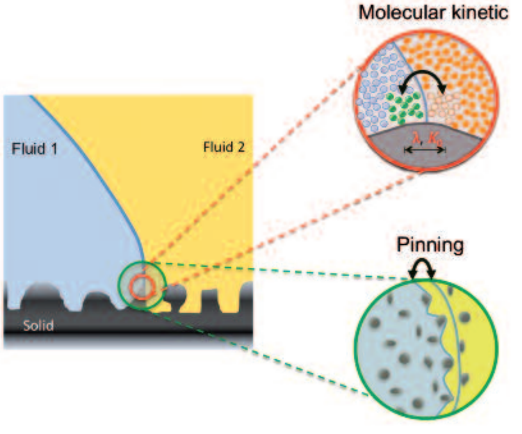
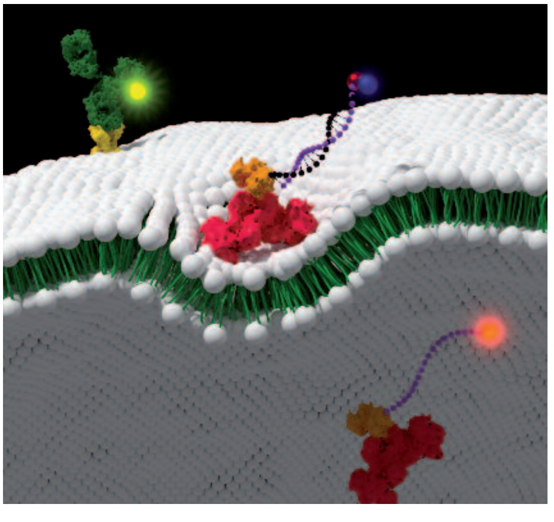
Radical orbital switching

A recent discovery made by researchers from the Australian National University and University of Wollongong appears to challenge several cornerstones of chemical reactivity (Gryn'ova G., Marshall D.L., Blanksby S.J., Coote M.L., *Nature Chem.* 2013, **5**, 474–81). According to the aufbau principle, the unpaired electron of a free radical should occupy the highest-energy orbital. However, the authors show that a broad range of distonic radical anions display so-called orbital energy-level conversion, in which their singly-occupied orbital is energetically lower than the doubly-occupied orbital(s) of the anionic functional group. As a result, the one-electron oxidation of such compounds produces high-spin species with potential applications in molecular electronics. Moreover, it is generally assumed that remote charges (beyond *c.* 5 Å separation) do not significantly affect the stability and reactivity of radicals (and vice versa), yet these distonic radical anions are more stable than their closed-shell or protonated counterparts by as much as four orders of magnitude. This ability to pH-switch radical reactivity can be harnessed to develop radical protecting groups for free-radical polymerisation and organic synthesis, and is likely to be important in radical biochemistry and, particularly, enzyme catalysis.

Thermal activation and surface wetting

The wetting of structured surfaces is critical in microfluidics, printing, self-cleaning materials and many natural phenomena. The motion of a liquid contact line over nano-textured surfaces controls the outcome of these wetting processes; however, the mechanisms involved are not understood. Physical chemists at the Ian Wark Research Institute, University of South Australia, together with international collaborators, have shown how nanoscale surface roughness influences how a surface wets (Ramiasa M., Ralston J., Fetzer R., Sedev R., Fopp-Spori D., Morhard C., Pacholski C., Spatz J. *J. Am. Chem. Soc.* 2013, **135**, 7159–71). The dynamics of the contact line on nanorough substrates is thermally activated. Both solid–liquid interactions and surface pinning strength contribute to the energy barriers, hindering the contact line motion. The activation free energy of wetting is the sum of surface wettability and surface topography contributions, linking contact line dynamics and roughness parameters. The coating of surfaces, movement of liquids through micropores and fast printing phenomena may all benefit from the application of this research.





SHIP – live cell internalisation probe

Understanding how cells internalise proteins and nanoparticles plays an important role in drug delivery, immunity and cell development.
Dr Angus Johnston and his team in the NanoMaterials for Biology group, at the Monash Institute for Pharmaceutical Sciences, have developed a new molecular sensor, SHIP (specific hybridisation internalisation probe), that enables simple, high-throughput and quantitative analysis of the uptake of materials into cells (Liu H., Johnston A.P.R. *Angew. Chem. Int. Ed.* 2013, **52**, 5744–8). By using a nucleic acid sensor that specifically quenches the fluorescence of material on the surface of the cell, the kinetics of nanoparticle and protein internalisation can be performed on live cells, without affecting the fluorescence of other cellular markers. A variety of materials, including proteins and nanoparticles, can be studied using this technique and it is likely to find application in the fields of drug delivery, cell biology and immunology.