

Chemical Science

www.rsc.org/chemicalscience

The Royal Society of Chemistry is the world's leading chemistry community. Through our high impact journals and publications we connect the world with the chemical sciences and invest the profits back into the chemistry community.

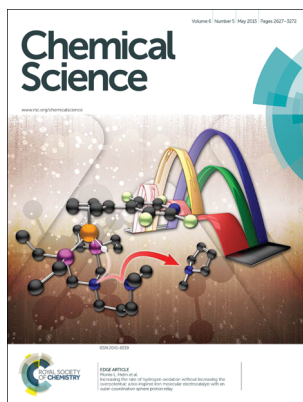
IN THIS ISSUE

ISSN 2041-6539 CODEN CSHCBM 6(5) 2627–3272 (2015)



Cover

See Erwin Reisner *et al.*,
pp. 2727–2736.
Image reproduced by
permission of Erwin Reisner
from *Chem. Sci.*, 2015, 6, 2727.



Inside cover

See Monte L. Helm *et al.*,
pp. 2737–2745.
Image reproduced by
permission of Tomiann Parker,
Authorized Agent for Battelle
Memorial Institute from
Chem. Sci., 2015, 6, 2737.

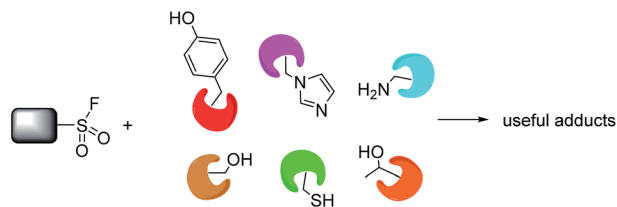
PERSPECTIVES

2650

Sulfonyl fluorides as privileged warheads in chemical biology

Arjun Narayanan and Lyn H. Jones*

The use of sulfonyl fluoride probes in chemical biology is reviewed.

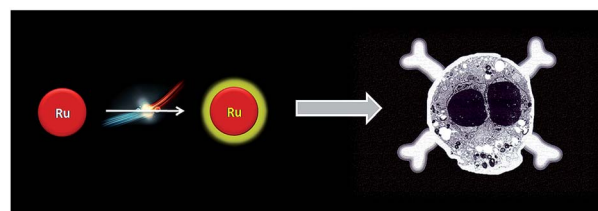


2660

Combination of Ru(II) complexes and light: new frontiers in cancer therapy

Cristina Mari, Vanessa Pierroz, Stefano Ferrari and Gilles Gasser*

In this perspective article, we present the recent achievements in the application of ruthenium complexes as photosensitizers and as photoactivatable prodrugs.



Editorial staff

Interim executive editor

May Copsey

Deputy editor

Jeanne Andres

Editorial production manager

Philippa Ross

Development editors

Alessia Millemaggi

Cesar Palmero

Publishing editors

Matthew Bown, Sage Bowser, Hugh Cowley,
Ruth Dilleen, Cally Haynes, Alan Holder,
Samantha Ivell, James Moore, Liisa Niitsoo,
Victoria Richards, Susan Weatherby, Rachel Wood

Publishing assistants

Natalie Ford, Bethany Johnson, Rebecca Wojturska

Publisher

Jamie Humphrey

For queries about submitted articles please contact
Philippa Ross, Editorial production manager, in the
first instance. E-mail chemicalscience@rsc.org

For pre-submission queries please contact
May Copsey, Interim executive editor.
E-mail chemicalscience-rsc@rsc.org

Chemical Science (electronic: ISSN 2041-6539)
is published monthly by the Royal Society of
Chemistry, Thomas Graham House, Science Park,
Milton Road, Cambridge, CB4 0WF, UK.

Chemical Science is a Gold Open Access journal
and all articles from 2015 onwards are free to
read. Please email orders@rsc.org to register
your interest or contact RSC Order Department,
Royal Society of Chemistry, Thomas Graham
House, Science Park, Milton Road, Cambridge,
CB4 0WF, UK

Tel +44 (0)1223 432398; E-mail orders@rsc.org

Advertisement sales: Tel +44 (0) 1223 432246;

Fax +44 (0) 1223 426017; E-mail advertising@rsc.org

For marketing opportunities relating to this journal,
contact marketing@rsc.org

Chemical Science

www.rsc.org/chemicalscience

Editorial board

Editor-in-chief

Daniel G. Nocera, Harvard University

Associate editors

Alán Aspuru-Guzik, Harvard
University
Zhenan Bao, Stanford University
Christopher C. Cummins,
Massachusetts Institute of
Technology
Kazunari Domen, University of Tokyo

Vy Dong, University of California,
Irvine
Matthew Gaunt, University of
Cambridge
Hubert Girault, Federal Polytechnic
School of Lausanne
Christopher A. Hunter, University of
Cambridge
David A. Leigh, University of
Manchester
Kopin Liu, Academia Sinica

James K. McCusker, Michigan State
University
Wonwoo Nam, Ewha Womans
University
Carsten Schultz, European Molecular
Biology Laboratory
F. Dean Toste, University of California,
Berkeley
Haw Yang, Princeton University
Jihong Yu, Jilin University

Advisory board

Takuzo Aida, University of Tokyo
Markus Antonietti, Max Planck
Institute of Colloids and Interfaces
Polly Arnold, University of Edinburgh
Xinhe Bao, Dalian Institute of
Chemical Physics
Guy Bertrand, University of California,
Los Angeles
Jeffrey Bode, Swiss Federal Institute of
Technology Zurich
Christopher Chang, University of
California, Berkeley
Chi-Ming Che, University of Hong
Kong
Jason Chin, Medical Research Council
Laboratory of Molecular Biology
Daniel Chiu, University of Washington
Graham Cooks, Purdue University
Eugenio Coronado, University of
Valencia
Lee Cronin, University of Glasgow
Gautam R. Desiraju, Indian Institute of
Science, Bangalore
James Durrant, Imperial College
London
Ben Feringa, University of Groningen
Cynthia Friend, Harvard University
Makoto Fujita, University of Tokyo
Philip Gale, University of Southampton
Song Gao, Peking University
Jinlong Gong, Tianjin University
Justin Gooding, University of New
South Wales
Michael Graetzel, Federal Polytechnic
School of Lausanne
Duncan Graham, University of
Strathclyde
Boxing Han, Chinese Academy of
Sciences

Jeremy Harvey, University of Bristol
Christy Haynes, University of
Minnesota
Johan Hofkens, Catholic University
of Leuven
Linda Hsieh-Wilson, California
Institute of Technology
Eric Jacobsen, Harvard University
Takashi Kato, University of Tokyo
Seong Keun Kim, Seoul National
University
Jerome Lacour, University of Geneva
James Leighton, Columbia University
Steve Ley, University of Cambridge
Chao-Jun Li, McGill University
Wenbin Lin, University of North
Carolina
Watson Loh, Instituto de Quimica
Julie Macpherson, University of
Warwick
Stephen Mann, University of Bristol
Bert Meijer, Eindhoven University of
Technology
Nils Metzler-Nolte, Ruhr University
Bochum
Scott Miller, Yale University
Daniel Mindiola, Indiana University
Mohammad Movassaghi,
Massachusetts Institute of
Technology
Jonathan Nitschke, University of
Cambridge
Kyoko Nozaki, University of Tokyo
Takashi Ooi, Nagoya University
Rachel O'Reilly, University of Warwick
Michel Orrit, Leiden University
Oleg Ozerov, Texas A&M University
Hongkun Park, Harvard University

Rasmita Raval, University of Liverpool
Paul Reider, Princeton University
Stuart Rowan, Case Western Reserve
University
Richmond Sarpong, University of
California, Berkeley
Gregory Scholes, University of
Toronto
Oliver Seitz, Humboldt University of
Berlin
Kay Severin, Federal Polytechnic
School of Lausanne
Mikiko Sodeoka, RIKEN
Brian Stoltz, California Institute of
Technology
Weihong Tan, University of Florida
He Tian, East China University of
Science and Technology
Zhong-Qun Tian, Xiamen University
Andrei Tokmakoff, University of
Chicago
Jan Van Hest, Radboud University
Tom Welton, Imperial College London
Christina White, University of Illinois
Martin Wolf, Fritz Haber Institute of
the Max Planck Society
Omar Yaghi, University of California,
Los Angeles
Vivian Yam, University of Hong Kong
Yang Yang, University of California,
Los Angeles
Shu-Hong Yu, University of Science
and Technology of China
Qi-Lin Zhou, Nankai University

Information for authors

Full details on how to submit material for publication
in Chemical Science are given in the Instructions for
Authors (available from <http://www.rsc.org/authors>).
Submissions should be made via the journal's homepage:
<http://www.rsc.org/chemicalscience>.

Authors may reproduce/republish portions of their
published contribution without seeking permission
from the RSC, provided that any such republication is
accompanied by an acknowledgement in the form:
(Original Citation)–Reproduced by permission of
The Royal Society of Chemistry.

This journal is ©The Royal Society of Chemistry 2015.
Apart from fair dealing for the purposes of research or
private study for non-commercial purposes, or criticism
or review, as permitted under the Copyright, Designs and

Patents Act 1988 and the Copyright and Related
Rights Regulation 2003, this publication may only be
reproduced, stored or transmitted, in any form or by
any means, with the prior permission in writing of the
Publishers or in the case of reprographic reproduction
in accordance with the terms of licences issued by the
Copyright Licensing Agency in the UK. US copyright law is
applicable to users in the USA.

The Royal Society of Chemistry takes reasonable care in
the preparation of this publication but does not accept
liability for the consequences of any errors or omissions.

