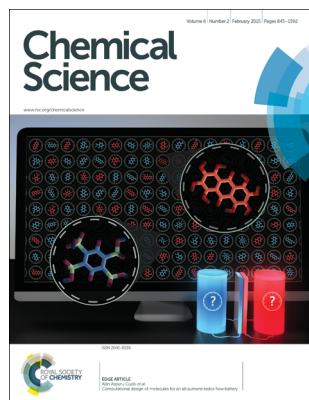


IN THIS ISSUE

ISSN 2041-6539 CODEN CSHCBM 6(2) 845–1592 (2015)



Cover
See Alán Aspuru-Guzik *et al.*, pp. 885–893.
Image designed by Lauren Aleza Kaye and reproduced by permission of Alán Aspuru-Guzik from *Chem. Sci.*, 2015, **6**, 885.



Inside cover
See Chung-Hang Leung, Dik-Lung Ma *et al.*, pp. 871–884.
Image reproduced by permission of Chung-Hang Leung from *Chem. Sci.*, 2015, **6**, 871.

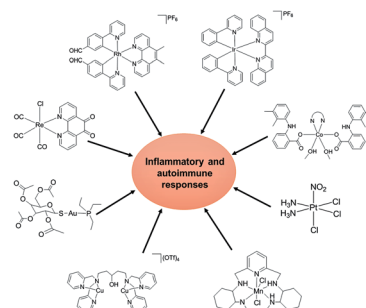
PERSPECTIVE

871

Metal complexes as potential modulators of inflammatory and autoimmune responses

Chung-Hang Leung,* Sheng Lin, Hai-Jing Zhong and Dik-Lung Ma*

In this perspective, we highlight recent examples in the development of transition metal complexes as modulators of inflammatory and autoimmune responses.



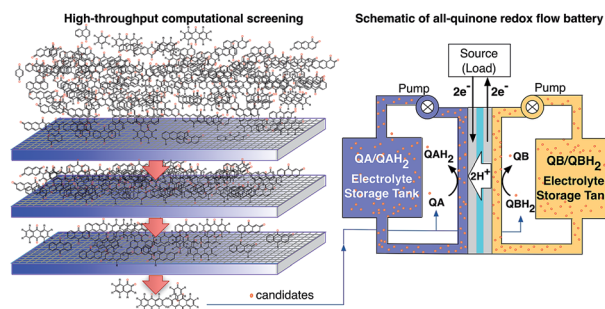
EDGE ARTICLES

885

Computational design of molecules for an all-quinone redox flow battery

Süleyman Er, Changwon Suh, Michael P. Marshak and Alán Aspuru-Guzik*

We demonstrate a successful high-throughput screening approach for the discovery of inexpensive, redox-active quinone molecules for organic-based aqueous flow batteries.



Editorial staff

Executive editor

Robert Eagling

Deputy editor

Jeanne Andres

Editorial production manager

Philippa Ross

Development editors

Alessia Millernaggi, Cesar Palmero-Palos

Publishing editors

Matthew Bown, Sage Bowser, Hugh Cowley,
Ruth Dilleen, Cally Haynes, Alan Holder,
Samantha Ivel, 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
Robert Eagling, 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

Associate editors

Zhenan Bao, Stanford University
Christopher W. Bielawski, University
of Texas at Austin
Christopher C. Cummins,
Massachusetts Institute of
Technology
Kazunari Domen, University of Tokyo

Matthew Gaunt, University of
Cambridge
Hubert Girault, Federal Polytechnic
School of Lausanne
David A. Leigh, University of
Manchester
Kopin Liu, Academia Sinica

Wonwoo Nam, Ewha Womans
University
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
Buxing 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
Christopher Hunter, University of
Sheffield
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
James McCusker, Michigan State
University
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
Daniel Nocera, Massachusetts
Institute of Technology
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.

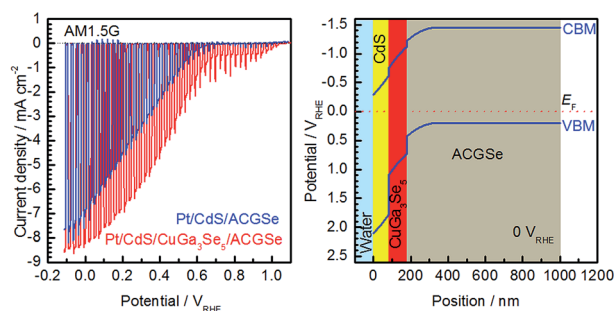


894

Durable hydrogen evolution from water driven by sunlight using (Ag,Cu)GaSe₂ photocathodes modified with CdS and CuGa₃Se₅

Li Zhang, Tsutomu Minegishi, Mamiko Nakabayashi, Yohichi Suzuki, Kazuhiko Seki, Naoya Shibata, Jun Kubota and Kazunari Domen*

The multilayer structure enhances the hydrogen evolution from water under simulated sunlight.

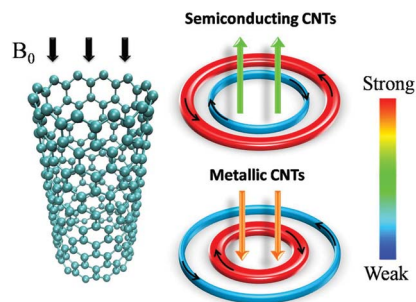


902

Exploring the ring current of carbon nanotubes by first-principles calculations

Pengju Ren, Anmin Zheng, Jianping Xiao, Xiulian Pan and Xinhe Bao*

The ring currents by the axial component of B_0 depend on the semiconducting or metallic properties of CNTs and hence determine the overall magnetic responses and the aromatic characters.

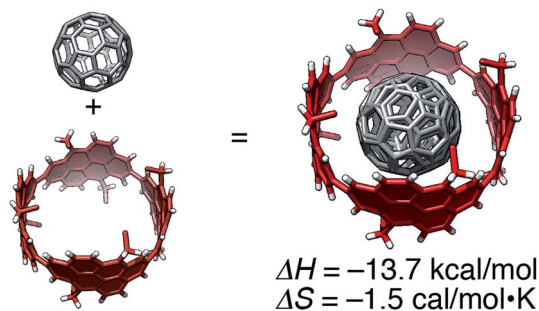


909

Molecular recognition in curved π -systems: effects of π -lengthening of tubular molecules on thermodynamics and structures

Taisuke Matsuno, Sota Sato, Ryosuke Iizuka and Hiroyuki Isobe*

The thermodynamics and molecular structure of a supramolecular complex between a tubular molecule, (P)-(12,8)-[4]cyclo-2,8-anthanthrenylene, and fullerene were investigated.

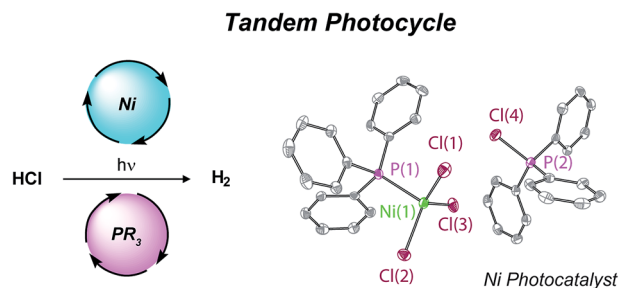


917

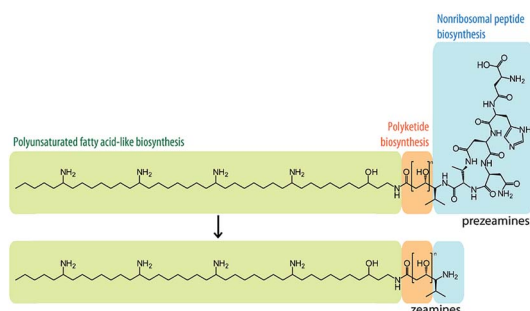
Tandem redox mediator/Ni(II) trihalide complex photocycle for hydrogen evolution from HCl

Seung Jun Hwang, David C. Powers, Andrew G. Maher and Daniel G. Nocera*

The challenge that short excited state lifetimes of first-row transition metal complexes present to the photoactivation of M–X bonds has been overcome with a phosphine mediator coupled to a nickel metal catalyst.



923

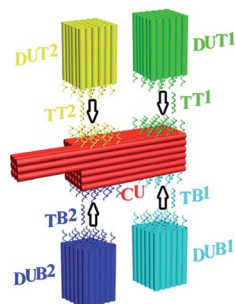


A combination of polyunsaturated fatty acid, nonribosomal peptide and polyketide biosynthetic machinery is used to assemble the zeamine antibiotics

Joleen Masschelein, Charlien Clauwers, Ufedo R. Awodi, Karen Stalmans, Wesley Vermaelen, Eveline Lescrinier, Abram Aertsen, Chris Michiels, Gregory L. Challis* and Rob Lavigne*

Zeamine assembly involves nonribosomal peptide, polyketide and polyunsaturated fatty acid-like biosynthetic pathways.

930

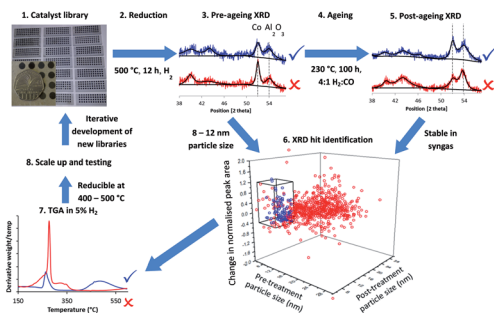


Multiplexed DNA detection based on positional encoding/decoding with self-assembled DNA nanostructures

Sha Sun, Huaxin Yao, Feifei Zhang and Jin Zhu*

A multiplexed DNA detection strategy with fast hybridization kinetics based on positional encoding/decoding with self-assembled DNA nanostructures has been developed.

935

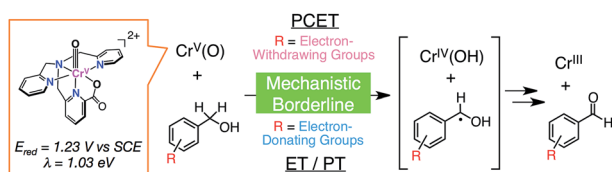


Proxy-based accelerated discovery of Fischer–Tropsch catalysts

Paul Boldrin, James R. Gallagher, Gary B. Combes, Dan I. Enache, David James, Peter R. Ellis, Gordon Kelly, John B. Claridge and Matthew J. Rosseinsky*

High-throughput XRD and TGA are used to screen hundreds of candidate Fischer–Tropsch synthesis catalyst samples per month for particle size, reducibility and stability under operating conditions. A series of highly stable catalysts based on Co–Ru–Mg–Al₂O₃ are identified.

