applying this thin-film technique to a variety of substrates, the researchers observed that the decomposition of a cyclodextrin (a cyclic oligomer of glucose) gave similar products to that of cellulose. Glucose monomers are linked in different ways in the two molecules, but linkage was found to have a negligible effect on the pyrolysis products.

Dauenhauer and colleagues used the cyclodextrin as a surrogate molecule for cellulose in theoretical studies, and suggest that cellulose is directly converted into furans and small oxygenated species through homolytic cleavage rather than through intermediates such as glucose. *AP*

PHOTOREDOX CATALYSIS

## Rapid reaction discovery

*Science* **334,** 1114–1117 (2011)

Any practitioner of synthetic organic chemistry will be aware that luck can play a part in the discovery of new chemical reactions or improved conditions, but is it possible to make your own luck by performing a very large number of random reactions? Now, David MacMillan and co-workers from Princeton University used this idea to shift the odds in their favour and discovered a previously unknown C–H arylation reaction.

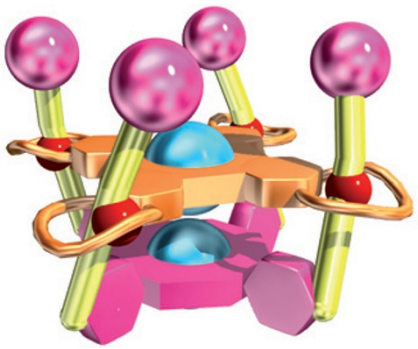
Realizing that they may find more previously unknown reactions by exploring a relatively new field, MacMillan and co-workers decided to use serendipity to seek new reactions that relied on photoredox catalysis. Using a typical high-throughput format — a 96-well plate — they made pair-wise combinations of common substrates with a variety of functional groups. They then examined the reactions of each combination with various photoredox catalysts under irradiation with a household 26 W fluorescent lamp. Gas chromatography–mass spectrometry analysis of the reaction mixtures allowed any usefully productive reactions to be quickly identified.

A 'hit' was found for the combination of *N*,*N*-dimethylaniline with 1,4-dicyanobenzene in the presence of an iridium pyridyl catalyst. The reaction product, an α-aryl amine, is commonly found in medicinally active agents so this reaction was selected for optimization. The original reaction formed the product in 11% yield, but the changes in solvent, base and the specific photocatalyst used enabled the yield to be improved to 85%. They were then able to use these optimized conditions to produce a variety of α-aryl and α-heteroaryl amines. *SD*

INTERLOCKED MOLECULES

## Switching spin

*Angew. Chem. Int. Ed.* http://dx.doi.org/10.1002/anie.201107104 (2011)





Molecules comprising mechanically interlocked components that are not covalently bonded to one another often form the basis of nanoscale switches and machines. Although constrained as part of a larger assembly, significant changes in the relative positions of the components can be achieved by modifying how they interact with each other. In rotaxanes, for example, the location of a macrocycle threaded on a linear chain can be altered by changing how strongly different sites along the chain bind to it.

Now, a team in Japan led by Kentaro Tanaka at Nagoya University have made a four-fold rotaxane that can be used to control the intramolecular distance and, therefore, the electronic coupling, between two copper(II) ions. The rotaxane is made up of two building blocks: a phthalocyanine ring with four crown-ether loops fixed around its edge and a porphyrin with four 'arms' that each thread through one of the loops. The structure is prevented from unravelling by bulky groups fixed to the end of each arm. The large porphyrin and phthalocyanine rings — each with a central copper(II) ion — stack on top of one another and their relative positions can be controlled by tuning the interactions between the crown-ether loops and the dialkylamine-containing arms.

When the dialkylamine groups are protonated, the crown ethers bind to them and the porphyrin and phthalocyanine rings are held too far apart for the copper(II) ions to interact. Once deprotonated, however, there is no thermodynamic driving force for the crown ethers to encircle the amine groups and the two large aromatic systems move close enough to enable antiferromagnetic coupling between the copper(II) ions. *SC*

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

blogroll

## Better by design

**The differences between planes and drugs, engineers and medicinal chemists… and Jimmy Stewart.**

Have you ever wondered about the similarities and differences between drug design and aeroplane design? If not, don't worry because Ashutosh Jogalekar at the Curious Wavefunction has blogged (http://go.nature.com/lltzKb) about a paper that does just that (http://go.nature.com/Z91DGQ). Both of these design processes use modelling, but "compared with the aeronautical industry where modelling has been applied to airplane design for decades, why has it taken so long for modelling to catch on in the pharmaceutical industry?" Jogalekar takes us through the three reasons he sees: the complexity of biological systems compared with aeronautical ones; the natural inclination of engineers to learn programming and modelling is generally not shared by the mix of people who work in pharma; and the lack of a "comprehensive knowledge base for validating modelling techniques". As a molecular modeller himself, Jogalekar finds the paper upbeat and hopes that "the pharmaceutical industry makes a concerted effort to test, refine, retain and discard modelling approaches to drug design at all levels".

Derek Lowe blogged his own thoughts on the paper (http://go.nature.com/YRhIKi), noting that, in biological systems, "there are so many nonlinear effects, so many crazy little things that can add up to so much more than you'd ever think". The "Andy Grove fallacy" — which is what Lowe calls the propensity of engineers and other outsiders to underestimate the complexity of drug discovery — is a favourite topic on In The Pipeline, so a lot of comments came from both sides of the fence — from engineers and biologists.

And finally … after pursuing exciting research on artificial photosynthesis, he left college and became a banker. A modern-day tale of the priorities of under-funded young scientists? No! It's a scene from the Jimmy Stewart movie *You Can't Take it with You*, released in 1938, which Nick Uhlig shared the clip on the Chemistry Blog (http://go.nature.com/9vrmaW).