Ⓢ The paper used in this publication meets the
requirements of ANSI/NISO Z39.48–1992
(Permanence of Paper).
Registered Charity No. 207890.



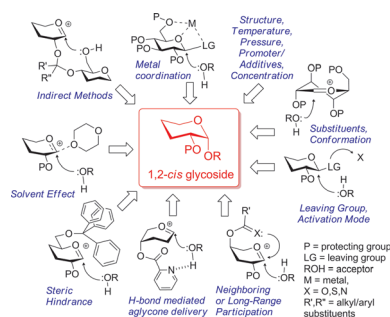
PERSPECTIVES

2687

Stereocontrolled 1,2-*cis* glycosylation as the driving force of progress in synthetic carbohydrate chemistry

Swati S. Nigudkar and Alexei V. Demchenko*

Recent developments in stereoselective 1,2-*cis* glycosylation that have emerged during the past decade are surveyed herein.

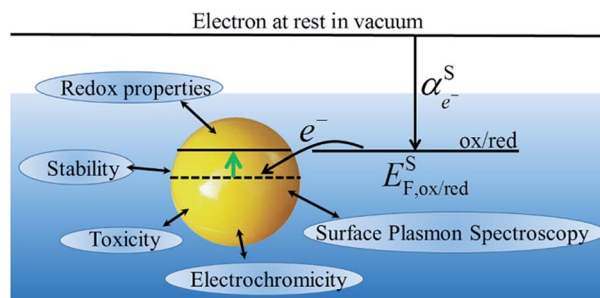


2705

Charging and discharging at the nanoscale: Fermi level equilibration of metallic nanoparticles

Micheál D. Scanlon, Pekka Peljo, Manuel A. Méndez, Evgeny Smirnov and Hubert H. Girault*

Surrounding environment, excess charge and size affect the Fermi level of the electrons in nanoparticles, having a significant influence on their properties.



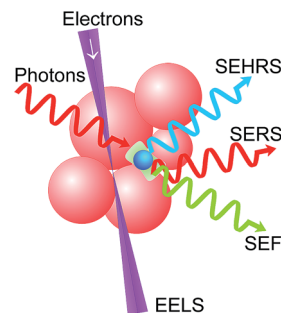
MINIREVIEW

2721

Probing plasmonic nanostructures by photons and electrons

Katrin Kneipp, Harald Kneipp and Janina Kneipp

Exploiting photons and electrons opens up exciting new capabilities to study complex plasmonic nanostructures and related local fields.



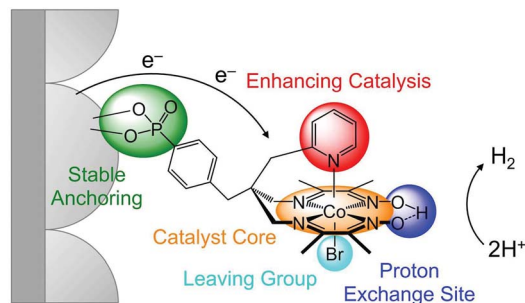
EDGE ARTICLES

2727

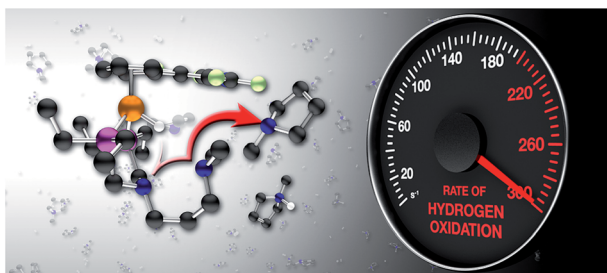
Enhancing H₂ evolution performance of an immobilised cobalt catalyst by rational ligand design

Janina Willkomm, Nicoleta M. Muresan and Erwin Reisner*

Rational ligand design was employed to improve the proton reduction activity of an immobilised cobalt diimine-dioxime catalyst.



2737

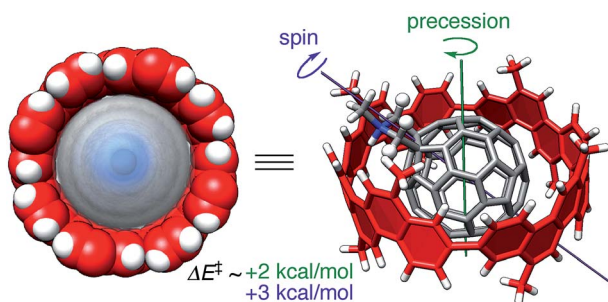


Increasing the rate of hydrogen oxidation without increasing the overpotential: a bio-inspired iron molecular electrocatalyst with an outer coordination sphere proton relay

Jonathan M. Darmon, Neeraj Kumar, Elliott B. Hulley, Charles J. Weiss, Simone Raugei, R. Morris Bullock and Monte L. Helm*

H₂ oxidation by a molecular electrocatalyst is dramatically improved by controlling proton movement from iron to the outer coordination sphere.

2746

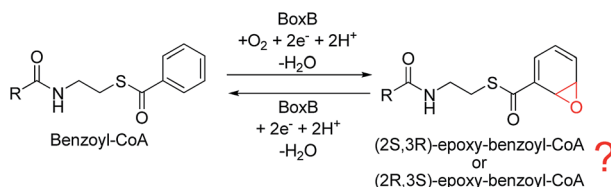


Theoretical studies on a carbonaceous molecular bearing: association thermodynamics and dual-mode rolling dynamics

Hiroyuki Isobe,* Kosuke Nakamura, Shunpei Hitosugi, Sota Sato, Hiroaki Tokoyama, Hideo Yamakado, Koichi Ohno and Hirohiko Kono*

The dynamics of a carbonaceous molecular bearing were investigated by DFT methods to reveal dual-mode motions with a minute energy barrier.

2754

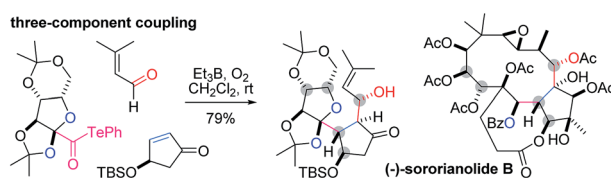


Mechanism and selectivity of the dinuclear iron benzoyl-coenzyme A epoxidase BoxB

Rong-Zhen Liao* and Per E. M. Siegbahn*

DFT calculations are used to elucidate the reaction mechanism and selectivity of BoxB catalyzed benzoyl-CoA epoxidation.

2765



Et₃B-mediated two- and three-component coupling reactions *via* radical decarbonylation of α -alkoxyacyl tellurides: single-step construction of densely oxygenated carboskeletons

Masanori Nagatomo, Daigo Kamimura, Yuki Matsui, Keisuke Masuda and Masayuki Inoue*

We devised new radical-based two- and three-component coupling reactions of sugar derivatives, and realized one-step construction of contiguously substituted polyol structures.

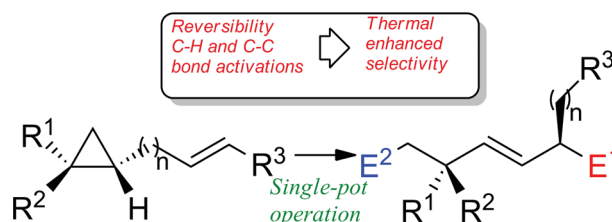


2770

Remote functionalization of hydrocarbons with reversibility enhanced stereocontrol

Alexandre Vasseur, Lionel Perrin,* Odile Eisenstein and Ilan Marek*

Remote functionalization of hydrocarbons could be achieved through successive zirconocene-mediated allylic C–H bond activations followed by a selective C–C bond cleavage.

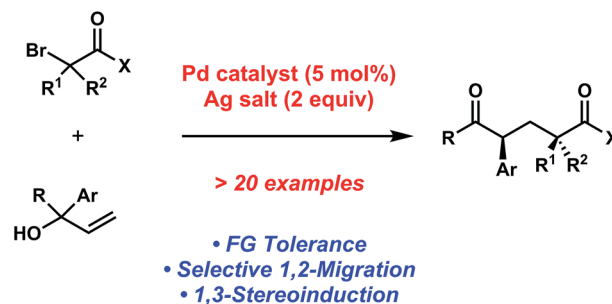


2777

Palladium-catalyzed cross-coupling of α -bromocarbonyls and allylic alcohols for the synthesis of α -aryl dicarbonyl compounds

Yang Yu and Uttam K. Tambar*

A palladium-catalyzed coupling of α -bromocarbonyl compounds and allylic alcohols has been developed for the generation of acyclic aryl-substituted dicarbonyl compounds.

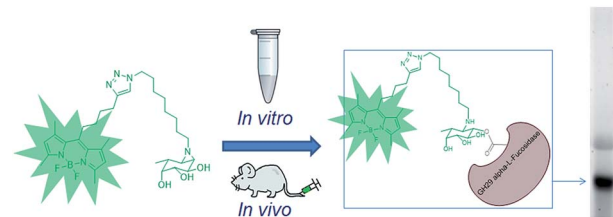


2782

In vitro and *in vivo* comparative and competitive activity-based protein profiling of GH29 α -L-fucosidases

J. Jiang, W. W. Kallemeijn, D. W. Wright, A. M. C. H. van den Nieuwendijk, V. Coco Rohde, E. Colomina Folch, H. van den Elst, B. I. Florea, S. Scheij, W. E. Donker-Koopman, M. Verhoek, N. Li, M. Schürmann, D. Mink, R. G. Boot, J. D. C. Codée, G. A. van der Marel, G. J. Davies, J. M. F. G. Aerts* and H. S. Overkleeft*

Development of probes for active GH29 α -L-fucosidases.

