Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

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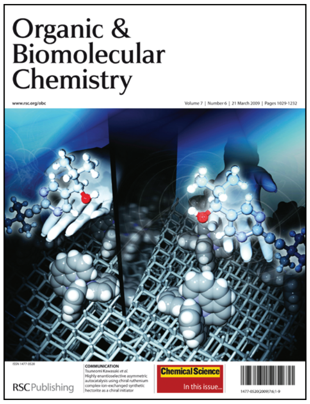
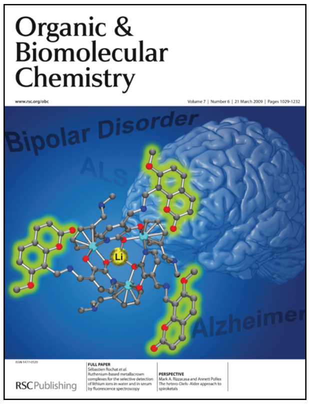
ISSN 1477-0520 CODEN OBCRAK 7(6) 1029–1232 (2009)



Cover
See Tsuneomi Kawasaki *et al.*, pp. 1073–1075.
Clay mineral exercises its asymmetric power to synthesize highly enantioenriched organic compounds in combination with asymmetric autocatalysis.

Image reproduced by permission of Kenso Soai from *Organic & Biomolecular Chemistry*, 2009, **7**, 1073.



Inside cover
See Sébastien Rochat *et al.*, pp. 1147–1153.
A fluorescent metallacrown complex can be used as a turn-on chemosensor for the pharmacologically important lithium ion.

Image reproduced by permission of Kay Severin from *Organic & Biomolecular Chemistry*, 2009, **7**, 1147.

CHEMICAL SCIENCE

C17

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

March 2009/Volume 6/Issue 3

www.rsc.org/chemicalscience

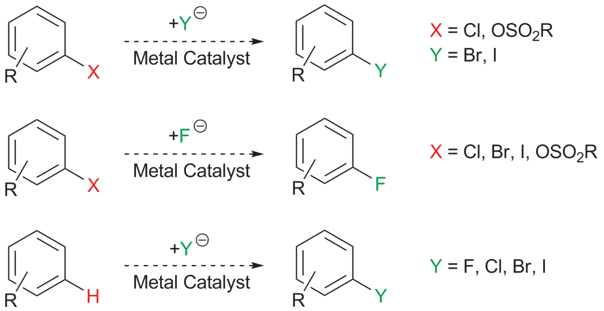
EMERGING AREA

1043

Metal-catalysed halogen exchange reactions of aryl halides

Tom D. Sheppard*

Metal-catalysed methods for the interconversion of aryl halides and for direct halogenation of aromatic systems are reviewed and critically assessed. The possible mechanisms of these reactions are discussed, with a view to identifying areas for future investigation.



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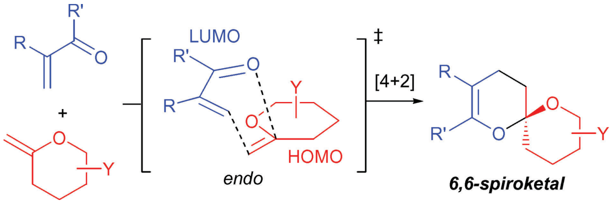
PERSPECTIVE

1053

The hetero-Diels–Alder approach to spiroketals

Mark A. Rizzacasa* and Annett Pollex

The hetero-Diels-Alder reaction can provide spiroketal systems with excellent stereoselectivity. This perspective article will briefly outline the scope and limitations of this approach for the production of naturally occurring spiroketals and derivatives.



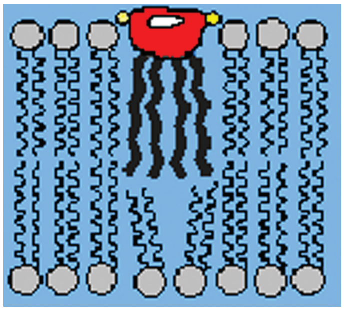
COMMUNICATIONS

1060

CyPLOS: a new family of synthetic ionophores

Sabina Licen, Cinzia Coppola, Jennifer D'Onofrio,
Daniela Montesarchio* and Paolo Tecilla*

The ion transport properties of novel synthetic ionophores based on cyclic phosphate-linked oligosaccharide (CyPLOS) macrocycles are described.

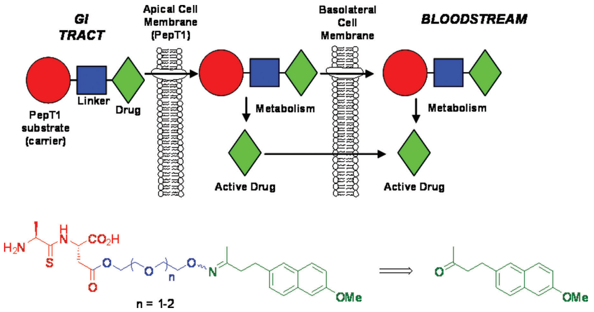


1064

Targeting ketone drugs towards transport by the intestinal peptide transporter, PepT1

David Foley, Patrick Bailey,* Myrtani Pieri and
David Meredith

Thiodipeptide prodrugs of the ketone nabumetone are shown to have affinity for, and be transported by, PepT1 *in vitro.*

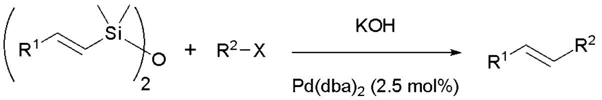


1068

Fluoride-free cross coupling using vinyldisiloxanes

Hannah F. Sore, Christine M. Boehner,
Simon J. F. MacDonald, David Norton, David J. Fox and
David R. Spring*

Vinyldisiloxanes equilibrate with the corresponding silanolates under basic conditions and subsequently undergo palladium catalysed cross coupling with aryl/heteroaryl iodides and bromides.



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Till Bachmann, Head of Biochip Research, University of Edinburgh
Riccardo Castagna, PhD Student, Politenico di Torino
Irina Piatkov, Senior Hospital Scientist, Diversity Health Institute
Johan Skog, Instructor at Harvard Medical School, Assistant in Neurology Massachusetts General Hospital
Andrey Alexeyenko, Researcher, Stockholm Bioinformatics Centre
Mats Nilsson, Associate Professor, Uppsala University
Jean Schleipen, Philips Research Europe
Manuel Salto-Tellez, Director, Molecular Diagnostic Oncology Centre, National University Health System
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- Commercial & Regulatory Perspectives

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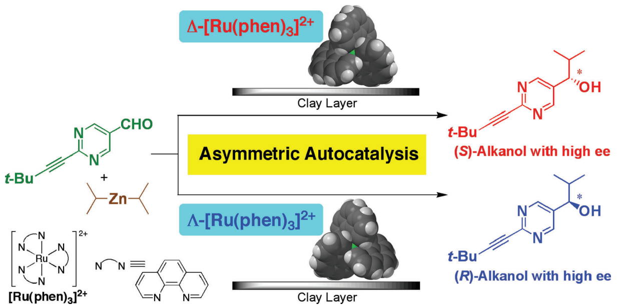
COMMUNICATIONS

1073

Highly enantioselective asymmetric autocatalysis using chiral ruthenium complex-ion-exchanged synthetic hectorite as a chiral initiator

Tsuneomi Kawasaki, Toshiki Omine, Kenta Suzuki,
Hisako Sato, Akihiko Yamagishi and Kenso Soai*

Synthetic hectorite containing intercalated Δ- and Λ-tris(1,10-phenanthroline)ruthenium(II) ions is a heterogeneous chiral catalyst in the addition of diisopropylzinc to pyrimidine-5-carbaldehyde, affording 5-pyrimidyl alkanol with high ee by asymmetric autocatalysis.



