular functions include ion pumps and ion channels. I will talk about the structural foundation of these pump-type and channel-type rhodopsins and discuss how biological pores with different shapes and properties can exert diverse molecular functions.



**Figure 1.** Biological pores with different molecular functions in rhodopsin family proteins

# Shape-shifting porous crystals

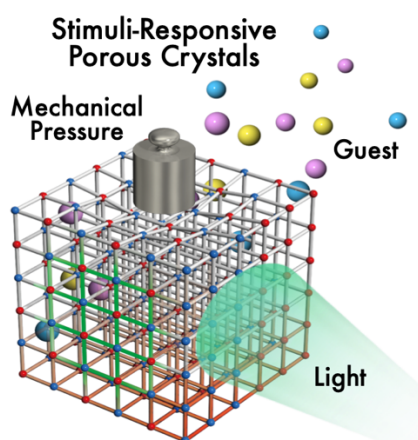
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**Keywords:** Porous materials, Crystals, Stimuli-response

Porous materials with nanometer-sized pores have long been used in our daily lives as functional materials that efficiently separate and remove small molecules such as gaseous molecules. As a new family of porous materials, metal–organic frameworks (MOFs) are synthesized by combining metal ions and organic ligands, and the size, shape, and chemical properties of their pores can be designed and tuned by taking advantage of the combination diversity of the constituents. Compared to conventional porous materials, MOFs are unique in that they can flexibly change their structures in response to the environment, despite their crystalline nature<sup>[1–4]</sup>. We are studying the synthesis and unprecedented function of such unique porous materials in which "hardness" and "softness" operate in concert. In this presentation, I would like to introduce MOF-based porous crystals that respond to external stimuli (**Figure 1**) with shape-shifting properties. Especially, I will present crystals that respond to guest molecules<sup>[5–7]</sup>, light<sup>[8–12]</sup>, and mechanical forces<sup>[13]</sup>.



**Figure 1.** Stimuli-responsive porous crystals.

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## Hydrogen Separation Membrane Technology for Net-Zero Carbon Dioxide Economy

### 水素分離膜技術で CO<sub>2</sub> ネットゼロ経済を

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#### **Opportunity for membrane technology in hydrogen economy**

A hydrogen economy has the potential to solve many problems caused by the direct use of fossil fuels *via* clean energy and transportation<sup>1</sup>. More than 90% of about 70 million tons worldwide demand for hydrogen is currently generated *via* steam reforming and the water-gas-shift (WGS) reaction of fossil fuel sources<sup>2</sup>. This produces an almost 50:50 mixture of hydrogen and carbon dioxide saturated with steam<sup>3,4</sup> from which hydrogen is subsequently purified by selectively adsorbing the CO<sub>2</sub> using aminated solvents. Unlike amine adsorption processes, membrane separation requires no changes in phase behavior and is in principle the most energetically cost-effective route for primary purification of H<sub>2</sub> and CO<sub>2</sub><sup>4,5</sup>.

