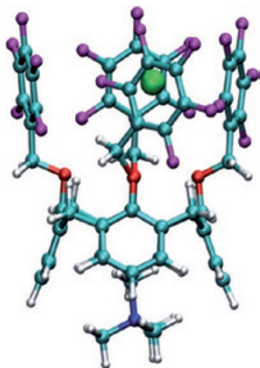


ION TRANSPORT

Weaker way to go

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201104966> (2011)



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Anion- π interactions and halogen bonds are weaker and much less common than their cation- π interactions and hydrogen bond counterparts. Yet when it comes to carrying ions through lipid bilayer membranes, stronger binding does not necessarily lead to better transport. Using a series of calixarenes as ion transporters, Stefan Matile and co-workers at the University of Geneva and the Politecnico di Milano have now

unravellled the contributions of anion- π interactions, halogen bonds and hydrogen bonds to anion transport.

The researchers prepared calixarenes that bind anions through one rim and counter-cations through the other. Transport only occurred when the cation was tetramethyl ammonium — behaviour consistent with counter-ion activations previously observed with other synthetic transporters. The anion-binding rim consists of arene rings, which, through substitutions between fluorine, iodine and hydrogen atoms at specific positions, were devised to form anion- π interactions, halogen bonding of various strengths, or hydrogen bonding.

The calixarenes' transport abilities were determined using vesicles made of lipid bilayer membranes that encapsulate a pH-sensitive fluorophore in a basic solution. Calixarenes transported chloride and hydroxide anions through the membrane in opposite ways, causing a pH variation that was observed by fluorescence. The best transport system was the one featuring anion- π interactions. Halogen binding of the anions was initially too strong for transport to occur, but this was addressed by weakening the interaction or increasing its

distance — which shows that anions can be carried through membranes using halogen, rather than hydrogen, bonds. AP

SOLUTION-PHASE DYNAMICS

Separation and solvation

J. Phys. Chem. Lett. **2**, 2797–2804 (2011)

Solvents play a crucial role in chemistry and choosing the right one can make all the difference between a successful or a failed reaction. Using solvent mixtures is a way to control various bulk properties but it also complicates the local molecular-scale environment that a solute experiences, challenging our microscopic understanding of such systems. For example, issues such as the preferential solvation of the solute (by one solvent within the mixture) must be considered, as well as possible heterogeneities in the structure of the mixture. To better understand these matters Benjamin Schwartz and Godwin Kanu from UCLA and Arthur Bragg from John Hopkins University have now studied the dynamics of the solvated electron in a mixture of tetrahydrofuran (THF) and water.

They probed changes in the absorption band of an electron after being ejected from tetrabutylammonium iodide in a

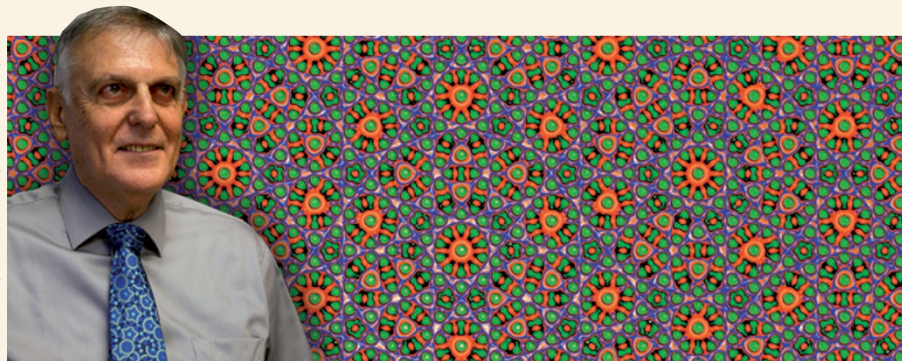
2011 NOBEL PRIZE IN CHEMISTRY

Crazy crystals?

"Ten fold??? There can be no such creature." It was with these words that Daniel Shechtman, 2011 Nobel Laureate in Chemistry, greeted the discovery of electron diffraction patterns that violated some of the fundamental laws of crystallography. The diffraction patterns had been collected from a crystal of an alloy of aluminium and manganese that had been rapidly cooled. The fact that the samples diffracted indicated they were crystalline, but the resulting symmetry — five- and ten-fold icosahedral — was impossible, according to the well-established rules of crystallography.

With his initially sceptical colleagues, Shechtman published the findings some two years after the initial observations, stating that they had "observed a metallic solid [...] with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice transitions" (*Phys. Rev. Lett.* **53**, 1951–1953; 1984). It is safe to say that reaction

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to the paper was mixed. On one side, some mathematicians and even crystallographers had been inspired to consider five-fold symmetry by the quasiperiodic tilings developed by Roger Penrose in the 1970s. Indeed, only six weeks after Shechtman and colleagues' paper was published, a theoretical explanation of quasicrystals — as they became to be known — was published by Paul Steinhard and Dov Levine (*Phys. Rev. Lett.* **53**, 2477–2480; 1984).

On the opposite side of the argument was Linus Pauling, who remained convinced that there was indeed 'no such creature' and argued that the observed phenomenon could be attributed solely to symmetrically intergrown crystals, known as twins. Such scepticism has dwindled in the face of overwhelming evidence and quasicrystals have since been found in nature (*Science* **324**, 1306–1309; 2009), as well as in rewritten crystallography textbooks. NW