PAPERS

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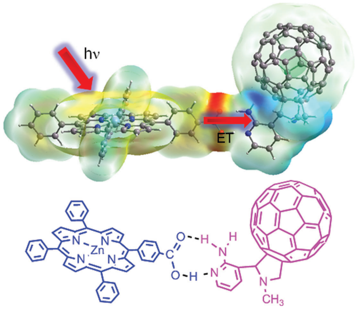
Through-bond photoinduced electron transfer in a porphyrin-fullerene conjugate held by a Hamilton type hydrogen bonding motif

Francis D'Souza,* Ganesh M. Venukadasula,
Ken-ichi Yamanaka, Navaneetha K. Subbaiyan,
Melvin E. Zandler and Osamu Ito*

Hamilton type hydrogen bonding is utilized to form a porphyrin-fullerene conjugate in which the donor–acceptor distance is suitably positioned to visualize through-bond electron transfer.

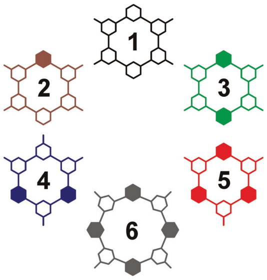


1081

Shape-persistent macrocycles comprising perfluorinated benzene subunits: synthesis, aggregation behaviour and unexpected μ-rod formation

Lijin Shu, Marcel Müri, Ralph Krupke and Marcel Mayor*

Six shape-persistent macrocycles, varying in number and/or spatial arrangement of perfluorinated corner units, were synthesized to investigate their aggregation behaviour.

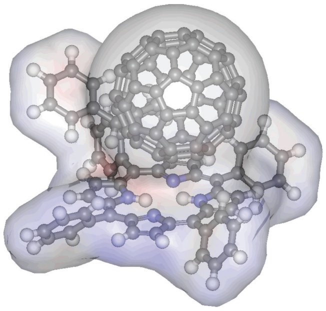


1093

A glycyl-substituted porphyrin as a starting compound for the synthesis of a π–π-stacked porphyrin–fullerene dyad with a frozen geometry

Angelo Lembo, Pietro Tagliatesta,* Daniel Cicero,
Alessandro Leoni and Alisa Salvatori

The synthesis of a new π–π-stacked porphyrin–fullerene dyad with a frozen geometry was accomplished by the use of a new synthesized glycyl porphyrin derivative. The new dyad shows a strong electronic interaction between the two chromophores in the ground state.



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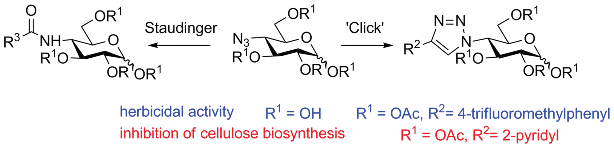
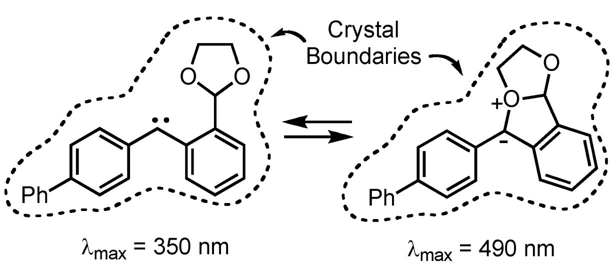


Synthesis of glucose derivatives modified at the 4-OH as potential chain-terminators of cellulose biosynthesis; herbicidal activity of simple monosaccharide derivatives

Emma van Dijkum, Ramona Danac, David J. Hughes, Richard Wood, Anne Rees, Brendan L. Wilkinson and Antony J. Fairbanks*

Glucose derivatives in which the 4-hydroxyl group had been modified were synthesised by click or Staudinger chemistry, and tested for herbicidal activity as putative inhibitors of cellulose biosynthesis.

1106

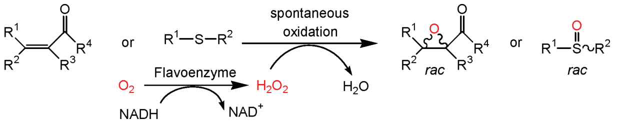


Photochemical generation, intramolecular reactions, and spectroscopic detection of oxonium ylide and carbene intermediates in a crystalline *ortho*-(1,3-dioxolan-2-yl)-diaryldiazomethane

Miguel A. Garcia-Garibay* and Hung Dang

Chemical and spectroscopic evidence was obtained for the generation of an intramolecular oxonium ylide in crystals of a diaryldiazomethane by trapping the corresponding diarylcarbene with a neighboring *ortho*-acetal. Different selectivities were observed in solution and in crystals.

1115

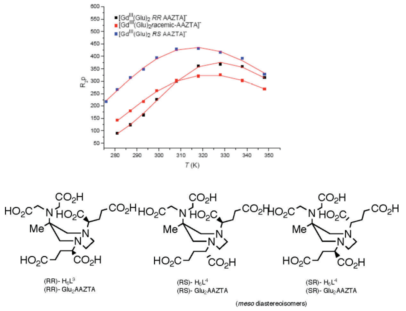


Epoxidation of conjugated C=C-bonds and sulfur-oxidation of thioethers mediated by NADH:FMN-dependent oxidoreductases

Nicole Jasmin Mueller, Clemens Stueckler, Melanie Hall, Peter Macheroux and Kurt Faber*

Epoxidation of alkenes and sulfoxidation of a thioether in presence of molecular oxygen and NADH was mediated by flavoproteins (YncD, YhdA and Lot6p) to furnish the corresponding epoxides and sulfoxide, respectively, in racemic form.

1120



Variation of water exchange dynamics with ligand structure and stereochemistry in lanthanide complexes based on 1,4-diazepine derivatives

Elisa M. Elemento, David Parker,* Silvio Aime, Eliana Gianolio and Luciano Lattuada

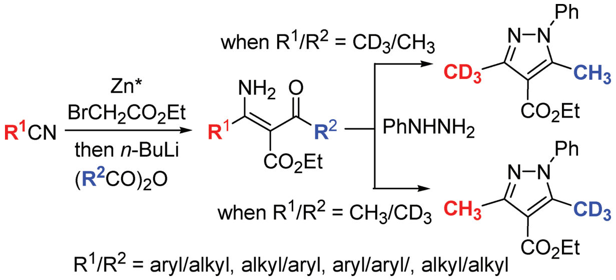
NMR studies with lanthanide complexes of diastereoisomeric heptadentate di-glutarate ligands based on a 6-methyl-6-aminoperhydrodiazepine moiety reveal the presence of two major species that undergo water exchange rates at Gd that differ by a factor of six.

