Organic & Biomolecular Chemistry

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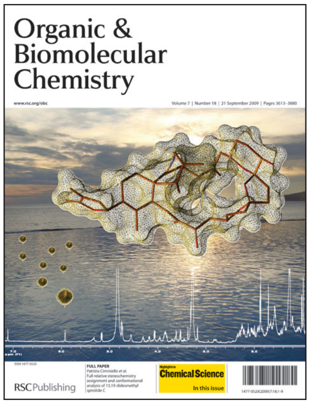
IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 7(18) 3613–3880 (2009)

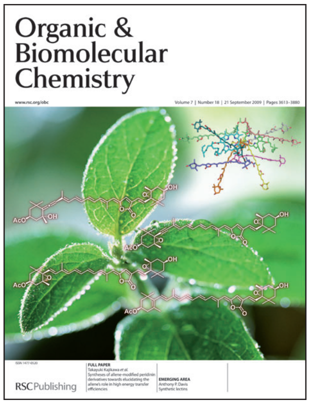


Cover

See Patrizia Ciminiello *et al.*, pp. 3674–3681.

A representation of the global minimum conformation of 13,19-didesmethyl spirolide C along with its ^{1}H-NMR spectrum, and of the toxic dinoflagellate *Alexandrium ostenfeldii* (the producing organism of the marine fast-acting spirolide toxins).

Image reproduced by permission of Martino Forino from *Organic & Biomolecular Chemistry*, 2009, **7**, 3674.



Inside cover

See Takayuki Kajikawa *et al.*, pp. 3723–3733.

The four structures in the picture are nor-carotenoid, peridinin, which is a representative auxiliary light harvesting pigment for photosynthesis in the sea, and its analogues. Another structure represents the PC complex which consists of eight peridinin and two chlorophyll a. Glittering leaves at the backside of the structures represent photosynthesis.

Image reproduced by permission of Shigeo Katsumura from *Organic & Biomolecular Chemistry*, 2009, **7**, 3723.

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C65

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Highlights in Chemical Science

September 2009/Volume 6/Issue 9

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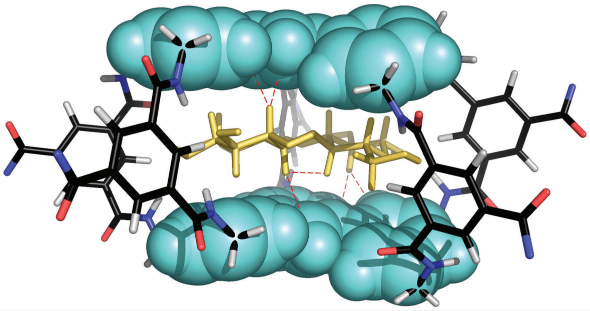
EMERGING AREA

3629

Synthetic lectins

Anthony P. Davis*

The mimicry of lectins (carbohydrate-binding proteins) is an attractive goal for supramolecular chemists. The challenge is difficult, but recent systems perform remarkably well when compared to their natural counterparts.



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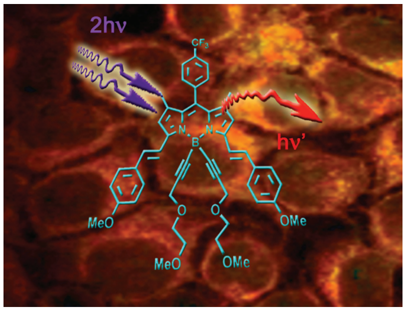
3639

Improved push-pull-push *E*-Bodipy fluorophores for two-photon cell-imaging

Pascal Didier, Gilles Ulrich, Yves Mély and
Raymond Ziessel*

Quadrupolar Bodipy dyes exhibiting TPA activity and high brightness with an emission at 660 nm were synthesized and their internalisation in HeLa cells as well as FLIM experiments were conducted.

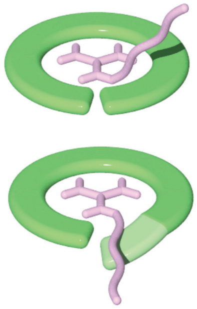


3643

Crescent oligoamides as hosts: conformation-dependent binding specificity

Kazuhiro Yamato, Lihua Yuan, Wen Feng, Amber J. Helsel,
Adam R. Sanford, Jin Zhu, Jingen Deng, Xiao Cheng Zeng
and Bing Gong*

Screening crescent oligoamides with various lengths and number of hydrogen bond acceptors has resulted in the identification of hosts that bind substituted guanidinium ions with high specificity and affinity.

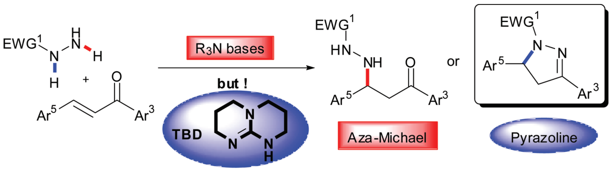


3648

TBD-organocatalysed synthesis of pyrazolines

Olivier Mahé, Denis Frath, Isabelle Dez, Francis Marsais,
Vincent Levacher and Jean-François Brière*

It was found that TBD, a cheap and commercially available guanidine, easily catalysed the synthesis of biologically important 3,5-diarylpyrazolines from chalcones and acylhydrazines.

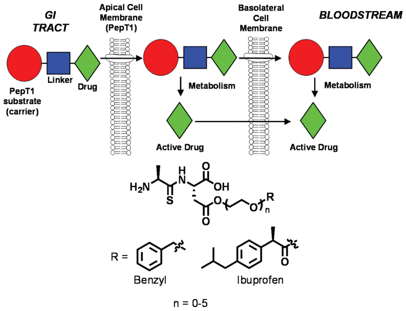


3652

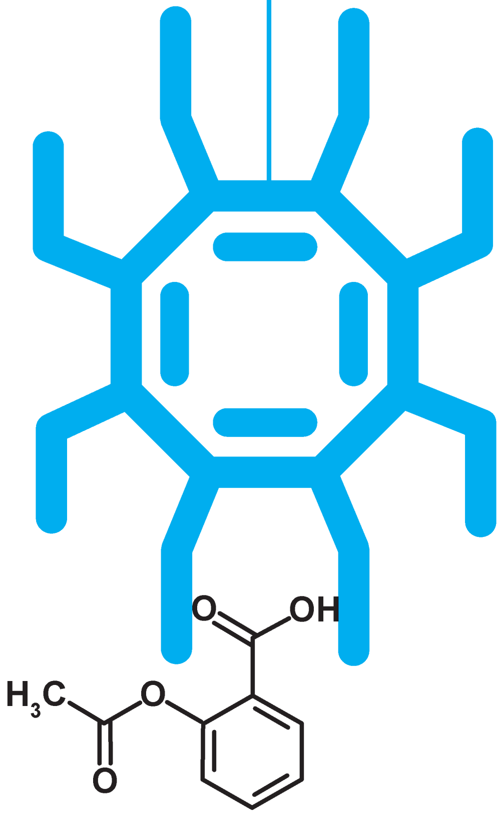
The *in vitro* transport of model thiodipeptide prodrugs designed to target the intestinal oligopeptide transporter, PepT1

David Foley, Myrtani Pieri, Rachel Pettecrew, Richard Price,
Stephen Miles, Ho Kam Lam, Patrick Bailey* and
David Meredith

Various thiodipeptide conjugates are shown to be substrates of the oligopeptide transporter PepT1, highlighting the potential of this approach for drug delivery.



