



nature
chemistry

JANUARY 2012 VOL 4 NO 1
www.nature.com/naturechemistry

NANOPARTICLE ASSEMBLY

Opening the toolbox

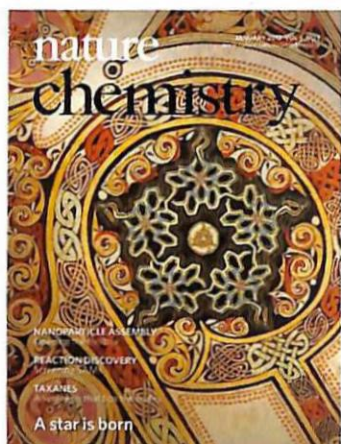
REACTION DISCOVERY

Screening SAMs

TAXANES

A synthesis that tips the scales

A star is born



COVER IMAGE

The cover image features the interlaced 'rho' character from Matthew 1:18 in the Lindisfarne Gospels as a backdrop for the X-ray crystal structure of the most complex non-DNA molecular knot synthesized so far. A team led by David Leigh prepared the 160-atom-long pentafoil knot in a one-step reaction from ten organic building blocks and five iron(II) cations. They use a single chloride anion as a template, which, in the solid-state structure, is located at the centre of the pentafoil knot and exhibits ten CH...Cl hydrogen bonds. Article p15; News & Views p7

IMAGE: JIM CALLAGHAN (EVOLUTION DESIGN)
BASED ON AN IMAGE © THE BRITISH LIBRARY
BOARD. (COTTON NERO D. IV. F.29)

COVER DESIGN: ALEX WING

ON THE COVER

Nanoparticle assembly
Opening the toolbox
Article p37

Reaction discovery
Screening SAMs
Article p45

Taxanes
A synthesis that tips the scales
Article p21

THESIS

- 1 **Judicial chemistry**
Bruce Gibb

BOOKS & ARTS

- 3 **The Case of the Poisonous Socks: Tales from Chemistry**
by William H. Brock
Reviewed by Philip Ball

RESEARCH HIGHLIGHTS

- 4 **Our choice from the recent literature**

BLOGROLL

- 5 **A hot topic**

NEWS & VIEWS

- 7 **Interlocked molecules: One-pot pentaknot**
Michaele J. Hardie
- 8 **Exciton dynamics: Electrons take an unexpected turn**
Heather M. Jaeger and Oleg V. Prezhdo
- 10 **Metallo-helical complexes: Resolutely pure helices**
Janice R. Aldrich-Wright
- 11 **Biomimetic chemistry: Merging the old with the new**
Marcetta Y. Darensbourg and Ryan D. Bethel
- 13 **Drug delivery: Relieving PEGylation**
Matthew C. Parrott and Joseph M. DeSimone



nature publishing group

Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group (Porters South, 4 Crinan Street, London N1 9XW, UK). Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, Fl 9, New York, NY, 10013-1917, US. Telephone: +1(212) 726-9200. Fax: +1(212) 696-9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Chemistry, Subscription Dept, PO Box 5054, Brentwood, TN 37024-5054, USA. Outside North America: Subscriptions Department, Brunel Road, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. Annual subscription rates: US/Canada US\$3520, Canada add 5% GST (institutional/corporate) US\$999, Canada add 5% GST (individual making personal payment), UK/Rest of World (excluding Europe and Japan) £1806 (institutional/corporate), £51 (individual making personal payment), Europe €2795 (institutional/corporate), €79 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group, c/o Mercury Airfreight International Ltd, 365 Blair Road, Avenel, NJ 07001, USA. Periodicals postage is paid at Rahway, NJ. Postmaster: send address changes to Nature Chemistry, c/o Mercury Airfreight International, 365 Blair Road, Avenel, NJ, USA. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. Postmaster: send address changes to Nature Chemistry Subscriptions Department, Brunel Road, Basingstoke, Hants, RG21 6XS, UK or Nature Chemistry Subscriptions Department PO Box 5054, Brentwood, TN 37024-5054, USA. © 2012 Macmillan Publishers Limited. All rights reserved.

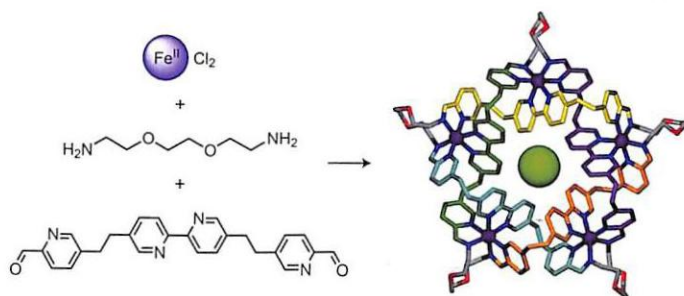
ARTICLES

15 A synthetic molecular pentafoil knot

Jean-François Ayme, Jonathon E. Beves, David A. Leigh, Roy T. McBurney, Kari Rissanen and David Schultz

The most complex non-DNA molecular knot prepared so far is self-assembled around a chloride anion from five metal cations, five bis-aldehyde and five bis-amine building blocks, in a one-pot reaction. The X-ray crystal structure of the 160-atom-loop pentafoil knot reveals a symmetrical closed-loop double helicate with a chloride anion held at its centre by ten $\text{CH}\cdots\text{Cl}^-$ hydrogen bonds.

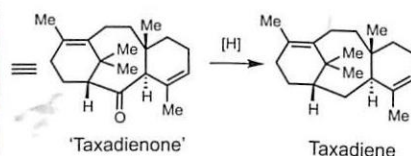
→N&V p7



21 Scalable enantioselective total synthesis of taxanes

Abraham Mendoza, Yoshihiro Ishihara and Phil S. Baran

The taxane diterpene family is structurally complex and exhibits a wide range of biological activities, best exemplified by the successful drug Taxol. Here, two of the least oxidized taxanes in the family, 'taxadienone' and taxadiene, are prepared by total synthesis on a gram scale. The concise synthetic route described herein provides a scalable, enantioselective entry to the taxane family of natural products.



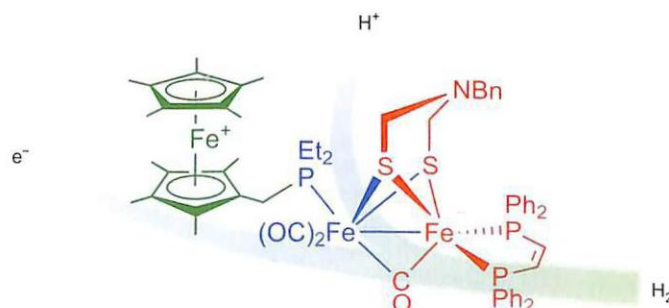
- Scalable
- Rapid (seven days with one chemist)
- Enantioselective
- Minimizes concession steps: seven steps

26 Combining acid-base, redox and substrate binding functionalities to give a complete model for the [FeFe]-hydrogenase

James M. Camara and Thomas B. Rauchfuss

The fastest catalysts in nature for producing and oxidizing hydrogen are [FeFe]-hydrogenases, which make use of an extra one-electron redox equivalent from an iron-sulfur cluster that is outside the core. Now, a ferrocene-based ligand that oxidizes at mild potential performs this cluster's role in an excellent synthetic hydrogenase model.

→N&V p11

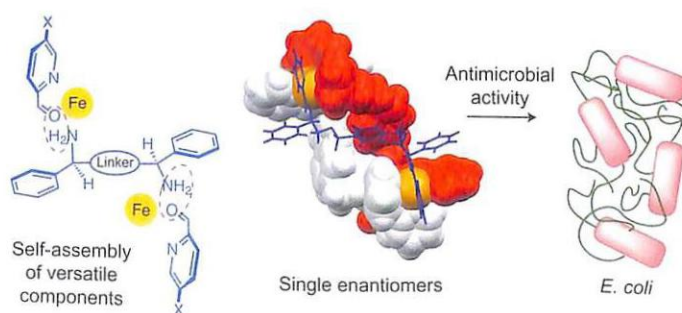


31 Optically pure, water-stable metallo-helical 'flexicate' assemblies with antibiotic activity

Suzanne E. Howson, Albert Bolhuis, Viktor Brabec, Guy J. Clarkson, Jaroslav Malina, Alison Rodger and Peter Scott

The self-assembly of monometallic moieties with organic ligands has proved to be a highly versatile approach for preparing a range of metal-ligand assemblies that are helical, optically pure and stable in aqueous solutions. One such iron(II) 'flexicate' system exhibits significant interactions with DNA, as well as promising antimicrobial activity properties.

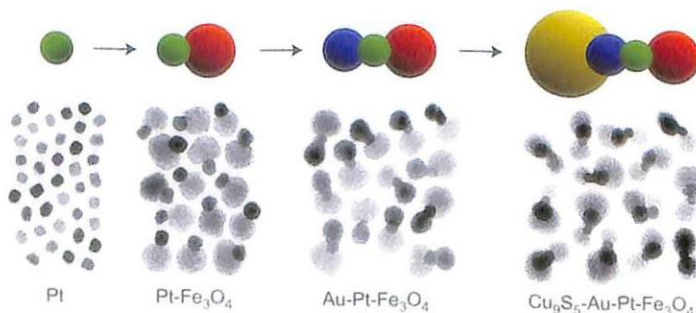
→N&V p10



37 A total-synthesis framework for the construction of high-order colloidal hybrid nanoparticles

Matthew R. Buck, James F. Bondi and Raymond E. Schaak

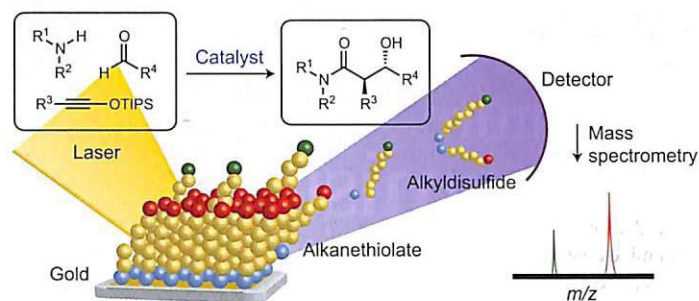
Colloidal hybrid nanoparticles represent an emerging class of multifunctional artificial molecules. However, unlike actual molecules, their complexity is limited by the lack of a mechanism-driven design framework. Here, nanoparticle analogues of chemoselectivity, regioselectivity, molecular substituent effects, and coupling reactions are used to predictably synthesize hybrid nanoparticle trimers, tetramers, and oligomers.



45 Three-component reaction discovery enabled by mass spectrometry of self-assembled monolayers

Timothy J. Montavon, Jing Li, Jaime R. Cabrera-Pardo, Milan Mrksich and Sergey A. Kozmin

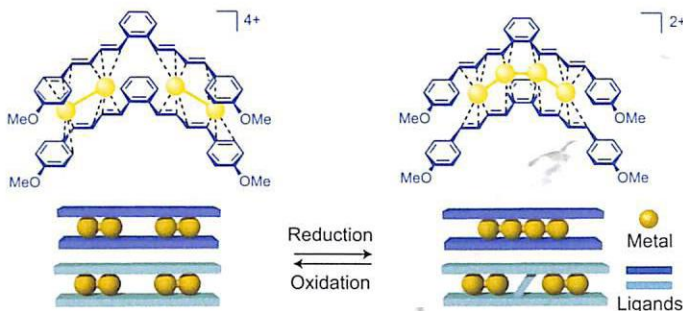
A general reaction-discovery platform has been used for identification of a new multicomponent transformation. The approach entails rapid analysis of interfacial chemical reactions on arrays of self-assembled monolayers using mass spectrometry. This enabled identification of a simple organic phosphine that catalyses a previously unknown condensation of siloxy alkynes, aldehydes and amines.



52 Redox-induced reversible metal assembly through translocation and reversible ligand coupling in tetranuclear metal sandwich frameworks

Tetsuro Murahashi, Katsunori Shirato, Azusa Fukushima, Kohei Takase, Tomoyoshi Suenobu, Shunichi Fukuzumi, Sensuke Ogoshi and Hideo Kurosawa

Despite their potential roles in catalysis and materials science, the redox-induced dynamic structural changes in (sp^2 -carbon ligand)-(multiple metals)-(sp^2 -carbon ligand) systems are not well understood. Now, tetra-palladium sandwich complexes have been described that exhibit redox-switchable assembly of the metal centres or coupling of the ligands.

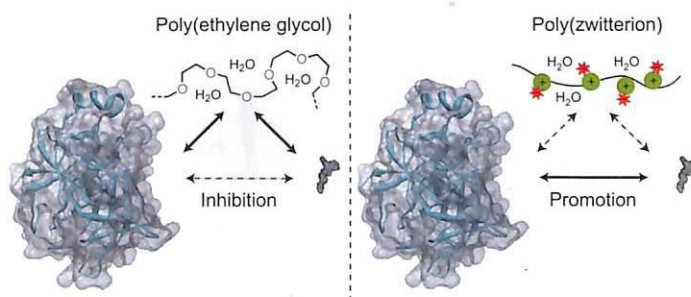


59 Poly(zwitterionic)protein conjugates offer increased stability without sacrificing binding affinity or bioactivity

Andrew J. Keefe and Shaoyi Jiang

Poly(ethylene glycol) conjugates have been widely used to improve the stability of proteins for use as therapeutics, but this stability comes at the expense of binding affinity. Here, poly(carboxybetaine) — a zwitterionic polymer — is shown to provide increased stability while also enhancing binding due to its super hydrophilic nature.

→N&V p13

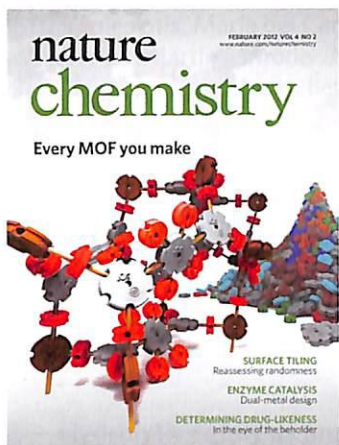


64 Erratum

IN YOUR ELEMENT

66 Oxygen origins

Mark H. Thiemens

**COVER IMAGE**

Randall Snurr and co-workers describe a computational approach for simulating every possible metal-organic framework (MOF) that can be built from a given set of building blocks (metal clusters and organic ligands) — represented conceptually on the cover using Tinkertoys. Some of the properties of MOFs can also be simulated to uncover structure-property relationships or materials suitable for specific applications. The MOF shown on the cover was identified for its methane storage capacity — a property that was subsequently confirmed experimentally.

Article p83

IMAGE: CHRISTOPHER E. WILMER

COVER DESIGN: ALEX WING

ON THE COVER**Surface tiling**

Reassessing randomness

Article p112

Enzyme catalysis

Dual-metal design

Article p118

Determining drug-likeness

In the eye of the beholder

Article p90

EDITORIAL

67 In praise of posters

RESEARCH HIGHLIGHTS

68 Our choice from the recent literature

BLOGROLL

69 Better by design

NEWS & VIEWS71 **Small-molecule libraries: Naturally inspired oligomers**

Jeffrey Aubé

72 **Laser control: Manipulating molecules**

Katharine Moore and Herschel Rabitz

74 **Molecular solids: Co-crystals give light a tune-up**

James D. Wuest

75 **Neurochemistry: Lighting up with azobenzenes**

G. Andrew Woolley

77 **Mechanochemistry: Measuring the force of sound**

Pedro Cintas and Giancarlo Cravotto

79 **DNA nanotechnology: The world's smallest assembly line**

Greg van Anders and Sharon C. Glotzer

80 **Dynamic materials: The chemistry of self-healing**

Marek W. Urban



nature publishing group

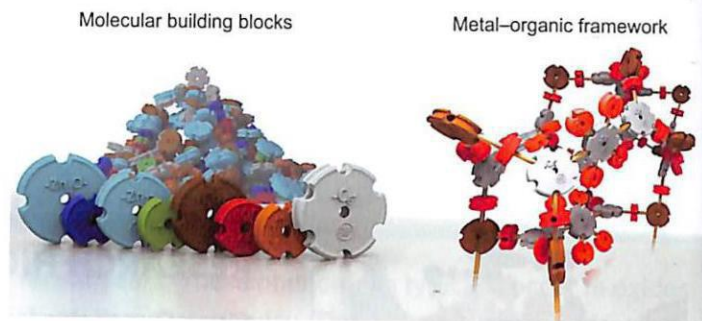
Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group (Porters South, 4 Crinan Street, London N1 9XW, UK). Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, Fl 9, New York, NY, 10013-1917, US. Telephone: +1(212) 726-9200. Fax: +1(212) 696-9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to - North America: Nature Chemistry, Subscription Dept, PO Box 5054, Brentwood, TN 37024-5054, USA. Outside North America: Subscriptions Department, Brunel Road, Basingstoke, Hants RG21 6XS, UK. Telephone: +44 (0)1256 329242; Fax: +44 (0)1256 812358. Annual subscription rates: US/Canada US\$3520, Canada add 5% GST (institutional/corporate), US\$999, Canada add 5% GST (individual making personal payment); UK/Rest of World (excluding Europe and Japan) £1806 (institutional/corporate), £51 (individual making personal payment); Europe €2795 (institutional/corporate), €79 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group, c/o Mercury Airfreight International Ltd, 365 Blair Road, Avenel, NJ 07001, USA. Periodicals postage is paid at Rahway, NJ. Postmaster: send address changes to Nature Chemistry, c/o Mercury Airfreight International, 365 Blair Road, Avenel, NJ, USA. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription information is available at <http://www.nature.com/naturechemistry>. Postmaster: send address changes to Nature Chemistry Subscriptions Department, Brunel Road, Basingstoke, Hants RG21 6XS, UK or Nature Chemistry Subscriptions Department PO Box 5054, Brentwood, TN 37024-5054, USA. © 2012 Macmillan Publishers Limited. All rights reserved.

ARTICLES

83 Large-scale screening of hypothetical metal-organic frameworks

Christopher E. Wilmer, Michael Leaf, Chang Yeon Lee, Omar K. Farha, Brad G. Hauser, Joseph T. Hupp and Randall Q. Snurr

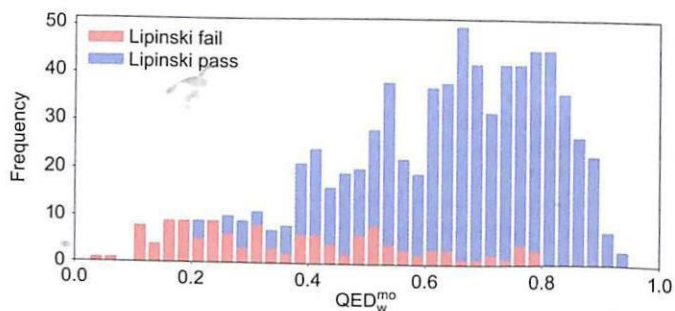
Chemists are able to prepare a wide variety of metal-organic frameworks by connecting together inorganic and organic building blocks of all sorts of shapes and properties. Now, a large-scale computational screening approach that simulates thousands of hypothetical MOFs from previously synthesized ones can help identify just which materials should be pursued.



90 Quantifying the chemical beauty of drugs

G. Richard Bickerton, Gaia V. Paolini, J r my Besnard, Sorel Muresan and Andrew L. Hopkins

Drug-likeness is a key consideration when selecting compounds during the early stages of drug discovery, but its evaluation in absolute terms does not adequately reflect the spectrum of compound quality. Here, an intuitive and transparent quantitative measure of drug-likeness is proposed that attempts to capture the abstract notion of aesthetics in medicinal chemistry.

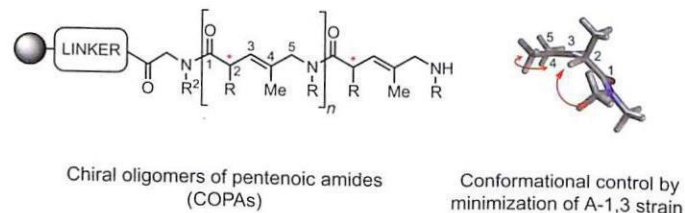


99 A biomimetic polyketide-inspired approach to small-molecule ligand discovery

Claudio Aquino, Mohosin Sarkar, Michael J. Chalmers, Kimberly Mendes, Thomas Kodadek and Glenn C. Micalizio

The design and synthesis of a family of chiral and conformationally constrained oligomers is described. Asymmetric synthesis of the monomers is presented and the preparation of a 160,000-member library of diverse tetramers via split-and-pool methods is discussed. From this library, a non-covalent ligand to the DNA-binding domain of p53 was discovered.

→N&V p71

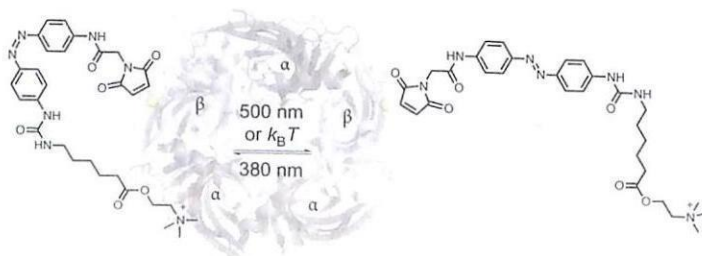


105 Optochemical control of genetically engineered neuronal nicotinic acetylcholine receptors

Ivan Tochitsky, Matthew R. Banghart, Alexandre Mour t, Jennifer Z. Yao, Benjamin Gaub, Richard H. Kramer and Dirk Trauner

Light-sensitive ligands can be used to regulate neurobiological receptors with high spatiotemporal precision. Here, the optochemical control of neuronal nicotinic acetylcholine receptors, using both photoswitchable tethered agonists and antagonists, is described. These rationally designed hybrid photoreceptors will facilitate the investigation of the physiological and pathological functions of nicotinic receptors in the brain.

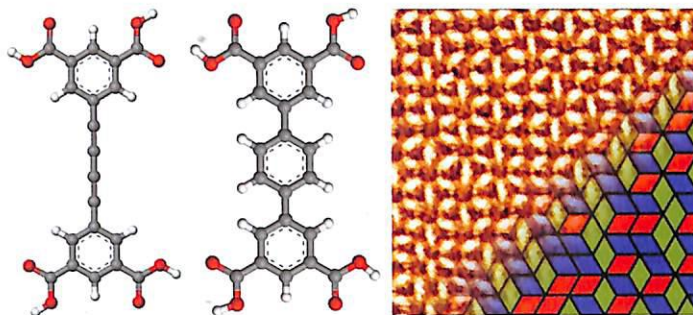
→N&V p75



112 Broken symmetry and the variation of critical properties in the phase behaviour of supramolecular rhombus tilings

Andrew Stannard, James C. Russell, Matthew O. Blunt, Christos Salesiotis, María del Carmen Giménez-López, Nassiba Taleb, Martin Schröder, Neil R. Champness, Juan P. Garrahan and Peter H. Beton

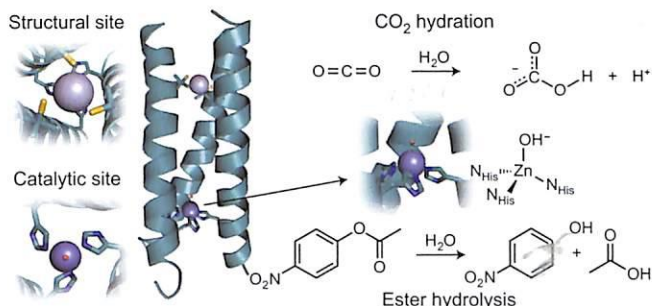
Assembling random networks on a surface is an intriguing — and potentially useful — phenomenon, but partial order is difficult to control. Researchers have now altered two-dimensional tetracarboxylic acid networks through only small chemical changes. This phase behaviour reveals that entropy, alongside energy, plays a crucial role in the order-disorder balance.