1132

An effective and general method for the highly regioselective synthesis of 1-phenylpyrazoles from β-enaminoketoesters, tandem Blaise–acylation adducts

Young Ok Ko, Yu Sung Chun, Cho-Long Park, Youngmee Kim, Hyunik Shin,* Sungho Ahn, Jongki Hong and Sang-gi Lee*

An effective and general route for the regioselective synthesis of a variety of pyrazoles, including isotopically discriminated ones, has been developed from the tandem Blaise–acylation adducts β-enaminoketoesters.

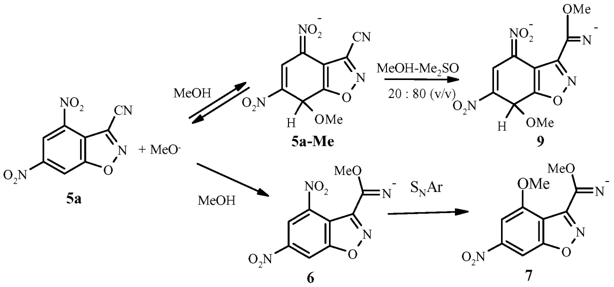


1137

The versatile electrophilic reactivity of 4,6-dinitrobenzo[d]isoxazole-3-carbonitrile

Betty Cottyn, Alexei Starosotnikov, Dominique Vichard, Régis Goumont, Svyatoslav Shevelev* and François Terrier*

The multifaceted electrophilic reactivity of the benzoisoxazole **5a** is shown to involve σ-complexation, S_NAr substitution and imidate formation.

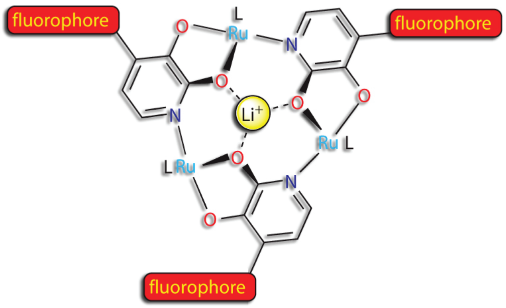


1147

Ruthenium-based metallacrown complexes for the selective detection of lithium ions in water and in serum by fluorescence spectroscopy

Sébastien Rochat, Zacharias Grote and Kay Severin*

A metallacrown complex with pendent methoxycoumarin fluorophores can be used to sense low millimolar concentrations of lithium ions in water or in a complex biological matrix such as human serum.



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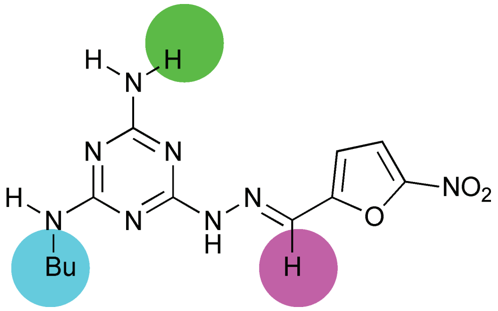
Novel functionalized melamine-based nitroheterocycles: synthesis and activity against trypanosomatid parasites

Alessandro Baliani, Valerie Peal, Ludovic Gros, Reto Brun, Marcel Kaiser, Michael P. Barrett and Ian H. Gilbert*

Conjugation of melamine to nitroheterocycles to give selective delivery to *Trypanosoma brucei* the causative organism of human African trypanosomiasis.



PAPERS

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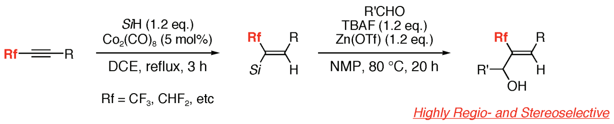
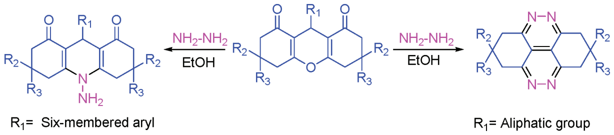


Remarkable access to fluoroalkylated trisubstituted alkenes *via* highly stereoselective cobalt-catalyzed hydrosilylation reaction of fluoroalkylated alkynes

Tsutomu Konno,* Ken-ichi Taku, Shigeyuki Yamada, Kazuki Moriyasu and Takashi Ishihara

A hydrosilylation of fluoroalkylated internal acetylenes and a following nucleophilic addition into various aldehydes gave the trisubstituted alkenes in high yields with high regio- and stereoselectivity.

1171

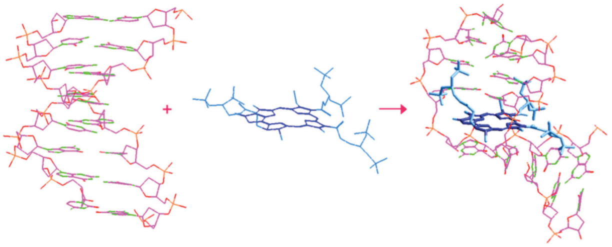


New domino reaction for the selective synthesis of tetracyclic cinnolino[5,4,3-*cde*]cinnolines

Bo Jiang, Wen-Juan Hao, Jin-Peng Zhang, Shu-Jiang Tu* and Feng Shi

A novel domino reaction for the highly selective synthesis of cinnolino[5,4,3-*cde*]cinnolines is described. The use of anthenes with aliphatic R_1 groups leads to cinnolino[5,4,3-*cde*]cinnolines, whereas anthenes with aryl R_1 groups result in *N*-amino-1,8-dioxoacridines.

1176

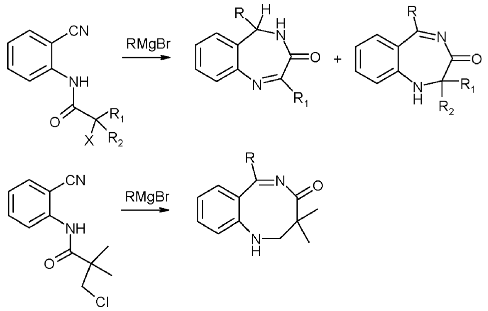


Synthesis and DNA-binding properties of water-soluble cationic pyropheophorbides derived from chlorophyll *a/b*

Hidetoshi Taima, Naoki Yoshioka and Hidenari Inoue*

Six water-soluble cationic pyropheophorbides *a/b* have been designed and synthesized. Dicationic pyropheophorbides bind outside the phosphate backbone of DNA, while tetra- and hexacationic pyropheophorbides intercalate between the base pairs of DNA. The binding mode depends on the number and position of the cationic peripheral substituents.

