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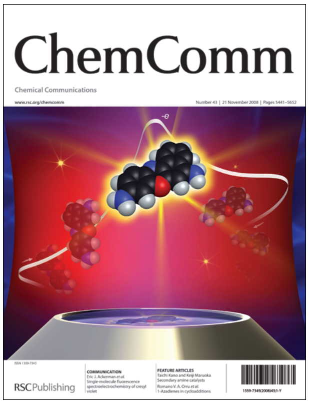
IN THIS ISSUE

ISSN 1359–7345 CODEN CHCOFS (43) 5441–5652 (2008)



Cover
See Eric J. Ackerman *et al.*,
pp. 5490–5492.
Single-molecule electron transfers have been studied by combining scanning fluorescence microscopy with cyclic voltammetric potential scanning.
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CHEMICAL SCIENCE

C81

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

November 2008/Volume 5/Issue 11

www.rsc.org/chemicalscience

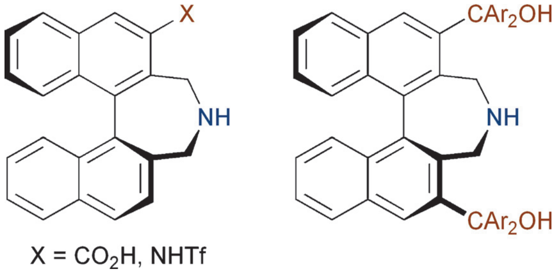
FEATURE ARTICLE

5465

Design of chiral bifunctional secondary amine catalysts for asymmetric enamine catalysis

Taichi Kano and Keiji Maruoka*

A series of binaphthyl-based secondary amine catalysts containing various functional groups have been designed as new chiral bifunctional amine catalysts. In several asymmetric reactions *via* enamine intermediates, these chiral organocatalysts exhibit unique reactivity and selectivity in comparison with proline and its derivatives.



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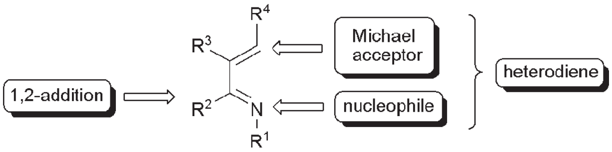
FEATURE ARTICLE

5474

1-Azadienes in cycloaddition and multicomponent reactions towards N-heterocycles

Bas Groenendaal, Eelco Ruijter and Romano V. A. Orru*

This *feature article* provides an overview of recent methods for the generation of 1-azadienes as well as their application in cycloaddition, electrocyclization and multicomponent reactions yielding various types of N-heterocycles.



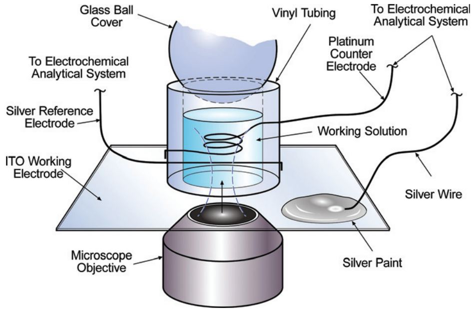
COMMUNICATIONS

5490

Single-molecule fluorescence spectroelectrochemistry of cresyl violet

Chenghong Lei, Dehong Hu and Eric J. Ackerman*

Here we report a new path to study single molecule electron transfer dynamics by coupling scanning fluorescence microscopy with a potentiostat *via* a conventional electrochemical cell to enable single-molecule fluorescence spectroelectrochemistry of cresyl violet in aqueous solution, demonstrating that the single-molecule fluorescence intensity of cresyl violet is modulated synchronously with the cyclic voltammetric potential scanning.

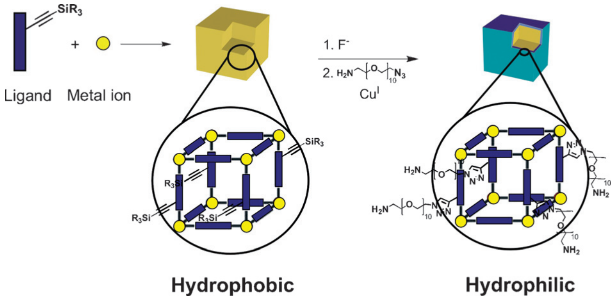


5493

Covalent surface modification of a metal–organic framework: selective surface engineering *via* Cu^I-catalyzed Huisgen cycloaddition

Tendai Gadzikwa, Guang Lu, Charlotte L. Stern, Scott R. Wilson,* Joseph T. Hupp* and SonBinh T. Nguyen*

A metal–organic framework bearing TMS-protected acetylenes has been synthesized. After selective external surface deprotection, the terminal alkynes are 'clicked' with organic azides to give a MOF with new surface properties.

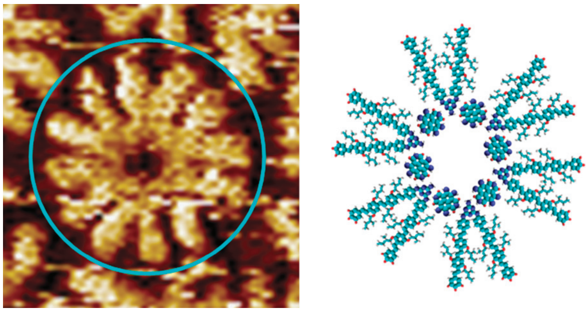


5496

Identification of oligo(*p*-phenylene vinylene)–naphthalene diimide heterocomplexes by scanning tunneling microscopy and spectroscopy at the liquid–solid interface

Inge De Cat, Cornelia Röger, Cameron C. Lee, Freek J. M. Hoeben, Maarten J. Pouderoijen, Albertus P. H. J. Schenning,* Frank Würthner* and Steven De Feyter*

Combining scanning tunneling microscopy and spectroscopy (STS) has unravelled the structural and electronic properties of quasi-crystalline multicomponent phases, including 12-membered electron donor–acceptor supramolecular rosettes.



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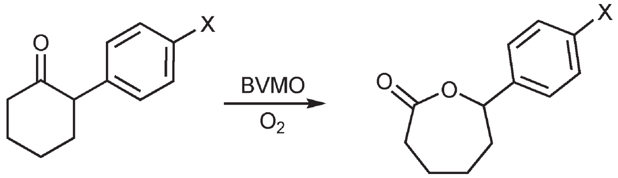
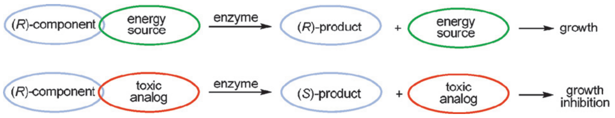


Greatly reduced amino acid alphabets in directed evolution: making the right choice for saturation mutagenesis at homologous enzyme positions

Manfred T. Reetz* and Sheng Wu

Enantioselective mutants of phenyl acetone monooxygenase (PAMO) as catalysts in Baeyer–Villiger reactions have been evolved by utilizing saturation mutagenesis.

5502

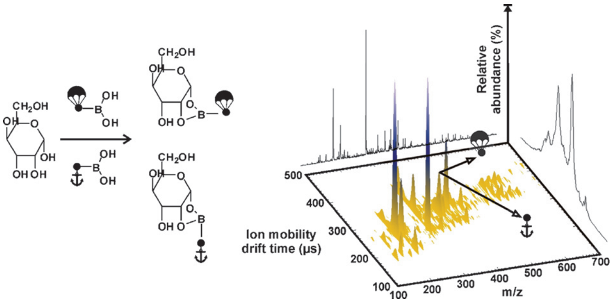


A genetic selection system for evolving enantioselectivity of enzymes

Manfred T. Reetz,* Horst Höbenreich, Pankaj Soni and Layla Fernández

As an alternative to screening in the directed evolution of enantioselective enzymes, a selection system has been implemented for a lipase-catalyzed hydrolytic kinetic resolution of a chiral ester.

5505

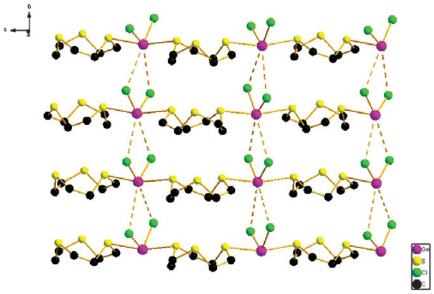


Enhanced carbohydrate structural selectivity in ion mobility-mass spectrometry analyses by boronic acid derivatization

Larissa S. Fenn and John A. McLean*

The boronic acid derivatization of carbohydrates is demonstrated as an ion mobility structural shift strategy to improve confidence in the identification and characterization of carbohydrate assignments for ion mobility-mass spectrometry analyses of complex biological samples.

5508



Coordination networks derived from germanium(II) thioether macrocyclic complexes—the first authenticated chalcogenoether complexes of Ge(II)

Fei Cheng, Andrew L. Hector, William Levason, Gillian Reid,* Michael Webster and Wenjian Zhang

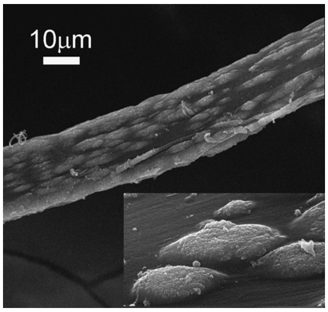
Exocyclic coordination of macrocyclic thioethers to germanium(II) halides leads to infinite chains (with weak Ge···X bridges between the chains) or sheet structures containing distorted octahedral Ge(II) with $[S_2X_2 + X_2]$ coordination and bridging thiacrowns.

5511

Templating effect of silk fibers in the oriented deposition of aragonite

Cheng Cheng, Yuhong Yang, Xin Chen and Zhengzhong Shao*

Parallel aligned aragonite depositions are obtained on degummed *Bombyx mori* silk fibers on account of both the ordered structure of the silk fiber and the directing-effect of silk fibroin.

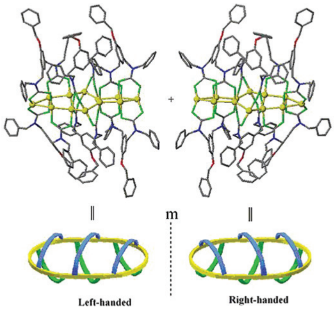


5514

Self-assembly of a neutral luminescent Au_{12} cluster with D_2 symmetry

Qing-Fu Sun, Terence Kwok-Ming Lee, Pei-Zhou Li, Liao-Yuan Yao, Jing-Jing Huang, Jing Huang, Shu-Yan Yu,* Yi-Zhi Li, Eddie Chung-Chin Cheng and Vivian Wing-Wah Yam*

The preparation of Au_{12} complexes is reported which show a cyclic framework consisting of twelve gold(I) ions arranged in a closed ring *via* non-covalent Au(I)···Au(I) interactions to give a chiral D_2 symmetrical structure.

