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ISSN 1359-7345 CODEN CHCOFS (25) 2545-2652 (2007)



Cover See Ben L. Feringa *et al.*, page 2578. Artistic rendering of amino acids subliming off of a meteor. Image reproduced by permission of Stephen P. Fletcher, Richard B. C. Jagt and Ben L. Feringa, from *Chem. Commun.*, 2007, 2578.

CHEMICAL BIOLOGY

B49

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.

Chemical Biology

July 2007/Volume 2/Issue 7 www.rsc.org/chembiology

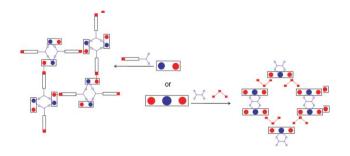
FEATURE ARTICLE

2565

Oligonuclear complexes as tectons in crystal engineering: structural diversity and magnetic properties

Marius Andruh*

Oligonuclear complexes can be efficiently employed as building blocks in designing heterometallic complexes with various nuclearities, dimensionalities and supramolecular solid-state architectures.



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2578

An astrophysically-relevant mechanism for amino acid enantiomer enrichment

Stephen P. Fletcher, Richard B. C. Jagt and Ben L. Feringa*

Significant enantioenrichment of a variety of amino acids is readily achieved by partial sublimation.



Incorporation of N-heterocyclic cations into proteins with a highly directed chemical modification

Nicola McMillan, Louise V. Smith, Jesus M. de la Fuente, Alexis D. C. Parenty, Nikolaj Gadegaard, Andrew R. Pitt, Katrina Thomson, Cameron MacKenzie, Sharon M. Kelly and Leroy Cronin*

The reaction of lysozyme with 5-(2-bromoethyl)phenanthridinium bromide targets lysine and cysteine residues by addition of an aromatic cation unit. These modifications have been found to manipulate the structure of the proteins on a surface, as shown by AFM.

2584

Metallized hyperbranched polydiyne: a photonic material with a large refractive index tunability and a spin-coatable catalyst for facile fabrication of carbon nanotubes

Matthias Häußler, Jacky Wing Yip Lam, Anjun Qin, Kalvin Ka Chun Tse, Martin Ka Shing Li, Jianzhao Liu, Cathy Ka Wai Jim, Ping Gao and Ben Zhong Tang*

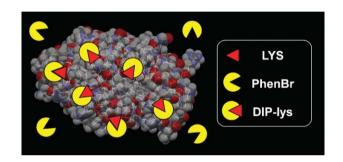
A cobalt-containing hyperbranched polymer readily forms thin film, whose photolyzed area shows a very different refractive index and whose pyrolyzed area serves as a nanosized catalyst for carbon nanotube growth.

2587

A physical gel made from hyperbranched polymer gelator

Yongwen Zhang, Wei Huang,* Yongfeng Zhou and Deyuan Yan*

A novel hyperbranched polymer gelator has been synthesized, which can self-assemble into the thermoreversible physical gel in DMF, DMAC, pyridine, DMSO or NMP with the driving force of hydrogen bonds among amide and amine groups of the highly branched macromolecules.



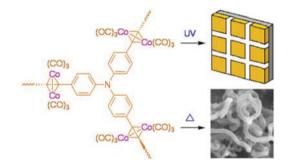
D- and L-Amino Acids with a Low Excess of the L-Enantiomer

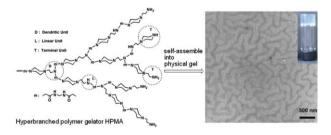
Evaporation with a Preference

for the Enantiomer in Excess

L D

L L L L Sublimate with a Higher Excess of L-Amino Acid





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2590



Tuning second-order NLO responses through halogen bonding

Elena Cariati,* Alessandra Forni,* Serena Biella, Pierangelo Metrangolo,* Frank Meyer, Giuseppe Resnati,* Stefania Righetto, Elisa Tordin and Renato Ugo

As a function of the ability of the solvent to behave as acceptor of halogen bonding, the NLO-phores under study give rise to $\mu\beta_{\lambda}$ values ranging from +192 × 10⁻⁴⁸ esu to -465 × 10⁻⁴⁸ esu.

2593

A new molybdenum-oxide-based organic-inorganic hybrid framework templated by double-Keggin anions

Yang-Guang Li, Li-Mei Dai, Yong-Hui Wang, Xin-Long Wang, En-Bo Wang,* Zhong-Min Su* and Lin Xu

A new double-Keggin-ion-templated, molybdenum-oxidebased organic-inorganic hybrid compound has been hydrothermally synthesized and its electrocatalytic properties investigated.

2596

Cyclic ureas as novel building blocks for bent-core liquid crystals

Benjamin Glettner, Sara Hein, R. Amaranatha Reddy, Ute Baumeister and Carsten Tschierske*

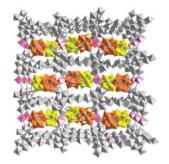
Cyclic ureas represent a novel class of bent units for the design of bent-core molecules with a wide variety of distinct polar (ferroelectric and antiferroelectric) liquid crystalline phases.

