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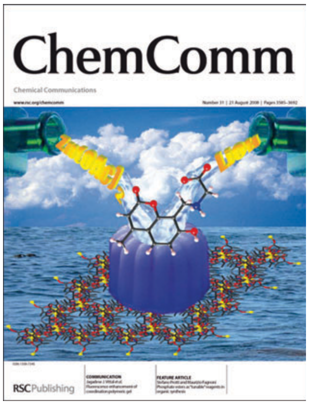
IN THIS ISSUE

ISSN 1359–7345 CODEN CHCOFS (31) 3585–3692 (2008)

Cover
See Véronique Gouverneur *et al.*, pp. 3622–3624.
The cover illustrates an exemplary transformation with the blossoming of an orchid flower. We demonstrate that fluorous allylsilanes were detagged with Selectfluor to deliver allylic fluorides purified by Fluorous solid Phase Extraction. This transformation, featuring a C–F bond-forming reaction as the detagging event, is particularly relevant for application in the area of medicinal chemistry and radiochemistry. Image reproduced by permission of Sophie Boldon, Jane E. Moore and Véronique Gouverneur from *Chem. Commun.*, 2008, 3622.



Inside cover
See Jagadese J. Vittal *et al.*, pp. 3628–3630.
The image illustrates the formation of a fluorescent hydrogel by a coordination polymer containing a ligand without any long alkyl chains. Image reproduced by permission of Wei Lee Leong, Anthony Yiu-Yan Tam, Sudip K. Batabyal, Lee Wah Koh, Stefan Kasapis, Vivian Wing-Wah Yam and Jagadese J. Vittal from *Chem. Commun.*, 2008, 3628.

CHEMICAL SCIENCE

C57

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

August 2008/Volume 5/Issue 8

www.rsc.org/chemicalscience

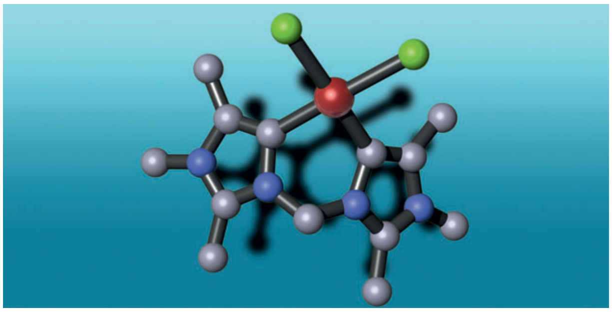
FEATURE ARTICLE

3601

C4-bound imidazolylidenes: from curiosities to high-impact carbene ligands

Martin Albrecht*

Imidazolium-derived *N*-heterocyclic carbenes that bind *via* C4 rather than C2 are becoming an increasingly popular class of ligands for implementing new reactivity patterns at the metal, for example for catalytic applications.



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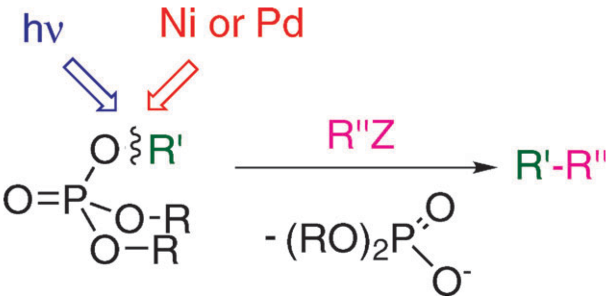
FEATURE ARTICLE

3611

Phosphate esters as "tunable" reagents in organic synthesis

Stefano Protti and Maurizio Fagnoni*

This *Feature Article* shows that phosphate esters (scarcely reactive towards nucleophilic substitution) can be activated by using metal catalysis and photochemistry thus obtaining conveniently tunable reactions.



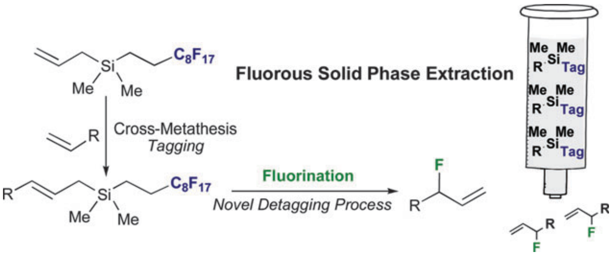
COMMUNICATIONS

3622

Fluorous synthesis of allylic fluorides: C–F bond formation as the detagging process

Sophie Boldon, Jane E. Moore and Véronique Gouverneur*

A novel fluorous tagging–detagging strategy has been developed featuring a fluorination as the detagging process. Fluorous allylsilanes were prepared by cross-metathesis and subjected to fluorodesilylation. The resulting allylic fluorides were successfully purified by fluorous solid phase extraction.

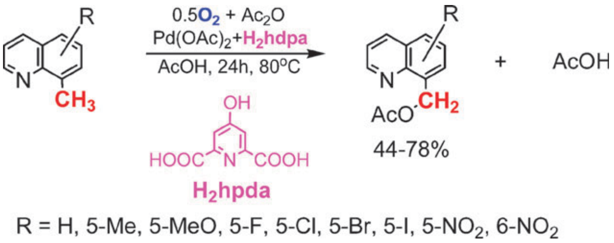


3625

Catalytic aerobic oxidation of substituted 8-methylquinolines in Pd^{II}-2,6-pyridinedicarboxylic acid systems

Jing Zhang, Eugene Khaskin, Nicholas P. Anderson, Peter Y. Zavalij and Andrei N. Vedernikov*

Palladium(II) 2,6-pyridinedicarboxylates catalyze homogeneous regioselective oxidation of substituted 8-methylquinolines with O_2 under mild conditions in AcOH–Ac_2O solution to produce corresponding 8-quinolylmethyl acetates.

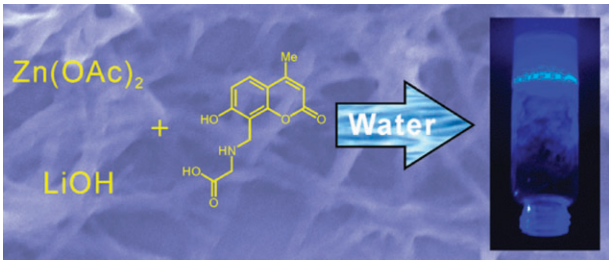


3628

Fluorescence enhancement of coordination polymeric gel

Wei Lee Leong, Anthony Yiu-Yan Tam, Sudip K. Batabyal, Lee Wah Koh, Stefan Kasapis,* Vivian Wing-Wah Yam* and Jagadese J. Vittal*

A 1D coordination polymer forms a hydrogel without the incorporation of hydrophobic long-chain alkyl groups in the ligand backbone. Furthermore, the fluorescence of the ligand chromophore is enhanced due to gelation.



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Sir J Fraser Stoddart, Northwestern University
Vivian W W Yam, The University of Hong Kong
Richard N Zare, Stanford University

For a detailed list of symposia, keynote speakers and to submit an abstract visit our website.