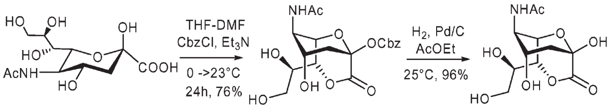


5517

The first synthesis of *N*-acetylneuraminic acid 1,7-lactone

Raffaele Colombo, Mario Anastasia, Paola Rota and Pietro Allevi*

N-Acetylneuraminic acid is transformed into its until now unavailable and rather unwieldy 1,7-lactone, *via* the manageable 2-benzyloxycarbonyl *N*-acetylneuraminic acid 1,7-lactone which generates the free lactone in quantitative yield by hydrogenolysis.

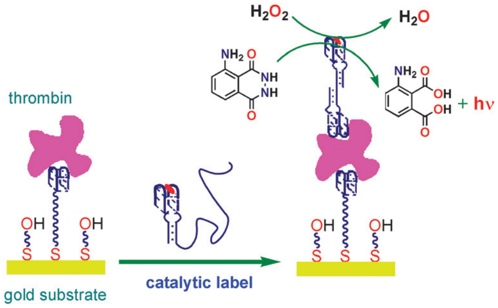


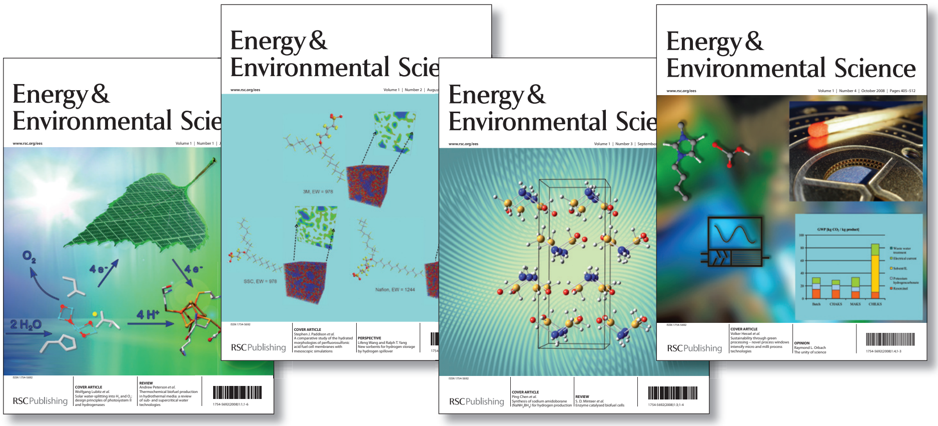
5520

Chemiluminescence thrombin aptasensor using high-activity DNAzyme as catalytic label

Tao Li, Erkang Wang and Shaojun Dong*

With a designed high-activity DNAzyme as the catalytic label, an ultrasensitive chemiluminescence thrombin aptasensor is developed, enabling a 10- to 100-fold improvement in the detection sensitivity as compared with previous counterparts.




Energy & Environmental Science
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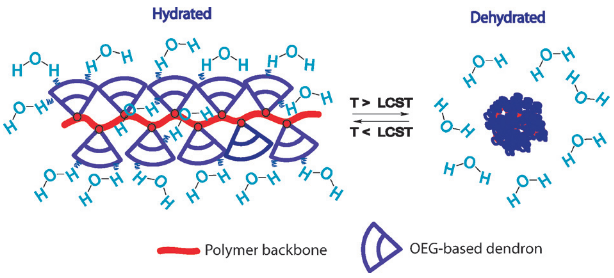
5523

Thermoresponsive dendronized polymers with tunable lower critical solution temperatures

Wen Li, Afang Zhang* and A. Dieter Schlüter

A series of first (**PG1**) and second generation (**PG2**) dendronized polymers were synthesized which exhibit fast and sharp phase transitions with negligible hystereses in aqueous solutions and apparent lower critical solution temperatures (LCSTs) in the range of 33–49 °C.

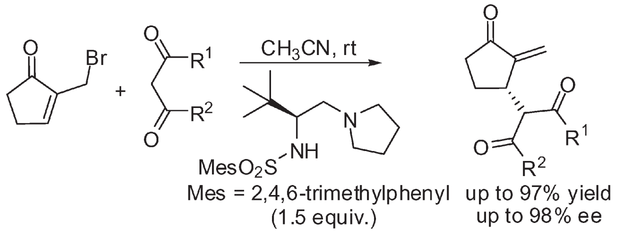


5526

Tandem conjugate addition–elimination reaction promoted by chiral pyrrolidinyl sulfonamide (CPS)

Junye Xu, Xiao Fu, Ruijuan Low, Yong-Peng Goh, Zhiyong Jiang and Choon-Hong Tan

Chiral pyrrolidinyl sulfonamides (CPS) have been found to promote the conjugate addition–elimination reaction between activated allylic bromides and 1,3-dicarbonyl compounds with high enantioselectivities. The highly functionalised products can be used to generate a variety of interesting enantiomerically pure compounds *via* simple transformations.

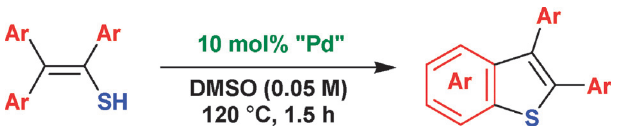


5529

Palladium-catalysed direct synthesis of benzo[*b*]thiophenes from thioenols

Kiyofumi Inamoto,* Yukari Arai, Kou Hiroya and Takayuki Doi*

The one-pot conversion of thioenols into benzo[*b*]thiophenes was achieved by using a simple palladium catalyst such as $PdCl_2$ or $PdCl_2$(cod). Various multi-substituted benzo[*b*]thiophenes were obtained from this process, generally in a high yield with a short reaction time.

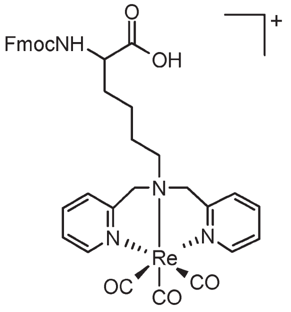


5532

A robust strategy for the preparation of libraries of metallopeptides. A new paradigm for the discovery of targeted molecular imaging and therapy agents

A. F. Armstrong, N. Oakley, S. Parker, P. W. Causey, J. Lemon, A. Capretta, C. Zimmerman, J. Joyal, F. Appoh, J. Zubieta, J. W. Babich, G. Singh and J. F. Valliant*

A robust method for the preparation and screening of a library of Re(I)-metallopeptides was developed as a way to accelerate the discovery of novel molecular imaging probes.



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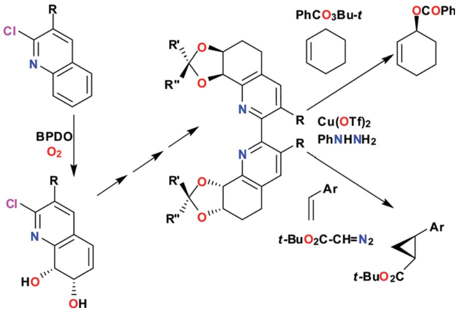
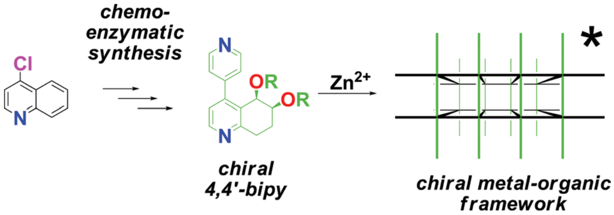


Azaarene *cis*-dihydrodiol-derived 2,2′-bipyridine ligands for asymmetric allylic oxidation and cyclopropanation

Derek R. Boyd,* Narain D. Sharma, Lenuta Sbircea, Deirdre Murphy, Tayeb Belhocine, John F. Malone, Stuart L. James, Christopher C. R. Allen and John T. G. Hamilton

Enantiopure 2,2′-bipyridine ligands derived from 2-chloroquinolines are efficient ligands for asymmetric allylic oxidation and cyclopropanation.

5538

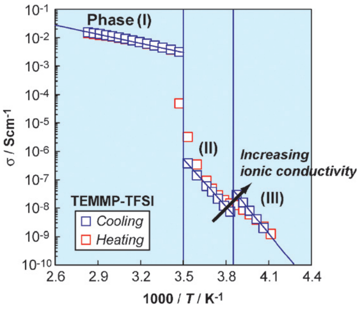


Chemoenzymatic synthesis of chiral 4,4′-bipyridyls and their metal–organic frameworks

Lenuta Sbircea, Narain D. Sharma, William Clegg, Ross W. Harrington, Peter N. Horton, Michael B. Hursthouse, David C. Apperley, Derek R. Boyd* and Stuart L. James*

Chemoenzymatic synthesis gives enantiopure 4,4′-bipyridyl derivatives which are excellent building blocks for making chiral metal–organic frameworks; the resulting MOFs exhibit some interesting structural and dynamic aspects.

5541

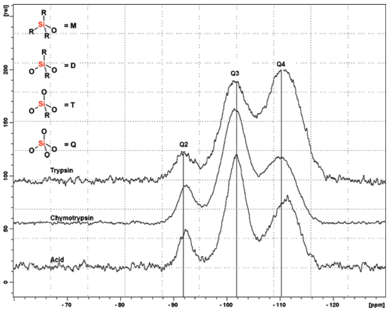


Phase transition and conductive acceleration of phosphonium-cation-based room-temperature ionic liquid

Shiro Seki,* Yasuhiro Umebayashi, Seiji Tsuzuki, Kikuko Hayamizu, Yo Kobayashi, Yasutaka Ohno, Takeshi Kobayashi, Yuichi Mita, Hajime Miyashiro, Nobuyuki Terada and Shin-ichi Ishiguro

An unusual ionic conduction phenomenon related to the phase transition of a novel phosphonium-cation-based room-temperature ionic liquid (RTIL) is reported.

5544



Enzyme-mediated sol–gel processing of alkoxysilanes

Mark Frampton, Ateeya Vawda, Jackie Fletcher and Paul M. Zelisko*

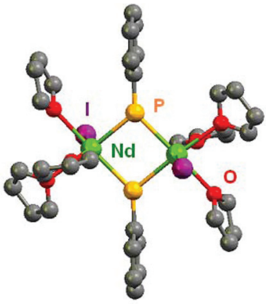
Through the judicious combination of enzyme and alkoxysilane species it is possible to affect the formation of particulate, but more importantly, monolithic silica; the latter being synthesized *via* the sol–gel process using ‘green’, solvent-free conditions.

