

ChemComm

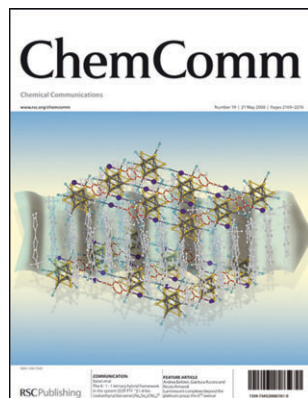
Chemical Communications

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IN THIS ISSUE

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Cover

See Batail *et al.*, pp. 2194–2196. Three types of noncovalent interactions direct the topology and achieve space partition. Image reproduced by permission of Anne-Lise Barrès, Abdelkrim El-Ghayoury, Leokadiya V. Zorina, Enric Canadell, Pascale Auban-Senzier and Patrick Batail from *Chem. Commun.*, 2008, 2194–2196.

CHEMICAL SCIENCE

C33

Drawing together research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences, showcasing newsworthy articles and significant scientific advances.

Chemical Science

May 2008/Volume 5/Issue 5

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FEATURE ARTICLE

2185

Luminescent complexes beyond the platinum group: the d^{10} avenue

Andrea Barbieri, Gianluca Accorsi and Nicola Armaroli*

The tuneability of the emission colour from red to blue, the variety of chemical structures, and significant progress in the emission performance make luminescent d^{10} complexes increasingly appealing as alternatives to traditional, but expensive, precious metal or rare earth emitting compounds.

The image shows a portion of the periodic table of elements. A blue arrow points to the right, highlighting a group of elements. The elements highlighted are Cu (29), Zn (30), Ag (47), Cd (48), and Au (79). These elements are labeled as 'd¹⁰ ions'. The periodic table is color-coded by groups, with the highlighted elements in a darker shade of blue.

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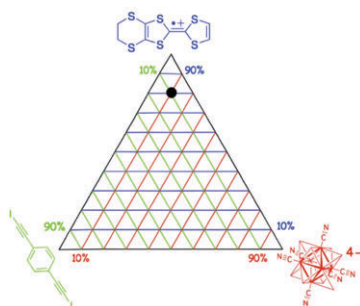
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2194

The 8 : 1 : 1 ternary hybrid framework in the system [EDT-TTF^{•+}][1,4-bis(iodoethyl)benzene][Re₆Se₈(CN)₆]⁴⁻: dual noncovalent expression of the octahedral halogen-bond hexa-acceptor nanonode

Anne-Lise Barrès, Abdelkrim El-Ghayoury, Leokadiya V. Zorina, Enric Canadell, Pascale Auban-Senzier and Patrick Batail*

Three types of noncovalent interactions direct topology, achieve space partition.

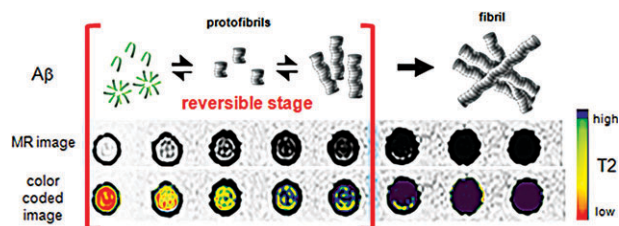


2197

Nanoparticle assisted magnetic resonance imaging of the early reversible stages of amyloid β self-assembly

Jin-sil Choi, Hyuck Jae Choi, Dae Chul Jung, Joo-Hyuk Lee and Jinwoo Cheon*

Co@Pt–Au nanoparticles, which have enhanced magnetism and high stability in aqueous media, are utilized in conjunction with MRI to monitor the structural evolution of A β assemblies, especially A β protofibrils in the early reversible stages.

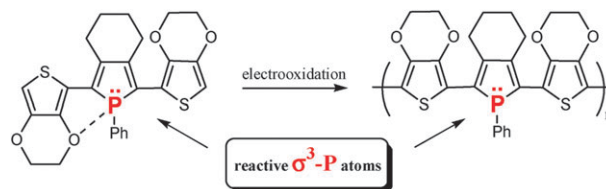


2200

Synthesis, electronic properties and electropolymerisation of EDT-capped σ^3 -phospholes

Vincent Lemau de Talancé, Muriel Hissler,* Ling-Zhi Zhang, Tamás Kárpáti, László Nyulászi,* Dolores Caras-Quintero, Peter Bäuerle* and Régis Réau*

The synthesis and physical properties of a new mixed σ^3 -phosphole–EDOT oligomer are described. This compound self-rigidifies due to an unprecedented P–O interaction and can be electropolymerised affording polymers incorporating functionalizable σ^3 -P moieties.

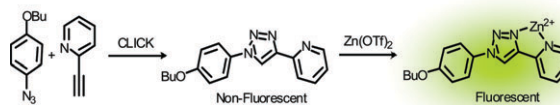


2203

1,3-Dipolar cycloaddition of alkynes to azides. Construction of operationally functional metal responsive fluorophores

David Schweinfurth, Kenneth I. Hardcastle and Uwe H. F. Bunz*

Click chemistry and metalloresponsive fluorophores: a copper catalyzed 1,3-dipolar cycloaddition of 4-butoxyphenylazide to 2-ethynylpyridine furnishes a dipolar cycloadduct that displays a strong fluorescence enhancement upon exposure to different divalent metal cations.



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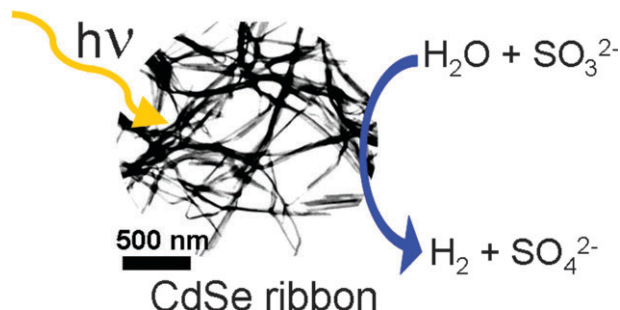
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2206

First demonstration of CdSe as a photocatalyst for hydrogen evolution from water under UV and visible light

F. Andrew Frame, Elizabeth C. Carroll, Delmar S. Larsen, Michael Sarahan, Nigel D. Browning and Frank E. Osterloh*

CdSe nanoribbons show activity for photocatalytic H₂ evolution from aqueous Na₂S/Na₂SO₃ solution under visible light irradiation. The activity is due to a quantum size effect. This is the first metal selenide active for this reaction.

