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IN THIS ISSUE

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

Cover
See Alán Aspuru-Guzik *et al.*, pp. 885–893.
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Inside cover
See Chung-Hang Leung, Dik-Lung Ma *et al.*, pp. 871–884.
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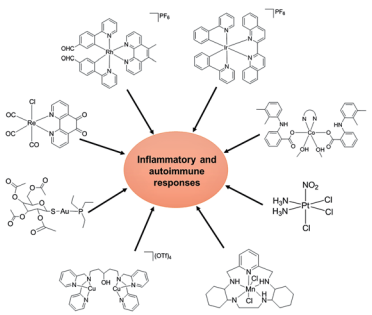
PERSPECTIVE



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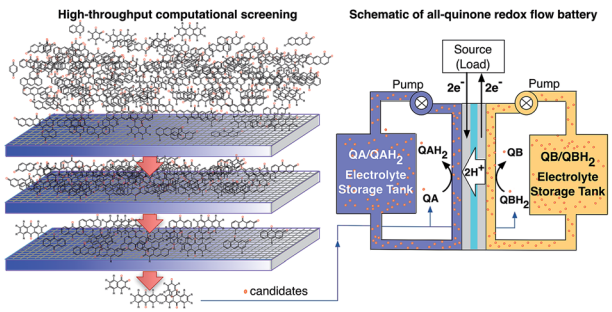

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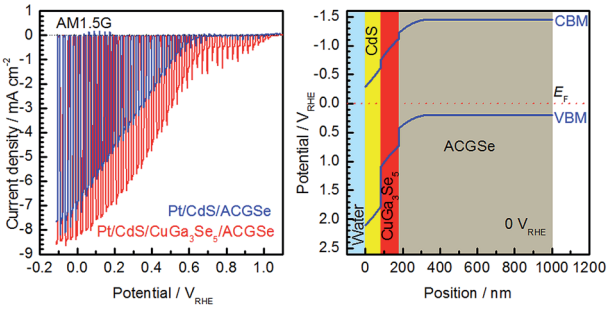

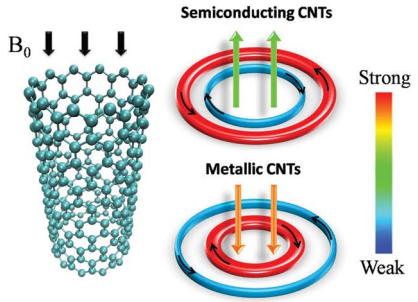

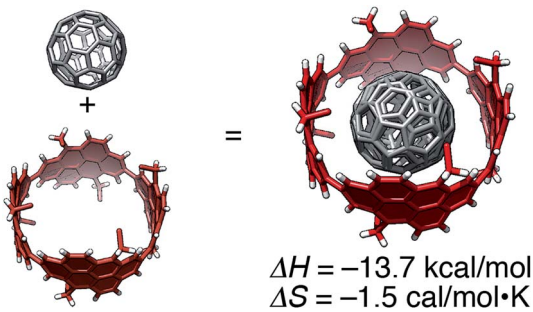

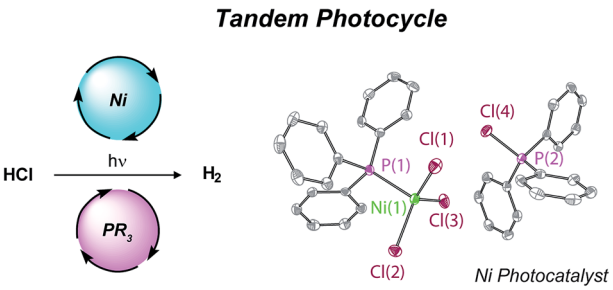

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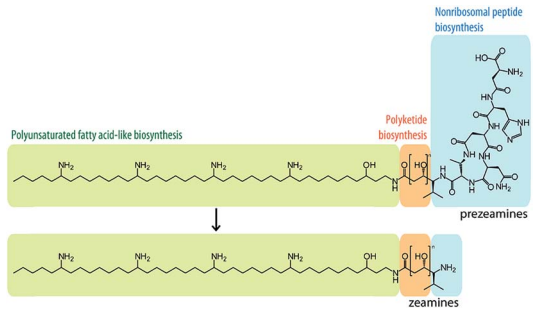
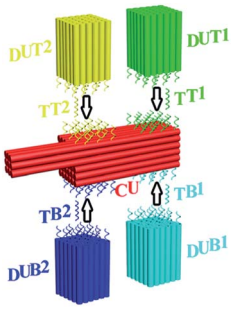