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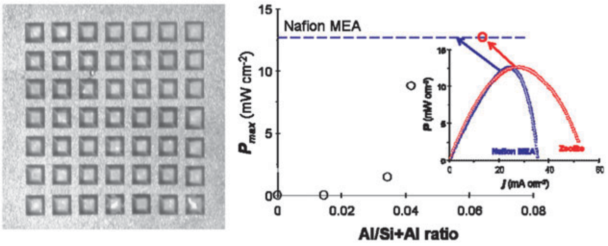
3631

Zeolite micro fuel cell

Siu Ming Kwan and King Lun Yeung*

Microfabricated HZSM-5 micromembranes were successfully employed as a proton-exchange membrane in a micro fuel cell and the energy generation is strongly dependent on the Al-content of the HZSM-5. A 6-μm thick HZSM-5 (Si/Al = 15) displays comparable performance to the Nafion® 117 generating OCV = 0.84 V, P_{max} = 12.8 mW cm^{-2} and j_{max} = 55 mA cm^{-2}.

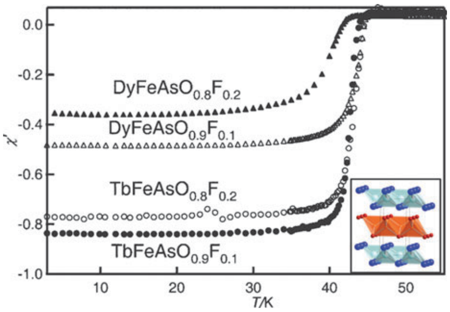


3634

High pressure synthesis of late rare earth RFeAs(O,F) superconductors; R = Tb and Dy

Jan-Willem G. Bos, George B. S. Penny,
Jennifer A. Rodgers, Dmitry A. Sokolov,
Andrew D. Huxley and J. Paul Attfield*

TbFeAs(O,F) and DyFeAs(O,F) superconductors with critical temperatures 46 and 45 K have been prepared by high pressure synthesis at 1100–1150 °C and 10–12 GPa. The superconductivity is found to be strongly 2-dimensional with very large critical fields at low temperatures.

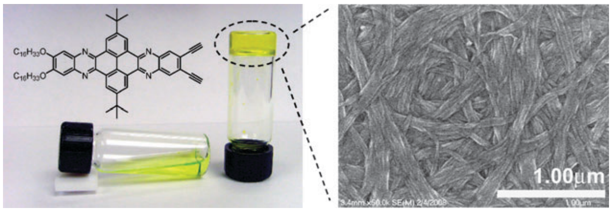


3636

Nanofibers of asymmetrically substituted bisphenazine through organogelation and their acid sensing properties

Dong-Chan Lee,* Kelly K. McGrath and Kyoungmi Jang

We report the organogelation of an asymmetric bisphenazine in select organic solvents through the growth of one-dimensional nanofibers *via* π–π interaction, hydrogen bonding, and van der Waals interaction and the colorimetric acid sensing property of the nanofibers.

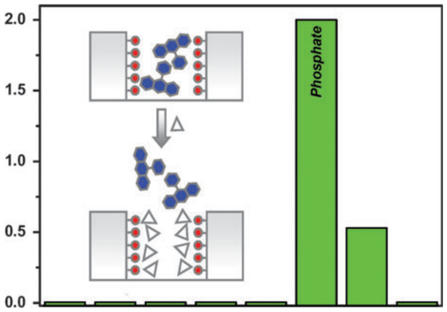


3639

Hybrid materials with nanoscopic anion-binding pockets for the colorimetric sensing of phosphate in water using displacement assays

María Comes, María D. Marcos,
Ramón Martínez-Máñez,* Félix Sancenón, Juan Soto,
Luis A. Villaescusa and Pedro Amorós

Mesoporous amino-functionalised solids containing certain dyes have been used as suitable anion hosts in displacement assays for the colorimetric signalling of phosphate in water.



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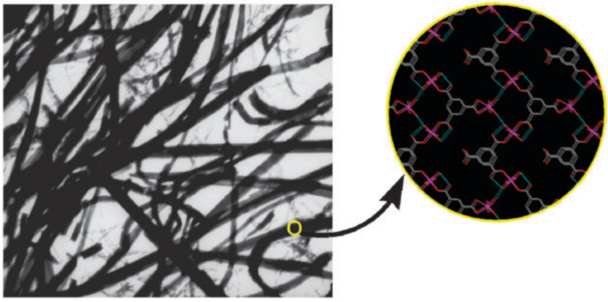
3642

Facile synthesis of nanocrystals of a microporous metal–organic framework by an ultrasonic method and selective sensing of organoamines

Ling-Guang Qiu,* Zong-Qun Li, Yun Wu, Wei Wang, Tao Xu and Xia Jiang

An ultrasonic method is employed for the first time to synthesize a nanoscale microporous metal–organic framework, by which a fluorescent sensor for the sensing of organoamines with remarkable size-selectivity has been developed.

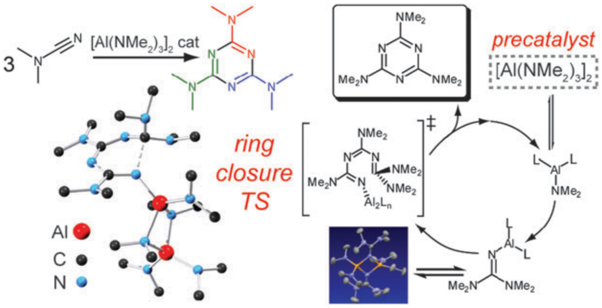


3645

Atom efficient cyclotrimerization of dimethylcyanamide catalyzed by aluminium amide: a combined experimental and theoretical investigation

Peter Dornan, Christopher N. Rowley, Jessica Priem, Seán T. Barry, Tara J. Burchell, Tom K. Woo* and Darrin S. Richeson*

$[Al(NMe_2)_3]_2$ catalyzes the cyclotrimerization of dimethylcyanamide to form hexamethylmelamine. DFT modelling confirms that the catalytic cycle includes triple cyanamide insertion, nucleophilic ring closure, and deinsertion.

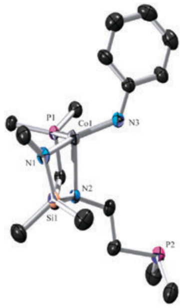


3648

Reactivity of a Co(I) $[N_2P_2]$ complex with azides: evidence for a transient Co(III) imido species

Wayne A. Chomitz and John Arnold*

Treatment of a Co(I) N_2P_2 complex with azides at low temperature generates a transient species whose derivative chemistry is consistent with imido (Co=NR) character.

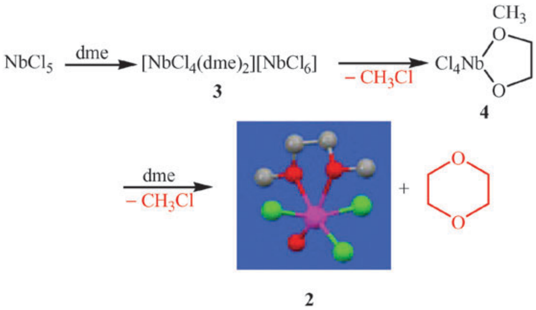


3651

From 1,2-dialkoxyalkanes to 1,4-dioxanes. A transformation mediated by $NbCl_5$ *via* multiple C–O bond cleavage at room temperature

Fabio Marchetti, Guido Pampaloni* and Stefano Zacchini

An unprecedented reaction, taking place through cleavage of three of the four dme C–O linkages, occurs between $NbCl_5$ and dme at room temperature and affords $NbOCl_3(dme)$, methyl chloride and 1,4-dioxane. Similar reactions occur with 1,2-diethoxyethane, 1,2-dimethoxypropane and diglyme.