945



Formation and characterization of a reactive chromium(v)–oxo complex: mechanistic insight into hydrogen-atom transfer reactions

Hiroaki Kotani,* Suzue Kaida, Tomoya Ishizuka, Miyuki Sakaguchi, Takashi Ogura, Yoshihito Shiota, Kazunari Yoshizawa and Takahiko Kojima*

Mechanistic insights were gained into hydrogen-atom transfer reactions from benzyl alcohol derivatives with different oxidation potentials to a highly reactive Cr(v)–oxo complex to reveal switching of reaction mechanisms.

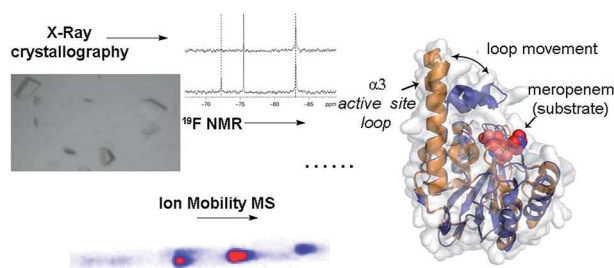


956

Studying the active-site loop movement of the São Paulo metallo- β -lactamase-1

Jürgen Brem, Weston B. Struwe, Anna M. Rydzik, Hanna Tarhonskaya, Inga Pfeffer, Emily Flashman, Sander S. van Berkel, James Spencer, Timothy D. W. Claridge, Michael A. McDonough, Justin L. P. Benesch* and Christopher J. Schofield*

A unique structural and biophysical characterization using crystallographic, native ion-mobility mass spectrometry and ^{19}F NMR identifies movement of a loop as being important in SPM-1 catalysis.

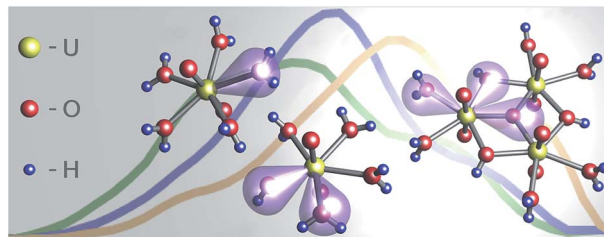


964

Combining luminescence spectroscopy, parallel factor analysis and quantum chemistry to reveal metal speciation – a case study of uranyl(VI) hydrolysis

Björn Drobot,* Robin Steudtner, Johannes Raff, Gerhard Geipel, Vinzenz Brendler and Satoru Tsushima*

The sensitive excitation of uranyl(VI) hydrolysis species in the UV (180 to 370 nm) is due to ligand-to-metal charge transfer.

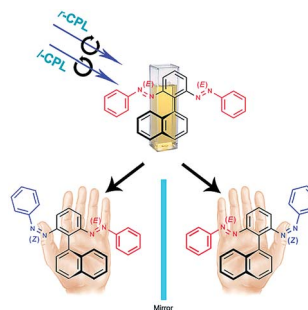


973

Dynamic induction of enantiomeric excess from a prochiral azobenzene dimer under circularly polarized light

K. Rijeesh, P. K. Hashim, Shin-ichiro Noro and Nobuyuki Tamaoki*

We demonstrate the simultaneous induction of chirality and enantiomeric excess from a prochiral azobenzene dimer *via* a chiral regioisomer formed *in situ* upon CPL irradiation.

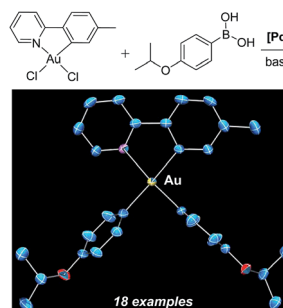


981

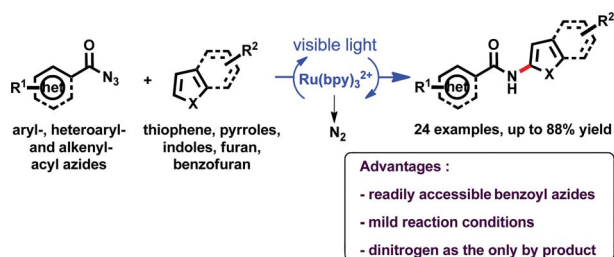
Suzuki–Miyaura coupling of arylboronic acids to gold(III)

Ayan Maity, Amanda N. Sulicz, Nihal Deligonul, Matthias Zeller, Allen D. Hunter and Thomas G. Gray*

Cyclometalated gold(III) aryls are prepared through palladium catalysis. Mono- and diarylation are demonstrated. A wide range of functional groups is tolerated.



987

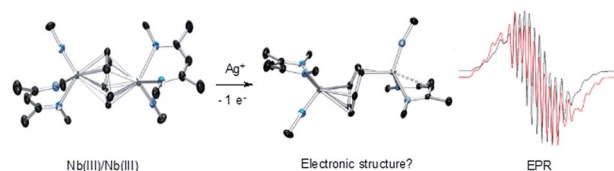


Visible light C–H amidation of heteroarenes with benzoyl azides

E. Brachet, T. Ghosh, I. Ghosh and B. König*

Benzoyl azides were used for the direct and atom economic C–H amidation of electron rich heteroarenes in the presence of phosphoric acid, a photocatalyst and visible light.

993

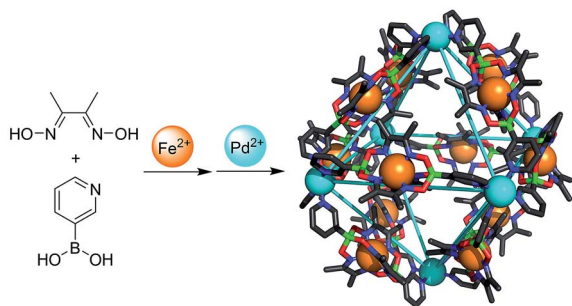


Electron localization in a mixed-valence diniobium benzene complex

Thomas L. Gianetti, Grégory Nocton,* Stefan G. Minasian, Nikolas Kaltsoyannis,* A. L. David Kilcoyne, Stosh A. Kozimor, David K. Shuh, Tolek Tylliszczak, Robert G. Bergman* and John Arnold*

One electron oxidation of a neutral diniobium benzene complex leads to a mixed-valence species. Single crystal X-ray diffraction, EPR, $L_{3,2}$ -edge XANES, and DFT indicate that the unpaired electron is localized on one metal center.

1004

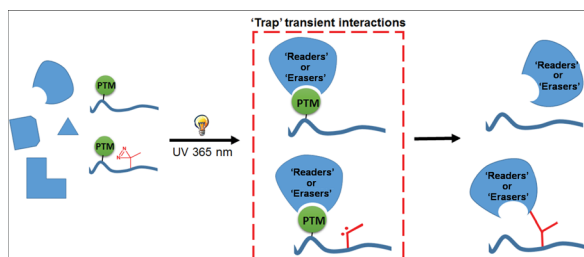


Large, heterometallic coordination cages based on ditopic metallo-ligands with 3-pyridyl donor groups

Matthew D. Wise, Julian J. Holstein, Philip Pattison, Celine Besnard, Euro Solari, Rosario Scopelliti, Gerard Bricogne and Kay Severin*

The two-step synthesis of large, heterometallic coordination cages based on ditopic 3-pyridyl ligands is described.

1011



Developing diazirine-based chemical probes to identify histone modification 'readers' and 'erasers'

Tangpo Yang, Zheng Liu and Xiang David Li*

New chemical tools to 'trap' post translational modification (PTM)-mediated protein–protein interactions.

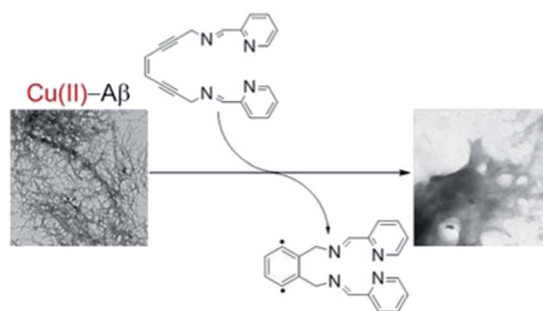


1018

Chelation-induced diradical formation as an approach to modulation of the amyloid- β aggregation pathway

Meghan R. Porter, Akiko Kochi, Jonathan A. Karty, Mi Hee Lim* and Jeffrey M. Zaleski*

We demonstrate that ligand-metal-A β interaction with subsequent radical generation is a relatively rapid mechanism for influencing A β structural integrity and thus, the aggregation pathway.

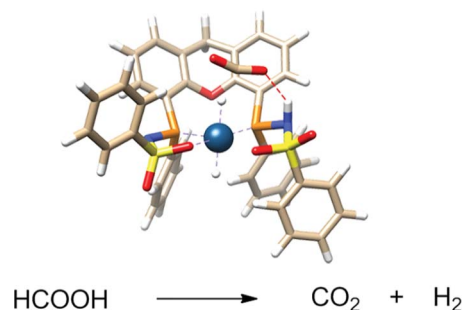


1027

Dehydrogenation of formic acid by Ir-bisMETAMORPhos complexes: experimental and computational insight into the role of a cooperative ligand

Sander Oldenhof, Martin Lutz, Bas de Bruin, Jarl Ivar van der Vlugt and Joost N. H. Reek*

The synthesis of Ir-complexes with three bisMETAMORPhos ligands is reported. The activity of these systems towards HCOOH dehydrogenation and the dual role of the ligand during catalysis is discussed, using spectroscopic and computational methods.

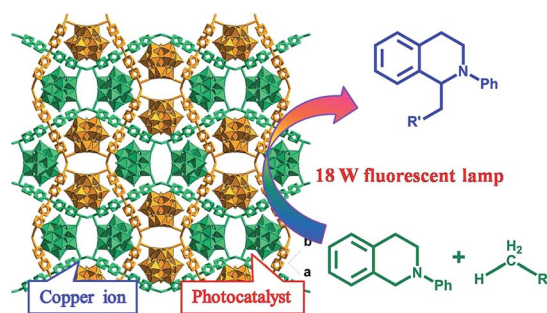


1035

Merging of the photocatalysis and copper catalysis in metal-organic frameworks for oxidative C-C bond formation

Dongying Shi, Cheng He, Bo Qi, Cong Chen, Jingyang Niu and Chunying Duan*

A new approach to merge Cu-catalysis/Ru-photocatalysis within one single MOF was achieved by incorporating [SiW₁₁O₃₉Ru(H₂O)]⁵⁻ into Cu-BPY MOFs.

