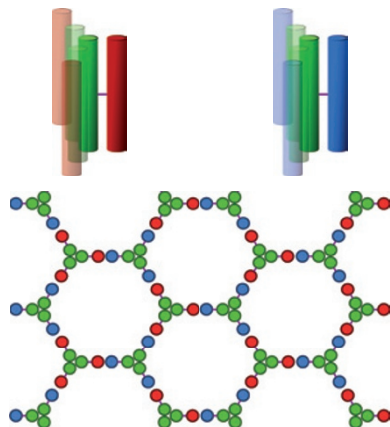


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that can also be used to create synthetic drug-delivery systems. However, fabricating such extended three-dimensional structures with a predetermined geometry requires control over the interactions that drive assembly. Now, Derek Woolfson and co-workers at the University of Bristol, UK, have designed peptides that self-assemble to form dimer or trimer bundles, which themselves self-assemble to form hollow peptide cages.

The peptides are derived from sequences known to assemble into a coiled-coil arrangement. One peptide was tailored to ensure that it self-assembles into a homotrimer. Adding peptides to the outside edges of the homotrimer — through disulfide bridges — enabled the formation of hexamer peptide hubs. To create a larger array, Woolfson and co-workers formed two different hexamer hubs by adding two different peptides to the outside of the homotrimer. These additional peptides were designed to dimerize with each other, therefore mixing these two hubs created a hexagonal array in which homotrimers, at the vertices of the array, are linked together by heterodimers.

Naively, one might expect the hexagonal array to form an extended planar structure, however, microscopy experiments showed that spherical particles were formed. These particles were hollow with a unilamellar construction — rather than being solid or formed with multiple walls — and Woolfson and co-workers called them self-assembled cage-like particles or SAGEs. The driving force behind the formation of their spherical cage structure is unclear; however, the extended hexagonal array retains some flexibility, which enables it to bend and close in on itself. Molecular dynamics simulations also suggest that repulsion between positive charges at one end of the assembled peptides may contribute to the hexamer hubs adopting a more wedge-like shape. Forming SAGEs also limits the number of unpartnered peptide edges in the hexagonal array, and maximizes the number of coiled-coil interactions. *RJ*

ALKENE SYNTHESIS

Activating iodoniums

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Tetrasubstituted alkenes are found in a variety of biologically active natural compounds, drugs and functional materials, but methods for their synthesis are limited. Steric congestion around the double bond is problematic for the classic Wittig-type reactions in terms of both substrate scope and stereoselectivity. There has been much recent interest in the use of metal catalysts to activate alkynes towards reaction with nucleophiles, however, a polarity-reversed process — activating a carbon electrophile towards reaction with an alkyne — which looks reasonable on paper, has not received the same attention. Now, Matthew Gaunt and co-workers from the University of Cambridge have reported a copper(I) catalysed addition of diaryl- or vinyl(aryl) iodonium triflates to alkynes.

Gaunt and co-workers have previously shown copper catalysts could activate diaryliodonium salts towards reaction with π -electron-rich nucleophiles such as indoles or anilines and wondered if this could be extended to reaction with alkynes. It is believed that the hypervalent iodine reagent reacts with the copper catalyst to give a Cu(III) complex, which then reacts with the alkyne to give a vinyl copper triflate intermediate. Reductive elimination would then return the copper(I) catalyst and produce the vinyl triflate product. In general, disubstituted alkynes react to produce *Z*-alkenes. And addition to unsymmetrical alkynes proceeds with useful regioselectivity when the substituents are sterically or electronically differentiated. Despite some potential pitfalls, terminal alkynes and even acetylene itself were also shown to be suitable substrates for the reaction. As yet, only a few examples are described involving transfer of an aryl group (rather than vinyl) from the iodonium reagent — which may be due to the need to synthesize the iodine reagents, or perhaps to a problem in controlling which of two groups is transferred to the copper catalyst.

The synthetic utility of the vinyl triflate products is unquestionable as they were then shown to undergo a wide variety of palladium-catalysed cross-coupling reactions. Suzuki and Sonagashira couplings gave alkenes with four carbon substituents, and Buchwald–Hartwig type amination and Miyaura borylation gave amido alkenes and alkenyl boronic esters, respectively, and all without loss of isomeric purity of the alkene. *SD*

Written by Stuart Cantrill, Stephen Davey, Russell Johnson and Anne Pichon.

blogroll

Welcome to the club

Twitter's new #chemclub aims to help you find exciting chemistry to read.

A weekly laboratory journal club is a great way to encourage researchers to read the literature and share their enthusiasm for great pieces of chemistry. Writing at Behind NMR Lines, Andrew Bissette found that he often caught wind of interesting papers via the watchful eyes of the chemistry crowd on Twitter. So he came up with an idea (<http://go.nature.com/pHRRZI>): why not form an online journal club that draws attention to 'cool papers' and spark some discussion? Thus began #chemclub.

Chemists of the Twitterverse have thrown themselves in with wild abandon. Andrew posts weekly round-ups of the best material, and the contributions so far range from the most cutting-edge total syntheses (<http://go.nature.com/v7UX4z>) to the dusty old classics of yesteryear (<http://go.nature.com/jmWc1Q>). Anyone can join in with #chemclub, so if you're reading a truly fascinating (or even slightly weird) paper, why not let the rest of us know about it?

Meanwhile, JessTheChemist who writes at The Organic Solution has been wondering just how academically interconnected the online chemistry community really is. Jess started out building her own chemistry 'family tree', but the project has since blossomed and is still growing (<http://go.nature.com/7z3QXf>). We're encouraged to add our own branches to the tree and who knows where your branch might lead. Perhaps even to the not-long-departed Maggie Thatcher? And on that note, Kat Day of The Chronicle Flask (<http://go.nature.com/v2a63E>) tells us to 'never mind the politics', Thatcher will always be one of those very famous female chemists who 'ignored the limits' (<http://go.nature.com/togjya>). Besides, once part of the club, always part of the club, right?

Written by Doctor Galactic, who blogs at www.doctorgalacticandthelabcoatcowboy.wordpress.com