118 Hydrolytic catalysis and structural stabilization in a designed metalloprotein

Melissa L. Zastrow, Anna F. A. Peacock, Jeanne A. Stuckey and Vincent L. Pecoraro

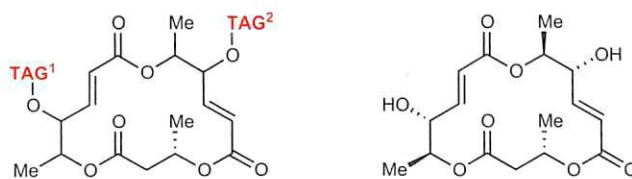
A designed metalloprotein containing an Hg(II) trithiolate centre that provides structural stability, and a Zn(II) tris histidine centre serving as a catalytic mimic of carbonic anhydrase, is shown to display rates that are comparable to the natural enzyme for ester hydrolysis and CO₂ hydration.



124 Binary fluororous tagging enables the synthesis and separation of a 16-stereoisomer library of macrophelides

Dennis P. Curran, Mantosh K. Sinha, Kai Zhang, Jesse J. Sabatini and Dae-Hyun Cho

A 16-member diastereoisomer library known to contain macrophelides A and E is synthesized as a mixture with the aid of a new encoding strategy for fluororous mixture synthesis. A simple process of sequential demixing and tag removal provides each of the isomers in individual, pure form. Analysis of the other library members ultimately leads to a structural reassignment for macrophelide D.



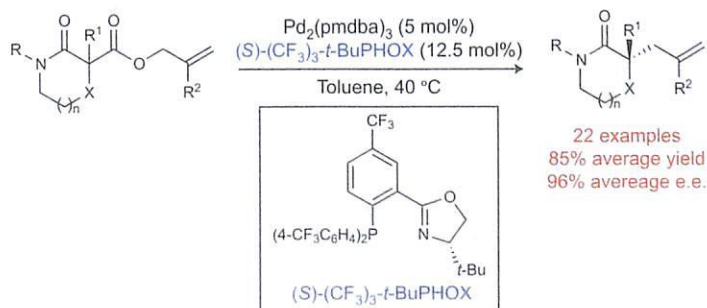
16 stereoisomers in a single mixture
Fluororous tags 1,2 share the same R_F groups

3S,8R,9S,14R,15S
macrophelide A

130 Enantioselective construction of quaternary N-heterocycles by palladium-catalysed decarboxylative allylic alkylation of lactams

Douglas C. Behenna, Yiyang Liu, Taiga Yurino, Jimin Kim, David E. White, Scott C. Virgil and Brian M. Stoltz

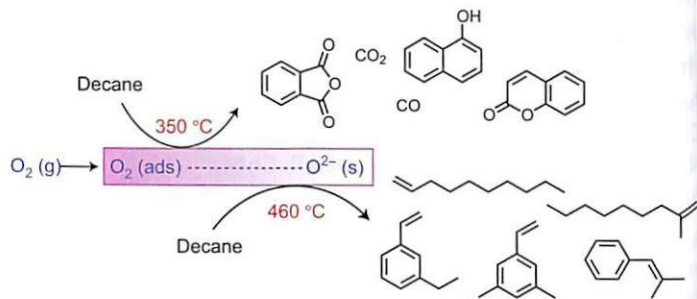
Nitrogen-containing heterocycles are ubiquitous in natural products, pharmaceuticals and in materials science. Here, the stereoselective synthesis of a wide array of structurally diverse, functionalized lactams by palladium-catalysed enantioselective enolate alkylation is described.



134 Non-lattice surface oxygen species implicated in the catalytic partial oxidation of decane to oxygenated aromatics

Sivaram Pradhan, Jonathan K. Bartley, Donald Bethell, Albert F. Carley, Marco Conte, Stan Golunski, Matthew P. House, Robert L. Jenkins, Rhys Lloyd and Graham J. Hutchings

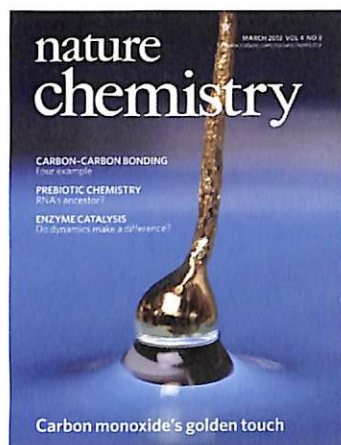
Mixed-metal oxide catalysts oxidize hydrocarbons into CO and CO₂ through surface oxygen species that have yet to form lattice oxide ions. The one-step oxidation of decane into a range of oxygenated aromatics by a fully oxidized iron molybdate catalyst has now revealed that these species can also be involved in selective oxygen insertion.



IN YOUR ELEMENT

140 Cool as helium

Christine Herman

**COVER IMAGE**

The cover image shows the gold electrode used by Rodriguez, Kwon and Koper in their study of gold-catalysed alcohol oxidation. The electrode is in the 'hanging-meniscus configuration' and is immersed in an aqueous solution.

When modified with carbon monoxide, the gold surface catalyses the oxidation of certain alcohols in alkaline media. Remarkably, the carbon monoxide acts as a reaction promoter, in contrast to its usual role as a poison.

Article p177

IMAGE: MARC DE HAAN,
PARAMACONI RODRIGUEZ, MARC KOPER

COVER DESIGN: ALEX WING

ON THE COVER

Carbon-carbon bonding
Four example
Article p195; N&V p154

Prebiotic chemistry
RNA's ancestor?
Article p183

Enzyme catalysis
Do dynamics make a difference?
Editorial p141;
Perspectives p161; p169

EDITORIAL

141 Of polemics and progress

THESIS

142 Zen and the art of molecules
Michelle Franci

RESEARCH HIGHLIGHTS

146 Our choice from the recent literature

BLOGROLL

147 For safety's sake

NEWS & VIEWS

149 **Surface chemistry: Making the right connections**
Neil R. Champness

150 **Chirality: Spin and gravity give a helping hand**
Laurence D. Barron

152 **Radiochemistry: Flipping fluoride's reactivity**
Véronique Gouverneur

154 **Quantum chemistry: Quadruply bonded carbon**
Jörg Grunenberg

155 **Nucleic acid hybridization: Robust sequence discrimination**
Grégoire Altan-Bonnet and Fred Russell Kramer

157 **Ultrafast chemical physics: In search of molecular movies**
Julia A. Weinstein and Neil T. Hunt

159 **Metamaterials: Turning a negative into a positive**
Jackie Y. Ying



nature publishing group

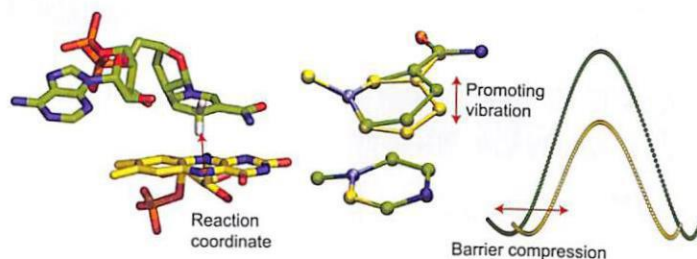
Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group (Porters South, 4 Crinan Street, London N1 9XW, UK) Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK Telephone: +44 (0)20 7833 4000 Fax: +44 (0)20 7843 4563 Email nchem@nature.com North American Advertising: Nature Chemistry, 75 Varick Street, Fl 9, New York, NY, 10013-1917, US Telephone: +1(212) 726-9200 Fax: +1(212) 696-9006 European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK Telephone: +44 (0)20 7833 4000 Fax: +44 (0)20 7843 4749 New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Chemistry, Subscription Dept, PO Box 5054, Brentwood, TN 37024-5054, USA Outside North America Subscriptions Department, Brunel Road, Basingstoke, Hants RG21 6XS, UK Telephone: +44 (0)1256 329242 Fax: +44 (0)1256 812358 Annual subscription rates: US/Canada US\$3520, Canada add 5% GST (institutional/corporate) US\$99, Canada add 5% GST (individual making personal payment), UK/Rest of World (excluding Europe and Japan) £1806 (institutional/corporate), £51 (individual making personal payment); Europe €2795 (institutional/corporate), €79 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan Telephone: +81 3 3267 8751 For single back issue prices: contact the publisher. Nature Chemistry (ISSN 1755-4330) is published monthly by Nature Publishing Group, c/o Mercury Airfreight International Ltd, 365 Blair Road, Avenel, NJ, USA Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. Postmaster: send address changes to Nature Chemistry Subscriptions Department, Brunel Road, Basingstoke, Hants, RG21 6XS, UK or Nature Chemistry Subscriptions Department PO Box 5054, Brentwood, TN 37024-5054, USA. © 2012 Macmillan Publishers Limited. All rights reserved.

PERSPECTIVES

161 Good vibrations in enzyme-catalysed reactions

Sam Hay and Nigel S. Scrutton

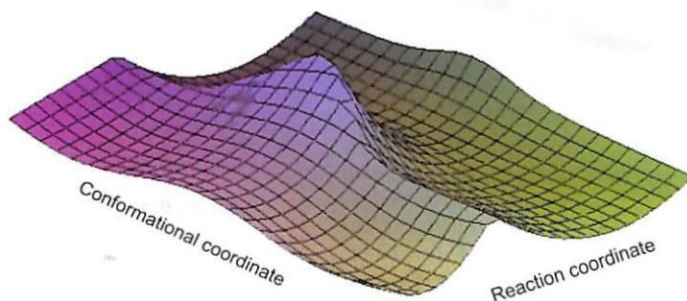
This Perspective discusses contemporary ideas for enzymatic reactions that invoke a role for fast 'promoting' (or 'compressive') motions or vibrations that, in principle, can facilitate enzyme-catalysed reactions. With an emphasis on hydrogen-transfer reactions, experimental, theoretical and computational approaches that have lent evidence to this controversial hypothesis are discussed.



169 Taking Ockham's razor to enzyme dynamics and catalysis

David R. Glowacki, Jeremy N. Harvey and Adrian J. Mulholland

Enzyme-catalysed reactions can involve significant quantum tunnelling and show kinetic isotope effects with complex temperature dependences. In this Perspective, reaction dynamics and enzyme catalysis are linked to transition-state-theory frameworks. It is shown that a multi-state model using standard transition-state theory can account for complex experimental data without invoking a role for enzyme dynamics.

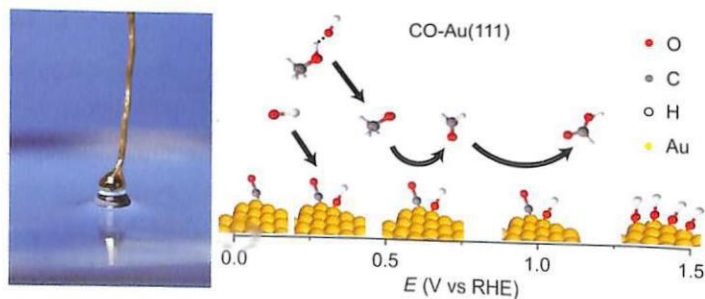


ARTICLES

177 The promoting effect of adsorbed carbon monoxide on the oxidation of alcohols on a gold catalyst

Paramaconi Rodriguez, Youngkook Kwon and Marc T. M. Koper

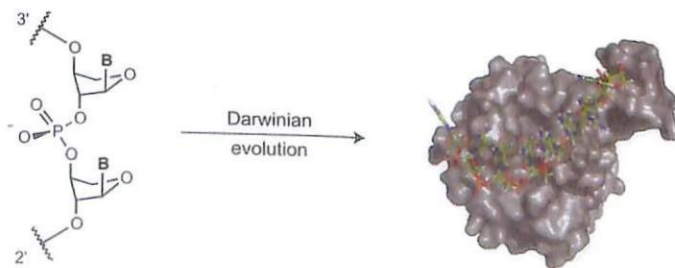
Adsorbed carbon monoxide typically acts to poison the oxidation of alcohols on heterogeneous catalysts and electrocatalysts. Here, it is shown that carbon monoxide that has been adsorbed irreversibly on a Au(111) surface can act as a promoter for this process by enhancing the scission of C-H bonds in the alcohol to yield the corresponding aldehyde.



183 Darwinian evolution of an alternative genetic system provides support for TNA as an RNA progenitor

Hanyang Yu, Su Zhang and John C. Chaput

The pre-RNA-world hypothesis postulates that RNA was preceded in the evolution of life by a simpler genetic material. Here, Darwinian evolution methods were used to generate a threose nucleic acid (TNA) aptamer. This result provides evidence that TNA could have served as an ancestral genetic system during an early stage of life.



188 Structure and catalytic properties of the most complex intergrown zeolite ITQ-39 determined by electron crystallography

Tom Willhammar, Junliang Sun, Wei Wan, Peter Oleynikov, Daliang Zhang, Xiaodong Zou, Manuel Moliner, Jorge Gonzalez, Cristina Martínez, Fernando Rey and Avelino Corma

Solving the structure of zeolites is often challenging because of their small particle size. Now, electron crystallography reveals the structure of a family of complex intergrown zeolite materials. These zeolites contain unique pairwise 12-ring channels that intersect with 10-ring channels, and are promising catalysts for converting gasoline into diesel fuel.

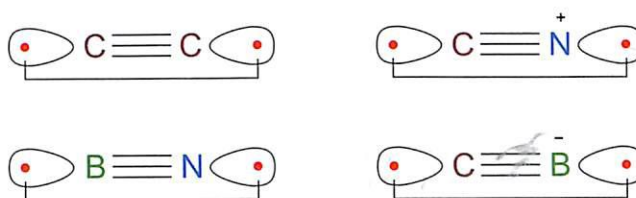


195 Quadruple bonding in C₂ and analogous eight-valence electron species

Sason Shaik, David Danovich, Wei Wu, Peifeng Su, Henry S. Rzepa and Philippe C. Hiberty

The bonding order of multiply bonded main-group elements is conventionally thought to be limited to triple bonds. Now, using high-level theoretical methods, it is shown that C₂ and its isoelectronic molecules CN⁺, BN and CB⁻ are quadruply bonded, featuring not only one σ - and two π -bonds, but also one weak 'inverted' bond.

→N&V p154

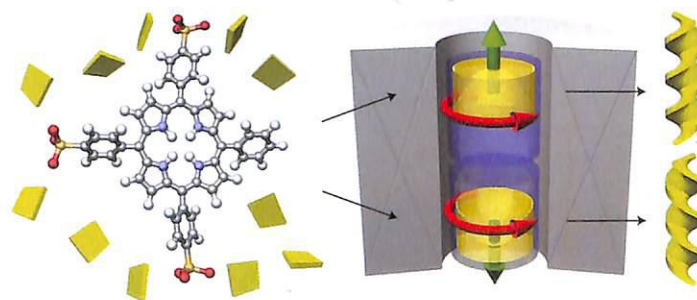


201 Selection of supramolecular chirality by application of rotational and magnetic forces

N. Micali, H. Engelkamp, P. G. van Rhee, P. C. M. Christianen, L. Monsù Scolaro and J. C. Maan

It is shown here that the proper combination of physical forces can induce chirality during the self-assembly of achiral molecules. Rotation and effective gravity created by high magnetic fields during the nucleation phase, together with the magnetic alignment of the nanoaggregates initially formed, control the enantioselectivity of porphyrin assemblies.

→N&V p150

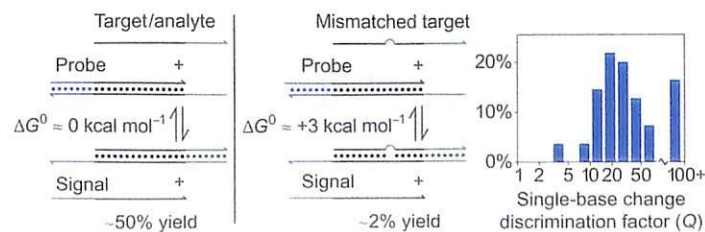


208 Optimizing the specificity of nucleic acid hybridization

David Yu Zhang, Sherry Xi Chen and Peng Yin

High-fidelity pairing of nucleic acid polymers is important in the development of sensors and for the application of DNA nanotechnology. Here, a set of hybridization probes is described that discriminates single-base changes with high specificity. The probes function robustly across many different temperatures, salinities and nucleic acid concentrations.

→N&V p155

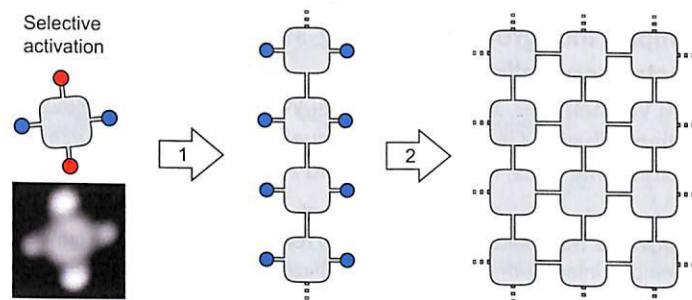


215 Controlling on-surface polymerization by hierarchical and substrate-directed growth

L. Lafferentz, V. Eberhardt, C. Dri, C. Africh, G. Comelli, F. Esch, S. Hecht and L. Grill

The bottom-up construction of covalently linked molecular architectures on surfaces has recently been demonstrated, but only rather simple structures can be obtained in such one-step connection processes. A sequential approach has now been used to induce the selective connection of molecules with a programmed reactivity, enabling network formation with high selectivity.

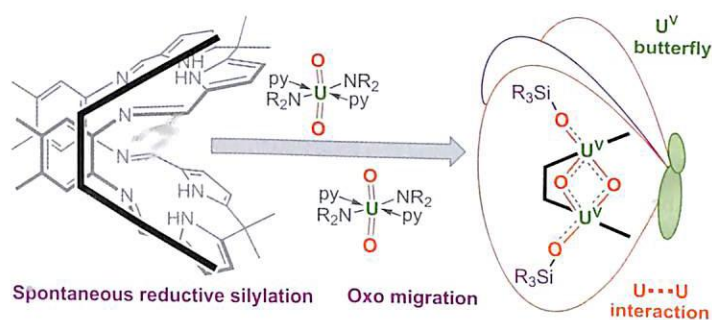
→N&V p149



221 Strongly coupled binuclear uranium-oxo complexes from uranyl oxo rearrangement and reductive silylation

Polly L. Arnold, Guy M. Jones, Samuel O. Odoh, Georg Schreckenbach, Nicola Magnani and Jason B. Love

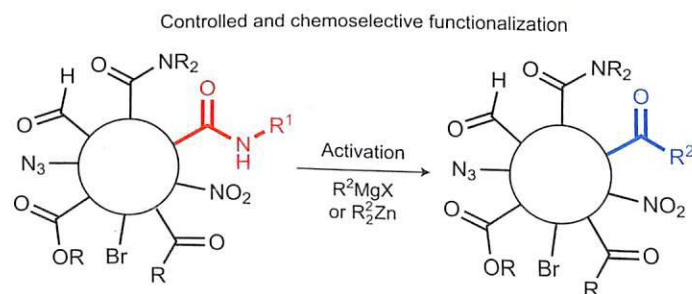
The oxo groups in the common *trans*-uranyl ion — present in the majority of known uranium compounds — are linear and inert. Now, a new reduced binuclear uranium-dioxo compound with very strong metal coupling and remarkable air stability has been formed through oxo migration and silylation.



228 Chemoselective synthesis of ketones and ketimines by addition of organometallic reagents to secondary amides

William S. Bechara, Guillaume Pelletier and André B. Charette

To achieve chemoselective additions of organometallics to carbonyls, it is important to consider the combination of acylating agent and organometallic as a reactive pair rather than either one in isolation. Here, a chemoselective, controlled and general methodology for the conversion of secondary amides to ketones and ketimines is described.

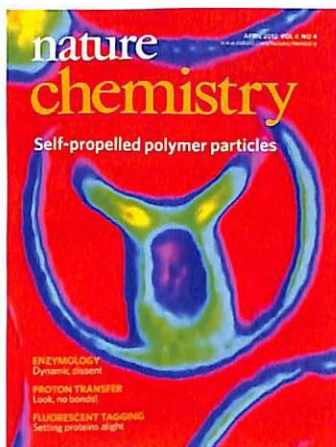


235 Erratum

IN YOUR ELEMENT

236 The deeds to deuterium

Dan O'Leary

**COVER IMAGE**

A team of researchers from Radboud University Nijmegen in The Netherlands have assembled a supramolecular system that is capable of self-propulsion. Platinum nanoparticles engulfed into bowl-shaped polymer vesicles — called stomatocytes — catalyse the decomposition of hydrogen peroxide, which serves as a fuel. The cover shows the colour-coded intensity profile of the opening of a stomatocyte, through which the water and oxygen formed in the decomposition process escape, thereby propelling the assembly.

Article p268; N&V p247

IMAGE: DANIELA WILSON

COVER DESIGN: ALEX WING

ON THE COVER

Enzymology
Dynamic dissent
Article p292

Proton transfer
Look, no bonds!
Article p323

Fluorescent tagging
Setting proteins alight
Article p298; N&V p248

THESIS

- 237 **Chemical intuition or chemical institution?**
Bruce Gibb

BOOKS & ARTS

- 239 **The Quest for the Cure: The Science and Stories Behind the Next Generation of Medicines** by Brent R. Stockwell
Reviewed by David Kroll

**INTERVIEW**

- 240 **A chronicler of chemistry**
Interview with Thomas Hager

RESEARCH HIGHLIGHTS

- 242 **Our choice from the recent literature**

BLOGROLL

- 243 **Scary chemicals**

NEWS & VIEWS

- 244 **Two-dimensional materials: Polymers stripped down**
Fernando J. Uribe-Romo and William R. Dichtel
- 245 **Ion dynamics: Wired-up water**
David Chandler, Christoph Dellago and Phillip Geissler
- 247 **Polymer vesicles: Autonomous propulsion**
Jonathan Howse
- 248 **Protein labelling: Playing tag with proteins**
Dante W. Romanini and Virginia W. Cornish
- 250 **Zeolite nanosystems: Imagination has no limits**
Javier Pérez-Ramírez
- 252 **Transparent conducting materials: Flexibility with a metallic skin**
Hideo Hosono
- 253 **Catalysis: Temporary intramolecularity**
Kian L. Tan



nature publishing group

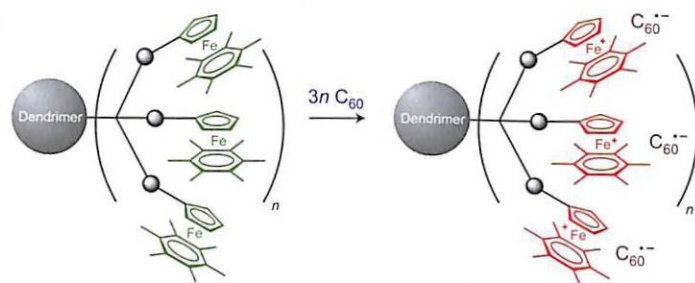
Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com North American Advertising: *Nature Chemistry*, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: *Nature Chemistry*, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2012 US annual subscription price is \$4412 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. UK/Rest of World (excluding Europe and Japan) £2264 (institutional/corporate), £55 (individual making personal payment). Europe €3503 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica NY 11431. *Nature Chemistry* is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to *Nature Chemistry*, Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Int'l 365 Blair Rd, Avenel, NJ 07001. Reprints: *Nature Chemistry* Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the *Nature Chemistry* homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

REVIEW ARTICLE

255 Electron-transfer processes in dendrimers and their implication in biology, catalysis, sensing and nanotechnology

Didier Astruc

Redox sites can be incorporated within dendrimers — highly branched, well-defined macromolecules — at specific locations, such as their core, branching points, periphery or inner cavities. These dendrimers can serve to functionalize surfaces, and electron-transfer processes at their redox sites show promise for various applications ranging from metallo-protein modelling to sensing to catalysis.



