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# IN THIS ISSUE

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Cover



See Sebastiano Campagna et al., pp. 4740–4742. A Pt(II) complex exhibits luminescence switching in the presence of HCl vapor. The luminescence switching can be reversed by heating or by  $NH_3$ vapor. Image reproduced by permission of F. Nastasi, E. Durdsteiner, N. Palmari

F. Puntoriero, N. Palmeri, S. Cavallaro, S. Campagna and S. Lanza from *Chem. Commun.*, 2007, 4740.

# CHEMICAL BIOLOGY

B89

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



December 2007/Volume 2/Issue 12

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# FEATURE ARTICLE

## 4717

# Catalytic enantioselective diboration, disilation and silaboration: new opportunities for asymmetric synthesis

Heather E. Burks and James P. Morken\*

Dimetalation of unsaturated substrates provides a reactive intermediate with two carbon-metal bonds. Stereospecific transformation of these elements can be accomplished in a number of ways thereby rendering catalytic asymmetric dimetalation a "springboard" for access to diverse classes of chiral compounds.



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# 4726

### Maximizing the relaxivity of HSA-bound gadolinium complexes by simultaneous optimization of rotation and water exchange

Stefano Avedano, Lorenzo Tei, Alberto Lombardi, Giovanni B. Giovenzana, Silvio Aime,\* Dario Longo and Mauro Botta\*

A new, compact, rigid and fast water exchanging Gd<sup>III</sup> complex exhibits a 14-fold relaxivity enhancement (30 MHz, 298 K) upon binding HSA non-covalently thanks to the lack of internal flexibility.

# 4729

# The first direct C-H arylation of purine nucleosides

Igor Čerňa, Radek Pohl and Michal Hocek\*

Pd-catalyzed direct C-H arylation of unprotected purine nucleosides (e.g. adenosine) with aryl iodides at position 8 was developed to allow a straightforward single-step introduction of diverse aryl groups.



GdL1  $= 5.7 \text{ mM}^{-1}\text{s}^{-1}$ GdL1-HSA  $r_{1p}^{b} = 78 \text{ mM}^{-1}\text{s}^{-1}$ 



GdL2  $= 7.0 \text{ mM}^{-1}\text{s}^{-1}$  $r_{lp}$ GdL2-HSA  $r_{1p}^{b} = 50 \text{ mM}^{-1}\text{s}^{-1}$ 



# 4731

A novel reaction of 7,7,8,8-tetracyanoquinodimethane (TCNQ): charge-transfer chromophores by [2 + 2]cycloaddition with alkynes

Milan Kivala, Corinne Boudon, Jean-Paul Gisselbrecht, Paul Seiler, Maurice Gross and François Diederich\*

A series of donor-acceptor chromophores featuring appealing optoelectronic and redox properties was prepared by a novel reaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and donor-substituted alkynes.

# 4734

### Selective binding of cucurbit[7]uril and β-cyclodextrin with a redox-active molecular triad $Ru(bpy)_3-MV^{2+}$ naphthol

Dapeng Zou, Samir Andersson, Rong Zhang, Shiguo Sun, Björn Åkermark and Licheng Sun\*

A 1:1:1 inclusion complex is formed by the binding interactions among  $\beta$ -CD, CB[7] hosts, and Ru(bpy)<sub>3</sub>terminated viologen-naphthalene guest in aqueous solution, in which the positions of both CB[7] and  $\beta$ -CD are closer to the Ru stopper than in the respective 1:1 inclusion complexes.







NMe<sub>2</sub>

NC

CN



# **Forthcoming Articles**

# Perspectives

Current molecular design of intelligent drugs and imaging probes targeting tumor-specific microenvironments

Sei-ichi Nishimoto, Japan

# **Emerging Area**

The development of yoctowells as a basis for modeling biological systems Sheshanath V. Bhosale, Australia

Generation, basic chemistry, and detection of *N*-nitrosotryptophan derivatives *Michael Kirsch, Germany* 

# Communication

Synthesis of novel ginkgolide photoaffinity-biotin probes

Sergei V. Dzyuba, USA

# Articles

Enantioselective catalysis of the Henry reaction by a chiral macrocyclic ytterbium complex in aqueous media

David Parker, UK

Nucleophilicities of amino acids and peptides

Herbert Mayr, Germany

Structural confirmation of the dihydrosphinganine and fatty acid constituents of the dental pathogen *Porphyromonas gingivalis* 

Michael B. Smith, USA

Carboxyl and carboxamide pyrazoles as protein kinase inhibitors in aberrant eukaryotic signal transduction: induction of growth arrest in MCF-7 cancer cells John Nielsen, Denmark

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### 4737

# Empirical determination of the absolute configuration of small chiral molecules using natural abundance <sup>2</sup>H NMR in chiral liquid crystals

Latifa Ziani, Philippe Lesot,\* Abdelkhrim Meddour and Jacques Courtieu

The absolute configuration of small chiral molecules containing a single asymmetric center is empirically determined using natural abundance deuterium 2D NMR spectroscopy in polypeptide liquid crystals.