A combination of polyunsaturated fatty acid, nonribosomal peptide and polyketide biosynthetic machinery is used to assemble the zeamine antibiotics

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

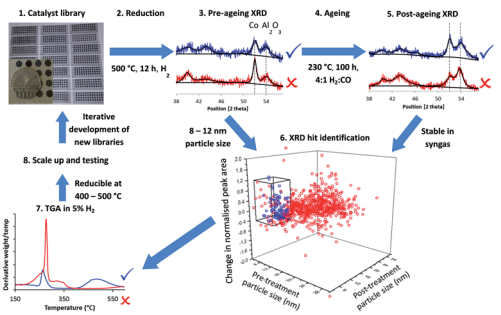


Multiplexed DNA detection based on positional encoding/decoding with self-assembled DNA nanostructures

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

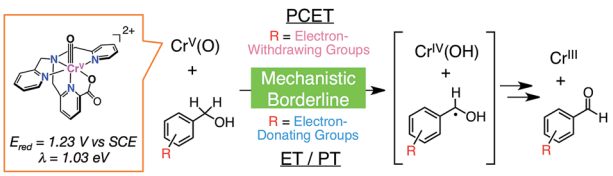


Proxy-based accelerated discovery of Fischer–Tropsch catalysts

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-Al_2O_3 are identified.

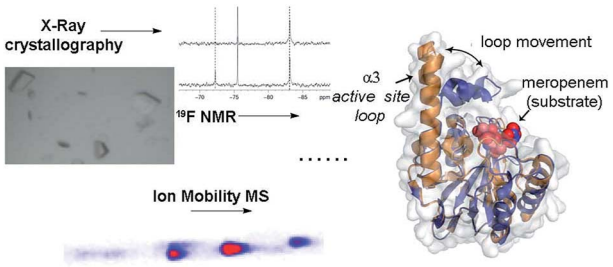
945

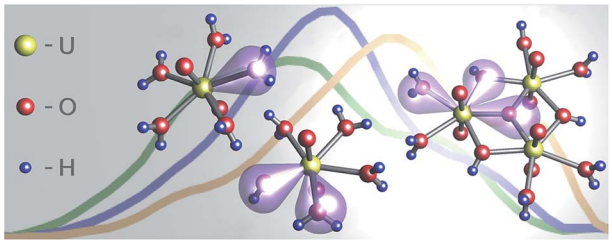


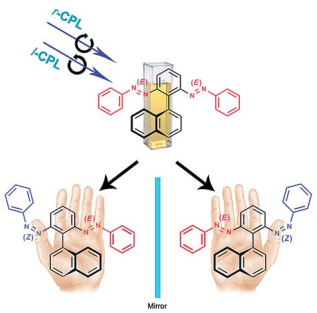
Formation and characterization of a reactive chromium(v)–oxo complex: mechanistic insight into hydrogen-atom transfer reactions

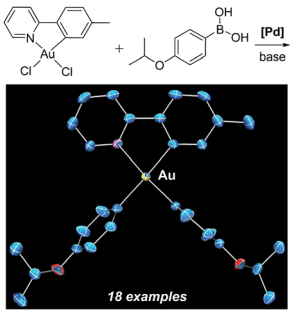
Hiroaki Kotani,* Suzue Kaida, Tomoya Ishizuka, Miyuki Sakaguchi, Takashi Ogura, Yoshihito Shiota, Kazunari Yoshizawa and Takahiko Kojima*