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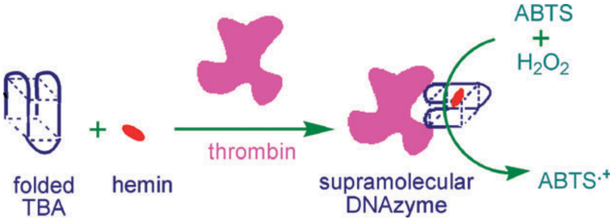
3654

G-quadruplex-based DNAzyme for facile colorimetric detection of thrombin

Tao Li, Erkang Wang and Shaojun Dong*

Thrombin is found to promote the binding of folded thrombin-binding aptamer (TBA) to hemin and thus a supramolecular complex with peroxidase-like activity is formed, which enables the colorimetric detection of thrombin in a facile way.

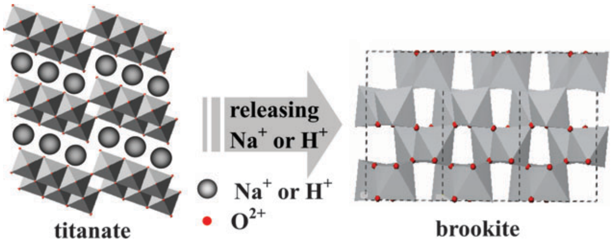


3657

Brookite-type TiO_2 nanotubes

Qixin Deng, Mingdeng Wei,* Xiaokun Ding, Lilong Jiang, Binghuo Ye and Kemei Wei

Brookite-type TiO_2 nanotubes with crystalline multilayer walls were synthesized for the first time *via* a simple hydrothermal route.

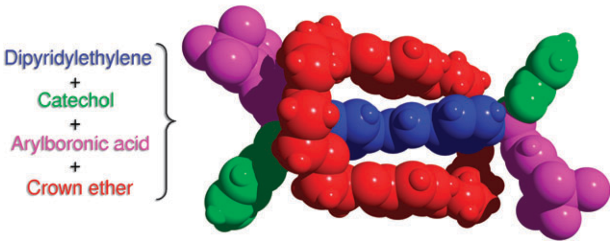


3660

Boron-based rotaxanes by multicomponent self-assembly

Nicolas Christinat, Rosario Scopelliti and Kay Severin*

Boron-based rotaxanes can be obtained by the reaction of 1,2-di(4-pyridyl)ethylene, catechol, 3,5-bis(trifluoromethyl)-phenylboronic acid and crown ethers.

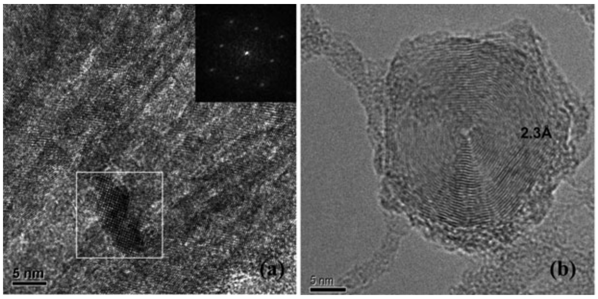


3663

High contrast solid state electrochromic devices based on Ruthenium Purple nanocomposites fabricated by layer-by-layer assembly

Vaibhav Jain, Rabindra Sahoo, Joerg R. Jinschek, Reza Montazami, Hank M. Yochum, Fredrick L. Beyer, Anil Kumar and James R. Heflin*

Electrochromic Ruthenium Purple–polymer nanocomposite films, fabricated by multilayer assembly, were found to exhibit sub-second switching speed and the highest electrochromic contrast reported to date for any inorganic material.

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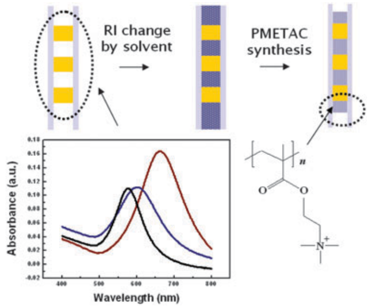
3666

Localized surface plasmon resonance (LSPR) sensitivity of Au nanodot patterns to probe solvation effects in polyelectrolyte brushes

Sarah Kim, Nan Cheng, Jong-Ryul Jeong, Se-Gyu Jang, Seung-Man Yang and Wilhelm T. S. Huck*

We report the use of localized surface plasmon resonance (LSPR) of hexagonal Au nanodot arrays to detect changes in the thickness and conformation of polymer brushes.

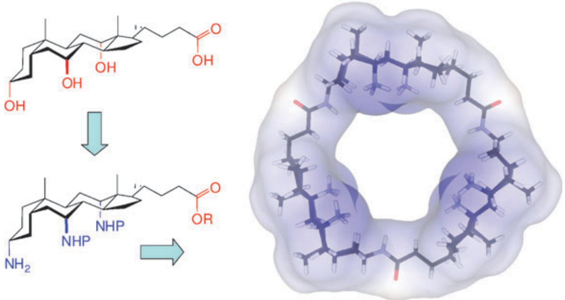


3669

Cationic cyclocholamides; toroidal facial amphiphiles with potential for anion transport

Samuel D. Whitmarsh, Adrian P. Redmond, Valentina Sgarlata and Anthony P. Davis*

Cholic acid has been transformed into cyclotrimeric and cyclotetrameric toroidal amphiphiles with inward-directed ammonium substituents; the cyclotrimer (shown) effects the transport of chloride anions across vesicle bilayer membranes.

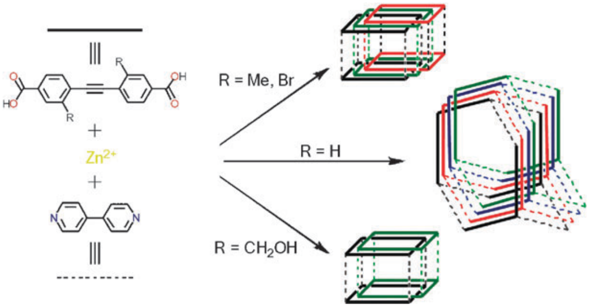


3672

Ligand-elaboration as a strategy for engendering structural diversity in porous metal–organic framework compounds

Tendai Gadzikwa, Bi-Shun Zeng, Joseph T. Hupp* and SonBinh T. Nguyen*

A series of Zn-based, mixed-ligand metal–organic frameworks with differing connectivities and varying levels of interpenetration were synthesized from 4,4′-ethynylenedibenzoic acids having tunable functionalities in the 3- and 3′-positions.