# Solid-state luminescence switching of platinum(II) dithiooxamide complexes in the presence of hydrogen halide and amine gases

Francesco Nastasi, Fausto Puntoriero,\* Natale Palmeri, Stefano Cavallaro, Sebastiano Campagna\* and Santo Lanza\*

Solid-state luminescence switching, coupled with significant color change, is obtained in a Pt(II) dithiooxamide compound by exposing the sample to HCl vapors; the process is fully reversed by heat or exposure to  $NH_3$  vapors.

### 4743

### Turbidimetric detection of ATP using polymeric micelles and DNA aptamers

Daisuke Miyamoto, Zhonglan Tang, Tohru Takarada\* and Mizuo Maeda

Turbidimetric detection of adenosine 5'-triphosphate (ATP) by the naked eye was achieved through a combination of noncross-linking aggregation of DNA-linked polymeric micelles and molecular recognition of ATP by a DNA aptamer.

## 4746

### A new functionalization strategy for pentacene

John E. Anthony,\* Johannes Gierschner, Chad A. Landis, Sean R. Parkin, Jes B. Sherman and Ronald C. Bakus, II

Appending the pentacene chromophore with alkyl-substituted dioxolane groups, where the substituents are held perpendicular to the pentacene plane, leads to materials with significantly improved solubility and solution stability. The derivatives exhibit a number of variations on the herringbone packing motif in their crystal structures.











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### 4749

# Novel one step hydrothermal synthesis of TiO<sub>2</sub>/WO<sub>3</sub> nanocomposites with enhanced photocatalytic activity

Valeria Puddu, Robert Mokaya and Gianluca Li Puma\*

The novel synthetic route and material properties that are demonstrated in this communication open up new opportunities for the easy synthesis of  $TiO_2/WO_3$  nanocomposites that have enhanced photocatalytic activities.

## 4752

# Optically sensed, molecular shuttles driven by acid-base chemistry

Sarah J. Vella, Jorge Tiburcio and Stephen J. Loeb\*

A pair of bistable [2]rotaxane molecular shuttles are prepared that combine 1,2-bis(pyridinium)ethane and benzylanilinium recognition sites; acid–base controlled shuttling of **DB24C8** is accompanied by either a change in colour or fluorescence intensity.

## 4755

### Intramolecular Stetter cyclisation of Morita–Baylis– Hillman adducts: a versatile approach towards bicycloenediones

Pierre Wasnaire, Thierry de Merode and István E. Markó\*

Bicyclic enediones of various sizes can be efficiently assembled by an original sequence involving, as key steps, a Morita– Baylis–Hillman coupling followed by a unique intramolecular Stetter cyclisation. During this ring closure, elimination of an acetate leaving group and double bond conjugation also take place.

# 4758

# A photochromic fluorescent switch in an organogel system with non-destructive readout ability

Shuzhang Xiao, Ying Zou, Mengxiao Yu, Tao Yi,\* Yifeng Zhou, Fuyou Li and Chunhui Huang\*

A fluorescent switch with non-destructive readout ability was fabricated in the gel state using a photochromic dithienylethene derivative.



base acid

0.7

0 4

0.3

0.2





6.0

E 5.0

slom 4.0

ate

adati

3.0

2.0

WG TIO2 1% 5% 10% 20% 40% P-25



### Chemo-, regio- and stereoselective preparation of silyl enol ethers from thiol esters and bis(iodozincio)alkane

Akihiro Ooguri, Zenichi Ikeda and Seijiro Matsubara\*

Treatment of thiol ester with bis(iodozincio)alkane in the presence of palladium catalyst and silylating reagent affords silyl enol ether chemo-, regio- and stereoselectively.



24.0 20.0

16.0 -

12.0

0.0 - L

0

4.0

0.2

Plastic-substrate DSC, n=7.4%

2.0

0.6

0.8

0.4

Voltage / V

# N-substituents, including demethylasterriquinone A1 Anthony J. Fletcher, Matthew N. Bax and Michael C. Willis\*

Palladium-catalysed N-annulation routes to indoles: the

synthesis of indoles with sterically demanding

Tandem palladium catalysed amination reactions can be used to prepare synthetically challenging indoles containing sterically demanding N-substituents; adamantyl, *tert*-butyl and 2,6-di(isopropyl)phenyl groups are all readily incorporated. The methodology delivered a short synthesis of the natural product demethylasterriquinone A1.

# Highly efficient plastic substrate dye-sensitized solar cells using a compression method for preparation of $TiO_2$ photoelectrodes

Takeshi Yamaguchi, Nobuyuki Tobe, Daisuke Matsumoto and Hironori Arakawa\*

The efficiency of a plastic-substrate dye-sensitized solar cell was much improved up to 7.4% under 100 mW cm<sup>-2</sup> (1 sun) AM1.5 illumination by a new method consisting of a press method without heat treatment, light confinement effect of TiO<sub>2</sub> film and water-based TiO<sub>2</sub> paste.



