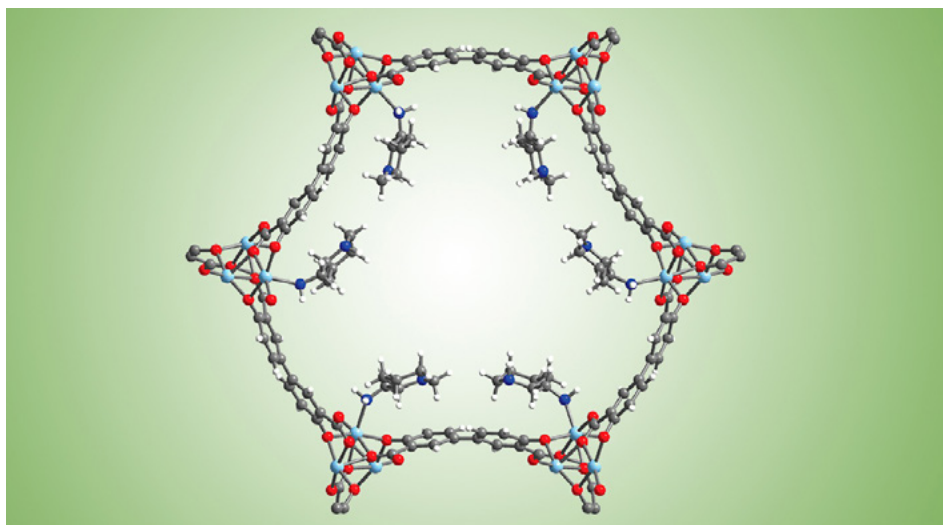
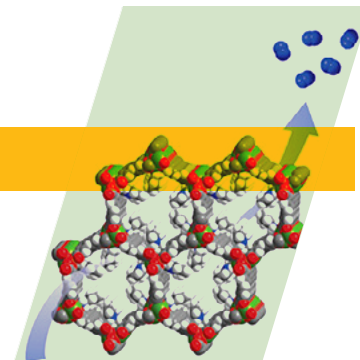


# Water Improves Material's Ability to Capture CO<sub>2</sub>



Single-crystal x-ray diffraction enables the precise determination of the positions of the atoms in metal-organic frameworks (MOFs), highly porous materials capable of soaking up vast quantities of a specific gas molecule, such as CO<sub>2</sub>. This structure represents 2-ampd-Zn<sub>2</sub>(dobpdc), a MOF with the same structure as 2-ampd-Mg<sub>2</sub>(dobpdc), the subject of this study. Light blue, blue, red, gray, and white spheres represent Zn, N, O, C, and H atoms, respectively.

## The power of natural gas

About 65% of anthropogenic greenhouse gas emissions comes from the combustion of fossil fuels in power plants. So far, efforts to capture CO<sub>2</sub> from power-plant flue gases and sequester it underground have mainly focused on coal-fired power plants. However, in the United States, natural gas has surpassed coal in terms of the amount CO<sub>2</sub> released, despite the fact that natural gas emits approximately half as much CO<sub>2</sub> per unit of electricity. Therefore, new materials are urgently needed to address this situation.

## Not all combustion is alike

Compared to coal-fired power plants, natural gas combined cycle (NGCC) plants produce flue gases with low CO<sub>2</sub> concentrations. This reduces the carbon footprint,

but increases the technical difficulty of CO<sub>2</sub> capture. Also, materials capable of adsorbing such low concentrations of CO<sub>2</sub> often require high temperatures to release it for sequestration, an important part of the cycle that offsets initial low-carbon benefits. NGCC emissions also have a higher concentration of O<sub>2</sub>, which has a corrosive effect on adsorbent materials, and both NGCC and coal flue streams are saturated in water, which can both degrade materials and reduce efficiency. Thus, an effective NGCC CO<sub>2</sub>-capture material must selectively bind low-concentration CO<sub>2</sub> under humid conditions while being thermally and oxidatively stable.

## Earlier discovery and optimization

At NGCC plants, CO<sub>2</sub> capture is currently done primarily using solutions of

## Scientific Achievement

With the help of the Advanced Light Source (ALS), researchers from UC Berkeley and ExxonMobil fine-tuned a material to capture CO<sub>2</sub> in the presence of water.

