LIQUID CRYSTALS

Inverted influences

Nature **485,** 86–89 (2012)

© 2012 NPG

Liquid crystals, elongated molecules formed by a rigid core bearing flexible terminal chains, are intrinsically anisotropic. Controlling their orientation over large domains at surfaces or interfaces — through mechanical or chemical treatment — leads to a variety of phases with different properties. This behaviour has been widely exploited for technical applications. Now, using computational simulations, Juan de Pablo at the University of Wisconsin–Madison and co-workers have shown that liquid crystals themselves are able to cause other species to orient at an interface.

The researchers modelled spherical nanodroplets consisting of ellipsoidal mesogens — the rigid units in liquid crystals that drive their ordering — surrounded by surfactant and water molecules. The model is set up so that the mesogens are fairly strongly anchored to the water and surfactant molecules. The latter two species do not interact with each other, but favour different orientations of the mesogens within the droplet.

On cooling, the initially disordered mesogens order into a nematic then a smectic liquid-crystal phase. This induced the formation of highly organized surfactant domains at the interface, which adopted different morphologies depending on the mesogens' ordering and the water/surfactant ratio. The surfactants formed, for example, circular or striped patterns around the droplet. Changing the spherical droplets to planar or cylindrical shapes also led to ordered surfactant domains, albeit organized to a lesser extent. This demonstration that anisotropic molecules can cause surfactant species to organize at liquid–liquid interfaces may make it possible in future to functionalize liquid droplets in a specific, segregated manner, and further assemble them into complex architectures. *AP*

MOLECULAR WALKERS

On the right track

Angew. Chem. Int. Ed. http://doi.org/fz4wr3 (2012)

Chemists often draw inspiration from nature when designing and making artificial molecular machines. In many cases, the goal is to mimic the function of a complex biomolecule with a relatively simple synthetic compound. Biological systems that researchers have tried to emulate in such a fashion include motor proteins — such as dynein and kinesin — that move progressively along a polymer-filament track. Molecular 'walkers' have typically been made in the laboratory using DNA building blocks, but small-molecule systems have also recently emerged.

Previous examples of small-molecule walkers have required the use of an external stimulus to trigger each step. Now, a team at the University of Edinburgh led by David Leigh have developed a system in which an α-methylene-4-nitrostyrene side chain can move in a stepwise manner along a polyamine backbone without any external input. The side chain is initially attached to one of the secondary amines on an oligoethyleneimine track, but it can step to an adjacent amine through a sequence of Michael and retro-Michael reactions. On average, each α-methylene-4-nitrostyrene

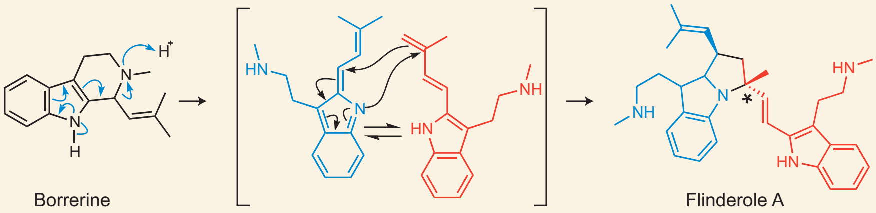
BIOMIMETIC SYNTHESIS

Flinderoles facilitated

J. Am. Chem. Soc. **134,** 6936–6939 (2012)

The emergence of drug-resistant strains of *Plasmodium falciparum* — the major cause of severe malarial infections — has resulted in much interest in the flindersial alkaloids, which are thought to act by a different mechanism than the commonly used drug chloroquine. With a goal of further testing and developing these natural products, Ravikrishna Vallakati and Jeremy May from the University of Houston have now described a biomimetic synthesis of several members of this family of alkaloids.

Prior work on the biosynthesis of the related natural products borreverine and isoborreverine led Vallakati and May to propose that the biosynthetic origin of flinderole A is an acid-catalysed ring-opening of borrerine followed by dimerization in a formal [3+2] cycloaddition (as pictured). Acid treatment of borrerine produced flinderole A along with its diastereomer desmethylflinderole C (at the starred position) and isoborreverine. To their surprise, and contrary to the previous reports, very little borreverine itself was produced under these conditions. The results, however, reflect the fact that borreverine and the flinderoles are not found together in nature. Furthermore, the Diels–Alder reaction to form borreverine would be energetically unfavourable with respect to that forming isoborreverine.



Borrerine

Flinderole A

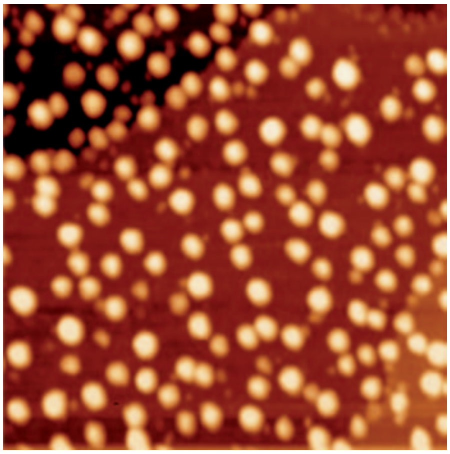
A one-pot reaction involving methylation of borrerine prior to acid treatment gave flinderoles B and C, meaning that all of the antimalarial flindersial alkaloids can be synthesized in as few as three steps from three simple commercially available materials. This convergent synthesis should make it possible to vary each of these three components to easily make analogues of the flinderoles and thus allow their testing for antimalarial activity. *SD* group can take over 500 steps on the same track before falling off.