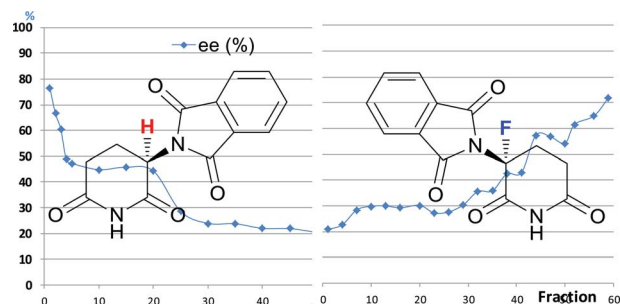


1043

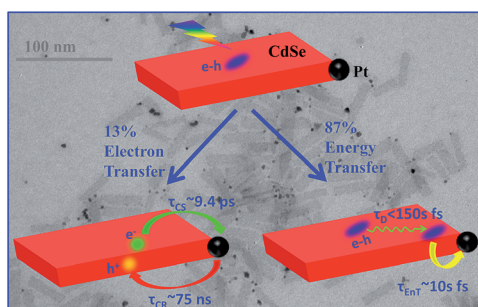
Self-disproportionation of enantiomers of thalidomide and its fluorinated analogue via gravity-driven achiral chromatography: mechanistic rationale and implications

Mayaka Maeno, Etsuko Tokunaga, Takeshi Yamamoto, Toshiya Suzuki, Yoshiyuki Ogino, Emi Ito, Motoo Shiro, Toru Asahi* and Norio Shibata*

We report on the self-disproportionation of enantiomers of non-racemic thalidomide (**1**) and 3'-fluorothalidomide (**2**) under achiral chromatography.



1049

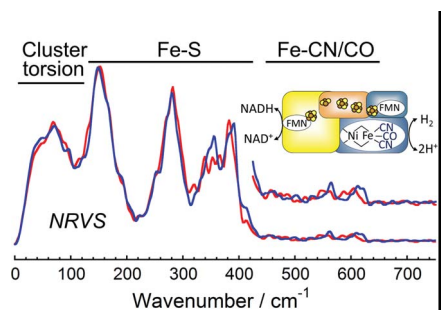


Ultrafast exciton quenching by energy and electron transfer in colloidal CdSe nanosheet–Pt heterostructures

Kaifeng Wu, Qiuyang Li, Yongling Du, Zheyuan Chen and Tianquan Lian*

Large in-plane exciton mobility in CdSe nanosheets leads to ultrafast exciton quenching by energy transfer to Pt.

1055

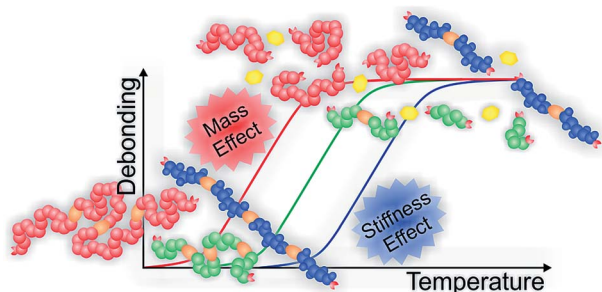


Nuclear resonance vibrational spectroscopy reveals the FeS cluster composition and active site vibrational properties of an O₂-tolerant NAD⁺-reducing [NiFe] hydrogenase

Lars Lauterbach,* Hongxin Wang, Marius Horch, Leland B. Gee, Yoshitaka Yoda, Yoshihito Tanaka, Ingo Zebger, Oliver Lenz and Stephen P. Cramer*

Nuclear resonance vibrational spectroscopy is used to characterize all Fe-containing cofactors in a complex multifactor enzyme.

1061

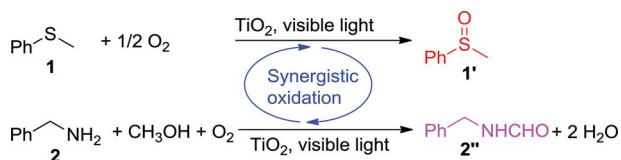


Entropy driven chain effects on ligation chemistry

Kai Pahnke, Josef Brandt, Ganna Gryn'ova, Peter Lindner, Ralf Schweins, Friedrich Georg Schmidt, Albena Lederer,* Michelle L. Coote* and Christopher Barner-Kowollik*

Entropic chain effects on dynamic bonding reactions are shown to enable the tuning of reaction equilibria not only by changing the mass of the reactants, but also by merely altering the building block side chain structure and thus the intrinsic stiffness. The findings enable a step change for the design of on-demand bonding systems and reversible ligation chemistry in general.

1075



Synergistic photocatalytic aerobic oxidation of sulfides and amines on TiO₂ under visible-light irradiation

Xianjun Lang, Wan Ru Leow, Jincai Zhao* and Xiaodong Chen*

Visible-light-induced selective oxygenation of sulfides and oxidative formylation of amines in methanol with dioxygen were synergistically achieved on titanium dioxide.

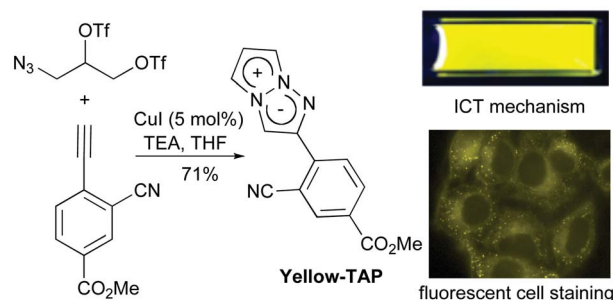


1083

Synthesis of yellow and red fluorescent 1,3a,6a-triazapentalenes and the theoretical investigation of their optical properties

Kosuke Namba,* Ayumi Osawa, Akira Nakayama,* Akane Mera, Fumi Tano, Yoshiro Chuman, Eri Sakuda, Tetsuya Taketsugu, Kazuyasu Sakaguchi, Noboru Kitamura and Keiji Tanino*

To expand the function of the fluorescent 1,3a,6a-triazapentalenes as labelling reagents, their fluorescence wavelength was extended to the red color region.

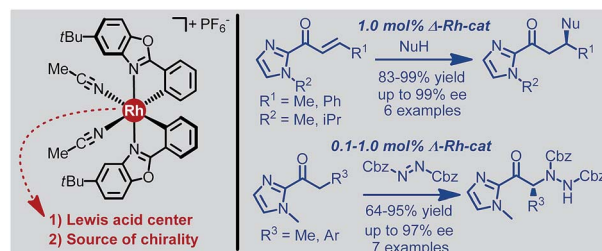


1094

Asymmetric Lewis acid catalysis directed by octahedral rhodium centrochirality

Chuanyong Wang, Liang-An Chen, Haohua Huo, Xiaodong Shen, Klaus Harms, Lei Gong and Eric Meggers*

A chiral-at-metal octahedral rhodium(III) complex serves as an effective asymmetric catalyst for Michael additions (electrophile activation) and α -aminations (nucleophile activation).

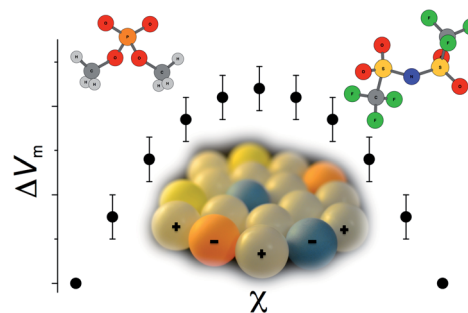


1101

A physicochemical investigation of ionic liquid mixtures

Matthew T. Clough, Colin R. Crick, John Gräsvik, Patricia A. Hunt,* Heiko Niedermeyer, Tom Welton* and Oliver P. Whitaker

A comprehensive study of ionic liquid mixtures reveals a remarkable adhesion to ideal mixing laws, with some consistent exceptions.

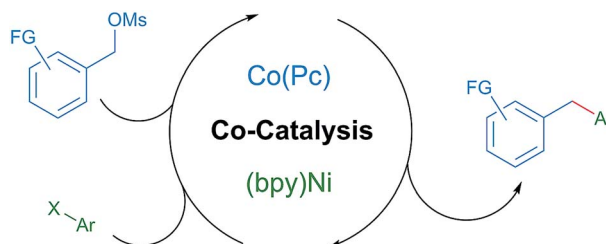


1115

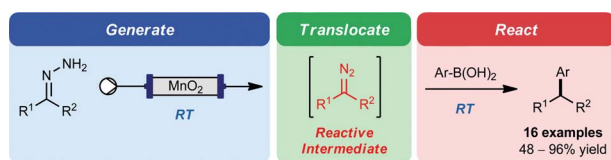
Cobalt co-catalysis for cross-electrophile coupling: diarylmethanes from benzyl mesylates and aryl halides

Laura K. G. Ackerman, Lukiana L. Anka-Lufford, Marina Naodovic and Daniel J. Weix*

Cobalt phthalocyanine mediated generation of benzylic radicals from benzylic sulfonate esters enables the selective nickel-catalyzed synthesis of diarylmethanes.



1120

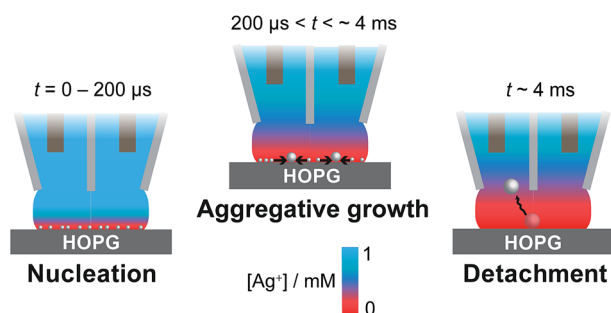


Flow chemistry as a discovery tool to access sp^2 – sp^3 cross-coupling reactions *via* diazo compounds

Duc N. Tran, Claudio Battilocchio, Shing-Bong Lou, Joel M. Hawkins and Steven V. Ley*

The room temperature sp^2 – sp^3 cross-coupling of flow-generated diazo compounds with boronic acids is reported.

