Finding new chemistry to capture double the carbon

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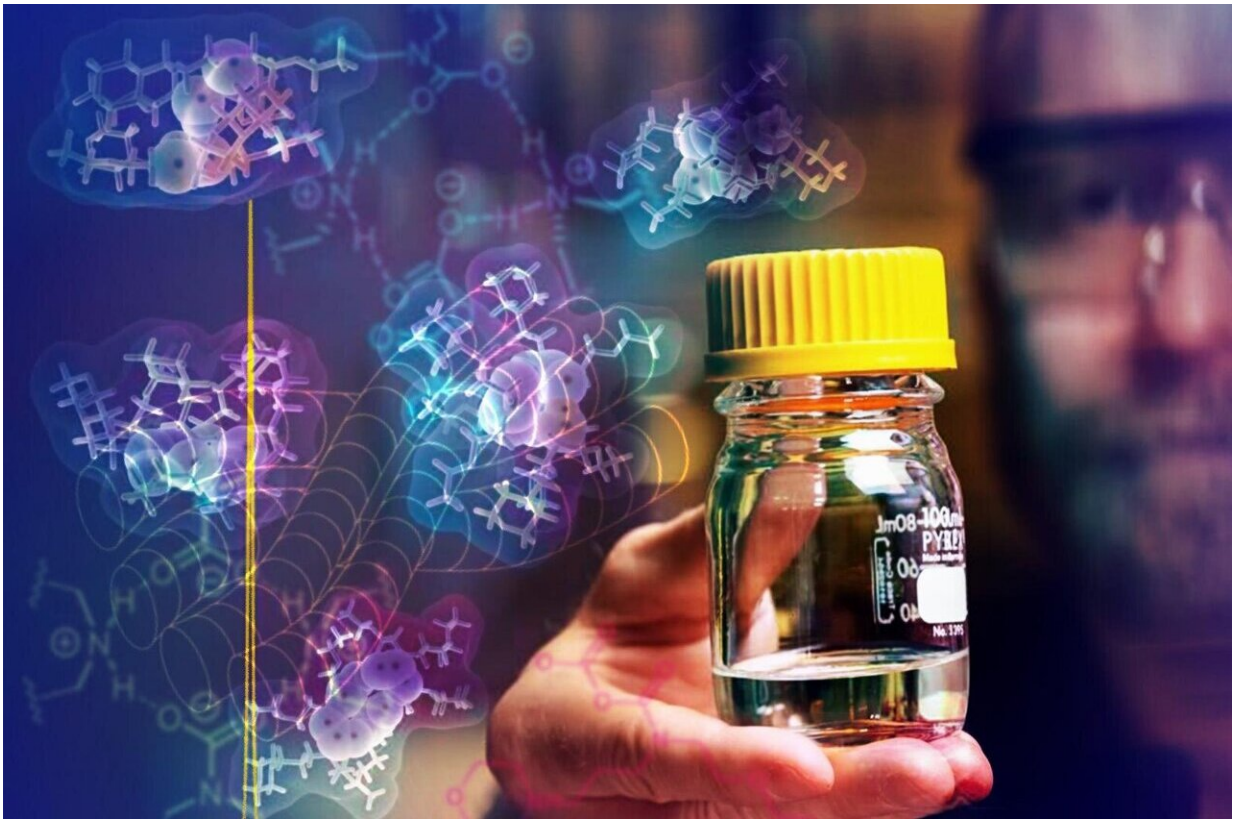


An established carbon capture solvent can form clusters that could significantly increase the amount of carbon dioxide stored. Credit: Photo: Andrea Starr; Composite image: Cortland Johnson | Pacific Northwest National Laboratory

Finding ways to capture, store, and use carbon dioxide (CO_2) remains an

urgent global problem. As temperatures continue to rise, keeping CO^2 from entering the atmosphere can help limit warming where carbon-based fuels are still needed.

Significant progress has been made in creating affordable, practical carbon capture technologies. Carbon-capturing liquids, referred to as solvents when they are present in abundance, can efficiently grab CO_2 molecules from coal-fired power plants, paper mills, and other emission sources. However, these all work through the same fundamental chemistry, or so researchers have assumed.