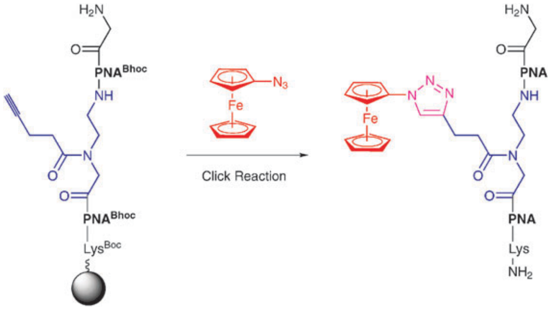


3675

Synthesis of organometallic PNA oligomers by click chemistry

Gilles Gasser, Nina Hüsken, S. David Köster and Nils Metzler-Nolte*

Click chemistry is used for the facile side-specific insertion of one or two ferrocene moieties into peptide nucleic acid (PNA) oligomers on the solid phase.



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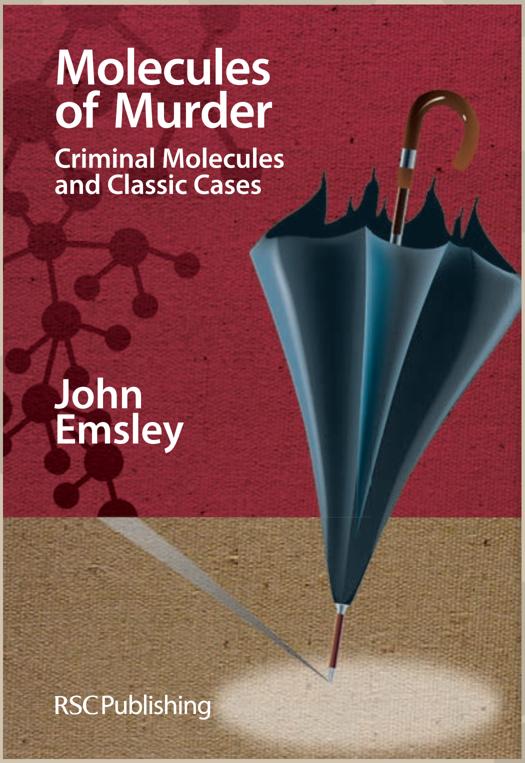

Molecules
of Murder

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This fascinating new book is about infamous murderers and famous victims! It includes the stories of people like Harold Shipman, Alexander Litvinenko, Adelaide Bartlett, and Georgi Markov. Few books on poisons analyse these crimes from the viewpoint of the poison itself, and doing so throws new light on how the murders or attempted murders were carried out and ultimately how the perpetrators were uncovered and brought to justice.

The reader is taken on a journey of discovery into the world of dangerous organic poisons. Ten highly toxic molecules are described all of particular interest due to their use in notorious murder cases. Each chapter explores the discovery of the molecules, their chemistry and effects in humans, followed by a re-examination of their deliberate misuse in high profile murder cases!

Title: Molecules of Murder
Sub Title: Criminal Molecules and Classic Cases
Author: John Emsley
ISBN: 9780854049653
Publication Date: August 2008
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Meet the Author…

Molecules of Murder Book Launch **30th July 2008, London, UK.**

236th ACS National Meeting & Exposition **17 – 21st August 2008, Philadelphia, USA.**

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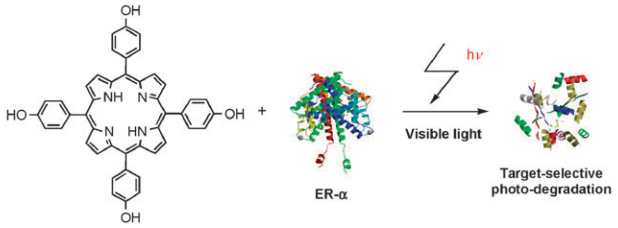
3678

Target-selective degradation of proteins by porphyrins upon visible photo-irradiation

Shuho Tanimoto, Shuichi Matsumura and Kazunobu Toshima*

A selected porphyrin derivative, when irradiated with visible light, effectively and selectively degraded the target transcription factor, human estrogen receptor-α (hER-α), in the absence of additives and under neutral conditions.

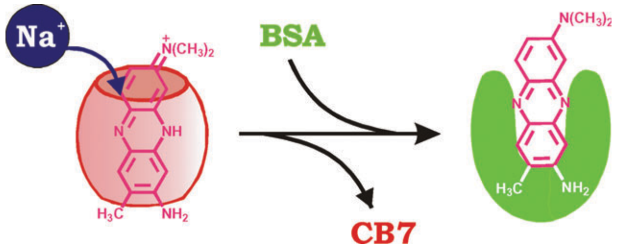


3681

Salt-induced guest relocation from a macrocyclic cavity into a biomolecular pocket: interplay between cucurbit[7]uril and albumin

Mhejabeen Shaikh, Jyotirmayee Mohanty,* Achikanath C. Bhasikuttan, Vanya D. Uzunova, Werner M. Nau and Haridas Pal*

The salt-induced tuning of the pK_a value of the dye Neutral Red in the presence of cucurbit[7]uril (CB7) and BSA is exploited to relocate the dye from the macrocyclic cavity of CB7 into the biomolecular pocket of bovine serum albumin.

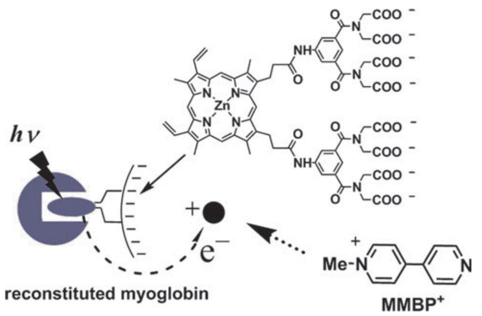


3684

Photocatalytic hydrogen generation using a protein-coated photosensitizer with anionic patches and a monocationic electron mediator

Takashi Matsuo, Atsushi Asano, Tsutomu Ando, Yoshio Hisaeda and Takashi Hayashi*

A reconstituted myoglobin with a synthetic cofactor having anionic binding sites effectively works as a photocatalyst for hydrogen generation in the presence of monomethylated bipyridinium.

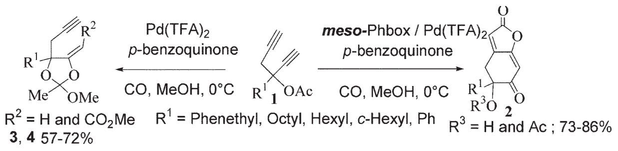


3687

meso-Phbox-Pd(II) catalyzed tandem carbonylative cyclization of 1-ethynyl-1-propargyl acetate

Keisuke Kato,* Ryuhei Teraguchi, Satoshi Motodate, Akira Uchida, Tomoyuki Mochida, Tat'yana A. Peganova, Nikolai V. Vologdin and Hiroyuki Akita*

The use of *meso*-Phbox-Pd(II) strikingly changed the course of carbonylation of 1-ethynyl-1-propargyl acetate **1**, yielding bicyclic lactone **2** by tandem carbonylative cyclization as a result of insertion of the second triple bond.



