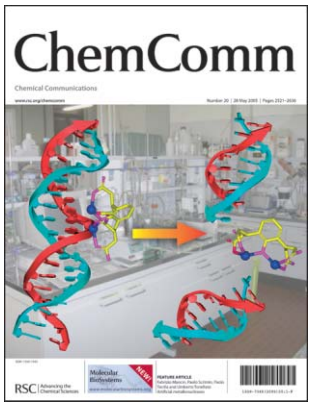
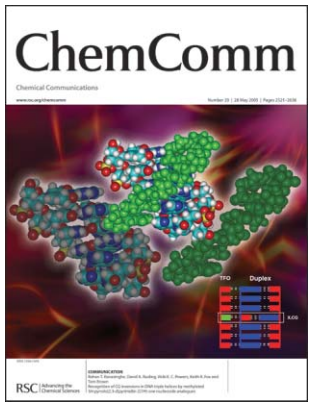
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (20) 2521–2636 (2005)



Cover
See Fabrizio Mancin, Paolo Scrimin, Paolo Tecilla and Umberto Tonellato, page 2540.
Chemists have taken up the fascinating challenge to develop artificial metallonucleases capable of competing with the natural enzymes. The picture shows a dicerium complex cleaving a DNA double strand. Image reproduced by permission of Paolo Tecilla *et al.*, from *Chem. Commun.*, 2005, 2540.



Inside cover
See Rohan T. Ranasinghe, David A. Rusling, Vicki E. C. Powers, Keith R. Fox and Tom Brown, page 2555. Pyrrolopyrimidine nucleoside analogues are synthesised and show selective CG base pair recognition in DNA triplexes. Image reproduced by permission of Tom Brown *et al.*, from *Chem. Commun.*, 2005, 2555.

EDITORIAL

New journal *Molecular BioSystems* has arrived

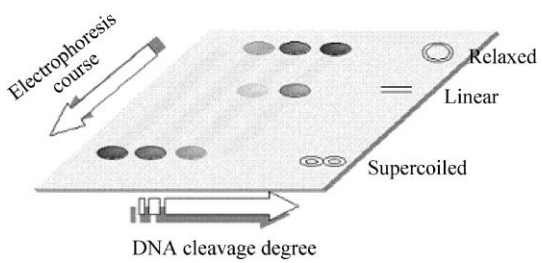
ChemComm is pleased to announce that the first issue of its sister journal *Molecular BioSystems* is now published.

FEATURE ARTICLE

Artificial metallonucleases

Fabrizio Mancin, Paolo Scrimin, Paolo Tecilla and Umberto Tonellato

Since the first report on the ability of metal ions to promote DNA hydrolysis, tremendous progress toward obtaining efficient synthetic DNA hydrolytic agents has been attained. However, several aspects need to be addressed before artificial catalysts are able to challenge the natural enzymes. This *Feature Article* highlights the progress toward the realization of synthetic nucleases with particular attention to the strategies that can be pursued to improve efficiency and selectivity.



Chemical Communications (print: ISSN 1359-7345; electronic: ISSN1364-548X) is published 48 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0)1206 226050; E-mail sales@rscdistribution.org

2005 Annual (print + electronic) subscription price: £1595; US$2635. 2005 Annual (electronic) subscription price: £1435; US$2370. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT. If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA. US Postmaster: send address changes to Chemical Communications, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight.
PRINTED IN THE UK

ChemComm

Chemical Communications

www.rsc.org/chemcomm

♾ The paper used in this publication meets the requirements of ANSI/NISO Z39.48–1992 (Permanence of Paper).

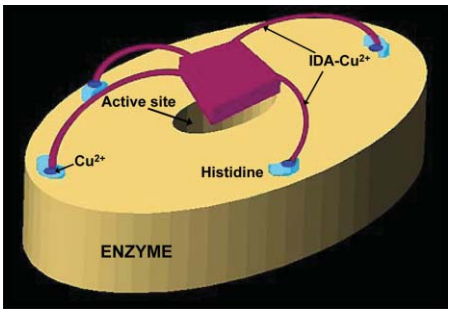
Royal Society of Chemistry: Registered Charity No. 207890.

2549

Inhibition of matrix metalloproteinase-9 by "multi-prong" surface binding groups

Abir L. Banerjee, Shakila Tobwala, Manas K. Haldar, Michael Swanson, Bidhan C. Roy, Sanku Mallik* and D. K. Srivastava*

A novel approach for blocking the active site accessibility of MMP-9 (but not MMP-10) and inhibiting the enzyme by "multi-prong" IDA-Cu^{2+} containing ligands is demonstrated.

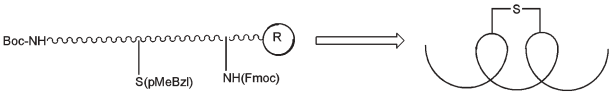


2552

Synthesis of constrained helical peptides by thioether ligation: application to analogs of gp41

Florence M. Brunel and Philip E. Dawson*

We present a procedure to constrain peptides in a helical conformation using thioether ligation. This simple, high-yielding method represents an attractive alternative to the use of lactam constraints.

