

(12,10) chirality CNTs in a slightly higher abundance than others.

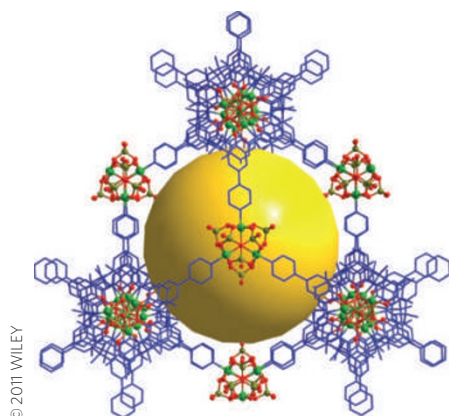
About 90% of the CNTs made using the ammonia route had a chiral angle in the range 20–30°, and 50% between 27 and 29°, a far greater proportion than those made using other methods. The group suggests that the ammonia does not affect the catalyst particle size, because there was only a slight increase in the average diameter of the CNTs grown using the ammonia method — 1.67 nm versus 1.60 nm. Instead, they infer that it must be etching off CNTs with smaller chiral angles, because these are more reactive.

#### METAL-ORGANIC FRAMEWORKS

### Triple twist for MOFs

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Helicate motifs, widespread in biomolecules, have long attracted scientists with their elegant morphologies and intrinsic chirality. Yong Cui and co-workers at Shanghai Jiao Tong University have now used a triple helicate cluster to construct homochiral metal-organic frameworks (MOFs). Those hybrid porous materials are typically prepared from metal salts and organic ligands by one-pot synthesis, but the researchers opted for a step-wise assembly.

A ligand (L) was first prepared, based on a twisted 1,1'-biphenol core, that features several coordination sites — terminal pyridyl, chelating nitrogen-oxygen, and pendant oxygen moieties. Subsequent coordination with copper atoms led to the formation of a triple-stranded heptametallic helicate cluster  $\{\text{Cu}_7\text{L}_3\}$  whose pyridyl sites remain free. The clusters were insoluble in most solvents, crystallizing into a three-dimensional, porous nanotubular architecture directed by anisotropic non-covalent CH- $\pi$ ,  $\pi$ - $\pi$  and hydrophobic interactions. In the next step, the helicate clusters  $\{\text{Cu}_7\text{L}_3\}$  and copper sulfate were dissolved in dimethyl sulfoxide (DMSO).

Although different metal-organic frameworks were obtained at different temperatures, the two architectures that formed between 80 and 100 °C could be identified. Characterization revealed that they both consisted of  $\{\text{Cu}_7\text{L}_3\}$  helicates linked together by multinuclear copper clusters into three-dimensional micro- and mesoporous networks. The symmetry and handedness of the helicate  $\{\text{Cu}_7\text{L}_3\}$  building blocks were retained during the assembly process, suggesting that this step-wise approach could be a general strategy for constructing homochiral MOFs. The two MOFs characterized resembled zeolites, exhibiting robust crystallinity and channel accessibility in solution — notable features for mesoporous frameworks, which tend to interpenetrate or collapse on solvent removal.

#### REACTION METHODOLOGY

### Coupling catalytic cycles

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In the simplest catalytic reaction, a small amount of one reaction partner is activated by a catalyst and the intermediate reacts with a second compound present in excess — the catalysis is successful because the rate of reaction between the two unactivated reaction partners is small. A large number of such simple catalytic reactions have been successfully developed. Dual catalysis — where two reaction partners, each activated by different catalysts, react — is attractive, but such reactions are rare.

Now, Barry Trost and Xinjun Luan from Stanford University have developed just such a process to couple together a  $\pi$ -allyl-palladium species and a vanadium allenolate in a type of process they call contemporaneous dual catalysis. A propargylic alcohol is activated by an oxyvanadium catalyst and an allyl carbonate by a palladium catalyst. A successful reaction outcome requires these two activated partners — one nucleophile and one electrophile — to react together more quickly than either can react with the starting materials from which they were generated, still present in a large excess. Once again, it is the relative reaction rates that are the important factor.

The scope for both reaction partners is broad, and the reaction product — an  $\alpha$ -allylated enone — is not one that can be easily obtained by conventional methodology. The delicate balance of reaction rates means that the outcome of the reaction is very sensitive to the ratio of the two catalysts with small changes resulting in dramatically larger amounts of unwanted side-products. Similarly, changes in the relative amounts of catalyst can be optimized for different reaction partners to maximize yield and selectivity.

## blogroll

### Mind-altering blogs

**What responsibilities are borne by the creators of compounds that end up as 'legal highs'?**

*Nature* kicked off the International Year of Chemistry in style, with its first issue of the year (<http://go.nature.com/94jluB>) containing lots of features, comment and papers on the central science. In its pages was a 'World View' column from David Nichols, in which he "describes how his research on psychedelic compounds has been abused — with fatal consequences." Nichols refers to the makers of 'legal highs', who use his work on psychedelic drugs for treating disease in rather less academic ways. Perhaps surprisingly for a one-page opinion article, this got quite a lot of attention — even reaching the BBC website (<http://go.nature.com/5JtEU1>). It certainly reached Derek Lowe and David Kroll at *In the Pipeline* (<http://go.nature.com/RJwWp8>) and *Terra Sigilata* (<http://go.nature.com/9QGGVT>) respectively. Lowe in particular expressed his "disgust for the people who are making and selling these things", and his sympathy for Nichols.

But the chemistry blogosphere was not entirely in agreement. Andrea Sella used his *Solarsaddle* blog to ask "Is David Nichols just a wee bit disingenuous?" (<http://go.nature.com/ydsJZR>). Sella had been on a BBC radio programme (<http://go.nature.com/QzFBCI>) discussing Nichols's article and was surprised to discover Nichols's close links to Alexander Shulgin, author of *PIHKAL: A Chemical Love Story*. He even goes so far as to say that Nichols's "opinion piece strikes me as a kind of lame attempt to deflect criticism of his work". Kroll responded in a second post (<http://go.nature.com/qraaP3>) acknowledging that Nichols did admit that "part of the reason" behind the article was to "distance himself from the psychedelic community".

And finally...KJHaxton launched a new series of posts on *Endless Possibilities* titled 'What Am I?' (<http://www.possibilitiesendless.com/?p=489>). Haxton gives some chemical clues to the ingredients of a household product and leaves the reader to deduce its identity.