In new work published in *Nature Chemistry*, scientists were surprised to find that a familiar solvent is even more promising than originally anticipated. New details about the solvent's underlying structure suggest that the liquid could hold twice as much CO_2 as previously thought. The newly revealed structure could also hold the key to creating a suite of carbon-based materials that could help keep even more CO_2 out of the atmosphere.

The Pacific Northwest National Laboratory (PNNL) team developed the solvent several years ago and has studied it in a variety of scenarios. The team has worked to dial down the costs of using the solvent and turn up its efficiency. Last year, they revealed the least costly carbon capture system to date. It was during this research that the team noticed something odd.

"We were trying to do a different type of high-pressure gas separation," said David Heldebrant, a PNNL chemist and co-corresponding author. "We saw that the solution got significantly thicker and a new peak appeared in our spectra, indicating something new had formed. It was totally unexpected and we knew we had to get to the bottom of it."

Heldebrant reached out to his collaborators at the University Claude

Bernard Lyon 1 and the University of Texas at El Paso to help untangle the molecular changes behind the results.

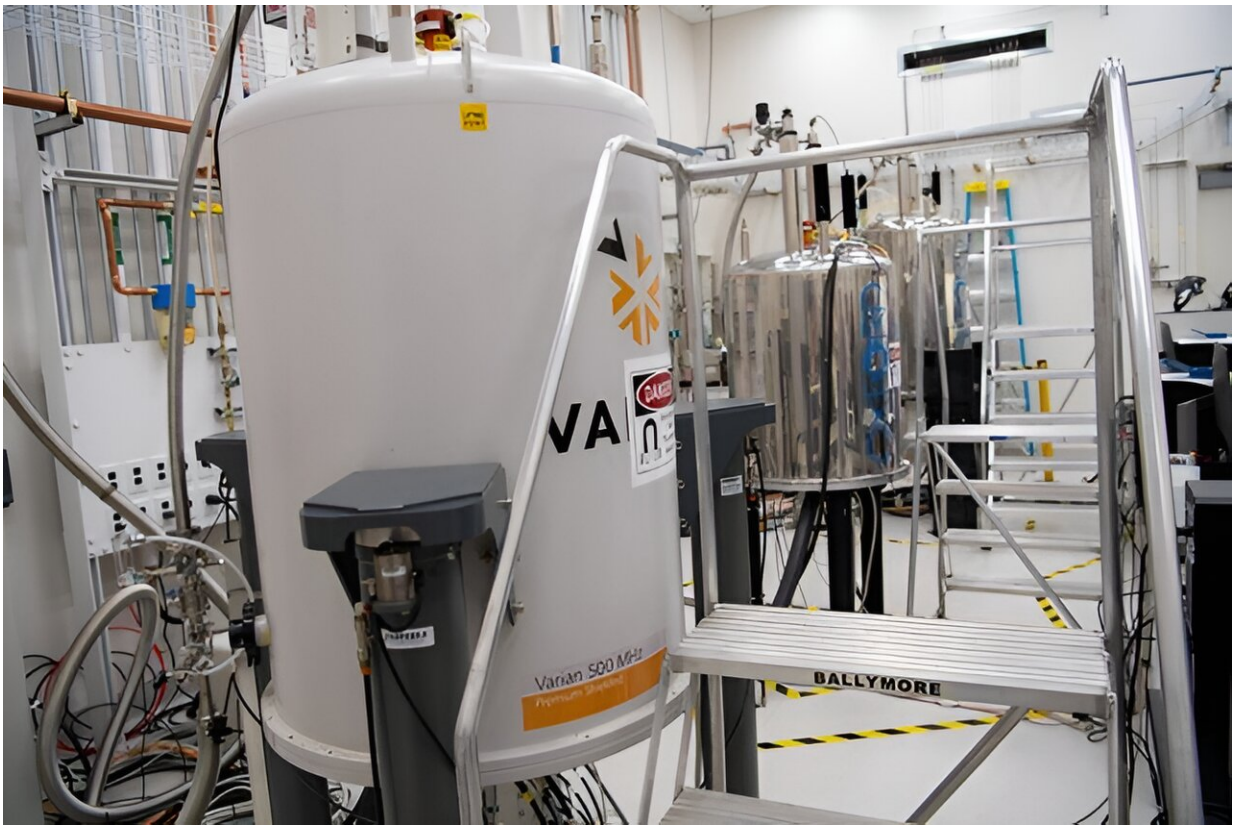
"This work is a truly interdisciplinary and collaborative effort," said Jose Leobardo Bañuelos, a professor at the University of Texas at El Paso. "The questions we needed to ask required more than just one type of expertise. We looked at the overall structure of the solvent when exposed to CO_2 and saw substantially more order than we expected."