1184



Synthesis of 1,4-benzodiazepin-3-ones and 1,5-benzodiazocin-4-ones by addition of Grignard reagents to derivatives of *o*-aminobenzonitrile

Birgitta Pettersson, Anna Rydbeck and Jan Bergman*

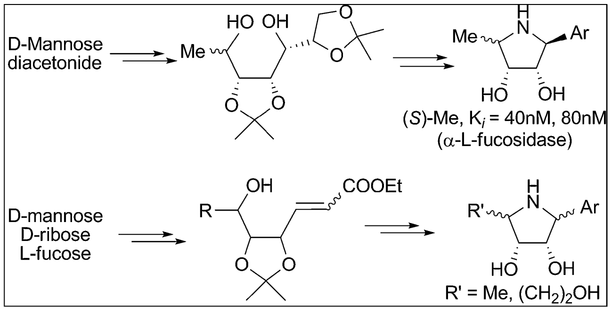
Addition of organometallics (such as Grignard reagents) to derivatives of *N*-(α-haloacyl)-*o*-aminobenzonitrile have been studied, which resulted in several 2,5-disubstituted 1,4-benzodiazepine-3-ones. The method was also applied to give 1,5-benzodiazocin-4-ones from certain derivatives of *N*-(β-haloacyl)-*o*-aminobenzonitrile.

1192

Synthesis of novel pyrrolidine 3,4-diol derivatives as inhibitors of α-L-fucosidases

Elena Moreno-Clavijo, Ana T. Carmona,*
Yolanda Vera-Ayoso, Antonio J. Moreno-Vargas,
Claudia Bello, Pierre Vogel and Inmaculada Robina*

New 3,4-dihydroxypyrrolidine derivatives were prepared by diversity oriented stereoselective syntheses starting from sugars. Some of the compounds are potent and selective inhibitors of α-L-fucosidases in the nM range.

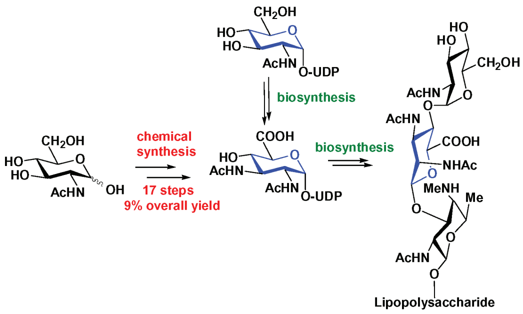


1203

Chemical synthesis of UDP-Glc-2,3-diNAcA, a key intermediate in cell surface polysaccharide biosynthesis in the human respiratory pathogens *B. pertussis* and *P. aeruginosa*

Martin Rejzek, Velupillai Sri Kannathasan, Corin Wing,
Andrew Preston, Erin L. Westman, Joseph S. Lam,
James H. Naismith, Duncan J. Maskell and Robert A. Field*

In the search for novel vaccine components to prevent whooping cough, analysis of the complex biosynthesis of *Bordetella pertussis* lipopolysaccharide has been enabled by synthetic carbohydrate chemistry.

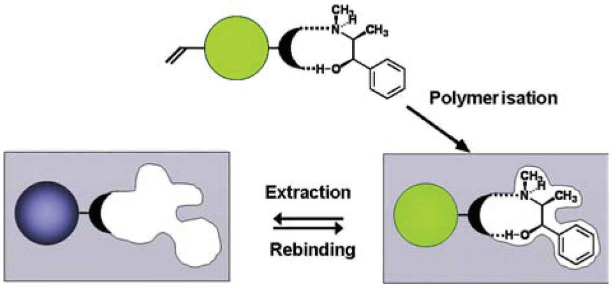


1211

Fluorescent imprinted polymer sensors for chiral amines

T. Hien Nguyen and Richard J. Ansell*

Two novel polymerisable carboxylate-functionalised coumarins have been designed and synthesised, and incorporated into imprinted polymers which show selective fluorescence responses in the presence of (−)-ephedrine.

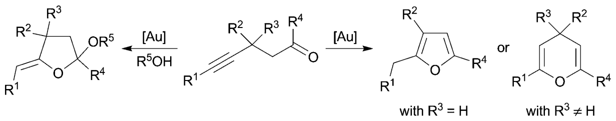


1221

Gold-catalyzed cycloisomerization of alk-4-yn-1-ones

Volker Belting and Norbert Krause*

Depending on the substitution pattern and the reaction conditions, the gold-catalyzed cyclization of alk-4-yn-1-ones affords substituted furans, 4*H*-pyrans, or alkylidene/benzylidene-substituted tetrahydrofuranyl ethers.



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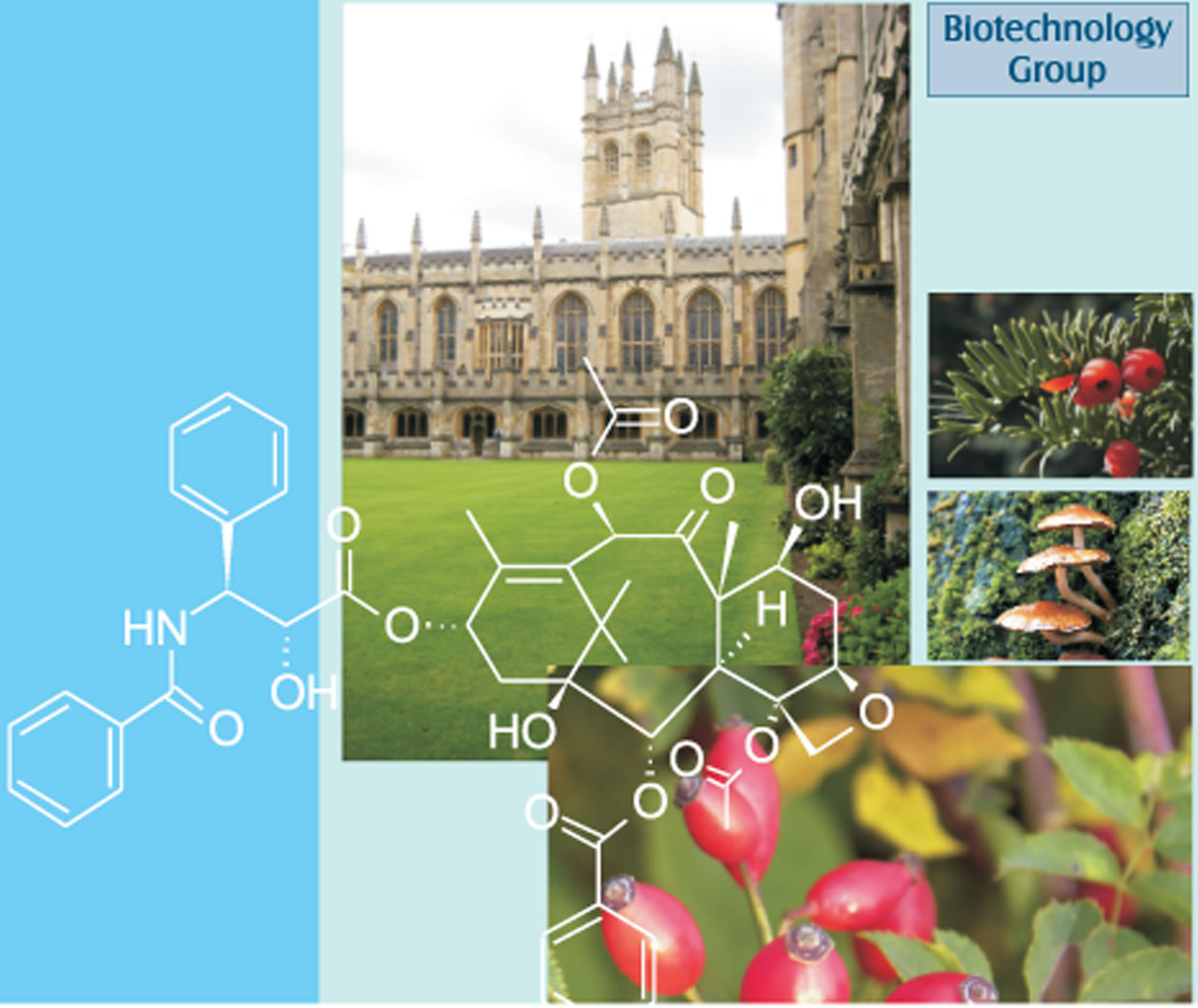