New adventures on the web



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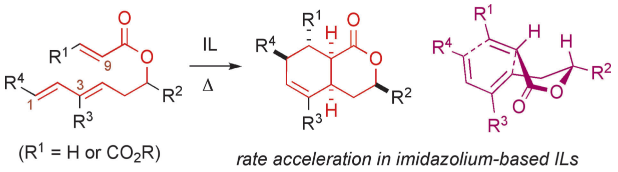
3657

Remarkable rate acceleration of intramolecular Diels–Alder reaction in ionic liquids

Hikaru Yanai, Hiroshi Ogura and Takeo Taguchi*

Intramolecular Diels–Alder reaction of ester-tethered 1,3,9-decatriene system was significantly accelerated in imidazolium-based ionic liquids to give *cis*-fused bicyclic lactones in good yield with high diastereoselectivity.

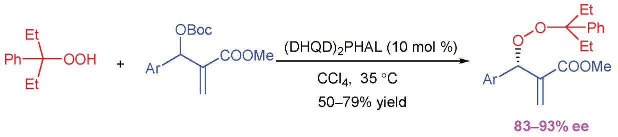


3660

Organocatalytic peroxy-asymmetric allylic alkylation

Xin Feng, Yu-Qing Yuan, Hai-Lei Cui, Kun Jiang and Ying-Chun Chen*

The organic Lewis base catalysed peroxy-asymmetric allylic alkylation of bulky hydroperoxyalkanes with Morita–Baylis–Hillman carbonates is reported (up to 93% ee), from which chiral α-methylene-β-hydroxy esters could be efficiently derived.

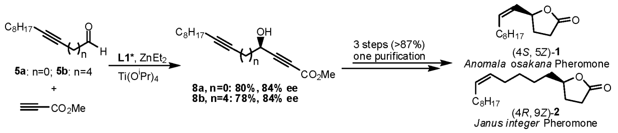


3663

Enantioselective synthesis of *Anomala osakana* pheromone and *Janus integer* pheromone: a flexible approach to chiral γ-butyrolactones

Li Lin, Qiangyang Zhao, A-Ni Li, Fengbo Ren, Fanzhi Yang and Rui Wang*

A concise and versatile enantioselective synthesis of chiral γ-butyrolactones has been achieved in a few steps without using any protecting groups. The synthesis uses γ-hydroxy-α,β-acetylenic esters as the key intermediates, which are obtained through an asymmetric alkynylation procedure.



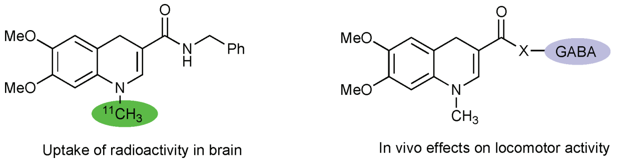
PAPERS

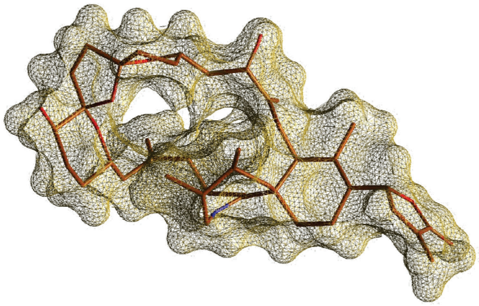
3666

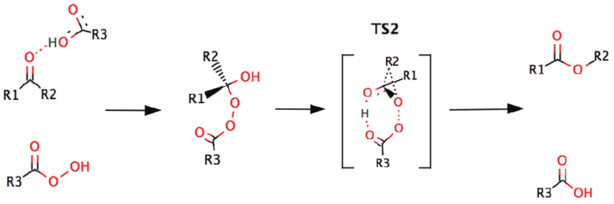
Synthesis, radiosynthesis and biological evaluation of 1,4-dihydroquinoline derivatives as new carriers for specific brain delivery

Lénaïg Foucout, Fabienne Gourand, Martine Dhilly, Pierre Bohn, Georges Dupas, Jean Costentin, Ahmed Abbas, Francis Marsais, Louisa Barré* and Vincent Levacher*

Synthesis, radiosynthesis and biological evaluation of 1,4-dihydroquinoline derivatives as new carriers for specific brain delivery.



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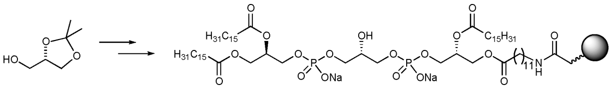
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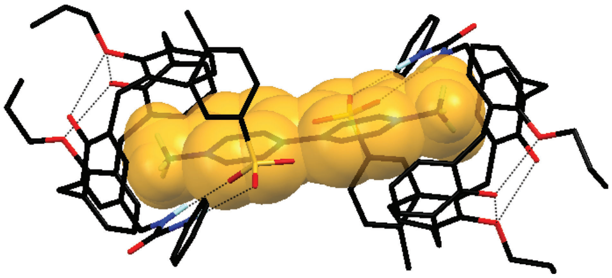

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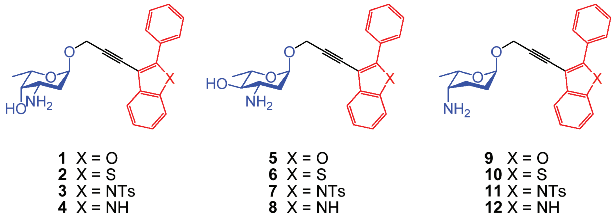
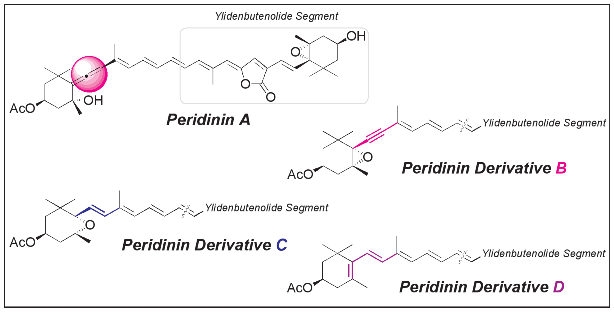


Synthesis and DNA-binding affinity studies of glycosylated intercalators designed as functional mimics of the anthracycline antibiotics

Wei Shi, Robert S. Coleman and Todd L. Lowary*

Twelve novel glycoconjugates mimicking the functional modules of anthracyclines in DNA binding have been synthesized. Their DNA binding affinity has also been investigated by using direct and indirect fluorescence measurements.

3723

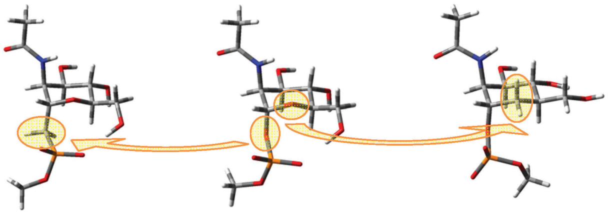


Syntheses of allene-modified derivatives of peridinin toward elucidation of the effective role of the allene function in high energy transfer efficiencies in photosynthesis

Takayuki Kajikawa, Kazuyoshi Aoki, Ram Shanker Singh, Takashi Iwashita, Toshiyuki Kusumoto, Harry A. Frank, Hideki Hashimoto and Shigeo Katsumura*

We describe the syntheses of three relatively unstable allene-modified derivatives of peridinin and the results of Stark spectroscopy studies toward elucidation of the exact role of the unique allene function.