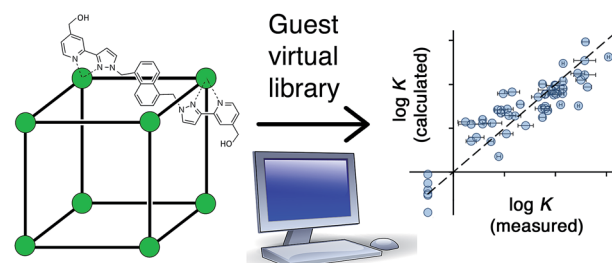


2790

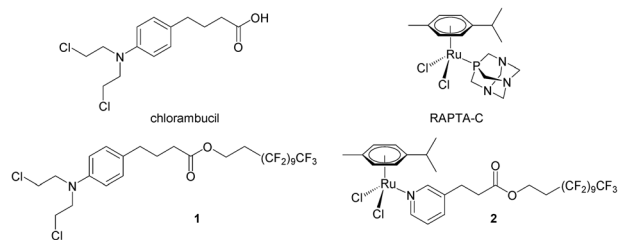
Virtual screening for high affinity guests for synthetic supramolecular receptors

William Cullen, Simon Turega, Christopher A. Hunter* and Michael D. Ward*

The protein/ligand docking programme 'GOLD' can be used to identify new strongly-binding guests for a synthetic coordination cage host.



2795

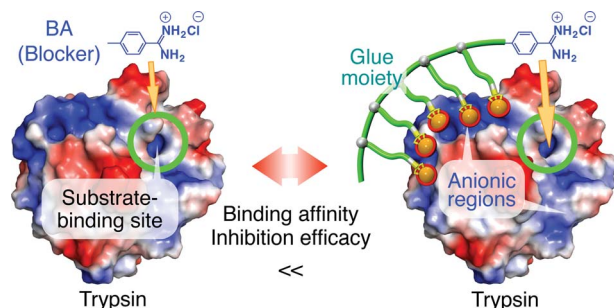


***In vivo* evaluation of small-molecule thermoresponsive anticancer drugs potentiated by hyperthermia**

Catherine M. Clavel, Patrycja Nowak-Sliwinska, Emilia Păunescu, Arjan W. Griffioen and Paul J. Dyson*

Hyperthermia used as an adjuvant with chemotherapy is highly promising in the treatment of certain cancers.

2802

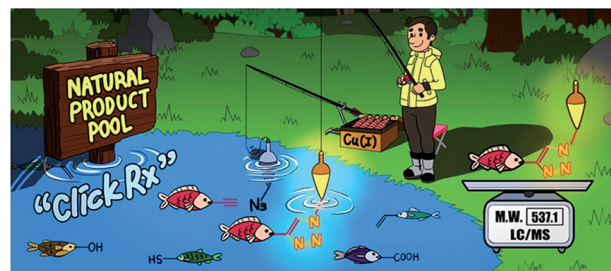


Molecular glues for manipulating enzymes: trypsin inhibition by benzamidine-conjugated molecular glues

Rina Mogaki, Kou Okuro* and Takuzo Aida*

The inhibitory effect of benzamidine as blocker on the protease activity of trypsin is enhanced by covalent conjugation with bioadhesive molecular glue.

2806

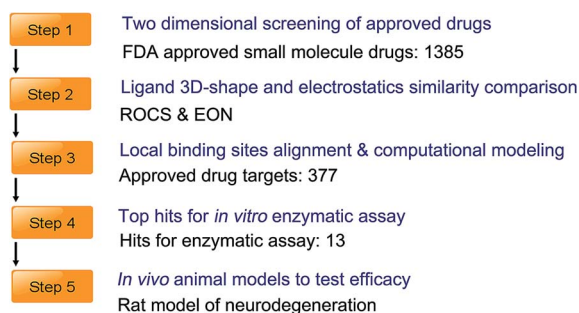


Chemical assay-guided natural product isolation via solid-supported chemodosimetric fluorescent probe

Hongjun Jeon, Chaemin Lim, Ji Min Lee and Sanghee Kim*

The fusion of click chemistry, fluorogenic chemodosimetry and a solid support offers advantages in identifying compounds in complex natural product mixtures.

2812



Computational discovery and experimental verification of tyrosine kinase inhibitor pazopanib for the reversal of memory and cognitive deficits in rat model neurodegeneration

Yongliang Yang,* Guohui Li,* Dongyu Zhao, Haoyang Yu, Xiliang Zheng, Xiangda Peng, Xiaoe Zhang, Ting Fu, Xiaoqing Hu, Mingshan Niu, Xuefei Ji, Libo Zou* and Jin Wang*

Pazopanib, a tyrosine kinase inhibitor marketed for cancer treatment, abrogates the course of neurodegeneration.

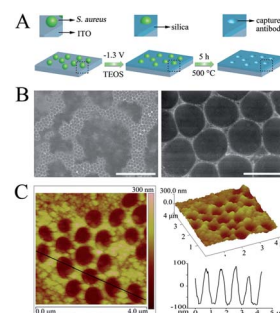


2822

Highly stable and reusable imprinted artificial antibody used for *in situ* detection and disinfection of pathogens

Zhijun Zhang, Yijia Guan, Meng Li, Andong Zhao, Jinsong Ren and Xiaogang Qu*

We fabricate artificial antibodies based on imprinting technology and develop a sandwich ELISA for pathogen detection.



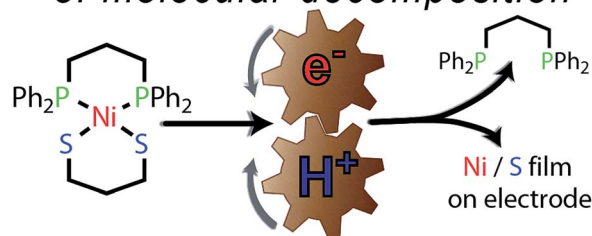
2827

Electrode initiated proton-coupled electron transfer to promote degradation of a nickel(II) coordination complex

Brian D. McCarthy, Carrie L. Donley and Jillian L. Dempsey*

Electrochemical analysis of a nickel compound that degrades permitted a peek into the decomposition mechanism.

peeking inside the black box of molecular decomposition

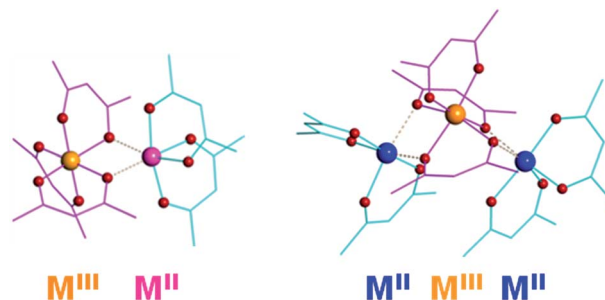


2835

Mixed-valent, heteroleptic homometallic diketonates as templates for the design of volatile heterometallic precursors

Craig M. Lieberman, Alexander S. Filatov, Zheng Wei, Andrey Yu. Rogachev, Artem M. Abakumov and Evgeny V. Dikarev*

A unique series of mixed-valent transition metal complexes ($M^{III} = Fe$; $M^{II} = Fe, Mn, Ni$) have been designed using a combination of diketonate ligands with electron-withdrawing (blue) and electron-donating (pink) substituents.

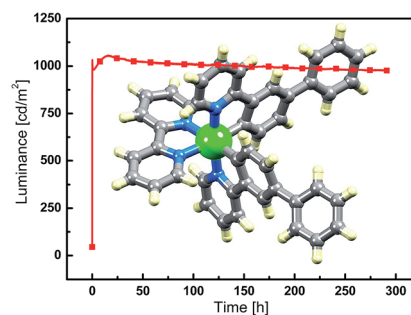


2843

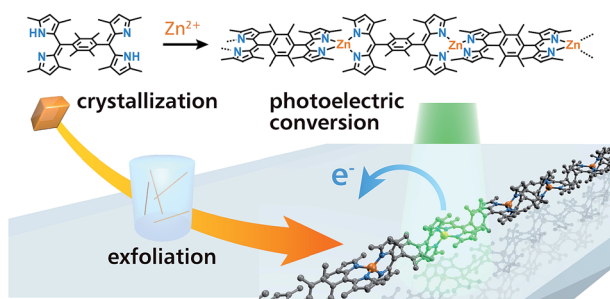
Exceptionally long-lived light-emitting electrochemical cells: multiple intra-cation π -stacking interactions in $[Ir(C^{\wedge}N)_2(N^{\wedge}N)][PF_6]$ emitters

Andreas M. Bünzli, Edwin C. Constable, Catherine E. Housecroft,* Alessandro Prescimone, Jennifer A. Zampese, Giulia Longo, Lidón Gil-Escrig, Antonio Pertegás, Enrique Ortí and Henk J. Bolink*

Extremely long-lived LEC devices have been achieved using $[Ir(C^{\wedge}N)_2(bpy)]^+$ complexes with phenyl-substituted $C^{\wedge}N$ ligands.



2853

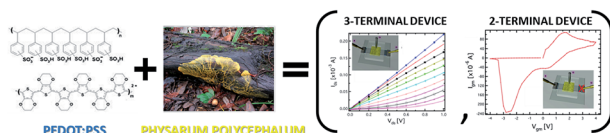


Bis(dipyrinato)metal(II) coordination polymers: crystallization, exfoliation into single wires, and electric conversion ability

Ryota Matsuoka, Ryojun Toyoda, Ryota Sakamoto,* Mizuho Tsuchiya, Ken Hoshiko, Tatsuhiko Nagayama, Yoshiyuki Nonoguchi, Kunihisa Sugimoto, Eiji Nishibori, Tsuyoshi Kawai and Hiroshi Nishihara*

The titled coordination polymers feature crystallization, single wire exfoliation, processability, and applicability to photoelectric and thermoelectric conversion systems.