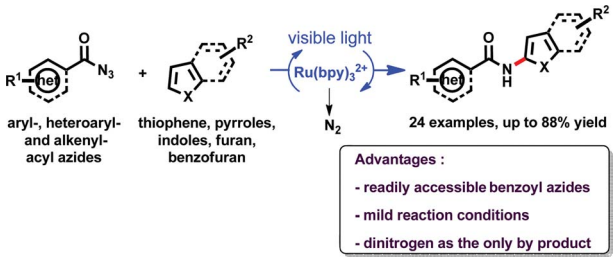
Mechanistic insights were gained into hydrogen-atom transfer reactions from benzyl alcohol derivatives with different oxidation potentials to a highly reactive Cr(v)–oxo complex to reveal switching of reaction mechanisms.







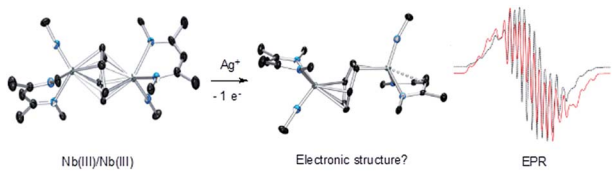




Visible light C–H amidation of heteroarenes with benzoyl azides

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

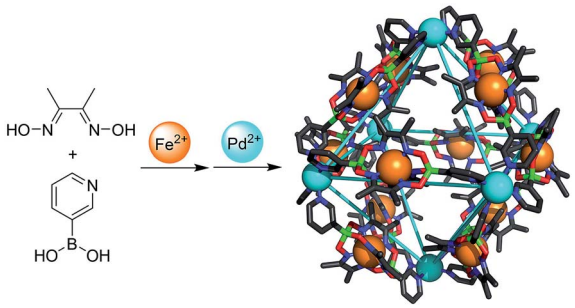
Benzoyl azides were used for the direct and atom economic C–H amidation of electron rich heteroarenes in the presence of phosphoric acid, a photocatalyst and visible light.



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 Tyliszczak, Robert G. Bergman* and John Arnold*

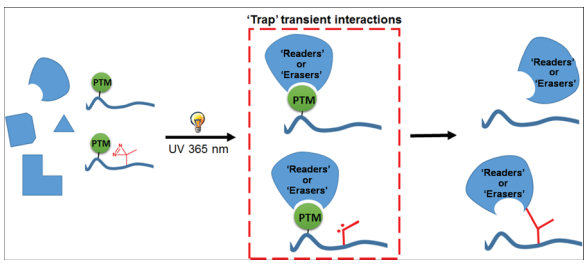
One electron oxidation of a neutral diniobium benzene complex leads to a mixed-valence species. Single crystal X-ray diffraction, EPR, $L_{3,2}$-edge XANES, and DFT indicate that the unpaired electron is localized on one metal center.



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.



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.

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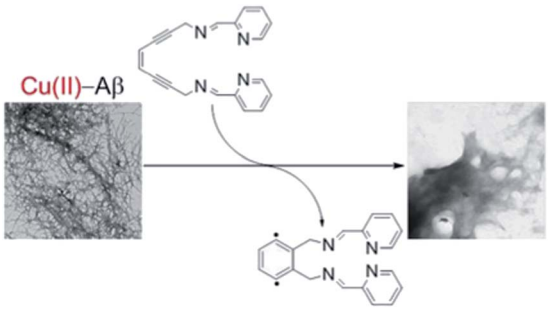