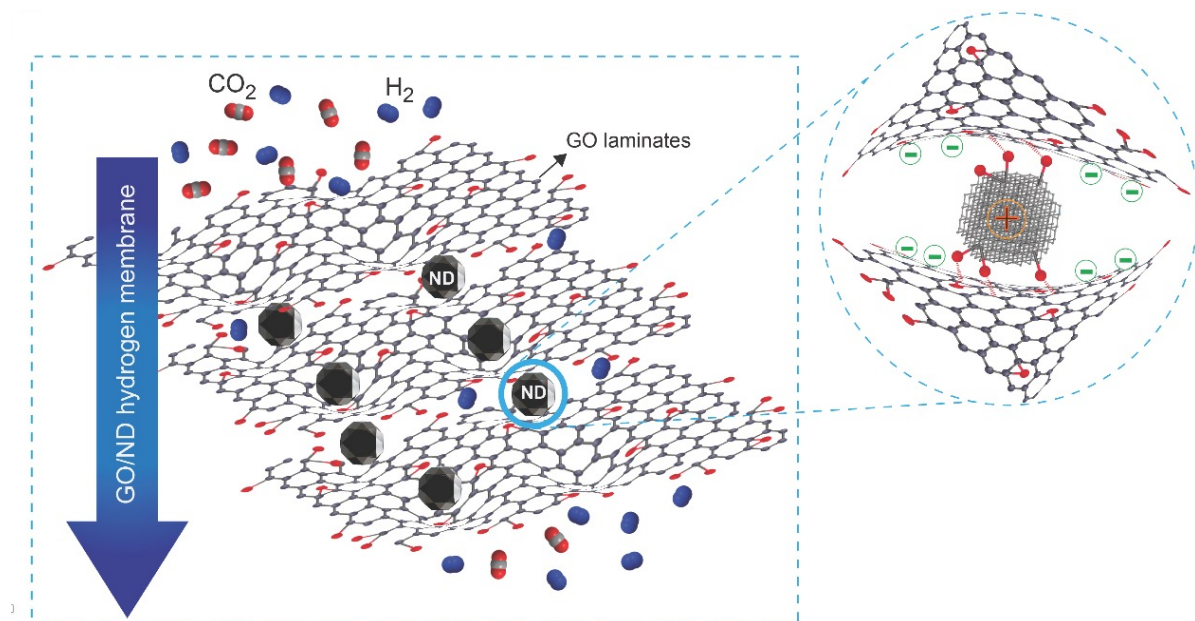
#### **Challenge for membrane technology in Hydrogen Economy.**

However polymeric membranes do not have adequate separation capability of CO<sub>2</sub> from H<sub>2</sub> due to the high level of solubility of CO<sub>2</sub> in organic materials<sup>6,7</sup>. Costly metallic membranes<sup>8</sup> and ceramic membranes<sup>9</sup>, operating on the principles of selective adsorption or molecular sieving have extraordinary selectivity for hydrogen against carbon dioxide; ~1000 and ~300 respectively and sufficient rates of permeance.

In the early 2010's, ultrathin graphene oxide (GO) was proposed as a step-change material for the separation of hydrogen and carbon dioxide *via* membrane separation processes<sup>10,11</sup>. Selectivities of up to 1000 and triple-digit (~000 GPU) permeances were reported. GO itself is cheaply sourced through controlled oxidation and exfoliation of graphite. These capabilities are ideal for highly efficient H<sub>2</sub> separation, to reach purity levels required for immediate use in fuel cells. However, swelling and disruption of the basal stacking of the carbon sheets in humid conditions is the Achilles heel of GO membranes, presenting an un-resolved obstacle to the practical implementation of this exciting technology<sup>12,13</sup>.

### Electrostatic stabilization of charged 2D materials.

Recently we reported how we specifically target the stabilization of GO membranes towards adverse humid conditions, whilst attempting to maintain its overall high performance towards H<sub>2</sub>/CO<sub>2</sub> separation. To do so, we employed the concept of pillared clays<sup>14</sup>, used in catalysis, where nearly compatible compounds are intercalated within layered silicates to strengthen their secondary structure (Figure). Taking the compatibility of carbonaceous materials into account, we surmised that robust nanodiamonds (NDs) with unique sp<sup>3</sup>/sp<sup>2</sup> core-shell structure and positive surface charge are capable of restraining the random restacking and aggregation of GO nanosheets.<sup>15</sup>



### Conclusion.

We have demonstrated the benefit of the intentional addition of positively charged carbonaceous nanoparticles, here exemplified through NDs that serve to stabilize negatively charged GO membrane sheets against humidity enhanced destabilization of the membrane's separation performance, whilst enhancing its intrinsic separation performance tremendously. Despite constraining our study to a single size scale of nanoparticle of different charge, and single size distribution of GO sheets, a significant data set was generated. However, a larger set of unanswered questions remain, such as relative size effects, the chemical nature of the particle, and more broadly, whether such charge stabilization can also be applicable to other novel materials such as MXenes (also a negatively charged 2D material). Answering such questions in the future will serve to generate high stability, 2D material composites, not only for membrane separation but also for other application areas where the field of 2D materials is gaining purchase.

