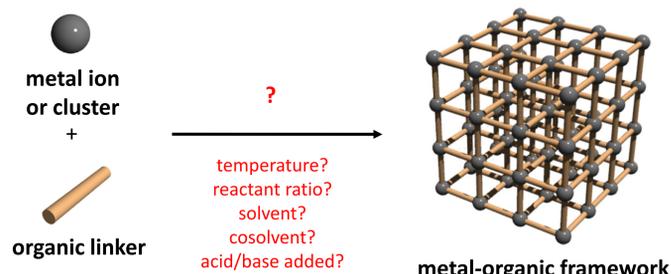


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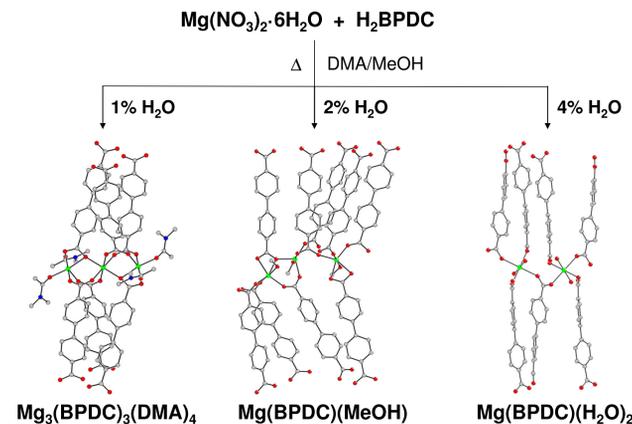
Introduction

Owing to their high internal surface areas and chemically tunable pore surfaces, metal-organic frameworks have a great potential to serve as next-generation CO₂ capture materials. However, the reaction conditions employed during synthesis can have a considerable impact on the purity and quality of the materials, and a high-throughput methodology is essential if optimized synthetic routes to new materials are to be discovered. Furthermore, despite the excellent selectivity of some metal-organic frameworks for CO₂ over N₂, their performance in the presence of other components of the flue gas (such as H₂O, NO_x, and SO_x) is currently not well understood. Our new initiative under ARPA-E will focus on the synthesis and full characterization of new metal-organic frameworks that will exhibit high long-term performance under realistic conditions for CO₂ capture. In addition, computational support will provide guidance for the synthetic experiments by identifying new target materials, as well as allowing detailed evaluation of the performance of each material. Cost analysis will also be performed on the most promising materials in order to identify the best materials for real-world applications.



Above: The formation of a metal-organic framework requires precise tuning of the reaction conditions.

Right: The reaction of Mg²⁺ ions with H₂BPDC (BPDC²⁻ = 4,4'-biphenyldicarboxylate) forms three different network structures depending on the H₂O content of the reaction solvent.



Accelerated Discovery of Metal-Organic Frameworks

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs



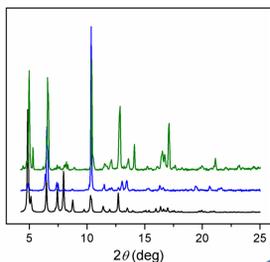
Automated solid and liquid dosing

Customized 96-vial plates

Powder X-ray diffraction

The synthesis of new metal-organic frameworks will be performed using a Symyx Core Module robot that allows automated powder and liquid dispensing into vials for small-scale reactions (1 mL capacity). The robot is installed within a glove box under a dinitrogen atmosphere, allowing precise control of the H₂O content of each reaction. Once the dispensing routine is completed, the individual reaction mixtures can be heated and stirred on the robot deck, and the products can be isolated and transferred to a glass plate for high-throughput X-ray diffraction.

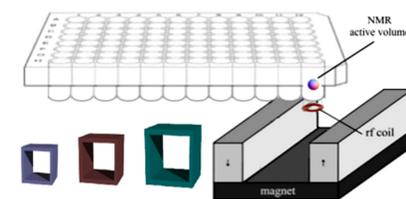
Powder diffraction patterns will be assessed based on their peak intensities, and the presence of low-angle diffraction peaks. Computational analysis of the powder patterns will be performed to determine the samples of highest quality for further scale-up and characterization. The powder patterns will also be compared against a database of known structure types and typical impurities to allow rapid identification of new phases.



