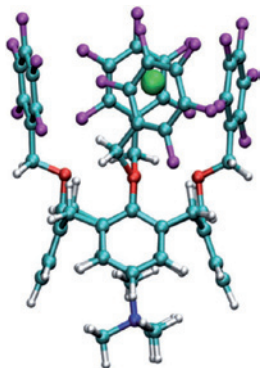


ION TRANSPORT

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

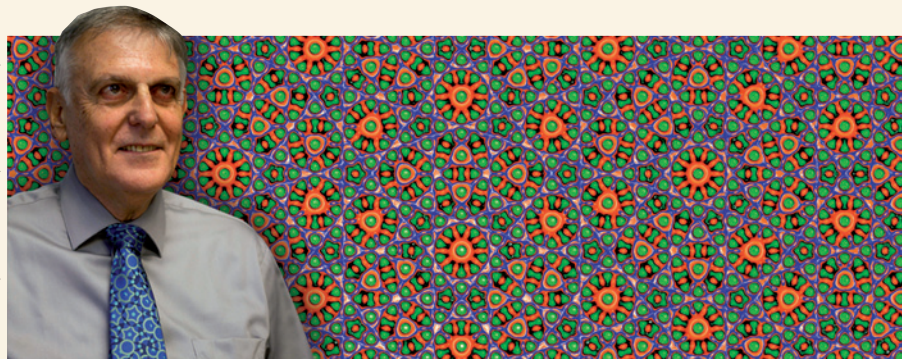
2011 NOBEL PRIZE IN CHEMISTRY

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*

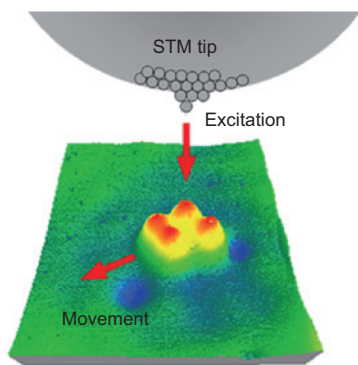
THF–water mixture. Their spectroscopic data suggests that the electrons are ejected into an environment of pure THF. Electrons, however, are preferentially solvated by water, and the discontinuous nature of the observed dynamics, in conjunction with a simple kinetic model, suggests that they diffuse through the THF until they find a group of water molecules within which they are then preferentially hydrated.

These results support the idea that the solvent mixture is phase-separated at the nanometre length-scale. They also show that the tetrabutylammonium iodide ion pair is differentially solvated within the mixture, with the iodide ion located on the edge of a region of water whereas tetrabutylammonium positions itself nearby within a region of THF. GA

MOLECULAR MACHINES

One-way traffic

Nature **479**, 208–211 (2011)



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Single molecules can be pushed or pulled across a surface with the tip of a scanning tunnelling microscope (STM). Depending on their structure, some molecules will simply slide over a surface without changing their relative orientation, whereas others can be made to roll if the whole molecule, or parts of it, rotate with respect to the surface. In all of these examples, however, the molecule is a passive participant and goes along for the ride without being actively involved.

Now, Tibor Kudernac and colleagues have shown that molecules with four unidirectional rotary motors as ‘wheels’ can be propelled across a Cu(111) surface because of changes in their conformation, rather than being pulled or pushed by an STM tip. An STM tip is still required, however, because rotation of the wheels is induced by applying a pulse with a voltage above 500 mV to the centre of the molecule. This electronic excitation causes each rotary motor to undergo a double-bond isomerization followed by a helix inversion

and results in a paddlewheel-like motion of each wheel on the surface.

Each wheel is chiral, however, and can only rotate in one direction. So that they can all act in concert and rotate in the same direction, the wheels on opposite sites of the molecule must have opposite chiralities. It is only in this case that the molecule moves forward in a more-or-less linear trajectory — it is not perfectly straight because it is difficult to excite all four wheels simultaneously — and other configurations lead to random motion or no movement at all. SC

CHIRAL NUCLEOPHILES

Ate complex is the answer

J. Am. Chem. Soc. **133**, 16794–16797 (2011)

Despite the wide use of organometallic nucleophiles in synthetic organic chemistry, there are only a few chiral examples of these useful reagents. This stands in stark contrast to the wide variety of chiral electrophilic reagents that have been developed. The most important property of chiral reagents — configurational stability — is often mutually exclusive with the features that are valued in organometallic reagents: high reactivity and ease of preparation. Now, Varinder Aggarwal and co-workers from the University of Bristol have described the use of ate complexes of boronic esters as chiral nucleophiles for asymmetric synthesis.

Aggarwal and co-workers recognized that chiral boronic esters would be configurationally stable and easy to synthesize, but that they were unreactive. They reasoned, however, that addition of an aryl lithium to a chiral boronic ester might result in formation of a reactive boronate complex — which would be able to react stereoselectively with a variety of electrophiles. The initial attempts — using *p*-methoxyphenyllithium to activate an alkyl boronic ester followed by reaction with iodine — were promising, giving an almost completely stereospecific reaction. Other electrophilic partners — such as an azodicarboxylate — were less successful, giving the product as an almost racemic mixture.

This result was assumed to be due to a competing single-electron reaction pathway, which involved an achiral alkyl radical intermediate. Tuning the electronic properties of the aryllithium was sufficient to bias the reaction in favour of the stereoselective two-electron pathway. The new methodology was shown to work with a wide variety of electrophile partners to produce chiral alkyl halides, alcohols and amines among others. SD

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey, Anne Pichon and Neil Withers.

blogroll

Trouble brewing

An oral history of pharma layoffs, the wonders of beer and some embarrassing artwork.

What do chemists do after they've just been laid off from their job in the pharmaceutical/chemical industry? Chemjobber is trying to gather useful information from people who have been through redundancy to “hear as much advice as possible for people who will be laid off”. Since the Layoff Project launch in mid-October (<http://go.nature.com/qi4mUR>), at the time of writing Chemjobber has been contacted by six people willing to tell their story. These have ranged from someone with 30 years' experience to someone 'freshly out of school', and from someone clearly having an understandably tough time adjusting to life without “being able to discuss chemistry” to someone whose personal circumstances changed so drastically they could easily put the loss of work into perspective.

Wort. Mash. India pale ale. German wheat beer. You probably expect to see words like these in a blog post about beer, but how about gibberellic acid, enzyme inactivation, dextrin oligomers (with structures!) and isomerization? Regular Blogroll readers won't be surprised to learn that the blogpost in question is by Martin Lersch, of Khymos (<http://go.nature.com/dkrxsu>). In his ~2,500 word post 'Wonders of extraction: Brewing beer', he takes readers through a thorough look at the first two steps of brewing beer: mashing and wort boiling. In his words, these “are really quite sophisticated extractions”.

And finally...what better way to decorate a new chemistry lab than to frost some pictures of molecules onto the glass doors, and onto a funky yellow glass artwork? Well, if you go ahead and decide to decorate your lab with molecular structures, perhaps you should check out at ChemBark what happened when Georgia Tech did this (<http://go.nature.com/H1kKJM>). If you don't like five-valent carbon or triply bonded bridge head atoms on fused rings, you have been warned!