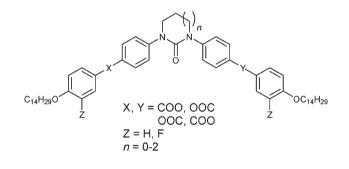
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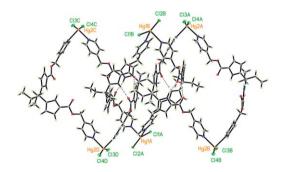
Hydrogen bond assisted helical self-assembly into [n]catenane

Zhenming Yin,* Yanhua Zhang, Jiaqi He and Jin-Pei Cheng*

A [*n*]catenane supramolecular structure has been constructed by combination of metal-directed self-assembly with interligand hydrogen bonds.







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2602

An azido–Cu^{II}–triazolate complex with utp-type topological network, showing spin-canted antiferromagnetism

Jian-Rong Li, Qun Yu, E. Carolina Sañudo, Ying Tao and Xian-He Bu*

The hydrothermal reaction of 1,2,4-triazole (Htrz) with $CuCl_2$ and NaN_3 afforded complex $[Cu(trz)(N_3)]_n$, the first example of an azido-metal-triazolate coordination polymer. It takes a rare non-interpenetrated **utp**-type [(10,3)-d] topology, and shows spin-canted antiferromagnetism.

2605

Surface modification of resorcinarene based selfassembled solid lipid nanoparticles for drug targeting

Stefan Ehrler, Uwe Pieles, Amina Wirth-Heller and Patrick Shahgaldian*

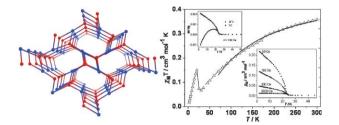
Prolyl-bearing amphiphilic resorcinarenes, *e.g.* tetrakis(*N*-methylprolyl)tetraundecylcalix[4]resorcinarene, self-assemble as stable solid lipid nanoparticles; these fully characterized systems could be further functionalized at their surface with proteins, and interact with specific antibodies bound on a sensor surface.

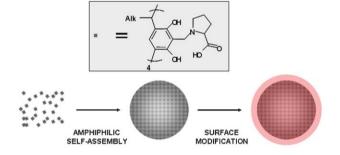
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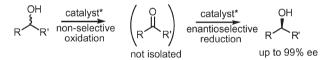
A catalytic deracemisation of alcohols

Gareth R. A. Adair and Jonathan M. J. Williams*

The deracemisation of secondary alcohols has been achieved using an oxidation and in situ reduction sequence using an Ru-based catalyst.





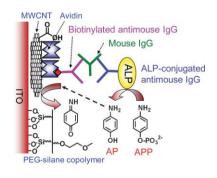


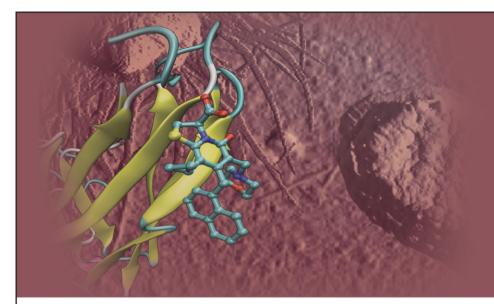
2610

Amperometric immunosensing using an indium tin oxide electrode modified with multi-walled carbon nanotube and poly(ethylene glycol)–silane copolymer

Md. Abdul Aziz, Sangjin Park, Sangyong Jon and Haesik Yang*

We describe a sensitive electrochemical immunosensor that takes advantage of the low background current of an indium tin oxide electrode, the good electrocatalytic properties of multi-walled carbon nanotubes, and the low biofouling properties of poly(ethylene glycol)–silane copolymer.





Forthcoming Articles:

Perspectives

Catalytic enantioselective construction of tetrasubstituted carbons by self-assembled poly rare earth metal complexes

Masakatsu Shibasaki, Japan

Polyketides, proteins and genes in fungi: programmed nano-machines begin to reveal their secrets

Russell J. Cox, UK

Emerging Area

Recent advances in the formation of luminescent lanthanide architectures and selfassemblies from structurally defined ligands

Thorfinnur Gunnlaugsson, Ireland

Articles

Agonistic and antagonistic properties of a *rhizobium sin-*1 lipid A modified by an ether-linked lipid

Geert-Jan Boons, USA

Identification of emissive lanthanide complexes suitable for cellular imaging that resist quenching by endogenous anti-oxidants

David Parker, UK

John Wilkie, UK

Synthesis of a new bifunctionalised fluorescent label and physical properties of the bound form on model peptide of Troponin C

Yukio Yamamoto, Japan

The role of metal ions in phosphate ester hydrolysis

Synthesis and chemical characterisation of target identification reagents based on an inhibitor of human cell invasion by the parasite *Toxoplasma gondii*

Nicholas J. Westwood, UK



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2613



Functionalized nanohybrid materials obtained from the interlayer grafting of aminoalcohols on kaolinite

Sadok Letaief and Christian Detellier*

New robust functionalized nanohybrid materials were prepared by the interlayer covalent attachment of aminoalcohols to the octahedral sheets of kaolinite.

2616

Deacylation studies on furanose triesters using an immobilized lipase: Synthesis of a key precursor for bicyclonucleosides

Ashok K. Prasad,* Neerja Kalra, Yogesh Yadav, Rajesh Kumar, Sunil K. Sharma, Shamkant Patkar, Lene Lange, Jesper Wengel* and Virinder S. Parmar*

Lipozyme $\mbox{\ensuremath{\mathbb{R}}}$ TL IM immobilized on silica catalyses the deacylation of compound X in a highly selective and efficient manner.