Pore Size Determination via NMR

Rapid screening process of new porous materials

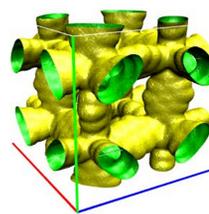
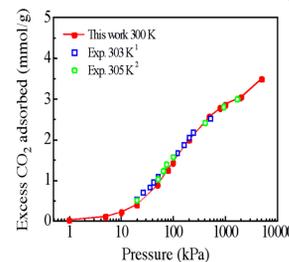
Although powder X-ray diffraction can allow the identification of materials with large unit cells (based on the presence of low-angle peaks), it does not afford information regarding the porosity of the samples. We will be developing NMR methods to allow the rapid screening of samples to identify new porous phases.



A dedicated instrument based on a single-sided NMR will be assembled from commercially available parts, and will allow the samples to be surveyed while in solution. The porosity can be probed by observing the relaxation times and diffusion rates of the solvent molecules, since the solvent molecules enclosed within the pores of the metal-organic framework will exhibit different dynamics to the bulk solvent. The rapid identification of porous phases will allow the number of samples to be studied for adsorptive properties to be reduced, allowing our efforts to be directed towards studying the most promising candidates for next-generation CO₂ capture materials.

Computational Support

Simulations, data analysis and lifecycle analysis

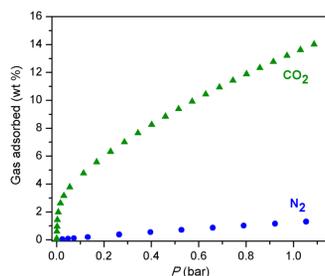
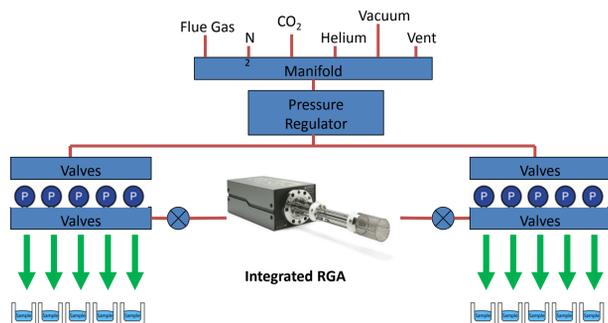


The computational methods will be developed upon a centralized database containing all data relating to each sample that is synthesized using the high-throughput synthesis system. Cheminformatics will be used to provide synthesis guidance, specifying target structures that should possess properties that are desirable for a CO₂ capture material. Moreover, gas adsorption simulations will be performed on both known and proposed metal-organic frameworks (left), such that the performance of any candidate material can be estimated.

Lifecycle analysis will also be performed on the most promising candidates, such that the economic and environmental impact of large-scale synthesis of the specific metal-organic framework, and the operation of the CO₂ capture system, can be estimated.

High-Throughput Gas Adsorption

Rapid screening of CO₂ capture performance



Following identification of crystalline and porous phases by powder X-ray diffraction and NMR screening, samples will be subjected to high-throughput gas adsorption experiments. The first-generation instrument, which will be an existing instrument retrofitted for the ARPA-E program, will enable the rapid collection of CO₂ and N₂ single-component isotherms (above right) for 28 samples in a single experiment. The large volume of data resulting from these experiments will be analyzed by automated methods, and materials exhibiting the most promising selectivity and adsorption capacities for CO₂ will be studied in further detail.

Design and assembly of the second-generation instrument is currently underway (above left), and will feature an integrated RGA for the analysis of mixed-component gas adsorption. The use of a mixed gas that accurately simulates a flue gas is a crucial aspect in the assessment of the performance of each material under the operating conditions encountered in CO₂ capture applications in the real world.

Optimization of sorbent use in power plants

The materials exhibiting the highest CO₂ capture performance in the adsorption experiments will be subjected to simulations in which the performance of the material within a real-world CO₂ capture system will be evaluated. The isotherms collected on the high-throughput sorption apparatus will enable the simulation of a typical four-step cycle (right). Metrics (energy penalties, product purity, product recovery) for such an assessment will be developed, and this will enable the optimal conditions for the use of each material to be established.

