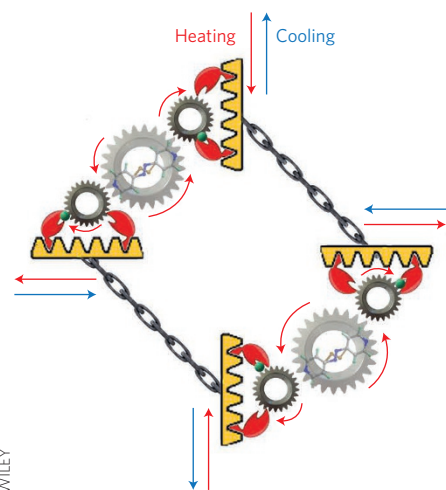


MOLECULAR MACHINES

**A cog in the machine**

*Angew. Chem. Int. Ed.* **55**, 14628–14632 (2016)



Proton transport is ubiquitous in biology — for example, through the hydrogen-bonded networks of protein channels. While some synthetic proton shuttles have been realized, such systems have rarely been used as a switching mechanism in functional materials. Now, Osamu Sato and colleagues at Kyushu University and the Institute for Materials Science in Japan have designed supramolecular organic frameworks (SOFs) that contract and expand at the macroscale on intramolecular proton shuttling.

The researchers first prepared a SOF from an azodipyridine and a tetracarboxylic acid. These two groups are hydrogen-bonded to one another to form a rhombic grid and act as the basis of a rack-and-pinion (gear) cascade. On a

temperature change, the pyridine groups facilitate an intra-carboxyl proton shuttle, resulting in rotation of the azodipyridine and a correlated translation of the tetra-acid. In other words, rotary motion is converted to linear motion. Density functional theory calculations suggested that ionization of the carboxyl groups kinetically aids the azodipyridine pedalling motion. This thermally-induced process involves a single crystal to single crystal phase transition. Propagation of the motion through the network causes a macroscopic expansion and contraction of the crystal of around 1.82 mm (123–333 K).

BLB

NANOMATERIALS

**Covalent welding**

*Nano Lett.* **16**, 7282–7289 (2016)

Carbon-based materials have been rapidly adopted in real-world applications. However, many of their outstanding electrical and mechanical properties only occur at the nanoscale, which imposes constraints on the design of macro-sized devices. In order to explore the potential of carbon nanomaterials, 2D building blocks have to be assembled into 3D nanostructures, ideally without compromising the nanoscale performance.

Liangbing Hu and co-workers at the University of Maryland have now proposed a route to bulk materials with enhanced electrical conductivity and tensile strength from carbon nanofibre networks. In the pristine matrix, amorphous interweaved nanofibres interact with one another via weak van der Waals forces. High temperature Joule heating

induced by ultrafast electric current pulses enables the gradual merging of adjacent carbon nanofibres where they intersect. The heating effect also leads to further carbonization of the nanofibres, and the resulting 3D matrix has high crystallinity and strong chemical and physical bonding. Compared to the amorphous nanofibres, the electrical conductivity of the covalently interconnected carbon network was more than four orders of magnitude higher. Interestingly, the same conditions didn't prove successful when applied to other carbon-based nanostructures. In highly crystalline carbon nanotubes, Joule heating resulted in deformation of the strong C–C bonds and overall deterioration of their electronic properties.

OB

NEUROMORPHIC COMPUTATION

**Clever analog memristors**

*Front. Neurosci.* **10**, 482 (2016)

The electrical resistance state of a memristor is a function of the history of currents and voltages previously applied to the device. Such behaviour closely resembles the activity-dependent plasticity of biological synapses, making memristors natural candidates to implement learning processes in neuromorphic hardware architectures. In analog memristors the possible resistance states are multi-valued, offering a closer analogy to biological synapses. However, the implementation of unsupervised learning processes based on networks of analog memristors has been rarely reported.

Now, Erika Covi and colleagues at the National Research Council in Italy and the University of Southampton in the UK have reported a network of 125 analog memristors capable of reproducing unsupervised learning tasks. Each memristor is a TiN/HfO<sub>2</sub>/TiN heterostructure and the researchers exploited filamentary resistive switching processes to mimic the synaptic plasticity therein. The memristor network connects two layers of artificial neurons — the so-called pre- and post-neurons. A 5 × 5 square array of pre-neurons, each of which act as a black or white pixel, provides images of letters as input signals to the network. The first activated post-neuron defines the output signal. After an unsupervised training process, the network was able to associate one specific post-neuron to each different letter being shown, demonstrating successful recognition. This was also verified for noisy or incomplete input images.

GP

Written by Bryden Le Bailly, Olga Bubnova, Ai Lin Chun and Giacomo Prando.

NANOPARTICLES

**Moved around**

*Sci. Adv.* **2**, e1601462 (2016)

Biological processes such as encapsulation, recognition and transportation are complex. Many methods have been used to translate the efficiency and specificity of these processes into simple and smart functional materials. Now, inspired by the way cells engulf debris and repair damage in the body, researchers in the US have created polymer-based droplets that can recognize, pick up and drop off hydroxyapatite nanoparticles from surfaces.

Hydroxyapatite — the main component in bone — is rich in calcium. To create a droplet that will bind to hydroxyapatite, Todd Emrick and co-workers at the University of Massachusetts functionalized phosphorylcholine-polyolefin with catechol and then shook an aqueous solution of this polymer in an organic solvent. When pumped through a flow cell over hydroxyapatite-coated substrates under laminar flow, the polymer-stabilized oil-in-water emulsion droplets were able to pick up the hydroxyapatite nanoparticles. Pick-up efficiency was lower under basic conditions and in solutions containing calcium ions. Furthermore, substrate composition also affected pick-up: greater efficiency was seen with PDMS and mica over plastic films. Exploiting this substrate-dependent pick-up efficiency, Emrick and colleagues showed that nanoparticles picked up from silicon substrates can be dropped off downstream on a polydopamine-coated silicon substrate. Such surface-to-surface nanoparticle transport is useful for transferring nanoparticle properties between materials.

ALC