5547

An unprecedented lanthanide phosphinidene halide: synthesis, structure and reactivity

Peng Cui, Yaofeng Chen,* Xin Xu and Jie Sun

The synthesis and structural characterization of an unprecedented lanthanide phosphinidene species $[(THF)_3(I)Nd(\mu\text{-}PC_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2$ are described; the phosphinidene moiety in this complex reacts as a carbene.

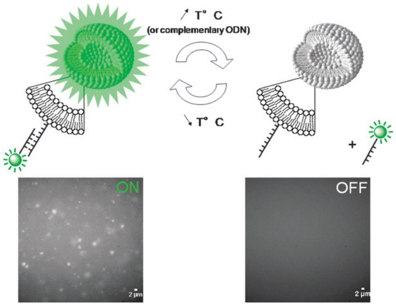


5550

Sensitive liposomes encoded with oligonucleotide amphiphiles: a biocompatible switch

Arnaud Gissot, Carmelo Di Primo, Isabelle Bestel, Gregory Giannone, Hubert Chapuis and Philippe Barthélémy*

DNA-tagged liposomes switch between an *on* and *off* fluorescent state depending on an external stimulus, either physical (temperature) or chemical (competitive complementary ON sequences). Both the platform and the switch are biocompatible.

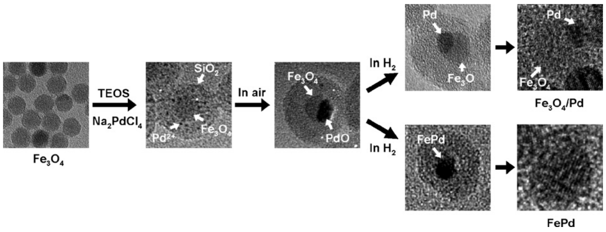


5553

Synthesis of Fe_3O_4/PdO heterodimer nanocrystals in silica nanospheres and their controllable transformation into Fe_3O_4/Pd heterodimers and FePd nanocrystals

Jongmin Shin, Hakwon Kim and In Su Lee*

The thermal annealing of silica nanospheres encapsulating Fe_3O_4 nanocrystals and Pd^{2+} complexes led to the formation of a heterodimer consisting of Fe_3O_4/PdO nanoparticles.

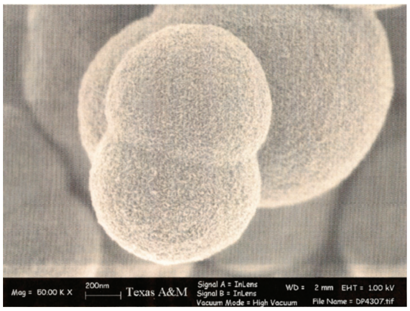


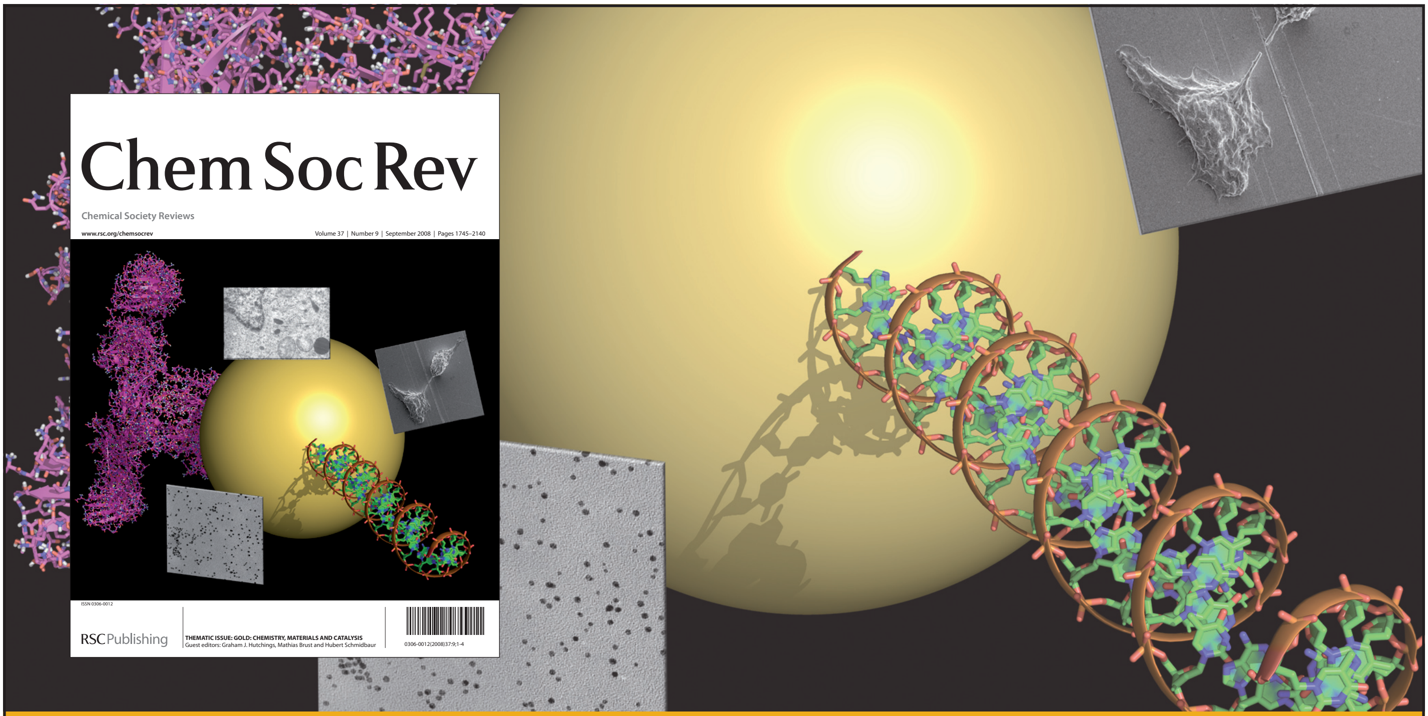
5556

Sn(IV) phosphonates as catalysts in solvent-free Baeyer–Villiger oxidations using H_2O_2

Sharath Kirumakki, Sandani Samarajeewa, Robert Harwell, Atashi Mukherjee, Rolfe H. Herber and Abraham Clearfield*

Porous Sn(IV)phosphonates behave as oxidation catalysts in Baeyer–Villiger oxidation in the presence of 30% H_2O_2 with no solvent required.





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THEMATIC ISSUE: GOLD: CHEMISTRY, MATERIALS AND CATALYSIS
Guest editors: Graham J. Hutchings, Mathias Brust and Hubert Schmidbaur
0306-0012(2008)37:9;1-4

Gold: Chemistry, Materials and Catalysis theme issue

This collection of reviews sets out the state of the art with respect to gold catalysis, the synthesis and application of gold nanoparticles and gold chemistry. As such the issue takes a very broad approach to the topic, which has now become a hot topic in chemistry as a whole. We hope the reviews will inspire new discoveries and new researchers into this exciting field. The issue is timely as the field is expanding rapidly and hence these articles allow us to take stock of the great progress already achieved, as well as highlighting the remaining challenges.

Reviews include:

The relevance of shape and size of Au_{55} clusters
Günter Schmid

The chemistry of gold as an anion
Martin Jansen

Catalytically active gold on ordered titania supports
Mingshu Chen and D. Wayne Goodman

Biological applications of gold nanoparticles
Ralph A. Sperling, Pilar Rivera Gil, Feng Zhang, Marco Zanella and Wolfgang J. Parak

Shape control in gold nanoparticle synthesis
Marek Grzelczak, Jorge Pérez-Juste, Paul Mulvaney and Luis M. Liz-Marzán

The use of aurophilic and other metal–metal interactions as crystal engineering design elements to increase structural dimensionality
Michael J. Katz, Ken Sakai and Daniel B. Leznoff

Supported gold nanoparticles as catalysts for organic reactions
Avelino Corma and Hermenegildo Garcia

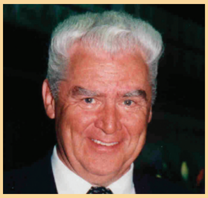
Guest editor

Graham J Hutchings
Cardiff University

Guest editor

Matthias Brust
University of Liverpool

Guest editor



Hubert Schmidbaur
Technische Universität München

'Catalysis is reaching a golden age, as gold is finding many new applications as a catalyst for selective oxidations and hydrogenations. It is a really exciting time to be working in the field of catalysis'

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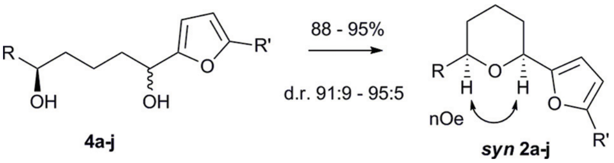
5559

A diastereoselective route to 2,6-*syn*-disubstituted tetrahydropyrans: synthesis of the civet compound (+)-2-((2*S*,6*S*)-6-methyltetrahydro-2*H*-pyran-2-yl) acetic acid

Matthew O'Brien,* Shane Cahill and Lyndsay A. Evans

The ability of furanyl–ether chiral centres to epimerise readily under acidic conditions allows rapid and diastereoselective access to 2,6-*syn*-disubstituted tetrahydropyrans.

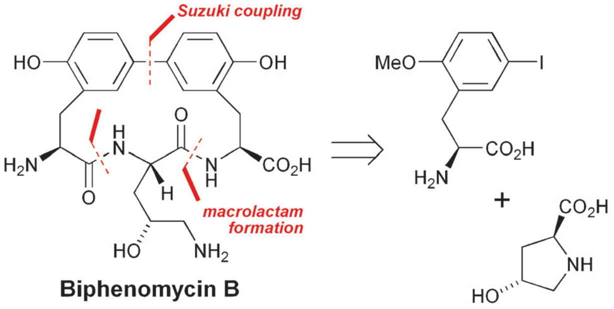


5562

Flexible total synthesis of biphenomycin B

Herbert Waldmann,* Yu-Peng He, Hao Tan, Lars Arve and Hans-Dieter Arndt*

A synthesis of biphenomycin B was accomplished with Suzuki coupling of unprotected amino acid building blocks and a high-yielding macrolactamization.

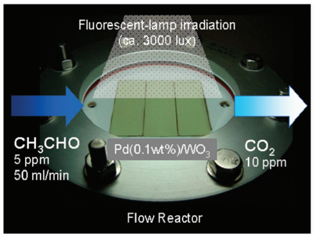


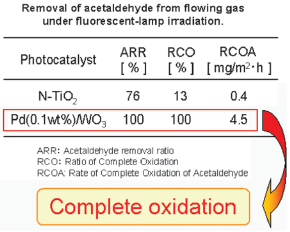
5565

Complete oxidation of acetaldehyde and toluene over a Pd/WO$_3$ photocatalyst under fluorescent- or visible-light irradiation

Takeo Arai, Masumi Horiguchi, Masatoshi Yanagida, Takahiro Gunji, Hideki Sugihara and Kazuhiro Sayama*

Acetaldehyde was completely oxidized to CO$_2$ over a Pd/WO$_3$ photocatalyst under fluorescent-light irradiation in a flow-type reactor, and Pd/WO$_3$ could also completely oxidize toluene in a batch reactor under visible-light irradiation.