2618

Supersilyl radicals from the dissociation of superdisilane observed by gas electron diffraction

Sarah L. Masters (née Hinchley),* Duncan A. Grassie, Heather E. Robertson, Margit Hölbling and Karl Hassler

Superdisilane is not observed in the vapour produced upon mild heating of the solid, and the observed radical is not the lowest-energy structure predicted *ab initio*.

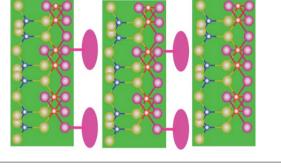
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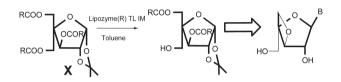
Patterning of lactoferrin using functional SAMs of iron complexes

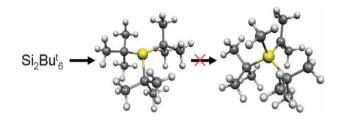
Nunzio Tuccitto, Nicoletta Giamblanco, Antonino Licciardello* and Giovanni Marletta

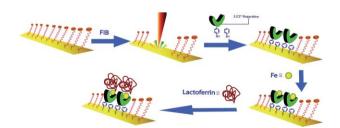
A new method is illustrated that allows spatially resolved immobilisation of lactoferrin on a surface, by means of non-covalent interaction between the native protein and a patterned self-assembled monolayer of an iron-containing terpyridine complex.











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September

24th-26th

Imperial College

Following the successful format of the previous meetings, the programme of the 2007 RSC-SCI 'flavours & fragrances' conference, organised by Philip Kraft and Karl A. D. Swift, will include these confirmed speakers: Angela Bassoli (University Milano), Constanze Brocke (Symrise), Robin A. Clery (Quest), Johannes le Coutre (Nestlé), Elisabet Duñach (University Nice), Céline Ellena (Charabot), Mark Erman (Millennium), Charles Fehr (Firmenich), Felix Flachsmann (Givaudan), Helmut Hügel (RMIT Melbourne), Thomas Hummel (University Dresden), Daniel Joulain (Robertet), Philip Kraft (Civaudan), Dietmar Krautwurst (Dt. Inst. Ernährungsf.), Christophe Laudamiel (IFF), Hiroyuki Matsuda (Takasago), Frank Ott (Symrise), Johannes Panten (Symrise), Caroline Plessis (Mane), Peter Schieberte (TU Munich), Geza Schoen (Escentric Molecules), Charles S. Sell (Quest), Roger Snowden (Firmenich), Reinhold Tacke (University Würzburg) and Chris Winkel (Quest).

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2624

Revisiting Perkin's dye(s): the spectroscopy and photophysics of two new mauveine compounds (B2 and C)

J. Seixas de Melo,* S. Takato, M. Sousa, M. J. Melo* and A. J. Parola

Two new components have been identified in an early sample prepared according to the original recipe of Perkin – designated as mauveine B2 and mauveine C – and these compounds were synthesized again and isolated by HPLC-DAD, identified by ¹H NMR, MS and their spectroscopic (UV/Vis and emission) and photophysical behaviour investigated.

2627

Ruthenium-catalysed double *trans*-hydrosilylation of 1,4-diarylbuta-1,3-diynes leading to 2,5-diarylsiloles

Takanori Matsuda, Sho Kadowaki and Masahiro Murakami*

Dihydrosilanes undergo double *trans*-hydrosilylation with 1,4-diarylbuta-1,3-diynes in the presence of a cationic ruthenium catalyst to afford 2,5-diarylsiloles. In particular, 9-silafluorene is a good hydrosilylating agent to produce spiro-type siloles in good yield.

2630

Landmine detection: Improved binding of 2,4-dinitrotoluene in a γ -CD/metal oxide matrix and its sensitive detection *via* a cyclic surface polarization impedance (cSPI) method

Myung-Jong Ju, Do-Hyeon Yang, Naoki Takahara, Kenshi Hayashi, Kiyoshi Toko, Seung-Woo Lee* and Toyoki Kunitake

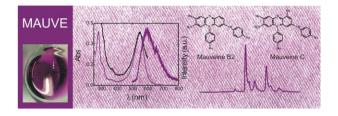
A chemically modified cSPI sensor that combines a molecular imprinting effect and host–guest interaction in TiO_2 matrices can detect 2,4-DNT at nM (sub-ppb) concentrations.

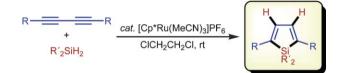
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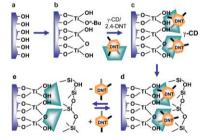
Formate as a CO surrogate for cascade processes: Rh-catalyzed cooperative decarbonylation and asymmetric Pauson–Khand-type cyclization reactions

Hang Wai Lee, Albert S. C. Chan and Fuk Yee Kwong*

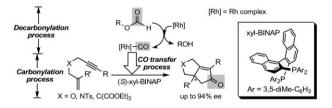
A Rh-(S)-xyl-BINAP complex-catalyzed cascade formate ester decarbonylation and asymmetric [2 + 2 + 1] carbonylative cyclization is described. This dual catalysis protocol provides up to 94% ee of the cycloadducts.



