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Molecular memories start to gel

Molecular logic devices based on switchable molecules have been mostly confined to solution. Fixing them into robust polymers should provide a technologically more attractive material.

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Images of the patterned films under ultraviolet illumination: the blue regions show the rotaxanes 'switched' by exposure to DMSO vapour. Image used with permission from ref. 1.

Molecules whose state can be switched abacus-style by moving threaded molecular beads have been fashioned into polymers, turning this potential 'information-bearing' molecular system into a robust material[1].

David Leigh of the University of Edinburgh in Scotland and his collaborators think that a polymeric 'molecular shuttle' might be better suited than solutions of the switchable molecules to applications such as sensing and data storage. They have already made a kind of logic gate from their polymer films, in which an optical output signal is switched by exposure to two chemical input signals. This change is visible to the naked eye in patterned regions of the films.

Molecular logic based on the movement, conformational changes or aggregation of molecules, triggering changes in their optical or electronic behaviour, has already been demonstrated in several systems of this sort[2–5]. In these cases, the molecules have been either in solution[2,3] or immobilized in monolayer films[4]. Typically, the idea is that some chemical change such as binding of metal ions or protonation alters a molecule's fluorescence properties, thereby providing an optical read-out signal of the chemical event. When such changes are induced by more than one chemical 'input', logic processes such as AND and OR operations can be encoded in molecular form.

The molecular shuttle[6] is one of the most appealing structures for this kind of chemical information processing. It involves a supramolecular assembly called a rotaxane, in which a hoop-shaped molecule is threaded on an axle-like molecule capped with two bulky end groups to prevent unthreading. When the axle contains two different units (stations) that interact favourably with the hoop under different circumstances, the hoop can shuttle back and forth between one and the other of them in response to external stimuli. In an early example, controlled motion of the hoop was induced electrochemically[3].

This shuttling involves no making or breaking of covalent bonds, and so it can be induced under mild conditions. The ability to switch rotaxanes between alternative states raises the possibility of encoding binary data in an array of molecular shuttles, in principle providing the extremely high storage density of one bit per molecule. This principle has been used to make electronically readable and writable molecular memories[4] from monolayers of rotaxanes sandwiched between electrodes. But, so far, many thousands of molecules are needed in these devices for the reliable and stable storage of a single bit.

The rotaxanes that Leigh and his colleagues have developed[1] are designed so that movement of the hoop between different docking positions is induced by changes in the solvent, and produces a change in the fluorescence of the assembly. The axle molecule contains a short hydrophilic station made from two glycine molecules, which can form hydrogen bonds with the hoop, and an alkyl chain where the hoop resides in polar solvents owing to a solvophobic effect. The glycine station is 'stoppered' with a bulky, fluorescent anthracene group. When the hoop binds to this station, molecular groups within its ring quench the anthracene fluorescence; when the hoop shifts further down the axle to the alkyl region, the anthracene 'lights up' again.

Leigh and colleagues showed that this switching of the optical output happened when the solvent was changed from the polar dimethylsulphoxide (DMSO, which produced a fluorescent 'on' state) to dichloromethane (where the fluorescence

was switched 'off'). Could this hoop motion be preserved in a polymeric system?

The researchers made a variant of their rotaxanes in which the non-fluorescent stopper on the axle contained two groups that could act as the initiators for polymerization of methyl methacrylate. Triggering polymerization produced rotaxanes that trail two long poly(methyl methacrylate) (PMMA) chains. The resulting polymer films were transparent and non-fluorescent: in the nonpolar PMMA environment, the hoops reside at the glycine stations and quench the anthracene chromophores.

But when the films were exposed to DMSO vapour through a patterned grid, an imprint of the grid pattern was revealed in the films when they were illuminated with UV light to induce fluorescence. Apparently, DMSO molecules lodged in the polymer network had caused the hoops to shuttle away from the glycine stations and onto the alkyl chains.

The researchers made an alternative version of their switchable polymer using hoop molecules that only quenched fluorescence when protonated. These materials could then be controlled using two chemical 'inputs': DMSO to shift the hoops, or trifluoroacetic acid vapour to protonate the hoops. The combination of these two inputs led to an output signal (either fluorescence (1) or quenching (0)) that corresponded to an INHIBIT logic gate. Patterns of data could again be written into the polymer films using grids to control which regions are exposed to vapour, creating patterned polymer 'memories'.

Although responsiveness to vapours might be useful for making chemical sensors, Leigh and colleagues think that this kind of molecular logic might be enacted in other applications using stimuli such as light, temperature, pH or electrical signals — all of which have been used previously to switch molecular shuttles in solution.

References

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