1126

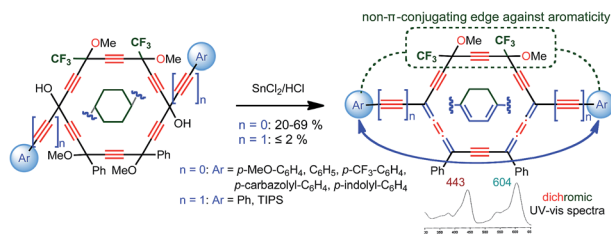


Nucleation, aggregative growth and detachment of metal nanoparticles during electrodeposition at electrode surfaces

Stanley C. S. Lai,* Robert A. Lazenby, Paul M. Kirkman and Patrick R. Unwin*

A nucleation-aggregative growth-detachment mechanism is proposed as an important feature of the electrodeposition of silver nanoparticles on basal plane highly oriented pyrolytic graphite (HOPG).

1139

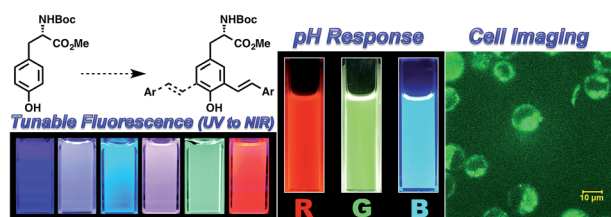


Carbo-cyclohexadienes vs. carbo-benzenes: structure and conjugative properties

Arnaud Rives, Iaroslav Baglai, Cécile Barthes, Valérie Maraval,* Nathalie Saffon-Merceron, Alix Saquet, Zoia Voitenko, Yulian Volovenko and Remi Chauvin*

Stable dichromic carbo-cyclohexadiene chromophores are synthesised, selectively with respect to the corresponding carbo-benzenes, by fluorine "chemical locking".

1150



Tyrosine-derived stimuli responsive, fluorescent amino acids

Pradeep Cheruku, Jen-Huang Huang, Hung-Ju Yen, Rashi S. Iyer, Kirk D. Rector, Jennifer S. Martinez and Hsing-Lin Wang*

A series of fluorescent unnatural amino acids (UAAs) bearing stilbene and *meta*-phenylenevinylene (*m*-PPV) backbone have been synthesized by palladium-catalyzed Heck couplings.

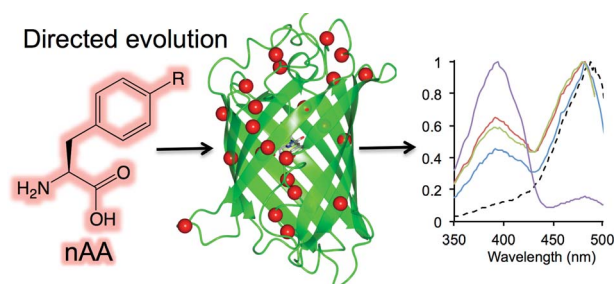


1159

Directed evolution of GFP with non-natural amino acids identifies residues for augmenting and photoswitching fluorescence

Samuel C. Reddington, Amy J. Baldwin, Rebecca Thompson, Andrea Brancale, Eric M. Tippmann and D. Dafydd Jones*

Genetic code reprogramming allows proteins to sample new chemistry through targeted introduction of non-natural amino acids. By combining with random codon replacement, residues traditionally overlooked can be identified as instilling new properties on a target protein.

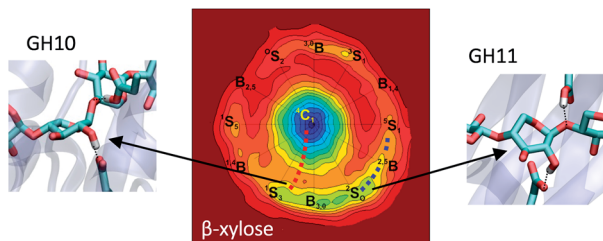


1167

The complete conformational free energy landscape of β -xylose reveals a two-fold catalytic itinerary for β -xylanases

Javier Iglesias-Fernández, Lluís Raich, Albert Ardèvol and Carme Rovira*

Ab initio conformational free energy landscapes, together with molecular dynamics simulations, enable to predict the catalytic itineraries of β -xylanase enzymes.

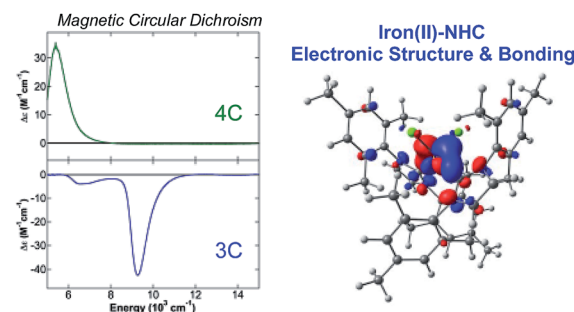


1178

A combined magnetic circular dichroism and density functional theory approach for the elucidation of electronic structure and bonding in three- and four-coordinate iron(II)–N-heterocyclic carbene complexes

Kathlyn L. Fillman, Jacob A. Przyowski, Malik H. Al-Afyouni, Zachary J. Tonzetich and Michael L. Neidig*

Studies of electronic structure and bonding in iron(II)–NHC complexes using a combined magnetic circular dichroism and DFT approach.

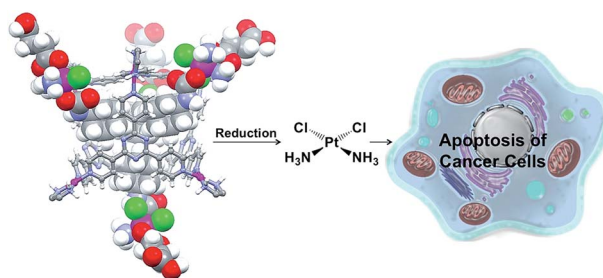


1189

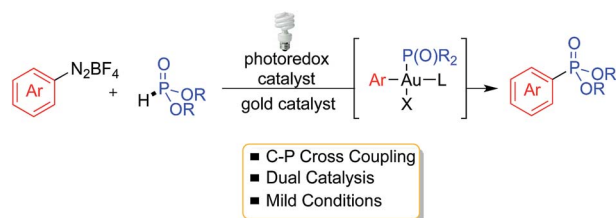
Encapsulation of Pt(IV) prodrugs within a Pt(II) cage for drug delivery

Yao-Rong Zheng, Kogularamanan Suntharalingam, Timothy C. Johnstone and Stephen J. Lippard*

This report describes a novel strategy for delivery of adamantyl-functionalized payloads using a supramolecular system, with a focus on Pt(IV) prodrugs.



1194

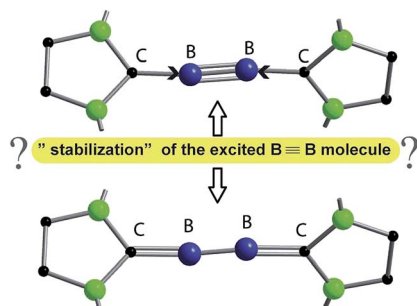


A dual catalytic strategy for carbon–phosphorus cross-coupling *via* gold and photoredox catalysis

Ying He, Hongmiao Wu and F. Dean Toste*

A new method for the *P*-arylation of aryldiazonium salts with *H*-phosphonates *via* dual gold and photoredox catalysis is described.

1199

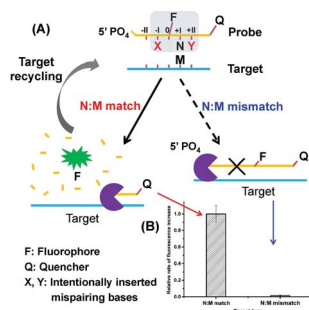


The boron–boron triple bond? A thermodynamic and force field based interpretation of the N-heterocyclic carbene (NHC) stabilization procedure

R. Köppe and H. Schnöckel*

From thermodynamic and force constant discussion a new description of bonding of $\text{B}_2(\text{NHC})_2$ (NHC = N-heterocyclic carbene $\text{C}_3\text{N}_2\text{H}_2(\text{C}_6\text{H}_3\text{Pr}_2-2,6)_2$) as $\text{NHC}\equiv\text{B}\equiv\text{B}\equiv\text{NHC}$ rather than $\text{NHC}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{NHC}$ is given.

1206

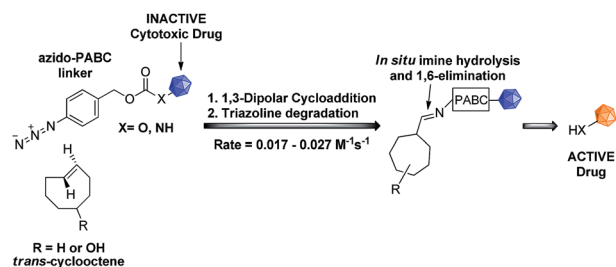


Enzyme-mediated single-nucleotide variation detection at room temperature with high discrimination factor

Tongbo Wu, Xianjin Xiao, Zhe Zhang and Meiping Zhao*

We present a novel strategy for the highly selective detection of single-nucleotide variation at room temperature, based on an extremely specific interaction between Lambda exonuclease (λ exo) and a chemically modified DNA structure.

1212



Bioorthogonal prodrug activation driven by a strain-promoted 1,3-dipolar cycloaddition

Siddharth S. Matikonda, Douglas L. Orsi, Verena Staudacher, Imogen A. Jenkins, Franziska Fiedler, Jiayi Chen and Allan B. Gamble*

Bioorthogonal prodrug activation controlled by the reaction of a *trans*-cyclooctene with an azide-functionalized prodrug is presented.



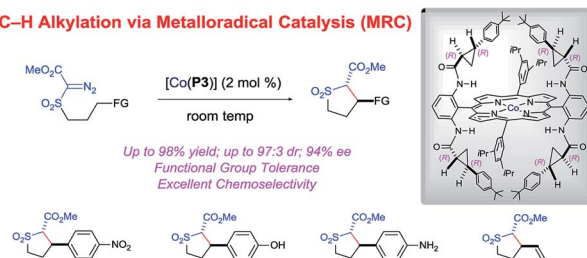
1219

Stereoselective radical C–H alkylation with acceptor/acceptor-substituted diazo reagents via Co(II)-based metalloradical catalysis

Xin Cui, Xue Xu, Li-Mei Jin, Lukasz Wojtas and X. Peter Zhang*

Co(II)-based metalloradical catalysis has, for the first time, been successfully applied for asymmetric intramolecular C–H alkylation of acceptor/acceptor-substituted diazo reagents.