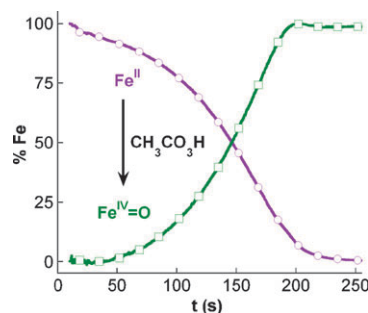


2209

Unexpected kinetic complexity in the formation of a nonheme oxoiron(IV) complex

Xiaopeng Shan and Lawrence Que, Jr.*

The stoichiometric formation of [Fe^{IV}(O)(L)(NCMe)]²⁺ from its iron(II) precursor and 1 equiv. peracid is kinetically more complex than expected, and an oxoiron(IV)-peracid adduct is proposed as the primary oxidant.

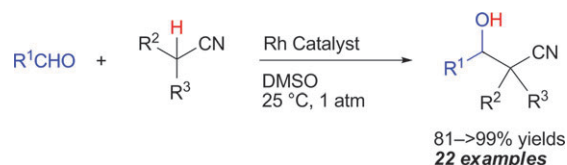


2212

Rh^I-catalyzed aldol-type reaction of organonitriles under mild conditions

Akihiro Goto, Kohei Endo, Yu Ukai, Stephan Irle and Susumu Saito*

An aldol-type reaction of organonitriles with aldehydes was catalyzed by a Rh^I(OR) species under ambient conditions, with the loading of catalyst precursor (as low as 0.005 molar equiv.) and organonitrile (as low as 2 molar equiv.) lower than previously reported.

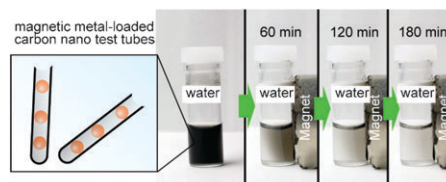


2215

Template synthesis of water-dispersible and magnetically responsive carbon nano test tubes

Hironori Orikasa,* Nobuhiro Inokuma, Somlak Ittisanronnachai, Xiao-Hui Wang, Osamu Kitakami and Takashi Kyotani

Water-dispersible and magneto-responsive carbon nano test tubes with a uniform size were synthesized, and the effect of magnetic interaction on the water dispersibility was analyzed in a semi-quantitative manner.





Surface enhanced Raman scattering

SERS theme issue

Since its discovery over 30 years ago SERS has enjoyed a high level of interest, which has increased significantly in the last few years. *Chem Soc Rev* issue 5, 2008 is a compilation of 2 critical and 15 tutorial reviews on the application of surface enhanced Raman scattering that brings together leading exponents in researching the technique and its applications. The result is a balanced portfolio that covers the main areas of current development and makes this a truly diverse yet up-to-date body of papers on the state of the SERS field.

Papers include:

Elena Bailo and Volker Deckert
Tip-enhanced Raman scattering

De-Yin Wu, Jian-Feng Li, Bin Ren and Zhong-Qun Tian
Electrochemical surface-enhanced Raman spectroscopy of nanostructures

Surbhi Lal, Nathaniel K. Grady, Janardan Kundu, Carly S. Levin, J. Britt Lassiter and Naomi J. Halas
Tailoring plasmonic substrates for surface enhanced spectroscopies

X.-M. Qian and S. M. Nie
Single-molecule and single-nanoparticle SERS: from fundamental mechanisms to biomedical applications

Matthew J. Banholzer, Jill E. Millstone, Lidong Qin and Chad A. Mirkin
Rationally designed nanostructures for surface-enhanced Raman spectroscopy

Guest editors:



Duncan Graham
University of
Strathclyde



Roy Goodacre
University of
Manchester

"ERS has emerged from the debates over the theory behind the phenomenon to come of age as a powerhouse of the modern spectroscopic world and this theme issue highlights the significant areas where SERS can be applied with unparalleled performance."

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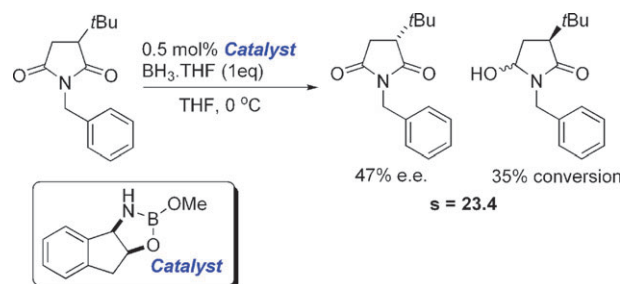
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2218

Kinetic resolution of racemic pyrrolidine-2,5-diones using chiral oxazaborolidine catalysts

Mike D. Barker, Rachel A. Dixon, Simon Jones* and Barrie J. Marsh

Chiral oxazaborolidine catalysts derived from *cis*-1-amino-indan-2-ol have been shown to be highly effective catalysts for the kinetic resolution of racemic pyrrolidine-2,5-diones with selectivity factors of up to 23 obtained with 0.5 mol% catalyst. The selectivity of the catalyst was very sensitive to the nature of the nitrogen protecting group.

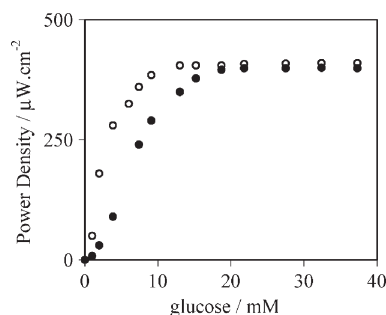


2221

A 280 $\mu\text{W cm}^{-2}$ biofuel cell operating at low glucose concentration

Nicolas Mano

We report the highest power biofuel cell, 280 $\mu\text{W cm}^{-2}$, operating at the lowest concentration to date: 5 mM glucose concentration.

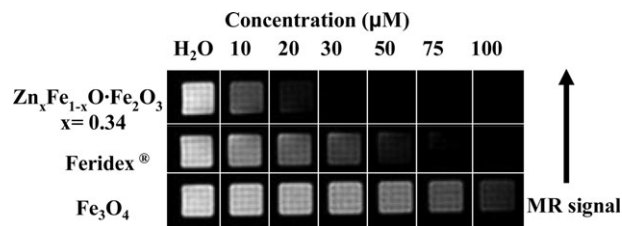


2224

Zinc ferrite nanoparticles as MRI contrast agents

Carlos Bárcena, Amandeep K. Sra, Girija S. Chaubey, Chalermchai Khemtong, J. Ping Liu and Jinming Gao*

Mixed spinel hydrophobic $\text{Zn}_x\text{Fe}_{1-x}\text{O} \cdot \text{Fe}_2\text{O}_3$ (up to $x = 0.34$) nanoparticles encapsulated in polymeric micelles exhibited increased T_2 relaxivity and sensitivity of detection over clinically used Feridex®.