There is no control over the direction in which the side chain steps along the track and the system simply equilibrates to give the most thermodynamically favourable distribution of nitrostyrene groups. Nevertheless, using a track with five amine stations Leigh and co-workers were able to show that a side chain could migrate from one end to the other and, in doing so, perform a rudimentary task, namely quenching a fluorescent group. *SC*

SURFACE CHEMISTRY

Panning for gold

J. Am. Chem. Soc. http://doi.org/hvr (2012)



© 2012 ACS

Many catalysts consist of active metal species adsorbed on an oxide surface, and they need to be highly dispersed to maintain activity. Unfortunately, metal atoms have a tendency to group into larger, less reactive particles, which has led to several attempts at reversing this process, but the mechanisms by which they worked were not understood. Now, Bing Yang from the Fritz Haber Institute in Berlin and colleagues have found that molecules of tris(phenylthio)benzene (TPB) are capable of trapping individual atoms of gold on either a gold or alumina surface.

Using scanning tunnelling microscopy, Yang and colleagues observed adsorbed gold atoms disappearing from the metal's surface as they coordinated to TPB ligands. This trapping of adatoms occurred with varying configurations of the TPB molecules, and so anything up to six atoms could become attached to the ligands. The team discovered that below 100 K, a flat-lying, single molecule of TPB bound to six gold atoms was stable. With TPB dimers the incorporation of six atoms was seen at room temperature.

When Yang and colleagues applied TPB to gold aggregates on an alumina surface, modelling a real catalyst, they observed several new aggregates, only 15 Å in size. The ability of TPB to trap gold atoms on both a gold and an oxide surface demonstrates its potential as a redispersion agent. Further research would need to be done to determine how to remove the ligand molecules from the surface after use, so as to avoid poisoning the catalyst. Yang and colleagues suggest photochemical bleaching or ozone etching as potential routes to do this. *HP*

ORGANIC SYNTHESIS

Catalytic compatibility

Science **335,** 1471–1474 (2012)

Diazomethane (CH_2N_2) is widely used in organic synthesis, for example as a reagent in esterification, dipolar cycloaddition and epoxidation. However, the use of diazomethane is limited by its toxicity and explosiveness, and even its precursors are unsafe.

Now, Bill Morandi and Erick Carreira from the Laboratory of Organic Chemistry in Zürich have developed a reaction in which diazomethane is formed *in situ* and then consumed by a metal catalyst, which avoids significant build-up of it, removing the potential hazard. A catalyst for this reaction has to be made compatible with the strongly oxidizing and strongly alkaline aqueous conditions in which the diazomethane is formed. The team tested catalysts formed by a range of transition metals and the highest yields were obtained with an iron porphyrin, which is non-toxic and inexpensive.

In Morandi and Carreira's method, diazomethane is generated in the aqueous phase and migrates to the organic phase, where it reacts with the catalyst. Separating the catalyst from the harsh conditions required to generate diazomethane means it resists decomposition. The researchers achieved up to 89% yield for the cyclopropanation of a range of alkenes using the iron porphyrin catalyst. A water-soluble rhodium catalyst gave no product, but a hydrophobic one resulted in 45% yield, demonstrating the importance of the catalyst being compatible with the organic phase. *HP*

Written by Stuart Cantrill, Stephen Davey, Anne Pichon and Heather Powell

Correction

In the Research Highlight 'Force microscopy takes charge' (N. Withers *Nature Chem.* **4,** 336; 2012), Fabian Mohn's surname was spelled incorrectly. Corrected in the HTML and PDF versions after print, 26 April 2012.

blogroll

Space dinosaurs!

Highly respected organic chemist publishes a Perspective in *JACS*, chaos ensues.

Ronald Breslow — past president of the ACS and Priestley medallist in 1999 — is a "well-respected research lion", in the words of SeeArOh at Just Like Cooking (http://go.nature.com/xO3kep). Few would dispute his place in the chemistry firmament. With many achievements behind him, surely he has earned the right to close a Perspective article in *JACS* (http://go.nature.com/i5DyA2) on the possible origin of homochirality in biological molecules with a chuckle — suggesting that humans would be better off not meeting the advanced dinosaurs, with amino acids of the opposite chirality, who may populate distant corners of the universe!

Apparently not. At least, not according to some of the dinosaur-focused bloggers/newshounds out there — such as Dinosaur Tracking (http://go.nature.com/tB19fD) or Discovery (http://go.nature.com/g31ylj). In their defence, however, they were reacting to the press briefing that the ACS somewhat mystifyingly released. It was mystifying because it ignored the six pages of discussion about the origin of chirality of amino acids to focus on the last two 'space dino' sentences.

The combination of Breslow and space dinos proved tempting for some chemistry bloggers, with SeeArrOh covering the paper and its final words in the good-humoured tone in which they were surely intended. Paul Bracher, who blogs at ChemBark (http://go.nature.com/ZibD8l), has worked in the origin-of-life field, and actually discussed the scientific content of the paper — how refreshing! But Bracher certainly doesn't mince his words giving his opinion of the ACS press office.

The final twist in the dinosaur's tale came in the comments on Just Like Cooking and ChemBark: hasn't Breslow written something quite similar in *Tetrahedron Letters* (http://doi.org/bs5wzc) and the *Israel Journal of Chemistry* (http://doi.org/csf7xr)? The similarity is such that, at the time of writing, *JACS* has removed the paper from its website, citing copyright concerns.