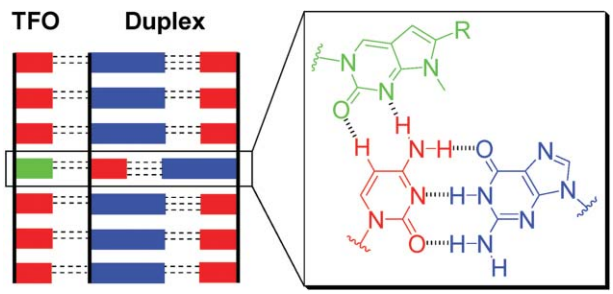


2555

Recognition of CG inversions in DNA triple helices by methylated 3*H*-pyrrolo[2,3-*d*]pyrimidin-2(7*H*)-one nucleoside analogues

Rohan T. Ranasinghe, David A. Rusling, Vicki E. C. Powers, Keith R. Fox and Tom Brown*

Substituted 3*H*-pyrrolo[2,3-*d*]pyrimidin-2(7*H*)-one nucleoside analogues have been synthesised from 5-alkynyl-uridine derivatives, incorporated into triplex forming oligonucleotides (TFOs) and found to selectively bind CG inversions with enhanced affinity compared to T.

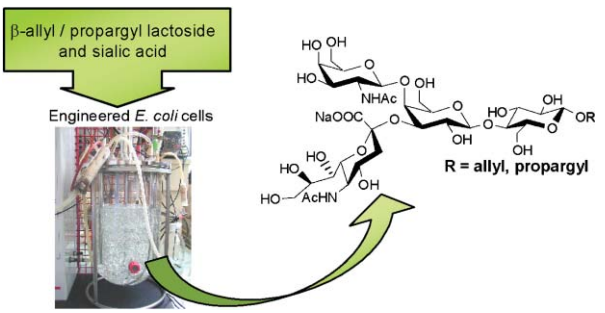


2558

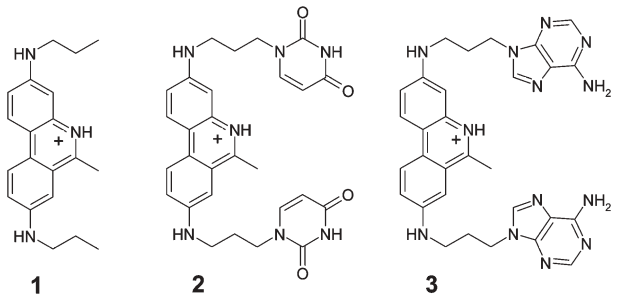
Biosynthesis of conjugatable saccharidic moieties of GM_2 and GM_3 gangliosides by engineered *E. coli*

Sébastien Fort,* Lemonia Birikaki, Marie-Pierre Dubois, Tatiana Antoine, Eric Samain and Hugues Driguez

Oligosaccharidic portions of gangliosides GM_2 and GM_3 bearing allyl or propargyl aglycons, are biosynthesized on the gram scale by growing metabolically engineered *Escherichia coli* cells.



2561

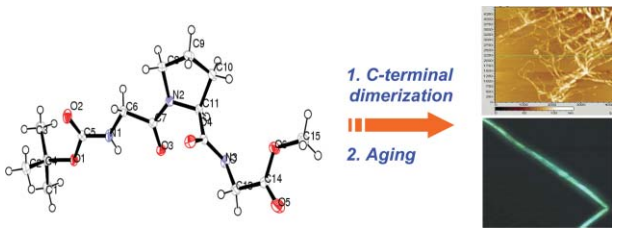


Recognition of homo-polynucleotides containing adenine by a phenanthridinium bis-uracil conjugate in aqueous media

Lidija-Marija Tumir, Ivo Piantanida,* Iva Juranović, Zlatko Meić, Sanja Tomić and Mladen Žinić*

A bis-uracil–phenanthridinium conjugate **2** significantly more strongly stabilized ds-polynucleotides containing poly-dA and poly-AH^+ strands than adenine analogue **3** and reference **1**, consecutive adenines in polynucleotide being essential for the observed selectivity.

2564

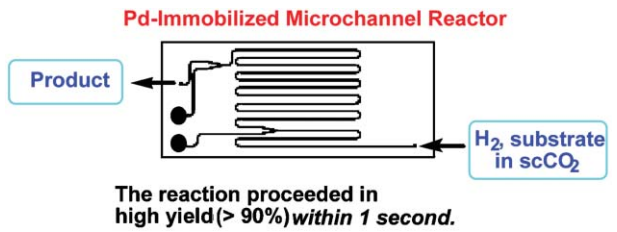


Enforcing solution phase nanoscopic aggregation in a palindromic tripeptide

K. Krishna Prasad, C. S. Purohit, Alok Jain, R. Sankararamakrishnan and Sandeep Verma*

This report describes nanosized fibril formation by a tripeptide conjugate derived from the highly evolutionary conserved V3 loop of HIV-1.