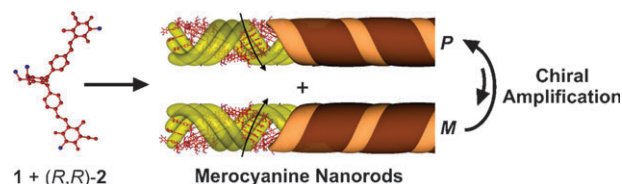


2227

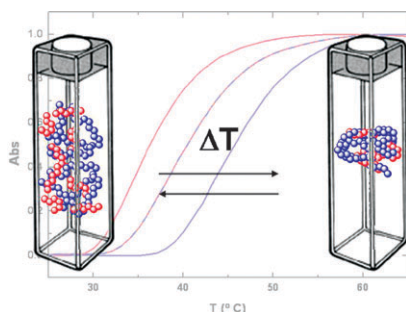
Time-dependent amplification of helical bias in self-assembled dye nanorods directed by the sergeants-and-soldiers principle

Andreas Lohr and Frank Würthner*

A pronounced sergeants-and-soldiers directed chiral amplification is observed for the self-assembly of merocyanine dye nanorods and the amplification process is shown to become slower for decreasing fraction of sergeant molecules.



2230

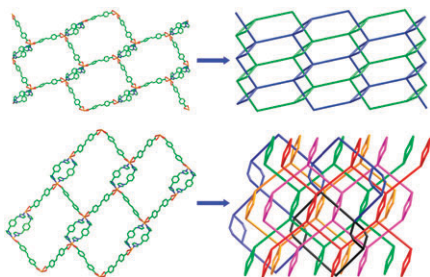


Fine-tuning the transition temperature of a stimuli-responsive polymer by a simple blending procedure

Francisco Fernández-Trillo, Jan C. M. van Hest, Jens C. Thies, Thierry Michon, Ralf Weberskirch and Neil R. Cameron*

Binary mixtures of well-defined, stimuli-responsive elastin-based side-chain polymers show a single transition temperature that depends on blend composition.

2233

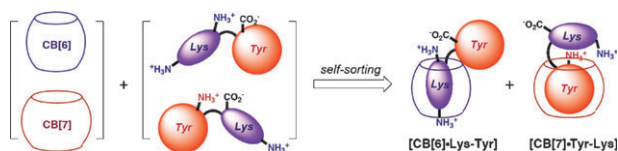


Unusual parallel and inclined interlocking modes in polyrotaxane-like metal-organic frameworks

Jin Yang, Jian-Fang Ma,* Stuart R. Batten* and Zhong-Min Su

We report here two unusual polyrotaxane-like metal-organic frameworks of $[\text{Co}_2(1,3\text{-bix})_2(\text{bpea})_2]$ **1** and $[\text{Cd}_4(1,4\text{-bix})_4(\text{bpea})_4] \cdot 4\text{H}_2\text{O}$ **2**, where both species contain loops and rods that are interlaced in a highly rare “parallel” fashion in **1**, but, uniquely, in an “inclined” fashion in **2**.

2236

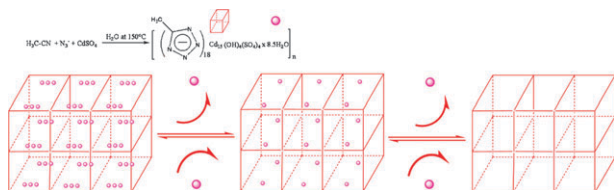


Sequence recognition and self-sorting of a dipeptide by cucurbit[6]uril and cucurbit[7]uril

Mikhail V. Rekharsky, Hatsuo Yamamura, Young Ho Ko, N. Selvapalam, Kimoon Kim* and Yoshihisa Inoue*

Cucurbit[7]uril forms very strong complex with zwitterionic dipeptide Phe-Gly with affinity exceeding 10^7 M^{-1} .

2239



Reversible shrinkage and expansion of a blue photofluorescent cadmium coordination polymer and *in situ* tetrazole ligand synthesis

Hong Deng,* Yong-Cai Qiu, Ying-Hua Li, Zhi-Hui Liu, Rong-Hua Zeng, Matthias Zeller and Stuart R. Batten

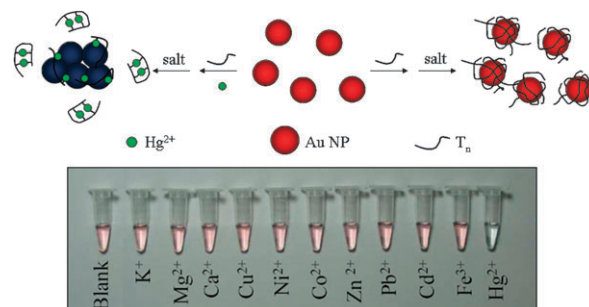
The metal-organic framework $[\text{Cd}_{15}(\text{SMT})_{18}(\text{OH})_4(\text{SO}_4)_4]$ with an unprecedented $\text{Cd}_3(\mu_3\text{-OH})(\mu_3\text{-SO}_4)$ core and two kinds of tetrazole coordination modes was formed by self-assembly and *in situ* synthesis of the 5-MT tetrazole ligand.

2242

Detection of mercury(II) based on Hg^{2+} -DNA complexes inducing the aggregation of gold nanoparticles

Chi-Wei Liu, Yi-Ting Hsieh, Chih-Ching Huang, Zong-Hong Lin and Huan-Tsung Chang*

A DNA-Au NP probe for sensing Hg^{2+} using the formation of DNA- Hg^{2+} complexes through T- Hg^{2+} -T coordination to control the negative charge density of the DNA strands—thereby varying their structures—adsorbed onto Au NPs.

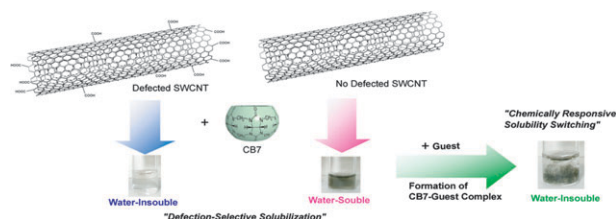


2245

Defection-selective solubilization and chemically-responsive solubility switching of single-walled carbon nanotubes with cucurbit[7]uril

Tomoki Ogoshi,* Ayumi Inagaki, Tada-aki Yamagishi and Yoshiaki Nakamoto*

Single-walled carbon nanotubes (SWCNTs) were homogeneously suspended in aqueous media with cucurbit[7]uril (CB7).