C–H Alkylation via Metalloradical Catalysis (MRC)

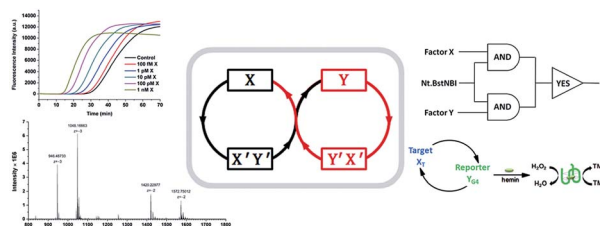


1225

DNA cross-triggered cascading self-amplification artificial biochemical circuit

Ji Nie, Ming-Zhe Zhao, Wen Jun Xie, Liang-Yuan Cai, Ying-Lin Zhou* and Xin-Xiang Zhang*

A novel DNA cross-triggered cascading self-amplification artificial biochemical circuit can be triggered by either of two fully independent oligonucleotide factors (~ 2 amol) and amplify both of them by 10^5 – 10^7 fold.

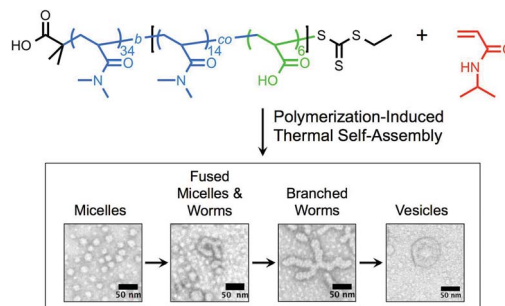


1230

Polymerization-induced thermal self-assembly (PITSA)

C. Adrian Figg, Alexandre Simula, Kalkidan A. Gebre, Bryan S. Tucker, David M. Haddleton and Brent S. Sumerlin*

Polymerization-induced thermal self-assembly (PITSA) was conducted using thermoresponsive poly(*N*-isopropylacrylamide) to result in micelle, worm, and vesicle polymeric morphologies.

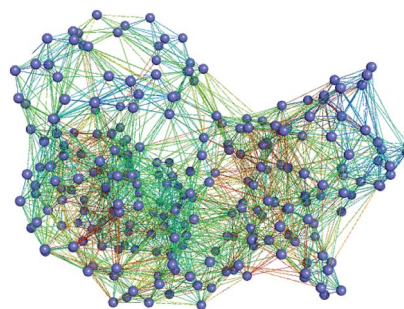


1237

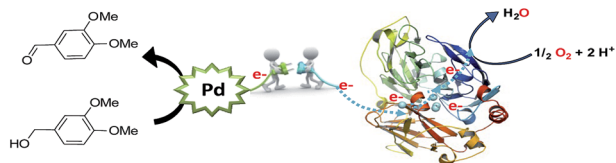
Rational coupled dynamics network manipulation rescues disease-relevant mutant cystic fibrosis transmembrane conductance regulator

Elizabeth A. Proctor, Pradeep Kota, Andrei A. Aleksandrov, Lihua He, John R. Riordan and Nikolay V. Dokholyan*

A novel approach identifying networks of residues involved in *trans*-protein dynamic coupling is applied to rescue mutant CFTR.



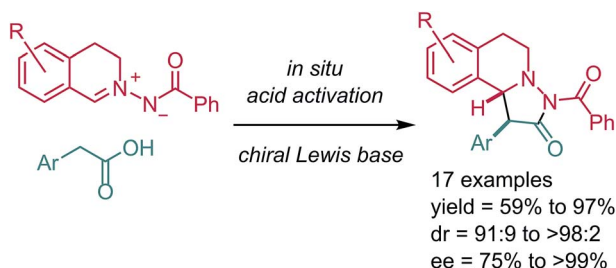
1247

**Laccases as palladium oxidases**

Yasmina Mekmouche,^{*} Ludovic Schneider, Pierre Rousselot-Pailley, Bruno Faure, A. Jalila Simaan, Constance Bochot, Marius Réglier and Thierry Tron^{*}

Combining a palladium-based complex with a laccase allows the oxidation of an alcohol substrate at room temperature and atmospheric pressure.

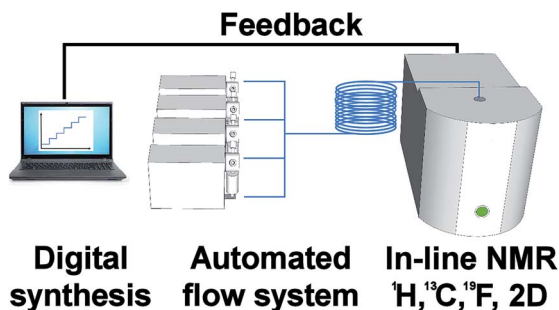
1252

**Stereoselective Lewis base catalyzed formal 1,3-dipolar cycloaddition of azomethine imines with mixed anhydrides**

Lena Hespig, Anup Biswas, Constantin G. Daniliuc, Christian Mück-Lichtenfeld^{*} and Armido Studer^{*}

Pyrazolidinones with a tetrahydroisoquinoline core are obtained with excellent diastereocontrol and high enantioselectivity. Theoretical studies give insight on the reaction mechanism.

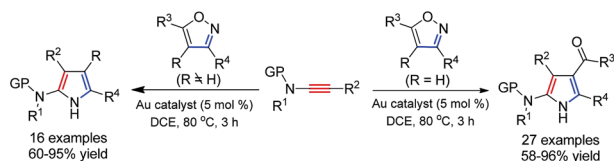
1258

**A self optimizing synthetic organic reactor system using real-time in-line NMR spectroscopy**

Victor Sans, Luzian Porwol, Vincenza Dragone and Leroy Cronin^{*}

A 'dial-a-molecule' platform for algorithm driven organic synthesis using real-time feedback, via in-line flow NMR spectroscopy, is demonstrated.

1265

**Atom-economic generation of gold carbenes: gold-catalyzed formal [3+2] cycloaddition between ynamides and isoxazoles**

Ai-Hua Zhou, Qiao He, Chao Shu, Yong-Fei Yu, Shuang Liu, Tian Zhao, Wei Zhang, Xin Lu^{*} and Long-Wu Ye^{*}

An unprecedented gold-catalyzed formal [3+2] cycloaddition between ynamides and isoxazoles has been developed, allowing rapid and practical access to a wide range of synthetically useful 2-aminopyrroles.

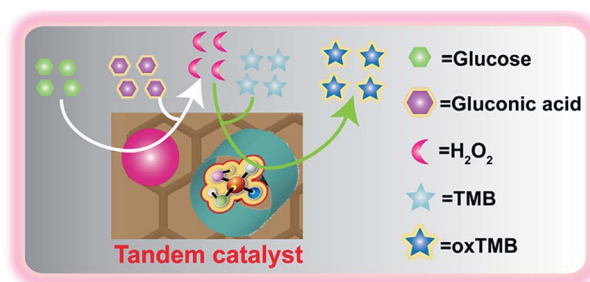


1272

Positional assembly of hemin and gold nanoparticles in graphene–mesoporous silica nanohybrids for tandem catalysis

Youhui Lin, Li Wu, Yanyan Huang, Jinsong Ren* and Xiaogang Qu*

A hybrid catalyst in which two different types of enzyme mimics are positioned in spatially separate domains within a graphene–mesoporous silica support is presented.

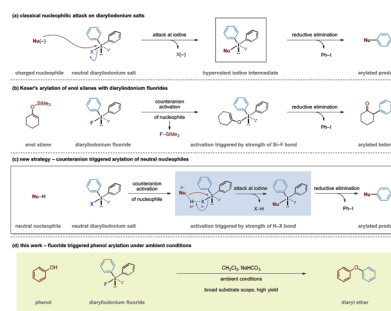


1277

A counteranion triggered arylation strategy using diaryliodonium fluorides

L. Chan, A. McNally, Q. Y. Toh, A. Mendoza and M. J. Gaunt*

A mild and transition metal-free counteranion triggered arylation strategy has been developed using diaryliodonium fluorides.

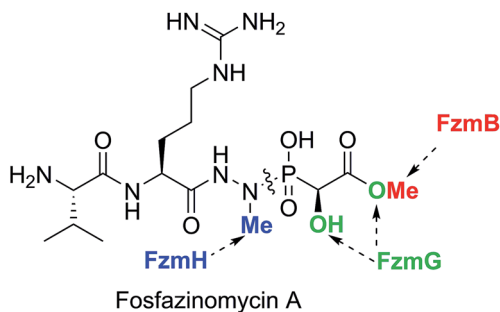


1282

Biosynthesis of fosfazinomycin is a convergent process

Zedu Huang, Kwo-Kwang A. Wang, Jaeheon Lee and Wilfred A. van der Donk*

Fosfazinomycin A is a phosphonate natural product in which the C-terminal methylhydrazide of a Val–Arg dipeptide is connected to methyl 2-hydroxy-2-phosphonoacetate (Me-HPnA).

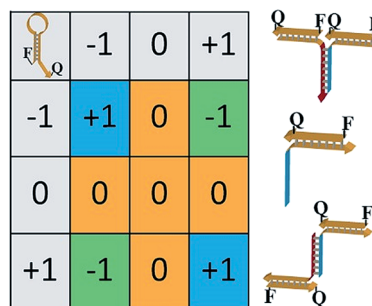


1288

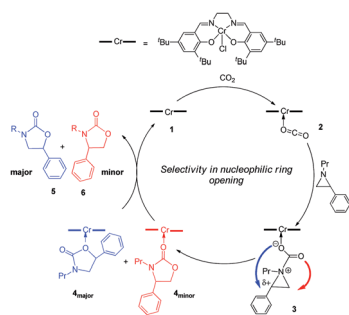
Ternary DNA computing using 3×3 multiplication matrices

Ron Orbach, Sivan Lilienthal, Michael Klein, R. D. Levine, Françoise Remacle and Itamar Willner*

Ternary computing, beyond Boolean logic, is anticipated to enhance computational complexity. DNA-based ternary computing is demonstrated by the assembly of a 3×3 multiplication table, and the parallel operation of three 3×3 multiplication matrices is highlighted.



