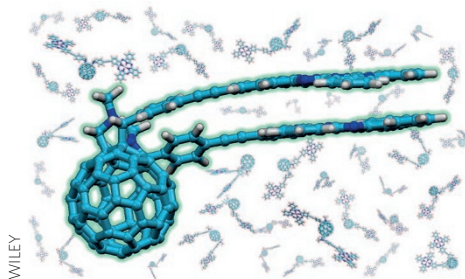


FULLERENES

Doubling down on C₆₀

Angew. Chem. Int. Ed. <http://doi.org/f3ms3z> (2016)



The controlled synthesis of fullerenes with two functional groups, known as bis-adducts, is a topic of keen interest for exploiting these molecules in materials. However, this is not trivial given the number of near-identical double bonds on C₆₀. Previous controlled syntheses have only been possible by tethering with a covalently linked spacer. Now, Dirk Guldi of the Friedrich-Alexander University in Nuremberg and Tomás Torres from the Autonomous University of Madrid, along with colleagues in Spain, Germany, Japan and the US, have devised a supramolecular-directed functionalization approach to form C₆₀ bis-adducts with regio-, stereo- and atropselectivity.

Zinc (II) phthalocyanine (Pc) aldehydes were mixed with *N*-methylglycine and C₆₀ to give the right- (*P*) and left-handed (*M*) helical forms of a single bis-adduct.

Without this control, up to 130 adducts with different regio- and stereochemistry could form. Non-covalent (π -stacking) interactions between the two Zn^{II}Pc arms give solely the *cis* C₆₀ addition product. Remarkably, the bis-adduct was isolated in 14% yield, a 2,800-fold increase from the theoretical yield, and significantly higher than those from untethered reactions (~1.4%). This also represents the first atropselective reaction with fullerenes; the atropisomerism results from the restricted rotation of the two macrocycles to give a fullerene derivative with point, axial and helical chirality.

BLB

NANOTHERMODYNAMICS

The power of one atom

Science **352**, 325–329 (2016)

A heat engine converts thermal energy into mechanical energy. While macroscopic engines were the basis of the industrial revolution, scaling down heat engines to the smallest possible scale might be the key to investigate fundamental concepts at the boundaries between quantum mechanics and thermodynamics. Now, Johannes Roßnagel, Kilian Singer and colleagues from the University of Mainz and other institutions in Germany report the realization of a single-atom heat engine.

The atom (a⁴⁰Ca⁺ ion) is confined along the axis of a conical electromagnetic trap. At the narrow end of the trap, an electric field noise generator acts as a hot reservoir. When the ion heats up, it moves towards a region of

higher potential energy, against the restoring force of the trap, and thus producing work. At the wide end of the cone, a blue-detuned laser cools the ion, sending it back to the narrow end and thus setting up a closed thermodynamic cycle. With each oscillation, the work done by the atom accumulates and if left unchecked would result in increasingly larger and larger amplitudes. To keep the system under steady state, the authors use a second cooling laser as a damping mechanism. In this way, they can measure the energy associated with each oscillation.

The efficiency of the engine is around 0.3%, but in terms of power generated per mass of active material, the value — 1.5 kW kg^{−1} — is similar to that of a car engine.

AM

GRAPHENE SPINTRONICS

Rashba or not Rashba?

Phys. Rev. Lett. **116**, 166102 (2016)

Thanks to its exceptionally long spin diffusion lengths and relaxation times, graphene is an ideal material for spintronics. However, the intrinsic spin–orbit coupling, arising from the atomic number of carbon atoms, is considered to be too weak to drive a spin-to-charge conversion via the inverse spin Hall effect. The Rashba interaction in graphene-based heterostructures is considered a more efficient mechanism, leading to the so-called inverse Rashba–Edelstein effect. The current lack of systematic experimental studies has not yet allowed researchers to discriminate clearly between these two scenarios.

Now, Sergey Dushenko and colleagues from Osaka University, along with collaborators at other Japanese institutions, demonstrate that the spin-to-charge conversion in single-layer graphene is surprisingly dominated by the intrinsic spin–orbit coupling. Single-layer graphene was deposited on a thin-film substrate made of yttrium iron garnet. The magnetization precession of the low-damping ferrimagnetic insulator was driven by an external magnetic field and efficiently injected spin currents in graphene under conditions of ferromagnetic resonance — the so-called spin pumping effect. The spin-to-charge conversion was then monitored by varying the charge carrier type and density of graphene by means of electrolytic gating. According to the authors, the actual dependence of the charge current on the gate voltage clearly ruled out any role of the Rashba interaction in the process.

GP

Written by Ai Lin Chun, Bryden Le Bailly, Alberto Moscatelli and Giacomo Prando.

NANOCRYSTALS

An enzyme that does it all

Proc. Natl Acad. Sci. USA **113**, 5275–5280 (2016)

Biological systems use a variety of ways to synthesize inorganic materials from aqueous solution. Control over material composition and structure is typically achieved through a complex process involving the assembly of different proteins or other biomolecules. Now, Bryan Berger and colleagues at Lehigh University in the US show that biomineralization is possible using a single enzyme, offering a green route to manufacture functional nanomaterials.

The researchers combined a purified form of the cystathionine γ -lyase enzyme with cadmium acetate and L-cysteine. The enzyme, which is obtained from the aerobic bacteria *Stenotrophomonas maltophilia*, is known to catalyse the production of H₂S from L-cysteine to form CdS in cell cultures. Using this combination, the researchers obtained monodisperse and crystalline CdS nanocrystals (2–4 nm in diameter) with optoelectronic properties similar to those synthesized in cells or by chemical methods. When L-cysteine was substituted with glutathione — which is not a substrate for the enzyme and is a capping agent known to stabilize water-soluble CdS nanocrystals — no nanocrystals formed, confirming that L-cysteine is the sulfur source. Replacing L-cysteine with Na₂S as the sulfur source still led to nanocrystal formation, suggesting that the enzyme can regulate nanocrystal growth independent of H₂S production. These results show that this single enzyme is capable of both catalysing the reactive precursors for mineralization and templating the subsequent nanocrystal growth.

ALC