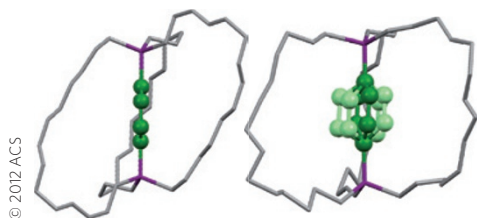


MOLECULAR MACHINES

Intracrystalline inflation

J. Am. Chem. Soc. **134**, 12458–12461 (2012)



There is much interest in the design of functional materials from the bottom up, so that their properties can be directly related to their molecular structures. Recently, a number of materials have been reported in which the properties depend on the control of motion within individual molecules. Now, Wataru Setaka and Kentaro Yamaguchi from Tokushima Bunri University in Japan have reported a compound that they describe as a ‘molecular balloon’, which ‘inflates’ when the temperature is increased.

These researchers have previously reported the synthesis of a molecular gyrotop — a system in which a phenylene rotor could freely rotate inside a cage formed by three long alkyl loops. The molecular balloon that they now describe was discovered when studying an intermediate structure in that prior synthesis. The alkyl-chain cage was constructed using ring-closing metathesis — producing a cage in which each chain contains an alkene. In contrast to the saturated alkyl cage of their original gyrotop — which is approximately spherical — an X-ray crystal structure of this compound (at 100 K) showed a cage that was ‘dented’ with the alkenyl chains collapsed inwards.

Analysis of the line shapes in the ^2H NMR of a deuterium-labelled version of this gyrotop enabled Setaka and Yamaguchi to estimate the rotation rate of the phenylene rotor. At low temperatures (<300 K), the phenylene ring flips slowly because its rotation is hindered by the collapsed cage structure. When the temperature was raised above 310 K, however, continuous rotation was observed.

To investigate the origin of this temperature-dependent behaviour the researchers performed a high-temperature X-ray crystallographic analysis. As expected, free rotation of the phenylene at high temperature results in a disordered structure in the centre of the cage. In addition, however, at this temperature the cage is inflated — apparently to avoid the steric clash with the rotor. The effect of this inflation is also seen in the macroscopic properties of the crystal — when the cage is inflated, the density of the unit cell is dramatically reduced. SD

‘ON WATER’ CHEMISTRY

Interfacial understanding

Angew. Chem. Int. Ed. **51**, 7981–7984 (2012)

Whereas nature chose water as the solvent to carry out the reactions necessary for life, chemists tend to choose organic media and even go to great lengths to make sure that they are working under dry conditions. One of the reasons for not using water is simple:

CLUSTER CHEMISTRY

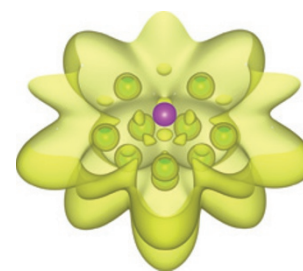
Filling in the blanks

Fully occupied orbitals endow compounds with particular stability — the Lewis 8-electron octet and the Langmuir 18-electron rule, which correspond to filled s , p and s , p , d orbitals, respectively, are firmly established. By the same token, it seems that 32-electron systems should be stable by virtue of their additional 14 electrons (the capacity of the f orbitals). Although $4f$ shells of lanthanides are too compact to allow the construction of 32-electron systems, the more diffuse $5f$ shells of the actinides have proven suitable. In previous work, 32-electron bonding has been proposed for endohedral clusters in which an actinide occupies the central cavity of a ligand cage, for an isoelectronic series based on $\text{U}@C_{28}$ and another based on $[\text{Pu}@M_{12}]^{2-}$ (where M is lead or tin).

In a separate study, another endohedral actinide@cage compound was characterized — an icosahedral silicon cage (Si_{20}) encapsulating a thorium atom. Noticing that $\text{Th}@Si_{20}$ falls short of fulfilling the 32-electron rule by only 8 electrons, a team of researchers from France and Finland led by Jean-Pierre Dognon and Pekka Pyykkö has now investigated its counterparts with heavier



actinides uranium, neptunium, plutonium, americium and curium. Calculations on these compounds revealed large binding energies — increasing from uranium to curium — that point to very stable actinide@ Si_{20} clusters (pictured). The actinides’ $7s$, $7p$, $6d$ and $5f$ electrons were found to participate in hybridization with the Si_{20} cage, in each case yielding an anionic 32-electron system. Furthermore, an analysis of the topology of electron densities — how electronic charges are distributed between two atoms, which provides an understanding of their bonding characteristics — also showed significant electron sharing occurred between actinide and silicon atoms.



These different analyses are all in agreement that notable covalency exists between the central actinides and the surrounding cages. Within this isoelectronic series, however, not all of the clusters have the same symmetry, and the plutonium- and americium-based structures were the most distorted. These findings provide significant support to the reliability of the 32-electron rule. Moreover, calculations also show that placing $[\text{U}@Si_{20}]^{6-}$ between two lanthanum centres leads to a neutral compound without disrupting its structure — which points to the possibility of further assembling actinide@ Si_{20} clusters into more complex architectures. AP

Chem. Sci. **3**, 2843–2848 (2012)

most organic reagents are not very soluble in it. This property, however, can actually be used to accelerate reaction rates in what are known as 'on water' reactions. These can occur for certain transformations when water-insoluble reactants are vigorously stirred in water to give aqueous emulsions or suspensions. Such reactions are thought to occur at the interface between the immiscible phases, but they are not fully understood. For example, the complicated structure of emulsions makes it difficult to quantify the effects of important reaction parameters such as water surface area and surface-to-volume ratio.