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August 2008 / Volume 5 / Issue 8 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

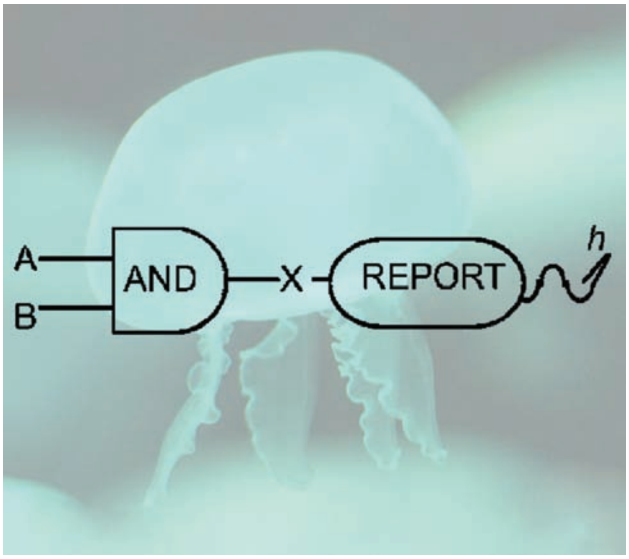
Jellyfish protein glows to demonstrate logic gate success

Fluorescent green logic

Japanese scientists are applying logic to the protein that causes jellyfish to fluoresce green.

Takahiko Nojima, and colleagues at the University of Tokyo, have created a system that uses protein synthesis to report on the success of four different biochemical logic gates. Analogous to computer logic gates, biochemical logic gates are used to direct simple biological functions.

The system consists of two parts: a logic gate that amplifies the DNA that codes for the protein and a report gate where the protein is expressed. In the first part a polymerase enzyme amplifies the DNA of interest – the template DNA – in a process called the polymerase chain reaction (PCR). Two pieces of complementary DNA called primers are required to start the PCR, and these act as the input signals for the gate. The amplified DNA contains not only a code for the protein but also sequences that recognise the 'machinery' in the report gate. As this enters the report gate the protein is expressed and the output measured by the green fluorescence coming from the protein.



The team successfully designed and constructed different primers and templates so that AND, OR, NOT and AND-NOT operations could be executed, with all four gates reporting successfully and fluorescing as expected.

Biochemical logic gates direct simple biological functions

Many DNA-based logic systems suffer from false positive signals, says Nojima. In our system, by adding the protein expression step, this possibility is cut off, he explains. This is because only a completely correct piece of DNA will express the protein, giving a fluorescent output. Nojima says he believes this definite on/off fluorescent signal is the most exciting aspect of his work.

A P de Silva, an expert in molecular logic at Queen's University, Belfast, UK, says that this work is valuable because it brings the important technique of PCR into the fold of biological versions of molecular logic.

Nojima says his group is now aiming 'to install the PCR-based logic gate into a microfluidic device.'

Frances Galvin

Reference

T Nojima *et al*, *Chem. Commun.*, 2008, DOI:10.1039/b807039c

In this issue

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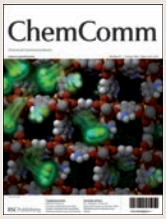


A snapshot of the latest developments from across the chemical sciences

Research highlights

A new type of molecular keypad lock is unveiled

Molecular data protection

Molecular keypad lock fluoresces in response to correct chemical input

Scientists in India have found the key to protecting information at a molecular level.

A molecular keypad lock, using a novel organic compound as a chemosensor, has been made by Amitava Das and his colleagues at the Central Salt and Marine Chemicals Research Institute, Gujarat.

Das synthesised 1-amino-8-naphthalene sulfonic acid ester, and found that it fluoresces when it comes into contact with copper and mercury. And that when more than one substrate is used, the fluorescence response depends on the order the substrates are added. For example, adding copper followed by fluoride produces a different response to adding fluoride followed by copper. The effect is caused by the different fluorescent properties and kinetic stabilities of the complexes formed.

The group then demonstrated the extension of this concept to a molecular keypad lock, with copper and fluoride acting as the two inputs and the fluorescence response as the output. Das hopes this idea will provide the basis of molecular logic gates for security purposes, 'Although the keypad lock demonstrated here can only process a password limited to two input bits, it inspires the imagination towards the development of the next generation of confidential identification technologies,' he says.

Uwe Pischel, an expert in molecular logic devices at the University of Huelva, Spain, agrees, 'The mimicking of complex logic functionality, like a keypad lock, with a surprisingly simple molecular structure underlines the potential of fluorescence control by chemical signals for the realisation of useful devices.'

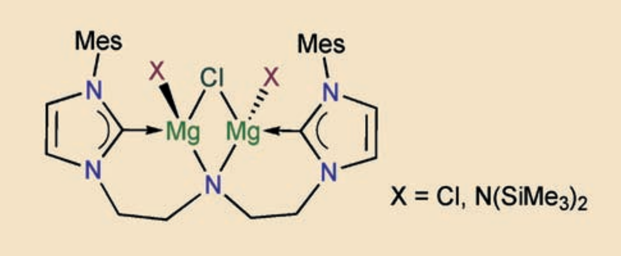
A real device using this idea is some way off; developing a system with more inputs and integrating the organic molecules into solid-state devices remains a challenge. 'The existing examples can hardly compete with the present silicon-based numeric locking and protection process,' Das explains, 'but these reported examples are a good demonstration of the concept as a proof-of-principle.'

Edward Morgan

Reference
M Suresh, *Chem. Commun.*, 2008, DOI: 10.1039/b807290f

Dimagnesium-carbene complex demonstrates catalytic credentials

Double the metal



The complex contains the shortest magnesium carbene bond ever seen

An unusual dimagnesium-carbene complex could make a useful new catalyst, claim UK chemists.

A new tridentate ligand that tightly binds two magnesium ions has been developed by Polly Arnold, of the University of Edinburgh, and colleagues. The complex holds the magnesium ions in place through two N-heterocyclic carbene groups and a central amine, with the two metals sitting in the open face of the ligand where their reactivity can be exploited.

'N-heterocyclic carbenes are being explored intensively as ligands for homogeneous catalysts based on the soft, platinum group metals. We've been studying their binding to harder metal cations,' says Arnold. 'This new ligand is very straightforward to make – we hope that these complexes will show a very different type of catalytic activity to the softer metal-based systems.'

The Edinburgh team confirmed that the dimagnesium in the complex was accessible for reaction by substituting two chlorine ligands from the top face. The resulting structure formed colourless crystals from which x-ray structures could be obtained – revealing that the complex contains the shortest magnesium carbene bond ever seen.