2567

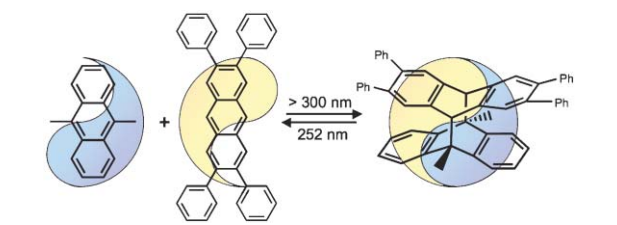


Hydrogenation reactions using $scCO_2$ as a solvent in microchannel reactors

Juta Kobayashi, Yuichiro Mori and Shū Kobayashi*

We developed an effective microfluidic hydrogenation system using $scCO_2$ as a reaction medium. It is remarkable that the reaction took place very rapidly (mean residence time: less than 1 second).

2569



Complementarity in bimolecular photochromism

David Bailey and Vance E. Williams*

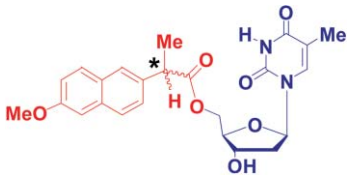
Irradiating 2,3,6,7-tetraphenylanthracene in the presence of 9,10-dimethylanthracene leads to exclusive formation of the cross-dimer. No photochemical reaction is observed when either of these chromophores is irradiated in the absence of the other.

2572

Stereo-differentiation in the excited state behaviour of naphthalene-thymine dyads

Susana Encinas, Maria J. Climent, Noureddine Belmadoui and Miguel A. Miranda*

Chiral discrimination has been found in the photophysical processes involving the naphthalene excited states of the title dyads: singlet deactivation by hydrogen bonding molecules, singlet energy transfer and triplet decay.

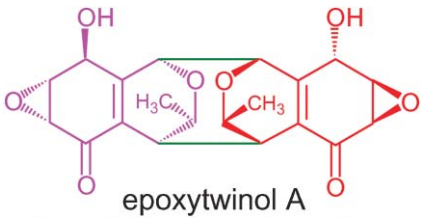


2575

Epoxytwinol A, a novel unique angiogenesis inhibitor with C_2 symmetry, produced by a fungus

Hideaki Kakeya,* Rie Onose, Hiroyuki Koshino and Hiroyuki Osada*

We isolated a novel unique pentaketide dimer designated as epoxytwinol A from the fermentation broth of a fungus. Its structure was determined to have a new carbon skeleton with C_2 symmetry *via* spectroscopic evidence. Epoxytwinol A inhibited endothelial cell migration stimulated by vascular endothelial growth factor (ED_{100} = 2.6 μM).

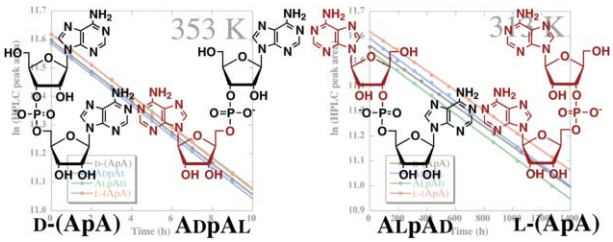


2578

Kinetic analysis of hydrolytic reaction of homo- and heterochiral adenylyl(3′–5′)adenosine isomers: breaking homochirality reduces hydrolytic stability of RNA

Hidehito Urata,* Rie Sasaki, Hiroyo Morita, Marina Kusumoto, Yoko Ogawa, Kozue Mitsuda and Masao Akagi*

The hydrolytic stabilities of the diastereomeric isomers of adenylyl(3′–5′)adenosine were carefully compared and the preferential hydrolysis of the heterochiral dimers over the homochiral ones was observed.

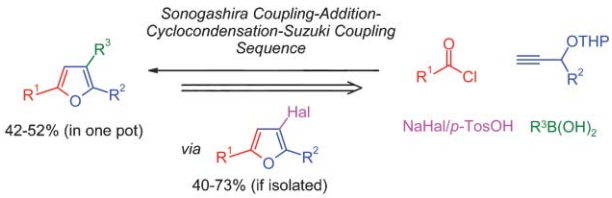


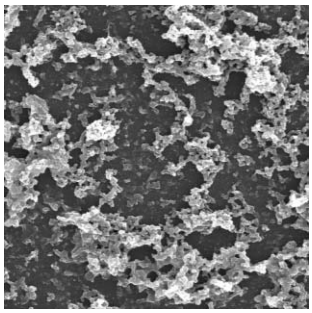
2581

A novel one-pot three-component synthesis of 3-halofurans and sequential Suzuki coupling

Alexei S. Karpov, Eugen Merkul, Thomas Oeser and Thomas J. J. Müller*

A novel Sonogashira–electrophilic addition sequence to ynones with concomitant deprotection and cyclocondensation opens a new one-pot synthesis of 3-halofurans and a sequential one-pot Sonogashira–addition–cyclocondensation–Suzuki reaction to furnish 2,3,5-trisubstituted furans.

