Unhealthy crystals

The toxicity of crystals is a somewhat mysterious phenomenon. It is believed that the negative surface charge and irregular morphology of crystals such as alpha-quartz or calcium pyrophosphate dihydrate might be responsible for the rupture of biological membranes and hence cause inflammation. But the detailed mechanism that causes these effects was hitherto unclear.

Molecular dynamics simulations of the interaction between a model bilayer membrane formed of dimyristoyl phosphatidylcholine (the prevailing phospholipid in our cellular membranes) and crystalline calcium pyrophosphate dihydrate (the mineral that accumulates in osteoarthritic joints and sometimes causes pain and swelling) performed by researchers in Florida now reveals the molecular mechanism responsible for the membrane rupture (Wierzbicki A., Dalal P., Madura J. D. & Cheung H. S. *Journal of Physical Chemistry B* **107**, 12346–12351; 2003). A crystal in the vicinity of the membrane is electrostatically attracted towards it. The interaction with the crystal limits the mobility of the phospholipids on the external side of the membrane relative to that of the phospholipids on the internal side. This difference perturbs the internal layer, which loses its ordered arrangement, becomes thinner, and eventually leaks water. Based on these findings, the authors propose a way to inactivate crystal surfaces and thus ameliorate crystal-induced arthritic conditions.

Mapping exciton motion

The exciton — a bound electron–hole pair — is a very useful particle responsible for the light emission in light-emitting diodes and lasers. Excitons can be confined within nanometre-scale structures such as quantum dots for short periods of time (around a nanosecond) before recombining to produce light. Using near-field photoluminescence imaging spectroscopy, Japanese and Canadian researchers have now managed to track the motion of an exciton within a quantum dot (K. Matsuda, *et al. Physical Review Letters* **91**, 177401; 2003). Kazunari Matsuda and colleagues created excitons by exciting a GaAs quantum dot with laser light delivered through a 20-nm aperture, and then collected the light emitted as a result of exciton recombination. Thanks to the high spatial resolution of their system (30 nm), they were able to collect numerous photoluminescence images and construct a detailed map of the emission, which reflects the spatial distribution of the excitons. Excitons were found to be spread over the quantum dot, whereas biexcitons (bound double excitons) were more strongly localized to its centre. Although the imaging technique is complex, Matsuda and colleagues expect that it can be applied to other nanoscale systems.

Monitoring oscillatory gels

Many materials in living organisms exhibit self-sustaining oscillations of chemical and/or physical organization, for example, the peristaltic motion of the intestinal tract. Some artificial materials have similar properties and thus the potential for mimicking biological functions. Now researchers in Japan have developed a polymer-gel system that undergoes colour changes such that the oscillations can be observed on the surface of the gel for the first time (Takeoka, Y., Watanabe, M. & Yoshida, R. *Journal of the American Chemical Society* 125, 13320–13321; 2003). The gel consists of two monomers, *N*-isopopylacrylamide, which controls the swelling and collapse of the gel in response to temperature, and a Ru-complex. Under certain chemical conditions, the Ru-complex ion catalyses a specific reaction (BZ) in which the ion is alternately oxidized and reduced as the reaction propagates, resulting in colour changes. When the gel is simultaneously subjected to changes in temperature, the swelling response of the gel occurs in parallel with the BZ reaction, resulting in waves of colour changes concomitant with the peristaltic motion. The colour tunability of these gels have the potential for use in devices used for determining oscillations in nonlinear chemical reactions.

Combinatorial synthesis

Modern drug discovery often involves screening small molecules for their ability to bind to selected protein targets or to modulate biological pathways in living organisms. The synthesis strategy most commonly used to produce collections of small molecules involves appending different sets of building blocks to a common molecular skeleton. But lack of efficient access to collections of synthetic compounds that have skeletal diversity has so far been a limiting factor in the discovery of small molecules. Stuart Schreiber and colleagues report the development of an alternative synthesis strategy that allows the generation of collections of compounds representing many molecular skeletons (Burke, M. D., Berger, E. M. & Schreiber, S. L. *Science* 302, 613–618; 2003). This approach, which is as efficient as previous methods of synthesis, can be used to generate a collection of compounds comprising overlapping matrices of molecular skeletons and appended building blocks in both enantiomeric and diastereomeric forms. The authors believe that this systematic screening of collections of compounds will allow us to gain fundamental insight into the interplay between building blocks, stereochemistry and skeletal diversity, and its role in small-molecule/protein interactions.

CRYSTALLINE MACROMOLECULAR REPLICANTS

Topotactic reactions — those in which there is a structural or orientational relationship between reactant and product — are of great interest to solid-state chemists because their nucleation step is easier than for chemical reactions in which there is no such relationship. Unfortunately, these reactions usually involve intramolecular processes that require laborious crystal engineering techniques. James Wuest and colleagues at the Université de Montréal now propose a synthetic strategy using permeable molecular crystals, specifically designed to allow external agents to enter, react within their pores and form new single-crystal structures which retain the original crystalline framework (*Angewandte Chemie International Edition* 42, 5303–5306; 2003). The construction of these permeable molecular crystals relies on the association of sticky molecules called tectons, which form directional interactions with neighbours according to well-established motifs. Topotactic processes caused by external reagents within the pores can also be used to cross-link the molecular crystals covalently, thereby creating supramolecular building blocks that can behave as permanent crystalline molecular replicas. The authors believe that this simple and generic way of designing stable porous networks with reactive interiors could be used to make a wide range of macromolecular materials with controlled ordered structures that would be impossible to obtain by traditional approaches.