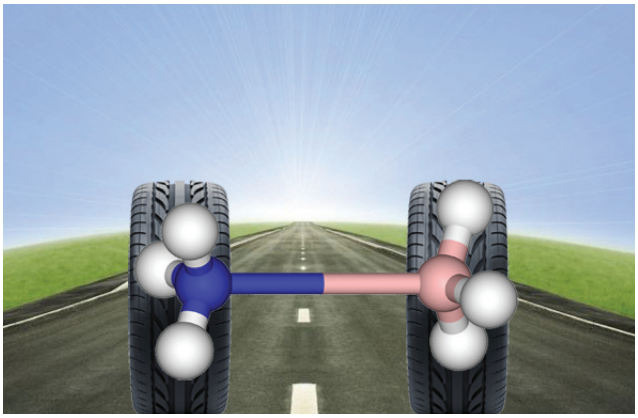
Andreas Danopoulos studies carbene complexes at the University of Southampton, UK, and agrees that the magnesium structure could make a useful catalyst. But the complex could also be a source of new metal structures, he adds. 'The complex could be used further, using a transmetallation reaction to give transition metal carbene complexes, or even lanthanide or actinide structures.'

James Mitchell Crow

Reference
P L Arnold *et al.*, *Dalton Trans.*, 2008, 3739 (DOI: 10.1039/b803253j)

Borane leads the way to alternative fuels

Fuelling the future



Materials which can store and release hydrogen on demand are sought after as petrol alternatives

New routes to hydrogen storage materials, which could offer alternative fuel for cars, have been developed by two teams of scientists in the US and Singapore.

Hydrogen is an important energy source as it reacts with oxygen to release energy with the only by-product being water. However, at atmospheric pressure it is gaseous, and therefore needs to be stored at high pressure to reduce the storage volume. By using a solid material with a high hydrogen content the volume required for hydrogen storage is considerably reduced, and the need for high pressure eliminated.

Ammonia borane (NH_3BH_3) has a high hydrogen content and is stable at room temperature, but has, in the past, proven difficult to prepare in high yield. Now, Tom Autrey and co-workers at the Pacific Northwest National Laboratory, Richland, US, have developed a new one-pot synthetic method to this solid material.[1]

Autrey's method requires in situ production of ammonium borohydride (NH_4BH_4) by the addition of NH_4X and MBH_4 salts (X = Cl, F, M = Na, Li) in liquid ammonia, followed by removal of the majority of the ammonia, then addition of tetrahydrofuran (THF) which causes the NH_4BH_4 to decompose to ammonia borane in high yield.

As Autrey explains, 'to be a viable hydrogen storage material economic routes to synthesis and regeneration are of the utmost importance.' At the moment hydrogen release from ammonia borane is not reversible, therefore Autrey says the 'long-term challenge is to regenerate ammonia borane from the spent storage material'.

Another problem with ammonia borane is that its decomposition leads to the production of the volatile compound borazine as a by-product. Borazine can poison proton exchange membrane fuel cells. This issue has been addressed by another team, led by Ping Chen at the National University of Singapore.[2]

Chen proposes the use of sodium aminoborane ($NaNH_2BH_3$) as an alternative to ammonia borane as it does not release borazine on decomposition. Traditionally sodium aminoborane is made using a mechano-synthetic route which requires additives to aid milling. But these additives cause a reduction in the hydrogen density of the product.

Chen's wet-chemical method allows pure sodium aminoborane to be made. He proposes two routes, the faster of which involves adding sodium hydride (NaH) to a solution of ammonia borane in THF. The reaction occurs within 10 minutes at –3 °C, giving solid sodium aminoborane which can be filtered off.

Xiong Zhitao, a member of Chen's team, says the most important aspect of this work is that 'it opened the road to a new class of materials comprising alkali or alkaline earth metal cation and $[NH_2BH_3]^-$ anion for storing hydrogen'.

Todd Marder at Durham University, UK, welcomes both teams' research, saying 'the study of materials which can store and release, under mild conditions, a significant percentage of their weight as hydrogen, is certainly one which is of considerable importance. However, given that the hydrogen release is not reversible, a major effort to develop economical methods for regeneration of ammonia borane is required if such materials are to result in commercially viable technologies for common use as hydrogen sources for automobiles.'

Vikki Chapman

References

1 D J Heldebrant *et al*, *Energy Environ. Sci.*, 2008, DOI: 10.1039/b808865a

2 Z Xiong *et al*, *Energy Environ. Sci.*, 2008, DOI: 10.1039/b805649h

News in brief

Natural solutions for malaria
French researchers have gained a new insight into the mechanism for fighting malaria which could be used to develop low cost drugs

Strontium strengthens imitation bones
New ceramics containing strontium, that has known anti-osteoporotic effects, offers a new approach to bone replacements

Model fireworks
Watching firework displays could be bad for both your health and the environment, claim UK scientists

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

This month in *Chemical Technology*

Fuel cell drives forward electric car
Scientists have made the first renewable fuel cell that can store more energy than petrol

Flow chemistry for the masses
Two new build-your-own microfluidic systems simplify the technology to make it assessable to all

Interview: Navy's sensing mission
Frances Ligler talks about portable, automated biosensors for fast detection of pollutants, drugs and explosives

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

This month in *Chemical Biology*

Dunking donuts into cells
Doughnut-shaped particles could help to reduce side effects from cancer treatments, says a team of scientists from the UK

Faster superbug detection
New chip technology offers a way to detect bacteria in blood plasma samples and simultaneously screen their response to antibiotics

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

Concern is growing about the fate of bismuth once it enters the environment

How non-toxic is non-toxic?

Canadian scientists have studied the effect of 'non-toxic' bismuth shotgun pellets on the environment with thought-provoking results.

Bismuth pellets were introduced as a non-toxic alternative to lead in 1994 in the US and 1997 in Canada, due to their similar ballistic properties. With spent pellets now spread across rural North America, little is actually known about the fate of bismuth once it enters the environment.

To help fill this knowledge gap, Nathan Fahey, University of Waterloo, Toronto, and co-workers placed bismuth pellets on the surface of a freshwater wetland, and tested the soil and plants for bismuth contamination each year for four years. The group's results suggest that, in this prime environment for the hunting of game birds, bismuth is leached into the soil but is not transferred from the soil into the plants.

Fahey hopes that his findings will encourage other researchers to further examine the non-toxic status of bismuth. He says that a variety of ecosystems must be studied and long term research is needed to trace the fate of bismuth from shot-gun pellets. *Fay Riordan*

Bismuth is widely used as a non-toxic alternative to lead in shotgun pellets

Reference
N S C Fahey *et al*, *J. Environ. Monit.*, 2008, DOI: 10.1039/b801535j

Click chemistry steers the way to a variety of multifunctional polymers

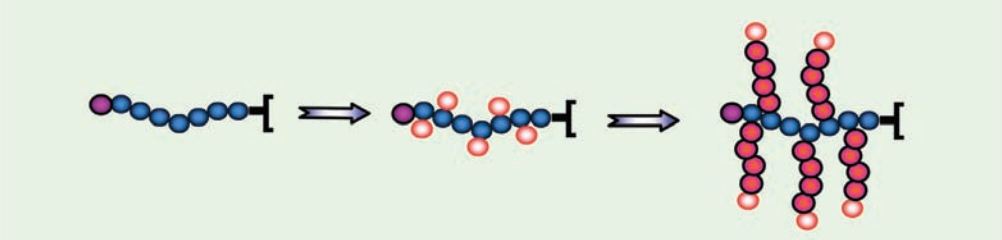
Polymers click in tune

Side chains of copolymers can now be clicked into place thanks to a new method developed by Dutch researchers.