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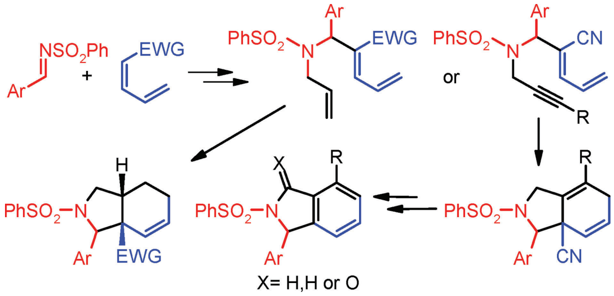

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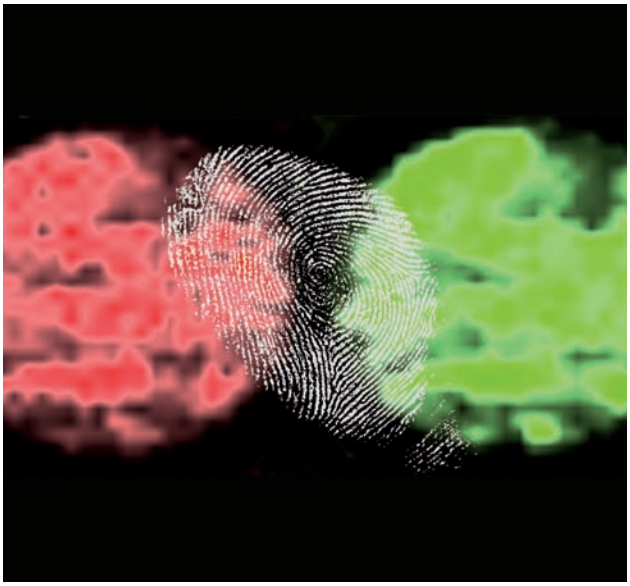
March 2009 / Volume 6 / Issue 3 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

Silica dusting agent allows drug detection in fingerprints

When the dust settles



The silica dust can give additional chemical information from fingerprints

UK scientists have devised a simple route to detecting illicit drugs and their metabolites in dusted fingerprints.

Frederick Rowell and colleagues of ROAR Particles Ltd in Durham, have developed a silica dusting agent that not only develops fingerprints, but also allows for the direct detection of drugs in the fingerprints by mass spectrometry. Rowell says that there is considerable interest in being able to obtain additional information from developed fingerprints, especially since a considerable fraction are smudged and therefore do not provide a clear image for routine identification purposes.

A hydrophobic silica dusting agent was used to develop fingerprints, which were then lifted using commercial tape. The lifted fingerprints subsequently underwent direct analysis by mass spectrometry, analysing for various chemical residues within the print. The procedure successfully confirmed the presence of parent drug compounds and their metabolites, providing unique fragmentation patterns for each chemical.

Graham Cooks of Purdue University in West Lafayette, US, says that the significance of this work lies in the fact that this technique 'can be used to record chemical fingerprints' and 'show the distribution of chemicals associated with latent fingerprints'. Cooks adds that the advantage of this method over existing ones is the 'dual use of powder as a latent print dust and as a mass spectroscopy matrix'.

'We need to undertake trials for these contact residues and for biomarkers with large numbers of individuals before our methods can be considered for routine forensic analysis,' says Rowell. 'In order to achieve maximum sensitivity for detecting chemicals present in trace amounts, it is necessary to reduce interference in the analysis step from the major components. This is proving a challenge but we think we have found a simple but effective solution.'

Mary Badcock

Reference

F Rowell, K Hudson and J Seviour, *Analyst*, 2009, DOI: 10.1039/b813957c

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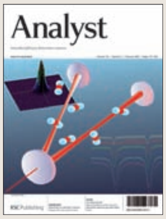
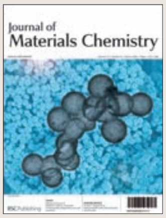
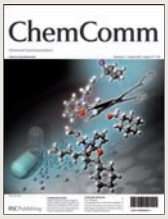






A snapshot of the latest developments from across the chemical sciences

Research highlights

Tagging a catalyst allows its progress through a reaction to be monitored

Fluorescent dyes to see catalysts in action

German researchers have used a fluorescent tag to monitor the state of a catalyst during a chemical reaction.

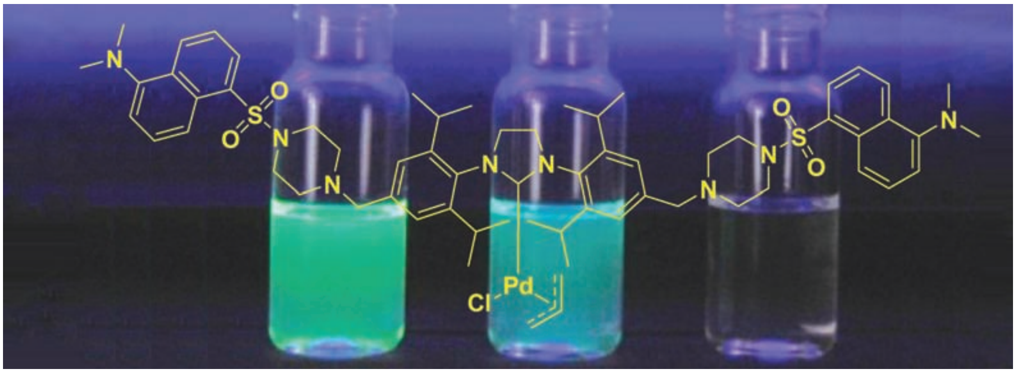
Herbert Plenio and colleagues from the Darmstadt University of Technology tagged an *N*-heterocyclic carbene ligand in a palladium catalyst with a fluorescent dye. They followed the catalyst's progress in a Suzuki cross-coupling reaction using fluorescence spectroscopy. The team found that the fluorescence signal changed at each stage of the reaction. When the catalyst was activated by a base, the signal decreased within a few seconds. It then remained stable until the substrate was added, then decreased gradually until the end of the reaction. The tag also allowed Plenio to see any catalyst impurities left in the product.

