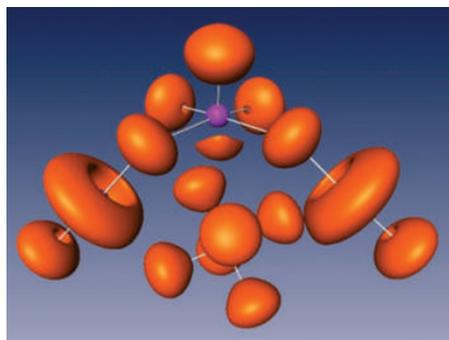


GROUP 18 COMPOUNDS

The krypton factor

J. Am. Chem. Soc. **132**, 3533–3542 (2010)

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Krypton, as expected for a relatively inert group 18 element, has a limited chemistry. Routes to all of its known compounds involve KrF_2 , which has been well characterized. There are a number of compounds featuring KrF^+ and Kr_2F_3^+ , but the Lewis acid–base adducts of KrF_2 (such as $\text{MoOF}_4 \cdot \text{KrF}_2$) have not been structurally characterized in full. Furthermore, there are no known compounds in which it acts as a ligand towards a main-group atom.

Now, Gary Schrobilgen and colleagues from McMaster University in Hamilton have prepared and fully characterized a KrF_2 coordination compound, $[\text{BrOF}_2][\text{AsF}_6] \cdot 2\text{KrF}_2$. They synthesized it by removing the XeF_2 species from a similar compound under dynamic vacuum at -78°C . Adding KrF_2 to a suspension of $[\text{BrOF}_2][\text{AsF}_6]$ in anhydrous HF produced

the unusual compound. It was stable in anhydrous HF for several days at -78°C and for over an hour at 25°C .

X-ray diffraction measurements performed at -173°C showed that the structure featured a central trigonal pyramidal BrOF_2^+ cation given a pseudo-octahedral geometry by the fluorine atoms from the KrF_2 and AsF_6 groups. The Kr–F bonds with bridging fluorine atoms are elongated by about 0.05 \AA with respect to free KrF_2 . This indicates more covalent character than in KrF^+ or Kr_2F_3^+ salts, showing that in this case KrF_2 is behaving as a coordinating ligand instead of a fluoride ion donor. The differences in Kr–F stretching modes shown by Raman spectroscopy confirmed this result, which was further explored computationally.

SURFACE CHEMISTRY

Hot to trot

Angew. Chem. Int. Ed. **49**, 1944–1948 (2010)

The chemistry that can take place on a solid surface is, in general, dictated by its composition and structure. The effects of harsh conditions such as high temperatures, however, must be considered in processes such as chemical vapour deposition (CVD). Now Gloria Tabacchi of the University of Insubria, Italy, and colleagues from the University of Padua, have used calculations to understand the activation of a CVD precursor molecule on a surface. They simulated the behaviour of an octahedral copper complex on a hydroxylated silica

surface at high temperature. The complex bears two pentanedionate ligands and an ethylenediamine ligand and is known to form Cu_xO nanostructures when deposited on a silicon surface.

Using first principles molecular dynamics, Tabacchi and colleagues identified three distinct types of motion. The complex initially undergoes slow back-and-forth diffusion on the surface for a few picoseconds, described by Tabacchi and co-workers as a “bump and rock” motion. This is followed by a regime of very limited movement that lasts for approximately 16 picoseconds, during which the complex remains within a very small region on the surface. Subsequently, the behaviour of the complex changes drastically, moving very quickly across the surface in a rolling motion while undergoing large conformational changes.

Tabacchi and co-workers examine how the complex bends and flexes as it passes through these regimes of motion by studying changes in the copper–ligand bond length. They observe that during the fast movement regime the hot surface vibrationally excites the complex, producing large bond oscillations and inter-ligand interactions that activate the complex for reaction and increase the chance of reactive collisions.

NANOPARTICLES

Sunscreen size studies

Nature Nanotech. **5**, 271–274 (2010)

Titania nanoparticles are a common ingredient in sunscreen with a high sun-protection factor (SPF). The small particles mean that such products are no longer the opaque white creams that were considered unattractive, and this has increased the uptake of these sunscreens. However, concerns have been raised about the safety of nanoparticles in such treatments. Although nanoparticles have been shown not to penetrate beyond the top layer of skin, titania nanoparticles react with UV light to produce potentially dangerous reactive oxygen species (ROS).

