

## ATMOSPHERIC CHEMISTRY

### Catalysis in the clouds

*Science* **340**, 727–730 (2013)



© STEPHAN MERTES/TROPOS

Clouds have a big impact on climate. Within them, aerosol particles scatter heat and light through 'aerosol radiative forcing'. The size and properties of these aerosol particles control a cloud's reflectivity — so, small droplets make brighter clouds that are more

reflective and block sunlight from reaching the Earth's surface. Thus, aerosol forcing typically works to oppose greenhouse gases and causes cooling. Sulfate aerosols are an important constituent of clouds, so understanding the in-cloud sulfur cycle is critical for modelling the impact of aerosol radiative forcing. Sulfates occur naturally from, for example, volcanic dust and sea salt, and anthropogenically through the combustion of fossil fuels. They are added to aerosol particles in clouds through both *in situ* oxidation of SO<sub>2</sub> and the direct uptake of H<sub>2</sub>SO<sub>4</sub> gas and ultrafine particulates by cloud droplets.

SO<sub>2</sub> can be oxidized by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and O<sub>2</sub>, but its reaction with O<sub>2</sub> can also be catalysed by transition metal ions (TMIs). The contribution of TMI catalysis is not fully understood, making it difficult to accurately predict the effect of sulfate aerosol radiative forcing in climate models. Now, a group of scientists, led by Eliza Harris and Bärbel Sinha from the Max Planck Institute in Mainz, have found that the pathway catalysed by naturally occurring TMIs is the main contributor to

the oxidation of sulfur in clouds. The team used instruments located in Mount Schmucke in Thuringia, Germany to measure upwind, downwind and within-hill cap clouds. By measuring sulfur isotope abundances in gas-phase SO<sub>2</sub> and sulfate particles they were able to discriminate between sulfate particles created through TMIs and those created through oxidation by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>.

As the dominant oxidation pathway involving natural TMIs takes place on large dust particles, which drop out of the clouds relatively quickly, the sulfate particles will actually have shorter lifetimes than previously estimated. The team maintain that this result will lead to significant changes in the contribution of aerosol forcing in major global climate models. RD

## POLYMER CHEMISTRY

### Spotlight on synthesis

*Chem. Commun.* **49**, 5453–5455 (2013)

Polymer synthesis has become increasingly sophisticated in recent years, and a

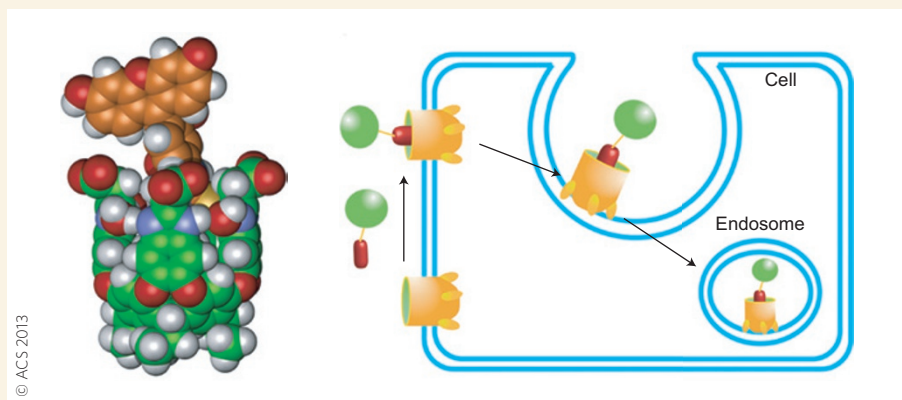
## CELLULAR IMAGING

### Buckets of binding

*J. Am. Chem. Soc.* **135**, 7090–7093 (2013)

Selective transport of molecules across cell membranes is a key step in drug delivery, live-cell imaging and other theranostic applications. Many drug and probe compounds are unable to simply burrow their way through the cell membrane, and typically a receptor is required to recognize appropriate species and mediate endocytosis to enable them to enter the cell. Moreover, the complex soup of molecules that make up the cellular environment can compete for the binding sites of artificial receptors and thwart efforts to develop a generalized transmembrane shuttling solution. These problems often limit successful synthetic transporters to single receptor–target systems.

Now a team of researchers from California State University, Long Beach and the University of California, Riverside, led by Richard Hooley have developed a carboxylate-decorated, non-cytotoxic cavitand molecule that can embed itself into cell walls and act as an anchor to facilitate the transport of guest molecules across lipid membranes. In contrast to other shape-based receptors, which tend to offer a wide target scope but poor selectivity, this cavitand specifically recognizes



© ACS 2013

choline-like salts. Once binding of a choline-tagged molecule occurs at the cell surface, the cavitand–target pair is endocytosed into the cell. Successful transport across cell membranes was demonstrated using a choline-modified fluorescein dye. In a control experiment using unmodified fluorescein there was virtually no internalized fluorescence, demonstrating that a choline-like group is essential for cavitand-mediated recognition and, in turn, transport into the cell.

Transmembrane transport also occurred — albeit at a slower rate — when an excess

of choline was added to the system, demonstrating that transport is not completely inhibited by competitive binding. This finding suggests that, in principle, such cavitand-based receptors could be used to mediate transport even in cell types where choline and its derivatives are present in high concentrations. The ability to selectively induce endocytosis with a range of target choline-tagged compounds could lead to a generalized cell membrane transport and delivery system for further use in drug-delivery systems. CH