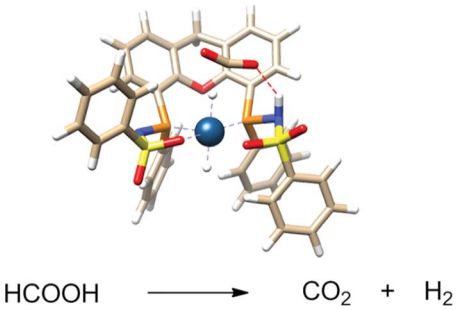

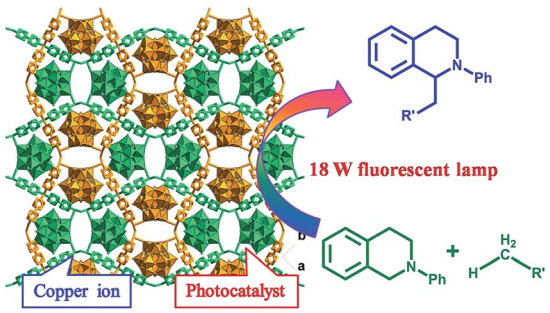

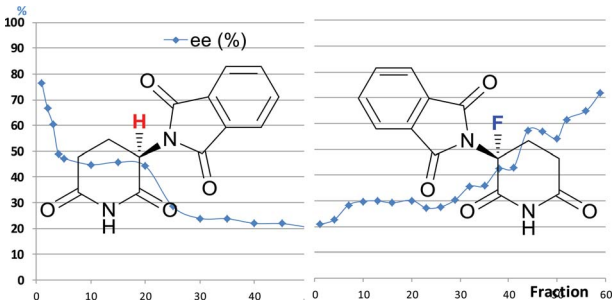

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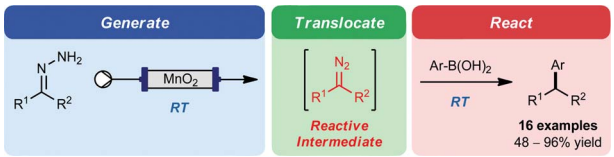
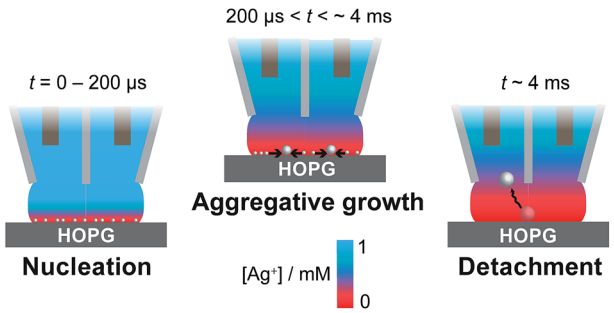


Flow chemistry as a discovery tool to access sp^2–sp^3 cross-coupling reactions *via* diazo compounds

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

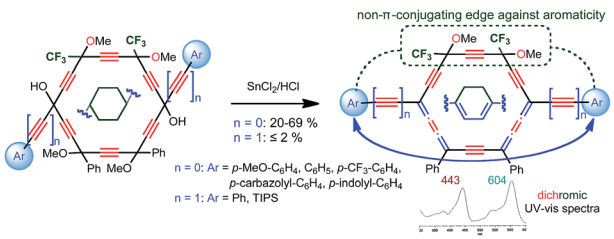
The room temperature sp^2–sp^3 cross-coupling of flow-generated diazo compounds with boronic acids is reported.



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*

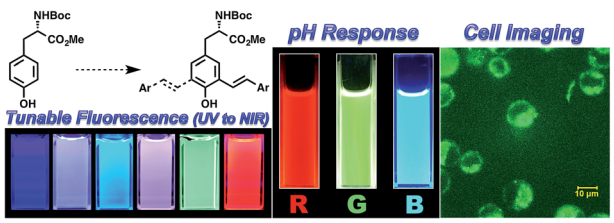
A nucleation-aggregative growth-detachment mechanism is proposed as an important feature of the electrodeposition of silver nanoparticles on basal plane highly oriented pyrolytic graphite (HOPG).



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".



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.