Removal of acetaldehyde from flowing gas under fluorescent-lamp irradiation.

Photocatalyst	ARR [%]	RCO [%]	RCOA [mg/m^2·h]
N-TiO$_2$	76	13	0.4
Pd(0.1wt%)/WO$_3$	100	100	4.5

ARR: Acetaldehyde removal ratio
RCO: Ratio of Complete Oxidation
RCOA: Rate of Complete Oxidation of Acetaldehyde

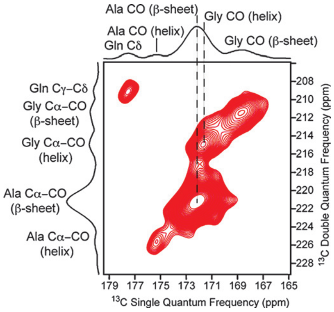
Complete oxidation

5568

Quantifying the fraction of glycine and alanine in β-sheet and helical conformations in spider dragline silk using solid-state NMR

Gregory P. Holland,* Janelle E. Jenkins, Melinda S. Creager, Randolph V. Lewis and Jeffery L. Yarger*

Solid-state two-dimensional refocused INADEQUATE MAS NMR experiments resolve distinct helical and β-sheet conformational environments for both alanine and glycine in *Nephila clavipes* dragline silk fibers.



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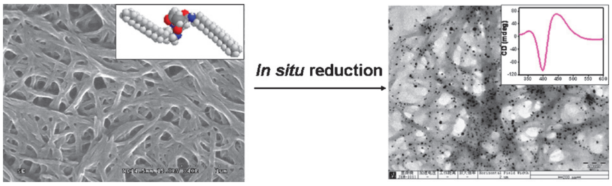
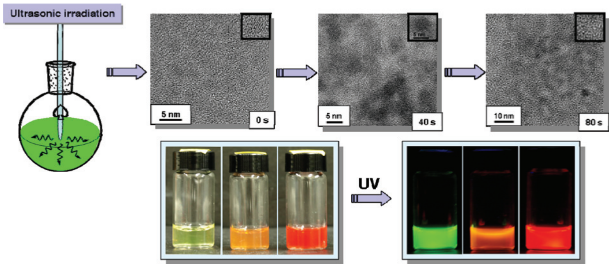


Fabrication of chiral silver nanoparticles and chiral nanoparticulate film *via* organogel

Yuangang Li and Minghua Liu*

Chiral silver nanoparticles and chiral nanoparticulate films were prepared through the *in situ* reduction of an organogel formed by a newly designed silver(I)-coordinated organogelator.

5574

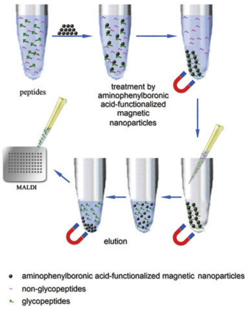


Sonication treatment of CdTe/CdS semiconductor nanocrystals and their bio-application

Seung Jae Lee, Kyung Nam Kim, Pan Kee Bae,
Hyun Ju Chang, Yong-Rok Kim and Joung Kyu Park*

CdTe/CdS nanocrystals were successfully synthesized by ultrasonic irradiation. Using ultrasonic irradiation of CdTe/CdS led to a red shift emission of up to 86 nm (from 542 to 628 nm). The water-soluble TGA-capped CdTe/CdS showed low toxicity and high quantum yields relative to thermally prepared samples.

5577

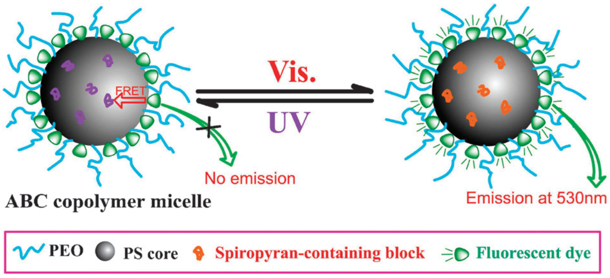


Facile synthesis of aminophenylboronic acid-functionalized magnetic nanoparticles for selective separation of glycopeptides and glycoproteins

Wei Zhou, Ning Yao, Guoping Yao, Chunhui Deng,*
Xiangmin Zhang and Pengyuan Yang*

In this work, aminophenylboronic acid-functionalized magnetic nanoparticles were synthesized, and applied to the selective separation of glycopeptides and glycoproteins.

5580



Reversible fluorescence modulation through energy transfer with ABC triblock copolymer micelles as scaffolds

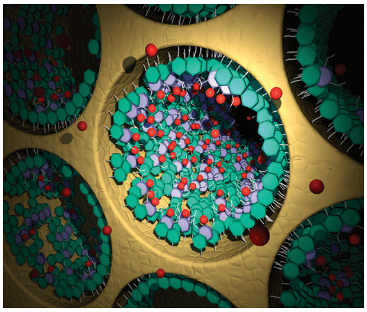
Jian Chen, Fang Zeng,* Shuizhu Wu,* Jianqing Zhao,
Qiming Chen and Zhen Tong

The micelles formed by an amphiphilic triblock copolymer in water serve as the scaffold for fluorescence resonance energy transfer as well as light-induced reversible fluorescence modulation for a hydrophobic fluorescent dye.

5583

New functional materials for heavy metal sorption: "Supramolecular" attachment of thiols to mesoporous silica substrates

Timothy G. Carter, Wassana Yantasee,
Thanapon Sangvanich, Glen E. Fryxell,
Darren W. Johnson* and R. Shane Addleman*

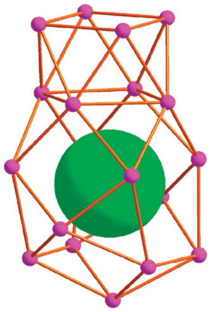


A new class of sorbent material, which exhibits exceptional metal (red spheres) capture from contaminated natural water, features aromatic thiol ligands (purple) reversibly bound to functionalized (green) mesoporous silica (yellow) through non-covalent interactions.

5586

Snowman-like silver alkynyl cluster consolidated by templating chloride and peripheral trifluoroacetates

Shu-Dan Bian and Quan-Ming Wang*

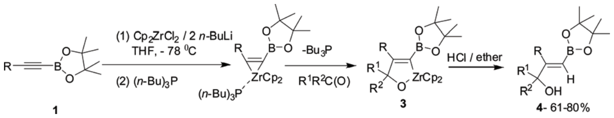


A novel nonadecanuclear silver double cage was isolated, in which a square antiprism and a pentacapped pentagonal prism templated by a chloride ion share a tetragonal face to form a cluster in the shape of a snowman.

5589

Synthesis of 3-hydroxy-1-alkenylboronates *via* phosphine stabilized borylzirconacyclopropenes

Abed Al Aziz Al Quntar, Alina Botvinik,
Abraham Rubinstein and Morris Srebnik*

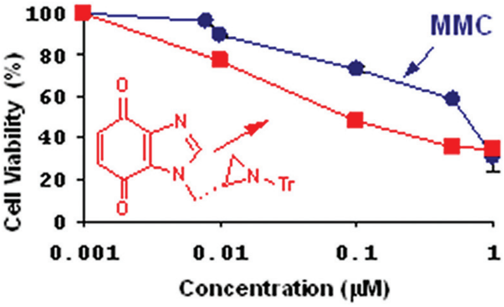


Zirconacyclopropenylboronates can be stabilized to dimerization by complexation with tributylphosphine. The phosphine stabilized zirconacycle boronates react with aliphatic and aromatic ketones and aldehydes at C2 of the triple bond to give the previously unknown 3-hydroxyvinylboronates in 61–80% isolated yields.

5592

First synthesis of *N*-[(aziridin-2-yl)methyl]benzimidazole-quinone and analysis of toxicity towards normal and Fanconi anemia cells

Liz O'Donovan, Michael P. Carty* and Fawaz Aldabbagh*



The first synthesis of benzimidazolequinone N-substituted with 2-methylaziridine is described along with its cytotoxicity against normal and Fanconi anemia fibroblast cells.

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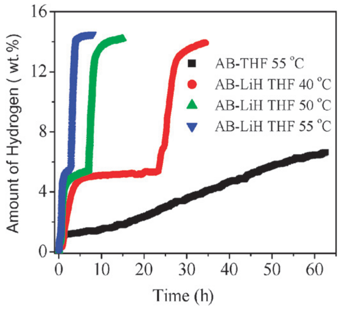
5595

Interaction of lithium hydride and ammonia borane in THF

Zhitao Xiong, Yong Shen Chua, Guotao Wu, Weiliang Xu, Ping Chen,* Wendy Shaw, Abhi Karkamkar, John Linehan, Tricia Smurthwaite and Thomas Autrey*

~14.3 wt% of hydrogen can be released from LiH–NH_3BH_3 THF suspension at 40 °C. The overall dehydrogenation is a two-step process; each step has an induction period.

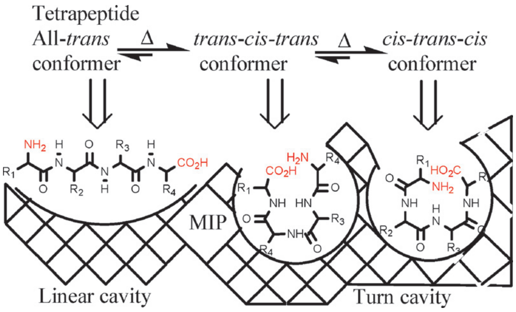


5598

Molecularly imprinted cavities template the macrocyclization of tetrapeptides

Dar-Fu Tai* and Yee-Fung Lin

Cavities formed using cyclic tetrapeptides (CTPs) or heat-induced conformers act as templates for cyclization. The cavities bind to linear tetrapeptides and enforce turn conformations to enhance cyclization to constrained CTPs.

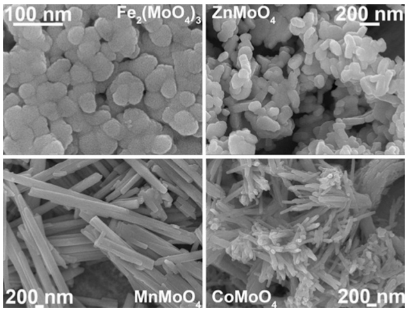


5601

A general precipitation strategy for large-scale synthesis of molybdate nanostructures

Cheng Peng, Lian Gao,* Songwang Yang and Jing Sun

A general precipitation strategy has been developed for the large-scale synthesis of molybdate nanostructures, and a series of molybdate nanostructures such as $Fe_2(MoO_4)_3$ nanoparticles, $ZnMoO_4$ nanoplates, $MnMoO_4$ nanorods and $CoMoO_4$ nanowires have been successfully prepared.