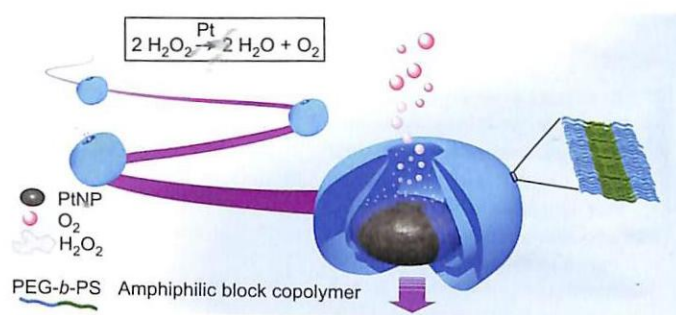
ARTICLES

268 Autonomous movement of platinum-loaded stomatocytes

Daniela A. Wilson, Roeland J. M. Nolte and Jan C. M. van Hest

A supramolecular system has been assembled that moves autonomously in the presence of a molecular fuel. Platinum nanoparticles entrapped in a polymer stomatocyte — a bowl-shaped polymer vesicle — catalyse the decomposition of the molecular fuel, hydrogen peroxide. The resulting generation of water and oxygen gas induces a directional movement of the stomatocyte.

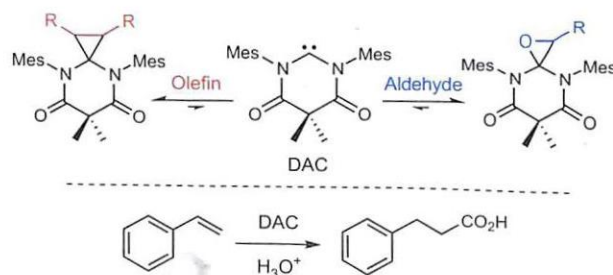
→N&V p247



275 Diamidocarbenes as versatile and reversible [2+1] cycloaddition reagents

Jonathan P. Moerdyk and Christopher W. Bielawski

An isolable diamidocarbene is shown to participate in reversible [2+1] cycloadditions with a variety of both electron-deficient and electron-rich olefins and aldehydes. Subsequent hydrolysis of a N,N'-diamidocyclopropane derived from styrene afforded the corresponding linear carboxylic acid, effectively establishing a metal- and carbon monoxide-free, anti-Markovnikov olefin hydrocarboxylation reaction.

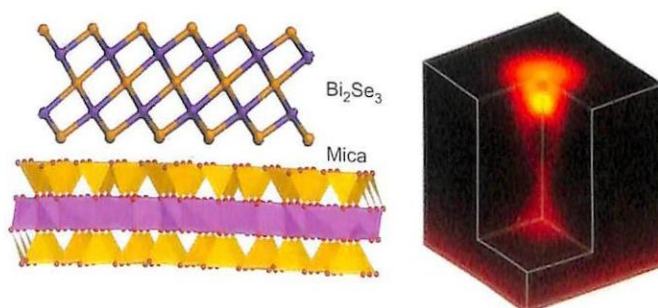


281 Topological insulator nanostructures for near-infrared transparent flexible electrodes

Hailin Peng, Wenhui Dang, Jie Cao, Yulin Chen, Di Wu, Wenshan Zheng, Hui Li, Zhi-Xun Shen and Zhongfan Liu

Transparent conductive electrodes are widely used in modern optoelectronic devices, but they are rarely transparent in the near-infrared, limiting their use. Nanostructured bismuth selenide, a topological insulator, is now shown to be a flexible near-infrared transparent electrode.

→N&V p252

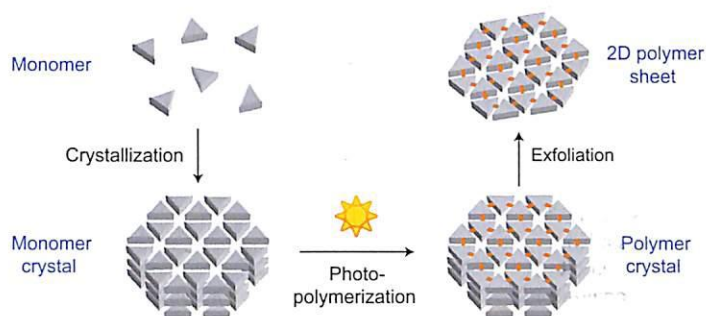


287 A two-dimensional polymer prepared by organic synthesis

Patrick Kissel, Rolf Erni, W. Bernd Schweizer, Marta D. Rossell, Benjamin T. King, Thomas Bauer, Stephan Götzinger, A. Dieter Schlüter and Junji Sakamoto

A two-dimensional polymer with internal periodicity has now been constructed. The procedure involves the rational molecular design of monomers, which first crystallize into a laminar lattice. A photo-induced polymerization then occurs laterally within each layer, and the resulting polymer crystals are subsequently delaminated into individual, free-standing two-dimensional polymers.

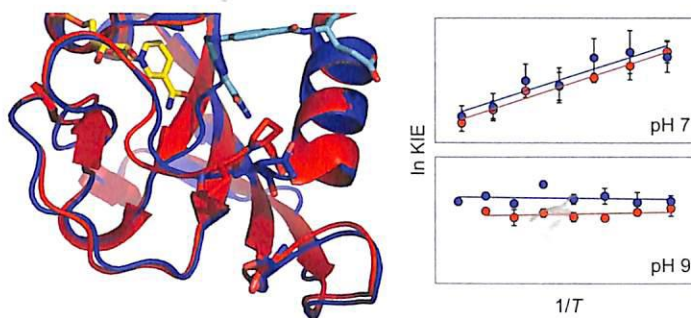
→N&V p244



292 Evidence that a 'dynamic knockout' in *Escherichia coli* dihydrofolate reductase does not affect the chemical step of catalysis

E. Joel Loveridge, Enas M. Behiry, Jiannan Guo and Rudolf K. Allemann

The connection between protein dynamics and catalysis is an issue of vigorous debate in enzymology. Conformational motions are known to be important for the physical steps in the catalytic cycle of dihydrofolate reductase, however, it is now reported that there is no evidence of a correlation between such motions and the actual chemical step, hydride transfer.

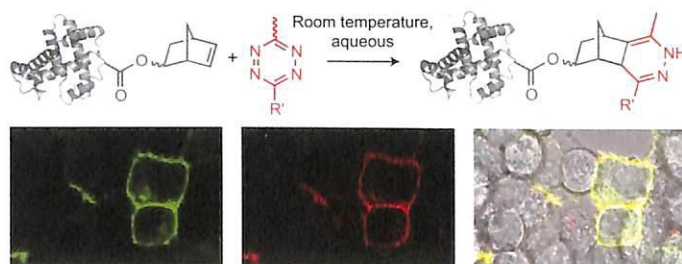


298 Genetically encoded norbornene directs site-specific cellular protein labelling via a rapid bioorthogonal reaction

Kathrin Lang, Lloyd Davis, Jessica Torres-Kolbus, Chungjung Chou, Alexander Deiters and Jason W. Chin

The site-specific incorporation of a norbornene amino acid into proteins via genetic code expansion, together with the synthesis of a series of tetrazine-based probes that exhibit turn-on fluorescence on their fast cycloaddition with norbornene, enables rapid protein labelling on mammalian cells.

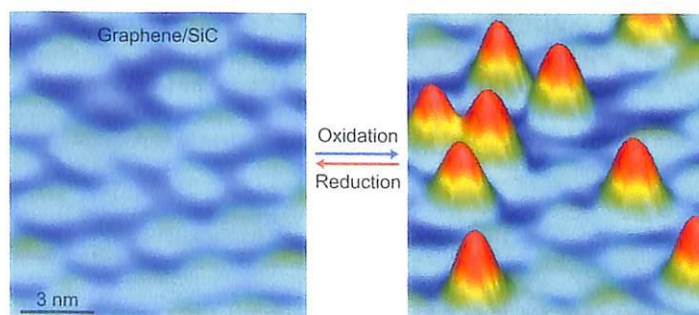
→N&V p248



305 Chemically homogeneous and thermally reversible oxidation of epitaxial graphene

Md. Zakir Hossain, James E. Johns, Kirk H. Bevan, Hunter J. Karmel, Yu Teng Liang, Shinya Yoshimoto, Kozo Mukai, Tatanori Koitaya, Jun Yoshinobu, Maki Kawai, Amanda M. Lear, Larry L. Kesmodel, Steven L. Tait and Mark C. Hersam

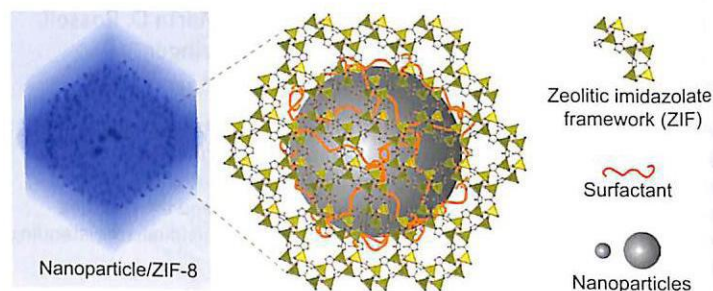
Graphene oxide produced via the standard Hummers method possesses a high degree of chemical inhomogeneity and limited reversibility. Now, it has been shown that an alternative ultra-high-vacuum approach for oxidizing epitaxial graphene yields uniform epoxy functionalization with thermal reversibility at temperatures as low as 260 °C.



310 Imparting functionality to a metal-organic framework by controlled nanoparticle encapsulation

Guang Lu, Shaozhou Li, Zhen Guo, Omar K. Farha, Brad G. Hauser, Xiaoying Qi, Yi Wang, Xin Wang, Sanyang Han, Xiaogang Liu, Joseph S. DuChene, Hua Zhang, Qichun Zhang, Xiaodong Chen, Jan Ma, Say Chye Joachim Loo, Wei D. Wei, Yanhui Yang, Joseph T. Hupp and Fengwei Huo

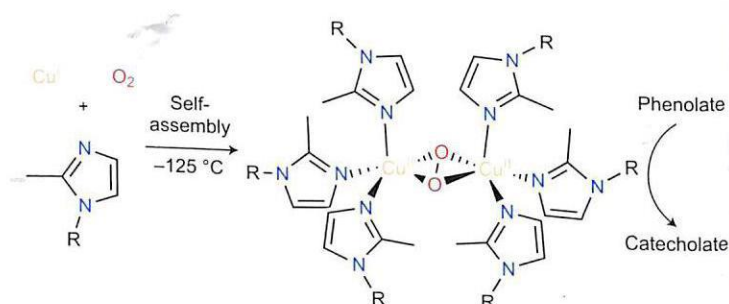
Surfactant-capped nanoparticles of various sizes, shapes and compositions have been completely enshrined within a metal-organic framework in a controlled, well-dispersed manner. The resulting hybrid materials exhibit active properties — catalytic, magnetic and optical — arising from the nanoparticles as well as sieving and orientation effects originating from the porous framework.



317 Self-assembly of the oxy-tyrosinase core and the fundamental components of phenolic hydroxylation

Cooper Citek, Christopher T. Lyons, Erik C. Wasinger and T. Daniel P. Stack

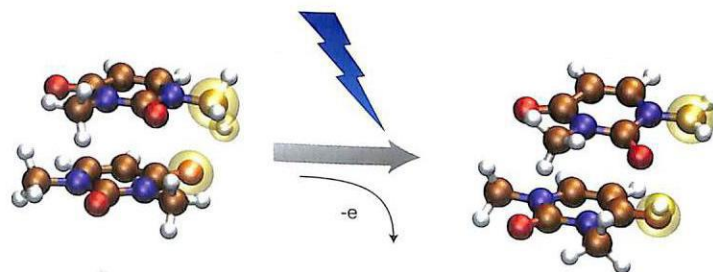
A functional active-site mimic of the oxy-tyrosinase enzyme forms through self-assembly of monodentate imidazole ligands, copper(I) and oxygen at $-125\text{ }^{\circ}\text{C}$. The fidelity of this copper-dioxygen complex to the native enzyme, its inherent stability and hydroxylation reactivity suggest that an organizational role of the protein matrix suffices to realize function.



323 Ionization of dimethyluracil dimers leads to facile proton transfer in the absence of hydrogen bonds

Amir Golan, Ksenia B. Bravaya, Romas Kudirka, Oleg Kostko, Stephen R. Leone, Anna I. Krylov and Musahid Ahmed

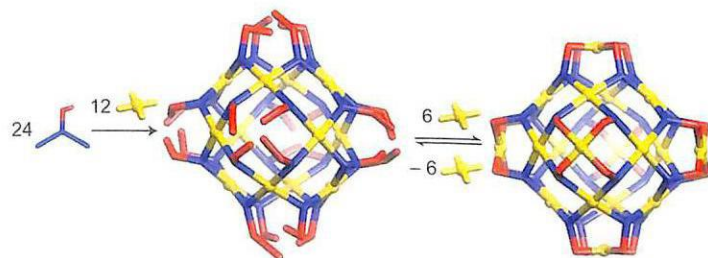
Proton transfer is usually considered in the context of hydrogen-bonding networks serving as proton-shuttling pathways. Now, an efficient ionization-induced proton transfer in the absence of hydrogen bonds has been observed in a model π -stacked system, the 1,3-dimethyluracil dimer.



330 An $M_{18}L_{24}$ stellated cuboctahedron through post-stellation of an $M_{12}L_{24}$ core

Qing-Fu Sun, Sota Sato and Makoto Fujita

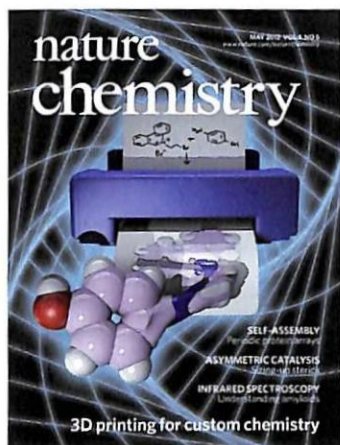
A molecular 'stellated polyhedron' with concave faces — constructed by extending the faces of its counterpart polyhedron until they intersect — has now been synthesized. Ligands that constitute the square faces of a metal-organic cuboctahedral cage were decorated with pendant side chains, which reversibly coordinate to additional metal centres to give rise to the stellated cage.



IN YOUR ELEMENT

334 Counting on copper

Tiberiu G. Moga



COVER IMAGE

There is growing interest in using 3D printing across a range of different industries, and Leroy Cronin and co-workers have now applied this technique to produce custom 'reactionware' for chemical reactions and analysis (shown conceptually on the cover). This approach enables active elements — such as catalysts — to be incorporated into the walls of printed vessels and also offers the opportunity to integrate components that facilitate the *in situ* analysis of a particular reaction. Article p349; News & Views p338

IMAGE: PHILIP KITSON

COVER DESIGN: ALEX WING

ON THE COVER

Self-assembly

Periodic protein arrays

Article p375; News & Views p346

Asymmetric catalysis

Sizing up sterics

Article p366; News & Views p344

Infrared spectroscopy

Understanding amyloids

Article p355; News & Views p339

BOOKS & ARTS

- 335 **Roald Hoffmann on the Philosophy, Art and Science of Chemistry**
Edited by Jeffrey Kovac and Michael Weisberg
 Reviewed by Ashutosh S. Jogalekar

RESEARCH HIGHLIGHTS

- 336 Our choice from the recent literature

BLOGROLL

- 337 Arnie and artemisinin

NEWS & VIEWS

- 338 **Custom labware: Chemical creativity with 3D printing**
 R. Daniel Johnson
- 339 **Infrared spectroscopy: Mapping protein-protein contacts**
 Minhaeng Cho
- 341 **Total synthesis: Welwitindolinone is well worth it**
 John L. Wood
- 343 **Main group chemistry: A heavier-element ketone at last**
 Philip P. Power
- 344 **Asymmetric catalysis: Correlating sterics in catalysis**
 Scott J. Miller
- 346 **Self-assembly: Proteins on parade**
 John C. Sinclair
- 347 **Magnetic anisotropy: The orientation is in the details**
 Muralee Murugesu



nature publishing group

Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2012 US annual subscription price is \$4412 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. UK/Rest of World (excluding Europe and Japan) £2264 (institutional/corporate), £55 (individual making personal payment), Europe €3503 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica NY 11431. Nature Chemistry is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to Nature Chemistry, Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

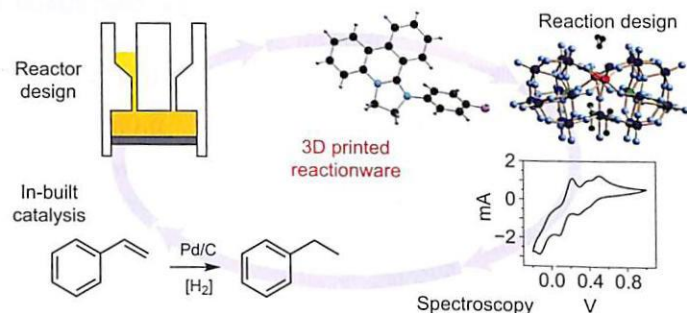
ARTICLES

349 Integrated 3D-printed reactionware for chemical synthesis and analysis

Mark D. Symes, Philip J. Kitson, Jun Yan, Craig J. Richmond, Geoffrey J. T. Cooper, Richard W. Bowman, Turlif Vilbrandt and Leroy Cronin

A low-cost 3D printer is used to combine chemical reactions and the reactor to produce an active 'reactionware' system for organic and inorganic synthesis. Active elements such as catalysts can be incorporated into the walls of printed reactors, and other printed-in components that enable electrochemical and spectroscopic analysis can also be included.

→N&V p338

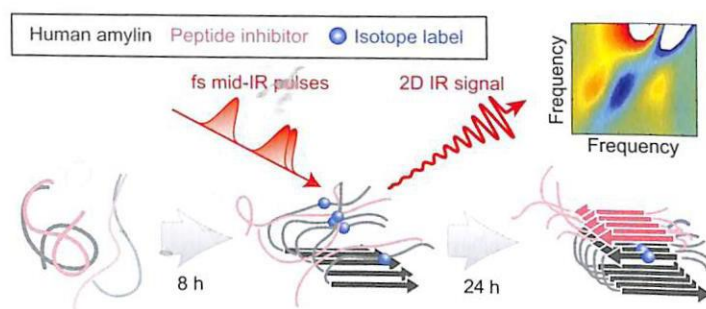


355 Two-dimensional infrared spectroscopy reveals the complex behaviour of an amyloid fibril inhibitor

Chris T. Middleton, Peter Marek, Ping Cao, Chi-cheng Chiu, Sadanand Singh, Ann Marie Woys, Juan J. de Pablo, Daniel P. Raleigh and Martin T. Zanni

Molecular inhibitors of amyloid formation could help combat Alzheimer's disease, type 2 diabetes, and other major human diseases. Here, two-dimensional infrared spectroscopy and residue-specific isotope labelling are used to obtain detailed structural information on amyloid-inhibitor complexes. The unexpected behaviour observed helps to explain the moderate activity of the inhibitor studied.

→N&V p339

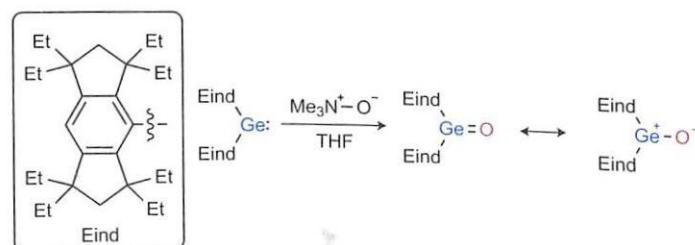


361 A stable germanone as the first isolated heavy ketone with a terminal oxygen atom

Liangchun Li, Tomohide Fukawa, Tsukasa Matsuo, Daisuke Hashizume, Hiroyuki Fueno, Kazuyoshi Tanaka and Kohei Tamao

Heavier analogues of ketones — containing a double bond between a group 14 element and oxygen — have so far not been isolated as stable compounds. Now, a stable monomeric germanone with a highly polarized Ge=O double bond has been isolated, stabilized by rigid bulky ligands.

→N&V p343

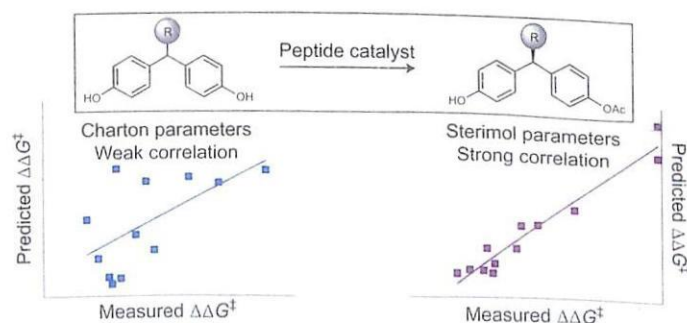


366 Multidimensional steric parameters in the analysis of asymmetric catalytic reactions

Kaid C. Harper, Elizabeth N. Bess and Matthew S. Sigman

Many parameters have been designed to describe steric size, but few have been able to explain consistently the selectivity of asymmetric catalytic reactions. Here, Sterimol parameters — originally used to develop quantitative structure-activity relationships in medicinal chemistry — have been used to quantify enantioselectivity in a diverse collection of asymmetric catalytic reactions.

→N&V p344

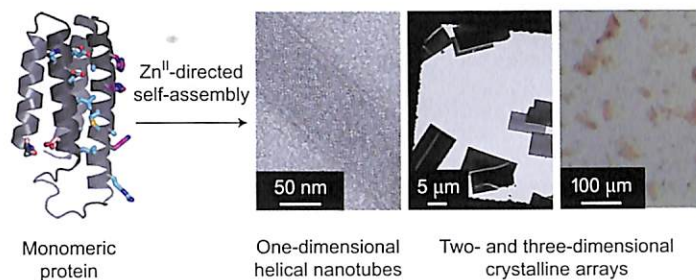


375 Metal-directed, chemically tunable assembly of one-, two- and three-dimensional crystalline protein arrays

Jeffrey D. Brodin, X. I. Ambroggio, Chunyan Tang, Kristin N. Parent, Timothy S. Baker and F. Akif Tezcan

The self-assembly of proteins into ordered yet dynamic nanoscale architectures is a crucial biological process and an inspiration for supramolecular chemistry, but has remained largely inaccessible synthetically. A monomeric protein has now been prepared that assembles with zinc ions into one-, two- and three-dimensional crystalline arrays with nano- and microscale order.