3734

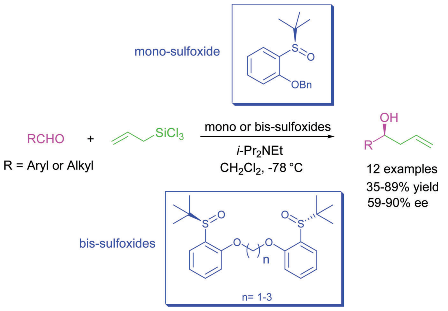


Modeling of synthetic phosphono and carba analogues of *N*-acetyl-α-D-mannosamine 1-phosphate, the repeating unit of the capsular polysaccharide from *Neisseria meningitidis* serovar A

Lucio Toma,* Laura Legnani, Anna Rencurosi, Laura Poletti, Luigi Lay* and Giovanni Russo

The conformational behavior of the title compounds was investigated with a DFT approach followed by ^{1}H NMR analysis, showing that the oxygen/methylene replacement does not modify the preference for the $^4C_1$ geometry of the hexacyclic ring.

3741



Aryl *tert*-butyl sulfoxide-promoted highly enantioselective addition of allyltrichlorosilane to aldehydes

Peng Wang, Junmin Chen, Linfeng Cun, Jingen Deng, Jin Zhu and Jian Liao*

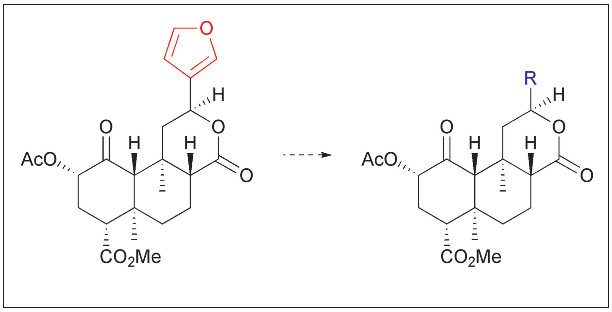
A series of enantiomerically pure mono- and bis-aryl *tert*-butyl sulfoxides were synthesised to promote the enantioselective allylation of aldehydes with allyltrichlorosilane. Moderate to high yields and up to 90% ee were obtained.

3748

Synthetic studies of neoclerodane diterpenes from *Salvia divinorum*: role of the furan in affinity for opioid receptors

Denise S. Simpson, Kimberly M. Lovell, Anthony Lozama, Nina Han, Victor W. Day, Christina M. Dersch, Richard B. Rothman and Thomas E. Prisinzano*

A series of furan modified analogues were prepared from salvinorin A as potential opioid receptor ligands. These compounds were evaluated for opioid affinity in CHO cells.

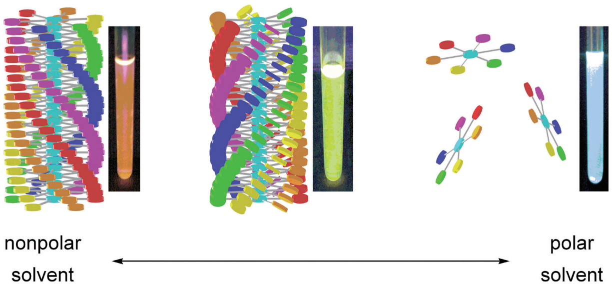


3757

Solvent-induced chirality inversion involving supramolecular helix transformation and color-tunable fluorescence of a C_6-symmetric hexakis(phenylethynyl)benzene derivative

Koichi Sakajiri,* Takeshi Sugisaki, Keiichi Moriya and Shoichi Kutsumizu

A C_6-symmetric disk-like molecule exhibits a solvent-induced supramolecular helix-sense inversion followed by destruction of the supramolecular helical column with concomitant change in fluorescent color over a wide visible range.

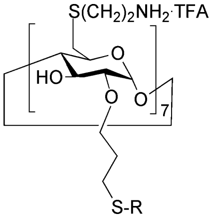


3763

Poly-6-cationic amphiphilic cyclodextrins designed for gene delivery

Colin Byrne, Florence Sallas, Dilip K. Rai, Julien Ogier and Raphael Darcy*

A synthetic route to a new class of amphiphilic cyclodextrins has been used to obtain polycationic cyclodextrins intended as gene delivery vectors.

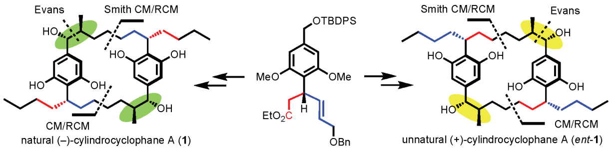


3772

Syntheses of naturally occurring cytotoxic [7.7]paracyclophanes, (−)-cylindrocyclophane A and its enantiomer, and implications for biological activity

H. Yamakoshi, F. Ikarashi, M. Minami, M. Shibuya, T. Sugahara, N. Kanoh, H. Ohori, H. Shibata and Y. Iwabuchi*

Enantiodivergent synthesis of cylindrocyclophane A enabled a preliminary SAR study, indicating that the chirality of this C_2-symmetric [7.7]paracyclophane is irrelevant to its cytotoxicity, which is attributed to the embedded resorcinol motifs.



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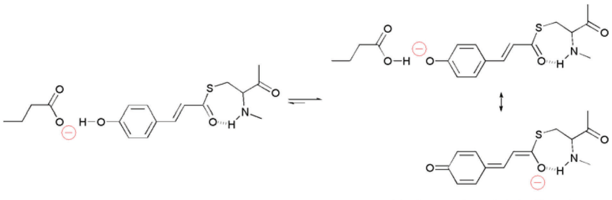
3782

Color regulation and stabilization of chromophore by Cys69 in photoactive yellow protein active center

Kentaro Okamoto, Norio Hamada, Taka-aki Okamura,
Norikazu Ueyama and Hitoshi Yamamoto*

The Cys69 residue plays an important role in the regulation of the color and the stabilization of the chromophore anion in the Photoactive Yellow Protein active center.

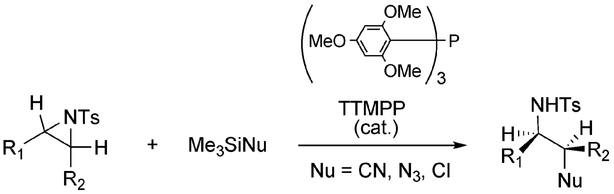


3792

TTMPP: An efficient organocatalyst in the ring-opening of aziridines with silylated nucleophiles

Satoru Matsukawa* and Kumiko Tsukamoto

The ring-opening of *N*-tosylaziridines with silylated nucleophiles catalyzed by tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) afforded the corresponding β-functionalized sulfonamides in excellent yield under mild reaction conditions.

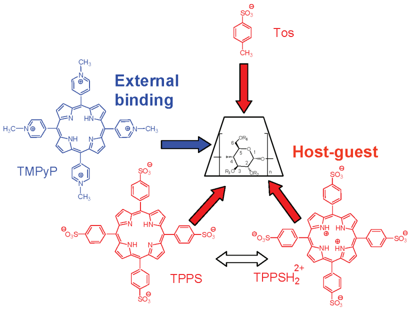


3797

Cyclodextrin carriers of positively charged porphyrin sensitizers

Jiří Mosinger,* Lenka Slavětínská, Kamil Lang,
Pavel Coufal and Pavel Kubát

Interaction of cationic 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) with the external cyclodextrin surface is the dominant binding mode. In contrast, tosylate counteranion (Tos) and diprotonated anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPSH_2^{2+}$) with two positive charges on the pyrrole rings form host–guest inclusion complexes.

