

# THE ADVANCED PHOTON SOURCE

## HINTS FROM HEMOGLOBIN LEAD TO BETTER CARBON MONOXIDE SEPARATION

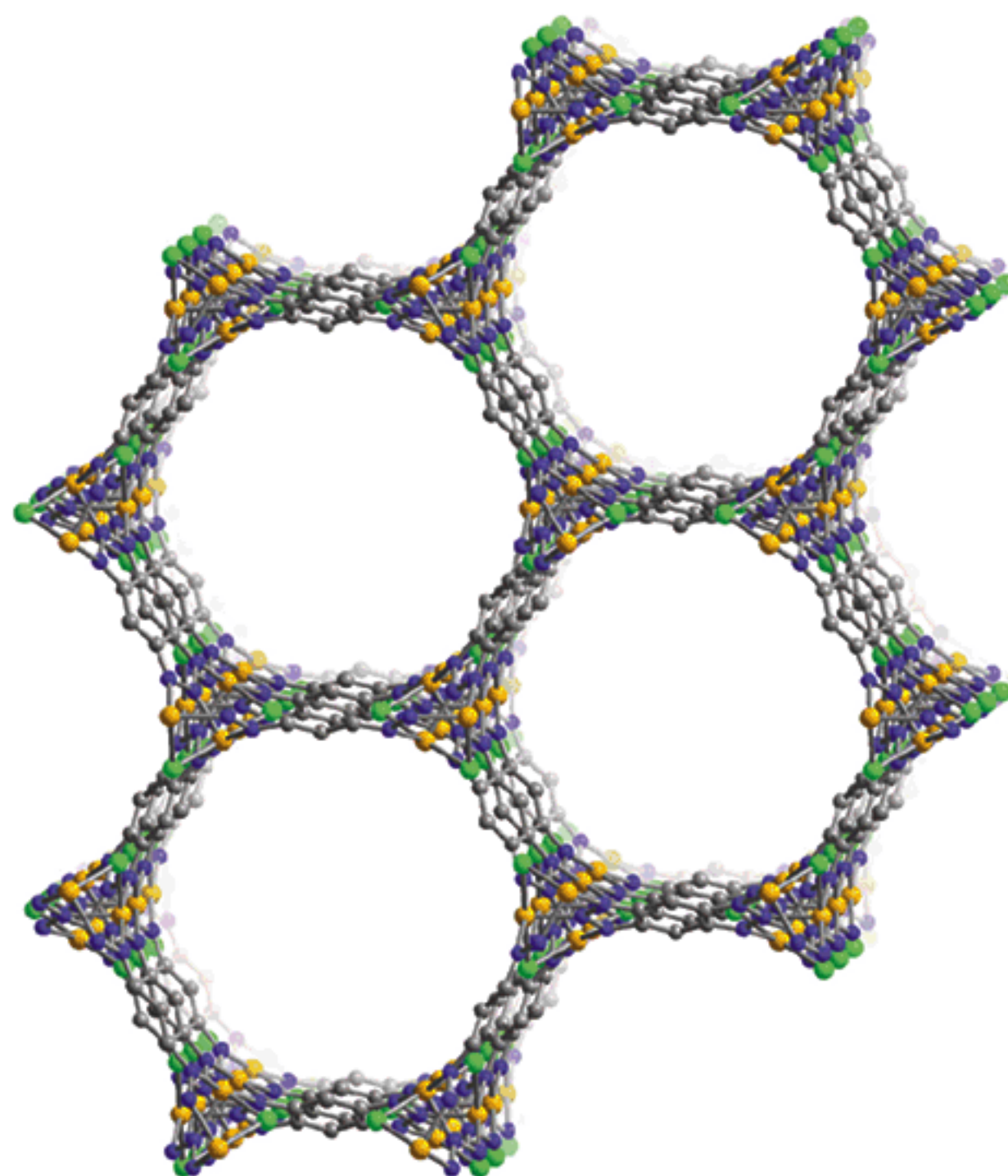
Carbon monoxide (CO) is an insidious poison because it loves the iron in our blood; it pushes oxygen out of iron-based hemoglobin, leading to painful asphyxiation. This affinity for iron comes in handy in a newly created material that can absorb carbon monoxide far better than other materials, with potential applications in industrial processes like syngas production, where CO is a key player, and reactions where CO is an unwanted contaminant. A number of characterization and measurement techniques contributed to this groundbreaking research, including critical experiments at the APS. The results of these studies were published online ahead of print in the journal *Nature*.

The new material is a metal-organic framework (MOF) that incorporates chains of iron atoms tuned to attract CO and exclude other chemical compounds. When CO binds to an iron atom in the MOF, it changes the environment of neighboring iron atoms to make them even more attractive to CO, creating a chain reaction. The research revealed a cooperative adsorption effect where binding at one site activates the neighboring sites, which means a change from very little adsorption to essentially saturating the material with CO.

The CO binding flips the spin state of iron, hence the researchers' terminology for the material: "spin-transition MOFs."

Two years ago, co-author Jeffrey Long accidentally stumbled across the first of this type of cooperative adsorbent when he created a MOF that adsorbed carbon dioxide far better than other materials.

The iron centers in the MOF form a helical chain structure down the vertices of the hexagonal pores. Binding of carbon



The porous MOF structure contains hexagonal channels lined with a high concentration of iron sites. These iron sites are able to bind carbon monoxide strongly and in a cooperative fashion. Gray, blue, green, and orange spheres represent carbon, nitrogen, chlorine and iron, respectively.

monoxide to a very small fraction of these iron sites causes the spin state of all the iron centers in the MOF to change, making CO binding at iron centers elsewhere in the pore more favorable. Gray, blue, green, and orange spheres represent carbon, nitrogen, chlorine and iron, respectively. The carbon dioxide capture material was a first-of-its-kind material for cooperative adsorption. Now, this research shows that cooperative MOF adsorbents can be built by design to target other key industrially relevant molecules for separation. It is a fundamental new mechanism where, by adjusting the ligands bound to the iron,

you might be able to get unsaturated hydrocarbons like acetylene, ethylene and propylene to bind also. High-resolution synchrotron x-ray powder diffraction data for two different MOFs, and versions of those MOFs dosed with CO, were collected at X-ray Science Division beamlines 11-BM-B and 17-BM-B at the APS. These studies revealed important information about the structures of the new materials, and about the method by which the MOFs absorbed CO.

*(Adapted from the original UC Berkeley press release by Robert Sanders.)*

**See:** Douglas A. Reed<sup>1</sup>, Benjamin K. Keitz<sup>1,2</sup>, Julia Oktawiec<sup>1</sup>, Jarad A. Mason<sup>1</sup>, Tomom Runčevski<sup>1,3</sup>, Dianne J. Xiao<sup>1</sup>, Lucy E. Darago<sup>1</sup>, Valentina Crocella<sup>4</sup>, Silvia Bordiga<sup>4</sup>, and Jeffrey R. Long<sup>1,3\*</sup>, "A spin transition mechanism for cooperative adsorption in metal-organic frameworks," *Nature*, published online 11 September 2017.

DOI: 10.1038/nature23674

**Author affiliations:** <sup>1</sup>University of California, Berkeley, <sup>2</sup>University of Texas at Austin, <sup>3</sup>Lawrence Berkeley National Laboratory, <sup>4</sup>University of Turin

**Correspondence:** \*jrlong@berkeley.edu

This research was supported through the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE) Office of Science-Basic Energy Sciences under award DE-SC0001015. D.A.R., J.O., J.A.M., D.J.X. and L.E.D. thank the National Science Foundation for graduate fellowship support. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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