LIQUID CRYSTALS

Inverted influences

Nature **485,** 86–89 (2012)

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

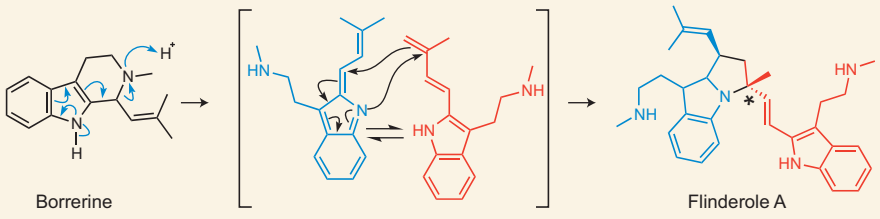
BIOMIMETIC SYNTHESIS

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.

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*