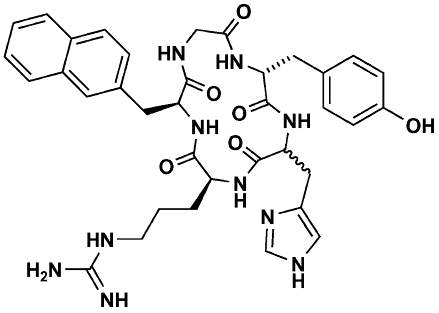


3805

Structure-activity relationship study on artificial CXCR4 ligands possessing the cyclic pentapeptide scaffold: the exploration of amino acid residues of pentapeptides by substitutions of several aromatic amino acids

T. Tanaka, W. Nomura,* T. Narumi, A. Esaka, S. Oishi,
N. Ohashi, K. Itotani, B. J. Evans, Z.-x. Wang, S. C. Peiper,
N. Fujii and H. Tamamura*

Cyclic pentapeptide libraries based on substitutions of several amino acids for D-Tyr¹ and Arg² in peptide **2** were prepared and screened to evaluate binding activity for CXCR4.



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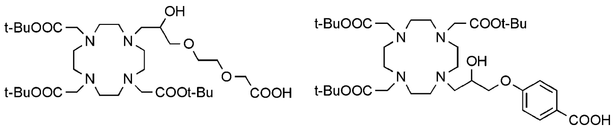
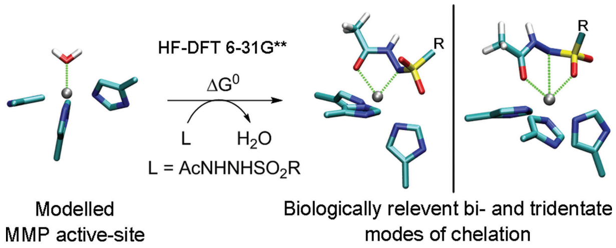


Synthesis of functionalised HP-DO3A chelating agents for conjugation to biomolecules

Alessandro Barge, Enrico Cappelletti, Giancarlo Cravotto, Aurelia Ferrigato, Luciano Lattuada,* Fabio Marinoni and Lorenzo Tei

Two new bifunctional chelating agents based on the HP-DO3A coordinating cage have been synthesised. Conjugation to an oxytocin derivative and labelling with ^{111}In(III) are reported.

3817

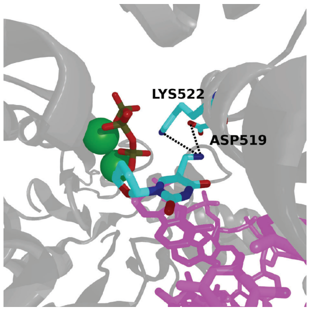


In silico study of MMP inhibition

Matthieu Rouffet, Clément Denhez, Erika Bourguet, Frédéric Bohr and Dominique Guillaume*

DFT and docking studies demonstrate that sulfonylhydrazides and the Zn ion afford mono-, bi- or tridentated complexes whose formation could represent the initial step leading to selective MMP inhibition.

3826

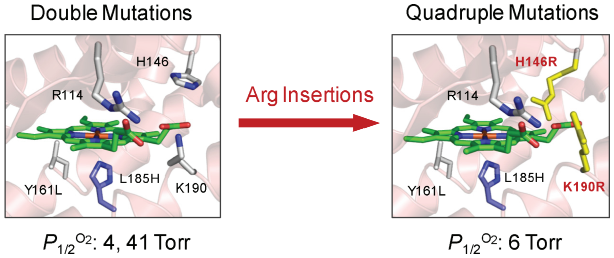


Synthesis and enzymatic incorporation of modified deoxyuridine triphosphates

Vinciane Borsenberger, Mikiembo Kukwikila and Stefan Howorka*

The synthesis of various 2′-deoxyuridine-5′-triphosphate derivatives bearing linkers at position 5 yielded an improved methodology for the Yoshikawa phosphorylation and molecular insight into the poor substrate properties of an amino-propargyl derivative in polymerisation reactions.

3836



The role of an amino acid triad at the entrance of the heme pocket in human serum albumin for O_2 and CO binding to iron protoporphyrin IX

Teruyuki Komatsu,* Akito Nakagawa, Stephen Curry, Eishun Tsuchida, Kenichi Murata, Nobuhumi Nakamura and Hiroyuki Ohno

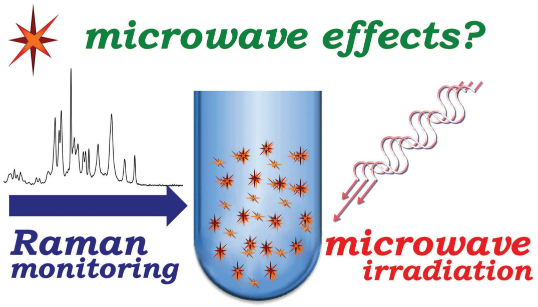
A basic amino acid triad at the entrance of the heme pocket in human serum albumin plays a crucial role for O_2 and CO binding the prosthetic iron(II) protoporphyrin IX group.

3842

Probing “microwave effects” using Raman spectroscopy

Jason R. Schmink and Nicholas E. Leadbeater*

Specific microwave effects? Non-thermal microwave effects? Localized superheating? Raman spectroscopy scrutinizes reactions under microwave irradiation in an attempt to confirm or refute these oft-cited phenomena.

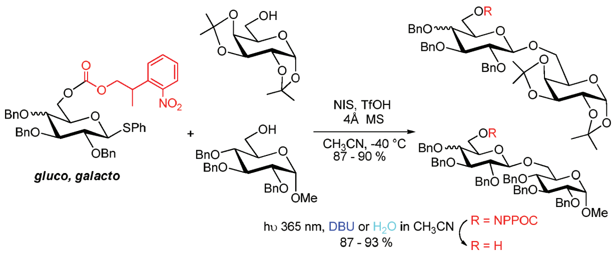


3847

Synthesis, glycosylation and photolysis of photolabile 2-(2-nitrophenyl)propyloxycarbonyl (NPPOC) protected glycopyranosides

Hua Yi, Stéphane Maisonneuve and Juan Xie*

The 6-*O*-NPPOC protected thio-glycopyranosides have been successfully used as glycosyl donors for the synthesis of NPPOC-protected disaccharides which can be easily photo-deprotected under neutral or basic conditions.

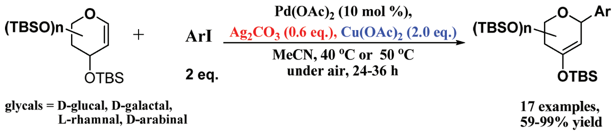


3855

Regio- and stereo-selective synthesis of aryl 2-deoxy-*C*-glycopyranosides by palladium-catalyzed Heck coupling reactions of glycals and aryl iodides

Hou-Hua Li and Xin-Shan Ye*

The Heck coupling of aryl iodides with pyranoid glycals using a catalytic amount of Pd(OAc)$_2$ to form pyranoid aryl *C*-glycosides has been achieved in the presence of Ag$_2$CO$_3$ and Cu(OAc)$_2$ (or DMSO) in acetonitrile. This arylation process, which occurs in a highly regio- and stereo-selective manner, provides a simple, mild, and efficient approach to the synthesis of aryl 2-deoxy-*C*-glycopyranosides.