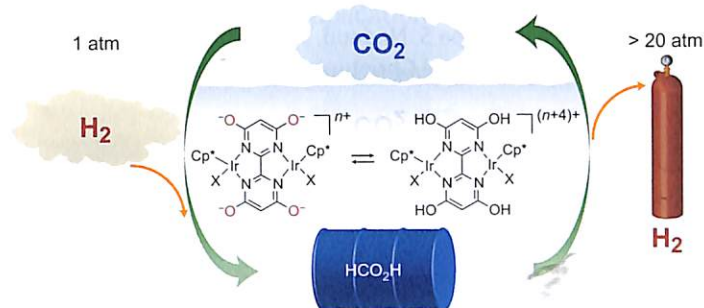
→N&V p346



383 Reversible hydrogen storage using CO₂ and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures

Jonathan F. Hull, Yuichiro Himeda, Wan-Hui Wang, Brian Hashiguchi, Roy Periana, David J. Szalda, James T. Muckerman and Etsuko Fujita

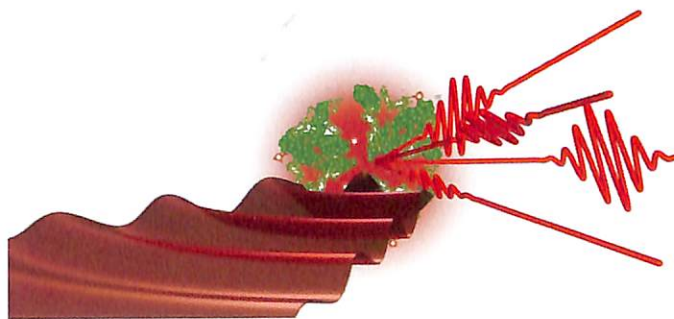
When operating at near-ambient conditions, using water as a solvent, a high-turnover iridium catalyst enables a reversible hydrogen storage system that uses carbon dioxide, formate and formic acid. Proton-responsive ligands in the catalyst allow it to be turned on or off by controlling the pH of the solution.



389 Elucidation of the timescales and origins of quantum electronic coherence in LHCII

Gabriela S. Schlau-Cohen, Akihito Ishizaki, Tessa R. Calhoun, Naomi S. Ginsberg, Matteo Ballottari, Roberto Bassi and Graham R. Fleming

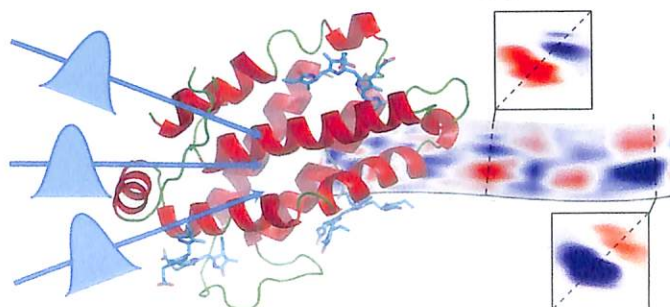
Quantum coherence has been observed in the major light-harvesting complex of photosystem II (LHCII) from green plants. By controlling the laser pulse polarization in two-dimensional electronic spectroscopy, signals from quantum coherence have been separated from other molecular processes, offering insight into the role of quantum coherence in photosynthetic light-harvesting.



396 Electronic coherence lineshapes reveal hidden excitonic correlations in photosynthetic light harvesting

Cathy Y. Wong, Richard M. Alvey, Daniel B. Turner, Krystyna E. Wilk, Donald A. Bryant, Paul M. G. Curmi, Robert J. Silbey and Gregory D. Scholes

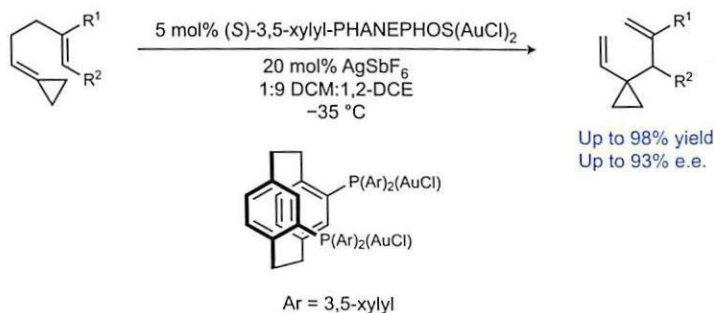
Quantum beating has been observed in photosynthetic systems, suggesting that energy-transfer processes in natural light harvesting could involve quantum effects. Now, extensive beating is found in the light-harvesting protein of a cryptophyte alga, and shown to be electronic. The implications of these observations on the free-energy surfaces and exciton delocalization were investigated.



405 A gold-catalysed enantioselective Cope rearrangement of achiral 1,5-dienes

Ryan J. Felix, Dieter Weber, Osvaldo Gutierrez, Dean J. Tantillo and Michel R. Gagné

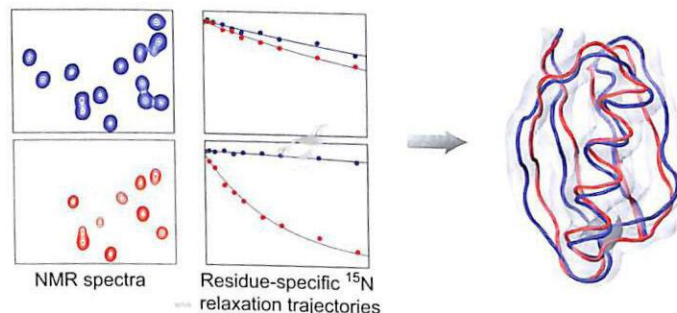
The Cope rearrangement has been known since the 1940s but, until now, no catalytic asymmetric variant has been reported. Here, a gold(I) catalyst is shown to induce an asymmetric Cope rearrangement of achiral 1,5-dienes containing a cyclopropylidene moiety to produce vinyl cyclopropanes in high yield and good to excellent enantioselectivities.



410 Protein fold determined by paramagnetic magic-angle spinning solid-state NMR spectroscopy

Ishita Sengupta, Philippe S. Nadaud, Jonathan J. Helmus, Charles D. Schwieters and Christopher P. Jaroniec

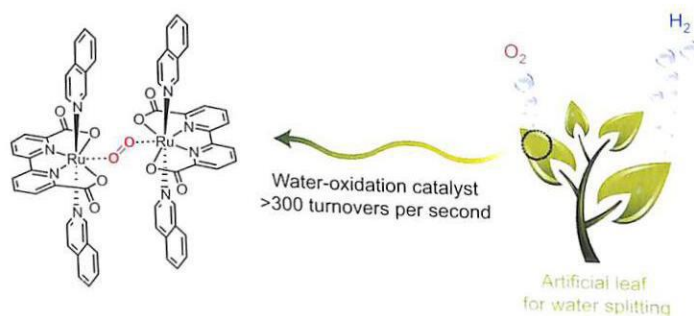
Despite recent progress, solving protein structures using solid-state NMR spectroscopy is not routine. Now, a method for the rapid determination of global protein fold is reported, based on measurements of ¹⁵N longitudinal paramagnetic relaxation enhancements in several protein variants modified with covalently attached cysteine-EDTA-Cu²⁺ tags.



418 A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II

Lele Duan, Fernando Bozoglian, Sukanta Mandal, Beverly Stewart, Timofei Privalov, Antoni Llobet and Licheng Sun

Increasing the efficiency and speed of the water-oxidation reaction is crucial to realizing light-driven water splitting. Now, a mononuclear ruthenium complex achieves fast water-oxidation catalysis with a high reaction rate of more than 300 turnovers per second, comparable to the activity of the oxygen-evolving complex in photosystem II.

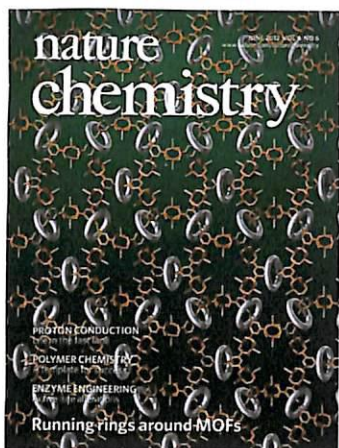


424 Addendum

IN YOUR ELEMENT

426 The four worlds of carbon

Simon H. Friedman

**COVER IMAGE**

A team of researchers from the University of Windsor in Canada have made a metal-organic framework (shown schematically on the cover) from [2]rotaxane linkers connected together with nodes comprising binuclear Cu(II) clusters. Heating the material under vacuum at 150 °C removes water molecules from the structure and creates void spaces that enable the crown ether rings of the rotaxane building blocks to rotate unimpeded. This work demonstrates how the dynamics associated with interlocked molecules can be integrated into a robust and ordered framework.

Article p456

COVER DESIGN: ALEX WING

ON THE COVER**Proton conduction**

Life in the fast lane

Article p461; News & Views p432

Polymer chemistry

A template for success

Article p491

Enzyme engineering

Active-site alterations

Article p478

THESIS

427 Chemical abstractions

Michelle Francl

RESEARCH HIGHLIGHTS

430 Our choice from the recent literature

BLOGROLL

431 Space dinosaurs!

NEWS & VIEWS

432 Proton conduction: Hopping along hydrogen bonds

Rodolphe Vuilleumier and Daniel Borgis

433 Flow chemistry: A light touch to a deadly problem

Kevin Booker-Milburn

435 Self-repairing polymers: Materials that heal themselves

Howard M. Colquhoun

437 Enzyme mimics: Halogen and chalcogen team up

Pierangelo Metrangolo and Giuseppe Resnati

438 Asymmetric catalysis: The power of pairing

Hajime Ito

440 Fluorescent sensors: Bright ideas

A. Prasanna de Silva

441 Alkaloid synthesis: Indolizidines with ease

Peter Shapland



nature publishing group

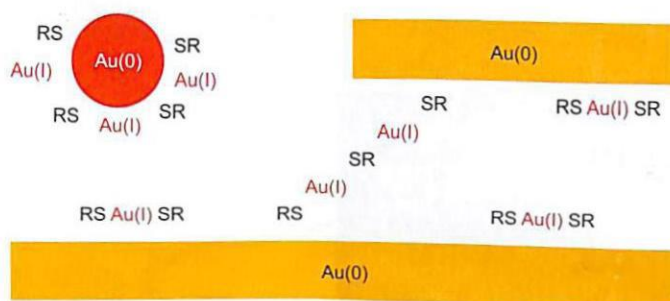
Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2012 US annual subscription price is \$4412 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. UK/Rest of World (excluding Europe and Japan) £2264 (institutional/corporate), £55 (individual making personal payment), Europe €3503 (institutional/corporate), €85 (individual making personal payment). Japan contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica, NY 11431. Nature Chemistry is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to Nature Chemistry, Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

REVIEW ARTICLE

443 The gold-sulfur interface at the nanoscale

Hannu Häkkinen

Thiolate-protected gold surfaces and interfaces are archetypal systems in various fields of current research in nanoscience, materials science, inorganic chemistry and surface science. Examples include self-assembled monolayers of organic molecules on gold, passivated gold nanoclusters and molecule-gold junctions. This Review discusses recent experimental and theoretical breakthroughs that highlight common features of gold-sulfur bonding in these systems.

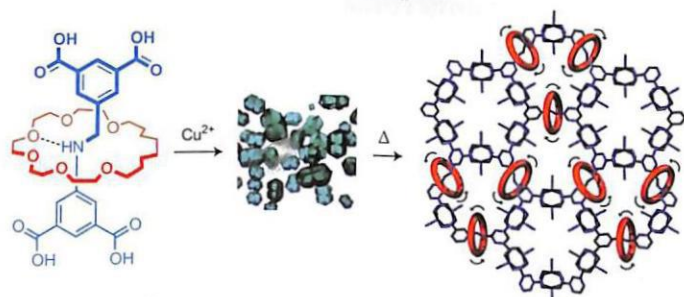


ARTICLES

456 Metal-organic frameworks with dynamic interlocked components

V. Nicholas Vukotic, Kristopher J. Harris, Kelong Zhu, Robert W. Schurko and Stephen J. Loeb

The dynamics of mechanically interlocked molecules such as catenanes and rotaxanes have been studied in solution as examples of rudimentary molecular switches and machines. A metal-organic framework with a [2]rotaxane as a building block demonstrates that such dynamic processes can also operate inside a solid-state material.

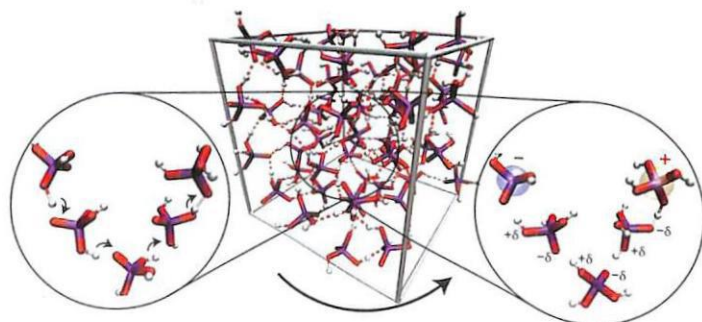


461 The mechanism of proton conduction in phosphoric acid

Linas Vilčiauskas, Mark E. Tuckerman, Gabriel Bester, Stephen J. Paddison and Klaus-Dieter Kreuer

Proton transport in phosphate-based systems is important in biology and clean energy technologies, and phosphoric acid, being the best known intrinsic proton conductor, represents an important model. *Ab initio* molecular dynamics simulations now reveal that the interplay between extended, polarized, hydrogen-bonded chains and a frustrated hydrogen-bond network gives rise to the high conductivity in liquid phosphoric acid.

→N&V p432

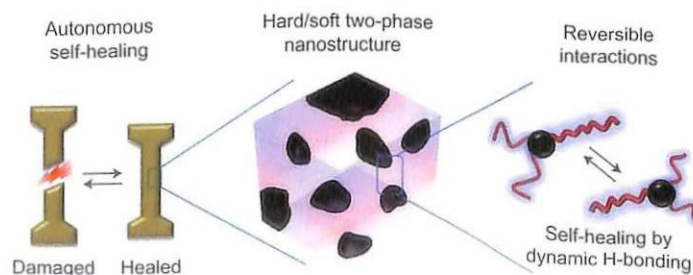


467 Multiphase design of autonomic self-healing thermoplastic elastomers

Yulin Chen, Aaron M. Kushner, Gregory A. Williams and Zhibin Guan

Polymer materials that could spontaneously heal like tissues in living systems would significantly improve the safety, lifetime, energy efficiency and environmental impact of man-made materials. Now, a general multiphase design of autonomic self-healing elastomeric materials that do not require the input of external energy or healing agents is reported.

→N&V p435

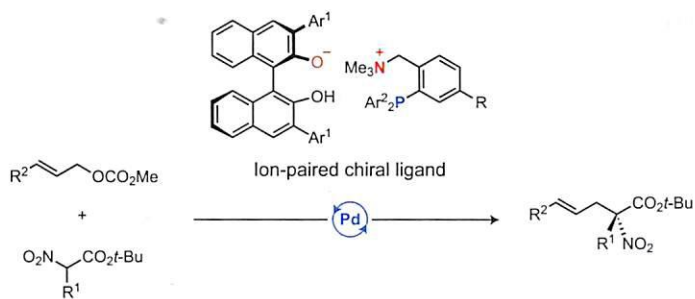


473 Ion-paired chiral ligands for asymmetric palladium catalysis

Kohsuke Ohmatsu, Mitsunori Ito, Tomoatsu Kunieda and Takashi Ooi

Rather than create a chiral catalyst by combining a chiral ligand with a metal, here an achiral phosphine ligand endowed with a cationic ammonium group is ion-paired with a chiral binaphtholate. A palladium catalyst based on this strategy is shown to be effective for highly enantioselective allylic alkylation of α -nitrocarboxylates.

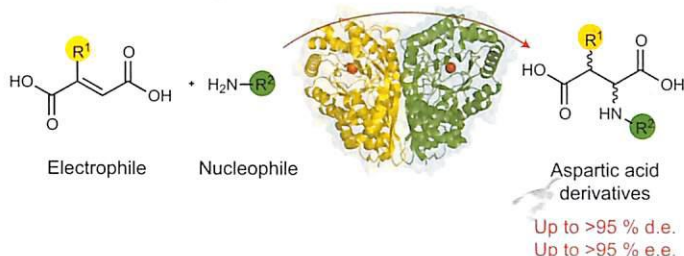
→N&V p438



478 Engineering methylaspartate ammonia lyase for the asymmetric synthesis of unnatural amino acids

Hans Raj, Wiktor Szymański, Jandr  de Villiers, Henri tte J. Rozeboom, Vinod Puthan Veetil, Carlos R. Reis, Marianne de Villiers, Frank J. Dekker, Stefaan de Wildeman, Wim J. Quax, Andy-Mark W. H. Thunnissen, Ben L. Feringa, Dick B. Janssen and Gerrit J. Poelarends

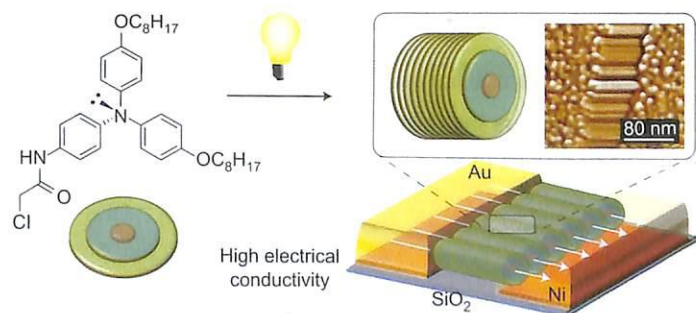
Substituted aspartic acids are highly valuable as tools for biological research and as chiral building blocks for pharmaceuticals. Here, engineering of the enzyme methylaspartate ammonia lyase to accept a large variety of substituted amines and fumarates and catalyse the asymmetric synthesis of aspartic acid derivatives is described.



485 Light-triggered self-construction of supramolecular organic nanowires as metallic interconnects

Vina Faramarzi, Fr d ric Niess, Emilie Moulin, Mounir Maaloum, Jean-Fran ois Dayen, Jean-Baptiste Beaufrand, Silvia Zanettini, Bernard Doudin and Nicolas Giuseppone

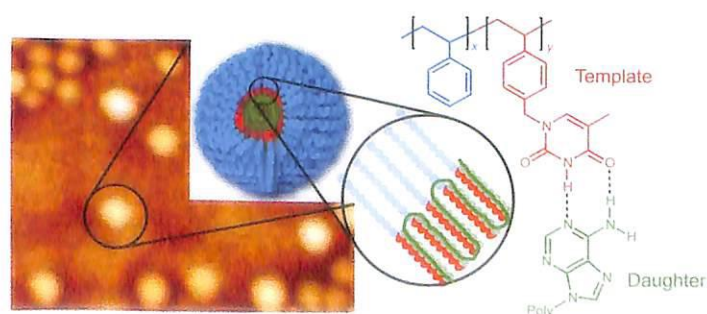
Triarylamine derivatives in solution have been self-assembled into organic nanowires between two electrodes, under white-light irradiation and in the presence of a voltage. The resulting fibres possess a very high electric conductivity as well as a metallic behaviour when cooled down to a temperature of 1.5 K.



491 Biomimetic radical polymerization via cooperative assembly of segregating templates

Ronan McHale, Joseph P. Patterson, Per B. Zetterlund and Rachel K. O'Reilly

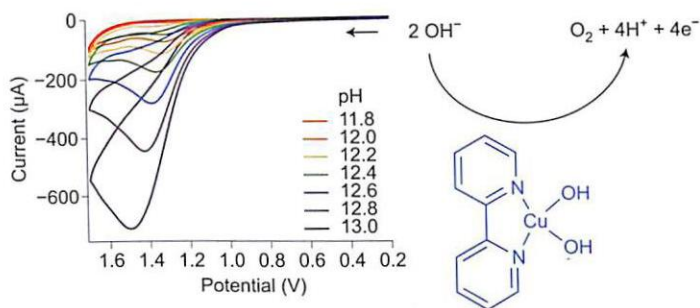
Nature synthesizes proteins and nucleic acids by polymerization methods that use well-regulated and segregated templates. Now, synthetic block-copolymer templates have been designed to assemble in a biomimetic fashion to segregate, and thus control, the synthetic radical polymerization of complementary nucleobase-containing vinyl monomers, to yield high-molecular-weight, low-polydispersity polymer chains.



498 A soluble copper-bipyridine water-oxidation electrocatalyst

Shoshanna M. Barnett, Karen I. Goldberg and James M. Mayer

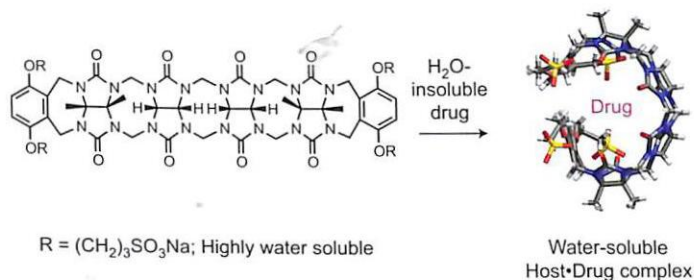
Copper and bipyridine (bpy) self-assemble in aqueous solutions at high pH into an active electrocatalyst for the oxidation of water to O_2 , one of the great challenges in energy catalysis. These solutions contain primarily $(bpy)Cu(OH)_2$, and are robust and active catalysts, albeit at high overpotentials.



503 Acyclic cucurbit[n]uril molecular containers enhance the solubility and bioactivity of poorly soluble pharmaceuticals

Da Ma, Gaya Hettiarachchi, Duc Nguyen, Ben Zhang, James B. Wittenberg, Peter Y. Zavalij, Volker Briken and Lyle Isaacs

Acyclic cucurbituril-type molecular containers have been found to increase the solubility of insoluble pharmaceutical agents in water by up to 2,750-fold. *In vitro* and *in vivo* toxicology studies suggest that the containers are well tolerated, and paclitaxel solubilized in this manner efficiently kills HeLa and SK-OV-3 cancer cells.

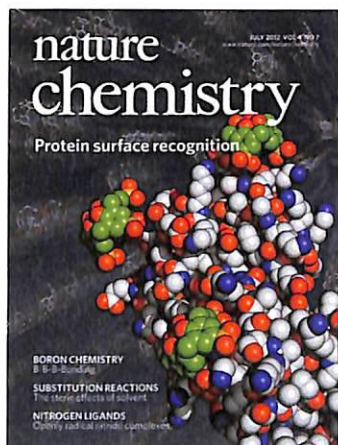


511 Corrigendum

IN YOUR ELEMENT

512 Ambiguous bromine

Matt Rattley

**COVER IMAGE**

Peter Crowley and co-workers have revealed how a sulfonated calixarene interacts with the outer surface of the cytochrome *c* protein. A combination of NMR spectroscopy and single-crystal X-ray crystallography shows that the calixarene 'explores' the surface of the protein through dynamic binding at multiple sites (depicted on the cover). Gaining understanding of these interactions may aid the crystallization of proteins and the design of ligands for protein recognition. Article p527; News & Views p519

IMAGE: PETER CROWLEY

COVER DESIGN: ALEX WING

ON THE COVER

Boron chemistry
B-B-B-Bonding
Article p563

Substitution reactions
The steric effects of solvent
Article p534; News & Views p522

Nitrogen ligands
Openly radical nitrido complexes
Article p552

THESIS

- 513 **Lies, damned lies and *h*-indices**
Bruce Gibb

RESEARCH HIGHLIGHTS

- 516 **Our choice from the recent literature**

BLOGROLL

- 517 **#WhatsInLemiShine**
Written by Chemjobber

NEWS & VIEWS

- 519 **Protein recognition: Calixarene connection**
Thomas Schrader
- 520 **Natural product biosynthesis: Tackling tunicamycin**
Ethan D. Goddard-Borger and Stephen G. Withers
- 522 **Reaction mechanisms: Stripping down S_N2**
Andrew J. Orr-Ewing
- 523 **Photochemistry: Molecular motor speed limits**
R. J. Dwayne Miller
- 525 **Main group chemistry: Breaking the limits with silylenes**
Matthias Driess



nature publishing group

Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: *Nature Chemistry*, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: *Nature Chemistry*, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2012 US annual subscription price is \$4412 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA; UK/Rest of World (excluding Europe and Japan) £2264 (institutional/corporate), £55 (individual making personal payment), Europe €3503 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica NY 11431. *Nature Chemistry* is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to *Nature Chemistry*, Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: *Nature Chemistry* Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the *Nature Chemistry* homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

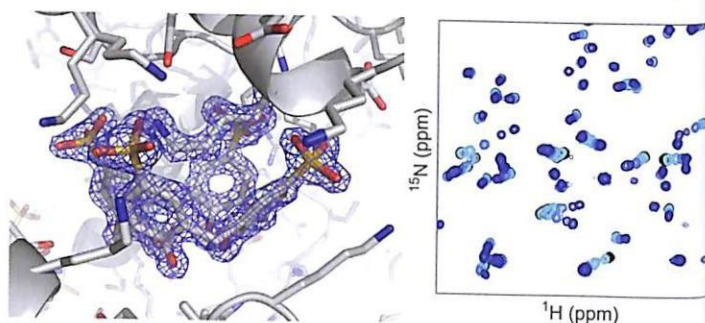
ARTICLES

527 Protein camouflage in cytochrome *c*-calixarene complexes

Róise E. McGovern, Humberto Fernandes, Amir R. Khan, Nicholas P. Power and Peter B. Crowley

A calixarene-protein host-guest complex has been characterized in detail by using a combination of NMR spectroscopy and X-ray crystallography. The water-soluble sulfonato-calix[4]arene binds to cytochrome *c* at various lysine residues to yield a dynamic complex. This interaction may serve to facilitate crystallization by mediating protein-protein contacts.