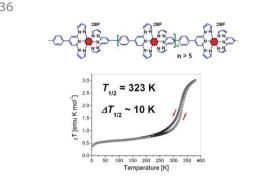


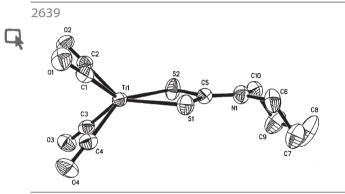


a: Surface activation, b: Ti(O°-Bu)₄ adsorption and hydrolysis, c: adsorption of a γ -CD/2,4-DNT complex, d: Si(OMe)₄ adsorption, and e: removal of 2,4-DNT.

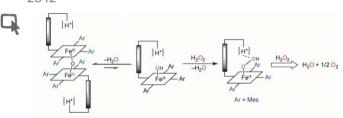






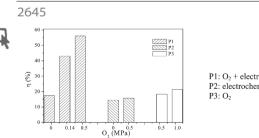


2642



 $Ar = C_6F_5 \text{ or } 2,6-(OMe)C_6H_3$





P1: O_2 + electrochemical oxidation P2: electrochemical oxidation P3: O_2

Above room temperature spin transition in a metallosupramolecular coordination oligomer/polymer

Chandrasekar Rajadurai, Olaf Fuhr, Robert Kruk, Mohammed Ghafari, Horst Hahn and Mario Ruben*

A novel metallo-supramolecular iron(II) coordination chain $[Fe^{II}(L)]_n(BF_4)_{2n}$ (L = 1,4-bis(1,2':6',1"-bispyrazolylpyridin-4'-yl)benzene) shows a reversible spin transition at 323 K with a *ca.* 10 K wide hysteresis loop.

Zerovalent titanium–sulfur complexes. Novel dithiocarbamato derivatives of $Ti(CO)_6$: $[Ti(CO)_4(S_2CNR_2)]^-$

Robert E. Jilek, Giovanna Tripepi, Eugenijus Urnezius, William W. Brennessel, Victor G. Young, Jr. and John E. Ellis*

Spectral, chemical and structural data indicate that the dithiocarbamato ligands in these unprecedented examples of isolable mononuclear six-coordinate Ti(0) carbonyls function as electronic equivalents of the η^5 -cyclopentadienyl ligand and are thereby best considered to be 18-electron complexes.

Stereochemical control of H_2O_2 dismutation by Hangman porphyrins

Joel Rosenthal, Leng Leng Chng, Stephen D. Fried and Daniel G. Nocera*

Incorporation of different aryl groups appended to the *meso*positions of iron(III) Hangman xanthene porphyrins dramatically impacts their catalase activity.

Oxygen as a promoter for efficient degradation of organic pollutants by high-temperature and high-pressure electrochemistry

Minghua Zhou,* Lecheng Lei and Qizhou Dai

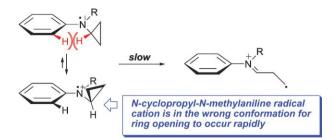
The introduction of oxygen in electrochemical oxidation at relatively high temperature and pressure as a promoter resulting in synergetic effects, greatly improves the mineralization of high-concentrated organic pollutants.

2648

The first calibration of an aminiumyl radical ion clock: why *N*-cyclopropylanilines may be poor mechanistic probes for single electron transfer

Xiangzhong Li, Michelle L. Grimm, Kazuo Igarashi, Neal Castagnoli, Jr. and J. M. Tanko*

Using direct and indirect electrochemical methods, the rate constant for ring opening of the radical cation generated from *N*-cyclopropyl-*N*-methylaniline was found to be $4.1 \times 10^4 \text{ s}^{-1}$.



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Chemical Biology

Health survey serves fish liver a boost Liver back on the menu?

Fish liver consumption is not associated with increased cancer risk, say Norwegian scientists.

Fish liver is a traditional food in northern Norway and an important source of vitamin D for Norwegians during dark winter months. But, it is also one of the most contaminated food items in the country, containing high levels of persistent organic pollutants (POPs), including dioxins. POPs have been associated with negative health effects, including an increased cancer risk.

The Norwegian Food Control Authority (now the Norwegian Food Safety Authority) has advised that children and women of childbearing age should avoid eating fish liver. This is based on EU recommendations for tolerable weekly intakes of toxic compounds and the health-related risks associated with long-term exposure to dioxins and similar compounds.

In 2006, however, Magritt Brustad and co-workers from the University of Tromsø showed that



POP levels in human blood are not significantly affected by fish liver intake.¹ Now, the team has studied whether consumption of the traditional food affects cancer rates.² From a survey of nearly 65000 Norwegian women, they have shown that eating fish liver is not associated with increased cancer risk; in fact, the total cancer

Fish liver is a traditional food in northern Norway

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1 T M Sandanger et al, J. Environ. Monit., 2006, 8, 552 (DOI: 10.1039/b600046k) 2 M Brustad et al, J. Environ. Monit., 2007, DOI: 10.1039/ b706302b

risk was slightly reduced for fish liver consumers.

'This is reassuring,' said Tim Key, deputy director of the Cancer Research UK Epidemiology Unit at the University of Oxford, who praised the study as 'well-designed.'

Brustad said the survey implies 'that the contribution to POPs from the traditional fish liver diet in Norway is below the limit that could give increased cancer risk.' The team suggests that the potential health gain of eating fish liver - from fat-soluble vitamins and essential fatty acids - is greater than the possible negative effects caused by contaminants.

