

has been aimed at understanding whether a membrane compartment encapsulating a genetic polymer can self-replicate. Previous investigations have shown that it is possible to synthesize lipid vesicles that can grow and divide, transferring any enclosed genetic material; however, there has been less success in the generation of a genetic polymer that can also self-replicate.

Modified amino-sugar nucleotides may provide a means of creating artificial cells using chemical copying of genetic material without the need for enzymes. This is because amino groups are more nucleophilic than the 3'-hydroxyl groups of ribo- and deoxyribo-nucleotides, therefore the formation of phosphoramidate-DNA polymers without enzymes is far more rapid than that of either DNA or RNA. Advancing this prospect, a team of researchers led by Jack Szostak of the Howard Hughes Medical Institute investigated further modifications to the chemistry of amino-sugar nucleotides to achieve fast and non-enzymatic copying with high fidelity.

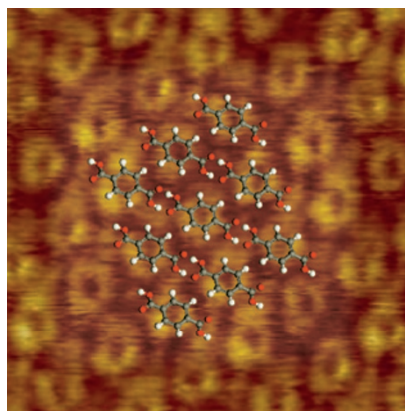
They synthesized 3'-amino-sugar analogues of RNA nucleotides, each with an imidazole-activated phosphate. In the presence of a template strand of homopolymeric DNA, RNA or phosphoramidate DNA, they found that addition of the complementary activated monomer resulted in the spontaneous synthesis of phosphoramidate DNA; however, a lack of fidelity was encountered in the copying of adenine bases due to its apparent weak bond with the thymine-based 3'-amino-sugar. Thermodynamic data was used to analyse the strength of these bonding interactions, and Szostak and colleagues rectified the problem by using a 2-thiothymidine monomer to promote a stronger bond in this pairing, which increased the accuracy and the rate of replicating polymerization. Through the use of these A, G, C and thioT monomers, it was further demonstrated that fast and accurate chemical copying of template genetic material could also be achieved using mixed sequence templates. *JH*

SELF-ASSEMBLY

Laying down the law

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Understanding the self-assembly of small molecules into predictable patterns on surfaces — particularly at the liquid/solid interface — is important in the bottom-up synthesis of functional nanostructures. That these processes occur spontaneously reveals that the associated overall free-energy change is positive. There are, however, a large number of factors to the overall process, both enthalpic



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and entropic in nature, all competing with each other, and understanding their subtle balance is challenging. Now, Markus Lackinger from the Technical University of Munich and co-workers have created a Born-Haber cycle that allows them to assess the enthalpic contributions.

Lackinger and co-workers decided to apply their process to the widely studied assembly of terephthalic acid on a graphite surface from a solution of nonanoic acid. The overall enthalpy change, which is associated with molecules in solution assembling on the surface in a solvated monolayer, is difficult to measure directly. The Born-Haber approach avoids this by combining several more easily measured enthalpies: those of substrate dissolution, sublimation and deposition from a vacuum in an unsolvated monolayer. Each of these values could be assessed experimentally and they compared well with values obtained by molecular mechanics and molecular dynamics simulations. A further important contribution in the overall process is dewetting of the surface — where molecules of the solvent need to make way for the substrate — and this had to be evaluated solely through simulations.

Several surprising conclusions arise from this treatment of self-assembly thermodynamics, and they can begin to explain observed phenomena. For example, the enthalpy barrier to desorption into solution is only a small fraction of that in a vacuum — a fact that explains the mobility of large substrates in a solvated monolayer. At the same time as reducing the enthalpic benefit of self-assembly, however, solvation also reduces the entropic penalty: solvent molecules removed from the surface in the process of dewetting gain entropy, and interactions between solvent and substrate in solution mean that the solution state is not as disordered as it may first seem. *SD*

Written by Gavin Armstrong, Stephen Davey, James Hennessy and Anne Pichon

blogroll

Turf wars

Molecular modellers scoop Nobel and a publishing 'trash heap' uncovered.

Nobel season has come and gone, with this year's chemistry prize awarded to Martin Karplus, Michael Levitt and Arieh Warshel. Once more, Paul Bracher at ChemBark must be thanked for collating the runners and riders on his blog (<http://go.nature.com/qrY5o2>). That the prize was awarded for computational chemistry delighted Ash Jogalekar at the Curious Wavefunction (<http://go.nature.com/u4TEfb>), who noted that it recognized both a whole field and the lifetime achievements of the three winners. Realizing that not everyone was happy with the decision, Jogalekar's delight soon turned to frustration (<http://go.nature.com/kytmTT>) at those chemists who snipe at researchers in other fields of chemistry. As Ash put it, these 'turf wars' hardly help improve the public image of chemists.

Speaking of turf wars, a recent sting investigation reported in *Science* on open-access (OA) publishers caused a stir both in the blogosphere and the mainstream press (<http://go.nature.com/mCNMVJ>). John Bohannon, under the superb alias Ocorrafoo Cobange, sent a spoof paper describing the new (non-existent) anticancer properties of a new (equally non-existent) wonder drug to 304 OA journals. It was accepted in 157, occasionally without peer review, despite clear scientific and ethical shortcomings.

"An Open Access Trash Heap" cried Derek Lowe at In The Pipeline (<http://go.nature.com/GMJ2ST>), with his two barrels aimed directly at those journals who rip off authors for "whatever fees they can scam". Open Access advocates, including PLOS founder Michael Eisen, were quick to defend OA publishing, suggesting similar failings would also occur in subscription-only journals. As Jon Tennant, guest-blogging on Matthew Shipman's SciLogs page, pointed out, Bohannon's sting uncovered deeper issues with peer review and editorial processes in general, regardless of publishers' business models (<http://go.nature.com/hXfj5>).

Written by Alasdair Taylor, who blogs at <http://attheinterface.wordpress.com>