→N&V p519

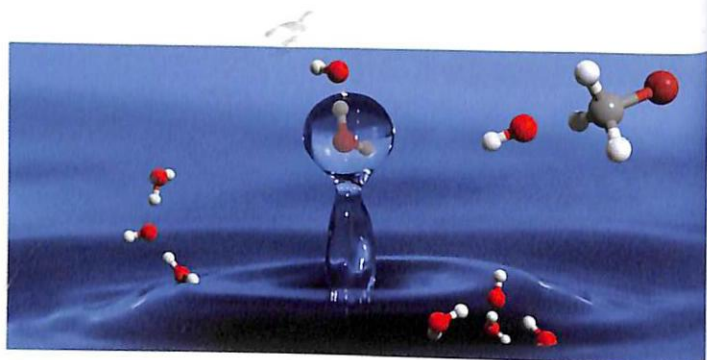


534 Single solvent molecules can affect the dynamics of substitution reactions

R. Otto, J. Brox, S. Trippel, M. Stei, T. Best and R. Wester

How do solvent molecules influence the dynamics of a chemical reaction? Crossed-beam molecular imaging experiments reveal how different reaction mechanisms can be either suppressed or enhanced by the presence of one water molecule. The study finds that steric effects are responsible for the observed dynamics.

→N&V p522

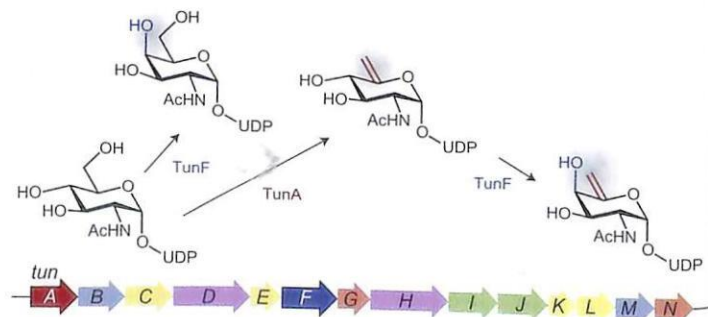


539 Biosynthesis of the tunicamycin antibiotics proceeds via unique exo-glycal intermediates

Filip J. Wyszynski, Seung Seo Lee, Tomoaki Yabe, Hua Wang, Juan Pablo Gomez-Escribano, Mervyn J. Bibb, Soo Jae Lee, Gideon J. Davies and Benjamin G. Davis

Construction of the remarkable 11-carbon frame of the antibiotic tunicamycin is shown to use cyclic enol ethers (exo-glycals) — the first time such intermediates have been seen in biology. Exo-glycal synthase TunA uses an elegantly subtle mechanism to control regioselectivity and with exo-glycal epimerase TunF sets a logical chemical stage for downstream radical C-C coupling.

→N&V p520

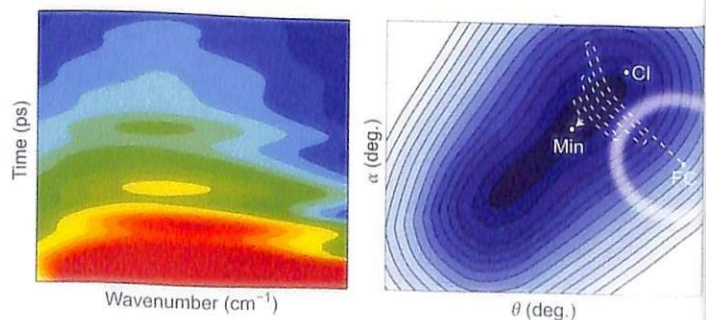


547 Ultrafast dynamics in the power stroke of a molecular rotary motor

Jamie Conyard, Kiri Addison, Ismael A. Heisler, Arjen Cnossen, Wesley R. Browne, Ben L. Feringa and Stephen R. Meech

The light-driven power stroke of a unidirectional molecular motor is studied using ultrafast fluorescence spectroscopy. The evolution on the excited-state energy surface is observed on the 100 fs timescale and is accompanied by damped coherent molecular motion. The implications of these observations for the operation of the molecular motors are discussed.

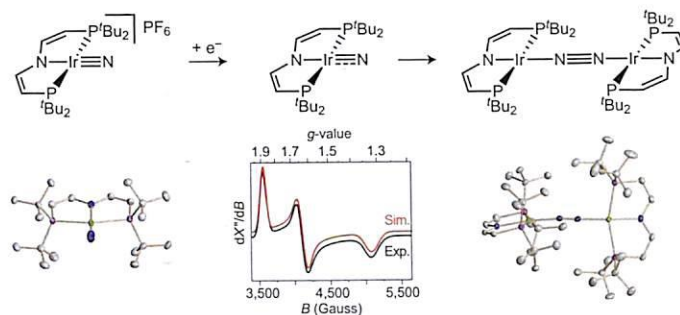
→N&V p523



552 Closed-shell and open-shell square-planar iridium nitrido complexes

Markus G. Scheibel, Bjorn Askevold, Frank W. Heinemann, Edward J. Reijerse, Bas de Bruin and Sven Schneider

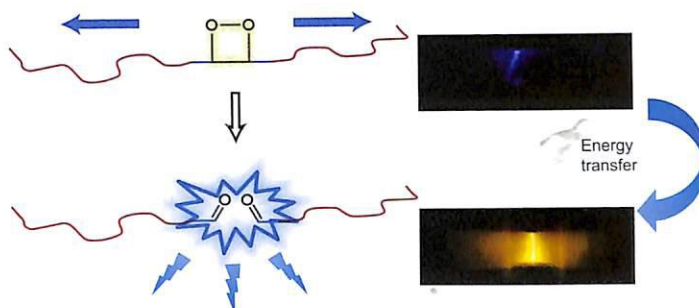
Coupling reactions of nitrogen atoms represent elementary steps to many important, heterogeneously catalysed reactions, such as the Haber-Bosch process or selective catalytic reduction of NO_x to N_2 . Here, the synthesis and characterization of closed- and open-shell, square-planar iridium nitrido complexes is described, indicating considerable nitridyl radical character for the open shell complex.



559 Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain

Yulan Chen, A. J. H. Spiering, S. Karthikeyan, Gerrit W. M. Peters, E. W. Meijer and Rint P. Sijbesma

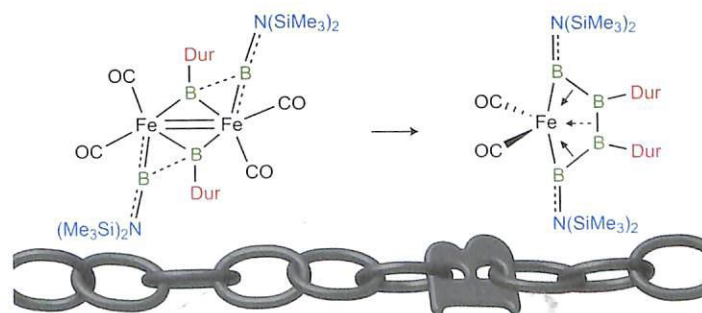
Bisadamantyl 1,2-dioxetane is a luminescent mechanophore that, when incorporated into polymer chains or networks, emits visible light when its 4-membered ring is opened by sonication in solution or by deformation of a bulk sample. This phenomenon mimics biological mechanoluminescence and highlights the potential to study the failure of polymeric materials with high spatial and temporal resolution.



563 Controlled homocatenation of boron on a transition metal

Holger Braunschweig, Qing Ye, Alfredo Vargas, Rian D. Dewhurst, Krzysztof Radacki and Alexander Damme

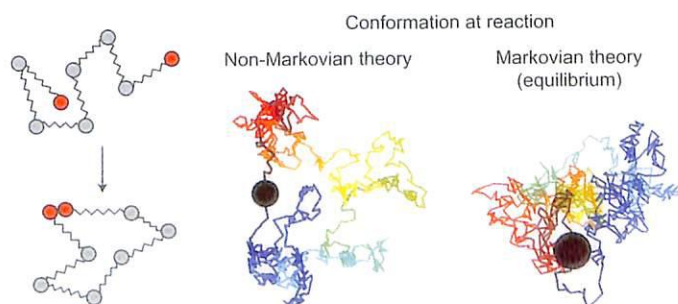
Mild, controllable homocatenation of many elements is a considerable challenge, usually due to their low homonuclear σ -bond enthalpy. This is particularly difficult for boron, despite its high homonuclear σ -bond enthalpy. The controllable metal-templated catenation of four boron atoms is now demonstrated — a step towards oligomers of monovalent boron and polyboranes.



568 Non-Markovian polymer reaction kinetics

T. Guérin, O. Bénichou and R. Voituriez

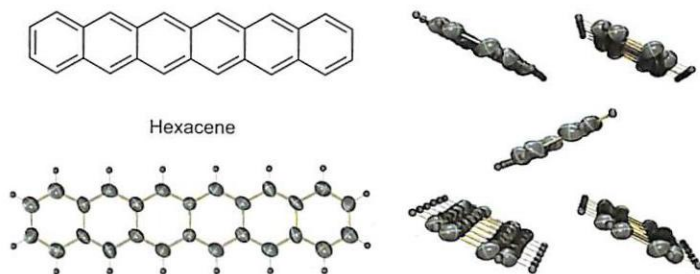
Quantifying polymer reaction kinetics requires the non-Markovian dynamics of monomer motion to be taken into account. This difficulty is overcome by explicitly determining the typical reactive conformations of the polymer, which are found to be more extended than equilibrium conformations, leading to reaction times significantly shorter than predicted by existing Markovian theories.



574 The synthesis, crystal structure and charge-transport properties of hexacene

Motonori Watanabe, Yuan Jay Chang, Shun-Wei Liu, Ting-Han Chao, Kenta Goto, Md. Minarul Islam, Chih-Hsien Yuan, Yu-Tai Tao, Teruo Shinmyozu and Tahsin J. Chow

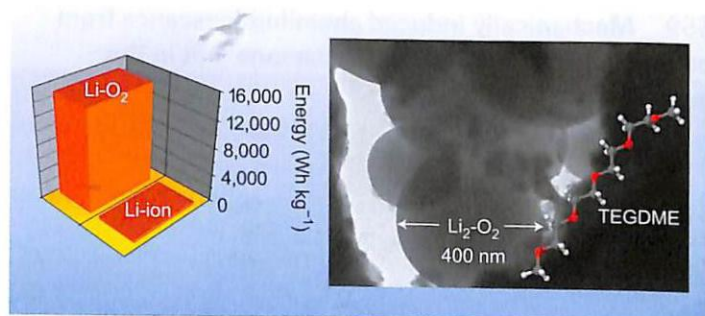
Crystals of hexacene prepared from a monoketone precursor are found to be stable up to 300 °C in the dark, but readily decompose when exposed to light. An organic-field transistor made with a single crystal of hexacene was found to have superior properties to one made from pentacene under analogous conditions.



579 An improved high-performance lithium-air battery

Hun-Gi Jung, Jusef Hassoun, Jin-Bum Park, Yang-Kook Sun and Bruno Scrosati

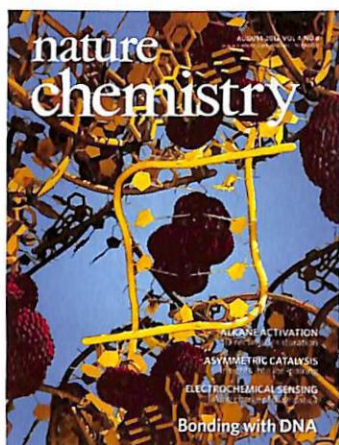
Lithium-air batteries have the possibility of having a very high energy density, but their use has been hampered by a limited number of charge-discharge cycles and a low current-rate capability. Now, exploiting a suitable, stable electrolyte allows an advanced lithium-air battery to operate with many cycles at various capacity and rate values.



IN YOUR ELEMENT

586 Peculiar protactinium

Richard Wilson



COVER IMAGE

Photosensitive metal complexes that are able to bind to DNA duplexes (an example of which is depicted on the cover) hold promise for diagnostic and therapeutic applications — but the precise details of how they interact with DNA need to be better understood. A collection of articles in this issue highlight some of the latest advances in elucidating their binding modes as well as challenges associated with this area of research.

Editorial p587; Interview p591;
News & Views p594;
Articles p615; p621

IMAGE: CHRISTINE CARDIN AND JAMES HALL

COVER DESIGN: ALEX WING

ON THE COVER

Alkane activation

Directing desaturation
Article p629

Asymmetric catalysis

Insights into ion-pairing
Review Article p603

Electrochemical sensing

Taking charge of diagnostics
Article p642; News & Views p595

EDITORIAL

587 Double-helix disruption

THESIS

588 Slow science
Jean-François Lutz

BOOKS & ARTS

590 App: SANROS created by László Kürti and Barbara Czako
Reviewed by Jon T. Njardarson

INTERVIEW

591 Binding manners
Interview with Claudia Turro

RESEARCH HIGHLIGHTS

592 Our choice from the recent literature

BLOGROLL

593 Toxicity and death
Written by Paul Bracher

NEWS & VIEWS

594 Interactions with DNA: Into the minor groove
Stephen Neidle

595 Electrochemical sensors: Taking charge of detection
Anthony M. Burke and Alon A. Gorodetsky

597 Catalyst-support interactions: Electronic perturbations
Charles T. Campbell

598 Supramolecular dye aggregates: Nanotube knockout
Jürgen Köhler

600 Protein folding: Turbo-charged crosslinking
David J. Craik

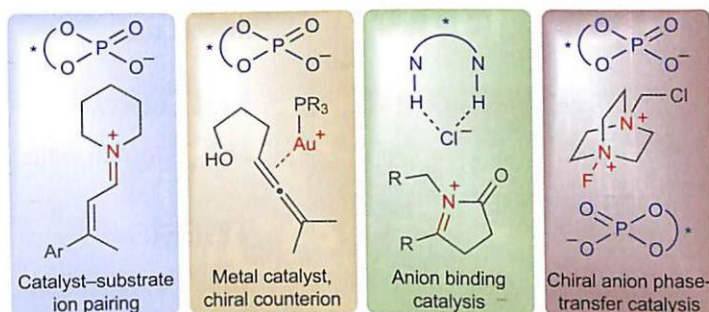


REVIEW ARTICLE

603 The progression of chiral anions from concepts to applications in asymmetric catalysis

Robert J. Phipps, Gregory L. Hamilton and F. Dean Toste

Novel concepts in asymmetric catalysis have the potential to open up previously inaccessible reaction space. This Review reflects on the origins of an area that has undergone dramatic recent advancement: the use of chiral anions in asymmetric catalysis. Details of a selection of the latest examples are also given.



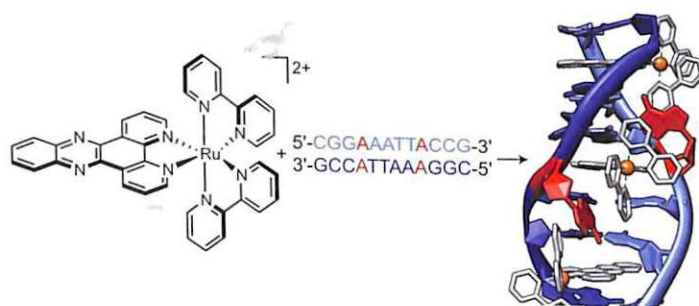
ARTICLES

615 Crystal structure of Δ -[Ru(bpy)₂dppz]²⁺ bound to mismatched DNA reveals side-by-side metalloinsertion and intercalation

Hang Song, Jens T. Kaiser and Jacqueline K. Barton

A 'light switch' ruthenium complex is known to show enhanced luminescence in the presence of DNA mismatches — emerging targets for cancer diagnostics and therapeutics — but the way it interacts with DNA has remained unclear. Now, metalloinsertion into and metallointercalation at the minor groove of the double helix have been unambiguously observed in a high-resolution crystal structure.

→N&V p594

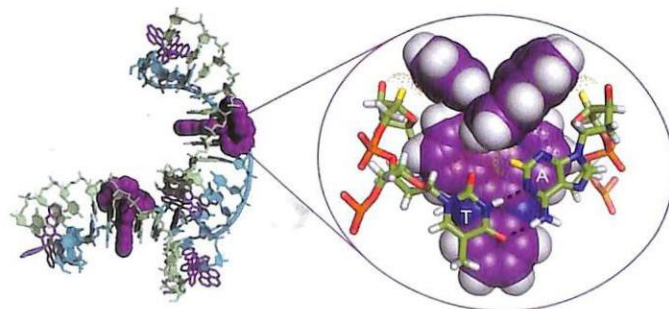


621 Crystal structures of Λ -[Ru(phen)₂dppz]²⁺ with oligonucleotides containing TA/TA and AT/AT steps show two intercalation modes

Hakan Niyazi, James P. Hall, Kyra O'Sullivan, Graeme Winter, Thomas Sorensen, John M. Kelly and Christine J. Cardin

Elucidating how small molecules bind to DNA is crucial to bio-sensing and therapy applications. Two crystal structures now show the binding modes of a 'light switch' ruthenium complex — whose luminescence in solution increases in the presence of DNA — with oligonucleotide duplexes containing either TA/TA or AT/AT central steps, revealing a specific intercalation mode with the TA/TA species.

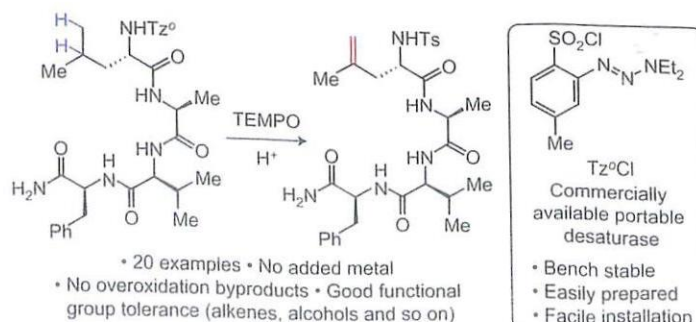
→N&V p594



629 Guided desaturation of unactivated aliphatics

Ana-Florina Voica, Abraham Mendoza, Will R. Gutekunst, Jorge Otero Fraga and Phil S. Baran

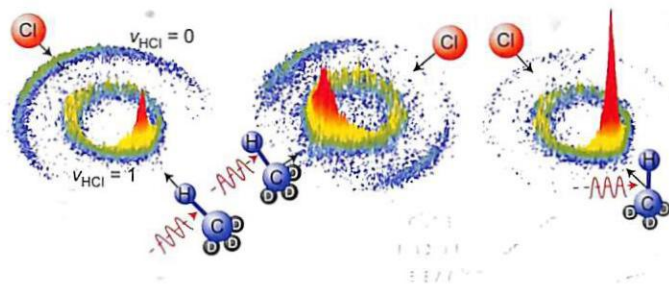
A bench-stable, aryl sulfonyl triazene is described that can be appended to alcohols or amines and used as a directing group to effect remote desaturation of unactivated aliphatics to produce olefins. The reaction is mild, operationally simple, requires no added metals and produces unsaturated tosylates or tosylamides available for further functionalization.



636 Revealing the stereospecific chemistry of the reaction of Cl with aligned CHD₃ ($\nu_1=1$)

Fengyan Wang, Kopin Liu and T. Peter Rakitzis

Steric effects are a key concept for understanding chemical reactivity. Now, by aligning reactants through control of the polarization of the infrared laser in a crossed-beam experiment, a three-dimensional view of how a reaction proceeds is reported. The results show striking dependences on the direction from which the laser-aligned reagents approach.

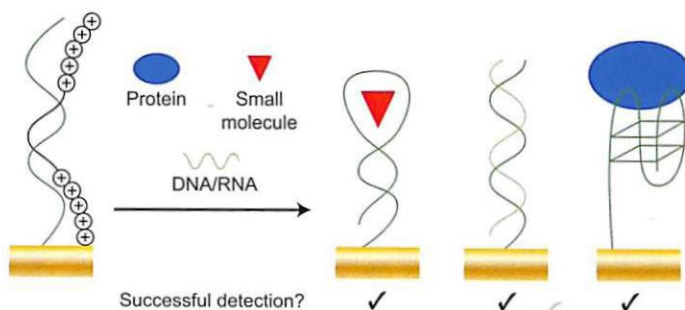


642 An ultrasensitive universal detector based on neutralizer displacement

Jagotamoy Das, Kristin B. Cederquist, Alexandre A. Zaragoza, Paul E. Lee, Edward H. Sargent and Shana O. Kelley

A universal detector of small molecules, proteins and nucleic acids is described that relies on the displacement of a neutralizer molecule from a sensor surface. When the neutralizer is displaced by an analyte, an electrochemical signal is generated. Ultrasensitive limits of detection are achieved, and a new record for the electrochemical detection of bacteria (0.15 colony-forming units per microlitre) is reported.

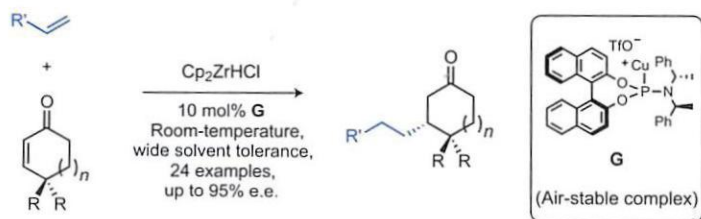
→N&V p595



649 Catalytic asymmetric carbon-carbon bond formation using alkenes as alkylmetal equivalents

Rebecca M. Maksymowicz, Philippe M. C. Roth and Stephen P. Fletcher

Organometallic reagents are widely used as nucleophiles in asymmetric catalysis. Here, alkylmetal species generated *in situ* by hydrometallation of alkenes are used in enantioselective copper-catalysed C-C bond formation. The process is formally an asymmetric reductive coupling of an alkene to an enone, and tolerates many functional groups.