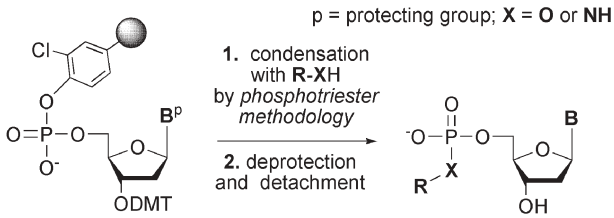




Direct electrochemistry and electrocatalysis with hemoglobin in water-soluble quantum dots film on glassy carbon electrode

Qing Lu, Shengshui Hu,* Daiwen Pang and Zhike He

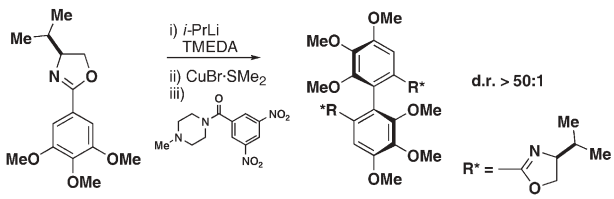
The direct electrochemistry of hemoglobin can be performed by immobilizing hemoglobin in a water-soluble quantum dots (CdSe–ZnS) film on glassy carbon electrode.



An efficient solid phase synthesis of 5′-phosphodiester and phosphoramidate monoester nucleoside analogues

Lorenzo De Napoli, Giovanni Di Fabio,* Jennifer D'Onofrio and Daniela Montesarchio

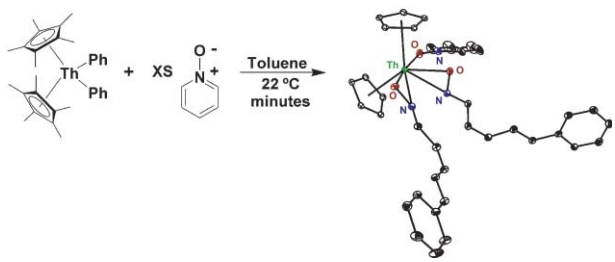
An easy and efficient strategy to obtain libraries of 5′-phosphodiester and 5′-phosphoramidate monoester nucleoside analogues in a highly pure form has been developed, starting from a new nucleoside based solid support.



Aryl–aryl coupling *via* directed lithiation and oxidation

David S. Surry, David J. Fox, Simon J. F. Macdonald and David R. Spring*

Organocuprates formed by a directed lithiation–transmetallation sequence may be oxidised to give biaryls. Inter- and intramolecular reactions are both successful and a highly diastereoselective reaction is possible if a valinol-derived chiral oxazoline is used as a directing group.



Carbon–nitrogen bond cleavage in pyridine ring systems mediated by organometallic thorium(IV) complexes

Jaime A. Pool, Brian L. Scott and Jaqueline L. Kiplinger*

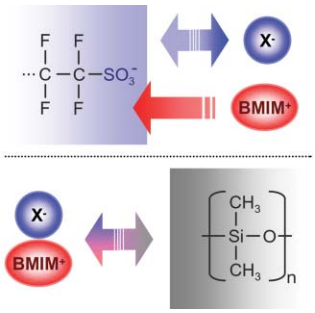
Thorium(IV) alkyl and aryl complexes of the type $(C_5Me_5)_2ThR_2$ (R = CH_2Ph, Ph) have been found to mediate the facile ring-opening and dearomatization of the pyridine ring of pyridine *N*-oxide under ambient conditions to afford the first thorium η^2-(*O*,*N*)-oximate complexes.

2594

Elucidating interactions of ionic liquids with polymer films using confocal Raman spectroscopy

Thomas Schäfer,* Roberto E. Di Paolo, Ricardo Franco and João G. Crespo

Ionic liquids and membranes are materials for emerging cleaner processing and composites in sensors, but little is known about their molecular interaction. Using confocal Raman microscopy, it was revealed how ionic liquids interact with PDMS and Nafion® membranes.

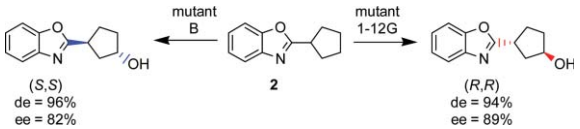


2597

Stereoselective hydroxylation of an achiral cyclopentanecarboxylic acid derivative using engineered P450s BM-3

Dieter F. Münzer, Peter Meinhold, Matthew W. Peters, Sabine Feichtenhofer, Herfried Griengl, Frances H. Arnold,* Anton Glieder and Anna de Raadt*

Substrate engineered, achiral carboxylic acid derivative **2** was biohydroxylated with various mutants of cytochrome P450 BM-3 to give two out of the four possible diastereoisomers in high de and ee.