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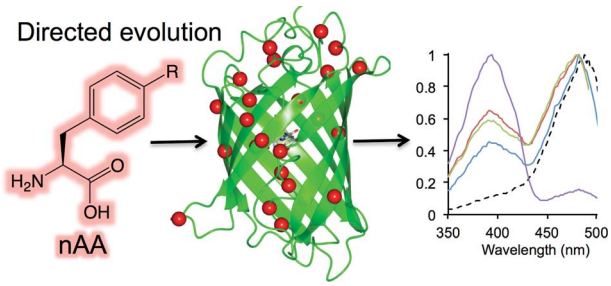

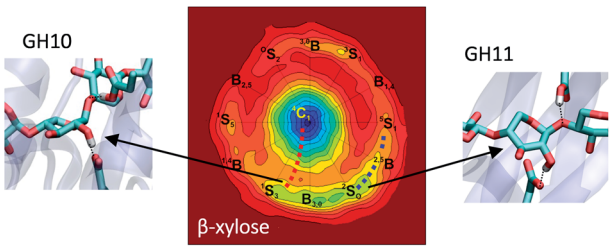

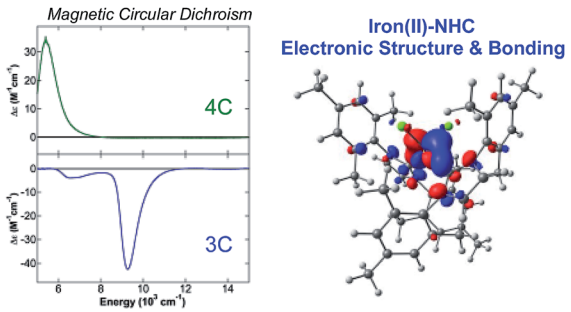

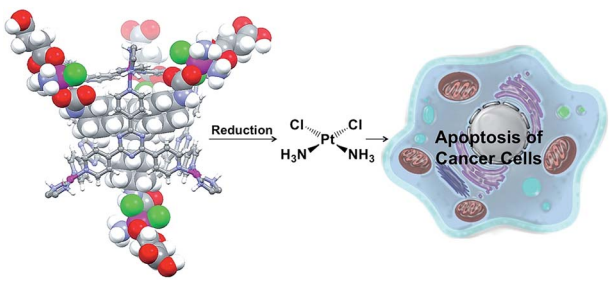

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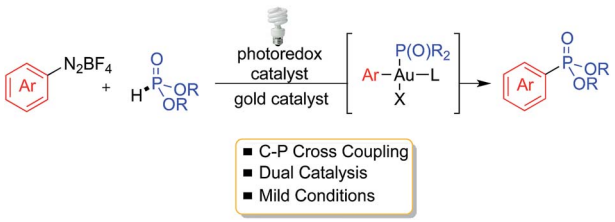


A dual catalytic strategy for carbon–phosphorus cross-coupling *via* gold and photoredox catalysis

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.

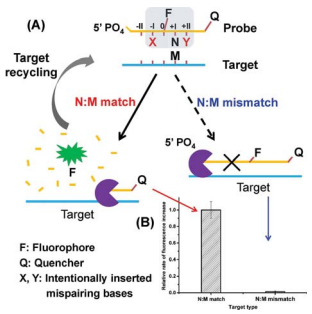
1199

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 $B_2(NHC)_2$ (NHC = N-heterocyclic carbene $C_3N_2H_2(C_6H_3Pr^i_2\text{-}2,6)_2$) as NHC⋍B⋍B⋍NHC rather than NHC → B≡B ← NHC is given.

1206

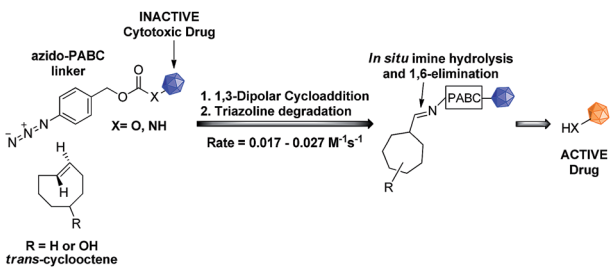


Enzyme-mediated single-nucleotide variation detection at room temperature with high discrimination factor

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.