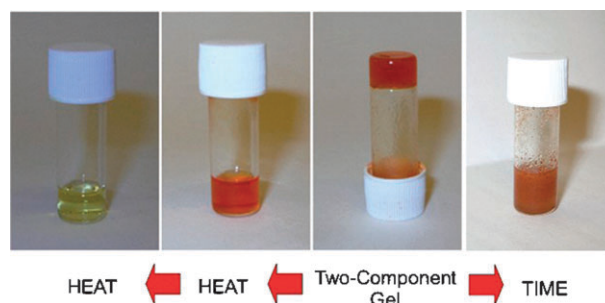


2248

Metastable two-component gel—exploring the gel-crystal interface

Jamie R. Moffat and David K. Smith*

A two-component system in which molecular recognition rapidly leads to the formation of a homogeneous molecular gel that subsequently aggregates *via* fibre-fibre interactions to yield microcrystals.

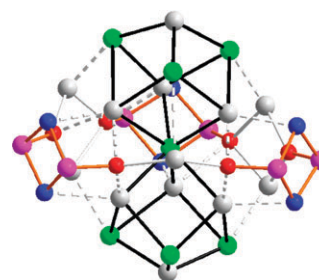


2251

Synthesis and structure of the Li_{13} cage $[\{\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{Li}_2\}_3(\text{LiCl})_6\text{Li}(\text{Cl}/\text{O}^t\text{Bu})_{0.5}(\text{thf})_7]$, containing a $[\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianion

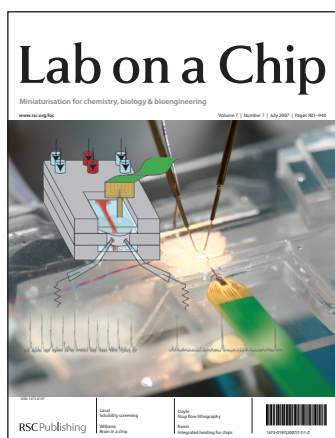
Wesley Ting Kwok Chan, Dana Eisler, Felipe García, Silvia Gonzalez-Calera, Mary McPartlin, James V. Morey, Robert E. Mulvey, Sanjay Singh,* Alexander Steiner and Dominic S. Wright*

The first complex containing the $[\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianion has been obtained.



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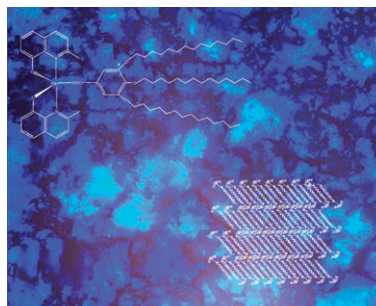
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2254

A “jellyfish” shaped green emitting gallium(III)-containing metallomesogen

Daniela Pucci,* Iolinda Aiello, Anna Bellusci, Alessandra Crispini, Irene De Franco, Mauro Ghedini and Massimo La Deda

The first example of a gallium(III)-based liquid crystal has been synthesized and structurally characterized, giving rise to a new smart multifunctional complex being also a good emitting species.

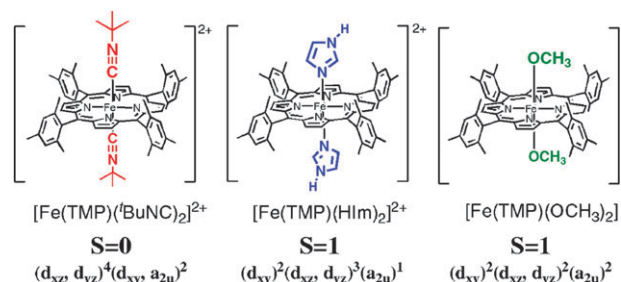


2257

Control of electronic structure of a six-coordinate iron(III) porphyrin radical by means of axial ligands

Akira Ikezaki, Hideyuki Tukada and Mikio Nakamura*

Addition of *tert*-butylisocyanide (*t*BuNC) to a CD₂Cl₂ solution of the iron(III) tetramesitylporphyrin (TMP) radical cation [Fe(TMP[•])(ClO₄)₂] at 195 K leads to the formation of [Fe(TMP[•])(*t*BuNC)₂]²⁺ with an *S* = 0 (*d*_{xy}, *d*_{yz})⁴ (*d*_{xy}, *a*_{2u})² ground state.

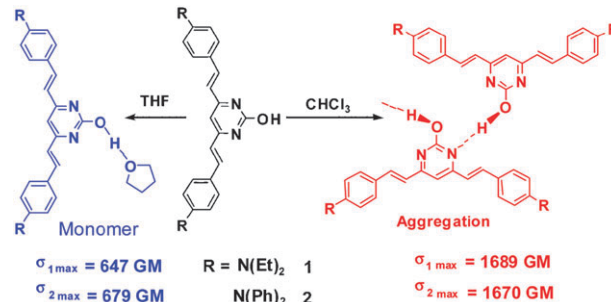


2260

Two-photon absorption enhancement induced by aggregation due to intermolecular hydrogen bonding in V-shaped 2-hydroxypyrimidine derivatives

Zijun Liu, Pin Shao, Zhenli Huang,* Bo Liu, Tao Chen and Jingui Qin*

The aggregation-induced large enhancement of two-photon absorption due to intermolecular hydrogen bonding is observed in solution.

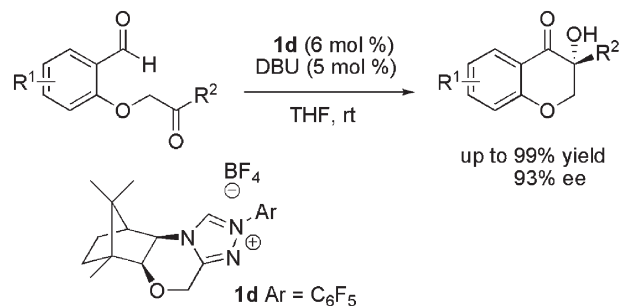


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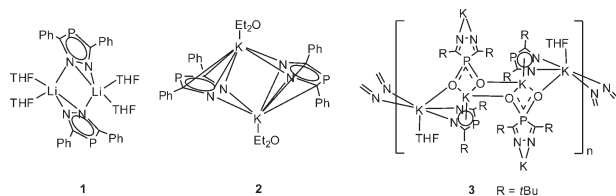
D-Camphor-derived triazolium salts for catalytic intramolecular crossed aldehyde–ketone benzoin reactions

Yi Li, Zhen Feng and Shu-Li You*

A series of triazolium salts has been synthesized from D-camphor and the *N*-heterocyclic carbene derived from **1d** and DBU could catalyze the intramolecular crossed aldehyde–ketone benzoin reaction in excellent yields with high ees.