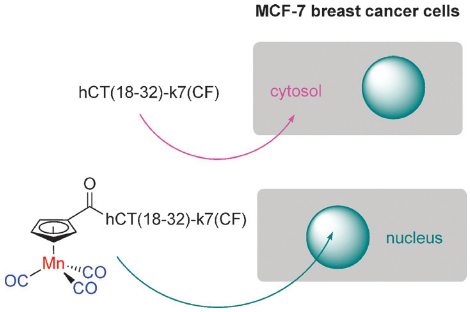


5604

Cymantrene conjugation modulates the intracellular distribution and induces high cytotoxicity of a cell-penetrating peptide

Ines Neundorf,* Jan Hoyer, Katrin Splith, Robert Rennert, Harmel W. Peindy N'Dongo and Ulrich Schatzschneider*

Coupling of the organometallic cymantrene moiety to a cell-penetrating peptide generates bioconjugates with a biological activity very distinct from that of the individual building blocks.



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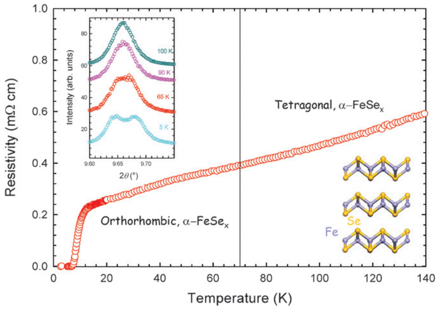
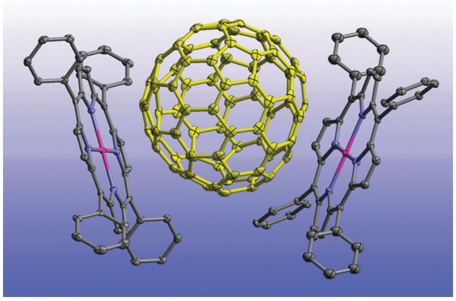


Crystal structure of the new $FeSe_{1-x}$ superconductor

Serena Margadonna,* Yasuhiro Takabayashi,
Martin T. McDonald, Karolina Kasperkiewicz,
Yoshikazu Mizuguchi, Yoshihiko Takano,
Andrew N. Fitch, Emmanuelle Suard and
Kosmas Prassides*

The simple binary iron selenide, α-$FeSe_{0.92}$ with a resistive superconductive transition temperature of 13.5 K shows a structural phase transition from tetragonal to orthorhombic crystal symmetry below 70 K.

5610

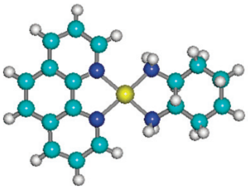


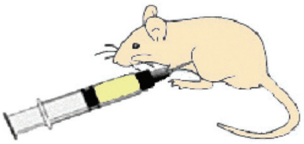
Crystallographic characterization and identification of a minor isomer of C_{84} fullerene

Lars Epple, Konstantin Amsharov, Kalin Simeonov,
Ina Dix and Martin Jansen*

We report the synthesis and single crystal X-ray analysis of C_{84} (14) · AgTPP (Ag tetraphenylporphyrin) cocrystal—the first ordered crystal structure containing a pristine higher fullerene.

5613



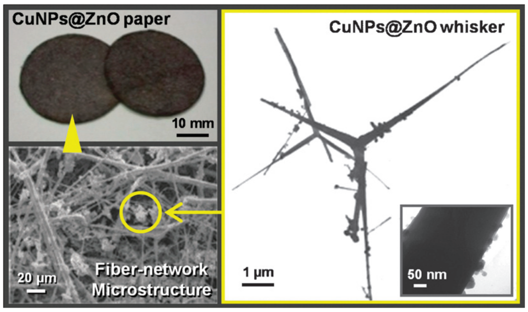


In vivo studies of a platinum(II) metallointercalator

Dianne M. Fisher, Ronald R. Fenton* and
Janice R. Aldrich-Wright*

An *in vivo* study for determining the toxicity and efficacy of [Pt(*S*,*S*-dach)(phen)Cl_2 · 1.5H_2O · 0.5HCl in female Specific Pathogen Free Swiss nude mice bearing PC3 tumour xenografts revealed the drug to be non-toxic and effective in decreasing tumour growth.

5616



In situ synthesis of Cu nanocatalysts on ZnO whiskers embedded in a microstructured paper composite for autothermal hydrogen production

Hirotaka Koga, Takuya Kitaoka* and Hiroyuki Wariishi

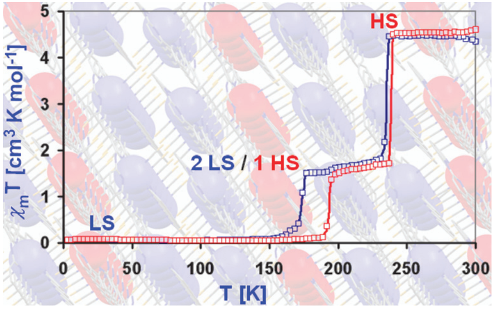
A facile and direct *in situ* synthesis of Cu nanocatalysts on a paper-like matrix with a fiber-network microstructure was successfully achieved by using ZnO whiskers as a selective catalyst support.

5619

A two-step spin crossover mononuclear iron(II) complex with a [HS–LS–LS] intermediate phase

Sylvestre Bonnet, Maxime A. Siegler, José Sánchez Costa, Gábor Molnár, Azzedine Bousseksou, Anthony L. Spek, Patrick Gamez and Jan Reedijk*

The two-step spin crossover of the new mononuclear complex [Fe(bapbpy)(SCN)$_2$] reveals two successive first-order phase transitions and an ordered intermediate phase built by the repetition of the unprecedented [HS–LS–LS] motif.

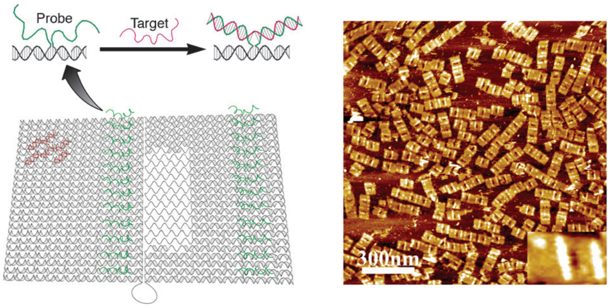


5622

Developing DNA tiles for oligonucleotide hybridization assay with higher accuracy and efficiency

Yonggang Ke, Jeanette Nangreave, Hao Yan, Stuart Lindsay and Yan Liu*

Nucleic acid tile systems with an internal hole were designed to achieve improved target/probe hybridization efficiency. The length of DNA target detected can be as short as 10 nt.

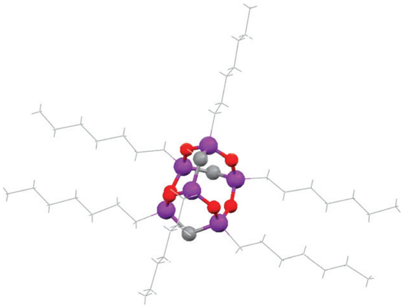


5625

A simple route to novel D spherosilicones; the first crystallographic structures of D_6 and D_8 cages

Alan R. Bassindale,* Zhihua Liu, Peter G. Taylor,* Peter N. Horton and Michael B. Hursthouse

The synthesis, characterisation and crystal structure of D_8 and D_6 cages from the corresponding bis(dialkoxy)methane is reported.

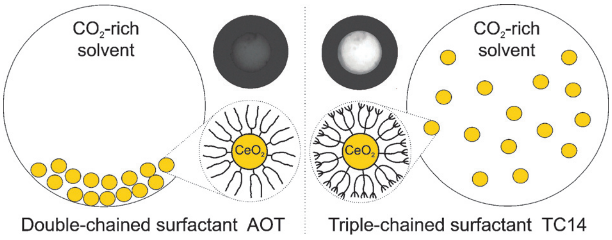


5628

Stabilization of CeO_2 nanoparticles in a CO_2 rich solvent

Martin J. Hollamby, Kieran Trickett, Ana Vesperinas, Carl Rivett, David C. Steytler, Zoe Schnepp, Jon Jones, Richard K. Heenan, Robert M. Richardson, Otto Glatter and Julian Eastoe*

The chemical nature of outer organic surfactant layers used to stabilize inorganic nanoparticles (NPs) is a key factor controlling solubility in a mixed liquid CO_2–heptane (10% vol) solvent.

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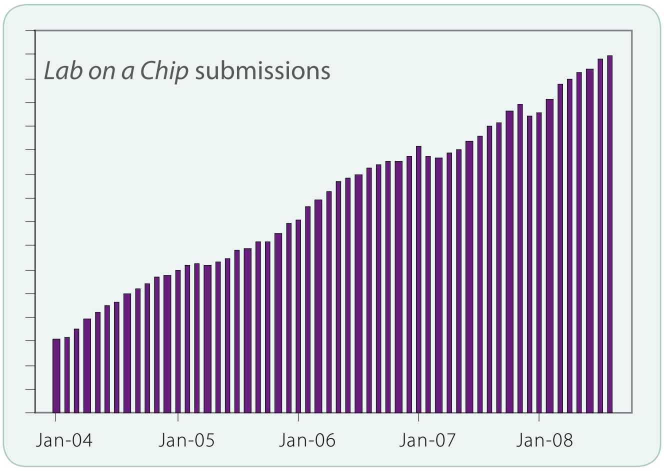
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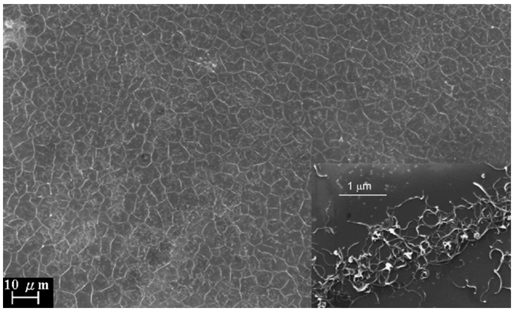
Jan-06
Jan-07
Jan-08

5631

Fabrication of porous carbon nanotube network

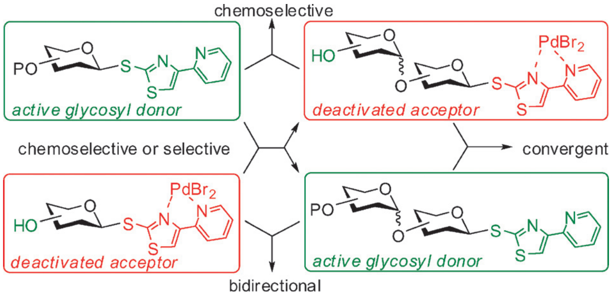


Jun-Wei Su, Shu-Juan Fu, Shangjr Gwo* and
Kuna-Jiuh Lin*

We used the spin-coating method combined with ultrasonic atomization as a continuous, one-step process to generate a two-dimensional honeycomb network that was constructed from pure multi-walled carbon nanotubes.