4767



# Synthesis and structure of the new complex hydride $Li_2BH_4NH_2$

Philip A. Chater, William I. F. David and Paul A. Anderson\*

The crystal structure of the new mixed anion amide– borohydride  $Li_2BH_4NH_2$  can be viewed as a mixture of nanosized clusters of  $LiNH_2$  embedded in a  $LiBH_4$  matrix and provides important clues about how the two compounds interact at low temperatures to form complex crystal structures.

## 4773

# Enhancing the reactivity of 1,2,3-triazoles in "click" macrocycles by face-to-face dibenzylammonium ion binding

Yi Liu,\* Xiyun Zhang, Liana M. Klivansky and Gayane Koshkakaryan

The reactivity of 1,2,3-triazoles in macrocycles synthesized *via* the copper catalyzed azide–alkyne cycloaddition reaction can be tuned by controlling its face-to-face binding with dibenzylammonium guests.

# 4776

# Supramolecular single-walled carbon nanotubes (SWCNTs) network polymer made by hybrids of SWCNTs and water-soluble calix[8]arenes

Tomoki Ogoshi,\* Tada-aki Yamagishi and Yoshiaki Nakamoto\*

The authors report on hybrids of water-soluble calix[8]arenes and single-walled carbon nanotubes (SWCNTs). The hybrids formed supramolecular SWCNTs network polymer by adding guest dimer.

4779

# Centripetal molecules as multifunctional building blocks for coordination networks

Yan-Qiong Sun, Jun He, Zhengtao Xu,\* Guo Huang, Xiao-Ping Zhou, Matthias Zeller and Allen D. Hunter

We introduce a class of branchy molecules with back-folded, centripetal geometry as functional building blocks for coordination networks. Crystallization of these molecules with  $AgSbF_6$  yielded networks featuring novel coordination modes, network connectivity and chiral/helical structures.

# 4782

# A concise organocatalytic and enantioselective synthesis of isotetronic acids

Jean-Marc Vincent,\* Chrystèle Margottin, Muriel Berlande, Dominique Cavagnat, Thierry Buffeteau and Yannick Landais\*

Benzoimidazole-pyrrolidine (BIP) was shown to catalyze the one-pot synthesis of isotetronic acids from  $\alpha$ -oxocarboxylic acids and aldehydes with enantioselectivities of up to 90%. Absolute configuration of the lactones was determined through vibrational circular dichroism (VCD) associated with *ab initio* calculations.













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# **Critical Review**

Advanced nuclear analytical techniques for metalloproteomics Yuxi Gao, Chunying Chen and Zhifang Chai, *J. Anal. At. Spectrom.*, 2007, **22**, 856 DOI: 10.1039/b703323k

# Articles:

Investigation of the selenium species distribution in a human B-cell lymphoma line by HPLC- and GC-ICP-MS in combination with HPLC-ESIMS/MS and GC-TOFMS after incubation with methylseleninic acid

Heidi Goenaga Infante, Simon P. Joel, Emma Warburton, Christopher Hopley, Ruth Hearn and Simone Jüliger, *J. Anal. At. Spectrom.*, 2007, **22**, 888 **DOI:** 10.1039/b708620b

# Laser ablation-ICP-MS assay development for detecting Cd- and Zn-binding proteins in Cd-exposed *Spinacia oleracea* L.

Aleksandra Polatajko, Marisa Azzolini, Ingo Feldmann, Thomas Stuezel and Norbert Jakubowski, *J. Anal. At. Spectrom.*, 2007, **22**, 878 DOI: 10.1039/b703245e

# Analysis of phytochelatins in nopal (Opuntia ficus): a metallomics approach in the soil-plant system

Julio Alberto Landero Figueroa, Scott Afton, Kazimierz Wrobel, Katarzyna Wrobel and Joseph A. Caruso, *J. Anal. At. Spectrom.*, 2007, **22**, 897 DOI: 10.1039/b703912c

# Mass spectrometric analysis of ubiquitin-platinum interactions of leading anticancer drugs: MALDI versus ESI

Christian G. Hartinger, Wee Han Ang, Angela Casini, Luigi Messori, Bernhard K. Keppler and Paul J. Dyson, *J. Anal. At. Spectrom.*, 2007, **22**, 960 **DOI:** 10.1039/b703350h

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### 4785

### Single-crystal metal–organic microtubes self-assembled from designed $D_3$ symmetrical nanoclusters with a capped triple-helix pentanuclear $M_5O_6$ core

Sisi Feng, Miaoli Zhu,\* Liping Lu\* and Maolin Guo

Single-crystal metal–organic microtubular architectures have been fabricated from designed  $D_3$  symmetrical nano clusters with a capped triple-helix pentanuclear  $M_5O_6$  core under hydrothermal conditions.

## 4788

## Direct organocatalytic synthesis of enantiopure succinimides from β-lactam aldehydes through ring expansion promoted by azolium salt precatalysts

Benito Alcaide,\* Pedro Almendros,\* Gema Cabrero and M. Pilar Ruiz

A single-step catalytic ring expansion approach from 4-oxoazetidine-2-carbaldehydes to enantiopure succinimides has been achieved by the use of a base (DBU) and a thiazolium salt precatalyst.