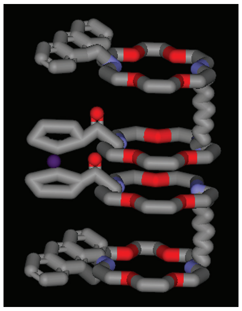


3862

Synthesis and characterization of a redox-active ion channel supporting cation flux in lipid bilayers

M. Tsikolia,* A. C. Hall, C. Suarez, Z. O. Nylander, S. M. Wardlaw, M. E. Gibson, K. L. Valentine, L. N. Onyewadume, D. A. Ahove, M. Woodbury, M. M. Mongare, C. Dennis Hall, Z. Wang, B. Draghici and A. R. Katritzky

The synthesis, cation binding and transmembrane conductive properties of a novel synthetic ion channel containing a redox-active centre are described. BLM and NMR studies confirm and describe its transport kinetics.



PAPERS

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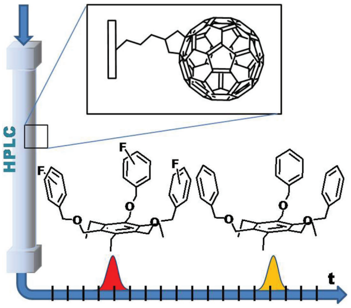


Aromatic tripodal receptors for (C_{60}-I_h)[5,6]fullerene

Gian Maria Dell'Anna, Rita Annunziata, Maurizio Benaglia, Giuseppe Celentano, Franco Cozzi,* Oscar Francesconi and Stefano Roelens*

Flexible tripodal receptors endowed with aromatic side-arms bind to fullerene through π–π interactions in a polar environment, but cannot compete with solvation in apolar media.

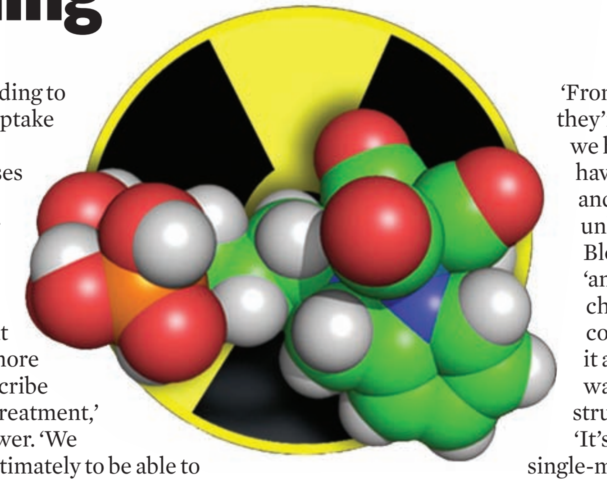
AUTHOR INDEX

September 2009 / Volume 6 / Issue 9 / ISSN 2041-580X / HCSIA3 / www.rsc.org/highlightschemsci

Highlights in Chemical Science

Dual function agents allow more control of radiopharmaceutical doses for cancer

Image is everything



The molecule consists of a bisphosphonate bone-seeking agent and a radio-labelled part separated by a spacer

Improved radiopharmaceutical agents to detect and treat cancer in bones have been developed by UK scientists.

Philip Blower and colleagues from King's College London and Barts and The London School of Medicine made a dual function molecule containing a bisphosphonate to target bones and a radio-labelled part to image in just two steps.

Cancer spreading from a tumour into bone, known as bone metastasis, is a common problem in cancer patients and can cause pain. Treatment involves injecting ^{99m}technetium or $^{188/186}$rhenium bisphosphonates into the body. The bisphosphonates accumulate in the bone and treat the area and the radio-labelled metals aid imaging by single photon emission computed tomography. But technetium bisphosphonates exist as mixtures of compounds, making it difficult to establish each component's role, explains Blower. Rhenium complexes are easily degraded by enzymes, leading to lower bone uptake and higher radiation doses in soft tissue, he adds. 'Our motivation was to reduce these effects so that doctors are more likely to prescribe this form of treatment,' explains Blower. 'We would like ultimately to be able to give doses that are high enough not just to relieve pain but to treat the cancer and extend life expectancy.'

In current treatments, the bisphosphonates both chelate the metal and bind to bone. Blower separated the bisphosphonate and metal with a spacer, which bound strongly to the metal leaving the bisphosphonate free to perform just one role – targeting bone. The two-step synthesis is easy and results in single, well-defined complexes.

'From a chemical perspective they're far superior to the agents we have already because we have a single compound and not a mixture of really unknown compounds,' says Blower of his molecules, 'and once we know what the chemistry is, it is under our control and we can optimise it and make it do what we want to do by changing the structure.'

'It's interesting that a single-molecule complex with bisphosphonates accumulates in the bone matrix as it is commonly maintained that only polymeric species can do this job,' says Adriano Duatti, an expert in molecular imaging at the University of Ferrara, Italy. 'A truly remarkable achievement would be to produce the corresponding ^{188}Re complex in high specific activity, as currently, there is no effective ^{188}Re agent for the treatment of bone metastases.'

Ian Coates

Reference

R Torres Martin de Rosales *et al*, *Chem Commun*, 2009, 4847 (DOI: 10.1039/b908652h)

In this issue

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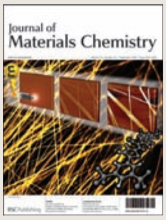
Superhydrophobicity saves scalding
Clothes coated with a Teflon–carbon nanotube composite could repel hot water

Ice gels take the heat
A non-toxic scaffold for stem cell tissue engineering

Uranium chemistry: the final frontier
New uranium compounds for the future of nuclear power

Bending the rules
Guy Bertrand talks about creating dream compounds, tennis and setting up international labs in this month's interview



A snapshot of the latest developments from across the chemical sciences

Research highlights

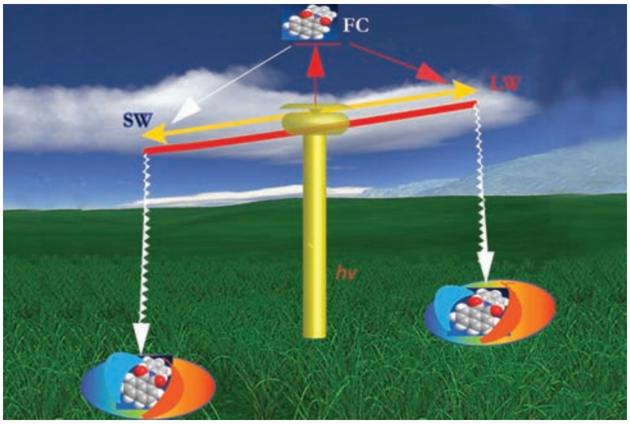
A seesaw helped scientists to discover dual fluorescent dyes

Dyes get the green, and red, light

With the help of a photophysical model, scientists in the US have discovered dual fluorescent dyes (where two colours are emitted from the same fluorophore), which could prove useful in detecting clinically important molecules.

Michael Heagy and co-workers from the New Mexico Institute of Mining and Technology synthesised a matrix of nine naphthalimide dyes. They used a seesaw balanced photophysical model to balance the dyes' electronic properties by directing substituent groups on the dyes to the correct positions. Four out of the nine dyes in the matrix showed dual fluorescence.