'Our work provides a highly sensitive tool to monitor catalysts in action in low concentrations,' says Plenio. 'Little is known about the nature of catalyst complexes involved in catalytic transformations. By definition, the amount of a catalyst is small compared to the substrates and, to make things worse, this often acts as only a reservoir for the even smaller amount of active species that is actually doing the work.'

Fluorescence has the high sensitivity required to detect these very small quantities, even with just a few nanograms of palladium. 'This is a nice application of fluorescence that allows a deeper insight into catalytic processes,' says Jay Winkler, an expert in the photochemistry of transition metal complexes at the California Institute of Technology, Pasadena, US.

Plenio says he hopes that in the future, he will have tags that are sensitive enough to reveal the concentration of the active species in the catalytic cycle and the nature of the metal complexes involved. 'We still need to understand so much more about fluorescence dyes and the photophysics behind them,' he says, 'but I am optimistic – Shimomura, Chalfie and Tsien's 2008 Nobel Prize award for the discovery and development of the green fluorescent protein is providing a strong stimulus.'

Michael Spencelayh



The fluorescence signal changes at each stage of the reaction

Reference
V Sashuk, D Schoeps and H Plenio, *Chem. Commun.*, 2009, 770 (DOI: 10.1039/b820633c)

Chinese scientists find the key to self-healing polymer

Smoothing the cracks in epoxy resin

Researchers in China have developed a self-healing epoxy resin which can be repaired by heating when cracks form.

Epoxy resin is a tough polymer with many uses from glues to circuit boards, aerospace engineering to art restoration. Epoxy materials are often used under harsh conditions where long-term service and durability are needed. So, it would be ideal if damaged epoxy resin could self-heal, a property recently developed for other polymers.

Conventional epoxy resin is based on epoxides to which an additive (or curing agent) is added to form cross-linking between the chains strengthening the polymer. However, these cross-linked bonds are usually irreversible meaning that if cracks form, the bonds cannot be remade to repair the material.

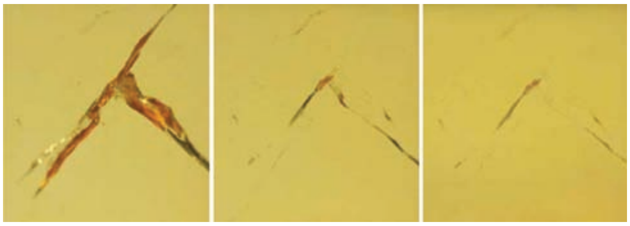
Min Zhi Rong and co-workers from Zhongshan University, Guangzhou, China, have solved this problem by making a new epoxy material which contains both epoxide and furan groups in the same molecule. To this they add a maleimide-based curing agent, as well as the conventional anhydride curing agent.

The anhydride forms irreversible strong bonds with the epoxide groups but the maleimide makes bonds with the furan groups which are reversible at 110°C. So when cracks form in the cured polymer, it is heated to 120°C to break the reversible bonds and then cooled to 80°C so the broken bonds could reform.

Fred Wudl, a polymer expert from University of California, Los Angeles, US, says Rong's work 'is an interesting step towards creating remendable epoxy resins, following on from previous work in the field.'

Rong says that his group is currently working to make an epoxy resin which will be able to self-heal at lower temperatures.

Ruth Doherty



Heating mends the cracks in damaged epoxy resin

Reference
Q Tian *et al*, *J. Mater. Chem.*, 2009, 1289 (DOI: 10.1039/b811938d)

Scientists turn waste plastic into useful ultra-strong carbon spheres

New lease of life for used cola bottles

JUPITER IMAGES

Discarded plastic bottles can be broken down to make ultra-strong carbon spheres that could be used in lubricants.

Vilas Pol from Bar-Ilan University, Ramat-Gan, Israel, and colleagues produced strong carbon microspheres from waste polyethylene terephthalate (PET). They heated used cola bottles at 700 °C for three hours in a closed reactor. The plastic then decomposed under self-generated pressure to form the hard carbon spheres with diameters between two and ten micrometres. 'We broke one diamond knife and damaged a second while cutting a cross-section of the spheres,' says Pol.

'The strength of these materials is interesting,' says Neil Coville, coordinator of the Carbon Nanotubes and Strong Composites group at the University of the Witwatersrand, Johannesburg, South Africa. 'The results are impressive and suggest others should be measuring this property in the future.'

'The process is particularly interesting,' says Philippe Serp, an expert in carbon nanostructures at the National Center for Scientific Research, Toulouse, France, 'as it does not use any catalyst.' Pol's scalable process also does not require solvents and improves on existing methods that can be limited by low yields and poor separation of the spheres from carbon soot.

Carbon spheres are used in energy storage and nanodevices. Pol's microspheres can withstand significant pressure, so they could be used in lubricants. Lowering the reaction temperature to below 700 °C gives larger carbon particles that could be used in printers, toners and filtration technology.

'The challenge facing today's scientific community to find an innovative solution to the degradation of waste polymers motivated us,' explains Pol's colleague Aharon Gedanken. 'Our process demonstrates a way to remediate waste PET polymer to fabricate value-added products.'

Kathryn Wills

Carbon spheres from decomposed plastic could be used in lubricants

Reference

S V Pol *et al, Green Chem.*, 2009, DOI: 10.1039/b819494g

Life's building blocks may have travelled to Earth on interstellar silica dust

Did space dust start life on Earth?

Amino acids could have found their way from deep space to start life on Earth, say scientists in Italy.

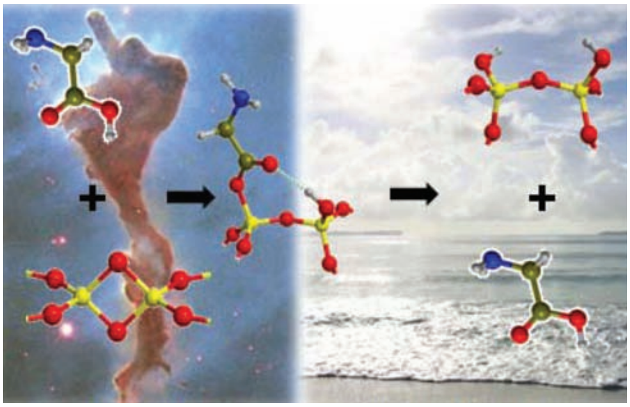
Piero Ugliengo and Albert Rimola from the University of Turin used quantum mechanics to show that amino acids synthesised in deep space molecular clouds can be captured by interstellar dust particles. Ugliengo says that the particles could have travelled to Earth, where the amino acids were released into the 'primordial soup' ready for the synthesis of early proteins.