### 4791

# Samarium(II) iodide-mediated intramolecular pinacol coupling reactions with cyclopropyl ketones

Sarah L. Foster, Sandeep Handa,\* Michael Krafft and David Rowling

The first successful SmI<sub>2</sub>-mediated pinacol coupling of cyclopropyl ketones shows that 5-*exo*-trig cyclisation of ketyl radical anions can compete with cyclopropyl ring-opening.

## 4794

# New trifluoromethylated derivatives of [60]fullerene, $C_{60}(CF_3)_n$ with n = 12 and 14

Nadezhda A. Omelyanyuk, Alexey A. Goryunkov, Nadezhda B. Tamm, Stanislav M. Avdoshenko, Ilya N. Ioffe, Lev N. Sidorov, Erhard Kemnitz and Sergey I. Troyanov\*

 $C_{60}(CF_3)_{12}$ , with two skew-pentagonal-pyramids on the opposite poles, and the first isomers of  $C_{60}(CF_3)_{14}$  have been isolated and characterized by X-ray crystallography, allowing more insight into of trifluoromethylation of [60]fullerene.





DBU (10 mol%)

MeCN, reflux



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### 4797





# Transition metal dinitrogen complexes supported by a versatile monoanionic $[N_2P_2]$ ligand

Wayne A. Chomitz and John Arnold\*

The reduction of a number of first and second row transition metal-halide complexes supported by a new monoanionic ligand [N<sub>2</sub>P<sub>2</sub>] has resulted in the isolation of four new transition metal dinitrogen compounds.

### 4800

### NO-disproportionation, promoted by Pd-cluster: formation and X-ray structure of $Pd_8(\mu-CO)_4(\mu-OOCCMe_3)_8[\mu-N(=O)O-]_4$

Tatiana A. Stromnova,\* Oleg N. Shishilov, Andrei V. Churakov, Lyudmila G. Kuz'mina and Judith A. K. Howard

Pd-clusters [Pd(CO)(OCOR)]<sub>n</sub> were found to promote the NO disproportionation into  $N_2$  and  $NO_2^-$  in mild conditions; an eight-nuclear palladium cluster with a new type of structure and an uncommon set of ligands was characterized by X-ray diffraction analysis.

### 4803

### Rapid ligand substitution reactions in ionic liquids studied by stopped-flow technique

Peter Illner, Simon Kern, Svetlana Begel and Rudi van Eldik\*

The kinetics of fast ligand substitution reactions of [M(terpy)Cl]Cl (M = Pt(II) and Pd(II)) with thiourea as entering nucleophile were for the first time studied in an ionic liquid, [emim][NTf<sub>2</sub>], as a function of nucleophile concentration and temperature, using stopped-flow techniques.

### 4806

One-step synthesis of SBA-15 containing tungsten oxide nanoclusters: a chemoselective catalyst for oxidation of sulfides to sulfoxides under ambient conditions

Ankur Bordoloi, Ajayan Vinu and S. B. Halligudi\*

Tungsten oxide nanoclusters supported highly ordered mesoporous SBA-15 material has been synthesized in a single step using a non-ionic surfactant as a template and used for the selective oxidation of sulfur compounds.



Pd<sub>6</sub>(CO)<sub>6</sub>(OCOR)<sub>6</sub>

Pd<sub>8</sub>(CO)<sub>4</sub>(OCOR)<sub>8</sub>(NO<sub>2</sub>)<sub>4</sub>







### Magnetic nanoparticle-supported proline as a recyclable and recoverable ligand for the CuI catalyzed arylation of nitrogen nucleophiles

Gagan Chouhan, Dashan Wang and Howard Alper\*

Magnetic nanoparticle-supported proline ligand was prepared and used for the CuI catalysed Ullmann-type coupling reactions of aryl/heteroaryl bromides with various nitrogen heterocycles to form the corresponding *N*-aryl products in good to excellent yields.

4812



# Rapid polymerisation of $S_2N_2$ within Na-ZSM-5 channels

Roberto S. P. King, Paul F. Kelly,\* Sandra E. Dann and Roger J. Mortimer

Exposure of Na-ZSM-5 to  $S_2N_2$  vapour results in very rapid darkening of the colour of the zeolite as the nitride enters its channels and polymerises to  $(SN)_x$ .

Multicomponent polymer coating to block photocatalytic

Wilson A. Lee,\* Nadine Pernodet, Bingquan Li, Chien H. Lin, Eli Hatchwell and Miriam H. Rafailovich Scanning electron microscopic image of fully coated uniform

4815



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### ADDITION AND CORRECTION

4818

Brian E. Mann and Roberto Motterlini

CO and NO in medicine

activity of TiO<sub>2</sub> nanoparticles

TiO<sub>2</sub> nanoparticles.