2859

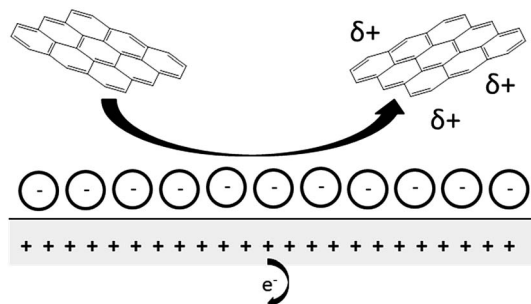


A hybrid living/organic electrochemical transistor based on the *Physarum polycephalum* cell endowed with both sensing and memristive properties

G. Tarabella, P. D'Angelo,* A. Cifarelli, A. Dimonte, A. Romeo, T. Berzina, V. Erokhin and S. Iannotta*

A hybrid bio-organic electrochemical transistor based on the *Physarum polycephalum* cell, showing a multifunctional operation (transistor and memristive-like response), has been demonstrated.

2869

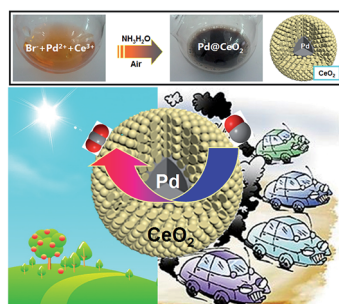


Single graphene nanoplatelets: capacitance, potential of zero charge and diffusion coefficient

Jeffrey Poon, Christopher Batchelor-McAuley, Kristina Tschulik and Richard G. Compton*

A nano-impact chronoamperometric experiment is presented here as a powerful technique for simultaneously probing important physical properties of graphene nanomaterials.

2877



γ -Al₂O₃ supported Pd@CeO₂ core@shell nanospheres: salting-out assisted growth and self-assembly, and their catalytic performance in CO oxidation

Xiao Wang, Dapeng Liu,* Junqi Li, Jiangman Zhen, Fan Wang and Hongjie Zhang*

Highly active Pd@CeO₂ core@shell nanospheres with tunable Pd core sizes for catalytic CO oxidation.

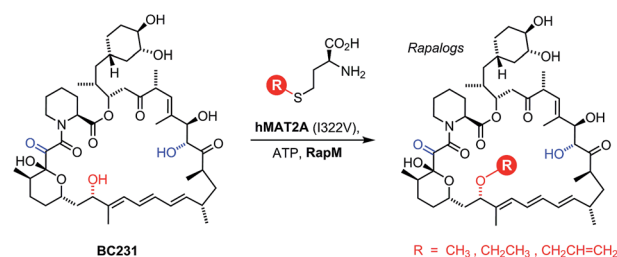


2885

Site-specific bioalkylation of rapamycin by the RapM 16-O-methyltransferase

Brian J. C. Law, Anna-Winona Struck, Matthew R. Bennett, Barrie Wilkinson and Jason Micklefield*

Characterisation of a rapamycin O-methyltransferase (RapM) and its utilisation in coupled reactions, with an improved variant of the human methionine adenosyl transferase (hMAT2A), results in new regioselectively alkylated rapamycin derivatives.

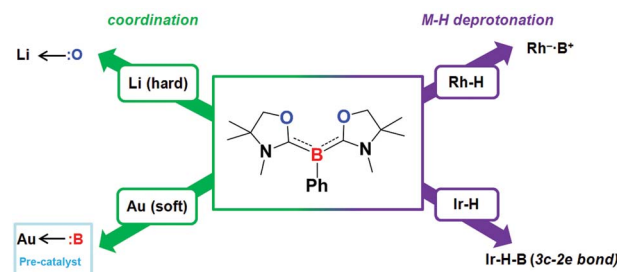


2893

Diverse reactivity of a tricoordinate organoboron L₂PhB: (L = oxazol-2-ylidene) towards alkali metal, group 9 metal, and coinage metal precursors

Lingbing Kong, Rakesh Ganguly, Yongxin Li and Rei Kinjo*

The reactivity of a tricoordinate organoboron L₂PhB: (L = oxazol-2-ylidene) **1** towards metal precursors and its coordination chemistry were comprehensively studied.

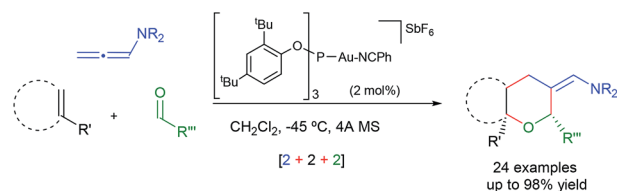


2903

Gold(I)-catalyzed [2 + 2 + 2] cycloaddition of allenamides, alkenes and aldehydes: a straightforward approach to tetrahydropyrans

Hélio Faustino, Iván Varela, José L. Mascareñas* and Fernando López*

A novel fully intermolecular gold-catalyzed [2 + 2 + 2] cycloaddition involving an allenamide, an alkene and an aldehyde provides a straightforward entry to tetrahydropyrans.

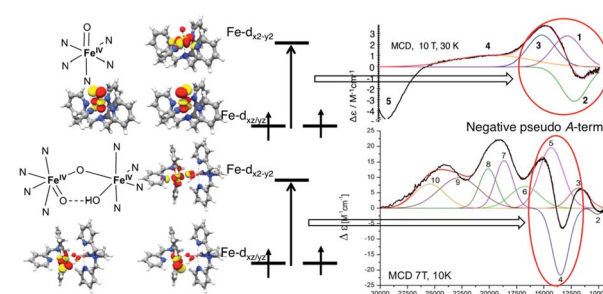


2909

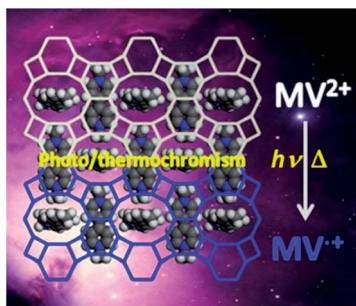
Magnetic circular dichroism and computational study of mononuclear and dinuclear iron(IV) complexes

Shengfa Ye,* Genqiang Xue, Itana Krivokapic, Taras Petrenko, Eckhard Bill,* Lawrence Que Jr* and Frank Neese*

The electronic structures of mononuclear and dinuclear iron(IV) complexes are studied using magnetic circular dichroism and wavefunction-based *ab initio* methods, and then correlated with their similar reactivities toward H- and O-atom transfer.



2922

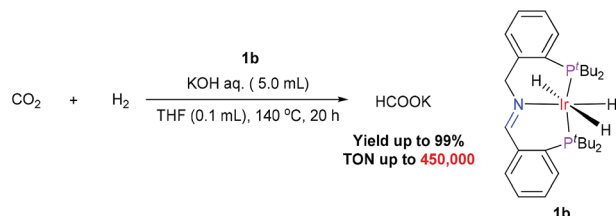


Methyl viologen-templated zinc gallophosphate zeolitic material with dual photo-/thermochromism and tuneable photovoltaic activity

Junbiao Wu, Chunyao Tao, Yi Li, Jiyang Li* and Jihong Yu*

The first zeolitic material templated by MV^{2+} cations exhibits dual photo-/thermochromism with ultralong-lived charge separation and high thermal stability, as well as tuneable photovoltaic activity.

2928

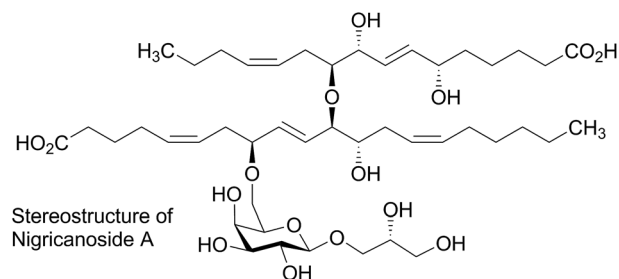


Highly efficient hydrogenation of carbon dioxide to formate catalyzed by iridium(III) complexes of imine–diphosphine ligands

Chong Liu, Jian-Hua Xie, Gui-Long Tian, Wei Li and Qi-Lin Zhou*

A new iridium catalyst containing an imine–diphosphine ligand was developed for the hydrogenation of CO_2 to formate.

2932

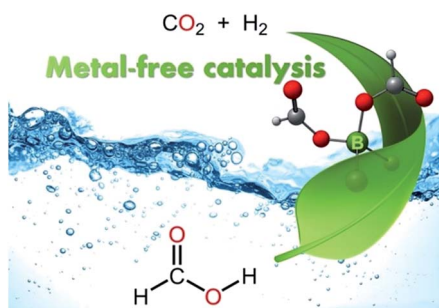


Structure elucidation of nigricanoside A through enantioselective total synthesis

Jie Chen, Panduka Koswatta, J. Robb DeBergh, Peng Fu, Ende Pan, John B. MacMillan* and Joseph M. Ready*

Total synthesis enabled the assignment of relative and absolute stereochemistry of nigricanoside A, which was reported to show potent cytotoxicity.

2938



Metal-free dehydrogenation of formic acid to H_2 and CO_2 using boron-based catalysts

Clément Chauvier, Anis Tlili, Christophe Das Neves Gomes, Pierre Thuéry and Thibault Cantat*

The decomposition of formic acid to H_2 and CO_2 under metal-free conditions has been unveiled using dialkylborane derivatives as catalysts.