1293

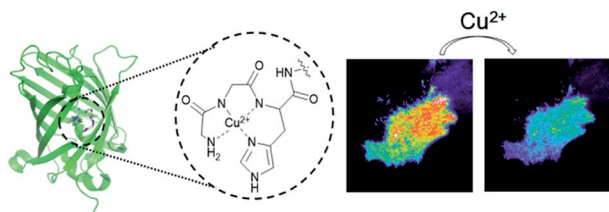


Intramolecular ring-opening from a CO₂-derived nucleophile as the origin of selectivity for 5-substituted oxazolidinone from the (salen)Cr-catalyzed [aziridine + CO₂] coupling

Debashis Adhikari, Aaron W. Miller, Mu-Hyun Baik* and SonBinh T. Nguyen*

The (salen)Cr-catalyzed [aziridine + CO₂] coupling to form oxazolidinone was found to exhibit excellent selectivity for the 5-substituted oxazolidinone product in the absence of any cocatalyst.

1301

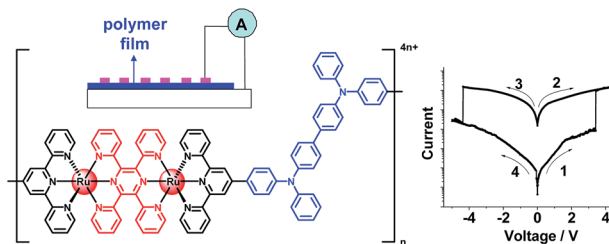


A novel copper-chelating strategy for fluorescent proteins to image dynamic copper fluctuations on live cell surfaces

Yoon-Aa Choi, Joo Oak Keem, Cha Yeon Kim, Hye Ryeon Yoon, Won Do Heo, Bong Hyun Chung* and Yongwon Jung*

A strong but selective copper-binding tripeptide was employed to develop a highly sensitive and selective copper(II) protein reporter.

1308

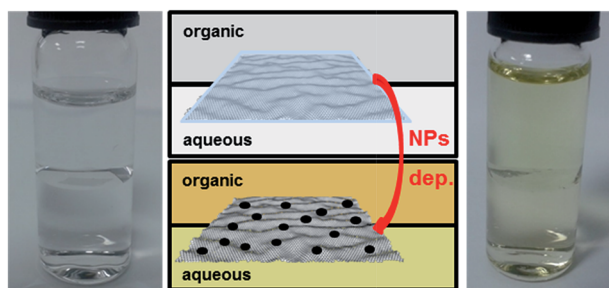


Tuning of resistive memory switching in electropolymerized metallopolymeric films

Bin-Bin Cui, Zupan Mao, Yuxia Chen, Yu-Wu Zhong,* Gui Yu,* Chuanlang Zhan* and Jiannian Yao*

Sandwiched electrical devices of an electropolymerized diruthenium metallopolymeric film show excellent resistive memory switching.

1316



Functionalization of graphene at the organic/water interface

Peter S. Toth, Quentin M. Ramasse, Matěj Velický and Robert A. W. Dryfe*

A simple method for the deposition of noble metal (Pd, Au) nanoparticles on a free-standing chemical vapour deposited graphene monolayer is reported. Metal deposition can proceed using either spontaneous or electrochemically-controlled processes. The resultant nanoclusters are characterized using atomic force and electron microscopy techniques, and mapping mode Raman spectroscopy.

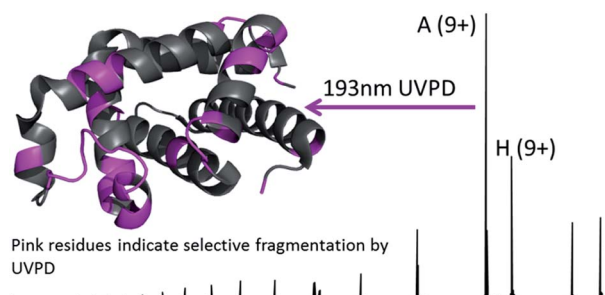


1324

Structural characterization of holo- and apo-myoglobin in the gas phase by ultraviolet photodissociation mass spectrometry

Michael B. Cammarata and Jennifer S. Brodbelt*

193 nm UV photodissociation of myoglobin in the gas phase showed preferential backbone cleavages in regions with higher relative *B*-factors.

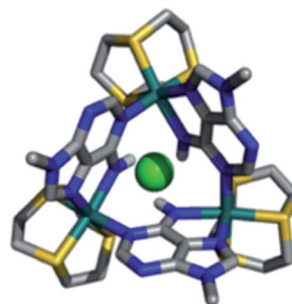


1334

Modulating the electron-transfer properties of a mixed-valence system through host–guest chemistry

Ahmed Zubi, Ashley Wragg, Simon Turega, Harry Adams, Paulo J. Costa, Vítor Félix* and Jim A. Thomas*

Herein, we report that the interplay between the binding properties and redox activity of a self-assembled trinuclear Ru^{II} macrocycle leads to an hitherto unreported phenomenon, in which access to specific MV states is gated by host–guest chemistry.

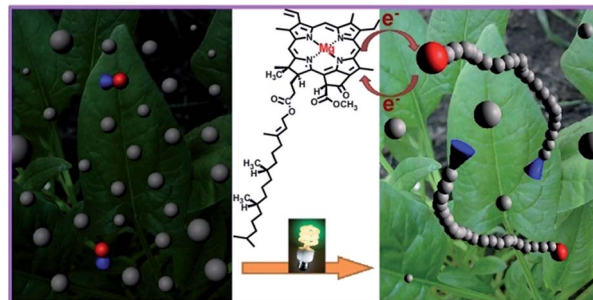


1341

Utilizing the electron transfer mechanism of chlorophyll a under light for controlled radical polymerization

Sivaprakash Shanmugam, Jiangtao Xu* and Cyrille Boyer*

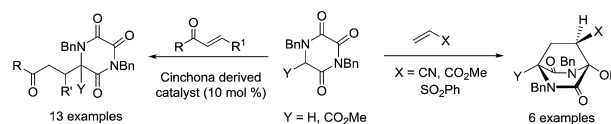
We report an efficient photoinduced living radical polymerization process that involves the use of chlorophyll as the photoredox catalyst, which allows the preparation of well-defined polymers.



1350

Highly enantioselective access to diketopiperazines via cinchona alkaloid catalyzed Michael additions

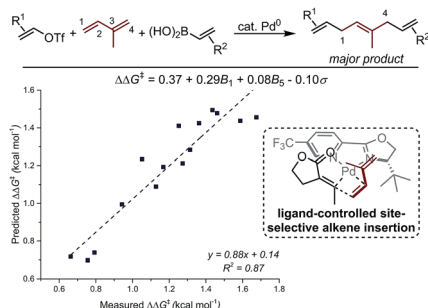
Alejandro Cabanillas, Christopher D. Davies, Louise Male and Nigel S. Simpkins*



Alkaloid catalysed additions to triketopiperazines gives products in high yield and er (88 : 12 to 99 : 1), including bridged hydroxy-DKPs *via* Michael-addition–ring closure.



1355

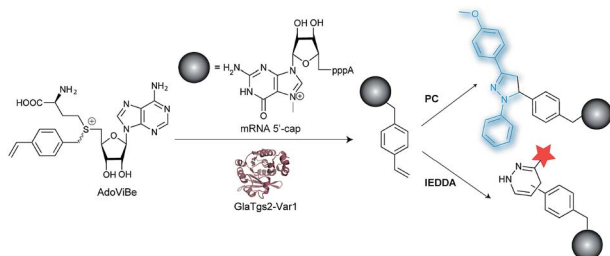


Development and investigation of a site selective palladium-catalyzed 1,4-difunctionalization of isoprene using pyridine–oxazoline ligands

Matthew S. McCamant and Matthew S. Sigman*

Palladium-catalyzed 1,4-difunctionalizations of isoprene that produce skipped polyenes are reported.

1362

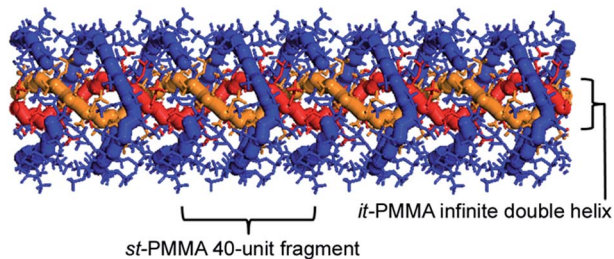


Enzymatic modification of 5'-capped RNA with a 4-vinylbenzyl group provides a platform for photoclick and inverse electron-demand Diels–Alder reaction

Josephin Marie Holstein, Daniela Stummer and Andrea Rentmeister*

Enzymatic transfer of 4-vinylbenzyl to the mRNA 5'-cap gives access to the fluorogenic photoclick and the inverse electron-demand Diels–Alder reaction.

1370

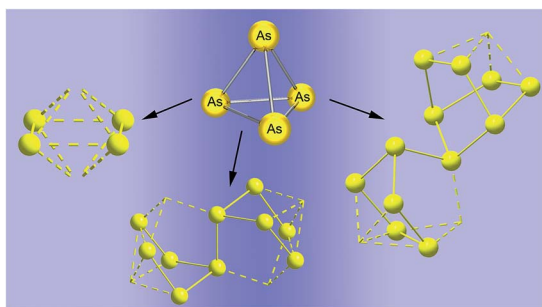


Molecular mapping of poly(methyl methacrylate) super-helix stereocomplexes

Andrew Joseph Christofferson, George Yiapanis, Jing Ming Ren, Greg Guanghua Qiao, Kotaro Satoh, Masami Kamigaito and Irene Yarovsky*

The structure of the it-/st-poly(methyl methacrylate) (PMMA) triple-helix stereocomplex is composed of a double helix of it-PMMA of 9 units per turn surrounded by a single helix of st-PMMA with an average of 20 units per turn.

1379



Synthesis of arsenic-rich As_n ligand complexes from yellow arsenic

C. Graßl, M. Bodensteiner, M. Zabel and M. Scheer*

A triple-decker complex of cobalt is able to consume As₄ moieties of yellow arsenic to build-up the to-date largest known As_n ligands.