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# Chemical Biology

Molecular probes get the measure of oxidase activity **Emotional enzymes** 

Chemists in the US have created fluorescent probes that can detect enzymes affecting our emotions. The team, led by Christopher Chang at the University of California, Berkeley, is the first to develop chemical tools that measure directly monoamine oxidase (MAO) activity in living cells.

MAOs catalyse amine oxidation and the enzymes are responsible for breaking down amine-containing neurotransmitters such as serotonin and dopamine. Altered MAO activity levels have been linked with diseases such as depression and MAO inhibitors are often used to treat both depression and anxiety. Our MAO levels, determined by our genes, may also affect aspects of our personality, said Chang.

Chang's MAO probes are amine derivatives of the redfluorescent dye, resorufin. The probes are oxidised by MAOs to give intermediates which break down to generate the dye. As MAO activity increases, more resorufin is produced, causing an increase in red



fluorescence which is measured.

The new probes can move through cell membranes, making them capable of detecting MAOs within cells. Also, unlike earlier methods, these probes detect MAO activity directly without the need for external secondary activating enzymes or reagents. Emotional link: MAO activity is measured as probes (left) break down to dye resorufin (right)

In the future, said Chang, these tools could be used in drug discovery in screens for new inhibitors, or for diagnosis of diseases where altered levels of MAO activity are typical. *Sarah Corcoran* 

Reference

A E Albers, K A Rawls and C J Chang, *Chem. Commun.*, 2007, 4647 (DOI: 10.1039/b713190a)

# In this issue

# **Cells surface in semisynthesis**

Scientists in Japan are using cells as protein factories

# OH to be in a position of power

French scientists are unravelling the anticancer secrets of ferrocenyl phenols

# **Plasma screening**

Norbert Jakubowski explains what he means by element-omics and outlines what he'd like to learn from Einstein

# **DNA** hitchhikers

Brian Jones and Julian Marchesi take a closer look at the genetic swap shops in our midst

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# **Research highlights**

Scientists see red as they analyse 65000 peptides
Substrate screening made simple



A simple assay for identifying protease substrates will make such experiments accessible to everyone, say scientists in Switzerland.

Proteases are enzymes that hydrolyse peptide bonds, and are involved in many important processes in the body. Identifying protease substrates is important for studying the structure and function of these enzymes, and can also produce leads for drug development, explained Jean-Louis Reymond, a bioorganic chemist from the University of Bern. Proteases Members of a peptide library are hydrolysed by a protease leaving free amino groups that react with a selective dye

Reference

J Kofoed and J-L Reymond, *Chem. Commun.*, 2007, 4453 (DOI: 10.1039/b713595e) are implicated in diseases such as cancer, and viral proteases are also important drug targets, he said.

There are currently many techniques for screening protease substrates, but according to Reymond they all involve complex experiments and remain inaccessible to most laboratories. Following calls for a simpler method, he and colleague Jacob Kofoed have developed a system that Reymond says is 'very simple, very reliable, and can be repeated by students with a minimum of training.' In the new method a library of peptides carried on polymer beads is exposed to a protease. This step leaves a free amino group on the peptides that are hydrolysed by the enzyme. A selective dye then reacts with the amino groups, colouring the beads carrying protease substrates red. The peptide sequences on the red beads are then analysed, thus identifying the substrates.

Reymond and Kofoed used their method to find substrates for various proteases among a library of over 65 000 peptides. The results from the assay agreed with those found by other methods.

Reymond said he would be able to use the technique in several projects, including studying the function of the intestinal proteases meprin  $\alpha$  and  $\beta$ . To extend the method's potential uses he also plans to include nonnatural peptides in the substrate libraries. 'This should provide peptides with higher selectivities for their target,' said Reymond. Danièle Gibney

# Ruthenium chromophore proves effective at inactivating protein target Bringing warhead efficiency to light

US scientists can now compare molecular warheads that inactivate proteins.

Chromophore assisted light inactivation (CALI) of proteins involves generating highly reactive species (often singlet oxygen) from a chromophore (the warhead) using light. The reactive species damages the target protein, inactivating its biological function. Thomas Kodadek, a chemical biologist at the University of Texas Southwestern Medical Centre in Dallas, explained that CALI can be used to 'knockout the function of a protein to validate pharmaceutical targets or alternatively provide temporal control of protein inactivation for mechanistic studies.<sup>2</sup>

Organic chromophores often react with the reactive species they produce, limiting their effectiveness as CALI warheads.



In CALI, chromophores (red) produce reactive species to inactivate a target protein

# Reference

J Lee et al, Mol. BioSyst., 2007, DOI: 10.1039/b712307h In this new research, Kodadek and his co-workers have developed a system for comparing warhead effectiveness. The system allows different chromophores to be covalently attached to a standard target protein through a simple coupling mechanism. This allows the chromophore efficiencies to be compared by measuring the remaining activity of the target.