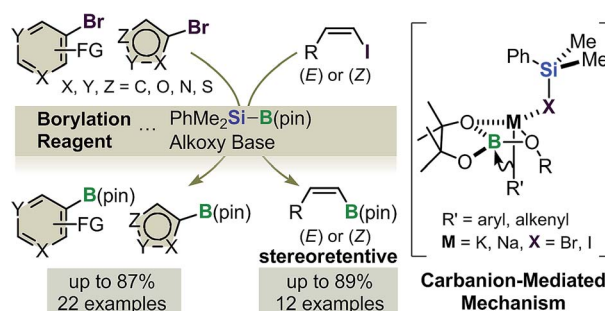


2943

Boryl substitution of functionalized aryl-, heteroaryl- and alkenyl halides with silylborane and an alkoxy base: expanded scope and mechanistic studies

Eiji Yamamoto, Satoshi Ukigai and Hajime Ito*

A transition-metal-free method has been developed for the boryl substitution of functionalized aryl-, heteroaryl- and alkenyl halides using a silylborane/alkoxy-base reagent. Borylation of (Z)-alkenyl halides proceeded in a stereoretentive manner.

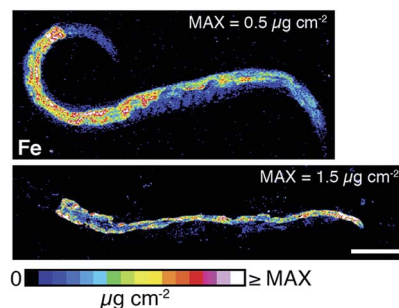


2952

Direct *in vivo* imaging of ferrous iron dyshomeostasis in ageing *Caenorhabditis elegans*

Simon A. James, Blaine R. Roberts, Dominic J. Hare, Martin D. de Jonge, Ian E. Birchall, Nicole L. Jenkins, Robert A. Cherny, Ashley I. Bush and Gawain McColl*

Synchrotron-based X-ray fluorescence imaging and metalloproteomics reveals a loss of iron homeostasis in ageing *Caenorhabditis elegans*.

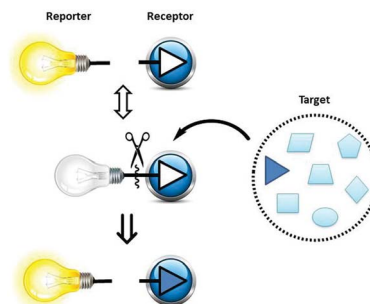


2963

Reaction-based Indicator displacement Assay (RIA) for the selective colorimetric and fluorometric detection of peroxynitrite

Xiaolong Sun, Karel Lacina, Elena C. Ramsamy, Stephen E. Flower, John S. Fossey, Xuhong Qian, Eric V. Anslyn,* Steven D. Bull* and Tony D. James*

Using the self-assembly of aromatic boronic acids with Alizarin Red S (ARS), we developed a new chemosensor for the selective detection of peroxynitrite.



2968

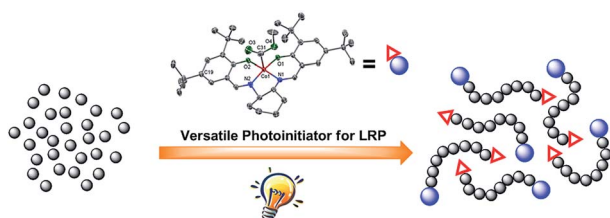
Expanding discriminative dimensions for analysis and imaging

Jérôme Querard, Arnaud Gautier,* Thomas Le Saux* and Ludovic Jullien*

OPTIMAL can discriminate – without any separation or washing step – a targeted photoswitchable probe used as labelling or titration contrast agent among various interfering compounds, photoswitchable or not.



2979

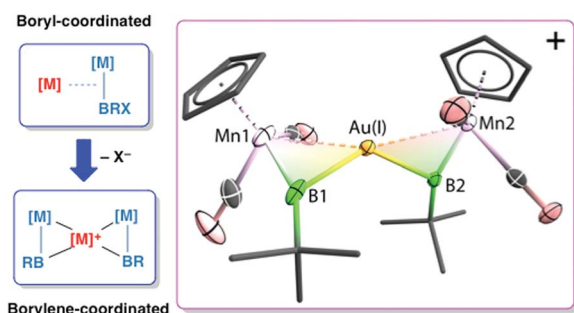


A well-defined, versatile photoinitiator (salen)Co–CO₂CH₃ for visible light-initiated living/controlled radical polymerization

Yaguang Zhao, Mengmeng Yu, Shuailin Zhang, Zhenqiang Wu, Yuchu Liu, Chi-How Peng* and Xuefeng Fu*

A well-defined organocobalt salen complex (salen)Co–CO₂CH₃ is used as a versatile photoinitiator for visible light-initiated living radical polymerization.

2989

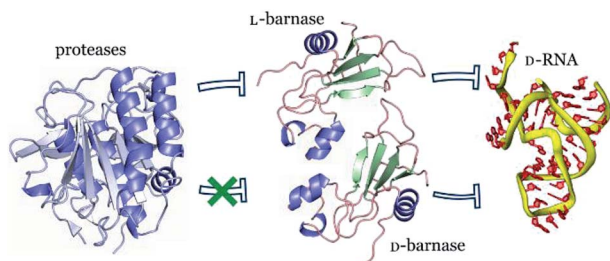


Side-on coordination of boryl and borylene complexes to cationic coinage metal fragments

Holger Braunschweig,* Krzysztof Radacki and Rong Shang

The M-(η^2 -BMn) complex [(η^5 -C₅H₅)(OC)₂Mn{ μ -B(Cl)(tBu)-Au(PPh₃)}] (2) can be functionalized via halide substitution reactions to afford isostructural complexes [(η^5 -C₅H₅)(OC)₂Mn{ μ -B(R)(tBu)Au(PPh₃)}] (R = Ph, CPh and NCS).

2997

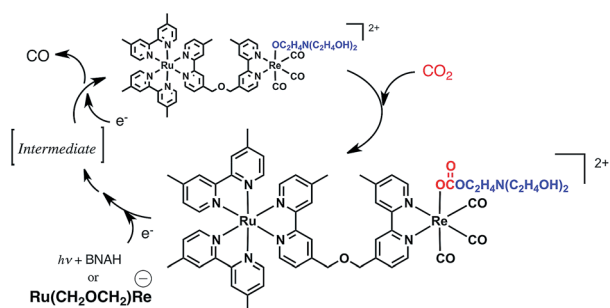


Total synthesis and biochemical characterization of mirror image barnase

Alexander A. Vinogradov, Ethan D. Evans and Bradley L. Pentelute*

Chemically prepared D-barnase catalyzes hydrolysis of native RNA and appears to be extremely stable to proteolysis.

3003



Ru(II)–Re(I) binuclear photocatalysts connected by –CH₂XCH₂– (X = O, S, CH₂) for CO₂ reduction

Eishiro Kato, Hiroyuki Takeda, Kazuhide Koike, Kei Ohkubo and Osamu Ishitani*

New Ru(II)–Re(I) diads with bridging ligands constructed of two diimines connected by –CH₂OCH₂– or –CH₂SCH₂– were synthesized and investigated as photocatalysts with enhanced oxidation power.

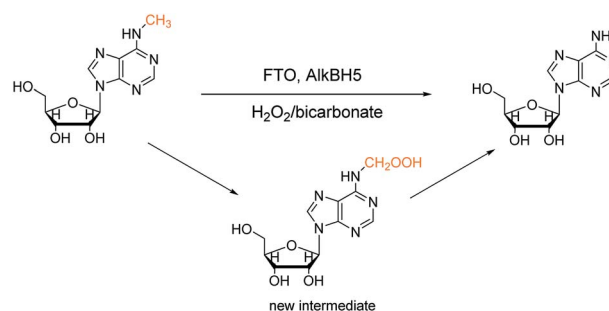


3013

***N*⁶-Hydroperoxymethyladenosine: a new intermediate of chemical oxidation of *N*⁶-methyladenosine mediated by bicarbonate-activated hydrogen peroxide**

Jinjun Wu, Heng Xiao, Tianlu Wang, Tingting Hong, Boshi Fu, Dongsheng Bai, Zhiyong He, Shuang Peng, Xiwen Xing, Jianlin Hu, Pu Guo and Xiang Zhou*

A new route is found in the chemical oxidation of *N*⁶-methyladenosine using a H₂O₂/bicarbonate system through the *N*⁶-hydroperoxymethyladenosine (oxm⁶A) intermediate.

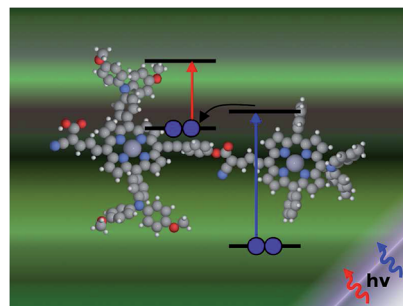


3018

Design of two-photon molecular tandem architectures for solar cells by *ab initio* theory

Kristian B. Ørnsø*, Juan M. Garcia-Lastra, Gema De La Torre, F. J. Himpsel, Angel Rubio and Kristian S. Thygesen*

We present new two-photon molecular architectures for photovoltaics where atomic precision can be obtained by synthetic chemistry.