2266

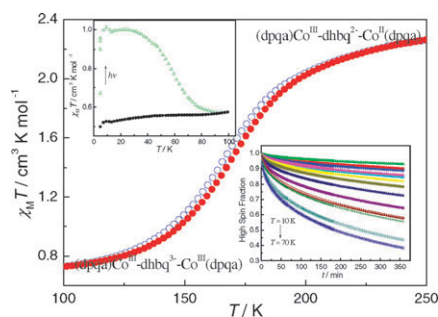


Structural diversity of 1,2,4-diazaphospholide complexes with alkali metals

Li Wan, Chengfu Pi, Lan Zhang, Wenjun Zheng,*
Linhong Weng, Zhenxia Chen and Yong Zhang

Several alkali metal complexes bearing 1,2,4-diazaphospholide ligands have been investigated and they represent novel structural motifs with σ -, π -bonding between the metal and the ligands.

2269

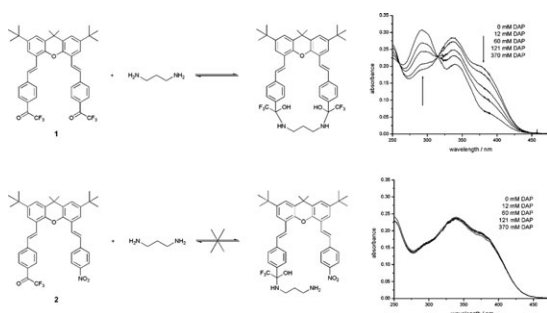


Side-effect of ancillary ligand on electron transfer and photodynamics of a dinuclear valence tautomeric complex

Bao Li, Jun Tao,* Hao-Ling Sun, Osamu Sato,*
Rong-Bin Huang and Lan-Sun Zheng

A cobalt complex was prepared and studied by X-ray diffraction, electrochemistry, ESR, thermally and photo-induced magnetic measurements. The results show that the ancillary ligand finely tuned structural factors and intermolecular interactions.

2272



Chemosensor for the optical detection of aliphatic amines and diamines

Susanne Reinert* and Gerhard J. Mohr

Two new chemosensor dyes with either one or two trifluoroacetophenone recognition moieties have been investigated in terms of reversibly interacting with amines and diamines to form hemiaminals causing changes in absorbance. The pre-organised structure of one of these chemosensors enhanced the selectivity towards diamines..

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Chemical Science

High levels of inorganic arsenic found in milk made from rice

Arsenic exposure from rice milk

Researchers have found that levels of arsenic in rice milk exceed EU and US drinking water standards.

Andrew Meharg and colleagues at the University of Aberdeen, UK, have shown that people drinking rice milk are exposed to high levels of inorganic arsenic. It is well known that rice can contain high levels of, predominately inorganic, arsenic – a known human carcinogen. However the levels of inorganic arsenic in milk made from rice, a cow milk alternative for vegans and lactose intolerant sufferers, have not previously been of concern.

Meharg's team analysed samples of rice milk to see if inorganic arsenic transfers from the rice into the milk. They tested commercially available and home-made milks, made from globally sourced white and brown rice grains. And they also looked at arsenic levels in soy and oat milk.

EU regulations set limits on the amount of arsenic allowed in drinking water, and the US specifically limits inorganic arsenic



levels. Neither closely regulates arsenic in foods, and it is not clear which category rice milk falls into.

Meharg found that all the commercial rice milks exceeded the EU standard for water of $10 \mu\text{g l}^{-1}$ and 80 per cent also

All the rice milks tested exceeded the EU drinking water standards

failed the US standard of $10 \mu\text{g l}^{-1}$ inorganic arsenic. The median total arsenic value was seven times greater than those found in soy and oat milk samples.

David Polya at the University of Manchester, UK, is an expert on the risks of environmental chemicals to humans, and says that the research highlights 'an inconsistency in the regulatory treatment of carcinogens, such as arsenic, between food and drink. Groups particularly at risk, such as vegans, are not identified by average exposure estimates,' he adds.

Meharg says that his research group has recently received funding to begin breeding rice plants that take up less arsenic. He also intends to characterise the bio-availability of arsenic from rice in humans to add to the evidence that this exposure route is concerning.

Harriet Brewerton

Reference

A A Meharg *et al.*, *J. Environ. Monit.*, 2008, **10**, 428 (DOI: 10.1039/b800981c)

In this issue

Cleaning up after nerve agents

Single-step destruction method for organophosphate chemical warfare unveiled

Zooming in on nanoparticles' defects

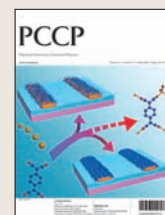
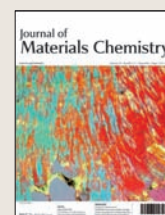
Bumpy surfaces are vital for nanoparticles catalytic activity

Interview: In the beginning....

Kenso Soai and Joanne Thomson discuss the origin of chirality in life

Instant insight: Nano-forms of carbon

Juan Luis Delgado, María Ángeles Herranz and Nazario Martín explore the cutting-edge in nanostructures made from carbon



A snapshot of the latest developments from across the chemical sciences

Research highlights

Puzzle of unexpectedly high levels of deuterated ammonia in space cracked

Solving a smelly space mystery

Researchers in Sweden have developed a new method to account for the vast abundance of deuterated compounds in space.

Terry Frankcombe and Gunnar Nyman at the University of Gothenburg in Sweden have focussed their interest on ammonia, a gas with a pungent odour. 'The fraction that is deuterated vastly exceeds what would be statistically expected,' says Frankcombe. 'We have developed a combined dynamics and statistically based model to investigate the formation of NH_2^+ , one of the ammonia precursors. Our model leads us to suggest a new explanation for how the deuterium enrichment happens during the formation of the ion. In all isotopically substituted $\text{NH}^+ + \text{H}_2$ reactions in which both hydrogen and deuterium are present, the NHD^+ product is preferred.'

More earthly applications have partly motivated this work: 'In collaboration with the Copenhagen Centre for Atmospheric Research, Denmark, isotope effects have



been used to understand better the composition of Earth's atmosphere and pin down sources and sinks for various species in the atmosphere,' says Frankcombe. But that isn't all. This is also an interesting system to study simply because developing a practical yet accurate treatment is challenging, he explains.

Chris Williams, a theoretical chemist at Ohio State University, Columbus, US, explains that theoretical calculations are

Researchers have developed a model to explain deuterium enrichment in space

Reference
T Frankcombe and G Nyman, *Phys. Chem. Chem. Phys.*, 2008, DOI: 10.1039/b801384e

necessary because 'it is hard to reproduce the low temperatures and pressures of the interstellar environment in the laboratory. Conventional reactive scattering calculations can simulate this type of reaction but the computational cost is considerable.' This new route using the 'adiabatic capture centrifugal sudden approximation has proved to be invaluable for finding overall rate constants on this class of reactions'.

Frankcombe notes that even in the vacuum of interstellar space, treating the molecules in isolation isn't the whole story. 'The focus may shift to reactions occurring on and in grains of dust to complement the gas phase work, as it is has become clear that interstellar chemistry cannot be understood without understanding the condensed-phase chemistry occurring in and on grains.' They warn that in that case, 'performing accurate dynamics studies with presently available methods becomes essentially impossible'.