## Significance and Impact

The parties have applied for a patent on the material, which was developed for use on the relatively humid flue gases emitted by certain natural gas power plants, a cleaner-burning alternative to coal.

ammonia derivatives (amines). However, releasing the CO<sub>2</sub> from these liquids is energy intensive and expensive. In previous work done at the Center for Gas Separations (a DOE Energy Frontier Research Center), UC Berkeley researchers discovered a metal-organic framework (MOF) that releases CO<sub>2</sub> with much less energy. The work attracted the attention of ExxonMobil, which was interested in optimizing the new material to make it even more effective. In this work, the Berkeley group, with support from ExxonMobil, worked on fine-tuning the MOF by functionalizing it with cyclic diamine compounds.

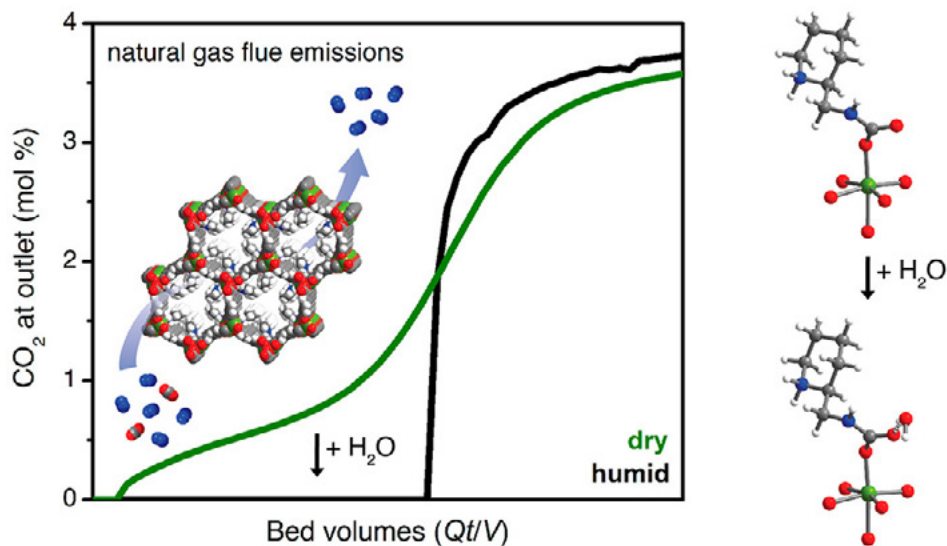
## Characterization by diffraction

At ALS Beamline 12.2.1, the researchers used single-crystal x-ray diffraction to precisely determine the

structure of 2-ampd-Zn<sub>2</sub>(dobpdc), a crystal with the same structure as the functionalized MOF. The information made clear how the diamines—the organic molecules that actually react with CO<sub>2</sub>—are organized. The researchers were thus able to compare the structure with predictions from computational work and recognize how water might affect CO<sub>2</sub> adsorption. The beamline also offers the ability to dose samples with gas, an experiment the researchers are currently working on to see how CO<sub>2</sub> actually interacts with the MOF binding sites and to further correlate structure with adsorption behavior.

### A surprising watery advantage

Adsorption measurements confirmed that 2-ampd-Mg<sub>2</sub>(dobpdc) is capable of adsorbing over 90% of the CO<sub>2</sub> in humid natural gas emissions. The researchers also discovered that humidity actually improves the material's CO<sub>2</sub> adsorption. Based on spectroscopic studies and theoretical calculations, they concluded that certain structures that form upon CO<sub>2</sub> binding are affected by the presence of water, making the CO<sub>2</sub> bind more strongly while preserving the ability to cycle CO<sub>2</sub> in and out with small temperature swings. UC Berkeley and ExxonMobil have applied for a patent on this particular MOF variant, in light of its exceptional and unique ability to capture CO<sub>2</sub> from NGCC flue gases.



Left: Plot of the CO<sub>2</sub> content in simulated flue gases after passage through a column of the optimized MOF. Under humid conditions (black curve), CO<sub>2</sub> leakage is effectively zero until a saturation point is reached. Under dry conditions (green), some CO<sub>2</sub> leaks through, even at very early stages. The inset depicts CO<sub>2</sub> and N<sub>2</sub> entering the material, but only the N<sub>2</sub> exiting. Top right: The MOF's Mg cluster (red/green) was functionalized with cyclic diamine (gray/blue/white). Bottom right: In humid conditions, H<sub>2</sub>O forms hydrogen bonds with the cyclic diamine.

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