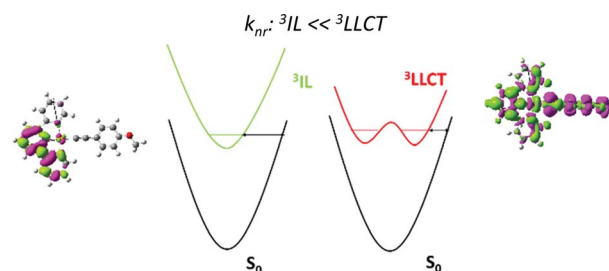


3026

Theoretical studies on the photophysical properties of luminescent pincer gold(III) arylacetylide complexes: the role of π -conjugation at the C-deprotonated [C[≡]N[−]][−] ligand

Glenna So Ming Tong*, Kaai Tung Chan, Xiaoyong Chang and Chi-Ming Che*

The facile non-radiative decay for gold(III) complexes is due to the thermally accessible ³LLCT, but not the usually assumed ³dd excited state.

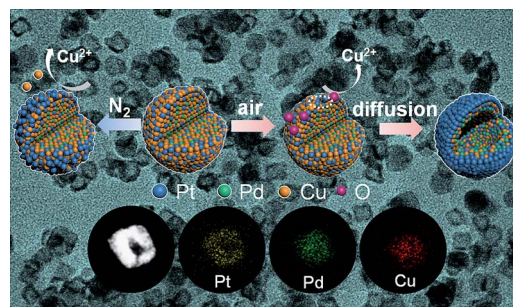


3038

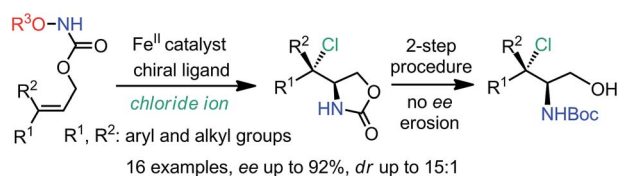
Hollow ternary PtPdCu nanoparticles: a superior and durable cathodic electrocatalyst

Xiao-Jing Liu, Chun-Hua Cui, Hui-Hui Li, Yong Lei, Tao-Tao Zhuang, Meng Sun, Muhammad Nadeem Arshad, Hassan A. Albar, Tariq R. Sobahi and Shu-Hong Yu*

Hollow PtPdCu nanoparticles with a Pt-enriched surface, formed by the dealloying action of acetic acid, exhibit superior durability and catalytic activity toward the ORR.



3044

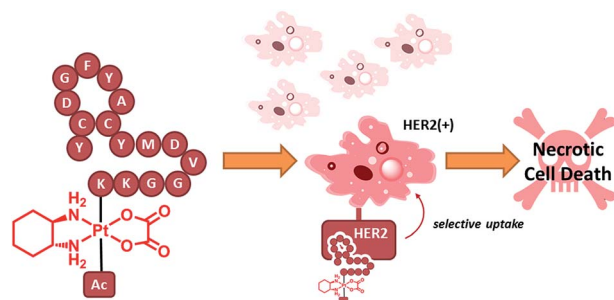


Iron(II)-catalyzed asymmetric intramolecular olefin aminochlorination using chloride ion

Cheng-Liang Zhu, Jun-Shan Tian, Zhen-Yuan Gu, Guo-Wen Xing and Hao Xu*

We report an iron-catalyzed asymmetric aminochlorination method for internal olefins; it tolerates valuable olefins that are incompatible with existing methods.

3051

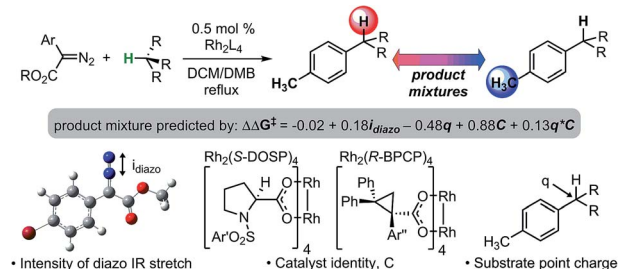


Induction of targeted necrosis with HER2-targeted platinum(IV) anticancer prodrugs

Daniel Yuan Qiang Wong, Jun Han Lim and Wee Han Ang*

Platinum(IV) prodrug complexes based on the cisplatin/oxaliplatin pharmacophore, containing anti-HER2/neu targeting peptides, were designed to deliver their cytotoxic platinum(II) payload selectively to highly HER2-expressing cells. Through induction of necrotic cell death, these platinum(IV)-peptide conjugates can circumvent apoptosis-resistance pathways in targeted HER2-positive cells.

3057

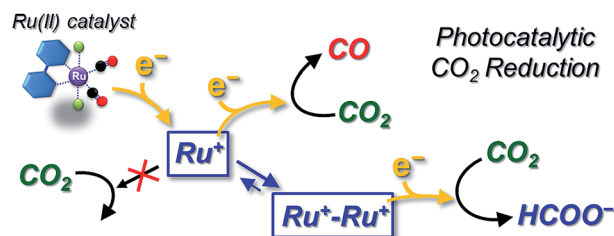


Using IR vibrations to quantitatively describe and predict site-selectivity in multivariate Rh-catalyzed C-H functionalization

Elizabeth N. Bess, David M. Guptill, Huw M. L. Davies* and Matthew S. Sigman*

Achieving selective C-H functionalization is a significant challenge that requires discrimination between many similar C-H bonds.

3063



Unexpected effect of catalyst concentration on photochemical CO₂ reduction by *trans*(Cl)-Ru(bpy)(CO)₂Cl₂: new mechanistic insight into the CO/HCOO⁻ selectivity

Yusuke Kuramochi, Jun Itabashi, Kyohei Fukaya, Akito Enomoto, Makoto Yoshida and Hitoshi Ishida*

We found catalyst concentration dependence of the product ratio in the photochemical reduction of CO₂, and proposed a new mechanism involving a Ru(I)-Ru(I) dimer intermediate.

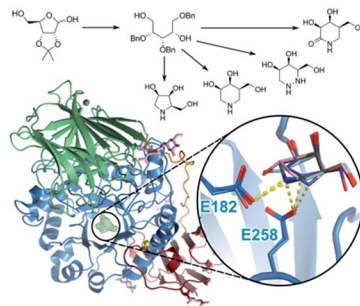


3075

Azasugar inhibitors as pharmacological chaperones for Krabbe disease

Chris H. Hill, Agnete H. Viuff, Samantha J. Spratley, Stéphane Salamone, Stig H. Christensen, Randy J. Read, Nigel W. Moriarty, Henrik H. Jensen* and Janet E. Deane*

Modified azasugar molecules have been synthesized and characterized as excellent pharmacological chaperone candidates to treat the neurodegenerative disorder Krabbe disease.

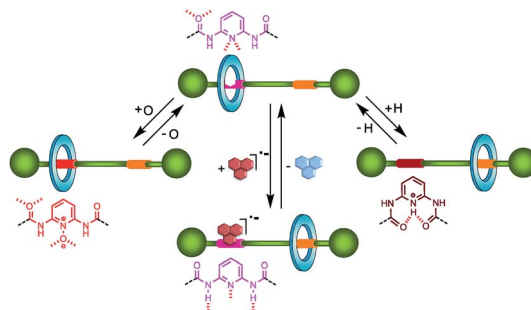


3087

Versatile control of the submolecular motion of di(acylamino)pyridine-based [2]rotaxanes

Alberto Martinez-Cuezva, Aurelia Pastor, Giacomo Cioncoloni, Raul-Angel Orenes, Mateo Alajarin, Mark D. Symes and Jose Berna*

Di(acylamino)pyridine motifs enable the building of switchable interlocked systems in which their dynamics can be exchanged between different states.

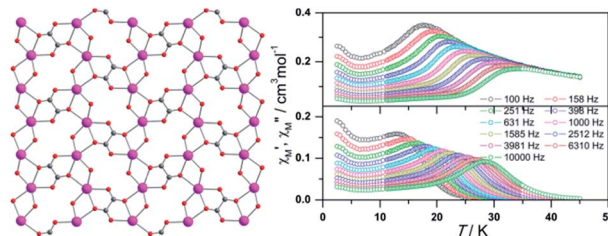


3095

Slow magnetic relaxation in a novel carboxylate/oxalate/hydroxyl bridged dysprosium layer

Dan-Dan Yin, Qi Chen, Yin-Shan Meng, Hao-Ling Sun*, Yi-Quan Zhang* and Song Gao*

2D dysprosium complex exhibiting slow magnetic relaxation originating from the strong Ising anisotropy of single Dy^{3+} ions has been reported.

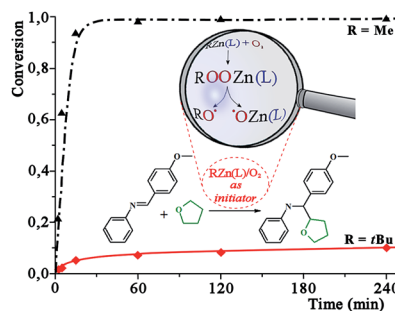


3102

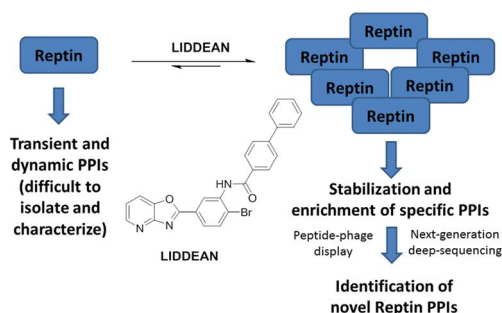
Development of zinc alkyl/air systems as radical initiators for organic reactions

Marcin Kubisiak, Karolina Zelga, Wojciech Bury, Iwona Justyniak, Krzysztof Budny-Godlewski, Zbigniew Ochal and Janusz Lewiński*

A novel organozinc initiator with a clear mechanistic signature for organic radical reactions has been developed.