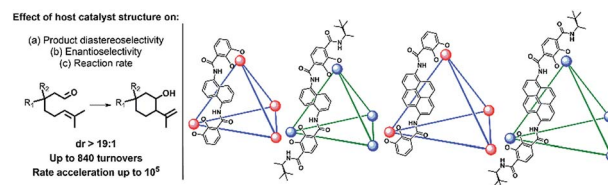


1383

The effect of host structure on the selectivity and mechanism of supramolecular catalysis of Prins cyclizations

William M. Hart-Cooper, Chen Zhao, Rebecca M. Triano, Parastou Yaghoubi, Haxel Lionel Ozores, Kristen N. Burford, F. Dean Toste*, Robert G. Bergman* and Kenneth N. Raymond*

Catalyst and substrate modification, product selectivity and kinetic studies comprehensively describe a new class of terpenoid cyclase mimics.

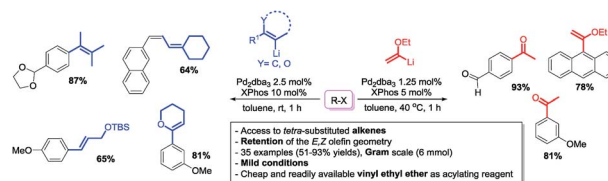


1394

Direct catalytic cross-coupling of alkenyllithium compounds

Valentín Hornillos, Massimo Giannerini, Carlos Vila, Martín Fañanás-Mastral and Ben L. Feringa*

The direct cross-coupling of alkenyllithium reagents with aryl and alkenyl halides is described. The use of a catalyst comprising $\text{Pd}_2(\text{dba})_3/\text{XPhos}$ allows for the stereoselective preparation of a wide variety of substituted alkenes in high yields under mild conditions.

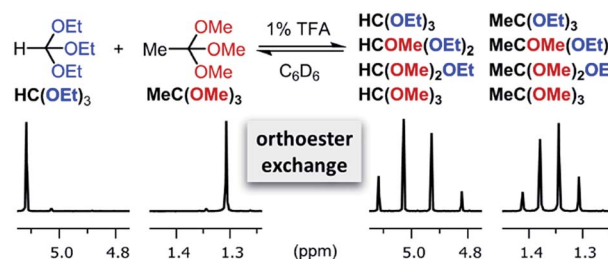


1399

Orthoester exchange: a tripodal tool for dynamic covalent and systems chemistry

René-Chris Brachvogel and Max von Delius*

We demonstrate that acid-catalyzed orthoester exchange is a promising tool for applications in dynamic covalent and systems chemistry.

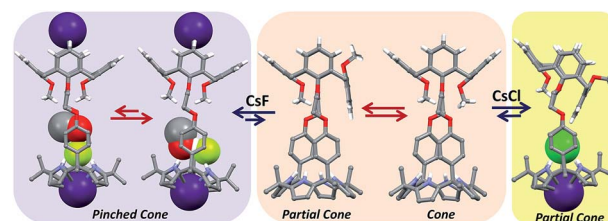


1404

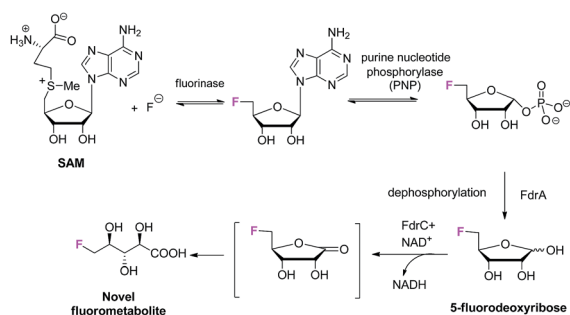
Ion pair-induced conformational motion in calix[4]arene-strapped calix[4]pyrroles

Sung Kuk Kim, Vincent M. Lynch, Benjamin P. Hay, Jong Seung Kim* and Jonathan L. Sessler*

Cone- and conformationally mobile calix[4]arene-strapped calix[4]pyrroles bind cesium salts via various different binding modes.



1414

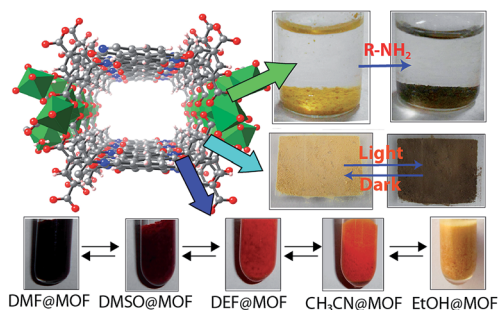


Identification of a fluorometabolite from *Streptomyces* sp. MA37: (2R3S4S)-5-fluoro-2,3,4-trihydroxypentanoic acid

Long Ma, Axel Bartholome, Ming Him Tong, Zhiwei Qin, Yi Yu, Thomas Shepherd, Kwaku Kyeremeh, Hai Deng* and David O'Hagan*

(2R3S4S)-5-Fluoro-2,3,4-trihydroxypentanoic acid (5-FHPA) has been discovered as a new fluorometabolite in the soil bacterium *Streptomyces* sp. MA37.

1420

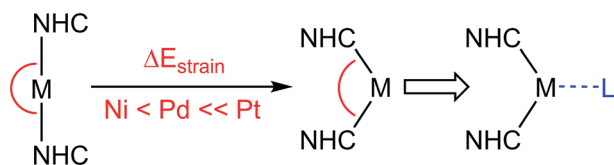


Solid state organic amine detection in a photochromic porous metal organic framework

Arijit Mallick, Bikash Garai, Matthew A. Addicoat, Petko St. Petkov, Thomas Heine and Rahul Banerjee*

A new Mg(II) based porous metal-organic framework (MOF) has been synthesized from naphthalenediimide (NDI) chromophoric unit containing linker. This MOF (Mg-NDI) shows instant and reversible photochromism as well as solvatochromic behavior. Due to the presence of electron deficient NDI moiety, this MOF exhibits selective organic amine (electron rich) sensing in solid state.

1426

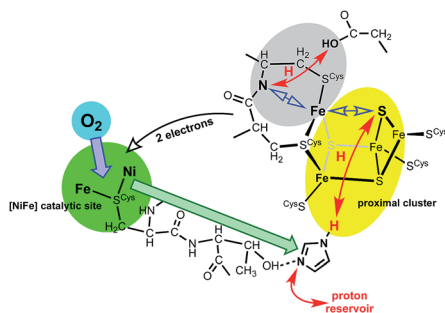


Bite-angle bending as a key for understanding group-10 metal reactivity of d¹⁰-[M(NHC)₂] complexes with sterically modest NHC ligands

Florian Hering, Jörn Nitsch, Ursula Paul, Andreas Steffen, F. Matthias Bickelhaupt* and Udo Radius*

Experimental and theoretical investigations on the novel 14 VE complexes [M⁰(iPr₂Im)₂] (M = Pd **3**, Pt **4**; iPr₂Im = 1,3-di-isopropyl-imidazolin-2-ylidene) and a comparison to their Ni congener reveal that NHC-M-NHC angle bending is a key to understand the reactivity of d¹⁰-[M(NHC)₂] complexes.

1433



What is the trigger mechanism for the reversal of electron flow in oxygen-tolerant [NiFe] hydrogenases?

Ian Dance

A new mechanistic model is developed for the sequence of events by which oxygen-tolerant [NiFe] hydrogenase enzymes respond to O₂.

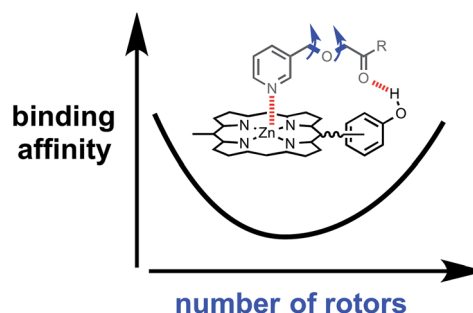


1444

The flexibility–complementarity dichotomy in receptor–ligand interactions

Hongmei Sun, Christopher A. Hunter* and Eva Marina Llamas

Binding affinity does not increase uniformly with preorganization, because there is a trade off between flexibility and fit.

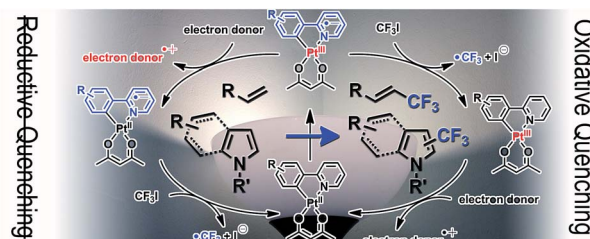


1454

Mechanisms and applications of cyclometalated Pt(II) complexes in photoredox catalytic trifluoromethylation

Won Joon Choi, Sungkyu Choi, Kei Ohkubo, Shunichi Fukuzumi,* Eun Jin Cho* and Youngmin You*

Pt(II) complexes catalyse the visible light-driven trifluoromethylation of alkenes and heteroarenes with improved quantum yields, due to strict adherence to an oxidative quenching pathway.

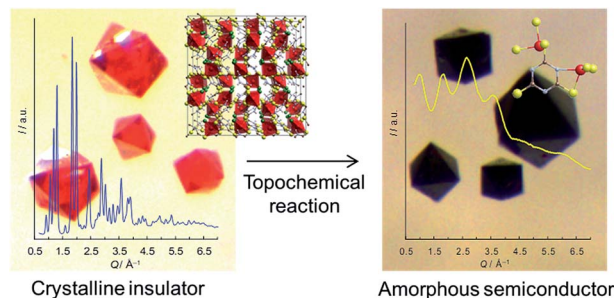


1465

Topochemical conversion of a dense metal–organic framework from a crystalline insulator to an amorphous semiconductor

S. Tominaka,* H. Hamoudi, T. Suga, T. D. Bennett, A. B. Cairns and A. K. Cheetham*

A dense, insulating metal–organic framework (MOF), is successfully converted into a semiconducting amorphous MOF *via* a topochemical route.