Ugliengo and Rimola simulated the reaction between the amino acid glycine and interstellar silica dust. Their calculations show that glycine can bond to defects on the silica particles' surface – defects that could have been caused by extreme heat given off by young stars. They tested the particles' stability by simulating conditions in space, such as cosmic rays and UV radiation. They also showed that hydrolysis of the particles, which would have happened when the dust landed in the ocean, released the glycine to become part of the primordial soup.

Ugliengo says that he hopes that experimental evidence will match their findings. 'The key role of the mineral surfaces as a catalyst in the prebiotic era is a very broad and promising one,' he says. 'We need to merge accurate quantum-mechanical modelling studies with carefully designed experimental measurements if any real progress in this exciting field is to be seen.'

'This work not only helps us understand the survival of amino acids formed in the harsh conditions of the interstellar medium, but it also suggests that some of these compounds may have arrived intact to the primitive Earth,' says Antonio Lazcano, a leading scientist in the origin of life and prebiotic chemistry fields, National Autonomous University of Mexico, Mexico City. 'The primitive soup was likely formed by chemical reactions that took place on the Earth but it was clearly spiced by extraterrestrial compounds arriving on board micrometeorites. The richer the broth, the tastier it becomes!'

Sarah Dixon



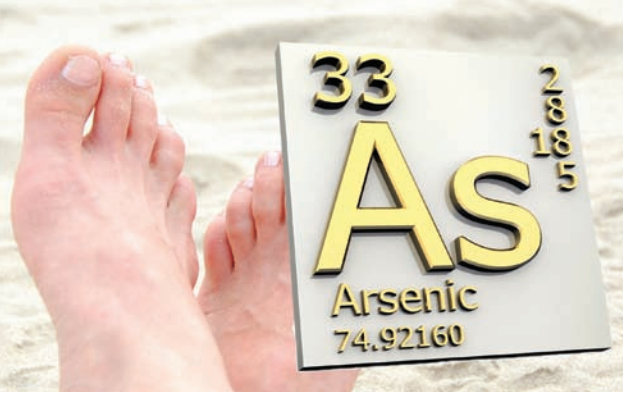
Amino acids may have been captured by silica particles in deep space and released in the primordial ocean

Reference

A Rimola and P Ugliengo, *Phys. Chem. Chem. Phys.*, 2009, DOI: 10.1039/b820577a

Poisonous element detected in toenail exam

Toenails reveal arsenic exposure



UK scientists have finally found a use for toenail cuttings. Mark Button at the British Geological Survey in Nottingham, UK, and colleagues are using the clippings to detect human exposure to elevated environmental levels of arsenic.

Button's group collected toenails from residents living near a former arsenic mine in Devon, UK. They washed and acid digested the samples under microwave irradiation. They then analysed the samples using inductively coupled plasma mass spectrometry. The toenails showed significantly elevated arsenic levels compared to those seen in samples taken from people that had no contact with the element.

Arsenic occurs naturally in the environment and people can be exposed to it in several ways, for example through contaminated water, food or soil. Chronic exposure is associated with increases in lung, liver, bladder and kidney cancers.

Once ingested, arsenic is absorbed into the bloodstream and then accumulates in several body parts. Evidence disappears from blood and urine after a few days but arsenic accumulates long term in keratin rich materials such as hair and nails. This makes them potentially more useful as biomarkers of chronic arsenic exposure. Toenail samples in particular are an attractive possibility as they are easy to collect, store and transport and are less liable to contamination than hair samples.

'This research', says Button, 'highlights the suitability of toenails as a biomarker of exposure to potentially harmful elements in areas such as the south-west of the UK where more extensive biomonitoring studies are long overdue.'

Richard Kelly

Reference

M Button *et al*, *J. Environ. Monit.*, 2009, DOI: 10.1039/b817097e

Instant insight

Metal detectors for clean fuel

Guilhem Caumette, University of Pau - IFP, France, outlines the techniques used to find metal contaminants in petroleum and how they will lead to superior fuels

Petroleum is, and always has been, the primary source of energy on our planet. The shortage of oil reserves, combined with increasing energy demands has brought a surge of interest in revisiting petroleum processing technology in the quest for better performing and cheaper fuels. Oil companies are searching for alternative sources of carbonaceous fuels, such as biofuels and gas condensates, or are trying to improve the efficiency of heavy crude oil (and heavy distillation fractions') conversion to transportation fuels.

Metals and sulfur found in these heavy petroleum fractions can poison the catalysts used during refining processes. They also corrode equipment and contaminate the environment. So investigations focus on detecting metal content in petroleum and petroleum products. The metals' behaviour during the refining processes depends on their speciation – their chemical form. Knowing the size and structure of metal complexes is crucial in choosing catalysts suitable for removing them. Their identity can also give information about the geological origin and migration of oils, and can be used to find new oil fields.

Yet, despite progress in analytical methodology, relatively little is known about the metal species in crude oils. Metalloporphyrin complexes with nickel and vanadium are often cited, but non-porphyrin complexes with molecular weights reaching several thousand Daltons should also be present. More information is available about the forms of sulfur in petroleum or mercury and arsenic in gas condensates but there is no definite agreement on their exact nature.

Reference
G Caumette *et al*, *J. Anal. At. Spectrom.*, 2009, DOI: 10.1039/b817888g

Analysing the elements in petroleum is a nightmare for analysts as the fuel contains thousands of molecules of different sizes and polarities, which interact with different forces. Direct analysis is barely possible and multistep analytical techniques are required to separate and properly identify target metallomolecules.

Relatively little is known about the metal species in crude oils

The interest in speciation of metals and other heteroelements in petroleum-related products has led analysts to develop dedicated analytical techniques and methods. They include direct analytical techniques such as x-ray absorption spectroscopy, electron paramagnetic resonance and molecular mass spectrometry (using laser desorption, electrospray and chemical ionisation) as well as hyphenated techniques that combine chromatography's high separation potential (for example, high performance liquid chromatography or gas chromatography) with an element specific detector's sensitivity (for example, atomic absorption spectrometry).

As these dedicated techniques become more widely available, identifying metal species in complex organic mixtures such as petroleum becomes easier and meeting the challenge of removing them for cleaner fuels becomes a step away.

Read more in 'Element speciation analysis of petroleum and related materials' in issue 3, 2009 of Journal of Analytical Atomic Spectrometry.

Chemistry, life and longevity

Jyoti Chattopadhyaya talks to Marie Cote about chemistry's role in our lives, the secrets of a successful business and delivers his message to younger scientists

Jyoti Chattopadhyaya

Jyoti Chattopadhyaya is Professor of Bioorganic Chemistry at the University of Uppsala, Sweden. His research focuses on a biophysical/bioorganic approach towards understanding the structure–function of nucleic acids, encompassing the design of biological mimics with synthetic chemistry and their structural studies *via* NMR and computation, and kinetics, for a better understanding of the chemistry–biology interface.