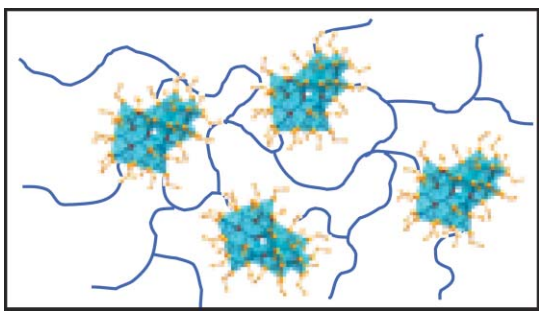


2600

New hybrid organic–inorganic nanocomposites based on functional $[Ti_{16}O_{16}(OEt)_{24}(OEMA)_8]$ nano-fillers

Sergio Bocchini, Giulia Fornasieri, Laurence Rozes, Sondes Trabelsi, Jocelyne Galy, Nick E. Zafeiropoulos, Manfred Stamm, Jean-François Gérard and Clément Sanchez*

New hybrid nanocomposites based on a methacrylate functionalized titanium-oxo cluster as nano-cross-linker show improved mechanical properties, optical transparency and photochromic activity.

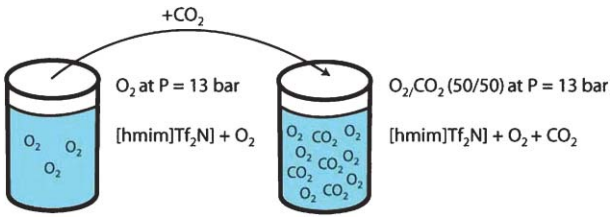


2603

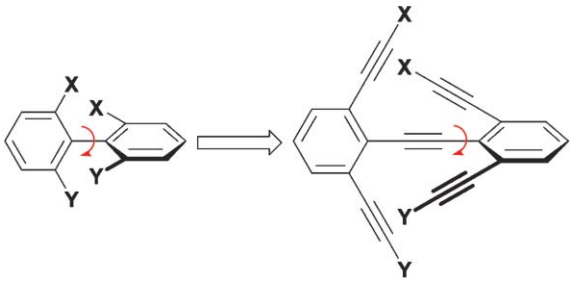
Enhancement of oxygen and methane solubility in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide using carbon dioxide

Daniel G. Hert, Jessica L. Anderson, Sudhir N. V. K. Aki and Joan F. Brennecke*

Low pressure CO_2 can be used to increase the solubility of gases like O_2 and CH_4 in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide.



2606

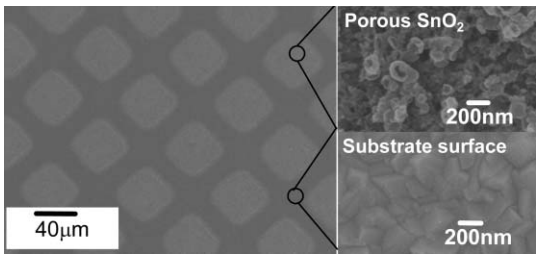


Hindered rotation in an "exploded" biphenyl

Ognjen Š. Miljanić, Sangdon Han, Daniel Holmes, Gaston R. Schaller and K. Peter C. Vollhardt*

The first cases of hindered rotation around the triple bond in simple diphenylacetylenes were observed, including that in chiral 2,2′-bis(trimethylsilyl)-6,6′-bis(dimethylthexylsilyl)diphenylacetylene.

2609

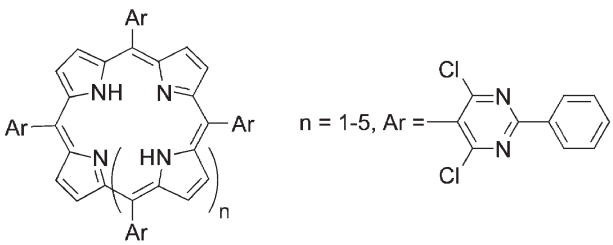


Fabrication of highly porous and micropatterned SnO_2 films by oxygen bubbles generated on the anode electrode

Eiji Hosono, Shinobu Fujihara, Hiroaki Imai, Itaru Honma and Haoshen Zhou*

Porous SnO_2 films and patterned films are fabricated by electrochemical assisted chemical bath deposition.

2612

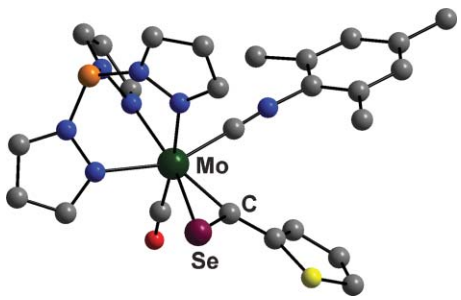


meso-Dichloropyrimidinyl substituted expanded porphyrins

Wouter Maes, Jeroen Vanderhaeghen and Wim Dehaen*

4,6-Dichloro-2-phenylpyrimidine-5-carbaldehyde can be used for the synthesis of novel *meso*-aryl substituted expanded porphyrins and the introduction of this heteroaromatic moiety shows great potential for the simplification and extension of post-macrocyclization synthetic modifications.