Now, Amanda Barnard from the Materials Science and Engineering division of CSIRO in Australia has made a theoretical comparison of the three key properties — SPF, transparency and ROS generation — of titania nanoparticles in sunscreen. The models show that both SPF and transparency increase as the nanoparticles become smaller. The two most common phases of titania — rutile and anatase — have different reactivity for the production of ROS, however, and the amount of each phase present is dependent on nanoparticle size. This interplay results in

ORGANIC SUPERCONDUCTORS

Turning on hydrocarbons

Nature **464**, 76–79 (2010)

Superconductivity in organic compounds is quite rare; important examples include charge-transfer salts and metal-doped all-carbon materials, such as graphite or fullerenes. Relatively high transition temperatures (T_c) have been reported for calcium-intercalated graphite (CaC_6 ; $T_c = 11.5 \text{ K}$) and $\text{RbC}_5\text{S}_2\text{C}_{60}$ ($T_c = 33 \text{ K}$). It is notable that these examples all feature extensive π -electron networks.

Now, Yoshihiro Kubozono and colleagues from several institutions in Japan have discovered superconductivity in a simple hydrocarbon doped with an alkali metal. The hydrocarbon is picene, which is flat and resembles five benzene rings fused together. When crystals of picene were heated to 440 K with potassium metal in an evacuated glass tube, they changed from white to black and showed metallic properties. The researchers made a range of compositions from just one atom of potassium per picene molecule to over five. When cooled, the compositions with around three atoms of potassium showed superconducting behaviour, with T_c ranging from 6.5 to 18 K ; although only accessible by liquid-helium cooling, this is still extremely high for organic superconductors.

The suddenness of the transition — the temperature range between the onset of the transition and its finish — for picenes (at around 0.5 K) is similar to that observed in CaC_6 , but much more rapid than for K_3C_{60} (over 10 K) or the recently discovered pnictide superconductors. Kubozono and colleagues have also investigated intercalating other alkali metals into picene, and although the sodium and rubidium materials did not show superconductivity, the caesium analogue did at 6.9 K .

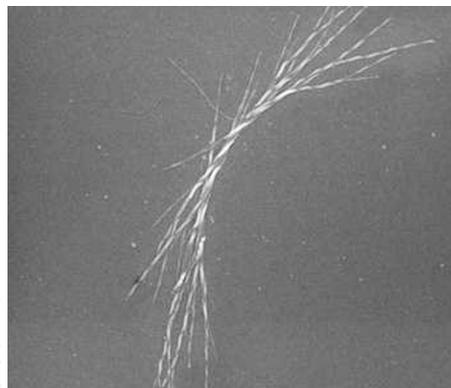
a peak in ROS production for nanoparticles at approximately 33 nm in size.

On balancing these factors, Barnard found that the most effective and least toxic nanoparticles would be those with an average diameter of less than 13 nm. The only toxicity taken into account in the study is that related to ROS generation, so further studies into risks associated with nanoparticles of this size remain important.

NANOPARTICLE SELF-ASSEMBLY

An illuminating twist

Science **327**, 1355–1359 (2010)



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The assembly of nanoparticles into complex architectures results in interesting morphologies and properties — helices, in particular, have continued to intrigue chemists and materials scientists. Now, an international team led by Sharon Glotzer and Nicholas Kotov at the University of Michigan has used visible light irradiation to control the self-assembly of cadmium telluride (CdTe) nanoparticles into helical ribbons.

Semiconductor CdTe nanoparticles were dispersed in an aqueous solution, with a lower concentration of stabilizer (thioglycolic acid) than that normally used — the concentration influences the geometry, dipole and reactivity of the nanoparticles. After precipitation and re-dispersion in solution, the nanoparticles self-assembled over 72 hours into left- and right-handed helical ribbons, aggregated into bundles of the same chirality. A closer look at the ageing process revealed that it was accompanied by the oxidation of tellurium — from Te^{2-} to Te^0 — and the replacement of some tellurium by sulfur. The cadmium sulfide, predominant in the resulting CdS/CdTe nanoparticles, is most likely to be located at the surface, preventing re-crystallization into thin CdTe nanowires.