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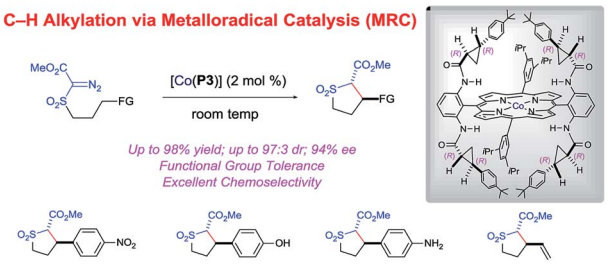
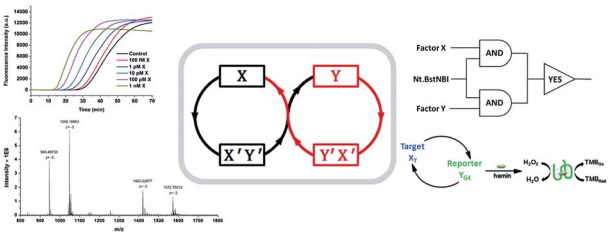
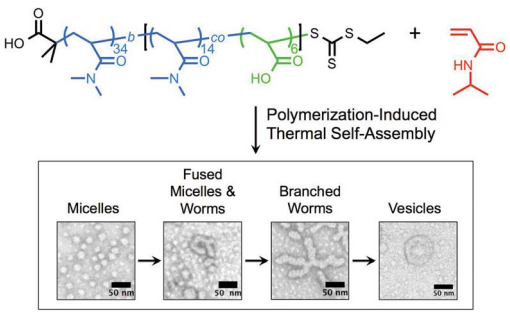
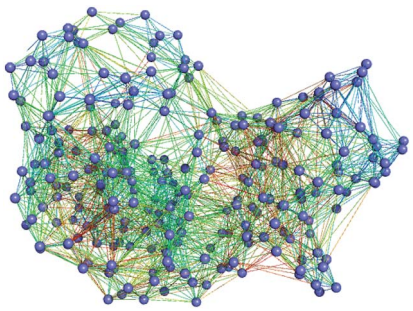
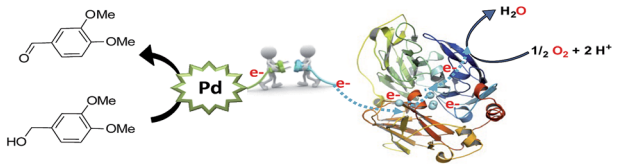






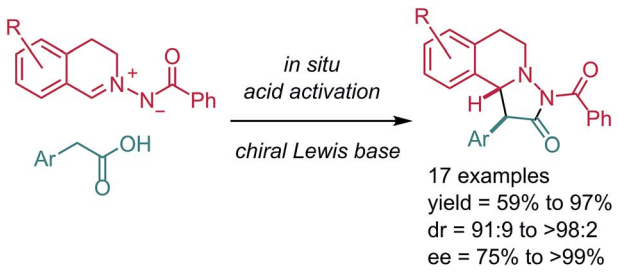




Laccases as palladium oxidases

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

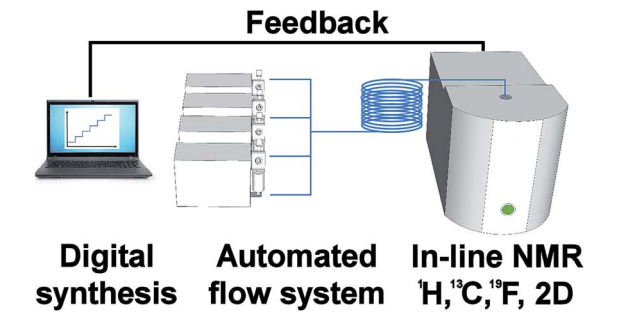
Combining a palladium-based complex with a laccase allows the oxidation of an alcohol substrate at room temperature and atmospheric pressure.



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

Lena Hesping, Anup Biswas, Constantin G. Daniliuc, Christian Mück-Lichtenfeld* and Armido Studer*

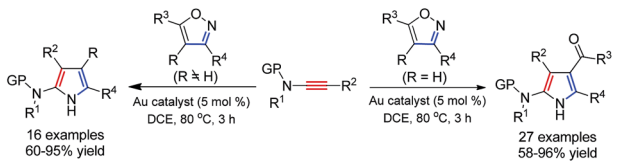
Pyrazolidinones with a tetrahydroisoquinoline core are obtained with excellent diastereocontrol and high enantioselectivity. Theoretical studies give insight on the reaction mechanism.