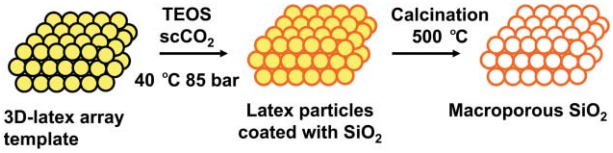
2615

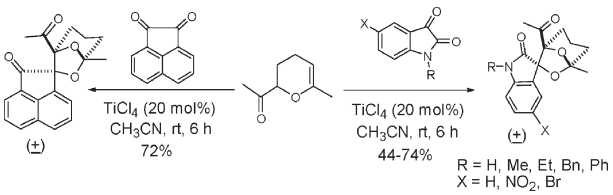


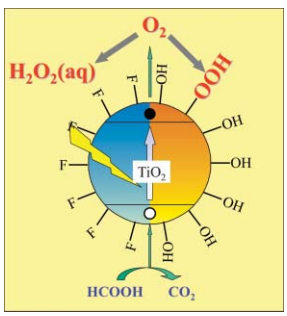
Selenoaroyl complexes of molybdenum

Lorraine M. Caldwell, Anthony F. Hill* and Anthony C. Willis

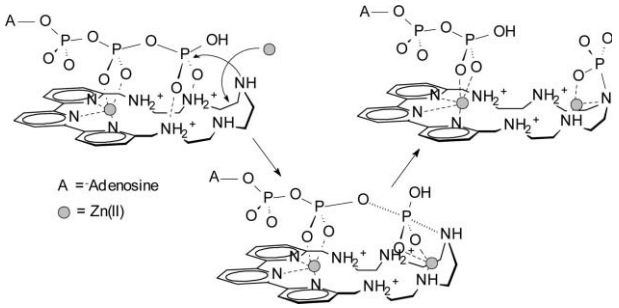
The reaction of mesityl isoselenocyanate with molybdenum alkylidynes provides the first structurally characterised examples of mononuclear selenoaroyl complexes, which may also be obtained directly from elemental selenium in the presence of a catalytic amount of mesityl isocyanide.







2630

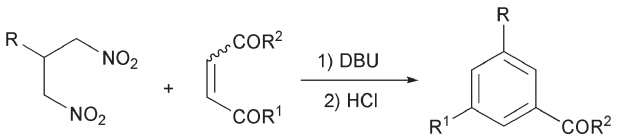


A zinc(II)-based receptor for ATP binding and hydrolysis

Carla Bazzicalupi, Andrea Bencini,* Antonio Bianchi,* Andrea Danesi, Claudia Giorgi, Carlos Lodeiro, Fernando Pina, Samuele Santarelli and Barbara Valtancoli

A protonated Zn(II) complex with a terpyridine-containing macrocycle catalyses ATP hydrolysis only in the presence of a second Zn(II) ion, which acts as cofactor assisting the phosphoryl transfer from ATP to an amine group of the macrocycle.

2633



One pot synthesis of 3,5-alkylated acetophenone and methyl benzoate derivatives *via* an anionic domino process

Roberto Ballini,* Luciano Barboni,* Dennis Fiorini, Guido Giarlo and Alessandro Palmieri

The one pot synthesis of 3,5-alkylated acetophenones and methyl benzoate derivatives starting from 1,3-dinitroalkanes and 2-ene-1,4-dicarbonyl derivatives is reported. The reactions occur *via* an anionic domino process.

AUTHOR INDEX

FREE E-MAIL ALERTS

Contents lists in advance of publication are available on the web *via* www.rsc.org/chemcomm – or take advantage of our free e-mail alerting service (www.rsc.org/ej_alert) to receive notification each time a new list becomes available.

* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

Professor Barbara Imperiali, FRSC

US Associate Editor for Chemical Biology, *ChemComm*

ChemComm is the leading international journal for the publication of communications on important new developments in the chemical sciences.

Each one of ChemComm's US Associate Editors is happy to receive submissions from the Americas in their subject area.

Professor Imperiali is the Ellen Swallow Richards Professor of Chemistry and Professor of Biology at Massachusetts Institute of Technology (MIT). Her research interests are concerned with the diverse aspects of protein structure, function and design. A multidisciplinary approach involving synthesis, state-of-the-art spectroscopy, molecular modelling, enzymology and molecular biology is employed to address fundamental problems at the interface of chemistry and biology.

Call for papers!