Comparative experiments showed a ruthenium-based chromophore to be a more effective warhead than the commonly used organic dye fluorescein. The scientists demonstrated that the ruthenium chromophore can enter cells and inactivate a target, opening up the possibility of CALI experiments on living cells as well as cell extracts. *Russell Johnson* 

# Exploiting cells as protein producers Cells surface in semisynthesis



Scientists in Japan are using cells as protein factories.

In protein semisynthesis, a target, modified protein is made by combining a synthetic molecule with a protein. The method can be used to incorporate artificial groups, such as labels, into a protein and so provide a way to study the protein's structure and function. However, protein semisynthesis can be low-yielding and requires high concentrations of reactive components. Now Teruyuki Nagamune and colleagues at the University of Tokyo have improved the efficiency of the process.

Protein semisynthesis often uses a split intein, a section of a protein that can excise itself and reattach the remaining portions - the exteins - to give a newly active protein called the splicing product. Nagamune's group focused on a bacterial intein that splits into two fragments. They fused one fragment to a reductase enzyme, which acts as a receptor, and the other, smaller, fragment to a ligand, in this case a reductase inhibitor. As the inhibitor binds to the enzyme, the two fragments are brought together and their proximity leads to an improved vield of the splicing product.

The Japanese researchers adapted the concept in cells to make splicing products of synthetic inteins. They used cells that expressed the fragment bound to the reductase receptor and then incubated the cells A ligand (pink) binds to its receptor, bringing together two exteins for improved protein yield

'an elegant

merger of

and protein

approaches

to improving

semisynthesis'

chemical

protein

small molecule

with the fragment bound to the ligand. Using a fluorescent assay, Nagamune showed that the ligand binds to the receptor as before, but this time the splicing product is made on the cell surface. 'This represents the first demonstration of a semisynthesis of cell surface protein on living cells,' said Shinya Tsukiji, a co-worker on Nagamune's team.

Nagamune's system works at low concentrations and, since the ligand-attached fragment is short, it can be made synthetically and a variety of functionalities can be incorporated easily.

Philip Cole, an expert in protein semisynthesis at Johns Hopkins University in Baltimore, US, views the work as an elegant merger of small molecule and protein chemical approaches to improving protein semisynthesis. 'The Holy Grail is *in vivo* protein semisynthesis, which no method works particularly well with,' said Cole. 'This approach has the chance to be powerful here.'

In the future, Tsukiji proposes to adopt this approach to incorporate a number of chemical probes such as fluorescent dyes and phosphorylated amino acids into target proteins. '[The system] will be invaluable in cell biology research and biotechnology,' said Tsukiji. Kathleen Too

### Reference

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# **News in brief**

### Activity assay goes for gold

An electrochemical biosensor for kinase activity could help in the search for new cancer treatments.

See **www.rsc.org**/**chembiology** for a full version of this article.

### This month in *Chemical Science*

Instant insight: Mutants make more How genetically modified microbes are offering a short-cut to natural product derviatives.

### Solid state NMR takes on Taxol

US scientists have developed a technique for investigating the biologically active forms of the anticancer drug.

### The changing colour of gold

DNA and gold nanoparticles provide a more sensitive way to detect copper ions in nature.

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

### This month in Chemical Technology

# Ready-to-use enzyme reactors within minutes

A fast multi-step microreactor for enzymatic synthesis has been developed by scientists in Germany.

# Cell culture and lysis on a chip is **BASIC**

US researchers have come up with a strategy to integrate biological steps in one microchip reactor.

# Microbes fuel the way to better water treatment

Microbial fuel cells for detecting pollutant levels in wastewater have been developed in Korea.

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# Substitution pattern affects cytotoxicity and electrochemistry **OH to be in a position of power**

French scientists are unravelling the anticancer secrets of ferrocenyl phenols.

Some breast cancer cells have oestrogen receptors and so natural oestrogen can stimulate their growth. A number of effective treatments are available for these hormone-receptor-positive breast cancers; one example being selective oestrogen receptor modulators such as tamoxifen, which can be used to occupy the hormone receptors, thus blocking oestrogen from them. But few effective therapies exist for hormone-independent breast cancers.

Recently, Gérard Jaouen, from the Ecole Nationale Superieure de Chimie de Paris, and his co-workers found that ferrocenyl phenols can act against not only hormonedependent but also hormoneindependent breast cancer cells. Now they are discovering how these cytotoxic compounds work.

The key to this mystery seems to be the position of the hydroxyl group on the phenol ring. The most cytotoxic of the ferrocenyl phenols are those with the hydroxyl group at the *para* position. Jaouen's team found that *meta*-OH substitution



Ferrocenyl phenols can act against hormone-independent breast cancer cells not only dramatically reduced a phenol's binding affinity for one form of the oestrogen receptor, but also lowered its cytotoxicity in hormone-independent breast cancer cells.