Ulrich Schubert and co-workers at Eindhoven University of Technology, The Netherlands, started by making a copolymer backbone with para-fluorine groups called poly(pentafluorostyrene-b-styrene). Next they used click chemistry to graft simple side chains – amine-containing macromonomers – onto the backbone. In this reaction the para-fluorine groups on the backbone undergo nucleophilic substitution with the primary amines. Schubert found that a variety of functionalised polymers could then be added into the side-chains of the graft copolymer using both atom transfer radical polymerisation and ring opening polymerisation.

The extension of the side chains using functionalised polymers allows the properties of the graft copolymer to be fine tuned. 'The diversity makes this method so unique,' says Schubert. 'The scope of this approach is seemingly unlimited since it might be applied in any area that includes polymers' he adds.

Fluorinated polymers show high thermal stability, chemical resistance, good mechanical properties at high temperatures and low flammability. This makes them useful in microelectronic devices and antifogging agents. Schubert hopes his new polymers can be developed for a variety of functions including coupling catalysts to the polymer backbone and a drug carrier to target specific groups, for example sugars. *Sylvia Pegg*



Polymer properties can be tuned through side-chain extension

Reference
C Ott, R Hoogemboom and U S. Schubert, *Chem. Commun.*, 2008, DOI: 10.1039/b807152g

The chemistry [r]evolution

Mike Doyle talks to Emma Shiells about evolution in chemistry, from Doyle's catalyst to how water saved the day

Mike Doyle

Mike Doyle is Professor and Chair of the Department of Chemistry and Biochemistry at the University of Maryland, Baltimore, US. His research is focused on applications with metal carbene transformations, Lewis acid catalysed reactions, and selective catalytic oxidations. He is the new associate editor for organic chemistry in *Chemical Communications*.

What inspired you to become a scientist?

I came into science at a time when the Sputnik revolution was occurring in the US. I had a high school teacher who was very inspirational. He was a very short fellow, but when he talked about chemistry, he levitated! It was this teacher that taught me that chemistry was the place to go.

Why did you choose to study transition metal catalysis in organic synthesis?

I started my career looking at processes surrounding dinitrogen compounds, or nitrogen in general. Looking at the aspects of catalysis became a natural progression. We looked at catalysis in biological systems, then at rhodium-catalysed systems because they had just emerged on the scene. The work was a success; it evolved faster than all of the other areas we were working on.

Were any of your projects taken on commercially?

In the 1990s, we developed a set of rhodium catalysts – carboxamidates – that had chiral ligands; those systems became known as the Doyle catalysts. They were commercialised and have been used in industry and universities.

What achievement are you most proud of in your career to date?

Developing the Doyle catalysts was one achievement, but there was also the study on the role of nitrite in medicine in the 1980s. We had elaborated the mechanism of how nitrite acts as a nitric oxide donor in biological systems, in studies with haemoglobin and myoglobin. Unfortunately, in the mid 1980s, we had to drop this research due to lack of funding. Then, in the late 1990s, this became a very popular area and in early 2000, conferences were being held on the biological and physiological effects of nitrite. I attended a meeting in 2005, at the National Institutes of Health, talking about nitrite in medicine and physiology and I was introduced as the 'father' of the area. I took a lot of pride in that.

Is your research more biological now?

No, it is more catalytic now. You can't stay in a particular area for too long these days, because of the nature of how chemistry evolves. Whatever you are doing should evolve. It's not a revolution anymore – it's an evolution. We have evolved catalysis, starting from our initial work using catalysts for metal carbene formation, to Lewis acid catalysed reactions, to oxidation chemistry and, more recently, to materials.

Where do you get your ideas from? What inspires you?

Stress is one thing! Or knowing that you have to make changes. When something confounds you, but you can't understand how it happened or why it happened, that leads to change. Students also drive you. A very good student will say 'I'm not going to do the same thing as the person in front of me; I want to do something different.' And they head off in directions that you would never have taken yourself.

You are the new associate editor for *Chemical Communications*. What do you hope to achieve in your new role?

To increase the visibility of *Chemical Communications* in the organic chemistry community, by showing the advantages of *Chemical Communications*, and by highlighting the fact that it would be a very good component of an overall research publication portfolio.

Can you remember any tense moments in the lab?

Very early in my career, as a young assistant professor, I conducted preliminary experiments that involved the reduction of carbonyl compounds with organosilanes. Our group had submitted an abstract for a national meeting describing the methodology and, at the same time, had submitted a disclosure for a patent application. About a month after we had submitted the abstract, we realised that the method was wrong. It happened on the 4th of July. I was in the lab, carrying out the reaction. I made the correct mixture, as we had done before, and I had that moment where everything becomes clear and I realised I had got it wrong. I remember saying 'we got it wrong for the abstract, we got it wrong for the disclosure, my career is over!' Then, a few minutes later, I had the solution. All I had to do was add water. It was that simple!


400 MHz


OUT
^{2}H
IN
OUT
^{1}H
IN
^{13}C
IN
J1
J2
BRUKER
CP DCH400S1 C/H-D-05 Z

Instant insight

Reducing the waste

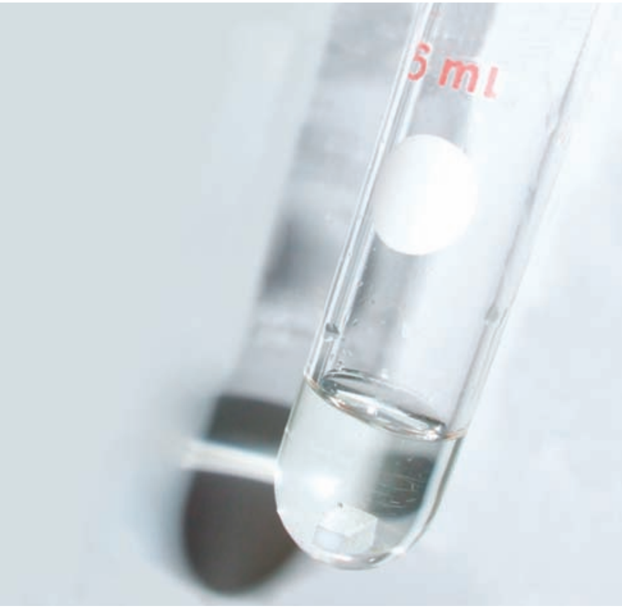
Tomislav Pintauer and Krzysztof Matyjaszewski from Duquesne University and Carnegie Mellon University, in Pittsburgh, US, reveal the magic ingredient that turns radical reactions 'green'

Morris Selig Kharasch, known for revolutionising radical reactions, first reported the addition of halogenated compounds to alkenes or alkynes in the 1940s. This process – coined an atom transfer radical addition (ATRA) reaction – is today considered to be a fundamental reaction in organic synthesis.

ATRA reactions work with a variety of alkyl halides and alkenes, and can be conducted inter- and intra-molecularly. The intramolecular version is particularly attractive because it enables the synthesis of functionalised cyclic systems, important building blocks for complex organic molecules from natural products to pharmaceuticals.

