

Water greases molecular machines

Molecular machines have been designed that can fulfill roles such as molecular switches, motors, and brakes. The mechanical behavior of these constructs differs from their macroscopic counterparts. For example, the concept of a conventional liquid lubricant makes no sense at the molecular scale. Despite this, water appears to have an accelerating effect on the movement of molecular machines based on hydrogen-bonded components, as described in the September 1 online edition of *Nature Chemistry* (DOI: 10.1038/NCHEM.1744).

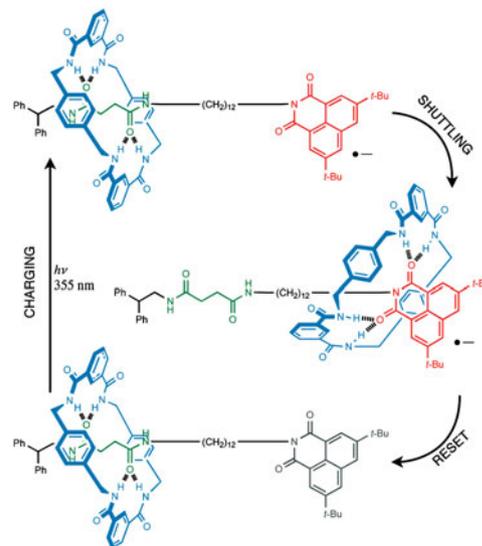
M.R. Panman of the University of Amsterdam, E.R. Kay of the University of Edinburgh, D.A. Leigh of Edinburgh and the University of Manchester, and their colleagues studied a rotaxane “molecular shuttle” in which a peptide-based macrocycle can bind to either of two hydrogen accepting “stations.” In the neutral state, the succinamide site is the more stable position, but a short pulse of UV light excites the naphthalimide group to a radical anion and induces the macrocycle to switch places.

The research team found that an addition of just 3% deuterated water to

the system brought about a twofold increase in the rate of movement, while other hydrogen bonding solvents such as methanol, ethanol, and butanol had an insignificant or negative effect. A similar effect was also found for the thermal rotation of the macrocycle around the succinamide site, where the rotation rate could be doubled by adding 5% deuterated water.

Possible straightforward explanations for this phenomenon such as changes in viscosity and solvent polarity could be ruled out as the solvent properties do not correlate with the observed trends. Instead, the researchers propose that the ability of water to form a three-dimensional hydrogen-bonded structure is key, as this can stabilize the detached state of the macrocycle and increase the probability of it leaving a binding site. The small size of the molecule also allows the structure to quickly rearrange as the parts reposition. Evidence for this is provided by observation of hydrogen bonding between the water and the macrocycle peptide linkages in infrared spectroscopy.

This research provides useful insight into the translation of biological motors, where it has already been speculated that water plays an important role in “lubricating” protein folding and molecular



The structure and operation cycle of the molecular shuttle in acetonitrile. In the uncharged state, the macrocycle (blue) binds to the succinamide (green) site, but laser excitation of the naphthalimide (red) site to a radical anion renders it a better hydrogen bond acceptor and induces the macrocycle to change places. Reproduced with permission from *Nature Chem.* **8** (2013), DOI: 10.1038/NCHEM.1744. © 2013 Macmillan Publishers Ltd.

rotors. While it is not possible to study biological systems in solvents other than water, synthetic machines such as these are able to put the principle to the test in a range of different solvents.

Toby Lockwood

Energy Focus

Perovskite-based planar heterojunction solar cell achieves record efficiency

Researchers looking for ways to reduce the cost of solar photovoltaics have recently begun studying perovskites. These are inexpensive materials with the same crystal structure as calcium titanium oxide, from which they draw their name. To date, researchers have demonstrated a series of photovoltaic cells that incorporate perovskites in relatively complex device architectures that generally require complex processing steps and high temperatures. Now, Mingzhen Liu and colleagues at the University of Oxford

have demonstrated a simple planar perovskite-based solar cell that avoids these issues and achieves over 15% efficiency. They reported their results in the September 19 issue of *Nature* (DOI: 10.1038/nature12509; p. 395).

The active layer in photovoltaic cells has three essential functions: absorption of light, generation of free carriers, and transport of those carriers to their respective contacts. Researchers have recently investigated the potential of organometallic trihalide perovskites to play one or more of these roles in nanostructured solar cells, although in all of these cases, other materials were also present to serve as a structured scaffold. The Oxford researchers hypothesized that it might be possible to build a high-efficiency device

using perovskites with a simple planar heterojunction architecture, eliminating the scaffolding and using the perovskite material to serve all three essential functions of the active layer. This would put the device in the same structural category as industrially relevant silicon and thin-film solar cells, and therefore be an important step forward.

To test this hypothesis, the researchers fabricated devices based on a fluorine-doped tin oxide (FTO)-coated glass (the device anode), followed by a spin-coated layer of compact TiO₂ as an electron-sensitive contact. Next, they deposited a layer of the mixed halide perovskite CH₃NH₃PbI_{3-x}Cl_x using two different methods: two-phase vapor deposition, and spin-coating. Both