

istic behavior of atoms and molecules.

This result also carries another surprising message. While it has been known for many years that electrons are paired in the superconducting state, the findings imply that they also form pairs (although localized and immobile) in the insulating state, unlike in any other

known material. That sets the researchers on a more focused search for what gets these immobilized pairs moving when the transition to superconductivity occurs.

Superconducting FETs might also have direct practical applications. Semiconductor-based FETs are power-

hungry, particularly when packed very densely to increase their speed. In contrast, superconductors operate with no resistance or energy loss. Here, the atomically thin layer construction is in fact advantageous—it enhances the ability to control superconductivity using an external electric field.

### Energy Focus

#### Conjugated microporous polymer networks chemically tuned for CO<sub>2</sub> adsorption

The capture and storage of CO<sub>2</sub> produced by the combustion of fossil fuels is a technical challenge with great impact to the environment. CO<sub>2</sub> uptake in metal-organic frameworks (MOFs) has been investigated, although under conditions—high pressure and low water vapor content—more relevant to pre-combustion CO<sub>2</sub> capture from syngas (a mixture of H<sub>2</sub>, CO<sub>2</sub>, and CO) or natural gas reserves. In a recent investigation of nanoporous organic polymers for CO<sub>2</sub> capture at ambient pressure, A.I. Cooper and co-researchers at the University of Liverpool postulated that rather than materials with very high surface areas, the introduction of tailored binding functionalities, and thereby increasing a material's heat of adsorption, would increase the amount of CO<sub>2</sub> adsorbed.

Cooper and co-researchers synthesized two conjugated microporous polymer (CMP) networks that incorporate primary amine and carboxylic groups, respectively. They found that the CO<sub>2</sub> uptakes and isosteric heats of adsorption of these CMPs are consistent with previously published computations showing that incorporation of carboxylic acid groups in MOFs, rather than amine groups, leads to the highest isosteric heat of adsorption, suggesting to the researchers a common design principle that spans the two materials classes.

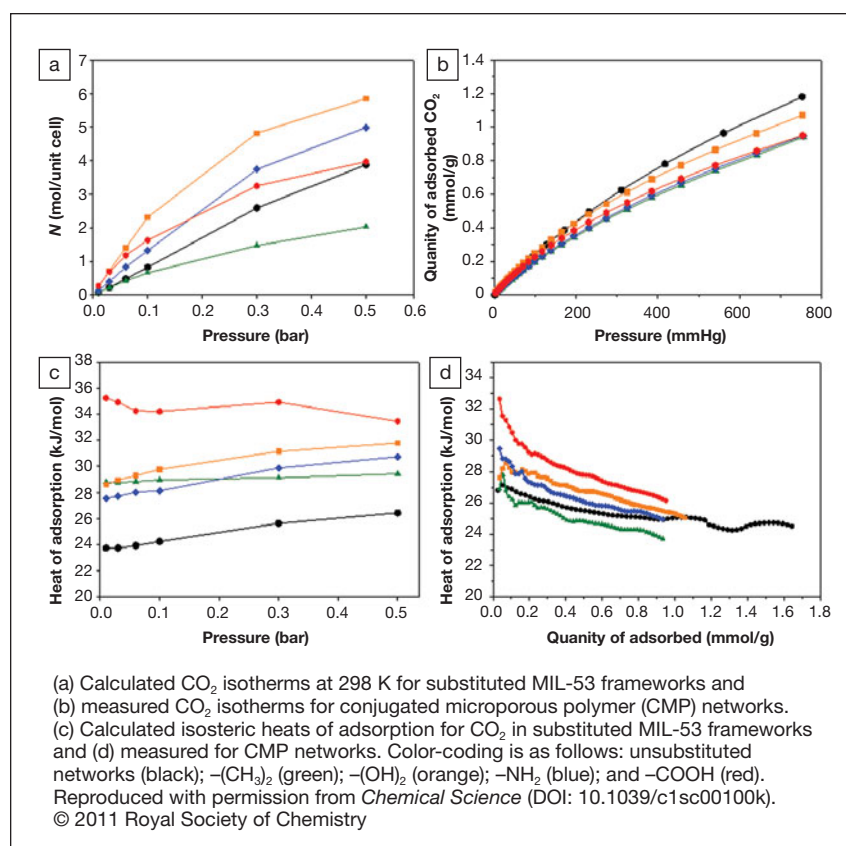
As reported in the May 6th online edition of *Chemical Science* (DOI: 10.1039/c1sc00100k), Cooper and co-researchers synthesized, isolated, and analyzed by Fourier transform infra-

red spectroscopy carboxylic acid and amine-functionalized CMP networks designated CMP-1-COOH and CMP-1-NH<sub>2</sub>, respectively. Insensitive to water, the CMP networks were also shown with thermal gravimetric analysis to be stable up to about 300°C. Scanning electron microscopy showed that the CMP network morphologies are similar to previous CMP networks. N<sub>2</sub> adsorption/desorption isotherms, measured at 77 K for CMP-1-COOH and CMP-1-NH<sub>2</sub> as well as for previously synthesized CMPs (see figure) are mainly Type I, that is, they show high gas uptake at low pressures (CMP-1-CH<sub>3</sub> and CMP-1-OH<sub>2</sub> are Type IV). From these isotherms the

researchers calculated surface areas and micropore volumes.