When asked whether the Norwegian Food Safety Authority should change its fish liver recommendation, Brustad suggested that, as well as basing dietary advice on toxicological estimations from animal models, 'population-based research methodology should be taken into consideration.' Freya Mearns

In this issue

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Why eating your greens could help night-time vision

Getting the measure of tears

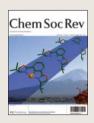
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Stephen Michnick talks about communication at the genomic level

Hair is news

In this month's Instant insight, Crisan Popescu and Hartwig Höcker put hair under the microscope



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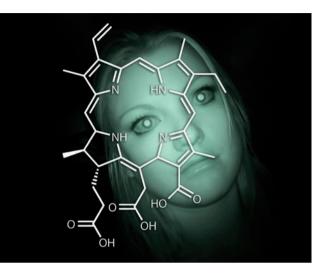
Chemical Biology

Research highlights

Improving colour vision by dosing on greens Chlorophylls help eyes see red...

Eating your greens rather than carrots could be the key to good night-time vision, according to scientists in the US. Ilyas Washington and colleagues at Columbia University, New York, have shown that a chlorophyll derivative can enhance eye sensitivity to red light.

In sight, light activates a visual pigment that sends an electrical signal to the brain. This process happens in the retina in cone and rod cells. Rod cells are insensitive to colour and the cone cells are mainly responsible for our colour vision. However, in dim light the cone cells cannot function and we largely perceive the world in black and white. This also means we are dependent on rod cells to see in the dark. Since these cells are particularly insensitive at the red end of the visible spectrum, Washington asked: 'How might



Taking a chlorophyll supplement could help you see in the dark one enhance red light night-time vision?'

Prompted by research suggesting that deep-sea dragonfish see using chlorophyll, the scientists gave mice a chlorophyll derivative, chlorin e_6 , to see if their red vision was improved. Using a technique called electroretinography, which measures retinal cell responses to a flash of light, the researchers found that the treated mice showed almost double the response to red light when compared to non-treated mice. The group also showed that the chlorin e_6 was localised in the retina and conclude that the increased visual sensitivity is a result of light absorption by the chlorophyll derivative.

Washington is currently performing similar research in people. It is possible that taking a chlorophyll derivative supplement could improve night vision, he said. *Nicola Burton*

Reference

I Washington et al, Photochem. Photobiol. Sci., 2007, DOI: 10.1039/b618104j

Protein fluctuations detected as indicators of infection **...Whilst Raman gets the measure of tears**





Doctors could one day drop tears to diagnose disease by Raman spectroscopy.

Nicholas Stone and Jacob Filik at the Gloucester Royal Hospital, UK, have used a technique called drop coating deposition Raman (DCDR) spectroscopy to detect changes in protein concentrations at the microlitre levels found in human tears. As Stone explained, 'infection causes the protein composition Tears are complex solutions of proteins

Reference

J Filik and N Stone, *Analyst*, 2007, **132**, 544 (DOI: 10.1039/ b701541k)

in body fluids to fluctuate so the ability to detect small changes in protein concentration is important for disease diagnosis.'

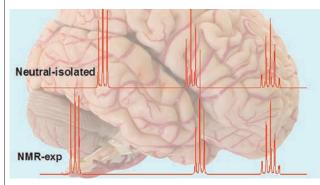
Tear-drying patterns are known to differ with infection and have been used in diagnosis for some time, but DCDR takes this a step further by analysing individual proteins to pinpoint which disease is present. DCDR concentrates solutions, moving them across a substrate by capillary flow, making it easier to obtain their Raman spectra. The weak solution is continually replenished by liquid from the centre and is concentrated in a characteristic coffee-ring drying pattern as the solvent evaporates. Stone and Filik were able to use the method to detect small concentration changes in mixtures of lysozyme, lactoferrin and albumin, which together make up 95% of the proteins in tears.

Andrew Berger, an expert in biomedical optics at the University

of Rochester, US, said that the 'work shows that DCDR can be a valuable tool for analytical chemists. Raman spectroscopy has great specificity, but the signals are often too weak. What's exciting is that the simple process of evaporation can be harnessed to increase the signal, shift the barrier, and open up a new range of possible applications.'

But Stone cautioned that 'there are a number of challenges to be overcome before DCDR can be reliably used for disease diagnosis. These include determining whether the technique is sensitive enough to detect the changes in fluids caused by disease and how non-proteins and contamination in the samples influence the results.' He added that there is also a 'difficulty of finding which diseases would benefit most from early detection and would also display large enough systematic protein changes to be detected.' Janet Crombie

Predicting neurotransmitter signals



Quantum chemical calculations could help scientists locate key neurotransmitters in the brain. The calculations should make the detection of small molecules in vivo much more accurate, claims the French team behind the research.

GABA (γ-aminobutyric acid) is a neurotransmitter involved in brain disorders such as epilepsy. In order to diagnose these disorders or monitor their treatment it is vital to be able to detect GABA in the brain. Usually this is done using nuclear

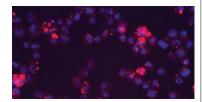
GABA's experimental (below) and theoretical (above) NMR spectra are similar

Reference

A R Allouche. M Aubert-Frécon and D Graveron-Demilly, Phys. Chem. Chem. Phys., 2007, 9, 3098 (DOI: 10.1039/b700631d) magnetic resonance spectroscopy (NMR). The problem is that GABA is present in the brain in very small amounts, and its signal is swamped by those of other molecules. Current detection methods involve filtering the NMR signals to separate overlapping spectra, but this relies on knowing precisely where to look for the peaks from GABA.