Further experiments showed that *para*-substitution also had an effect on the phenols' electrochemical properties, and suggested that the *para*-OH substituted phenols oxidise to form quinone methide-type structures. A *para*-OH would allow greater resonance stabilisation of the radical intermediate on the way to these structures. The researchers propose that oxidative activation to quinone methide species could be 'a key' to the phenols' biological activity. *Freya Mearns* 

Freya Mearn

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E A Hillard *et al, Dalton Trans.*, 2007, 5073 (DOI: 10.1039/b705030e)

# In the current issue of Research Articles...



The influence of anion species on the toxicity of 1-alkyl-3-methylimidazolium ionic liquids observed in an (eco) toxicological test battery Marianne Matzke *et al*, *Green Chem.*, 2007, **9**, 1198 (DOI: 10.1039/b705795d)

Design of a novel G-quenched molecular beacon: A simple and efficient strategy for DNA sequence analysis

Yoshio Saito *et al, Chem. Commun.*, 2007, 4492 (DOI: 10.1039/b709715h)

# Second-harmonic generation for studying structural motion of biological molecules in real time and space

Joshua S Salafsky, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5704 (DOI: 10.1039/b710505c)

# Some uses of transition metal complexes as anti-cancer and anti-HIV agents

Raymond Wai-Yin Sun *et al*, *Dalton Trans.*, 2007, 4884 (DOI: 10.1039/b705079h)

SEC-ICP-MS and ESI-MS/MS for analyzing *in vitro* and *in vivo* Cd-phytochelatin complexes in a Cd-hyperaccumulator *Brassica chinensis* 

Liqin Chen et al, J. Anal. At. Spectrom., 2007, **22**, 1403 (DOI: 10.1039/b707830g)

**Self-assembled cellular microarrays patterned using DNA barcodes** Erik S Douglas *et al, Lab Chip,* 2007, **7**, 1442 (DOI: 10.1039/b708666k)

# Optimization of non-natural nucleotides for selective incorporation opposite damaged DNA

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Photodynamic therapy—a promising treatment option for autoimmune skin ulcers: a case report

Stefania Motta and Marcello Monti, *Photochem. Photobiol. Sci.*, 2007, **6**, 1150 (DOI: 10.1039/b711920h)

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# Interview

# **Plasma screening**

Norbert Jakubowski talks to Laura Howes about childhood experiments, element-omics and what he'd like to learn from Einstein



## Norbert Jakubowski

Norbert Jakubowski works at the Institute for Analytical Sciences in Dortmund and researches the development of analytical methods for proteomics, especially those using plasma sources. He is also on the editorial board of the Journal of Analytical Atomic Spectrometry.

### Who or what inspired you to become a scientist?

I've always been attracted to flashes, lightning and high voltages. When I was a child of around sixteen years old, I used to generate my own plasmas using the high voltages from my parents' TV. My family did not like these experiments and afterwards, the TV didn't work so well any more!

# What motivated you to specialise in atomic spectrometry, and metallomics in particular?

I studied physics at the University of Essen, where plasma physics was the main focus. For my diploma, I had to design an ion source based on plasma and this really got me interested in the field.

My first job for the Institute of Analytical Sciences was to develop ion sources for mass spectrometry, including inductively coupled plasma mass spectrometry (ICP-MS). Once we had the prototypes of the ion sources, we used them for analytical problems.

For example, one of the big problems in Dortmund was the pathway of carcinogenic or toxic metals into the environment. We were able to trace these back to their source, the local steel industry. We then asked ourselves if these species of metal, once deposited, could enter the food chain or be inhaled. As a result, our research moved from environmental to biological applications. We learnt early on that with inorganic mass spectrometry, the high sensitivity could allow us to follow the pathways travelled by the metals.

# You use the phrase 'element-omics' when referring to your work. What do you mean by that?

Biomolecules cannot be seen with ICP-MS therefore we need tags on the biomolecules which we can measure. It is not just metals that can act as the tags; semi-metals and halogens can play a role too. This is why I prefer the word element-omics to metallomics. Really what we are doing is nothing other than method development in analytical chemistry, and, of course, these methods can be applied throughout the life sciences.

# How does atomic spectrometry help to solve biological problems that other fields cannot?

For us, it is because of the plasma that we use. The plasma is nothing but an extremely hot flame and every sample that is injected into it is completely decomposed, atomised and excited. All information about the molecular structure of the sample is lost, which is a disadvantage. On the other hand, because this process loses the structural information, the sensitivity we achieve for elements is identical for every molecule, which is an improvement on other spectroscopic methods.

# If you could solve any scientific problem in any field, what would it be?

I would put all my energy into one and the same problem: energy and water. The future problems of our world will be related to food, water, clean air and energy. A better and fairer distribution of these resources is urgently needed.

### Which scientist do you most admire and why?

Albert Einstein. I think I look up to him because of his personality. He was a genius, but also extremely modest. Einstein revolutionised physics with only a deep thought, without a lab, without a professorship, without money. He was a physicist, but did not specialise in a specific topic; he was more universal. To make things easier, to present them as simply as possible and to reduce everything to a common denominator is something we can all learn from him. The secrets of the universe and life look so difficult to understand but they are so perfectly organised and it is our challenge the find the right formula.