3109

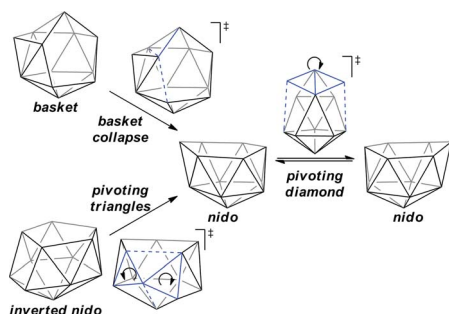


Discovery of a novel ligand that modulates the protein-protein interactions of the AAA+ superfamily oncoprotein reptin

Alan R. Healy, Douglas R. Houston,* Lucy Remnant, Anne-Sophie Huart, Veronika Brychtova, Magda M. Maslon, Olivia Meers, Petr Muller, Adam Krejci, Elizabeth A. Blackburn, Borek Vojtesek, Lenka Hernychova, Malcolm D. Walkinshaw, Nicholas J. Westwood* and Ted R. Hupp*

Discovery and use of a chemical tool.

3117

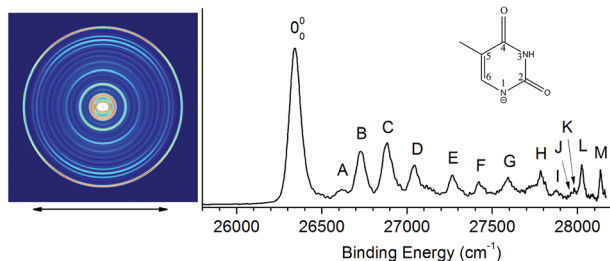


Isomerisation of *nido*-[C₂B₁₀H₁₂]²⁻ dianions: unprecedented rearrangements and new structural motifs in carborane cluster chemistry

David McKay,* Stuart A. Macgregor and Alan J. Welch

The formation and isomerisation of *nido*-[C₂B₁₀H₁₂]²⁻ species is investigated through DFT calculations, which reveal novel *basket* and *inverted nido* intermediates and unusual interconversion pathways, including *basket collapse* and *pivoting triangles* and *diamonds*.

3129

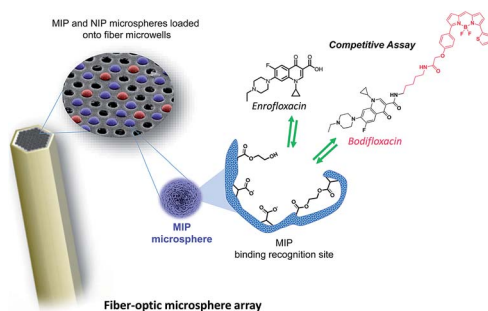


Probing the vibrational spectroscopy of the deprotonated thymine radical by photodetachment and state-selective autodetachment photoelectron spectroscopy via dipole-bound states

Dao-Ling Huang, Hong-Tao Liu, Chuan-Gang Ning, Guo-Zhu Zhu and Lai-Sheng Wang*

High-resolution state-selective autodetachment photoelectron spectroscopy via dipole-bound states and photodetachment spectroscopy of cryogenically cooled deprotonated thymine anions are reported.

3139



Fiber-optic array using molecularly imprinted microspheres for antibiotic analysis

Sergio Carrasco, Elena Benito-Peña,* David R. Walt* and María C. Moreno-Bondí*

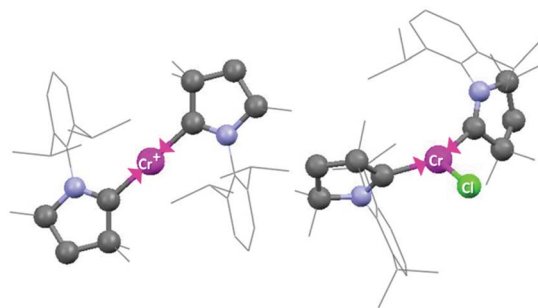
In this article we describe a new class of high-density optical microarrays based on molecularly imprinted microsphere sensors that directly incorporate specific recognition capabilities to detect enrofloxacin (ENRO), an antibiotic widely used for both human and veterinary applications.



3148

Cr(I)Cl as well as Cr⁺ are stabilised between two cyclic alkyl amino carbenes

Prinson P. Samuel, Roman Neufeld, Kartik Chandra Mondal, Herbert W. Roesky,* Regine Herbst-Irmer, Dietmar Stalke,* Serhiy Demeshko, Franc Meyer,* Vallyanga Chalil Rojisha, Susmita De, Pattiyil Parameswaran,* A. Claudia Stückl, Wolfgang Kaim, Jonathan H. Christian, Jasleen K. Bindra and Naresh S. Dalal*



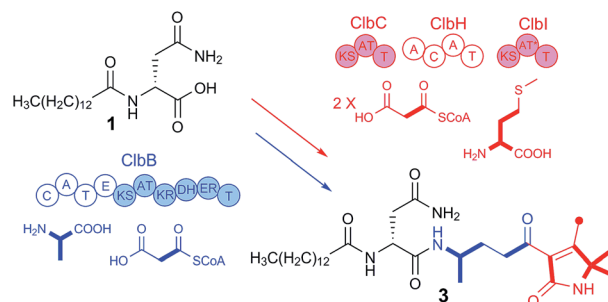
Complexes with two and three coordinate chromium(I).

3154

Two more pieces of the colibactin genotoxin puzzle from *Escherichia coli* show incorporation of an unusual 1-aminocyclopropanecarboxylic acid moiety

Xiaoying Bian, Alberto Plaza, Youming Zhang* and Rolf Müller*

Biosynthetic pathway intermediates related to genotoxin colibactin formation: a linear compound **3** bearing a rare 7-methyl-4-azaspiro[2.4]hept-6-en-5-one residue.

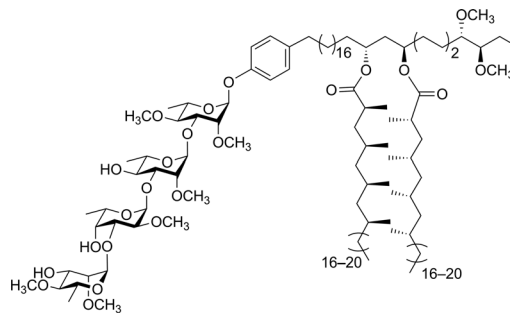


3161

Effect of phenolic glycolipids from *Mycobacterium kansasii* on proinflammatory cytokine release. A structure–activity relationship study

Hassan R. H. Elsaidi and Todd L. Lowary*

Mycobacterial Phenolic glycolipids (PGLs) are important cell wall virulence factors, which inhibit the production of host anti-inflammatory cytokines in a structure-dependent manner.

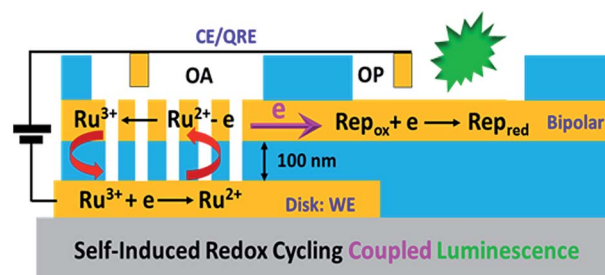


3173

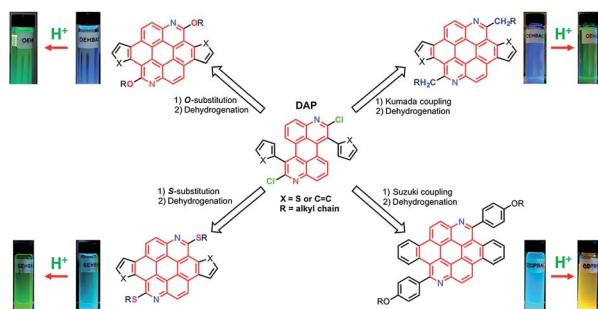
Self-induced redox cycling coupled luminescence on nanopore recessed disk-multiscale bipolar electrodes

Chaoxiong Ma, Lawrence P. Zaino III and Paul W. Bohn*

Self-induced redox cycling at nanopore ring-disk electrodes is coupled, through a bipolar electrode, to a remote fluorogenic reporter reaction.



3180

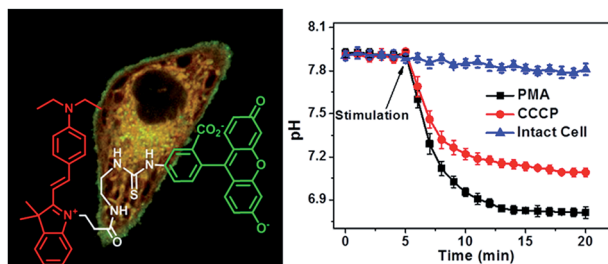


A divergent route to core- and peripherally functionalized diazacoronenes that act as colorimetric and fluorescence proton sensors

Bo He, Jing Dai, Danylo Zhrebetskyy, Teresa L. Chen, Benjamin A. Zhang, Simon J. Teat, Qichun Zhang, Linwang Wang and Yi Liu*

One-stop center for functional polycyclic aromatic hydrocarbons – a dichlorodiazaperylene intermediate has been synthesized and employed for the synthesis of highly functionalized coronene derivatives.