5633

4-(Pyridin-2-yl)thiazol-2-yl thioglycosides as bidentate ligands for oligosaccharide synthesis *via* temporary deactivation

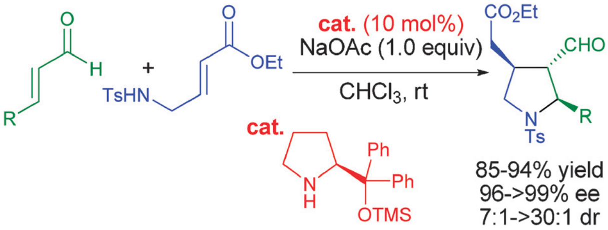


Papapida Pornsuriyasak, Nigam P. Rath and
Alexei V. Demchenko*

This study focusses on a new concept for oligosaccharide synthesis based on 4-(pyridin-2-yl)thiazol-2-yl thioglycosides that can either act as effective glycosyl donors or can be deactivated by stable bidentate complexation with palladium(II) bromide.

5636

Highly enantio- and diastereoselective organocatalytic cascade aza-Michael–Michael reactions: a direct method for the synthesis of trisubstituted chiral pyrrolidines

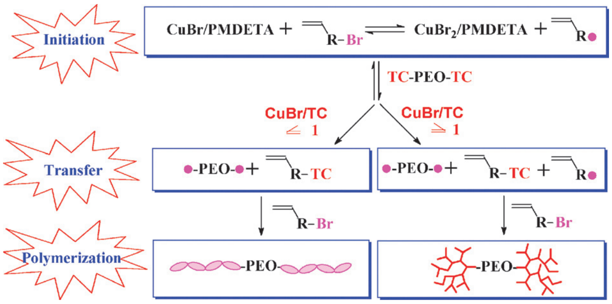


Hao Li, Liansuo Zu, Hexin Xie, Jian Wang and
Wei Wang*

An unprecedented highly enantio- and diastereoselective cascade aza-Michael–Michael reaction of α,β-unsaturated aldehydes with *trans*-γ-Ts protected amino α,β-unsaturated ester has been developed.

5639

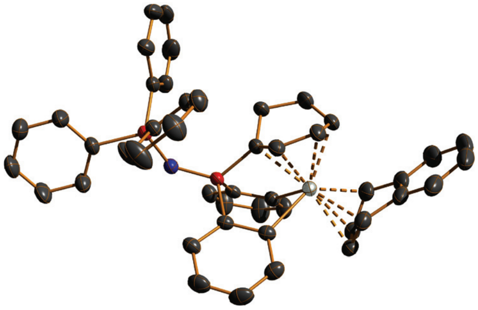
A facile strategy to control polymer topology by variation of controlled radical polymerization mechanisms



Wen-Ming Wan and Cai-Yuan Pan*

A facile strategy for control of the polymer topologies can be achieved simply by tuning the feed molar ratio of catalyst to transfer agent in the controlled radical polymerization.

5642

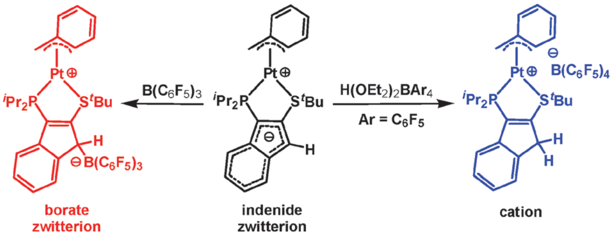


A total loss of innocence: double *ortho*-metallation of bis(triphenylphosphano)iminium cation, $[N(PPh_3)_2]^+$, by tris(η-naphthalene)tantalate(1 −)

Victor J. Sussman and John E. Ellis*

The generally unreactive counterion $[N(PPh_3)_2]^+$ reacts under ambient conditions with tris(naphthalene)tantalate(1 −) to afford a structurally-unique compound in which two phenyl groups bound to one phosphorus atom have undergone *ortho*-metallation.

5645

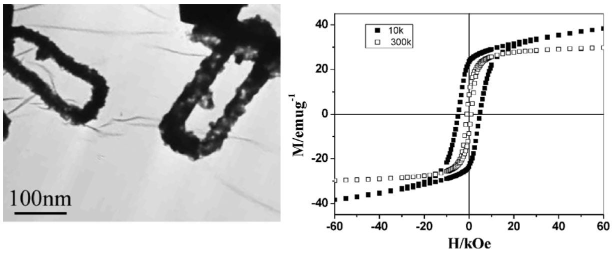


(κ^2-*P*,*S*)Pt(benzyl) complexes derived from 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene: facile synthesis of carbanion- and borate-containing zwitterions

Kevin D. Hesp, Robert McDonald, Michael J. Ferguson, Gabriele Schatte and Mark Stradiotto*

A new P,S-substituted indene serves as a versatile ligand precursor in the synthesis of neutral and cationic (κ^2-*P*,*S*)Pt(benzyl) complexes, as well as related zwitterions featuring indenide or borate ligation.

5648



Cobalt ferrite nanorings: Ostwald ripening dictated synthesis and magnetic properties

Hui Zhang, Chuanxin Zhai, Jianbo Wu, Xiangyang Ma and Deren Yang*

$CoFe_2O_4$ nanorings were synthesized by a simple solvothermal process, in which Ostwald ripening was definitely responsible for the formation of hollow structures, and their ferromagnetic behavior at room temperature was observed.

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Chemical Science

MRSA-beating compounds are key targets in human medicine

Inhibiting the spread of superbugs

UK chemists have found a small molecule with the potential to overcome one of the most serious problems facing the healthcare profession today – the spread of the deadly infection MRSA.

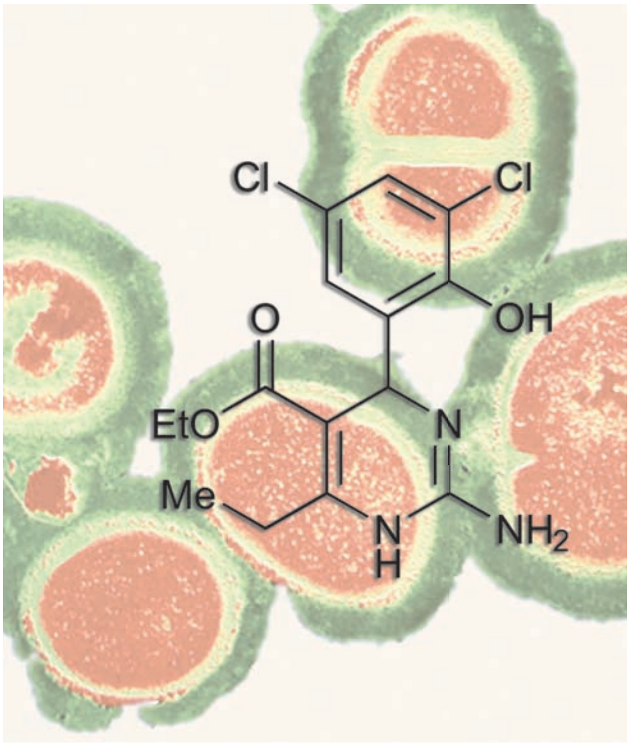
Methicillin-resistant *Staphylococcus aureus* (MRSA) is a multidrug resistant strain of the common *S. aureus* bacterium that causes difficult-to-treat infections in humans. The development of new antibacterial agents to overcome this and other 'superbugs' are key targets in human medicine. With this in mind David Spring and colleagues at the University of Cambridge, UK, have used diversity-orientated synthesis to indentify a small molecule which can inhibit the enzyme that controls cell division in an epidemic strain of MRSA.

The diversity-oriented synthesis used by Spring involved making a library of 200 structurally-diverse compounds and screening them for the required antibacterial activity against two epidemic strains of MRSA. The successful compounds were narrowed down to those with key frameworks and functional groups and were then subjected to further screening. The most potent of these was a substituted dihydropyrimidine named emmacin.

In further tests Spring showed that emmacin can selectively inhibit the key dihydrofolate reductase (DHFR) enzyme in an epidemic strain of MRSA, known as EMRSA-16. He also found that it exhibits no cytotoxic properties in mammalian systems.

Spring suggests that emmacin may be representative of a whole new class of bacteria selective DHFR inhibitors which could be exploited in the development of critically needed new antibacterial agents. 'Bacteria are becoming resistant to DHFR inhibitors, so the more classes of compound which we can discover, the better we can tackle this problem,' he adds.

Richard Kelly



Emmacin (above) was the most potent anti-MRSA agent found

Reference

E E Wyatt *et al*, *Chem. Commun.*, 2008, 4962 (DOI:10.1039/b812901k)

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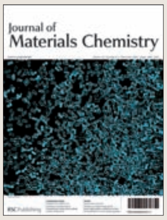
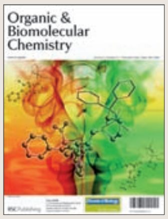




A snapshot of the latest developments from across the chemical sciences

Research highlights

New computer software speeds up the analysis of X-ray diffraction patterns

Crystal phases get ID'd

It is now easier to automatically ID crystal phases in zeolites, thanks to scientists in Spain

Laurent Baumes at the University of Valencia and co-workers have developed a new method for automatically deciphering X-ray diffraction patterns – allowing crystallographic phases to be identified quickly and reliably.

X-ray diffraction is used for a wide range of purposes, from routine characterisation in industrial production control through to in-depth research investigations of the most complex high-technology materials. However, the analysis of the diffraction data can be very complex explains Baumes. The synthesis of crystalline materials such as zeolites often produces a mixture of phases, he says, which need to be identified in order to determine how different synthetic methods influence the structure obtained and also to identify new phases that may have been made.

Zeolite structures can now be rapidly identified

Baumes' method, called adaptable time warping, is a piece of advanced computer software that can be coupled with existing high throughput synthesis technologies to help speed up the whole process of experimental and data analysis.

The new technique has been compared with existing software, says Baumes, and it shows a clear improvement in the error rate which is even more apparent when there is a mixture of crystalline and noncrystalline phases.

'The main application is the reduction of the time to market for new materials through the use of advanced software combined with high throughput technologies,' says Baumes.

Stephan Schunk, a scientist at hte - the high throughput experimentation company, Heidelberg, Germany, says 'the work is a breakthrough'. 'It enables the scientist to embark on complex synthetic programs and puts him in a position of ease and comfort when analysing the data,' he adds.