### If you weren't a scientist, what would you do?

I would become a psycho-analyst. The problem is that there aren't enough quantitative tools in psycho-analysis. Even nowadays, there aren't many instruments to measure what we do, why we do it and how we know who we are. This would be a challenge: psychomics?



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# Instant insight DNA hitchhikers

Brian Jones and Julian Marchesi, of University College Cork in Ireland, take a closer look at the genetic swap shops in our midst

When most people think about their gut, it usually means they are hungry, sated or feeling unwell. Very few of us would pause to consider what else may be going on in there and would only ever associate microbes with the gut in a negative sense, focusing on the pathogens that cause various gastro-intestinal (GI) upsets. However, for the majority of our lives, our guts are home to myriad micro-organisms that co-exist with us and even play crucial roles in our development and wellbeing.

The human gastrointestinal tract is home to up to 1000 different species of bacteria and populations can reach 100 trillion cells in the large intestine. Collectively, these microbial passengers are referred to as the gut microbiota and form a highly complex ecosystem within the human GI tract. This community begins to develop shortly after birth and is involved in shaping our development from our earliest days.

Over time, the gut microbiota has co-evolved with humans, resulting in a microbial community that performs many beneficial functions for the host. These include preventing our colonisation by pathogens, extracting nutrients from the food we eat, controlling cell division in the intestinal epithelium and developing our immune system. However, studies have also highlighted that gut microbiota contribute to diseases such as colorectal cancer and inflammatory bowel disease.

The microbial community's significance in human development and its impact on host health, means understanding the ecosystem's activities and capabilities should facilitate enhancements in human health and disease prevention, especially when coupled with data regarding the host genome. Unfortunately, analysing this activity is not easy. Of the plethora of bacterial species residing in our guts, we can grow relatively few



The microbiota is the collection of bacteria in the gut and its collective genetic material is the metagenome

# Reference

B V Jones and J R Marchesi, *Mol. BioSyst.*, 2007, **3**, 749 (DOI: 10.1039/b705657e) in the laboratory. So, instead, we use powerful culture-independent approaches in which the individual genomes of the population are treated as one collective genome, broken into smaller pieces and transferred into bacteria that we can easily grow in the lab. This collective genome is referred to as the metagenome.

For most of our lives the composition of our microbiota is stable and so are the functions it performs. However, the composition can vary between individuals and so too could the relative outputs from these different communities. This difference makes the gut microbiota an important source of variation between individuals and potentially affects risk factors for numerous diseases. Ultimately, differences in our gut microbes may serve to increase the risk of certain diseases for some people while reducing it for others.

Further variation can be introduced by bacteria being able to swap genes amongst themselves, allowing them to acquire new abilities. This process is called horizontal gene transfer (HGT) and is a major driving force in bacterial evolution and adaptation. HGT is mediated by mobile pieces of DNA, which are like hitchhikers that grab a ride with a bacterial host and use its cellular machinery to replicate. In return, these mobile genetic elements (MGE) often encode genes that are lacking in the host bacterium, but which provide it with a survival advantage such as antibiotic resistance.

MGE can also pick up genes from a host bacterium and then carry these with them when they move. This promiscuity promotes gene flow within bacterial populations, and allows genes to move into an established population from bacteria that are just passing through. In the human gut, HGT could introduce new functions to the bacterial community and is likely to be important in its adaptability to changes in the gut environment.

So, if human and bacterial co-evolution has selected for a microbiota adapted to life in the gut, and in an intimate symbiotic relationship with the human host, the pool of genes in the microbiota has likely been shaped to reflect this. By looking at the gene pool - the mobile metagenome - we are likely to identify important functions of the gut microbiota. It may also lead to strategies for manipulating these functions and, considering the link between the microbiota and human health, could have important implications for disease treatment.

Read Jones and Marchesi's highlight 'Accessing the mobile metagenome of the human gut microbiota' in Molecular BioSystems.

# **Essential elements**

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# And finally...



Molecular BioSystems unzips ...

# Tokeshi wins Pioneers in Miniaturisation prize

Manabu Tokeshi has been named as the 2007 winner of the Pioneers in Miniaturisation prize.

The prize, first awarded in 2006, was established by two of the major players in the miniaturisation sector, *Lab on a Chip* and Corning Incorporated.

Joydeep Lahiri, research director at Corning Inc., commented 'Tokeshi's multi-disciplinary research exemplifies the essential outreach that is necessary – particularly to the molecular biology or medical areas – in order to find "the next big thing" that will succeed, for example, Cornings µPlate technology.'

The prize aims to promote miniaturisation through micro and nanotechnologies to the wider scientific community and encourage both young and new scientists into the field.

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From left: Harp Minhas, editor, *Lab on a Chip*; Manabu Tokeshi (2007 Award Winner); Joydeep Lahiri, research director, Corning Inc.; and Andreas Manz, chair of the *Lab on a Chip* editorial board.

Yoshinobu Baba of the Plasma Nanotechnology Research Center Nagoya University, Japan, said 'Tokeshi has been the powerhouse behind many interdisciplinary publications as his record shows.'

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