3187

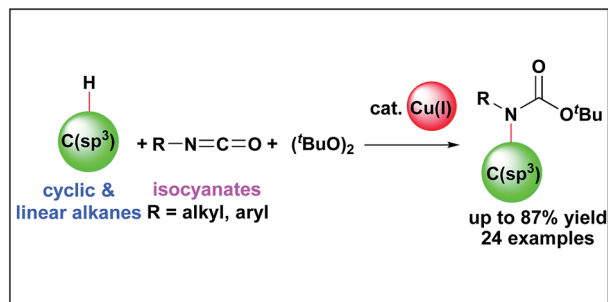


Ratiometric detection of pH fluctuation in mitochondria with a new fluorescein/cyanine hybrid sensor

Yuncong Chen, Chengcheng Zhu, Jiajie Cen, Yang Bai, Weijiang He* and Zijian Guo*

The first small-molecular ratiometric pH sensor with mitochondria targeting ability was constructed. With this sensor, the stimulated pH_m fluctuation in MCF-7 cells was monitored via both fluorescence confocal microscopy and flow cytometry.

3195

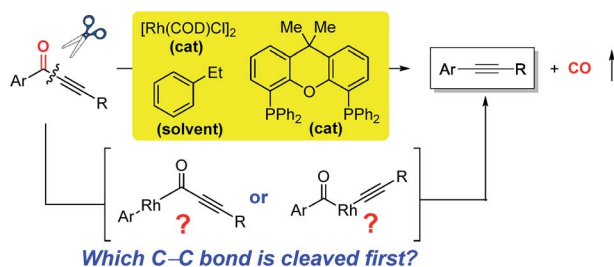


Copper-catalyzed intermolecular C(sp³)-H bond functionalization towards the synthesis of tertiary carbamates

Prasanna Kumara Chikkade, Yoichiro Kuninobu* and Motomu Kanai*

We describe the development of an intermolecular unactivated C(sp³)-H bond functionalization towards the direct synthesis of tertiary carbamates.

3201



Rh-catalyzed decarbonylation of conjugated ynones via carbon-alkyne bond activation: reaction scope and mechanistic exploration via DFT calculations

Alpay Dermenci, Rachel E. Whittaker, Yang Gao, Faben A. Cruz, Zhi-Xiang Yu* and Guangbin Dong*

We report a catalytic C-C bond activation of unstrained conjugated monoyones via decarbonylation to synthesize disubstituted alkynes.

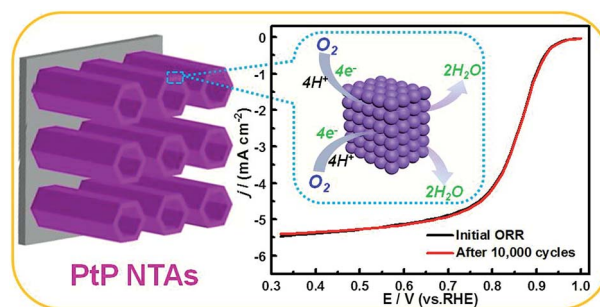


3211

Highly stable PtP alloy nanotube arrays as a catalyst for the oxygen reduction reaction in acidic medium

Lili Zhang, Meng Wei, Suqing Wang, Zhong Li, Liang-Xin Ding* and Haihui Wang*

Self-supporting PtP alloy nanotube arrays composed of interconnected PtP alloy nanocrystals exhibited excellent activity and durability for the ORR in acidic medium.

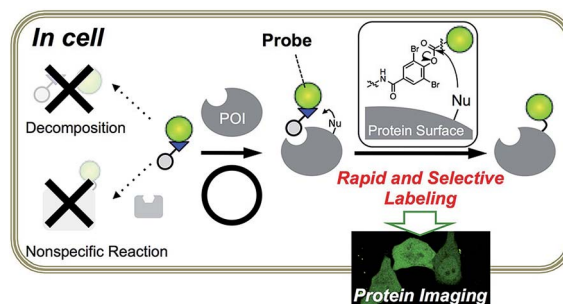


3217

Ligand-directed dibromophenyl benzoate chemistry for rapid and selective acylation of intracellular natural proteins

Yousuke Takaoka, Yuki Nishikawa, Yuki Hashimoto, Kenta Sasaki and Itaru Hamachi*

A rapid and selective protein labeling method, LDBB chemistry is a useful tool for natural protein imaging in living cells.

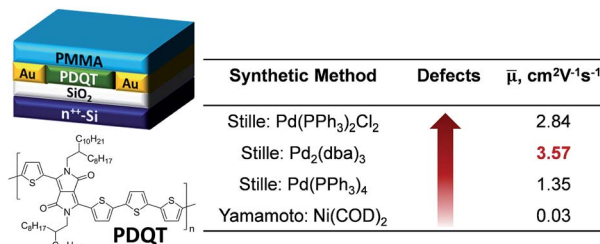


3225

Is a polymer semiconductor having a "perfect" regular structure desirable for organic thin film transistors?

Wei Hong, Shaoyun Chen, Bin Sun, Mark A. Arnould, Yuezhong Meng and Yuning Li*

Appreciable amounts of structural defects produced during Stille coupling polymerization have unexpected beneficial effects on the molecular ordering and charge transport performance of polymers.

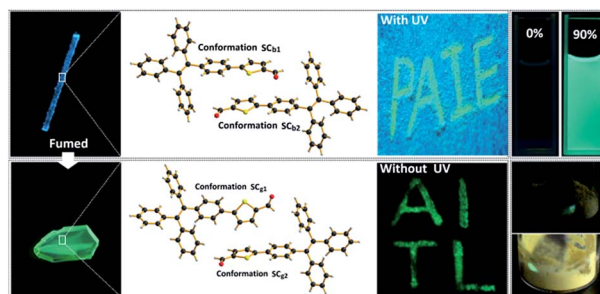


3236

Very bright mechanoluminescence and remarkable mechanochromism using a tetraphenylethene derivative with aggregation-induced emission

Bingjia Xu, Jiajun He, Yingxiao Mu, Qiangzhong Zhu, Sikai Wu, Yifan Wang, Yi Zhang,* Chongjun Jin, Changcheng Lo, Zhenguo Chi,* Alan Lien, Siwei Liu and Jiarui Xu*

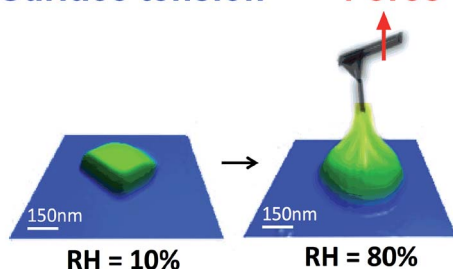
Two photoluminescent polymorphs exhibit different mechanoluminescence activities and mechanochromic behaviors.



EDGE ARTICLES

3242

Surface tension ↔ Force

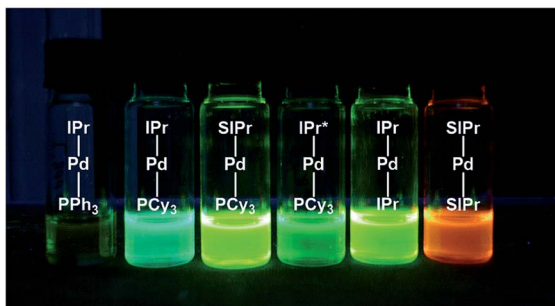


Humidity-dependent surface tension measurements of individual inorganic and organic submicrometre liquid particles

Holly S. Morris, Vicki H. Grassian* and Alexei V. Tivanski*

Atomic force microscopy has been utilized to measure the surface tension of atmospherically relevant droplets smaller than one micron.

3248

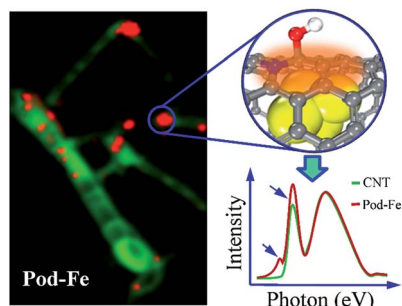


Palladium(0) NHC complexes: a new avenue to highly efficient phosphorescence

Adam F. Henwood, Mathieu Lesieur, Ashu K. Bansal, Vincent Lemaur, David Beljonne, David G. Thompson, Duncan Graham, Alexandra M. Z. Slawin, Ifor D. W. Samuel,* Catherine S. J. Cazin* and Eli Zysman-Colman*

We report the first examples of highly luminescent di-coordinated Pd(0) complexes.

3262



Visualizing electronic interactions between iron and carbon by X-ray chemical imaging and spectroscopy

Xiaoqi Chen, Jianping Xiao, Jian Wang, Dehui Deng,* Yongfeng Hu, Jigang Zhou, Liang Yu, Thomas Heine, Xiulian Pan and Xinhe Bao*

Pod-like carbon nanotube with encapsulated iron particles (Pod-Fe) was used as a well-defined model to study the electronic interaction between carbon shells and the iron particles by scanning transmission X-ray microscopy (STXM).

CORRECTIONS

3268

Correction: Electrostatic control of regioselectivity via ion pairing in a Au(I)-catalyzed rearrangement

Vivian M. Lau, Craig F. Gorin and Matthew W. Kanan*



CORRECTIONS

3269

Correction: Photoinduced dynamics of a cyanine dye: parallel pathways of non-radiative deactivation involving multiple excited-state twisted transients

Srigokul Upadhyayula, Vicente Nuñez, Eli M. Espinoza, Jillian M. Larsen, Duoduo Bao, Dewen Shi, Jenny T. Mac, Bahman Anvari and Valentine I. Vullev*