The researchers noted that CO<sub>2</sub> uptake, measured at low pressure for the entire series of CMP networks, does not correlate solely with surface area or pore volume. However, the researchers found that the isosteric heats of adsorption depended on the functional group, increasing as: COOH > (OH)<sub>2</sub> > NH<sub>2</sub> > H > (CH<sub>3</sub>)<sub>2</sub>, with the heat of adsorption for CMP-1-COOH being substantially higher than all other CMP networks in this series, higher than activated carbon, but lower than for some MOF networks.

The researchers said that their data corroborates the fundamental compu-





tational conclusion that carboxylic acids are good targets for CO<sub>2</sub> capture. Although the CO<sub>2</sub> binding might be too strong for CO<sub>2</sub> capture applications

because of the energy penalty due to recycling the material, the researchers said that “the ability to fine tune CO<sub>2</sub> affinity in this way [with the selection of

functional groups] is of potential value for both CO<sub>2</sub> capture and storage as well as gas separation.”

**Steven Trohalaki**

### Bio Focus

#### Liquid STEM used for particle uptake studies in living cells

The uptake of nanoparticles into cells has conventionally been studied with transmission electron microscopy of thin sections. However, the preparation into thin sections leads to a loss of nanoparticles, and also prevents the analysis of the whole three-dimensional cellular volume. Furthermore, conventional electron microscopy is not capable of studying live cells. D.B. Peckys and N. de Jonge from Vanderbilt University Medical Center have now improved upon a liquid scanning transmission electron microscopy (STEM) method that allows for quantitative assessment of nanoparticle uptake in living cells. The researchers used a microfluidic chamber composed of microchips where fibroblast cells were imaged with minimal radiation damage to reveal the distribution of gold-nanoparticles (Au-NP) within the cells.

In the March 16th issue of *Nano Let-*

*ters* (DOI: 10.1021/nl200285r; p. 1733), the research team described the application of a novel microfluidic chamber device for live-cell examination. The device was made from two parallel silicon microchips. Each microchip contained a central silicon nitride (SiN) membrane of 50 nm thickness that was transparent to the electron beam as well as light. One microchip was coated with poly-L-lysine (PLL) for increased cell adherence; the other chip had an attached 6 μm spacer to form a reservoir for the cells and buffer. Live green monkey kidney fibroblast cells (COS-7) were incubated for 2 hours in the presence of 30 nm Au-NPs. The cells were then washed and incubated in a medium. Twenty-four hours later, the cells were enclosed in the chamber and imaged live with a STEM under a continuous flow of buffer. Experiments demonstrated that COS-7 cells remained viable in the microfluidic chamber.

STEM analysis was carried out shortly after the cells were loaded. The cells were viewed at 16,000x magnification using an accelerating voltage of

200 kV and a probe current of 0.16 nA. The researchers were seeking to identify several quantitative values pertaining to the number and placement of the Au-NPs inside the cell vesicle. The STEM images showed high concentrations of Au-NPs as dark spots clustered inside cell vesicles, which were 200–300 nm in diameter. However, there was a degree of image distortion due to certain factors including beam-specimen interaction, the liquid medium, distance to focal plane, and the degree of pixelation.

Despite these conditions, the researchers were still able to resolve separate nanoparticles by enhancing the image using image processing software, Image J. They conducted quantitative measurements of several factors such as the total number of Au-NPs per vesicle cluster and the average density of Au-NPs on the surface of the vesicles.

The researchers concluded that their research showed this method of liquid STEM is suitable for further study of nanoparticles uptake into living cells.

**Tara D. Washington**

### Nano Focus

#### Nanofiltration membrane improves performance of vanadium redox flow battery

Integrating renewable energy sources such as wind and solar into the electric grid will require energy storage systems to handle their intermittent nature. One promising possibility is the vanadium redox flow battery (VRB), based on active species of vanadium dissolved in electrolyte. To date, VRBs have been limited by their use of perfluorinated-polymer ion-exchange membranes, which are expensive and have low selectivity between vanadium and other ions. Now a group from the Dalian Institute of Chemical

Physics in China has demonstrated a VRB based on a much cheaper nanofiltration membrane. H. Zhang and colleagues reported their findings in a recent issue of *Energy & Environmental Science* (DOI: 10.1039/c1ee01117k; p. 1676).

VRBs were first proposed and demonstrated 25 years ago, and have a number of advantages for grid-scale storage, including fast response times and the ability to scale to essentially unlimited storage capacity. They function by flowing solutions of vanadium ions in a sulfuric acid electrolyte by either side of an ion-exchange membrane. The researchers hypothesized that it would be possible to eliminate the use of the expensive ion-exchange membrane by using a nanofil-

tration (NF) membrane, which conducts ions mechanically through nanometer-scale pores, and costs (by their estimate) roughly 1/20th as much.

To test this idea, the researchers prepared samples of polyacrylonitrile NF membranes using a phase-inversion method, varying the polymer concentration and the addition of volatile co-solvents in order to control the distribution of pore sizes. They next tested the ionic selectivity of the membranes by measuring the permeation rate of VO<sup>2+</sup> and H<sup>+</sup> in a 3 M H<sub>2</sub>SO<sub>4</sub> solution across the samples into deionized water, finding that the rate for H<sup>+</sup> exceeded that of VO<sup>2+</sup> by factors ranging from 6.9 to 14.9, with the largest ratio occurring for the sample