'Just as green and red traffic signals convey far more information to a motorist than a single yellow caution flasher, so also is the greater information obtained from dyes that emit in two colours to researchers who are attempting to detect a molecule, an ion or another clinically important system,' explains Heagy.



'The ability to obtain two colours from an organic dye improves biological analyses by providing a second signal or output to monitor. This enables better accuracy as the second colour provides internal calibration of the signal.'

Obtaining dual fluorescent dyes has previously proved difficult because of factors such as substituent groups on the molecule and the solvent affecting whether dual fluorescence will occur. Chemists have had to synthesise large libraries of dyes where only a small fraction turn out to be dual fluorescent.

A seesaw model was used to balance the dyes' electronic properties by directing substituent groups on the dyes to the correct positions

Robert Strongin, who develops new organic reagents used in diagnosing, understanding and treating diseases at Portland State University, US, says, 'It's not often that simple and elegant predictive models for tuning fluorophore photophysics are reported.' He adds that the work of Heagy's group represents 'a breakthrough that will allow better understanding of fluorophore properties, and enable the design of improved optical materials.'

Heagy envisions dual fluorescent naphthalimide dyes being used in chemosensory devices for ion and molecule detection because of their advantages over conventional one-colour dyes. *Fay Nolan-Neylan*

Reference

P Nandhikonda *et al*, *Chem. Commun.*, 2009, 4941 (DOI: 10.1039/b911768g)

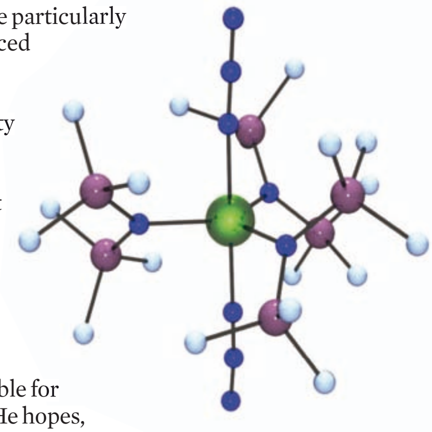
Scientists have made new uranium compounds for the future of nuclear power

Uranium chemistry: the final frontier

US scientists have synthesised complexes that could provide us with a new insight into the chemistry of uranium, with far reaching consequences for the nuclear industry and beyond.

Trevor Hayton and colleagues at the University of California, Santa Barbara, have made and isolated new uranium compounds containing an azide group, including uranium(V) azides. It is the first time, says Hayton, that uranium(V) azides have in fact been made. The team now hopes to harness the azide group's well-known reactivity to synthesise uranium nitride complexes.

Uranium nitride is a ceramic compound used as a nuclear fuel. NASA is interested in using it as a future fuel for nuclear reactors used in space exploration. The compounds have also received attention recently as potential fuels for the next-generation of nuclear power systems.



Uranium azides could be used to make nitrides, which are particularly promising as advanced nuclear fuels

Actinide nitrides are particularly promising as advanced nuclear fuels since they exhibit higher thermal conductivity and higher metal density compared with the oxides that are currently used.

Nitrides are a relatively rare functional group for uranium, says Hayton, and so few examples are available for scientists to study. He hopes, by using his new uranium azides, to carry out small-scale synthesis of uranium nitride and improve the understanding of its chemical properties. This would help scientists to predict its behaviour in nuclear waste and in the environment resulting in breakthroughs in waste processing and environmental remediation.

Uranium is also of great fundamental interest as it possesses chemical traits that are not found in any other element, says Hayton. These unique features may result in the development of novel catalytic reactivity. Many challenges remain in uranium chemistry and in actinide chemistry in general, adds Hayton, describing it as being 'the last frontier of the periodic table'.

Christopher Cummins, from the Massachusetts Institute of Technology, Cambridge, US, welcomes the work and says 'it elegantly unfurls a larger uranium(IV/V) coordination chemistry of azide as a nitrogen-rich pseudo-halide.'
Sarah Corcoran

Reference

S Fortier, G Wu and T W Hayton, *Dalton Trans.*, 2010, DOI: 10.1039/b909879h

Clothes could repel hot water with a Teflon-carbon nanotube composite coating

Superhydrophobicity saves scalding

A coating designed for clothing could help reduce industrial injuries due to scalding, say Chinese scientists.

Victims of hot water scalds often experience substantial burns as a result of the water wetting their clothing. 'The use of superhydrophobic textiles seems to be a promising way to protect the victims from deeper scalding,' says Yuyang Liu at The Hong Kong Polytechnic University and colleagues.

Superhydrophobic surfaces, such as Teflon and lotus leaves, exhibit high repellency to cool water. However, Liu and co-workers have discovered that a number of such surfaces show significantly reduced repellency to hot water. Their study led them to develop a fabric coated with a Teflon and carbon nanotube composite, which demonstrated promising repellency properties to hot beverages including tea and coffee.

Liu's work quantified water repellency both in terms of the shape of droplets placed on the surface (static water) and the ability of sprayed droplets (dynamic water) to slide off the surface. While a standard Teflon-coated fabric scores well with regards to static water, its response to dynamic water is poor. Liu's material aimed to rectify this by using carbon nanotubes to increase the surface roughness, which improves superhydrophobicity by trapping air bubbles in tiny pores.

'It is possible that the smaller length scale associated with the carbon nanotubes means that the superhydrophobic surface effect can withstand higher water impact pressures,' suggests Glen McHale of Nottingham Trent University, UK, who studies superhydrophobic surfaces. He warns that 'further work would be needed to repeat these tests and verify the mechanism.' Liu acknowledges that 'the creation of superhydrophobic surfaces which can repel pressured hot liquids is still a great challenge to scientists.'

Erica Wise

A water droplet on a superhydrophobic surface

Reference

Y Liu, X Chen and J H Xin, *J. Mater. Chem.*, 2009, **19**, 5602 (DOI: 10.1039/b822168e)

Scientists have made a non-toxic scaffold for stem cell tissue engineering

Ice gels take the heat

Chinese scientists have combined two separate scaffold-making techniques to create an artificial biomaterial that can withstand conditions in the body.

Biomaterials are materials designed to replace or improve a natural function of a living structure. These materials can either be natural or man-made.

Xiang Yao from Tsinghua University, Beijing, and colleagues combined ice-segregation-induced self-assembly (ISISA) and electrostatic self-assembly (ESA) to fabricate macroscale biomaterials from nanoscale building blocks.

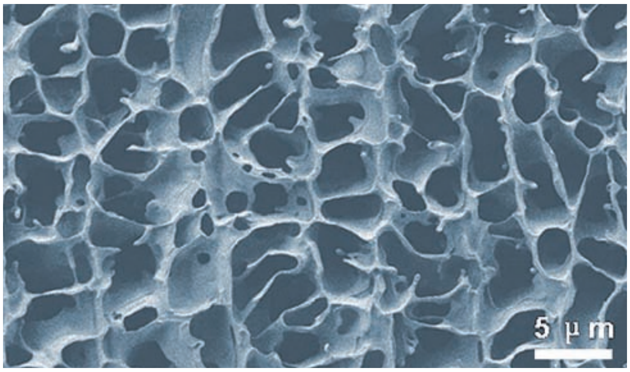
In ISISA, ice is used as a template to fabricate a porous structure whereas ESA uses two oppositely charged particles, suspended in a fluid, to attract each other. The ESA process has mainly been used to make 2D biomaterials, but Yao says his goal was 'to achieve a three dimensional and nanometre level biomimetic control of cell behaviour.' ISISA has been used to create 3D scaffolds but because the scaffolds are held together with weak forces with this method, a water soluble polymer such as polyvinyl alcohol is often used to bind them together. Unfortunately, the polymer is toxic, which limits its use in tissue engineering.