## Conclusion.

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# Looking Beyond Crystallinity in

## Metal-Organic Frameworks

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**Keywords:** MOFs, Glass, Liquid

Metal-organic framework (MOF) materials are often ordered, (crystalline) solids. Order—or uniformity—is frequently held to be advantageous, or even pivotal, to our ability to engineer useful properties in a rational way. Here, we will look at the difference between amorphous, and glassy solids, and cover the mechanisms underpinning the shear-induced collapse of MOFs. Using the crystalline MIL-100 / amorphous Fe-BTC pairing as an example, we will then address the poorly understood structure of the latter. Specifically, we show an experimental-computational approach to generate a ‘structure’ for Fe-BTC, and show it may outperform MIL-100 in terms of gas separation.<sup>1</sup>

We will demonstrate the several families of MOFs known to form stable liquids at high temperature,<sup>2,3</sup> with quenching leading to the formation of glasses which retain the three-dimensional inorganic-organic bonding of the crystalline phase. The uses of such materials will be evaluated, before we finally show how the formation of composites containing both MOF, and glass phases may find use in applications.<sup>4,5</sup>

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# Building pores with the power of DNA nanotechnology

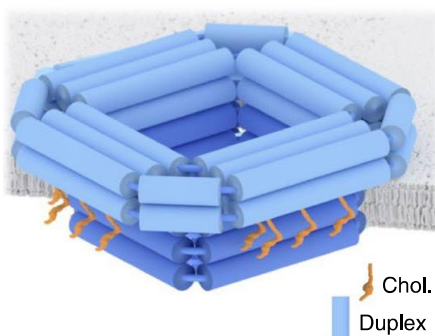
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**Keywords:** pores, nanopores, DNA, nanotechnology, membranes, bilayers, sensing, single-molecule analysis, biophysics

Porous structures are relevant in many areas of science, technology, and society. Porous 3D materials are used in chemical catalysis and storage, while thin, porous films are essential for purification of water, foodstuffs, and medicine. Furthermore, thin membranes with single pores have delivered portable DNA sequencing and biosensing of single molecules. Conventionally, porous structures are fabricated with organic, polymeric, or solid-state-materials. By comparison, DNA nanotechnology offers another, powerful route to create highly defined and simple-to-build nanostructures.

In my talk, I will present nanopores composed of DNA. The pores are rationally designed to self-assemble from a few to hundreds of DNA strands using base pair-specific interactions. The pores mimic natural membrane proteins which span biological lipid bilayer membranes<sup>(1)</sup> and have pioneered single-molecule sensing<sup>(2)</sup> and portable DNA sequencing<sup>(3)</sup>. The DNA pores go beyond the scope of biology in terms of size and shape<sup>(4)</sup> or controlled nanomechanical movement<sup>(5)</sup>. The design and assembly of the pores follows newly established protocols<sup>(6)</sup> and yields unique nanostructures whose assembly<sup>(7)</sup>, structural dynamics<sup>(8)</sup>, membrane transport<sup>(9)</sup>, and membrane interactions<sup>(10)</sup> have been characterised with an array of techniques. The DNA pores can be custom-engineering for portable sensing of diagnostic proteins using commercial handheld-devices<sup>(4)</sup>. The work on DNA nanopores can inspire the wider field of bioengineering<sup>(11)</sup> and materials science, and -given its interdisciplinary nature- leads to unexpected changes in graduate teaching<sup>(12)</sup> and research management<sup>(13)</sup>.



**Figure 1.** A single nanopore composed of assembled DNA duplexes (cylinders, blue) inserted into a bilayer membrane (grey). The square pore has an inner lumen of 10 nm by 10 nm. Cholesterol tags (orange) anchor the hydrophilic structure into the hydrophobic bilayer membrane<sup>(4)</sup>.

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