Colin Batchelor

NASA

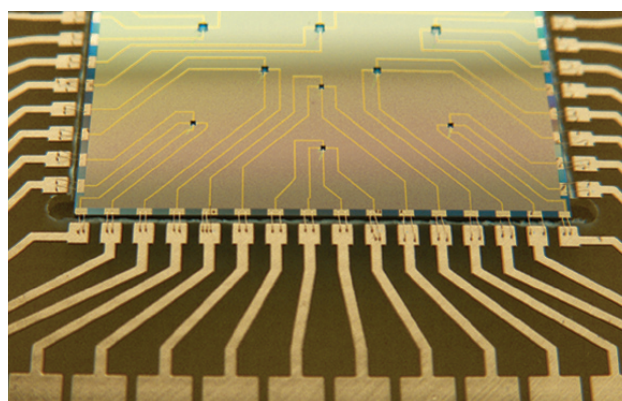
A new, innovative device for the ultrafast screening of anticancer drugs

3D chips assess drug viability

Scientists in Germany have developed a new 3D chip for the rapid and cheap assessment of potential anticancer drugs.

Andrea Robitzki and colleagues at the University of Leipzig have made a chip for the ultrafast characterisation of both 3D tissue samples, and for screening compounds to assess their anticancer activity.

3D multicellular cultures are commonly used to mimic in vivo conditions in tumours, as single cell assays do not give sufficiently realistic responses to anticancer drugs. However, to date screening devices for these 3D cultures are not advanced enough to become commercially available. 'The advantage of this novel chip is the microcavity structure keeps the tissue samples in culture



and in a viable state for real time measurements of cellular changes,' explains Robitzki.

The technique used in the chip is impedance spectroscopy: a current is applied to the biological sample which then flows through

Cellular changes can be measured in real time

Reference
D Kloß *et al*, *Lab Chip*, 2008, DOI:10.1039/b800394g

to a counter electrode beneath. By measuring the electrical responses different cellular processes can be analysed under normal conditions or after applying drugs, toxins or other active compounds. 'This approach is a novel innovation for drug screening and for producing cost-effective pharmaceutical products and therapeutical concepts in a short time frame,' says Robitzki.

'The results show a relevant technology that will be appealing to industry and academics alike,' comments Jon Cooper, a bioengineer at the University of Glasgow, UK. 'One could easily imagine it being implemented in a high throughput format appropriate for the pharmaceutical industry,' he adds.

Sarah Dixon

Single-step destruction method for organophosphate chemical warfare unveiled

Cleaning up after nerve agents

Destruction of nerve agents through a simple chemical reaction could help remove chemical weapon stockpiles and clean contaminated materials. US scientists have demonstrated that cheap, easily prepared chemicals can break down organophosphate nerve agents such as VX to a non-hazardous material.

Existing methods for destroying nerve agents such as oxidation with bleach are limited. Nerve agents in chemical weapons are often found as chemical mixtures, and bleach reacts indiscriminately - even explosively - with many chemicals such as propellants. It is also corrosive to materials and surfaces. Other approaches such as alkaline hydrolysis also have drawbacks, including low solubility and slow reaction rates. Furthermore some decontamination methods give by-products, such as thioic acids, which are almost as toxic as the original nerve agent.

Now David Atwood and Daniel Williams at University of Kentucky, Lexington, and Kennesaw State



University and co-workers have devised a destruction method based on dealkylating agents. Organophosphate-based nerve agents and pesticides can now be cleaved in a single reaction. 'This research demonstrates the first technique whereby nerve agents or pesticides can be made inactive in a direct reaction. The resulting non-

User is wearing a suit with a breathing unit, and is pointing a detector at a simulated agent shell

Reference
A Mitra, *New J. Chem.*, 2008, DOI:10.1039/b717041f

toxic byproducts would be solids that could be easily handled or disposed of,' explains Atwood. Looking to the future 'the technology could also be used to decontaminate vehicles or other objects that have been exposed to nerve agents', he adds.

The dealkylating agents are based on Schiff bases containing boron or aluminium and specifically cleave the phosphate ester bond in nerve agents or pesticides preventing unwanted side reactions or surface corrosion.

'The search for a non-corrosive decontamination of sensitive material and skin after exposure by toxic chemicals, for example pesticides and nerve agents, is an important but challenging task,' says Franz Worek an expert in organophosphate toxicology at the Bundeswehr Institute of Pharmacology and Toxicology, Munich, Germany. 'This new and promising approach may ultimately lead to a new type of mild and effective decontamination,' he adds.
Russell Johnson

New highly insulating aerogels inspired by bird nests

Strength in nanoworms

Scientists in the US have mimicked the structure of bird nests to overcome the extreme fragility of highly insulating aerogels.

Already used to protect NASA's Mars rovers' delicate electronics from the cold, aerogels are low-density materials prized for their insulating properties. However, the porous materials, made of interwoven nanoparticle strands, are also extremely fragile, limiting their use. Now Nicholas Leventis and colleagues at Missouri University of Science and Technology, Rolla, have made a stronger material by boosting the interlocking between strands.

Aerogels are typically made from pearl necklace-like strings of silica nanoparticles, and can be strengthened with a polymer coating, so that the strands form crosslinks wherever they meet. But inspired



Aerogels help keep this Mars rover's electronics warm

by the highly interlocked structures of bird nests, Leventis switched to vanadia-based structures, which form a more highly entangled worm-like nanostructure.

'Both crosslinked silica and vanadia are very strong materials. But crosslinked vanadia aerogels never fail under compression, and can absorb at least four times the kinetic energy of the silicon carbide ceramics used for armour,' said Leventis. 'Killer applications will be in areas

Reference
N Leventis *et al.*, *J. Mater. Chem.*, 2008, DOI: 10.1039/b801770k

where we can take advantage of the multifunctional character of these materials - strength in combination with acoustic and thermal insulation - such as lightweight structural materials for buildings, and the automotive and airplane industries.'

Bakul Dave who makes similar gel-based materials at Southern Illinois University, Carbondale, US, describes the work as a step forward. 'It seems the properties depend on the nanostructure morphology - so in principle, it should be possible to make these materials with components other than vanadium.'