When Yao combined the two methods by using ESA building blocks in an ISISA process, the team found that the resulting 3D scaffold was strong in water at 37 °C without the need to add toxic binders. This makes it suitable for use in physiological environments and Yao says he hopes his research can be used in biomedical applications such as stem cell tissue engineering.

'The absence of cross-linkers should improve their biocompatibility as biomaterials but this issue must still be addressed,' says Marisa Ferrer, an expert in biomaterial design and application at the Instituto de Ciencia de Materiales de Madrid, Spain, who adds: 'The combination of ice ISISA and ESA beats the challenge of preparing 3D scaffolds working at physiological pH.'

Paul Hatton, who works on tissue engineering and polymer biocompatibility at the University of Sheffield, UK, comments that Yao's work is 'an elegant solution to one of the more significant challenges faced by those seeking to fabricate biomimetic materials, that of how to "build in" a nanoscale level of hierarchy in order to contribute to functional properties.'

Rebecca Brodie



The 3D biocompatible structures were grown on ice

Reference

X Yao, H Yao and Y Li, *J. Mater. Chem.*, 2009, DOI: 10.1039/ b909059b

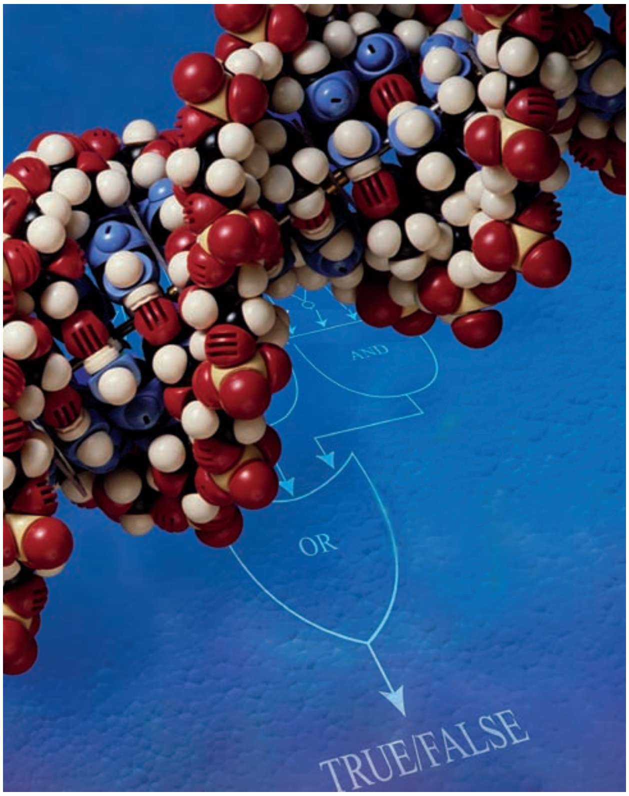
Simplified DNA logic gates detect biomarkers

A logical extension

DNA logic gates can now detect more than just DNA segments, and by exploiting nature's design, their preparation could be simpler than ever.

Atsushi Ogawa and Mizuo Maeda from The Institute of Physical and Chemical Research (RIKEN), Saitama, and Ehime University, Japan, have developed existing DNA logic gate systems to create a detection system where gold nanoparticle aggregation provides a visual marker for a variety of biomarkers.

Logic gates are used in digital circuits in computer chips. An input signal goes through a binary operation to give either a true (one) or false (zero) output. This system has been mimicked in biology using DNA inputs, outputs and switches. DNA logic gates detect oligonucleotides (short DNA segments) when they bind to the logic gate sensors. This concept has been developed to detect different molecules using aptamers–DNA or RNA molecules adapted to bind to other molecules and viruses. However, both DNA and aptamer logic gates have a drawback in that they rely on a hybridisation switch. When a target molecule binds, or hybridizes, to the sensor, the event has to be transmitted to a reporter system, which must be specifically engineered for each sensor/target system.



A true or false output that can be monitored by eye is given by the DNA logic gates

To avoid the need to design a hybridisation switch, Ogawa and Maeda based their logic gate on a cleavase aptazyme. An aptazyme is an enzyme which naturally produces a response upon interaction with a specific target or marker molecule. The aptazyme can be adapted to respond to virtually any species of interest, from a single ion, to a drug metabolite, which could have implications for medical diagnostic techniques. In this case, when activated by its target molecule, the cleavase aptazyme cleaves a length RNA from its own structure. The resulting free RNA transmits a signal to a reporter system; in this case, the pair used gold nanoparticles as reporters. They functionalised them with DNA strands that bind to the free RNA to form a duplex with a blunt end (where the ends of both strands are even rather than one strand being longer than the other). The duplexes facilitate nanoparticle aggregation, which can be seen with the naked eye by clearing of an otherwise cloudy reaction medium.

'We want to apply this method to construct more complex logic gates,' says Ogawa. 'Because the aggregation of gold nanoparticles depends on whether or not DNA on the nanoparticles forms a duplex with the cleaved RNA with a blunt end, we think an appropriate design of the cleaved RNA sequences may make them possible.'

Milan Stojanovic, an expert in diagnostic molecular devices based on nucleic acids, at Columbia University, New York, US, says that the work is an 'important contribution' towards a field that 'has a future if it moves in the direction of autonomous therapeutic devices, rather than towards competing with silicon.' *Katie Dryden-Holt*

Reference

A Ogawa and M Maeda, *Chem. Commun.*, 2009, DOI: 10.1039/b910288d

News in brief

This month in Highlights in *Chemical Technology*

Nanoparticles take on terrorism
Tiny amounts of explosives such as TNT can be detected

Sterile surfaces in a flash
European scientists have created light-activated antimicrobial surfaces by modifying a material used in medical devices with tiny amounts of commonly used dyes.

Corn waste converted to chemicals
Biofuel waste could be turned into building blocks for industrial chemicals.

Holography speaks volumes
Søren Hvilsted discusses how holograms could be the answer to the increasing demand for data storage

Raising the bar
In this month's interview, Scott Tanner talks about measuring cell biomarkers and Olympic gymastics

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

This month in Highlights in *Chemical Biology*

Nano-earthquake to shake up drug screening
A thumbnail-sized chip mimics the turbulent conditions a drug experiences on its journey through the body

Blood cells get active
A cell boosting peptide could help diabetics

Untangling Alzheimer's
Cures for Alzheimer's may come from understanding its chemistry. Arvi Rauk examines the disease at the molecular level

Genetic alphabets
In this month's interview, Ichiro Hirao talks about nucleic acid research, expanding the genetic code and the possibility of creating new life.

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

Interview

Bending the rules

Guy Bertrand talks to Marie Cote about creating dream compounds, tennis and setting up international labs

Guy Bertrand

Guy Bertrand is a Distinguished Professor of Chemistry at the University of California, Riverside (UCR), CA, US, where he heads the UCR/CNRS (National Center for Scientific Research) joint laboratory. His research interests concern main group elements and are at the interface between organic, organometallic and inorganic chemistry. Major ongoing projects in Guy Bertrand's group are the synthesis of stable carbenes, highly reactive intermediates and defying standard valence rules.

What led you to chemistry?