Monique Aubert-Frécon's team from the University of Lyon has performed quantum chemical calculations to work out how to locate these GABA peaks. Instead of the usual approach of predicting the peaks from experimental measurements, the group calculated GABA's electronic structure from first principles. From this they could predict GABA's signature spectrum and how it would change in different magnetic fields. The calculations should make it easier to pick GABA out from the complicated NMR spectrum of the brain, said Aubert-Frécon. Clare Boothby

Search and destroy



South Korean scientists have developed a proof-of-concept method for cancer detection and treatment. Seungjoo Haam and Yong-Min Huh at Yonsei University, Seoul, and their colleagues have made magnetic nanoparticles that can both detect breast cancer cells and deliver drugs to them.

The scientists combined iron nanocrystals and a biodegradable polymer to create their nanoparticles. The team encapsulated an anticancer drug, doxorubicin, inside the nanoparticles, and bound the antibody Herceptin, used to target breast cancer cells, to their surface.

The group then added the nanoparticles to a solution containing cancerous cells. They found that the nanoparticles bind to the cells and kill them by slowly releasing the trapped drug to them over a three week period.

According to the researchers, one advantage of the nanoparticles is that they can be detected using magnetic resonance imaging (MRI), a non-invasive method used routinely in medicine to image soft tissues. Since the nanoparticles bind cancerous cells, this could be of future use when identifying tumours.

Haam's major research interest lies in the construction of all-in-one nanoplatforms to simultaneously diagnose and treat cancer and in confirming their efficacies at the cellular level. 'This antibodyconjugated nanoparticle is a proof of concept,' explained Haam.

Haam will now continue with this work, and aims to develop integrated systems for anticancer treatments with targeted drug delivery and real-time monitoring. Susan Batten

Reference

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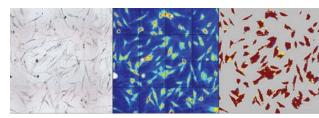
Snapshots of specialising cells

Researchers in Germany have used infrared spectroscopy to spot stem cells as they change into new cell types.

Christoph Krafft, at the Dresden University of Technology, and colleagues wanted to develop a spectroscopic technique that would tell if stem cells were differentiating, a process in which they become a specialised type of cell, such as a skin cell or a white blood cell.

Stem cells are used in medicine to restore damaged tissues and are being investigated to find new treatments. Krafft explained: 'A frequent problem in stem cell research is to determine the type and differentiation state of the cells. The standard techniques depend on antibodies, which recognise cell-specific antigens. However, antibodies are not available for each cell type or differentiation state and the antigen-antibody binding is sometimes not specific enough.'

Krafft and his team coupled an infrared (IR) spectrometer with a microscope so they could locate



In a computer image non-stimulated stem cells (left) appear red when their IR spectra (centre) are analysed (right); stimulated cells appear blue

Reference

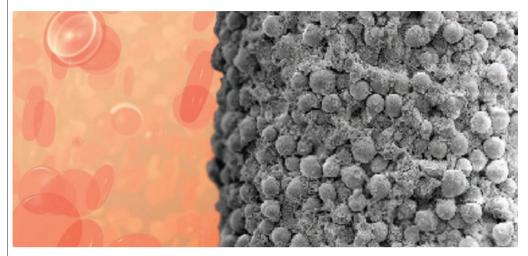
C Krafft et al, Analyst, 2007, DOI: 10.1039/b700368d

stem cells and measure their IR spectra. They grew some of the cells in a medium designed to stimulate them to turn into bone-forming cells, called osteoblasts. The IR spectra from these cells differed from those of non-stimulated cells. Both sets of spectra were used to train a computer model to distinguish between the cell groups.

The team used the IR microscope and computer model to produce images of stem cells; stimulated and non-stimulated cells appeared as different colours, showing whether they had differentiated.

Krafft explained that he hopes to develop the research to find out more about how stem cells form new bone. Rachel Warfield

Fast sampling system measures drug levels in blood in vivo **Designer drugs probe**



A simple method for measuring drug concentrations in vivo could be used in medical and drug tests, claim Canadian chemists.

Janusz Pawliszyn and colleagues from the University of Waterloo, developed their method, based on a technique called solid phase microextraction (SPME), to offer fast sampling and more accurate sample analysis.

The chemists used biocompatible SPME probes to measure diazepam levels in beagle bloodstreams - as a probe is placed in contact with the blood, it adsorbs a fraction of the diazepam, which can then be extracted and measured. 'The major contributions of our group were to develop the calibration procedure, which determines how the amount of compound found on the probe relates to the concentration in the sample, and to develop an automated analysis system that can DOI: 10.1039/b701423f

The biocompatible probe (right) adsorbs drugs from the bloodstream

Reference

A Es-haghi et al, Analyst, 2007,

handle large amounts of samples at a time,' said Pawliszvn.

According to Pawliszyn, a major advantage of SPME is that it measures the concentration of free compounds only. Methods that use whole blood samples also measure the amount of compound bound to, for example, blood proteins, but normally only the free compound determines the biological activity and is medically significant.