Replacing vanadium with a cheaper alternative is Leventis' first goal. 'We are applying lessons learned from vanadia to silica, which under certain conditions can also produce worm-like structures,' Leventis adds.
James Mitchell Crow

News in brief

This month in Chemical Technology

Designer thermometers rise to new levels

Ionic liquids have been used in liquid-in-glass thermometers as alternatives to mercury and ethanol

A bright future for solar cells

A highly efficient light harvesting molecule could lead to cheaper solar cells, claim international scientists

Cellular power plants fuel molecular motors

Mitochondria have been used to power miniature motors for microfluidic devices

Nerve agent detector on a chip

A microfluidic device that can identify exposure to sarin could help identify individuals needing treatment at sites of terrorist attack

See www.rsc.org/chemicaltechnology for full versions of these articles

This month in Chemical Biology

The science of smell

Chip technology is helping French scientists to unravel the mysteries behind our sense of smell

Analysing aneurysms

In the future, doctors may be able to spot life-threatening blood vessel swelling more accurately, thanks to work by French scientists

Spiky sponges share their secrets

Enzymes that make sponges spiky are promising leads for new silicon-based materials, say British scientists

Tumour treatments see the light

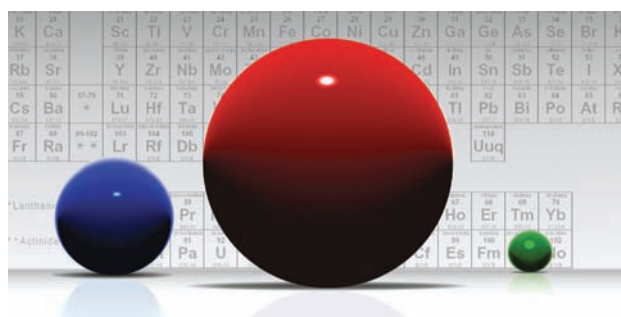
DNA-seeking probes could deliver anticancer agents right to the heart of tumour cells, say chemists in Italy

Computers get to the heart of gene expression

German scientists are unravelling the genetic basis of diseases by combining computational biology techniques

See www.rsc.org/chembiology for full versions of these articles

Refining atomic radii



A new set of covalent atomic radii that is more comprehensive and precise than previous lists has been compiled by Spanish scientists from the University of Barcelona.

The concept of atomic radii is used in structural chemistry and X-ray crystallography to give a rough idea of the size of an atom in a molecule or crystal, and to establish bonding and non-bonding interactions between atoms. The new list of radii covers elements up to curium (atomic number 96) and shows sensible trends along both the rows and groups of the

The new list shows sensible trends along both the rows and groups of the periodic table

Reference
B. Cordero *et al.*, *Dalton Trans.*, 2008, DOI: 10.1039/b801115j

periodic table, explains team leader Santiago Alvarez.

The work began when Alvarez's team were trying to decide when to expect structures to have a through-ring metal–metal interaction, and discovered that existing lists of radii contained gaps and inconsistencies. They found periodic trends were erratic and that in the previously most complete set used by the Cambridge Structural Database (CSD) important metals such as nickel, palladium, platinum and gold were given default unrefined values of 1.50 Å.

The Spanish team derived their radii from a systematic search of 228 000 experimental bond distances in structures held in the CSD and the Inorganic Crystal Structure Database. They determined the radii from bond distances to nitrogen, carbon and oxygen atoms, as there many examples of covalent bonds from these to most other elements.

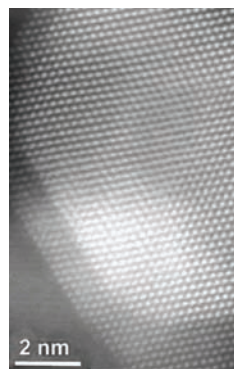
Michael Townsend

Zooming in on nanoparticles' defects

US researchers have found a way to study defects on surfaces of nanoparticles, which are thought to be critical for catalytic activity.

Metal nanoparticles are the key to the activity of many catalysts, including those in car catalytic converters. To improve these catalysts it is important to know what is happening at the atomic level. Miguel Jose-Yacamán and colleagues at the University of Texas at Austin have found that, using microscopy and computer modelling, they can obtain much more detail than before about nanoparticle surface defects.

Jose-Yacamán's method uses aberration-corrected TEM (transmission electron microscopy), which uses software to correct distortions introduced by the microscope lenses. This enables imaging of atoms in non-regular environments (such as at surface defects), which is not possible with regular TEM. The team applied this technique to a gold–palladium nanoparticle, and not only found



Nanoparticles bumpy surfaces are vital for their catalytic activity

Reference
D Ferrer *et al.*, *J. Mater. Chem.*, 2008, DOI: 10.1039/b801320a

that it was a single crystal, but that it consisted of three distinct spherical layers, each with a different ratio of the two metals. They also obtained electron density profiles along different axes through the particle. By comparing these with computer models, they found that the nanoparticle contains steps, edges and kinks on its surface.

Jose-Yacamán says their results show that 'the surface of the particle is rather rough at the atomic scale.'

David Cockayne, professor of materials chemistry at the University of Oxford, UK, is enthusiastic about the work, saying that it 'demonstrates the enormous potential for modern aberration-corrected TEM to explore the complex structures of nanoparticles'. Luis Liz-Marzán, an expert in nanoparticles from the University of Vigo in Spain, echoed these thoughts, saying this 'represents a leap in electron microscopy capabilities for nanoparticle analysis'.

David Barden

In the beginning....

Kenso Soai and Joanne Thomson discuss the origin of chirality in life



Kenso Soai

Kenso Soai is professor of applied chemistry at Tokyo University of Science, Japan. His research interests centre on chirality in organic synthesis, including asymmetric autocatalysis and spontaneous asymmetric synthesis.

What first inspired you to become a chemist?

I have been interested in the natural sciences since my childhood. My hope was to become a researcher in this area, although I hadn't decided on a specific subject. After entering university, I attended various lectures and seminars to help me decide. In the middle of my second year, I chose chemistry as the major subject because I thought that I would be able to contribute the most to this subject.

Much of your work focuses on asymmetric autocatalysis. Could you explain what this is and why it is important in understanding the origin of homochirality in life?

Asymmetric autocatalysis is a reaction in which the chiral product acts as a chiral catalyst for its own production. Because the structures of the catalyst and product are the same, consecutive asymmetric autocatalyses using the product of one round as the catalyst for the next significantly amplify the enantiomeric excess (ee) from extremely low to near enantiopurity. It also significantly increases the amount of product.

Living organisms use only L-amino acids and D-sugars. How this chirality originated and the method of enantioenrichment are questions of broad interest that are also related to the origin of life. Several theories have been proposed for the origin of chirality, but the ees induced by these mechanisms have been very low. Asymmetric autocatalysis could be the answer. An initial spontaneous fluctuation in the ratio of enantiomers could have led to asymmetric autocatalysis and the amplification of chirality in nature.

Asymmetric autocatalysis is not a mere purification or separation of enantiomers but an increase in the amount by self-replication, one of the essential features of life.

What else are you currently working on?