I do not think I was programmed to become a chemist. I wanted to be a tennis player, but I was better at school than on the court! Then, I studied science. I did not like mathematics and physics, and at that time I found biology too empirical, so I chose chemistry.

Where do you look for ideas?

All along my career, I have tried to demonstrate that some of the rules we learned at school are not totally correct, or at least that we can find tricks to get around them. A good illustration is given by our recent synthesis of push–push allenes, which are flexible and bent, whereas regular allenes were believed to be rigid and linear. Do not misunderstand, I am a deep admirer of ancient chemists who were working without the modern technological tools, and this is my way to render homage to them. In many of my papers there is a reference to a work from the beginning of the 20th century, or even earlier.

What is the most significant aspect of your work?

I guess that the synthesis of the first stable carbene in 1988 is the most important result of my career. At that time, very few chemists believed that carbenes could be isolated. Certainly nobody thought, including myself, that some twenty years later, carbenes would be ubiquitous ligands for transition metal based catalysts, and catalysts in their own right. Having said that, I have to recognise that our first stable carbene did not find applications by itself, and that the popularity of carbenes is mainly due to the so-called *N*-heterocyclic carbenes, discovered by my friend Bo Arduengo. This perfectly illustrates that it is difficult to predict if a discovery, as spectacular as it is, will be important for the future or not.

When we found stable diradicals, we thought that ourselves, or somebody else, would quickly find applications for them in materials science. So far, this has not been the case and diradicals are still laboratory curiosities! The future will also tell us if cyclic bent-allenes, which we have recently described, are important or not. Right now, I am quite optimistic. In any case, the most significant aspect of my work is hopefully what we will discover tomorrow!

What do you love about your job?

I can spend hours at the NMR or X-ray machine to be sure that we have really created the new chemical object we were dreaming of. The success of former PhD students or postdoctoral fellows is also very rewarding. To make a comparison, when I was young I played tennis, and I wanted to be the best; now I am more interested to see my kids winning a game, than winning a game by myself.

You are a keen communicator. How would you define the importance of teaching?

In the US, the barrier between the professors and the students is almost non-existent, and I like it. My aim here is to make chemistry as attractive as possible for every student. My great pleasure is to see some of the students majoring in biology change their mind and become chemistry majors!

Having worked both in Europe and in the US, what would you say the major differences are in the life of an academic?

To begin an academic career, I am quite convinced that the US system is better, although very brutal. For all scientists, it is more stressful to work in the US, especially at a time when the budgets are tight, but I find this very exciting and stimulating. However, to increase your chance of funding, you need to work in a 'fashionable area', and to demonstrate that your research will quickly find applications. This is an extremely important aspect, since most of the time practical applications of a fundamental discovery occur years afterwards. Lastly, there is the existence of a strong competition between the US universities, and that makes the faculty of a department a real team. I would advise young scientists to test both, via postdoctoral stays abroad. Then, they could choose the one that suits them best.

You point out that your laboratory is a joint venture between the University of California and the French CNRS. Can you comment on the collaboration?

I am very proud of this, and I believe that this is representative of the structure of fundamental research in the future. Globalisation is not only a word, it is a reality that we cannot ignore. I am quite confident that other agencies all over the world will follow and that many international labs will be created.

Finally, what would be your message to the younger generation?

A very simple but very important one: science and scientists are not boring! We travel all around the world, meet new friends at conferences, and what can be more exciting than to make a tiny contribution to improving the welfare of humanity.

Essential elements

IUPAC 2009

The RSC hosted the 42nd IUPAC Congress at the SECC, Glasgow, UK, and enjoyed meeting over 2000 delegates from 72 countries and 64 chemical societies. The programme featured seven themes: Analysis & Detection, Chemistry for Health, Education & Communication, Industry & Innovation, Materials, and Synthesis & Mechanism. RSC journals sponsored a variety of sessions within the 50 symposia taking place. Speakers presented key research topics demonstrating the impact of the chemical sciences, and highlighting exciting innovations with an overall focus on ‘Chemistry Solutions’.

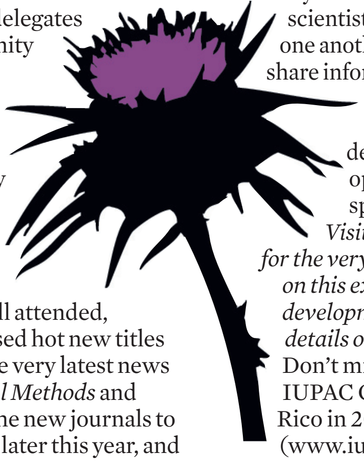
Following the RSC’s acquisition of ChemSpider, Graham McCann, Business Manager for ChemSpider, joined Antony Williams, ChemSpider Vice President of Strategic Development, on the ChemSpider stand to share future plans on what the collaboration will bring to scientists. The new website, demonstrated on the stand, gave delegates the opportunity to navigate around the website to see the new functionality it offers to users.

The RSC stand was also very well attended, and showcased hot new titles including the very latest news on *Analytical Methods* and *Nanoscale*, the new journals to be launched later this year, and *Polymer Chemistry*, a new journal for 2010.

This year’s IUPAC conference also saw the successful launch of RSC’s highly interactive social networking tool, MyRSC.

MyRSC allows chemical scientists to network with one another across the globe, share information about themselves and their research, receive details of career opportunities and join specialist groups. *Visit http://my.rsc.org for the very latest information on this exciting new development, and to find out details on how to join.*

Don’t miss out on the next IUPAC Congress in Puerto Rico in 2011! (www.iupac2011.org)



Working together

What do a free online source of structure-based chemical information, Twitter and a roadmap have in common?

They are all ways in which the RSC is working with the global scientific community – and they all feature in Issue 2, 2009 of *Fusion*, RSC Publishing’s newsletter, which has a distinct technology theme. We, as members of the community, have a vast range of new and emerging technologies at our disposal. We can alert you to an article immediately it is published online, and provide links to open online resources to help you enhance your knowledge. You can share your experiences with other scientists via virtual discussion groups, and allow a global audience to view details of your work on videos.

There are many other ways in which technology has facilitated international networking and dissemination of the latest scientific advances. Gone are the days when a researcher waited for a print journal to arrive on the desk to see the latest developments, or relied on the occasional overseas trip to a scientific conference to catch up with like-minded researchers!

So can these new technologies help us to work together to overcome some of the global challenges that are facing scientists? We’d like to think so.

Find out more on our website: www.rsc.org/publishing/fusion

ChemSpider sensation

August marks a milestone in ChemSpider’s 2009 calendar. Just two months after announcing RSC’s new partnership, we unveiled to the world at the 42nd IUPAC Congress in Glasgow a refreshed looking ChemSpider, now hosted on powerful RSC servers.

The ChemSpider booth at the event was abuzz: delegates searched for chemicals they didn’t expect ChemSpider to have...and found them! They deposited and curated data live. People who’d never heard of ChemSpider rushed to tell others. We heard comments like, ‘This is the best thing I have seen all day’ and ‘Do you realise how much this will do for the world of chemistry?’

Delegates were impressed by the fast text and structure searching capabilities, the size and diversity of the database (including videos, reactions and blog posts). They were also complimentary about the new ChemSpider look and feel delivered through the logo, exhibition booth and literature, and excited about ChemSpider’s vision for the future.

The ChemSpider team thanks everyone for their support.

Search, share and help refine the data at www.chemspider.com

ChemSpider
Building community for chemists

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