What inspired you to be a scientist?

Curiosity inspired me. I am driven by curiosity and the unknown. I also wanted to pass on my knowledge, to let people know what I know. Science is for society, and we, as scientists, have a duty to keep the public informed.

What motivated you to study chemistry?

Once I realised the bountiful gifts of nature as an undergraduate, I understood how chemistry has made our lives so successful. From drugs to clothes to hygiene, chemistry plays a fundamental role. Look at the longevity of the human race today: in Sweden, where I live, you can hope to reach 85–86 years old. Can such longevity be possible without chemistry?

With this in mind, we need to work towards a cleaner environment so that toxicity levels are lowered and controlled. In this way, the positive effects of chemistry will come into focus. If chemistry can find its way into the containment of carbon monoxide and carbon dioxide emissions, then let's hope it won't be unusual to live to 150! We want to live long and productive years, and not perish like the dinosaurs. To reduce carbon dioxide pollution, we need help from all corners of research, for example, to develop hybrid cars for the next generation. Politicians also need to take responsibility. More money should be invested in these research fields and chemistry and politics must work together.

What led you to specialise in the biophysical aspects of nucleic acids?

If you wish to carry out synthetic organic chemistry, you need to understand the physical chemistry behind it. In order to understand biological functions, there must be interplay between physical and synthetic chemistry. Chemistry cannot be distinguished into separate branches as it used to be 30–40 years ago.

How do you see nucleic acid chemistry progressing over the next 10 years?

There is a metamorphosis going on in this field, but nucleic acids do not stand alone – they have a role to play with other biopolymers and ligands. Nucleic acids alone cannot achieve the whole process from transcription and translation to glycosylation of proteins. This can only take place through the interaction of different ligands and biopolymers.

You have initiated many start-up companies. What is the secret to setting up a successful business?

The secret is to understand that we cannot have companies without patents, we cannot have patents without fundamental discoveries, and we cannot have fundamental discoveries without solid support behind us – it's a continuum. The dynamic of the process is very important and the market force alone cannot dictate what will actually make it to the market. I would like to see more commitment from the representatives of our democratic society; I would be happy to see some of the profits from the start-up companies go back to the tax payers.

What would your message for younger scientists be?

Have trust in yourself, and be ready to put your heart and soul into the game. We as teachers have a responsibility to communicate to the younger generation about the science of today and how it has developed. However, I can only paint my own picture: the students have to decide for themselves. Science pays off, but it demands a full commitment. The younger generation takes it for granted, because they have not seen days without antibiotics or a flushing toilet. We would not be what we are today without science and many people tend to forget this. That is the message I want to give to them.

What would you be if you were not a scientist?

I wasn't very good at sports. I played some chess, but I was not alpha plus in that either. But I am good at what I do, and that is what I want to be. I want to keep sharpening my mind and look forward: there is still much to learn.

Essential elements

2009 spring conferences

With the 2009 spring conference season about to begin, RSC Publishing staff will be spread around the globe at a number of major conferences over the forthcoming weeks.

Meet RSC staff at Pittcon in Chicago, US, from 8–12 March. This comprehensive annual meeting on laboratory science this year celebrates 60 years of service to the scientific community. Visit the RSC at booth #3410 and meet Niamh O'Connor, the editor of *Analyst* and *JAAS*, the market leader in spectrometric techniques. Pick up free copies of RSC journals and enter our competition to win an iPod touch when you sign up to journal e-alerts. Keep up-to-date with forthcoming RSC Pittcon announcements at www.rsc.org/publishing

The RSC will also be at the American Physical Society (APS) meeting in Pittsburg, PA, US, from 16–20 March, where around 7000 scientists gather to share research on a wide range of physics and physics-related topics. Visit us at booth #117.

Salt Lake City, US, hosts the 237th ACS National Meeting & Exposition, from 22–26 March. Enjoy the rich programme of scientific papers on a variety of multidisciplinary topics, including thematic programming around nanoscience. Meet Geoff Ozin (a speaker in the Naturally Nano session on Tuesday 24 March) who will be at RSC booth #1525 signing copies of his best selling book, *Nanochemistry*. The 2nd edition highlights the latest breakthroughs using more than eighty new case histories, problem sets and teaching principles.

If you're travelling to these or other conferences, look out for RSC Publishing staff – they will be happy to meet you. Visit our stand and pick up sample copies of journals, look out for special offers on the RSC book collection and keep up-to-date with the latest developments and exciting new announcements from RSC Publishing.

Faraday Discussions grow in popularity

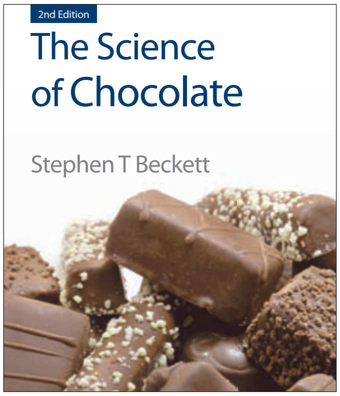
Faraday Discussions, the long-established series of meetings providing unique international views on newly acquired physical chemistry, chemical physics and biophysical chemistry results, has increased its frequency this year from three to four meetings. These meetings take a special format, in which papers are distributed to all participants in advance of the conference and almost all of the meeting is devoted to discussion of the papers. Previous *Faraday Discussions* volumes are available to buy online at www.rsc.org/books.

Faraday Discussions' latest impact factor is 5.0, emphasising its highly cited and well respected accounts by world-class experts in physical chemistry. Philip Earis, editor for *Faraday Discussions* comments: 'The unique format of *Faraday Discussions*, and the world-class speakers that discussions attract, lead to outstanding and stimulating debate in topical areas of physical chemistry.'

2009 sees the discussion of Cold and ultracold molecules; Soft nanotechnology; Multi-scale modelling of polymers, colloids, mesophases and membranes; and Frontiers in physical organic chemistry. Registration is now open for the first meeting in April which will be held at Durham University, UK. Visit www.rsc.org/faraday for further information on past and future *Faraday Discussions*.

And finally...

As part of this year's food theme, the RSC's book programme will showcase titles focused on, or related, to the food sciences. The RSC already has an extensive food science list catering for scientists at all levels from schools and universities through to industry. *The Science of Chocolate*, *Chemistry and Biology of Winemaking* and *Food: The Chemistry of its Components* (5th edition) are already established as best selling titles, used by the scientific community and professionals globally.



2009 begins with the publication of the *Microbiology Handbook (Diary)*, shortly followed by other exciting new food titles including *Nanotechnologies in Food* (from the RSC's landmark *Nanoscience and Nanotechnology* series) and *Handbook of Culture Media for Food and Water Microbiology*. These titles will be complemented further by other exciting projects to be published throughout the year.

For more information please visit www.rsc.org/books

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