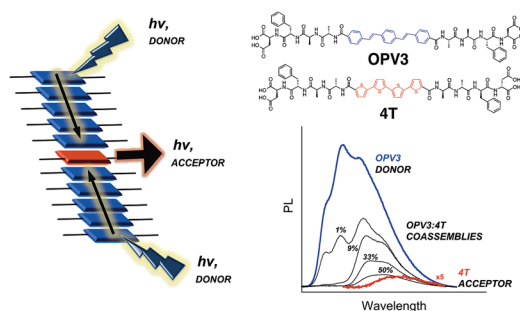


1474

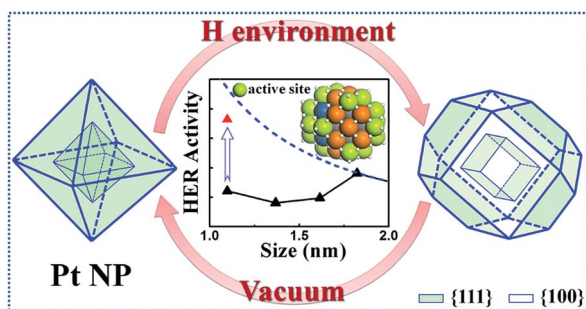
Energy transfer within responsive pi-conjugated coassembled peptide-based nanostructures in aqueous environments

Herdeline Ann M. Ardoña and John D. Tovar*

Energy transfer is demonstrated within a responsive donor–acceptor system which incorporates two different semiconducting units (oligo(*p*-phenylenevinylene and quaterthiophene) coassembled within peptide nanostructures in completely aqueous environments.



1485

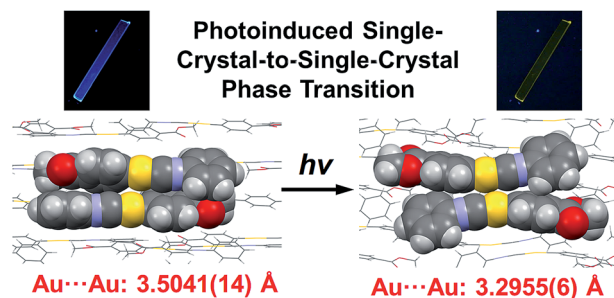


Restructuring and Hydrogen Evolution on Pt Nanoparticle

Guang-Feng Wei and Zhi-Pan Liu*

Dynamic catalyst structuring and the hydrogen evolution activity enhancement at nanoscale, as predicted by a first principles global optimization method.

1491

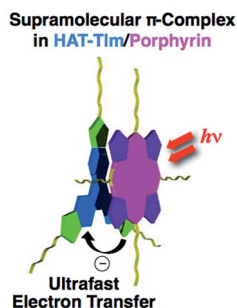


Photoinduced single-crystal-to-single-crystal phase transition and photosalt effect of a gold(I) isocyanide complex with shortening of intermolecular auropilic bonds

Tomohiro Seki, Kenta Sakurada, Mai Muromoto and Hajime Ito*

We report the first photoinduced single-crystal-to-single-crystal phase transition of a gold complex that involves shortening of intermolecular auropilic bonds. The gold(I) isocyanide complex also shows a photosalt effect.

1498

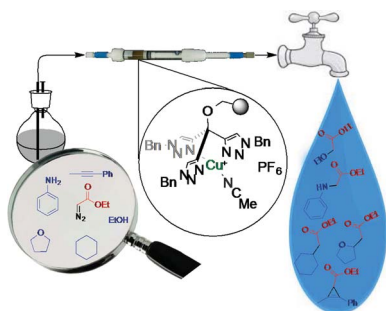


Ultrafast photoinduced electron transfer in face-to-face charge-transfer π -complexes of planar porphyrins and hexaazatriphenylene derivatives

Toru Aoki, Hayato Sakai, Kei Ohkubo, Tomo Sakanoue, Taishi Takenobu,* Shunichi Fukuzumi* and Taku Hasobe*

We have successfully observed ultrafast photoinduced electron transfer in face-to-face charge-transfer π -complexes of planar porphyrins and hexaazatriphenylene derivatives.

1510



A fully recyclable heterogenized Cu catalyst for the general carbene transfer reaction in batch and flow

Lourdes Maestre, Erhan Ozkal, Carles Ayats, Álvaro Beltrán, M. Mar Díaz-Requejo,* Pedro J. Pérez* and Miquel A. Pericàs*

Carbene transfer reactions can be performed in batch and flow with a highly active, chemically stable heterogenized tris(triazolyli)methyl copper(I) catalyst.

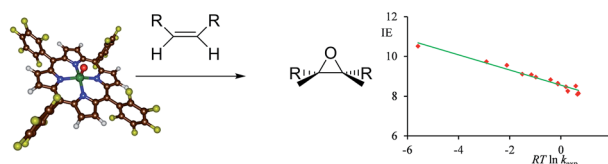


1516

A comprehensive test set of epoxidation rate constants for iron(IV)–oxo porphyrin cation radical complexes

Mala A. Sainna, Suresh Kumar, Devesh Kumar,* Simonetta Fornarini,* Maria Elisa Crestoni* and Sam P. de Visser*

Trends in oxygen atom transfer to Compound I of the P450 models with an extensive test set have been studied and show a preferred regioselectivity of epoxidation over hydroxylation in the gas-phase for the first time.

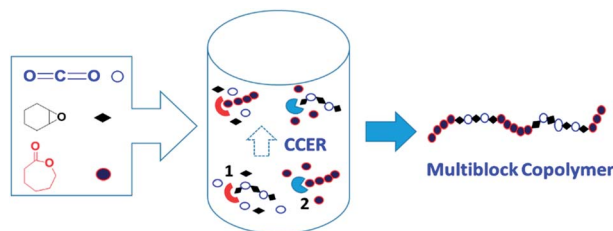


1530

Highly efficient one-pot/one-step synthesis of multiblock copolymers from three-component polymerization of carbon dioxide, epoxide and lactone

Y. Li, J. Hong, R. Wei, Y. Zhang, Z. Tong, X. Zhang,* B. Du, J. Xu and Z. Fan

Carbon dioxide-based multiblock copolymers were synthesized by a one-pot/one-step three-component polymerization of cyclohexene oxide, ε-caprolactone and CO₂ via cross-chain exchange reaction at two catalysts.

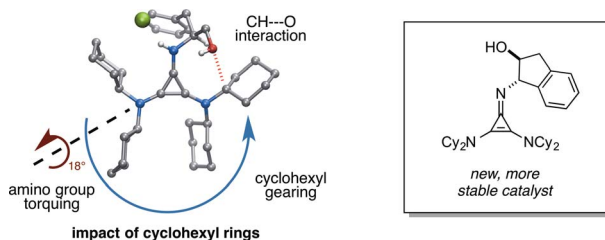


1537

Structure–activity relationship studies of cyclopropenimines as enantioselective Brønsted base catalysts

Jeffrey S. Bandar, Alexandre Barthelme, Alon Y. Mazori and Tristan H. Lambert*

New insights aid in the understanding and design of cyclopropenimine-based asymmetric catalysts.

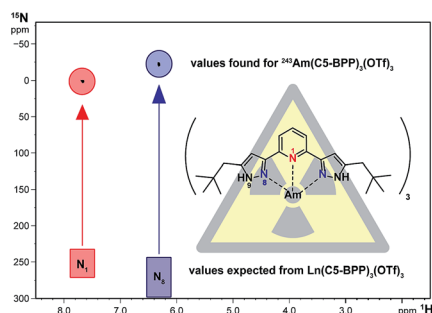


1548

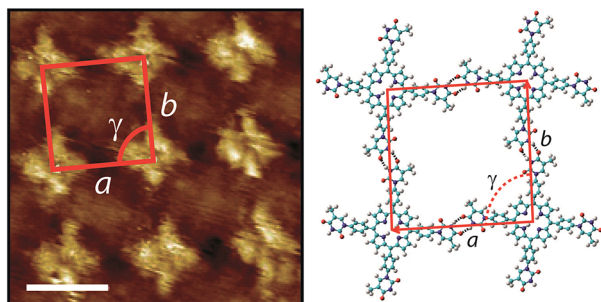
NMR and TRLFS studies of Ln(III) and An(III) C5-BPP complexes

Christian Adam,* Björn B. Beele, Andreas Geist, Udo Müllich, Peter Kaden and Petra J. Panak

NMR investigations of Am(C5-BPP)₃³⁺ show weak paramagnetism in Am(III), indicating significant covalence in metal–ligand bonds with N-donor ligands. This may explain the observed extraction selectivity for actinides over lanthanides.



1562

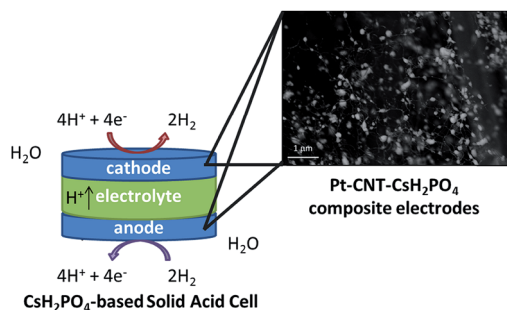


Thymine functionalised porphyrins, synthesis and heteromolecular surface-based self-assembly

Anna G. Slater, Ya Hu, Lixu Yang, Stephen P. Argent, William Lewis, Matthew O. Blunt* and Neil R. Champness*

The synthesis and surface-based self-assembly of thymine-functionalised porphyrins is described.

1570

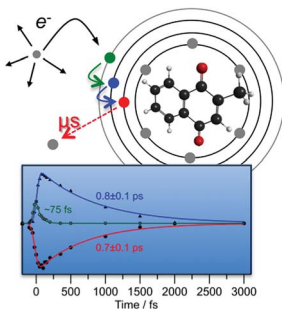


Platinum-decorated carbon nanotubes for hydrogen oxidation and proton reduction in solid acid electrochemical cells

V. Sara Thoi, Robert E. Usiskin and Sossina M. Haile*

Carbon nanotubes are used as interconnects between directly deposited Pt nanoparticles and a proton conducting solid acid electrolyte for proton reduction and hydrogen oxidation in CsH_2PO_4 -based solid acid cells. These composite electrodes significantly reduce the Pt loading and achieve record Pt utilization for solid acid cells.

1578



On the formation of anions: frequency-, angle-, and time-resolved photoelectron imaging of the menadione radical anion

James N. Bull, Christopher W. West and Jan R. R. Verlet*

Frequency-, angle-, and time-resolved photoelectron imaging of gas-phase menadione (vitamin K_3) radical anions is used to show that quasi-bound resonances of the anion can act as efficient doorway states to produce metastable ground electronic state anions on a sub-picosecond timescale.

EXPRESSION OF CONCERN

1590

Expression of concern: Homonuclear bond activation using a stable N,N' -diamidocarbene

Robert Eagling