The first ATRA reactions were conducted in the presence of light or radical initiators. These were later replaced with more efficient halogen-transfer agents based on transition metals such as copper, iron, ruthenium or nickel. However, to form the desired product selectively, large amounts of metal catalyst are needed (several million ppm). This causes problems in product separation and catalyst regeneration, making the process environmentally unfriendly and expensive. Limiting its use for making complex molecules and natural products, especially on the large scale.

Similar problems are also encountered with the copper-mediated atom transfer radical polymerisation (ATRP) reaction, which was discovered in 1995. Mechanistically similar to ATRA, the reaction conditions are modified so that the product of the initial addition reaction can be reactivated. The repetitive addition step is what makes ATRP a polymerisation process. It is a powerful, robust, and easy to conduct method that allows polymeric materials to be prepared with well-defined composition, architecture and functionality.


Adding a reducing agent means the amount of metal catalyst needed is so small the reaction mixture is colourless

In copper-catalysed ATRA and ATRP, the transition metal in its lower oxidation state activates the dormant alkyl halide species, generating radicals which are then deactivated by the metal in its higher oxidation state. Nevertheless, because the radical deactivation – known as termination – reactions cannot be totally suppressed, the higher oxidation state metal complex accumulates as the reaction proceeds. This means larger metal quantities are required as the catalyst is 'used up'. A recently discovered solution to this problem uses environmentally friendly reducing agents to continuously regenerate the metal complex in the lower oxidation state. These reducing agents include radical initiators, amines, glucose, ascorbic acid and tin(II) compounds.

These ARGET (activators regenerated by electron transfer) and ICAR (initiators for continuous activator regeneration) ATRP processes allow polymerisation to be conducted using very small amounts of copper catalyst (1–100 ppm). Generally the amount of catalyst required to carry out a reaction is reduced 500–10 000 times. The methodology also reduces catalyst-based side reactions.

A procedure developed for catalyst regeneration in copper- and ruthenium-catalysed ATRA reactions has also been successfully used here, achieving one of the highest turnover numbers for any metal mediated ATRA process.

These recent developments could have profound implications for the large-scale industrial synthesis of small organic molecules and well-defined polymeric materials.

Read Pintauer and Matyjaszewski's tutorial review on 'Atom transfer radical addition and polymerization reactions catalyzed by ppm amounts of copper complexes' in Issue 6, 2008 of Chemical Society Reviews

Reference

T Pintauer and K Matyjaszewski, *Chem. Soc. Rev.*, 2008, **37**, 1087 (DOI: 10.1039/b714578k)

Essential elements

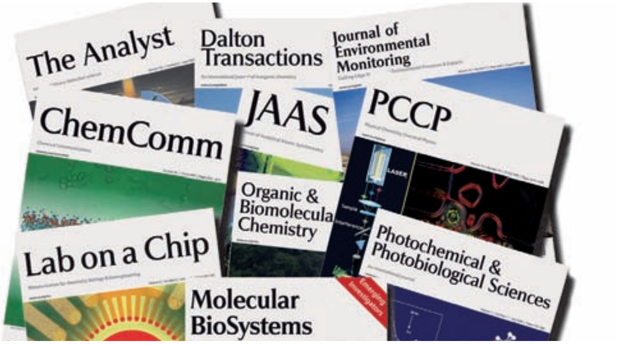
Even greater impact!

RSC authors, readers and publishing teams throughout the world are celebrating news of continued success for RSC journals, following the release of the 2007 Impact Factors, calculated by ISI®.

Titles from across the collection have again recorded impressive rises, while the latest immediacy indices confirm the relevance and topicality of research published by the RSC. According to Robert Parker, managing director of RSC Publishing, 'The number of citations to research published in RSC journals rose by an average of 36% in 2007, endorsement indeed to the efforts of our authors, referees and editorial teams.'

Flagship journal, *ChemComm* sees a 13% increase in impact factor to an all time high of 5.141, while *Chem Soc Rev* is ranked first for immediacy (3.406) in general chemistry review journals and third for impact factor (13.082).

Molecular BioSystems, now in its fourth year of publication, achieves a staggering increase of 68% to an impact factor of 4.121. *Soft Matter*, launched at the same time, retains its position as number one in the field for both impact and immediacy, at 4.703 and 0.784, respectively. Also in the materials field, *Journal of Materials Chemistry* has an impact factor of 4.339, representing an impressive 59% rise over three years.



Number one is a common theme across the RSC journal portfolio. *The Analyst* is first for immediacy in analytical chemistry at 1.032, and enjoys a rise in impact factor of more than 10% for the second year running to 3.553. *JAAS* (*Journal of Analytical Atomic Spectrometry*) maintains its position as the number one journal in the field (impact factor 3.269) and, with an immediacy index of 0.614, *CrystEngComm* moves to the number one position for crystal engineering. *Dalton Transactions* maintains its position as the general inorganic chemistry journal with the highest immediacy index (0.758) and shows the biggest increase in impact factor (6.6% to 3.212) of any inorganic chemistry journal.

Green Chemistry extends its lead as the number one green chemistry journal with a 15% rise in impact factor to 4.836. *Journal of Environmental Monitoring* also sees a substantial increase with a 20% rise in impact factor to 1.833, while *Photochemical & Photobiological Sciences* maintains its position as the number one journal for photochemical and photobiological research (2.208).

Natural Product Reports is first for immediacy in the field of organic chemistry (1.672) and *Organic & Biomolecular Chemistry* sees a 10% increase in impact factor to 3.167. *Lab on a Chip* remains one of the leading journals in micro- and nano-research with an impact factor of 5.068 and *PCCP* (*Physical Chemistry Chemical Physics*) clocks in with an impact factor of 3.343, representing an impressive 61% rise over three years.

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We would like to thank all our authors, referees and readers for their continued support.

Footnote:
The annual ISI® impact factors provide an indication of the average number of citations per paper. The impact factor for 2007 is calculated from the total number of citations given in 2007 to citeable articles published in 2005 and 2006, divided by the number of citeable articles published in 2005 and 2006. The immediacy index measures how topical and urgent the papers published in a journal are. The 2007 immediacy index is the total number of citations given in 2007 to citeable articles published in 2007 divided by the number of citeable articles published in 2007. Data based on 2007 impact factors, calculated by ISI®, released June 2008.

And finally...

With the conference season in full swing, RSC Publishing staff are spread around the globe at a number of major conferences over the coming weeks.

Are you attending the ACS National Meeting & Exposition in Philadelphia? Make sure you visit the RSC Publishing stand where staff will be on hand to answer any questions you may have. You can pick up a copy of Issue 1 of *Energy & Environmental Science*, our newest journal, as it makes its print debut, and find out the latest journals news. Book authors John Emsley (*Molecules of Murder*) and Stephen Beckett (*The Science of Chocolate*) will be signing copies of their books.


PHOTODISC

In September, the focus is Turin, Italy, for the 2nd Annual EuCheMS meeting. The wide-ranging themes provide scope for showcasing RSC products – including the recently announced *Metallomics* and *Integrative Biology*, both launching January 2009.

If you're travelling to these or other conferences, look out for RSC Publishing staff - they will be happy to meet you.

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