Comparing the ageing processes under visible light irradiation and in the dark revealed that in both cases the assemblies evolve through a variety of unusual shapes to

form bundled straight nanoribbons. In the dark, however, the ribbons remain straight, but under continuing irradiation with visible light photo-oxidation of CdS occurs, which increases the charge–dipole forces and causes the formation of helices. Stronger twisting was obtained under more intense irradiation. Calculations show that the formation of particular architectures — chains, ribbons or sheets — depends on the interplay between face–face attraction and electrostatic repulsion forces.

CHARGE TRANSPORT

Electron hopping in a hairpin

Angew. Chem. Int. Ed. **49**, 2385–2388 (2010)

Long-distance charge transport is an important characteristic for the components of organic electronic devices. Research has recently turned to DNA as a scaffolding material because it can hold molecules in helical arrangements, for example through the substitution or modifications of its base pairs. Perylene-based polyaromatic molecules have previously been attached to phosphate groups and incorporated into oligonucleotides. On photoexcitation, two adjacent perylene diimide (PDI) units were found to be coupled owing to co-facial π – π stacking. Now, Michael Wasielewski, Frederick Lewis and co-workers at Northwestern University have investigated the charge transport across such PDI moieties.

They prepared a series of DNA hairpins in which two to four adjacent bases in the double helix were substituted for a PDI moiety in a zipper-like manner — adjacent to each other but on opposite strands. UV–visible spectra of the species showed that adjacent, π – π stacked PDI moieties were exciton-coupled.

In each hairpin, one of the PDI units was reduced into its radical ion. The resulting singly reduced duplexes were then investigated by electron paramagnetic resonance spectroscopy. These revealed that an unpaired electron hopped between the two PDI units of the dimer, but only between two units of the trimer, and three units of the tetramer. The fact that not all PDI moieties participated in electron sharing could be due to a difference between energy levels across the moieties, or to imperfect stacking. The rapid electron hopping rate observed (above 10^7 s^{-1}) suggests that such DNA–PDI systems hold promise for charge transport materials.

The definitive versions of these Research Highlights first appeared on the *Nature Chemistry* website, along with other articles that will not appear in print. If citing these articles, please refer to the web version.

blogroll

Save our moles

ACS meeting highlights, a periodic table of science bloggers, and atomic spectroscopy knitwear

The spring ACS meeting prompted the usual flurry of blog posts, albeit possibly slightly reduced because of scarce internet connections in the venue. Katharine Sanderson blogged for Nature News at ‘In the field’ (<http://go.nature.com/nuRrX9>) on topics ranging from green chemistry to the reasons why Rosalind Franklin missed her chance to decode the structure of DNA. If you see people wearing t-shirts saying ‘Save the mole!’ or ‘Moles are units!’ then they’ve probably read Mitch’s post on the Chemistry Blog (<http://go.nature.com/wUbejd>). He reported from a talk given by Paul Karol of Carnegie Mellon University, who “argued passionately for the removal of the mole from the base set of units from the International System of Units.” The main point of his argument is that “a mole is just a numerical value, and has as much physical meaning as the term dozen.” Could this do for chemistry what the downgrading of Pluto did for astronomy?

When David Bradley of Science Base (<http://go.nature.com/iD847q>) issued a call for people to suggest their blogs to fill in his periodic table of science blogs, he probably wasn’t expecting the gold rush that followed. In a few short hours, people across the world responded by blog comment or twitter and all 118 elements were claimed. Our own blog nabbed sodium (Na for *Nature Chemistry*), whereas Nature Networks bagged neon (Ne). The final version is neatly colour-coded for various scientific disciplines and the diversity is such that I’d be surprised if anyone followed all of them.

And finally, have you ever wanted a scarf in the pattern of the emission spectrum of your favourite element? Well, now you can buy one, thanks to Becky Stern at The Stern Lab (<http://go.nature.com/8vxJnn>). They’re about six-and-a-half-feet long (around two metres) and look very stylish — the perfect gift for the chemist in your life.