'We have developed this technology to facilitate applications elsewhere,' Pawliszyn said. The technique can be adapted to almost any compound in any biological sample, he added. 'You can design probes that are very specific, for example, by using antibodies.'

'For some types of medical test, a patient could do his or her own sampling at home and then send the probes to the lab for analysis,' said Pawliszyn, highlighting the portability of the probes. The method could be used to determine compound metabolism rates and even be modified to measure compound concentrations in breath, he said. Danièle Gibney

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Interview

The dynamic cell

Stephen Michnick talks to James Mitchell Crow about communication at the genomic level



Stephen Michnick

Stephen Michnick is professor of biochemistry at the University of Montreal, Canada, and a member of the editorial board of *Molecular BioSystems*. His research in the area of chemical, structural and genome biology focuses on developing approaches to understand biochemical networks in cells.

Who inspired you to become a scientist?

My father – he had an infectious curiosity about things. He took any opportunity for a science lesson and I was brought up interested in science.

What are you working on at the moment?

We're interested in how regulatory and protein communication networks work in living cells. At the genome level, we are looking at protein complexes and how these are affected by physical or chemical perturbations. Assembly, disassembly or relocalisation of protein complexes reflects regulatory processes that underlie cellular adaptations to perturbations, including changing gene expression, metabolic pathway flux or cell shape or movement caused by reorganisation of the cytoskeleton. There are some simple mechanistic pictures of these adaptive responses but it is not entirely clear how these processes are orchestrated. We are trying to systematise the process of discovering how, when, where and what drives the assembly of protein complexes that underlie these adaptations.

How does your protein-fragment complementation assay (PCA) work?

PCA is a strategy to detect protein–protein interactions in biological systems. It takes advantage of nature's invention called protein folding. Since a linear polypeptide has all the chemical information necessary to fold into a three-dimensional structure, in principle, if you split the polypeptide into two pieces and throw them together in solution they might fold up, but generally that doesn't happen.

PCA is based on recreating the unimolecular process of folding by genetically fusing two proteins that interact with two fragments. If these proteins interact and bring the fragments together, you recreate unimolecular folding conditions and the two fragments spontaneously fold into the unique structure that the intact polypeptide would have formed. If the physical interaction of the two proteins fused to the fragments is absolutely necessary for folding to occur and the protein that folds catalyses a detectable reaction, then you have a reporter for the protein–protein interaction. We and others have developed a number of different PCAs that allow us to address how protein complexes assemble in living cells.

What will be the next big thing in your field?

An exciting area is the development of biosensors to detect rapid changes in enzyme activities, particularly those mediated by post-translational modifications. We look at physical interactions and how they change but we can't pick up these other events. Hopefully, biosensors of the future will enable us to detect these chemical transformations.

I am interested in the link between 'emergency responses,' how a cell responds immediately to a sudden change in environment, versus adaptive responses, those that occur in the gene expression program. For example, let's say you starve the cell of an essential nutrient. The cell has the enzymes to make this nutrient, but they are expressed at too low a level. The cell can't wait for the expression of the genes for these enzymes to be turned up. Maybe the existing enzymes are modified to increase their activity by chemosensory signalling pathways. However, we don't know how the chemosensory signal causes the reprogramming of the biochemical pathway that controls the synthesis of a nutrient and how this is done so quickly. Development of assays that detect these processes would help us to figure this out.

Will drug discovery ever become a more predictable science?

Everything we do makes it a little more predictable – but in incremental steps. We are not yet able to predict unintended affects of molecules on cells or humans. The problem, as always, is one of biological complexity. Even if we developed a magic technique that allowed us to identify all targets of a compound, we may find that they interact with hundreds of different things; we have to delve deeper into the biology. If we get better at predicting biological responses to small molecules our search for drugs may be more successful.

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

I can't imagine living in the 21st century and not being a scientist, but I've thought of writing science fiction. I've always admired scientists who are science fiction writers. My favourite is Gregory Benford because he takes real theories and turns them into dramatisations of things that could happen – like time travel and black holes coming out of cyclotrons.

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Instant insight Hair is the news

Crisan Popescu and Hartwig Höcker, of the DWI (German Wool Research Institute), Aachen University (RWTH), Germany, put hair under the microscope

Biologically, hair is the filamentous appendage on the skin of mammals. Chemically, it is a composite material in which both the reinforcing fibres and the matrix are made of proteins.

All kinds of hairs look alike under a light microscope; they are strands covered with scales overlapping like roof tiles, oriented from root to tip. Under the higher magnification of a scanning electron microscope, differences of geometry and scale height can clearly be recognised. These, and other criteria, serve to identify the source of a hair.

Hair fibres, roughly cylindrical with diameters ranging from 10µm to 100µm, are multicellular tissues. The heart of the fibre is surrounded by the cuticle, made of plate-like overlapping cells whose heights can reach up to 1µm. Each cuticle cell has four layers: the epicuticle; the a-layer; the exocuticle; and the endocuticle. Inside the cuticle, the cortex contains spindle-like interlocking cortical cells, with cell membrane complex in-between. Each cortical cell is composed of macrofibrils embedded in an intermacrofibrillar material. Each macrofibril consists of microfibrils, called the intermediate filaments (IF), themselves embedded in an intermicrofibrillar matrix composed of intermediate filament associated proteins (IFAP). Thus, hair is a composite material with a complex dual structure at all levels.