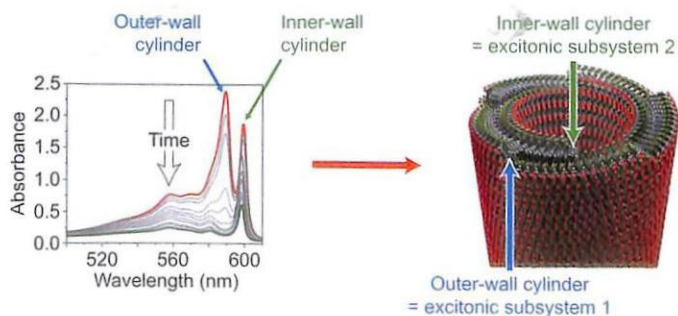


655 Utilizing redox-chemistry to elucidate the nature of exciton transitions in supramolecular dye nanotubes

D. M. Eisele, C. W. Cone, E. A. Bloemsmma, S.M. Vlaming, C. G. F. van der Kwaak, R. J. Silbey, M. G. Bawendi, J. Knoester, J. P. Rabe and D. A. Vanden Bout

The collective excited states (excitons) in supramolecular light-harvesting systems depend intimately on their structure and it is crucial to understand how these states interact. Now it is shown that simple redox chemistry can be used to address this fundamental question by simplifying the complex excitonic interactions in such multichromophoric systems.

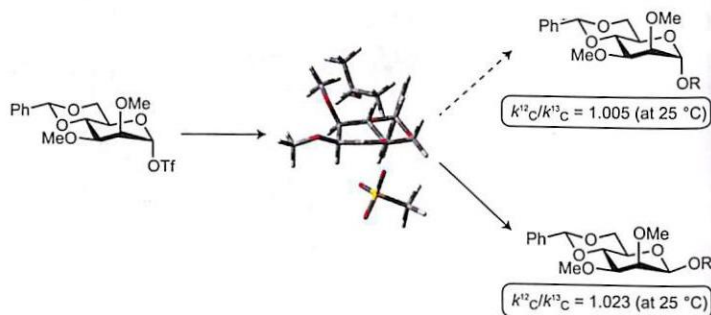
→N&V p598



663 Dissecting the mechanisms of a class of chemical glycosylation using primary ^{13}C kinetic isotope effects

Min Huang, Graham E. Garrett, Nicolas Birlirakis, Luis Bohé, Derek A. Pratt and David Crich

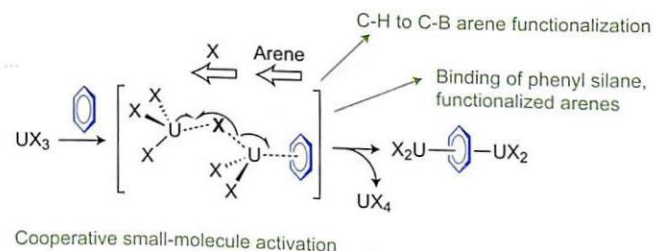
Chemical glycosylations are perhaps the most important reactions in glycoscience, but the mechanisms are not well understood. Here, quantum chemical calculations combined with natural-abundance NMR measurements of ^{13}C kinetic isotope effects reveal both associative and dissociative mechanisms at the extremes of a continuum that depends on the relative stereochemistry of the substrate and the anomeric configuration of the product.



668 Spontaneous reduction and C-H borylation of arenes mediated by uranium(III) disproportionation

Polly L. Arnold, Stephen M. Mansell, Laurent Maron and David McKay

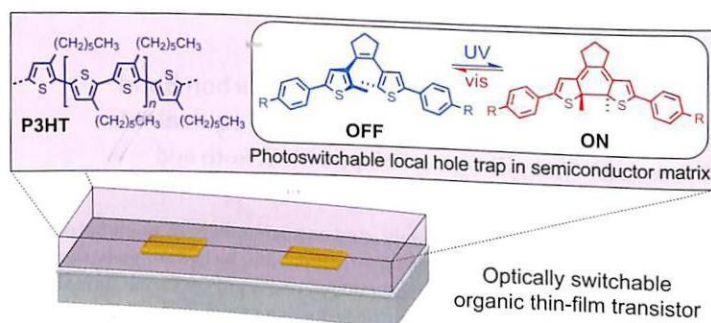
Simple uranium complexes, UX_3 , are shown to cooperatively bind and reduce arenes by disproportionation under mild conditions. This allows arene C-H bond activation and boryl functionalization, and trapping of reactive, substituted arenes in inverse sandwich complexes.



675 Optically switchable transistor via energy-level phototuning in a bicomponent organic semiconductor

Emanuele Orgiu, Núria Crivillers, Martin Herder, Lutz Grubert, Michael Pätzelt, Johannes Frisch, Egon Pavlica, Duc T. Duong, Guido Bratina, Alberto Salleo, Norbert Koch, Stefan Hecht and Paolo Samorì

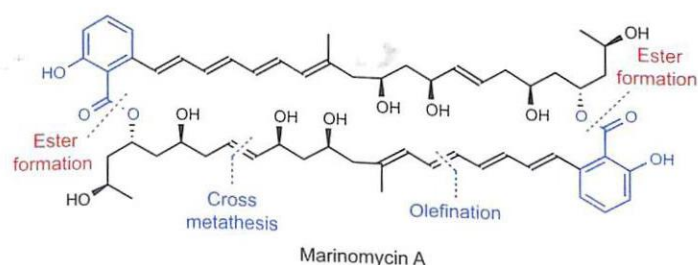
One of the goals for devices using organic semiconductors is to make the materials themselves multifunctional or tunable, reducing the complexity of the device. Now, a film created by blending two components is shown to be phototunable with bistable energy levels and has been used in an organic thin-film transistor.



680 Total synthesis of marinomycin A using salicylate as a molecular switch to mediate dimerization

P. Andrew Evans, Mu-Hua Huang, Michael J. Lawler and Sergio Maroto

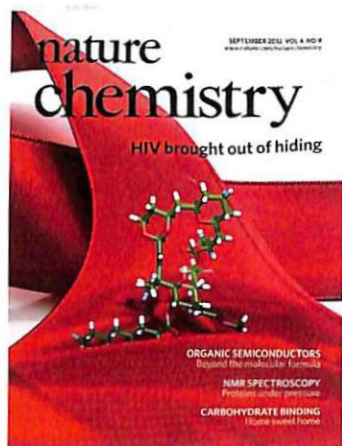
Marinomycin A is a member of a new class of bis-salicylate-containing polyene macrodiolide, with potent antibiotic activity against methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *Enterococcus faecium* (VREF). Here, a triply convergent synthesis of this agent is described that uses the salicylate moiety as a novel molecular switch for the chemoselective construction of the macrodiolide.



IN YOUR ELEMENT

686 Life and death with nitrogen

Michael Tarselli



COVER IMAGE

Current antiretroviral therapy (ART) can transform HIV infection from a terminal illness to a manageable chronic disease, but hidden HIV can re-ignite infection if treatment is stopped. Jerome Zack, Paul Wender and co-workers have now shown that a series of simplified — and thus synthetically accessible — analogues of the marine natural product bryostatin (one of which is shown on the cover) are able to activate latent HIV *in vitro*. It is hoped that this approach, in combination with ART, might ultimately lead to eradication of the infection.

Article p705; News & Views p692

IMAGE: BRIAN LOY

COVER DESIGN: ALEX WING

ON THE COVER

ORGANIC SEMICONDUCTORS
Beyond the molecular formula
Perspective p699

NMR SPECTROSCOPY
Proteins under pressure
Article p711; News & Views p693

CARBOHYDRATE BINDING
Home sweet home
Article p718; News & Views p697

THESIS

687 **Homemade chemists**
Michelle Francl

RESEARCH HIGHLIGHTS

690 **Our choice from the recent literature**

BLOGROLL

691 **But is it art?**
Written by See Arr Oh

NEWS & VIEWS

- 692 **Medicinal chemistry: Forcing an enemy into the open**
Christian Melander and David M. Margolis
- 693 **Protein NMR spectroscopy: Hydrogen bonds under pressure**
Gerd Nielsen and Harald Schwalbe
- 695 **Molecular switches: Hydrazones double down on zinc**
Shawn C. Burdette
- 697 **Carbohydrate recognition: A minimalistic approach to binding**
Stefan Kubik



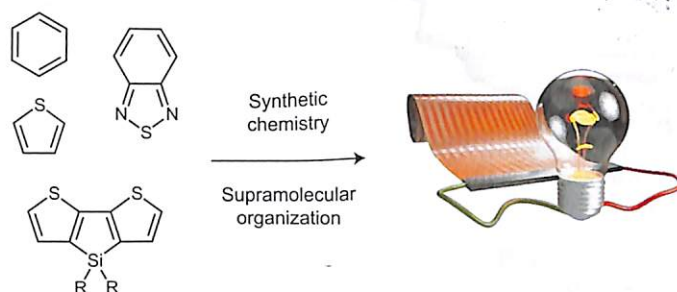
Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000 Fax: +44 (0)20 7843 4563 Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, 9th Floor, New York, NY 10013-1917 USA. Telephone: +1 212 726 9200 Fax: +1 212 696 9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000 Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860 Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242 Fax: +44 (0)1256 812358. The 2012 US annual subscription price is \$4412 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. UK/Rest of World (excluding Europe and Japan) £2264 (institutional/corporate), £55 (individual making personal payment); Europe €3503 (institutional/corporate), €85 (individual making personal payment); Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica NY 11431. Nature Chemistry is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to Nature Chemistry, Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

PERSPECTIVE

699 Design strategies for organic semiconductors beyond the molecular formula

Zachary B. Henson, Klaus Müllen and Guillermo C. Bazan

Although the molecular formula gives valuable information on the properties of isolated molecules or conjugated polymers, it fails to accurately predict their collective behaviour in the solid state. This Perspective highlights the importance of organization across multiple length scales on the optical and electronic properties of organic semiconductors, and how device performances poorly reflect the capabilities of a given material.



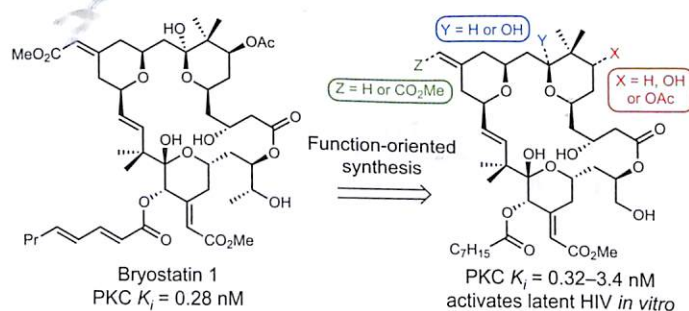
ARTICLES

705 Designed, synthetically accessible bryostatin analogues potentially induce activation of latent HIV reservoirs *in vitro*

Brian A. DeChristopher, Brian A. Loy, Matthew D. Marsden, Adam J. Schrier, Jerome A. Zack and Paul A. Wender

Simplified bryostatin analogues are shown to potentially induce latent HIV expression *in vitro*. These analogues display comparable or better potency when compared with bryostatin. Moreover, they are up to 1,000-fold more potent in inducing latent HIV expression than prostratin, the current lead preclinical candidate.

→N&V p692

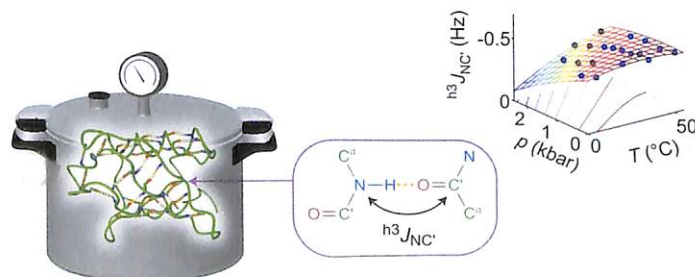


711 Key stabilizing elements of protein structure identified through pressure and temperature perturbation of its hydrogen bond network

Lydia Nisius and Stephan Grzesiek

The pressure- and temperature-dependent changes of various hydrogen bonds within ubiquitin have been determined at very high resolution using NMR H-bond scalar couplings. The measured perturbations show a correlation with the sequence separation between donor and acceptor residues, and indicate that certain topologically crucial H-bonds are specifically stabilized.

→N&V p693

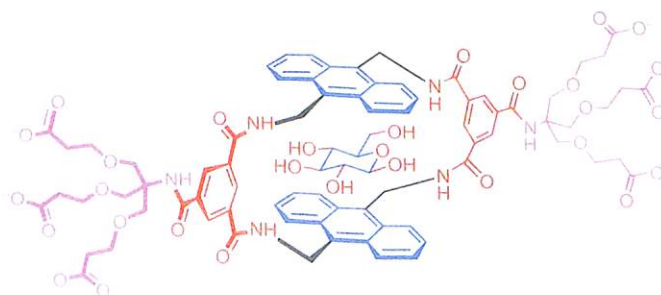


718 A simple and accessible synthetic lectin for glucose recognition and sensing

Chenfeng Ke, Harry Destecroix, Matthew P. Crump and Anthony P. Davis

Selective carbohydrate binding is a difficult task, usually accomplished by proteins (lectins) or complex synthetic analogues. It has now been achieved by a remarkably simple compound, accessible in just five steps from commercially available materials. This new receptor is highly selective for all-equatorial carbohydrates, and may be used to sense glucose through changes in anthracene fluorescence.

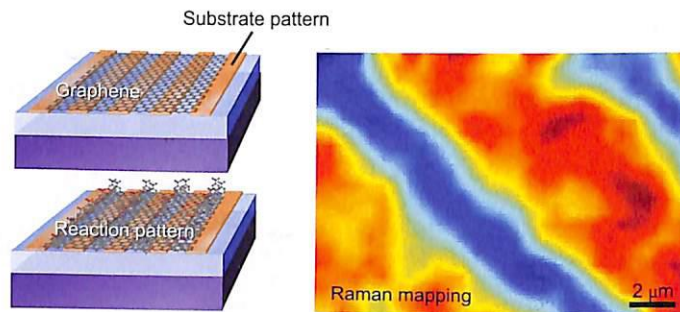
→N&V p697



724 Understanding and controlling the substrate effect on graphene electron-transfer chemistry via reactivity imprint lithography

Qing Hua Wang, Zhong Jin, Ki Kang Kim, Andrew J. Hilmer, Geraldine L. C. Paulus, Chih-Jen Shih, Moon-Ho Ham, Javier D. Sanchez-Yamagishi, Kenji Watanabe, Takashi Taniguchi, Jing Kong, Pablo Jarillo-Herrero and Michael S. Strano

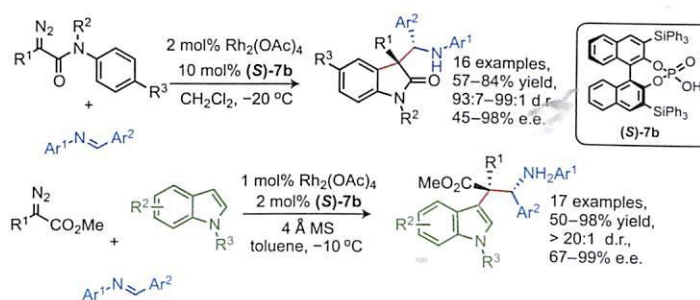
The chemical modification of graphene is important for its use in many applications. Now it is shown that the reactivity of graphene towards covalent modification varies widely depending on its underlying support substrate, and that the substrate can be patterned to induce spatial control of chemical reactions in graphene.



733 Highly enantioselective trapping of zwitterionic intermediates by imines

Huang Qiu, Ming Li, Li-Qin Jiang, Feng-Ping Lv, Li Zan, Chang-Wei Zhai, Michael P. Doyle and Wen-Hao Hu

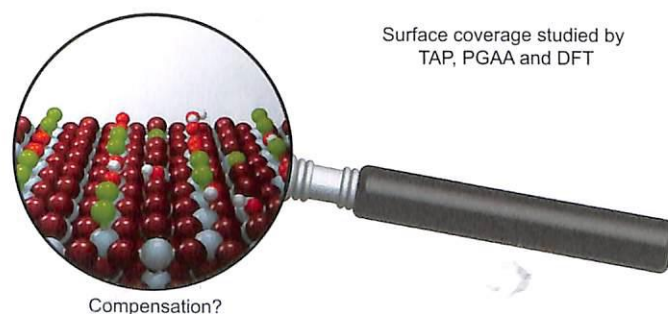
Reactions with unstable and highly reactive zwitterionic intermediates generated in transition-metal-catalysed processes provide new opportunities for molecular constructions. Here imines, activated by chiral organocatalysts, have been employed to trap the zwitterionic intermediates to give polyfunctionalized indole and oxindole derivatives in a single step with excellent diastereoselectivity and enantioselectivity.



739 *In situ* surface coverage analysis of RuO₂-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis

Detre Teschner, Gerard Novell-Leruth, Ramzi Farra, Axel Knop-Gericke, Robert Schlögl, László Szentmiklósi, Miguel González Hevia, Hary Soerijanto, Reinhard Schomäcker, Javier Pérez-Ramírez and Núria López

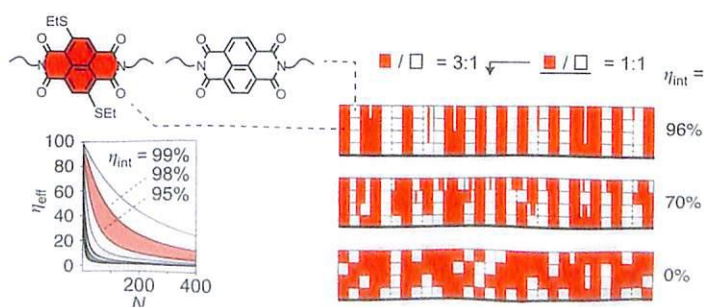
In heterogeneous catalytic processes the Arrhenius parameters are often found to be interrelated (compensation phenomenon). Using state-of-the-art experiments and density functional theory, the origin of compensation is studied. A similar dependence on the rate-limiting surface-coverage term is found for both apparent activation energy and prefactor terms, which can be translated into surface configurational entropy contributions.



746 A quantitative model for the transcription of 2D patterns into functional 3D architectures

Edvinas Orentas, Marco Lista, Nai-Ti Lin, Naomi Sakai and Stefan Matile

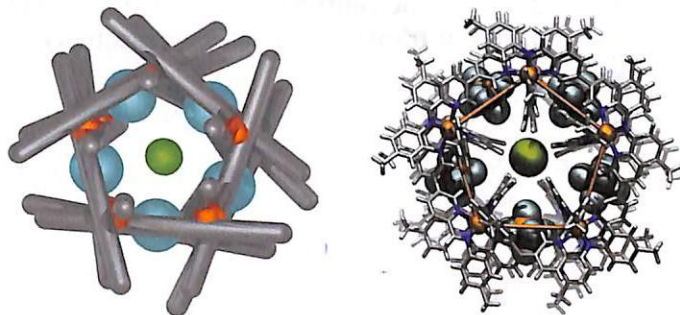
The self-sorting of molecular building blocks should allow 2D surface patterns to be transcribed into 3D functional materials. Here, a non-empirical approach to the templated synthesis of supramolecular architectures on surfaces is reported, starting with a theoretical model and followed by comprehensive experimental validation, including direct evidence for functional relevance of the produced materials.



751 Anion-induced reconstitution of a self-assembling system to express a chloride-binding $\text{Co}_{10}\text{L}_{15}$ pentagonal prism

Imogen A. Riddell, Maarten M. J. Smulders, Jack K. Clegg, Yana R. Hristova, Boris Breiner, John D. Thoburn and Jonathan R. Nitschke

A coordination cage has been prepared that self-assembles through second-order templation. Peripheral perchlorate or hexafluorophosphate template anions direct the formation of a hollow prism whose central pocket was able to bind a small anionic guest such as halide or azide, in a manner reminiscent to signal transduction in biological systems.

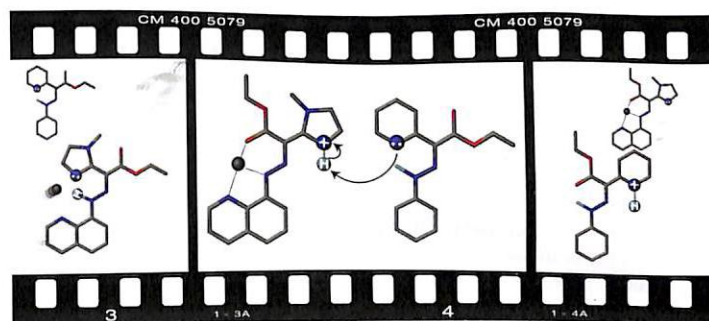


757 A switching cascade of hydrazone-based rotary switches through coordination-coupled proton relays

Debdas Ray, Justin T. Foy, Russell P. Hughes and Ivan Aprahamian

Metal cations play an important role in biological proton relays by modulating the $\text{p}K_a$ values of surrounding amino acids. This effect has now been used to induce the isomerization of two hydrazone switches using a single input. It is found that a combination of electrostatic repulsion and conformational changes are required for the proton relay to take place.

→N&V p695



IN YOUR ELEMENT

764 Reactions coupled to palladium

Matthew Hartings

nature
chemistryOCTOBER 2012 VOL 4 NO 10
www.nature.com/naturechemistryPolymers get
a little cagey

COVER IMAGE

A team of researchers led by Trevor Douglas have demonstrated that atom-transfer radical polymerization can be initiated from specific sites on the inside surface of a protein cage to produce a confined crosslinked polymethacrylate derivative (shown schematically on the cover). The pendant amine groups present in the polymer can be reacted with small molecules — such as fluorescent dyes or Gd-based contrast agents for magnetic resonance imaging — to produce hybrid protein-polymer conjugates with a high density of functional labels.

Article p781; News & Views p775

IMAGE: NIKKI SIMON

COVER DESIGN: ALEX WING

ON THE COVER

Water splitting
Occurring organically
Article p794

Aptameric protection
Shields for selective synthesis
Article p789; News & Views p774

Metal-organic frameworks
Carbon-capture calculations
Article p810; News & Views p777

CORRESPONDENCE

- 765** Dark channel fluorescence observations result from concentration effects rather than solvent-solute charge transfer
T. Z. Regier, A. J. Achkar, D. Peak, J. S. Tse and D. G. Hawthorn
- 766** Dips and peaks in fluorescence yield X-ray absorption are due to state-dependent decay
Frank M. F. de Groot
- 767** Reply to 'Dark channel fluorescence...' and 'Dips and peaks...'
Emad F. Aziz, Kathrin M. Lange, Sébastien Bonhommeau and Majed Chergui

THESIS

- 769** Knowledge management in chemistry
Bruce Gibb



RESEARCH HIGHLIGHTS

- 772** Our choice from the recent literature

BLOGROLL

- 773** Harder than flight
Written by BRSM

NEWS & VIEWS

- 774** Selective functionalization: Shields for small molecules
Scott K. Silverman
- 775** Chemical virology: Packing polymers in protein cages
Jeroen J. L. M. Cornelissen
- 777** Molecular simulations: Force fields for carbon capture
Rachel B. Getman
- 779** Main group chemistry: Bonsai phosphorus
Emma E. Coyle and Christopher J. O'Brien



nature publishing group

Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7833 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2013 US annual subscription price is \$4677 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. UK/Rest of World (excluding Europe and Japan) £2400 (institutional/corporate), £55 (individual making personal payment), Europe €3713 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica, NY 11431. Nature Chemistry is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to Nature Chemistry, Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

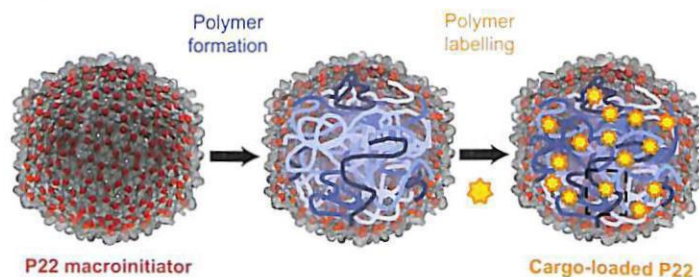
ARTICLES

781 Use of the interior cavity of the P22 capsid for site-specific initiation of atom-transfer radical polymerization with high-density cargo loading

Janice Lucon, Shefah Qazi, Masaki Uchida, Gregory J. Bedwell, Ben LaFrance, Peter E. Prevelige Jr and Trevor Douglas

The site-selective initiation and propagation of an atom-transfer radical polymerization reaction forms an addressable crosslinked polymer constrained within the interior cavity of a virus-like particle derived from the bacteriophage P22. This protein-polymer hybrid is useful as a new vehicle for high-density delivery of small-molecule cargos.