We are working on asymmetric induction in organic compounds by physical factors. We have found that quartz and circularly polarized light act as the origin of chirality to afford highly enantioenriched compounds. We have also demonstrated spontaneous absolute asymmetric synthesis, where enantioenrichment occurs without adding any

chiral material. For example, the reaction between pyrimidine-5-carbaldehyde and diisopropylzinc affords enantioenriched pyrimidyl alkanol product because the initial tiny enantiometric imbalance is amplified by asymmetric catalysis. Our dream is to induce chirality in compounds by these chiral physical factors.

What do you enjoy most about your job?

The best part is that I am really interested in the research I do. The moment when a promising result is obtained, especially if it is unexpected, is very stimulating.

Chemistry is a bridge combining people with the same interests and passions. Listening to the excellent lectures, discussions and collaborations about chirality with chemists all over the world makes my life really exciting.

You have received numerous awards and honours during your career, including the Chirality Medal in 2005. What do you think is the secret to successful research?


I have been working on the enantioselective addition reaction of alkylmetal reagents to aldehydes for nearly 30 years. We reported the first asymmetric autocatalysis in 1990, but it took us another 5 years to finally find asymmetric autocatalysis with amplification of enantiopurity. We kept at it because I thought it was a really fascinating project. Persistence, therefore, may be one of the conditions necessary to obtain success.

What do you do in your spare time?

I usually go for a walk along the banks of my local river and read a book. I like to read books about history. Although at school we learned the history of heroes and politicians, we didn't learn much about the lives of normal people in ancient and medieval centuries.

If you weren't a chemist, what would you be?

When I was a student, I was attracted to scientific subjects such as biology, chemistry, mathematics and geology. If I weren't a chemist, I would most likely be a biologist.

A close-up photograph of three Bruker CryoProbe NMR cryoprobes. The probes are white with blue and yellow accents. They are numbered 14, 15, and 16 from left to right. The background is a blurred blue and white pattern.

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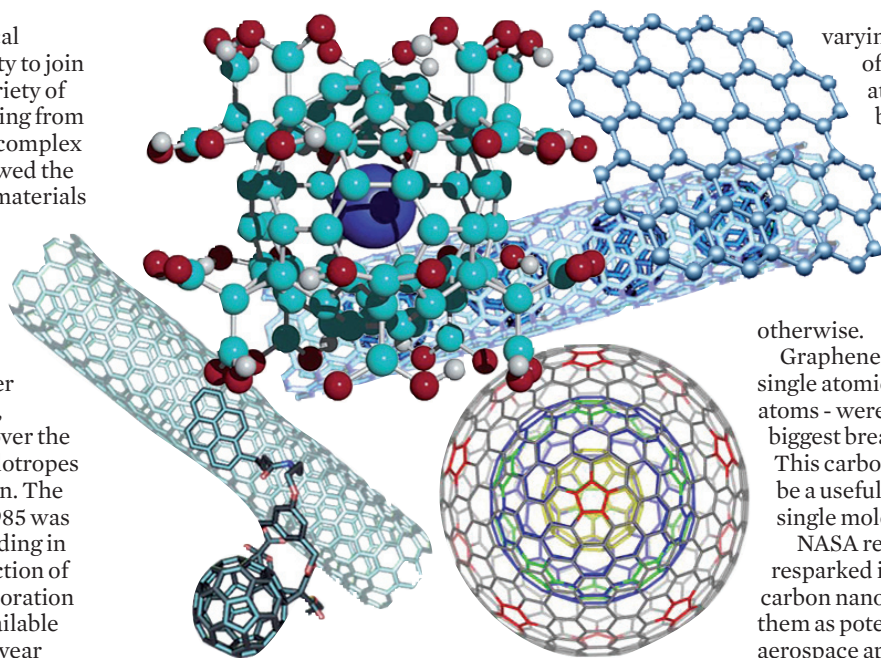
Nano-forms of carbon

Juan Luis Delgado, María Ángeles Herranz and Nazario Martín at Complutense University of Madrid, Spain, explore the cutting-edge in nanostructures made from carbon

Carbon is a singular chemical element with a unique ability to join together forming a wide variety of fascinating molecules, ranging from a few carbon atoms to long complex chains. This ability has allowed the creation of numerous new materials and molecules of interest for a very diverse range of applications.

The discovery over two decades ago that carbon can form stable and ordered structures other than graphite and diamond, stimulated researchers all over the world to search for other allotropes - structural forms - of carbon. The discovery of fullerenes in 1985 was followed by another key finding in 1990: the multigram production of C₆₀ using a simple arc-evaporation apparatus that is readily available in most labs. The following year using a similar evaporator, Sumio Iijima discovered fullerene-related multiwalled carbon nanotubes (MWNTs). This was followed two years later by tubes containing only one graphitic sheet, known as single-walled carbon nanotubes. These are made by doping one of the electrodes used to produce MWNTs with metals such as Fe or Co.

Also in the early 1990s, new types of structures started to be made that consist of carbon spheres of increasing diameters layered on top of each other, akin to the wooden Russian dolls. Due to their layered design these were coined nano-onions. The nano-onions were only the tip of the iceberg, with a wide variety of new carbon nanostructures such as endohedral



cup-stacked

nanotubes, nanohorns,

nanotori, nanobuds and graphenes now emerging as new and fascinating forms of carbon whose chemical and physical properties are currently being unravelled.

Of particular interest are endohedral fullerenes - carbon cages that encapsulate atoms or molecules in their inner space. Made using the so called 'molecular surgery' approach - the fullerene cage opens in a controlled way, allowing atoms or small molecules to enter, and then closes to reform the pristine fullerene structure. Alternatively, the interesting family of trimetallic nitride templated endohedrals are obtained directly with relatively high yields, by

varying the composition of the cooling gas atmosphere in the arc-burning process used in the production of fullerenes. They have an inner metal cluster that can stabilise a large variety of carbon cages that can not exist

otherwise.

Graphenes - materials that are single atomic flat layers of carbon atoms - were considered one of the biggest breakthroughs in 2007. This carbon form was found to be a useful sensor able to detect a single molecule of gas.

NASA researchers have resparked interest in the original carbon nano-onions, considering them as potential additives for aerospace applications. The nano-onions have demonstrated superior lubrication properties to other conventional lubricants, and we foresee a very promising future for these and other new and still unexplored forms of carbon.

Although the scientific community are not yet entirely satisfied with all the expectations and excitement that emerged from the initial discovery of fullerenes and carbon nanotubes, the spectacular properties that these species reveal day by day will make them play an essential role in the future.

Read Nazario Martín et al's feature article 'The nano-forms of carbon' in issue 13, 2008 of Journal of Materials Chemistry

Different nanoforms of carbon

Reference

J L Delgado, M A Herranz and N Martín, *J. Mater. Chem.*, 2008, **18**, 1417 (DOI: 10.1039/b717218d)

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