Now, Wilhelm Huck and colleagues at Radboud University Nijmegen and the University of Cambridge, have used a fluidic approach to control the interfacial features of two model 'on water' reactions to better understand and quantify the role played by the water surface. The reaction set-up consisted of a cross-junction fed by tubes containing either water or reagents dissolved in toluene. Monodisperse plugs of toluene and water form at the junction and, by controlling the flow rate of the immiscible phases or changing the diameter of the tubing, Huck and colleagues could control the interfacial surface-to-volume ratio of the reacting plugs. Using this set-up they studied the cycloaddition reaction of quadricyclane with diethyl azodicarboxylate (DEAD), and the ene reaction between β -pinene and DEAD, reactions known from previous studies to exhibit 'on water' behaviour.

Huck and colleagues observed a linear relationship between the percentage conversion of reactants into products (as analysed by NMR spectroscopy) and the interfacial surface area between the plugs, strongly supporting a role for the surface in enhancing the rate. They also calculated a decrease in the activation energy of the reactions when 'on water' in comparison to in toluene, which supports a mechanism involving a hydrogen-bond-stabilized transition state. GA

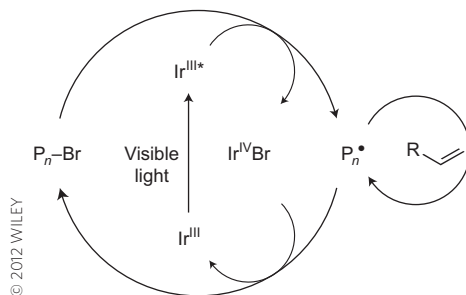
POLYMER CHEMISTRY

Alive with light

Angew. Chem. Int. Ed. <http://doi.org/fz5hsn> (2012)

The properties of any given polymeric material are influenced significantly by the molecular weights of the individual polymer chains and also the distribution of those values. Methods that offer very good control over these parameters are therefore prized in polymer synthesis. In particular, controlled living radical polymerization has attracted much attention and acronyms such as ATRP (atom transfer radical

polymerization) and RAFT (reversible addition fragmentation chain transfer polymerization) are now commonplace in the chemical literature. Some relatively recent developments in this area have focused on how to control these reactions with an external stimulus, such as light or an applied electrical current.



Previous attempts to photoregulate living radical polymerization processes have been somewhat limited, either giving rise to poor molecular weight control or only enabling the initiation step — rather than the subsequent chain-growth steps — to be controlled. Now, Brett Fors and Craig Hawker from the University of California, Santa Barbara, have shown that the living radical polymerization of methacrylates can be turned on and off at the flick of a (light) switch by using a commercially available iridium-based photoredox catalyst. The Ir(III) catalyst absorbs visible light to give an excited-state Ir(III)* species that can react with an alkyl bromide initiator to produce an alkyl radical and an Ir(IV)Br complex. The alkyl radical initiates the polymerization of a methacrylate monomer to give a propagating polymer radical, which can then react with the Ir(IV)Br species to give a dormant polymer chain with a bromide end group, at the same time as regenerating the original Ir(III) complex.

In the presence of light, this process (pictured) continues to cycle in this fashion, although the alkyl bromide is no longer a small-molecule initiator but a polymer chain. When the light is turned off, however, the propagation reaction stops almost immediately — importantly, Fors and Hawker show that no chain termination occurs during this resting period. When the light is turned back on an hour later, the polymerization reaction resumes and continues until the light source is removed once more. Further evidence for the living nature of the system is provided through the efficient formation of a diblock copolymer. SC

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey and Anne Pichon.

blogroll

But is it art?

Practical synthetic chemistry shows an artistic side with synthesized doodles, logos and colouring-book molecules.

It's been a busy summer in the blogosphere! Between 'arsenic life' and the newly discovered Higgs boson, science blogs seem more relevant than ever. In all the fuss, though, they may have overlooked some promising chemical artists in their midst.

First up, let's turn our attention to the 2012 London Olympic Games. Chemists at the University of Warwick decided to commemorate the event by synthesizing a new molecular version of the famed Olympic rings. ChemConnector's Antony Williams explains (<http://go.nature.com/oCerSJ>) that a chalkboard 'doodle' evolved into a synthesis of olympicene; the RSC's ChemSpider SyntheticPages later published (<http://go.nature.com/N4OM3p>) the step-by-step details. IBM-Zurich (of pentacene-imaging fame) posted a series of finely resolved atomic images to Flickr (<http://go.nature.com/uPSHll>).

Next we'll talk high fashion. At *Chemistry World*, Phillip Broadwith noted (<http://go.nature.com/VYtBww>) a neat undergraduate synthesis project: making a hydrocarbon to match a clothing label's logo. After just three steps, Plymouth University's Mark Cockerton and Simon Belt had their target...but still no word on whether they've tied up a sponsorship deal with the apparel company in question!

Speaking of synthetic art, we'd be remiss not to wish a happy belated birthday to organic chemist K. C. Nicolaou. Blogger BRSM prepared a special tribute (<http://go.nature.com/jkKft8>) to his penchant for flashy colours and ancient mythology in the figures that adorn his papers and the graphical abstracts that accompany them. A small group of Blogroll's 'usual suspects' — including Adam Azman, Chemjobber and Dr Freddy — re-imagined K.C.'s classic molecules with new artistic twists. Perhaps these entries will finally prompt publication of that chemical colouring book (<http://go.nature.com/dWIUMI>).

Written by See Arr Oh, who blogs at <http://justlikecooking.blogspot.com>