→N&V p775

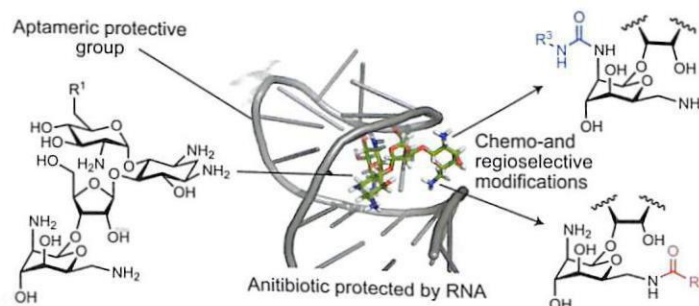


789 Selective transformations of complex molecules are enabled by aptameric protective groups

Andreas A. Bastian, Alessio Marcozzi and Andreas Herrmann

Selective modifications of structurally complex molecules bearing multiple reactive functional groups often require cumbersome multistep synthetic efforts. Here, aptameric protective groups based on short RNA sequences are described — they bind to neamine antibiotics, simultaneously protecting several functionalities and enabling regio- and chemoselective functionalizations.

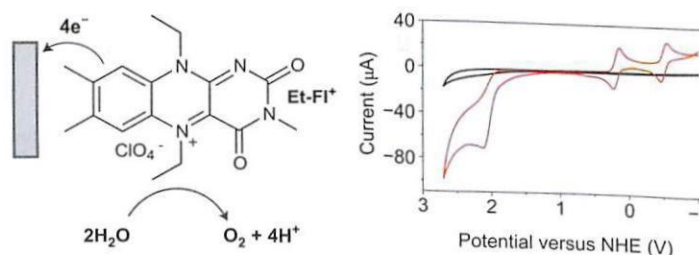
→N&V p774



794 Electrode-assisted catalytic water oxidation by a flavin derivative

Ekaterina Mirzakulova, Renat Khatmullin, Janitha Walpita, Thomas Corrigan, Nella M. Vargas-Barbosa, Shubham Vyas, Shameema Oottikkal, Samuel F. Manzer, Christopher M. Hadad and Ksenija D. Glusac

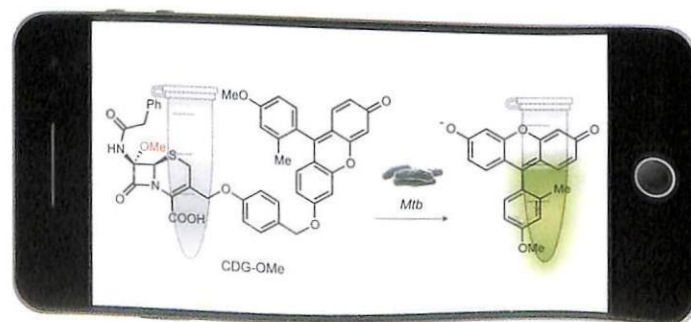
So far, reports of molecular electrochemical water oxidation have involved catalytic transition metal complexes. Now it is demonstrated that water can be oxidized, and oxygen evolved, using a simple organic, flavin derivative.



802 Rapid point-of-care detection of the tuberculosis pathogen using a BlaC-specific fluorogenic probe

Hexin Xie, Joseph Mire, Ying Kong, MiHee Chang, Hany A. Hassounah, Chris N. Thornton, James C. Sacchettini, Jeffrey D. Cirillo and Jianghong Rao

Rapid diagnostic methods that can be applied in resource-limited settings are important in the fight against tuberculosis. Here, fluorogenic probes are described that are activated by BlaC — an enzyme secreted by tubercle bacilli. The probes have enabled detection in unprocessed human sputum of live pathogen in less than 10 min.

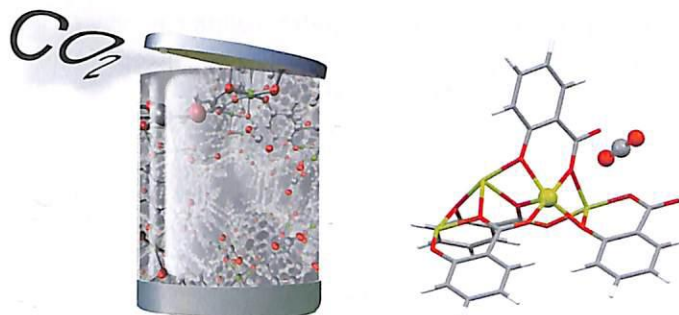


810 *Ab initio* carbon capture in open-site metal-organic frameworks

Allison L. Dzubak, Li-Chiang Lin, Jihan Kim, Joseph A. Swisher, Roberta Poloni, Sergey N. Maximoff, Berend Smit and Laura Gagliardi

Metal-organic frameworks featuring unsaturated metal sites have emerged as promising materials for CO₂ capture, but the host-guest interactions at play have remained poorly understood. An approach based on quantum chemical calculations has now been devised to generate force fields that accurately describe a MOF's metal sites and predict its gas uptake abilities.

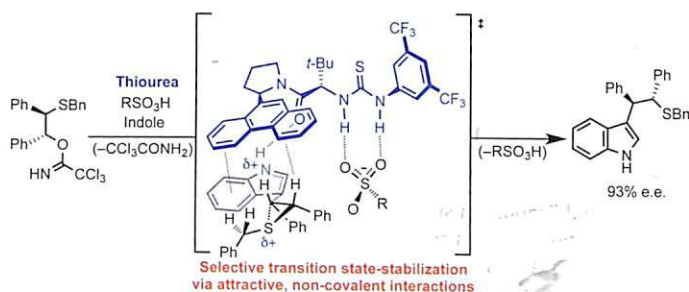
→N&V p777



817 Thiourea-catalysed ring opening of episulfonium ions with indole derivatives by means of stabilizing non-covalent interactions

Song Lin and Eric N. Jacobsen

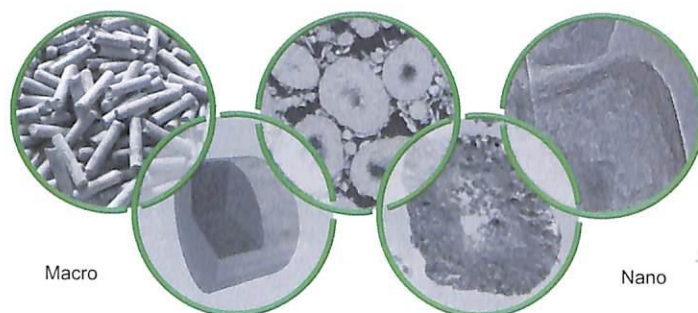
Arylpyrrolidino amidothiurea catalysts are shown to catalyse the enantioselective ring-opening of episulfonium ions by indole derivatives. Catalysis and enantioinduction are achieved by selective transition-state stabilization of the major pathway in the rate- and selectivity-determining step through a network of attractive anion-binding, cation- π and hydrogen-bonding interactions between the catalyst and the reacting partners.



825 Visualization of hierarchically structured zeolite bodies from macro to nano length scales

Sharon Mitchell, Nina-Luisa Michels, Karsten Kunze and Javier Pérez-Ramírez

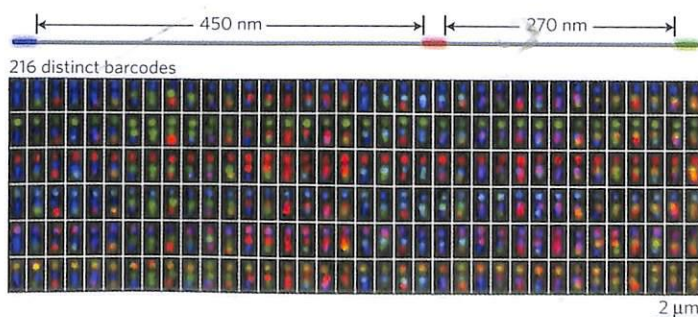
Understanding the nature of complex zeolite particles, used as catalysts in industrial reactors, is vital for their further development. Now, an integrated approach to visualizing granules of a hierarchical MFI-type zeolite, on length scales from nanometres to millimetres, is reported.



832 Submicrometre geometrically encoded fluorescent barcodes self-assembled from DNA

Chenxiang Lin, Ralf Jungmann, Andrew M. Leifer, Chao Li, Daniel Levner, George M. Church, William M. Shih and Peng Yin

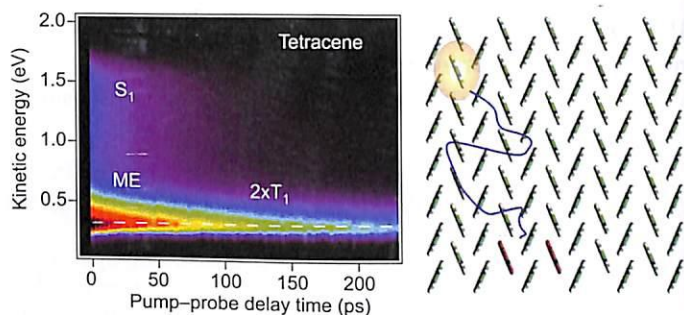
Life-science research and biomedical diagnostics call for robust fluorescence barcodes of compact size and high multiplexing capability. Here DNA-origami technology was used to construct a new kind of geometrically encoded barcode with excellent structural stiffness. They hold promise for both *in situ* and *ex situ* imaging of diverse biologically relevant entities.



840 The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain

Wai-Lun Chan, Manuel Ligges and X-Y. Zhu

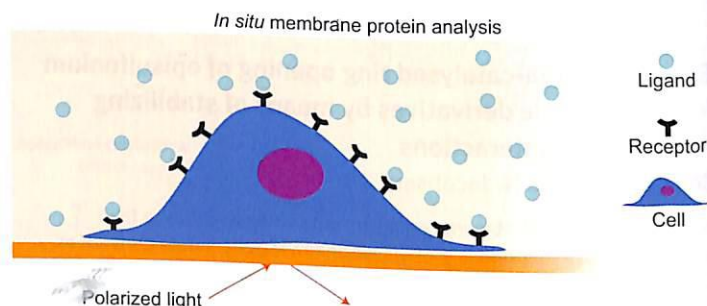
Better understanding of the mechanisms of singlet fission may facilitate its implementation in solar cells, improving their efficiency. Although singlet fission in tetracene is endothermic, it is now observed not to be thermally activated; rather a quantum coherent process allows access to the higher-energy multi-exciton state, which then forms two triplet excitons through an entropic driving force.



846 Label-free measuring and mapping of binding kinetics of membrane proteins in single living cells

Wei Wang, Yunze Yang, Shaopeng Wang, Vinay J. Nagaraj, Qiang Liu, Jie Wu and Nongjian Tao

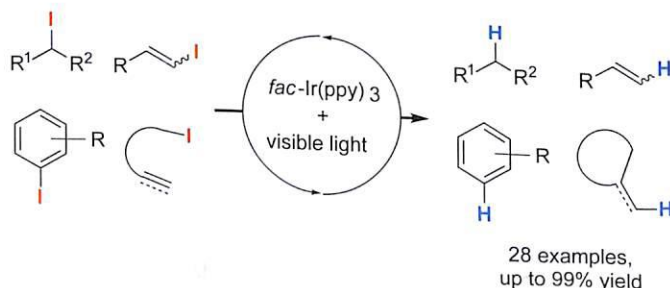
Many biological processes involve the binding of proteins to cell membrane receptors, making these proteins valuable disease biomarkers and therapeutic targets. A label-free plasmonic microscopy method has now been devised to determine the distribution and local binding kinetics of these 'membrane proteins', on the surface of single living cells rather than *ex situ*.



854 Engaging unactivated alkyl, alkenyl and aryl iodides in visible-light-mediated free radical reactions

John D. Nguyen, Erica M. D'Amato, Jagan M. R. Narayanam and Corey R. J. Stephenson

Visible-light-mediated photocatalytic generation of carbon-centred radicals from alkyl, alkenyl and aryl iodides, which then undergo subsequent hydrogen-atom abstraction or reductive cyclizations, is reported. The protocol is characterized by the use of inexpensive reagents, mild conditions, exceptional functional group tolerance, and good-to-high yields.

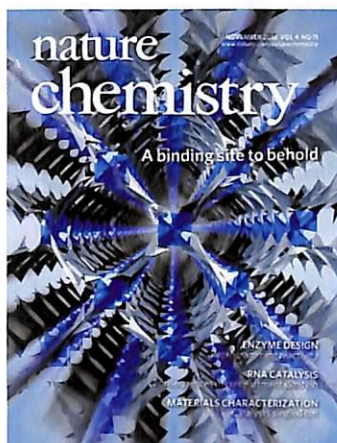


860 Erratum

IN YOUR ELEMENT

862 A touch of indium

Catherine Renouf



COVER IMAGE

Metal-organic frameworks (MOFs) are widely investigated for their potential to selectively separate and store environmentally harmful gases. The cover image of this issue shows the structure of a MOF — described by Martin Schröder and co-workers — whose promising capture capabilities rely on hydroxyl groups rather than the traditionally used amine ones. The hydrogen bonding interactions between the host framework and CO₂ and SO₂ gases were directly visualized by *in situ* static and dynamic characterization methods, and the results supported by modelling studies.

Article p887

IMAGE: SIHAI YANG

COVER DESIGN: ALEX WING

ON THE COVER

Enzyme design

Reprogramming reactivity

Article p900; News & Views p868

RNA catalysis

Consequences of compartmentalization

Article p941

Materials characterization

Catalysts singled out

Review Article p873

THESIS

863 100 years of the hydrogen bond

Patrick Goymer

RESEARCH HIGHLIGHTS

866 Our choice from the recent literature

BLOGROLL

867 Teaching the teacher

Written by Ashutosh Jogalekar

NEWS & VIEWS

868 Protein design: Engineering di-iron enzymes

Steven M. Berry

869 Heterogeneous catalysis: Teaching an old material new tricks

Elio Giamello

871 Molecular magnetism: A three-headed Janus material

Michel Verdaguer

IN YOUR ELEMENT

954 Osmium weighs in

Gregory Girolami



nature publishing group

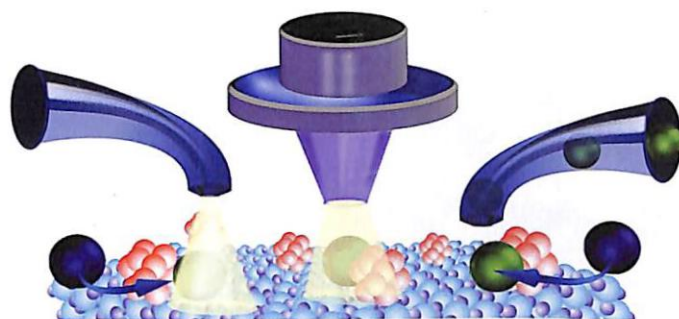
Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: Nature Chemistry, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: Nature Chemistry, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2013 US annual subscription price is \$4677 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA; UK/Rest of World (excluding Europe and Japan) £2400 (institutional/corporate), £55 (individual making personal payment); Europe €3713 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica NY 11431. Nature Chemistry is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to Nature Chemistry, Air Business Ltd, c/o Worldnet Shipping Inc., 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: Nature Chemistry Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the Nature Chemistry homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

REVIEW ARTICLE

873 Heterogeneities of individual catalyst particles in space and time as monitored by spectroscopy

Inge L. C. Buurmans and Bert M. Weckhuysen

This Review describes the general trends and implications of heterogeneities within individual catalyst particles as observed by modern spatiotemporal spectroscopy. It discusses how catalytic materials have been found to display heterogeneities in structure, composition and reactivity in space and time. The implications of these findings for future catalyst design are also described.

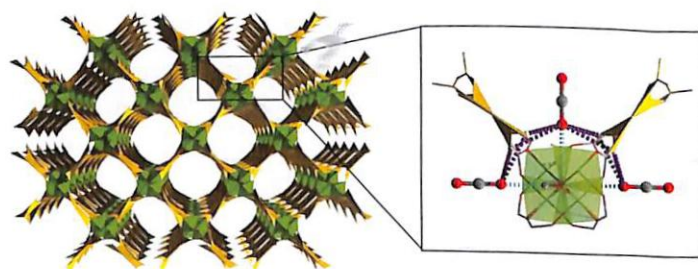


ARTICLES

887 Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host

Sihai Yang, Junliang Sun, Anibal J. Ramirez-Cuesta, Samantha K. Callear, William I. F. David, Daniel P. Anderson, Ruth Newby, Alexander J. Blake, Julia E. Parker, Chiu C. Tang and Martin Schröder

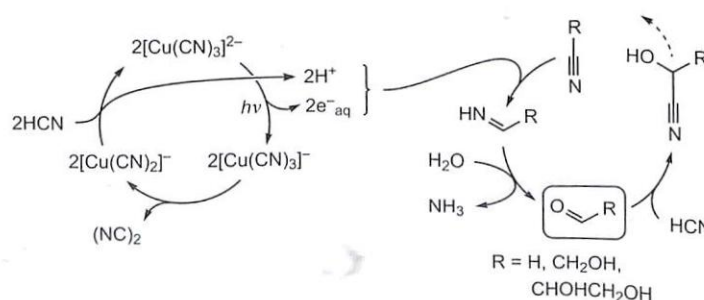
Porous solids are well suited to the capture of environmentally harmful gases, but further understanding of the solid-gas interactions involved is required. Combining dynamic and static characterization with modelling, researchers have now described how a metal-organic framework binds CO₂ and SO₂ selectively through hydroxyl groups — rather than amine ones as typically featured.



895 Prebiotic synthesis of simple sugars by photoredox systems chemistry

Dougal Ritson and John D. Sutherland

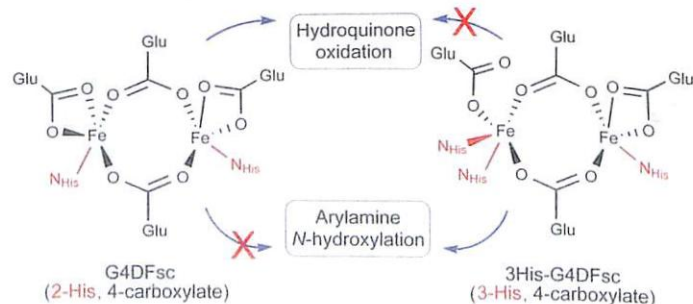
A demonstration of simple sugar synthesis from single carbon feedstocks would provide significant support for the involvement of RNA in the origin of life. Here, hydrogen cyanide is shown to feed a cyanocuprate photoredox cycle that ultimately provides both the starting material and the reducing power necessary for a Killiani-Fischer-type sugar synthesis.



900 Alteration of the oxygen-dependent reactivity of *de novo* Due Ferri proteins

Amanda J. Reig, Marcos M. Pires, Rae Ana Snyder, Yibing Wu, Hyunil Jo, Daniel W. Kulp, Susan E. Butch, Jennifer R. Calhoun, Thomas G. Szyperski, Edward I. Solomon and William F. DeGrado

Representing the first successful rational reprogramming of function in a *de novo* protein, the reactivity of a designed di-iron carboxylate protein from the Due Ferri family was altered from hydroquinone oxidation to arylamine *N*-hydroxylation through the introduction of a critical third histidine ligand in the active site.

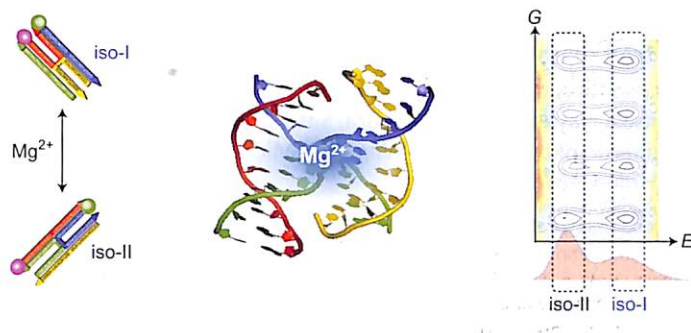


→N&V p868

907 Hidden complexity in the isomerization dynamics of Holliday junctions

Changbong Hyeon, Jinwoo Lee, Jeseong Yoon, Sungchul Hohng and D. Thirumalai

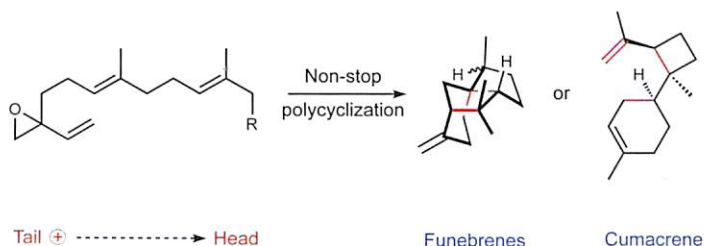
Single-molecule experiments reveal substantial molecule-to-molecule variation in the Mg^{2+} -induced isomerization dynamics of Holliday junctions (HJs). Effective ergodicity breaking of time trajectories results in the partitioning of HJ dynamics into multiple clusters. The observed dynamical heterogeneity is a consequence of various internal multiloop conformations that are frozen by Mg^{2+} ions.



915 Synthesis of highly strained terpenes by non-stop tail-to-head polycyclization

Sergey V. Pronin and Ryan A. Shenvi

Sesquiterpenes are biosynthesized from linear isoprenols through the intermediacy of multiple, high-energy carbocations. Here a strategy is demonstrated for mimicking these reactions in bulk solvent to yield strained, acid-labile terpenes. Key to the success of these reactions is the sequestration of the counteranion away from the reactive carbocation, a strategy that should enable further study of challenging polycyclizations.

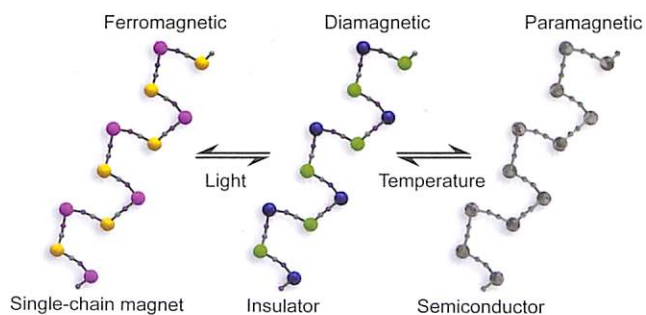


921 Three-way switching in a cyanide-bridged [CoFe] chain

Norihisa Hoshino, Fumichika Iijima, Graham N. Newton, Norifumi Yoshida, Takuya Shiga, Hiroyuki Nojiri, Akiko Nakao, Reiji Kumai, Youichi Murakami and Hiroki Oshio

Bistable materials, which exist in either one of two phases under identical conditions, are intriguing both from a fundamental perspective and for their practical applications. A cyanide-bridged [CoFe] coordination chain has now been prepared that shows both magnetic and electric bistabilities in the same temperature range, undergoing thermo- and photo-induced conversions between insulating, semiconducting and single-chain magnet-type phases.