The IFs consist of chains of the tough, insoluble protein α -keratin. Driven by the hydrophobic effect, two of these chains combine to form a coiled coil. Further packing into dimers and tetramers gives IFs with 32 chains in their cross section.

Dry hair consists of around 95% proteins and 2% lipids, a substantial amount of which are present as 18-methyl eicosanoic acid at the surface. The rest of the hair is made



Hair – a sophisticated composite material of nuclear remnants, carbohydrates and inorganic salts.

Total hydrolysis of hair fibre leads to the 20 common α -amino acids, ammonia, and small amounts of thiocysteine, cysteic acid and lanthionine. While the overall amino acid composition is similar for hairs from different mammals, it is strongly differentiated among the morphological components.

Elemental analysis of hair shows, remarkably independently of hair origin, 50wt% carbon, 7wt% hydrogen, 22wt% oxygen, 16wt% nitrogen and 5wt% sulfur. The sulfur comes from the high cystine content, specific to α -keratin fibres. Cystine disulfide bonds provide the cross-links that lead to hair's insolubility and thermal stability.

Hair absorbs moisture due to the polar amino acid residues of the inside; yet, hair's surface is hydrophobic, due to the lipid content of the epicuticle. This contradictory behaviour is known as the hair paradox. Increasing hair's moisture content from 0 to 33% results in a longitudinal swelling of only 2% but a radial swelling of 16%. Natural hair colour is caused by pigment granules of black to brown eumelanin and yellow to red pheomelanin, generated from tyrosine. Unpigmented hair results from an interruption of the synthesis chain of melanin. Bleaching is achieved by oxidation with hydrogen peroxide, which leads to a disintegration of the melanin granules.

A variety of functional (thiol, amino, hydroxyl) groups make hair eligible to chemical reactions important for the textile and cosmetic industries. The cleavage (with thioglycolic acid or bisulfite) and re-formation (upon oxidation with hydrogen peroxide) of disulfide cross-links after shaping is the key to the permanent wave.

Unfortunately, the growth of hair from the follicle, connected with the commonly desired cure for baldness, is far from being understood today.

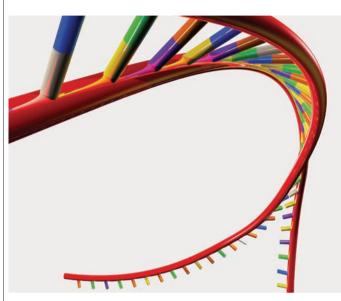
Read Popescu and Höcker's review 'Hair – the most sophisticated biological composite material' in a forthcoming issue of Chemical Society Reviews.

ent as C Popescu and H Höcker, at the Chem. Soc. Rev., 2007, DOI: ir is made 10.1039/b6045370

Chemical Biology

Essential elements

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'We're proud of the progress

Molecular BioSystems has made since its launch in 2005,' said Robert Parker, managing director at RSC Publishing. 'The journal has grown, the quality of science is excellent and feedback from readers has been overwhelmingly positive. Now is an appropriate time for this success to be translated into a solo publication.'

Since the publication of the first issue, Molecular BioSystems has been paired with Chemical Communications. This interaction with the host has resulted in an excellent communication channel for the published content, which has reached a wide and interdisciplinary audience. Online pairing with four other complementary publications (Organic & Biomolecular Chemistry, Lab on a Chip, The Analyst and Analytical Abstracts) ensured optimum visibility.

'Now is the perfect time to unzip *Molecular BioSystems* from its hosts,' commented Michael Smith, commissioning editor. 'We believe the journal has a great deal to offer to the chemical biology community.'

Read more at www. molecularbiosystems.org/unzip

The Chemistry and Biology of Winemaking

And finally...

In the past twelve months the RSC book *Kitchen Chemistry* has become an international bestseller! It is an exceptional learning resource and offers a fascinating insight into the science in our kitchens.

RSC Publishing also has an extensive food science book list that caters for scientists at all levels, from schools through to industry.

Newly published books include The Science of Bakery Products and The Chemistry and Biology of Winemaking, which now join other bestselling titles such as The Science of Chocolate and Gums and Stabilisers for the Food Industry.

For more information visit www.rsc.org/books



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Pioneers in Miniaturisation Prize

Leading the way in miniaturisation, *Lab on a Chip* has teamed up with Corning Incorporated to again host the Pioneers in Miniaturisation Prize. Spanning a variety of disciplines, this prize recognises outstanding achievements and significant contributions by a younger scientist to the understanding and advancement of micro- and nanoscale science.

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2007 annual subscription rate: £199; US \$376.

As a leading-edge science and technology organisation, Corning Incorporated is keen to reward, recognise and encourage the development of miniaturisation in the chemical and biological sciences and promotes interdisciplinary research required for the most significant innovations in this area.

The recipient of the award

All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017. Email: sales@rsc.org

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Associate editors: Neil Withers, Nicola Nugent Interviews editor: Alison Stoddart

Essential elements: Valerie Simpson, Caroline Wain and Ricky Warren

Publishing Assistant: Jackie Cockrill Publisher: Emma Wilson will receive a \$5000 bursary to support their continued contribution to the field. A deadline for applications has been set for 31st August 2007. Following the final decision, which will be made by committee, a winner will be announced at µTAS 2007 conference, in Paris, France.

For further information visit www.rsc.org/loc/pioneerprize

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