Sarah Dixon

Reference
L A Baumes *et al*, *CrystEngComm*, 2008, **10**, 1321 (DOI: 10.1039/b812395k)

Nanoparticle thermotherapy has 'great potential' for biomedical research

Cancer cells need salting before cooking

Korean scientists have used table salt to help them move closer to creating a porous silicon nanobomb that will literally blow up cancerous cells.

Thermotherapy – that uses near infrared (NIR) light to destroy cells – stopped being used in the 1990s, but thanks to new research is making a comeback as a possible alternative to currently available therapies for removing cancerous cells. Recently agents such as carbon nanotubes – that emit heat after irradiation with NIR – have been tried in combination with thermotherapy to kill cancer cells selectively.

Last year Chongmu Lee and co-workers at Inha University, Incheon, found that porous silicon offered a non-toxic and biodegradable alternative to carbon nanotubes for killing breast cancer cells. Now in vitro tests have shown that a suspension of porous silicon in sodium chloride solution offers better results still, say the researchers.

Salt improves the performance of porous silicon as a thermotherapy agent

The researchers avoid killing healthy cells by taking advantage of the folic acid- and antibody-receptors that are over abundant in most cancer cells. They pre-treat the porous silicon in sodium chloride solution with folic acid or antibodies, so that the agent binds selectively to the cancer cells before irradiation.

'Porous silicon can substantially lower the illumination intensities of NIR necessary to obtain a heating effect sufficient to destroy cancer cells down to a level which can be actually used in the clinic,' says Lee.

Lisa DeLouise, an expert in porous silicon at the University of Rochester Medical Centre in the US, says 'nanoparticle thermotherapy is an emerging field with great potential for biomedical research'.

Lee is continuing his research with in vivo tests, before moving on to clinical trials. He will go on to use the explosive properties of porous silicon to form a nanobomb for cancer treatment by finding a biocompatible oxidant to trigger heating. He is also working on a similar titanium dioxide system.

Sylvia Pegg

Reference
C Lee *et al*, *J. Mater. Chem.*, 2008, **18**, 4790 (DOI:10.1039/b808500e)

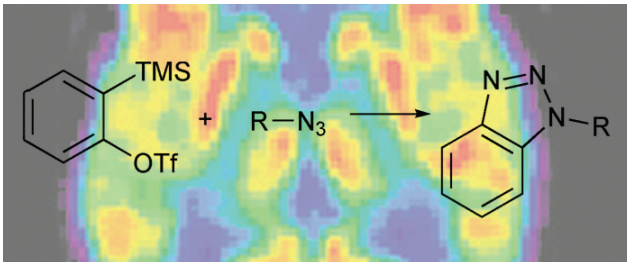
Non-toxic alternatives to current click chemistry are being explored

Copper-free clicking

Dutch scientists have developed a biologically-friendly click reaction which may lead to new tracers for improving the 3D imaging of cancerous tumours.

Click chemistry often includes copper catalysts that remove the need for the high temperatures and pressures. But copper is toxic to most living things so copper-free alternatives are highly sought after.

To achieve this Ben Feringa, University of Gröningen, and his team reacted a benzene ring, substituted with two leaving groups, with various functionalised azides to make benzotriazoles. The reactions could be activated using fluoride salts in combination with a complementary crown ether to give the product in yields of up to 82 per cent. This was achieved in less than two hours without the need for a copper catalyst, or elevated temperatures and pressures.



Benzothiazoles can be made using a copper-free click reaction

Feringa warns that this is just a first step in the right direction for 'developing alternatives to current click chemistry'. 'The problem with the use of this method in the context of living organisms would be that, although it is fast and does not need copper, fluoride is still needed to generate the reactive benzyne and we do not know if it will work in the aqueous environment of a cell.'

David Jackson, Syngenta, Muenchwilen, Switzerland – whose interests include reaction optimisation and clean chemistry – is impressed with the work: 'The benzotriazole unit continues to be of significant interest as a component in new potential new products in the life sciences industry. The triazole unit is particularly tricky to build at a multi kilogram scale due to the instability of building blocks and reagents. All new mild methods leading to their formation are sure to find applications.'

'With this method in hand our first goal is to introduce radiolabels like fluoride into relevant compounds for positron emission tomography (PET) tracer studies,' says Feringa. 'We are also exploring its use in labelling a range of bioactive compounds where copper-catalysed click reactions are currently used.'

Christina Hodkinson

Reference

L Campbell-Verduyn *et al*, *Org. Biomol. Chem.*, 2008, **6**, 3461 (DOI: 10.1039/b812403e)

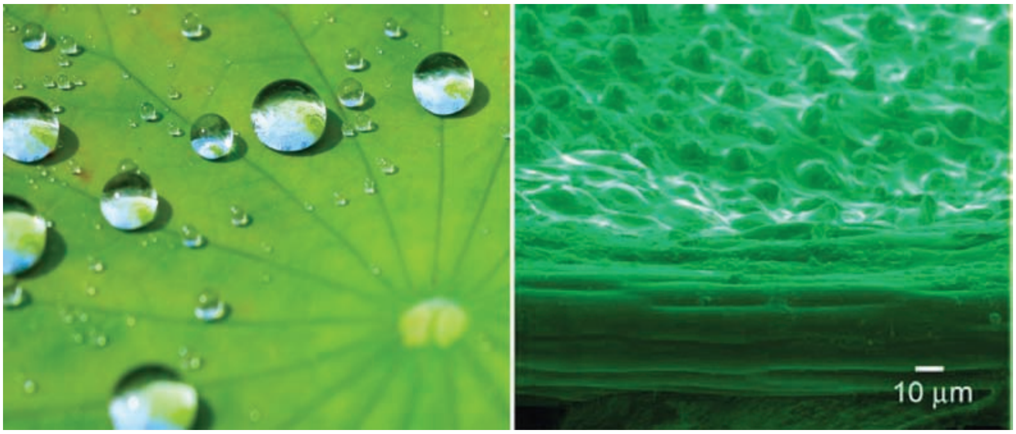
Lotus leaves are cleverly designed to prevent water flowing onto them

How water leaves lotus leaves

The mystery of how superhydrophobic lotus leaves remain completely dry whilst floating on water has been solved by Chinese scientists.

The top of a floating lotus leaf is a famous example of a superhydrophobic surface that sheds water, and has been used as a model for technologies such as self-cleaning windows. The leaf is covered in a rough surface of waxy projections, which causes water to form beads and slide off. Now Lei Jiang of the Chinese Academy of Sciences in Beijing and colleagues have found out why, when floating, no water flows onto the leaf.

Electron microscopy showed that, close to the leaf edge the projections are replaced by a smooth surface of folds and grooves, preventing the reverse-flow of water droplets. This means that the leaf is 50 per cent more resistant to submersion than a model leaf with a smooth surface.



Folds and grooves at the leaf margin help keep it dry

Jiang suggests that, just as the lotus leaf surface has provided inspiration for superhydrophobic surfaces, the leaf margin can serve as a model in applications such as tubes or microfluidic channels which require clean outflow or directional repellancy.

Abraham Marmur, a professor of water science and technology at Technion–Israel Institute of Technology, Haifa, says that 'the authors should be congratulated for opening a new angle for looking at the wonders of the lotus leaf'.

Michael Townsend

Reference

J Zhang *et al*, *Soft Matter*, 2008, **4**, 2232 (DOI: 10.1039/b807857b)

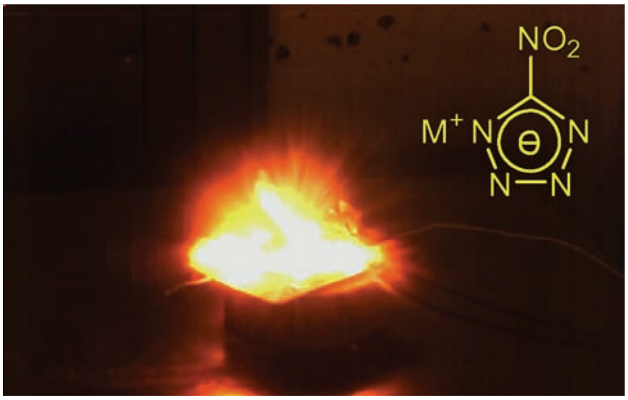
Lead contamination concerns at military training grounds lead to new detonators

Environmentally friendly explosives

Scientists in Germany have made lead-free detonators for reducing the environmental impact of military explosives.

Detonators contain primary explosives which can be easily ignited by a physical or electric stimulus. They are used to trigger the explosion of more stable energetic materials in guns and hand grenades. Currently, almost all primary explosives are based on lead azide which causes concern for human health and the environment.

Thomas Klapötke and colleagues at the Ludwig-Maximilian University of Munich made alkali metal salts as a replacement for lead azide. 'Lead is a toxic heavy metal and there are concerns about lead concentration at military training grounds,' says Klapötke. Over 90 000 hand grenades are used at these sites every year, explains Klapötke, therefore it is important to try to make the soldiers lives safer and healthier by removing toxic substances.



Alkali metal-based primary explosives are less toxic than the current lead-based ones

Klapötke's team made a family of alkali metal salts with the energetic 5-nitrotetrazolate anion. The salts with the harder lithium and sodium cations were found to contain crystal water, which gives them low sensitivity towards shock and friction. The rest of the alkali metal salts form as the anhydrous species, and show increased explosive sensitivities making them more useful as prospective replacements for commonly used primary explosives.

Klapötke says that the new primary explosives are good enough for military use, however more work is needed to improve their thermally stability for use in harsh conditions such as for oil drilling. In the future we also hope to look into environmentally friendly replacements for other explosives such as perchlorates which are used as oxidisers in pyrotechnics and solid rocket boosters, he adds.

Joseph Backofen, BRIGS Co., Herndon, US, an expert in ballistics, comments 'this work represents a clear path towards developing new energetic materials that are free from constituents deemed harmful to their users during routine work. This issue is important in primers used in rifle and pistol ammunition used in indoor training ranges by police and military personnel.'

Sarah Dixon

Reference
T M Klapötke, C M Sabaté and J M Welch, *Dalton Trans.*, 2008, DOI: 10.1039/b811410b

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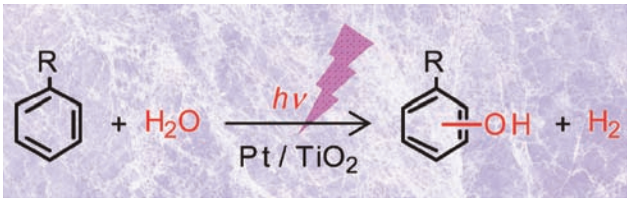
Tap water proves its worth in the synthesis of phenols

Water to wine...well alcohols actually

Japanese scientists have unleashed the power of water to improve the selectivity and green credentials of the synthetic route to industrially-important phenols.