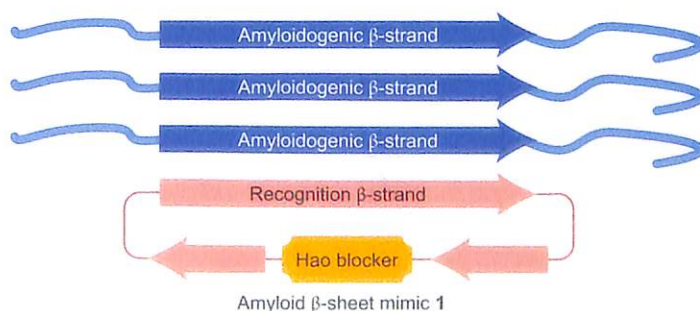
→N&V p871



927 Amyloid β -sheet mimics that antagonize protein aggregation and reduce amyloid toxicity

Pin-Nan Cheng, Cong Liu, Minglei Zhao, David Eisenberg and James S. Nowick

A family of robust β -sheet macrocycles that can display a variety of heptapeptide sequences from different amyloid proteins is introduced. These amyloid β -sheet mimics can be tailored to antagonize aggregation of the proteins, thereby reducing the toxicity associated with diseases such as Alzheimer's.

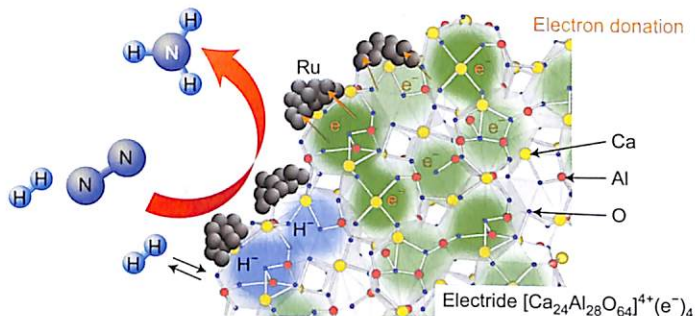


934 Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store

Masaaki Kitano, Yasunori Inoue, Youhei Yamazaki, Fumitaka Hayashi, Shinji Kanbara, Satoru Matsuishi, Toshiharu Yokoyama, Sung-Wng Kim, Michikazu Hara and Hideo Hosono

Methods that fix atmospheric nitrogen to ammonia under mild conditions could offer a more environmentally benign alternative to the Haber-Bosch process. Now, a Ru-loaded electride, $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(\text{e}^-)_4$, is reported that acts as an efficient electron donor and reversible hydrogen store, and is demonstrated to function as an efficient catalyst for ammonia synthesis.

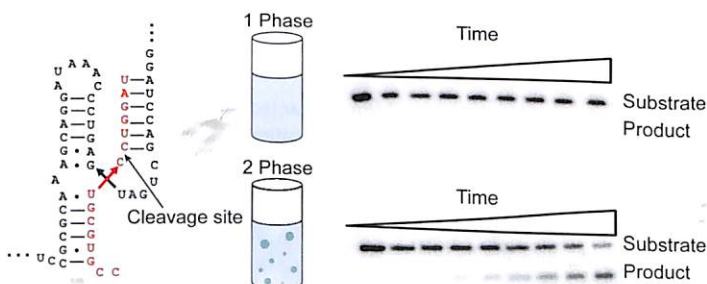
→N&V p869



941 RNA catalysis through compartmentalization

Christopher A. Strulson, Rosalynn C. Molden, Christine D. Keating and Philip C. Bevilacqua

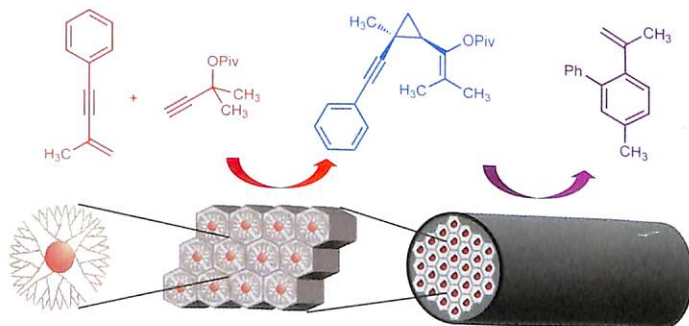
RNA compartmentalization is essential for cellular functions and may have played a pivotal role in the emergence of life. However, the consequences of compartmentalization on RNA catalysis have been largely unexplored. Here, partitioning of catalytic RNA in a two-phase aqueous polymer solution increased local RNA concentration, enhancing ribozyme kinetics.

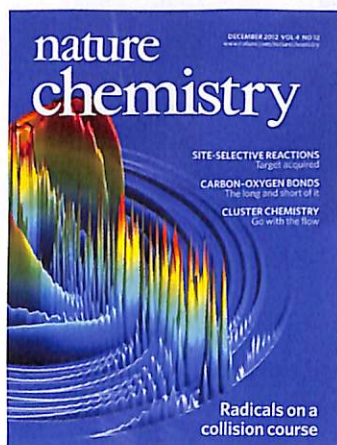


947 Control of selectivity in heterogeneous catalysis by tuning nanoparticle properties and reactor residence time

Elad Gross, Jack Hung-Chang Liu, F. Dean Toste and Gabor A. Somorjai

Heterogeneous catalysts are generally more readily recycled than homogeneous catalysts, but the latter are more easily modified to tune reactivity and selectivity. Here, the dendrimer coating of gold nanoparticle catalysts is shown to be a surrogate for the ligands of homogeneous catalysts. Tuning of product distribution and reaction selectivity is possible when these catalysts are employed in a fixed-bed flow reactor.



**COVER IMAGE**

Interest in the inelastic collisions of OH radicals stems from their importance in combustion and atmospheric chemistry, but measuring their velocities in specific internal quantum states has proved difficult. Now, David H. Parker and co-workers have demonstrated how velocity-map imaging can be applied to the study of the inelastic scattering of OH using crossed-molecular-beam methods. The cover image shows contour plots of normalized differential cross-sections versus velocity for OH collisions with Ar obtained from close-coupling calculations.

Article p985

IMAGE: SARANDIS MARINAKIS

COVER DESIGN: ALEX WING

ON THE COVER

Site-selective reactions
Target acquired
Articles p990 and p996;
News & Views p963

Carbon-oxygen bonds
The long and short of it
Article p1018

Cluster chemistry
Go with the flow
Article p1037

EDITORIAL

955 **Take aim**

THESIS

956 **Naming names**

Michelle Francl

958 **Free at last!**

Dennis P. Curran

BOOKS & ARTS

959 **Theatre: Tenure bubbles burst**

Abigail Klopper

RESEARCH HIGHLIGHTS

960 **Our choice from the recent literature**

BLOGROLL

961 **Eye of the beholder**

Written by Karl D. Collins

NEWS & VIEWS

962 **Lithium-air batteries: Something from nothing**

Fangyi Cheng and Jun Chen

963 **Site-selective reactions: Remodelling by diversity and design**

Pamela M. Tadross and Eric N. Jacobsen

965 **Water splitting: Catalyst or spectator?**

Daniel R. Gamelin

967 **Single-molecule magnets: Uranyl steps in the ring**

Polly L. Arnold

969 **Organic photochemistry: Exciting excited-state aromaticity**

Henrik Ottosson

971 **Anticancer agents: Unleash the forces within**

Weiwei Gao and Liangfang Zhang

IN YOUR ELEMENT

1052 **Plutonium's new horizons**

Jan Hartmann



nature publishing group

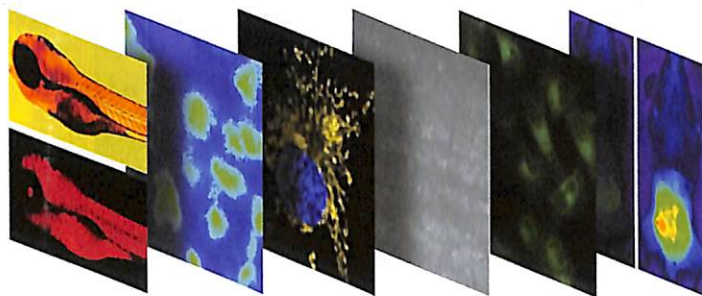
Nature Chemistry (ISSN 1755-4330, USPS 025131) is published monthly by Nature Publishing Group, Porters South, 4 Crinan Street, London N1 9XW, UK. Editorial Office: Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4563. Email: nchem@nature.com. North American Advertising: *Nature Chemistry*, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 212 726 9200. Fax: +1 212 696 9006. European Advertising: *Nature Chemistry*, Porters South, 4 Crinan Street, London N1 9XW, UK. Telephone: +44 (0)20 7833 4000. Fax: +44 (0)20 7843 4749. New subscriptions/renewals/changes of address/back issues and all other customer service questions should be addressed to: North America: Nature Publishing Group, Customer Services Department, 75 Varick Street, 9th Floor, New York, NY 10013-1917, USA. Telephone: +1 (866) 363 7860. Fax: +1 (212) 334 0879. Outside North America: Nature Publishing Group, Subscriptions Department, Brunel Road, Houndmills, Basingstoke, Hants, RG21 6XS, UK. Telephone: +44 (0)1256 329242. Fax: +44 (0)1256 812358. The 2013 US annual subscription price is \$4677 (Full), \$107 (Personal 1 year). Airfreight and mailing in the USA by agent named Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA; UK/Rest of World (excluding Europe and Japan) £2400 (institutional/corporate), £55 (individual making personal payment); Europe €3713 (institutional/corporate), €85 (individual making personal payment). Japan: contact Nature Asia-Pacific, Chiyoda Building, 2-37 Ichigayatamachi, Shinjuku-Ku, Tokyo, 162-0843, Japan. Telephone: +81 3 3267 8751. For single back issue prices contact the publisher. Periodicals postage paid at Jamaica, NY 11431. *Nature Chemistry* is published monthly by Nature Publishing Group, The Macmillan Building, 4 Crinan Street, London N1 9XW, UK. US Postmaster: Send address changes to *Nature Chemistry*, Air Business Ltd, c/o Worldnet Shipping Inc, 156-15, 146th Avenue, 2nd Floor, Jamaica, NY 11434, USA. Distributed in the USA by Mercury Intl 365 Blair Rd, Avenel, NJ 07001. Reprints: *Nature Chemistry* Reprints Department, Porters South, 4 Crinan Street, London N1 9XW, UK. Subscription records are maintained at Nature Publishing Group, Brunel Road, Basingstoke, Hampshire RG21 6XT, UK. Air Business Ltd is acting as our mailing agent. Subscription information is available at the *Nature Chemistry* homepage at <http://www.nature.com/naturechemistry>. © 2012 Macmillan Publishers Limited. All rights reserved.

REVIEW ARTICLE

973 Reaction-based small-molecule fluorescent probes for chemoselective bioimaging

Jefferson Chan, Sheel C. Dodani and Christopher J. Chang

The complexity of living systems makes attempts to gain a molecular-level understanding of them a unique and inspiring challenge. This Review summarizes progress in the development of bioorthogonal reaction-based fluorescent probes used to follow the spatial and temporal dynamics of biologically important analytes within living systems.

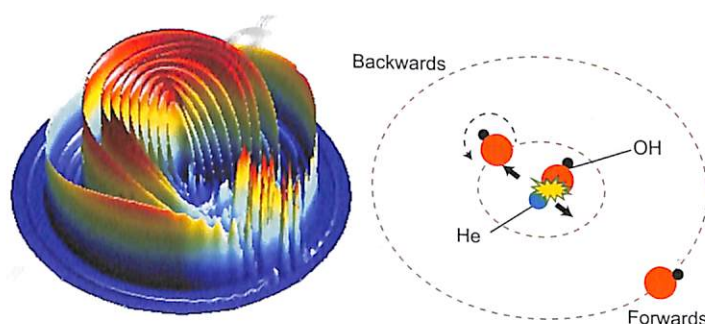


ARTICLES

985 Inelastic scattering of hydroxyl radicals with helium and argon by velocity-map imaging

Gautam Sarma, Sarantos Marinakis, J. J. ter Meulen, David H. Parker and Kenneth G. McKendrick

Hydroxyl radicals (OH) are important in many chemical systems, including combustion and atmospheric reactions, however experimentally measuring their velocities in specific internal quantum states has proved difficult. Now differential cross-sections for inelastic scattering of fully state-specified OH with He and Ar have been observed for the first time using velocity-map imaging in a crossed-molecular-beam arrangement.

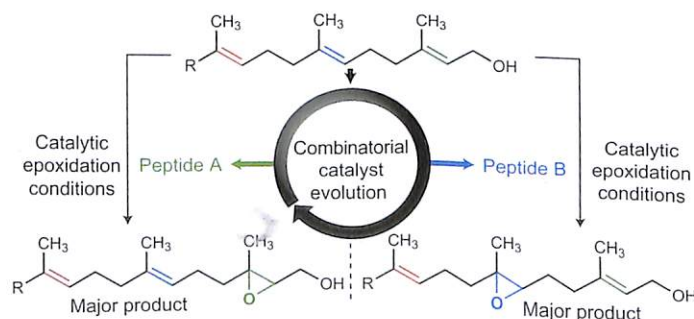


990 Combinatorial evolution of site- and enantioselective catalysts for polyene epoxidation

Phillip A. Lichtor and Scott J. Miller

Aspartic acid-based catalysts that are selective for oxidation of either the 2,3 position or the 6,7 position of certain isoprenols have been discovered. The catalysts emerged from a diversity-based approach employing the one-bead-one-compound libraries. The site-selectivity of the catalysis seems to derive from the hydroxyl group in the substrate, although the details of this are not yet known.

→N&V p963

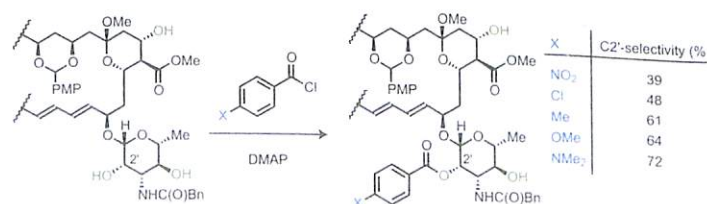


996 Electronic tuning of site-selectivity

Brandon C. Wilcock, Brice E. Uno, Gretchen L. Bromann, Matthew J. Clark, Thomas M. Anderson and Martin D. Burke

Site-selective functionalizations of complex small molecules can generate targeted derivatives with exceptional step-efficiency, but general strategies for maximizing selectivity in this context are rare. Investigations with the ion-channel-forming natural product amphotericin B have revealed that site-selectivity can be tuned by simply modifying the electronic nature of the reagents.

→N&V p963

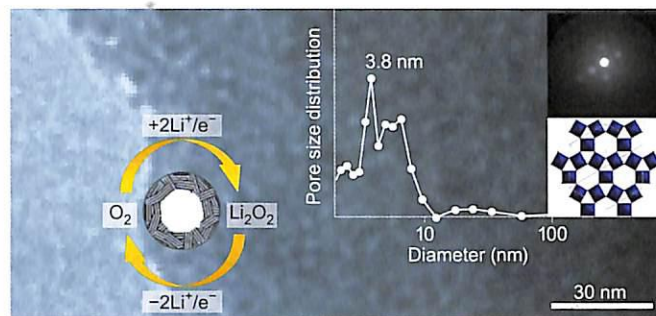


1004 Synthesis of a metallic mesoporous pyrochlore as a catalyst for lithium-O₂ batteries

Si Hyoung Oh, Robert Black, Ekaterina Pomerantseva, Jin-Hyon Lee and Linda F. Nazar

The lithium-O₂ battery can theoretically provide energy densities that greatly exceed that of Li-ion, but it requires more efficient catalysts (or 'promoters') than carbon for oxygen reduction and evolution. Here, we report a tailor-made mesoporous metallic oxide that results in high reversible capacities and operates over many cycles.

→N&V p962

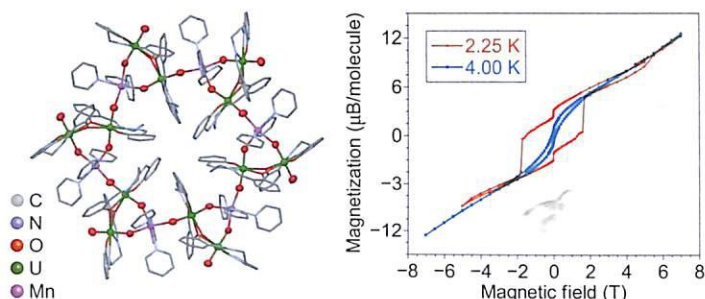


1011 Uranium and manganese assembled in a wheel-shaped nanoscale single-molecule magnet with high spin-reversal barrier

Victor Mougel, Lucile Chatelain, Jacques Pécaut, Roberto Caciuffo, Eric Colineau, Jean-Christophe Griveau and Marinella Mazzanti

A {U₁₂Mn₆} wheel-shaped cluster that has been assembled through cation-cation interactions exhibits single-molecule-magnet behaviour. Single-molecule magnets are promising for magnetic storage devices at the nanoscale, and the observation of magnetic bistability with an open hysteresis loop and high relaxation barrier in this 5f-3d complex suggests that uranium-based compounds could be useful components.

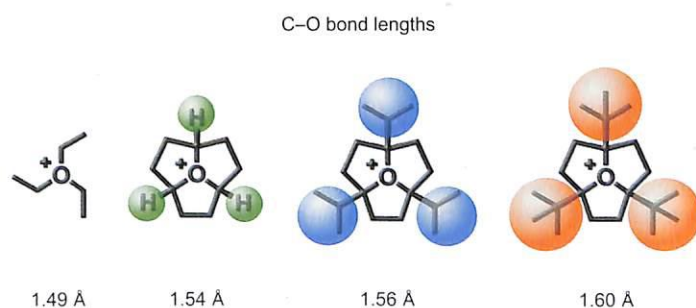
→N&V p967



1018 Extreme oxatriquinanes and a record C-O bond length

Gorkem Gunbas, Nema Hafezi, William L. Sheppard, Marilyn M. Olmstead, Irini V. Stoyanova, Fook S. Tham, Matthew P. Meyer and Mark Mascal

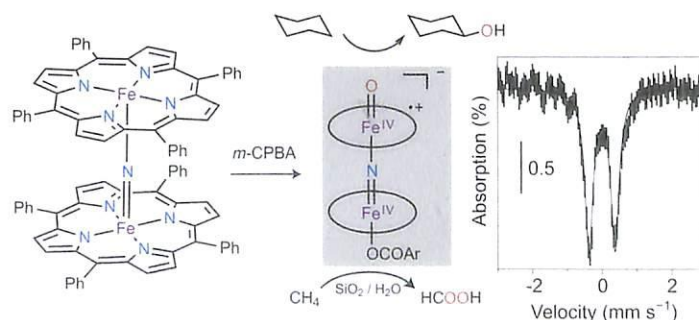
Oxatriquinane is a remarkably stable alkyl oxonium ion, despite the fact that its carbon-oxygen bond lengths are 1.54 Å. The robust nature of this fused tricyclic molecule enabled the addition of increasing steric bulk to the system, culminating in a tri-tert-butylloxatriquinane with a record 1.62 Å C-O bond distance.



1024 An N-bridged high-valent diiron-oxo species on a porphyrin platform that can oxidize methane

Evgeny V. Kudrik, Pavel Afanasiev, Leonardo X. Alvarez, Patrick Dubourdeaux, Martin Clémancey, Jean-Marc Latour, Geneviève Blondin, Denis Bouchu, Florian Albrieux, Sergey E. Nefedov and Alexander B. Sorokin

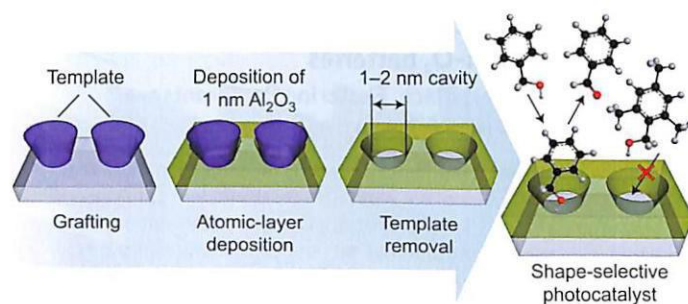
A short-lived diiron-oxo species — based on a nitrido-bridged bis-porphyrin platform — capable of efficiently oxidizing the strongest of C-H bonds has been prepared and spectroscopically characterized. The catalytic properties of this high-valent diiron(IV)-oxo complex were elucidated by studying the oxidation kinetics of a range of alkanes.



1030 Shape-selective sieving layers on an oxide catalyst surface

Christian P. Canlas, Junling Lu, Natalie A. Ray, Nicolas A. Grosso-Giordano, Sungsik Lee, Jeffrey W. Elam, Randall E. Winans, Richard P. Van Duyne, Peter C. Stair and Justin M. Notestein

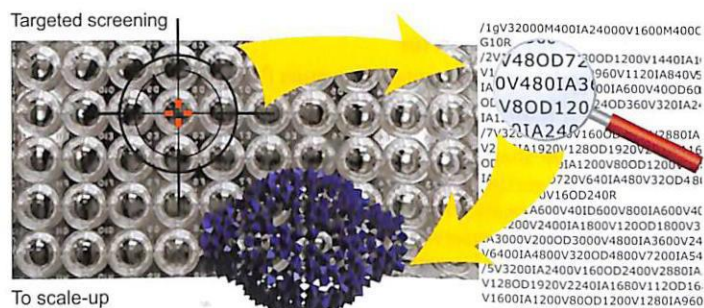
Templated atomic layer deposition (ALD) is used to create oxide 'nanocavities' on the surface of catalyst particles. Subnanometre films containing nanocavities act as sieves for the underlying catalyst, resulting in high selectivities for the smaller of two reactants in competitive oxidations or reductions.



1037 A flow-system array for the discovery and scale up of inorganic clusters

Craig J. Richmond, Haralampos N. Miras, Andreu Ruiz de la Oliva, Hongying Zang, Victor Sans, Leonid Paramonov, Charalampos Makatsoris, Ross Inglis, Euan K. Brechin, De-Liang Long and Leroy Cronin

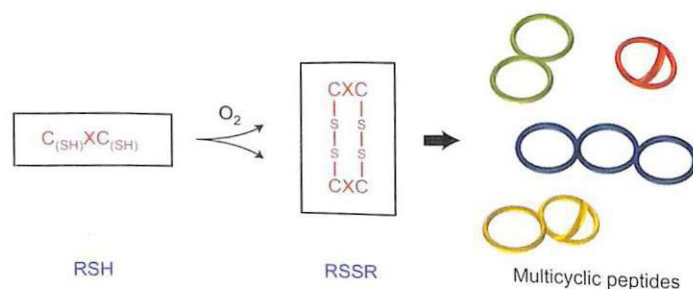
The discovery and synthesis of inorganic clusters can be both time consuming and limited by a lack of reproducibility. An automated flow process coupled with multiple batch crystallization has now been successfully used to rapidly screen and scale-up the syntheses of inorganic clusters, including polyoxometalates and manganese-based single-molecule magnets.



1044 Twin disulfides for orthogonal disulfide pairing and the directed folding of multicyclic peptides

Chuanliu Wu, Jean-Christophe Leroux and Marc A. Gauthier

The precise pairing of cysteine residues in proteins is routinely achieved in nature. However, the comparable pairing within polypeptides is a long-standing challenge for the preparation of multicyclic species. Here, a straightforward approach to direct the inter-/intramolecular pairing of cysteine residues within peptides using a minimal CXC motif is presented.



1050 Corrigendum