The molecules, it seemed, were clustering when they ought to be paired. But what did the new, tidily ordered structures mean?

Causing change through clusters

When the team took a fresh look at the solvent-CO_2 system using analytical chemistry tools, they detected self-assembled clusters of solvent molecules. At first, the researchers tried to fit the data to a model using only two molecules of solvent. Despite their starting expectation, the data just didn't fit.

When the researchers used a model with four solvent molecules, the results fell into place. A four-component cluster was actually the form of the solvent the team had been seeing. The flexible structure can undergo a series of shifts to accommodate incoming CO_2 molecules. The CO_2 eventually reaches the core of the cluster, home to an active site pocket that may be similar to those that exist inside enzymes. In fact, the overall cluster structure and interactions seem to resemble proteins.



Measurements of the solvent and carbon dioxide showed the presence of something unexpected. Credit: Andrea Starr | Pacific Northwest National Laboratory

The active site binding pocket is at the center of the newly observed chemistry. Typically, carbon capture systems work with a single CO_2 molecule which binds and may react to form something different. Having everything constrained to reactions involving one CO_2 limits the next steps of carbon conversion. The cluster enables something different.

The unexpected peak the team originally found corresponds to the formation of a new species that includes two different molecules of CO_2. The clusters incorporate CO_2 stepwise, first capturing and activating one molecule followed by the second. The data show a

cooperative effect—having one molecule of CO_2 bound changes how the second molecule binds.

"We're really excited about the new solvent design possibilities this opens up," said Heldebrant. "If we can find ways to intentionally build in cooperativity that enhances CO_2 binding, we could change how carbon capture systems operate."

Finding new reactivity

Once both CO_2 molecules are inside the cluster they can react with one another, creating different carbon-based molecules that could expand potential uses of captured CO_2.

"What we're doing here is changing a major variable in the process," said Heldebrant. "We've historically captured each CO_2 on its own. Binding two CO_2 together could help us effectively double the storage capacity of our capture systems."

The newly connected molecules have very different properties from CO_2. This changes the chemistry required to separate the captured carbon from the solvent. These CO_2-based molecules are larger and represent a first step towards creating CO_2-rich polymers.

One persistent issue with captured carbon is what to do with it. While long-term storage of CO_2 is an option, it presents logistical challenges and can add cost to an already expensive capture process. Finding ways to convert captured CO_2 into economically valuable products could help offset capture costs and provide a step toward a closed carbon cycle.

By joining two CO_2 molecules together during the initial capture step, this work presents a new way to approach carbon conversion and utilization. Instead of starting with CO_2, researchers could have different

options to create new chemicals. This opens doors to different types of chemistry previously considered unrealistic for CO_2 conversion. These potential next steps are only possible by focusing on the fundamental science behind carbon capture.

"There's so much urgency in deploying carbon capture systems," said Julien Leclaire, a professor at the University Claude Bernard Lyon 1 and co-corresponding author of the paper. "We don't always explore the molecular-scale details of these processes due to their complexity. But sometimes we can find insights that connect molecular and large-scale behavior."

In addition to Heldebrant, PNNL researchers include Katarzyna Grubel, Eric Walter, Ying Chen, Difan Zhang, Manh Thuong Nguyen, Debmalya Ray, Sarah Allec, Deepika Malhotra, Wontae Joo, and Jaelynne King. In addition to Leclaire, University Claude Bernard Lyon 1 researchers include Jean Septavaux and Marc Hennenbelle.

More information: Julien Leclaire et al, Tetrameric self-assembling of water-lean solvents enables carbamate anhydride-based CO2 capture chemistry, *Nature Chemistry* (2024). DOI: 10.1038/s41557-024-01495-z

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