Professor Imperiali is pleased to receive papers on important developments in chemical biology. Submit today at **www.rsc.org/resource**

For enquiries please contact:
Professor Imperiali at chemcomm@mit.edu

30030571

Why publish in ChemComm:

- Impact factor: 4.031
- Rapid publication – typically 60 days (from receipt to publication)
- Now: weekly publication
- 3 page communications – providing authors with the flexibility to develop their results and discussion
- 40 years publishing excellent research
- High visibility – indexed in MEDLINE
- 'Hot papers' are highlighted – helping authors to promote their work
- FREE colour where scientifically necessary
- FREE inclusion in Chemical Biology Virtual Journal

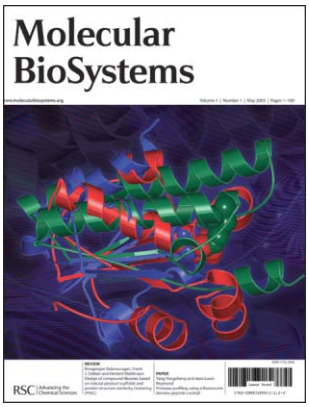
Submit today!

RSC | Advancing the Chemical Sciences

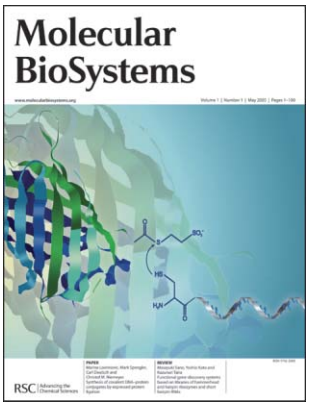
www.rsc.org/chemcomm

IN THIS ISSUE

ISSN 1742-206X CODEN MBOIBW 1(1) 1–100 (2005)



Cover
See Herbert Waldmann *et al.*, page 36. Clustering of protein domain cores according to structural similarity (here Cdc25A (red), 11βHSD1 (green), and AChE (blue)) is a new guiding principle for guiding compound library development for chemical biology and medicinal chemistry. Image reproduced by permission of Rengarajan Balamurugan, Frank J. Dekker and Herbert Waldmann, from *Mol. BioSyst.*, 2005, **1**, 36.



Inside cover
See Christof M. Niemeyer *et al.*, page 64. The synthesis of covalent DNA-protein conjugates is accomplished by expressed protein ligation of intein-fusion proteins and a DNA-cysteine conjugate.
Image reproduced by permission of Marina Lovrinovic, Mark Spengler, Carl Deutsch and Christof M. Niemeyer, from *Mol. BioSyst.*, 2005, **1**, 64.

EDITORIAL

Chemistry meets the -omic sciences and systems biology

Welcome to the first issue of *Molecular BioSystems*—an exciting new chemical biology journal with a particular focus on the interface between chemistry and the -omic sciences and systems biology.

HOT OFF THE PRESS

Hot off the Press

In the *Hot off the Press* section of *Molecular BioSystems*, members of the Editorial Board and their research groups highlight recent literature for the benefit of the community. This month the highlighted topics include enhancing the efficacy of RNA interference, identification of targets of kinase inhibitors, analysis of low-abundance peptides, and secretion of recombinant proteins.

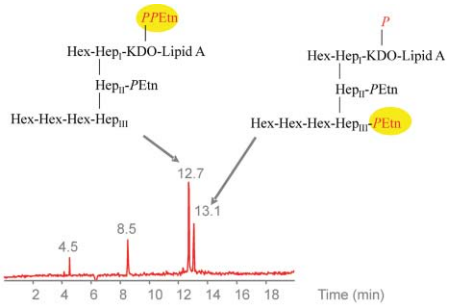
METHOD

46

Electrophoretic and mass spectrometric strategies for profiling bacterial lipopolysaccharides

Jianjun Li,* Andrew D. Cox, Derek W. Hood, Elke K. H. Schweda, E. Richard Moxon and James C. Richards

The CE–MS analysis of LPS from *Haemophilus influenzae* strain 375.1 revealed the presence of two isoforms varying by the location of the phosphoethanolamine groups on the core structure.



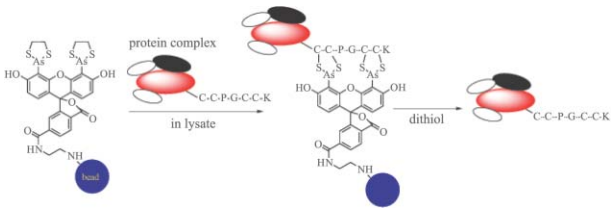
COMMUNICATION

53

One-step, non-denaturing isolation of an RNA polymerase enzyme complex using an improved multi-use affinity probe resin

M. Uljana Mayer,* Liang Shi and Thomas C. Squier

Isolation of intact protein complexes using a bisarsenical affinity reagent on a glass support permits the rapid identification of protein components by mass spectrometry.