Hisao Yoshida and colleagues from Nagoya University have developed a photocatalyst that activates water to oxidise functionalised aromatic rings in a selective manner.

Phenols are currently made using a multistep process which consumes a significant amount of energy. Selectivity is another well-known disadvantage of this route, as the side chains often oxidise in preference to the aromatic ring. Much research has been done into developing one-step, environmentally-friendly and more efficient routes which involve the direct oxidation of aromatic rings. However to date selectivity has remained an issue.



A photocatalyst activates water to selectively oxidise aromatic rings

Now, Yoshida has overcome this using a platinum-loaded titanium oxide catalyst that is activated by illumination with the appropriate wavelength of light. The activated catalyst then converts water into an oxygen species that selectively reacts with an aromatic ring to make the required phenol, with hydrogen as the waste product.

Added bonuses of this route include mild reaction conditions – room temperature and atmospheric pressure – and removal of the need for expensive or hazardous oxidants. Additionally Yoshida found that the intensity and wavelength of the light can be varied to finely control the reaction products.

Yoshida recognises that the rate of the reaction needs to be improved before this can be a useful industrial process. However, he says that 'our findings provide an important principle which may be widely valuable for many kinds of undiscovered chemical syntheses, especially selective oxidation.'

Stephen Poulston, an expert in photocatalysis at Johnson Matthey, Reading, UK, agrees: 'It is encouraging to see potential applications for photocatalysis beyond the more well-established research.' 'I think the challenge with this reaction, which is common to most photocatalytic processes, is how to scale the reaction up and how to increase the reaction rate,' he adds.

May Copsey

Reference
H Yoshida *et al*, *Chem. Commun.*, 2008, 4634 (DOI: 10.1039/b811555a)

Is your food safe to eat?

Gordon Shephard, South African Medical Research Council, Cape Town, highlights the analytical methods used to ensure our food is free from the natural toxins produced by fungi

Food is the essence of life, yet the majority of people give little thought to the role analytical chemistry plays in ensuring our food is safe to eat. When food safety issues are raised, it is normally the perceived problems of pesticide – or other man-made chemical – residues in our foods causing concern. Yet natural toxins, produced by a range of microbiological organisms, are actually more potent toxins and carcinogens and therefore a greater threat to food safety.

Amongst these natural toxins are the mycotoxins, secondary metabolites of filamentous fungi – more commonly known as mould. These can infect agricultural products both in the field, during plant growth, as well as in poorly stored produce. Many of the mycotoxins are extremely stable and can survive in the agricultural raw material through to the finished product on the supermarket shelf. Similarly, their presence in animal feed can result in the carry-over of the toxin or its metabolites into animal products for human consumption.

Although practically unknown in the developed world due to the vigilance of food safety authorities, human morbidity and mortality due to mycotoxin exposure is widespread in developing countries – especially in communities that are self-sufficient.

The mycotoxins have a diverse range of chemical structures and therefore biological effects. Although many hundreds of these toxins are known, researchers and food safety authorities concentrate on those produced by fungal pathogens of major crops – aflatoxins, fumonisins, trichothecenes (especially deoxynivalenol and T-2 toxin), zearalenone, ochratoxin A and patulin. And many countries now have legislated maximum levels of these toxins allowed in food.

Maize kernels infected with mould can enter the food system

A characteristic of mycotoxin contamination is that it is not uniformly spread throughout an agricultural product. This means that specific sampling methods for each different product and toxin combination are needed.

A wide range of analytical methods have been developed for detecting mycotoxins in food. All these methods – apart from near-infrared – require extraction of the toxin from the food, using polar solvent mixtures, prior to analysis. These extracts, which still contain many soluble food compounds, can be analysed directly in enzyme-linked immunosorbent assays (ELISAs) or applied to a variety of screening methods such as lateral flow devices, dipsticks and biosensors. These methodologies all rely on the use of mycotoxin-specific antibodies to discriminate the mycotoxin from the coextracted food components and generally give semi-quantitative results.

For more accurate determination of mycotoxins, the extracts require purifying. The clean-up method of choice is solid phase extraction, where the mycotoxin binds to the sorbent, the impurities are washed through the column and finally the mycotoxin is released. Also popular are multifunctional columns – packed with adsorbent mixtures such as alumina and charcoal – that absorb the impurites as the mycotoxin extract passes through.

After extract clean-up, mycotoxins can be analysed by thin-layer, gas or high-performance liquid chromatography. This last method coupled with ultraviolet, fluorescence or mass spectrometric detection is the most frequently used analysis technique. The use of tandem mass spectrometric detection here can provide multitoxin analysis combined with confirmatory evidence within the same experiment. Multitoxin analysis is useful for foods that can be contaminated by a number of different mycotoxins, produced by the same or different fungal species.

Interpretation of ancient writings suggests that mycotoxins have caused health problems since the earliest times of recorded history. And unless we can inhibit the toxin synthetic capability of the mycotoxin-producing fungi, we shall need to continue to tap into the advances in analytical chemistry to monitor these potent natural toxins.

Read Gordon Seymour Shephard's tutorial review 'Determination of mycotoxins in human foods' in issue 11, 2008 of Chemical Society Reviews

Reference
G S Shephard, *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b713084h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Interview

Chemistry is the business

A V Rama Rao talks to Joanne Thomson about how science has shaped development in India

A V Rama Rao

A V Rama Rao is founder and managing director of Avra Laboratories in Hyderabad, India, a research-focused company that caters to the process and product needs of the pharmaceutical industry. He has published more than two hundred and fifty papers on the isolation, structural elucidation and synthesis of natural products and has developed more than fifty drug technologies commercialised by the pharmaceutical industry.

What inspired you to become a scientist?
The science of natural products fascinated me in my early days. I was surrounded by inspiration. I lived close to poppy fields – my grandfather was addicted to the morphine made from them to relieve his knee pains. Malaria was common and I used to take quinine tablets whenever I suffered from it. I was also fascinated to see fabrics dyed with natural colours, especially indigo, which was cultivated in India.

What was your big break?
My two year stint with E J Corey at Harvard University. There I realised the importance in choosing the right product for synthesis. I also realised that the product should have some relevance to society. I returned to India to work at the National Chemical Laboratory (NCL) in 1977. Most of my senior colleagues at NCL discouraged me from taking on challenging synthetic projects as the institute (albeit a premier one) was not well equipped and it took months to import reagents at the time (the early 1980s). In spite of all these hurdles, I was always keen on tackling such fascinating projects.

You founded Avra Laboratories in 1995. What were your motivations, and what are your aspirations for the company for the years ahead?
When I retired as director of the Indian Institute of Chemical Technology in 1995, I wanted an exciting and viable alternative. I decided not to accept a distinguished scientist position at the Council for Scientific and Industrial Research because normally, such distinguished persons feel more like extinguished entities within the organisation. I decided to utilise my scientific expertise to tackle some industrial projects. Most people become consultants as it is an easy option. I wanted to offer more than paper solutions; I wanted to have a lab where I could work with a team of scientists and provide real solutions on a fee for service model. This idea led to the genesis of Avra Laboratories.

In the future, we would like to align with some of the big pharma companies and offer our R&D services on a long-term basis.

Your sons, Ramakrishna and Chandra, both work at Avra. How important is it to you to maintain these family connections in business?
For a medium-sized industry like us, I feel it is better to be run by family, provided that they are well qualified to lead the team. Ramakrishna has a Master's degree in industrial chemistry and an MBA. He meticulously plans the commercial operations. Chandra obtained a PhD in organic chemistry from Cambridge University.
He is a very good communicator and inspires young R&D personnel in Avra. All three of us have defined roles and operate professionally.

India is becoming a major player in chemical research. How important do you think chemistry is to the future development of India?
Since we joined the World Trade Organisation, the Indian pharma industry has been rapidly expanding and now employs even expats in top R&D positions. During the last three years, many international pharma companies have started R&D divisions in India and the government has doubled the R&D budget for public institutions.

I believe India is among the few developing nations that can boast of an indigenous but globally respected chemical industry. India thus has an established platform to enable it to gain further stature as a hub for manufacturing and innovation by taking advantage of the lower costs and abundant talent.

The generic market has always been the mainstay of the Indian pharmaceutical industry but competition has increased greatly in recent years. What strategies should companies adopt in the coming years to survive?
Competition is good for the consumer and puts pressure on manufacturers to innovate and bring in efficiencies of scale. If you cannot beat your competitor, the other option would be to join him. I believe there will be consolidation in the Indian chemical space with mergers and acquisitions. The pressure to survive might kindle innovating strategies that could cater to an unmet need at the time.

Essential elements

Good prospects for *Lab on a Chip*

Lab on a Chip, the miniaturisation journal for chemistry, biology and bioengineering is now taking miniaturisation science to the next level. With journal submissions steeply rising over the past years, 2009 will see the journal increase in frequency to 24 issues per year. The new year will also herald the arrival of George Whitesides as the new editorial board chair of *Lab on a Chip*. 'There is no one in the field who is better equipped than Professor Whitesides to help *Lab on a Chip* ascend to the next level in terms of quality, visibility and impact,' comments Harp Minhas, editor of *Lab on a Chip*.

George Whitesides, the new editorial board chair of *Lab on a Chip*

Lab on a Chip has established itself at the heart of the miniaturisation community through various sponsorships for prizes and awards, which recognise and highlight the contributions of young and emerging scientists in the field, to online support via new initiatives such as 'Chips & Tips'- the quick-fix online forum providing useful advice on common practical problems for scientists in the miniaturisation world.

More issues, more leading research and a new editorial board chair – 2009 promises to be an exciting year for the *Lab on a Chip* community.

For further information visit www.rsc.org/loc

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ChemComm in Korea

The Second *ChemComm* International Symposium on Supramolecular Chemistry will take place in Korea in November 2008 with one-day meetings in Seoul, Daejeon and Pohang. This follows a successful First *ChemComm* International Symposium on Polymers and Polymer Science in China in December 2007.

ChemComm, with an impact factor of 5.14, publishes some of the most significant work in the chemical sciences and is the fastest at publishing general chemistry communications. *ChemComm* Symposia aim to bring together scientists in an environment that fosters collaborations between the researchers and universities involved. All symposia are free to attend and each is devoted to a topical area of the chemical sciences, featuring an invited programme of international and locally-based expert speakers.

In this second symposium, the programme is supplemented by a poster session, showcasing the work of local universities.

As the second symposium approaches fast and promises to be as successful as the first, plans for a third symposium next year in China are already well underway. The Third *ChemComm* International Symposium on the topic of Organic Chemistry will be held in February 2009, with meetings in Beijing, Shanghai and Chengdu.

For more details on *ChemComm* Symposia, and full programme schedules for the Second Symposium on Supramolecular Chemistry in Korea, visit www.rsc.org/chemcommsymposia.

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