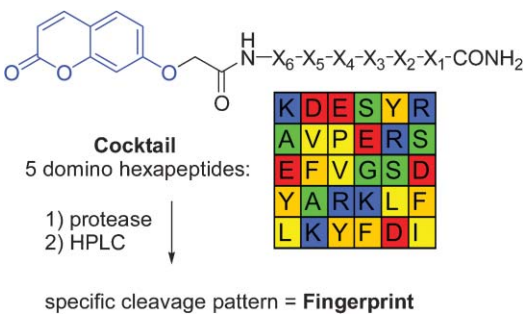
PAPERS

57

Protease profiling using a fluorescent domino peptide cocktail

Yang Yongzheng and Jean-Louis Reymond*

A cocktail of five coumarin-labeled hexapeptides with a domino sequence arrangement provides specific cleavage patterns allowing the functional identification of various proteases in a single HPLC assay.

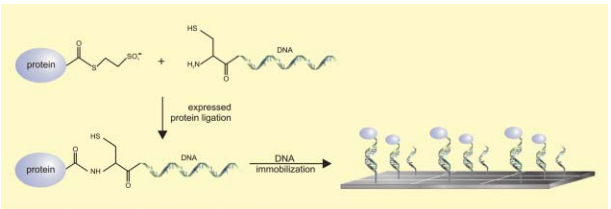


64

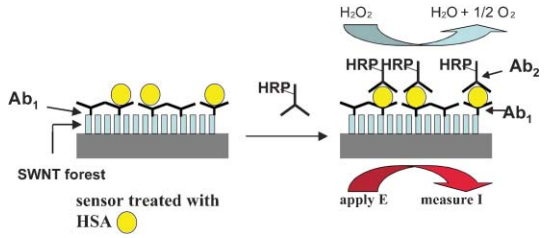
Synthesis of covalent DNA–protein conjugates by expressed protein ligation

Marina Lovrinovic, Mark Spengler, Carl Deutsch and Christof M. Niemeyer*

Efficient and site-specific covalent coupling of DNA oligomers and recombinant proteins is achieved by expressed protein ligation. The resulting conjugates, which retain their full biological activity, are versatile molecular tools.



70

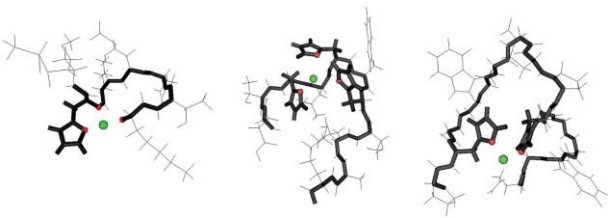


Protein immunosensor using single-wall carbon nanotube forests with electrochemical detection of enzyme labels

Xin Yu, Sang Nyon Kim, Fotios Papadimitrakopoulos* and James F. Rusling*

Vertically aligned single-wall carbon nanotube forests were used to fabricate enzyme-linked amperometric immunosensors featuring antibodies bioconjugated to nanotube ends. Using casein and detergent to minimize non-specific binding, a detection limit of 1 pmol mL^{-1} was achieved for human serum albumin.

79

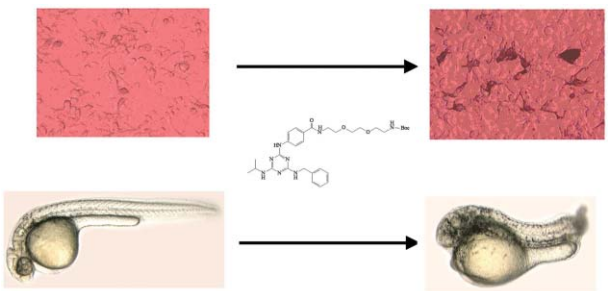


NMR studies on Cu(II)–peptide complexes: exchange kinetics and determination of structures in solution

Elena Gaggelli, Henryk Kozlowski, Daniela Valensin and Gianni Valensin*

Knowledge of structural and kinetic features of copper(II) strongly interacting with histidine-containing peptides taken from the human prion protein may shed light on relevant aspects of prion diseases. System-adapted NMR methods yield valuable geometrical restraints for determining structures in solution.

85

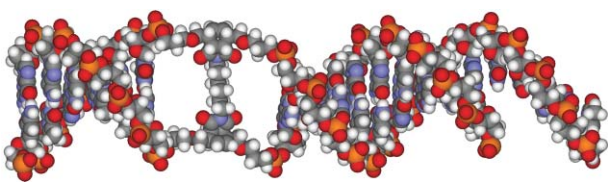


Identification of the F1F0 mitochondrial ATPase as a target for modulating skin pigmentation by screening a tagged triazine library in zebrafish

Da-Woon Jung, Darren Williams, Sonya M. Khersonsky, Tae-Wook Kang, Noushin Heidary, Young-Tae Chang and Seth J. Orlow*

A chemical probe identified from a zebrafish screening system has been successfully used in a forward chemical genetic approach to establish a link between the phenotype and the protein.

93



Crosslinking of diene-modified DNA with bis-maleimides

Rolf Tona and Robert Häner*

Crosslinked oligonucleotide hybrids produced *via* the Diels–Alder reaction were shown to behave like two separate, hairpin-like structures, rather than like a single, continuous duplex.