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.



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.

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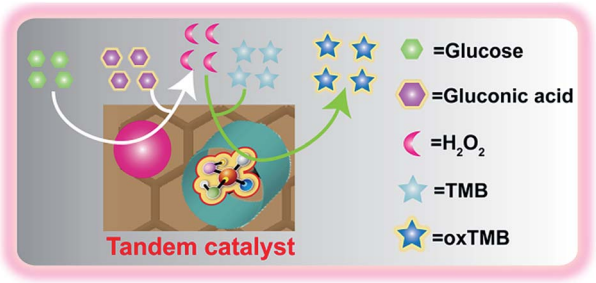
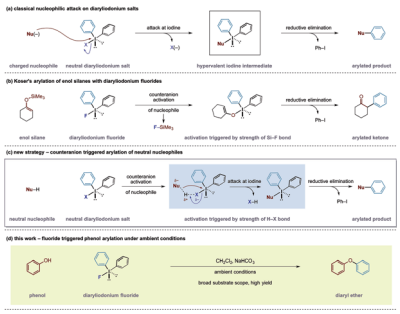
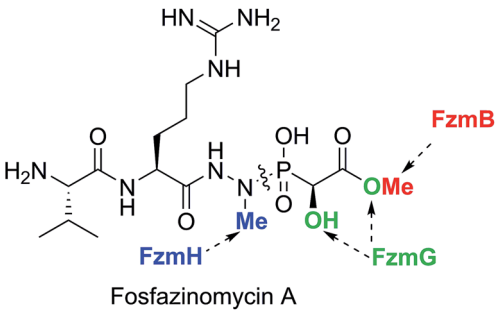
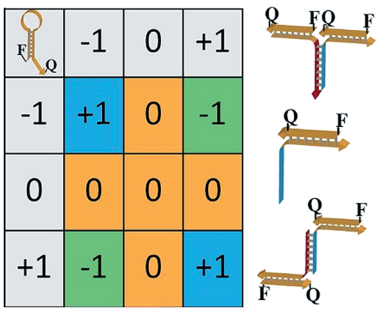






Fosfazinomycin A



EDGE ARTICLES

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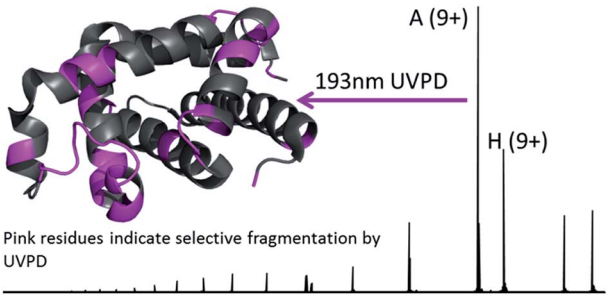
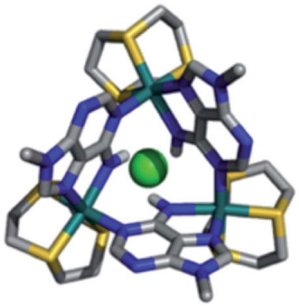
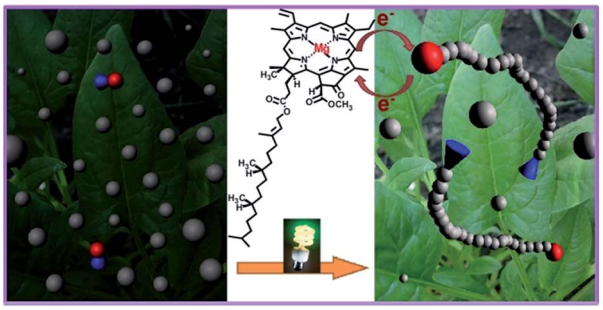
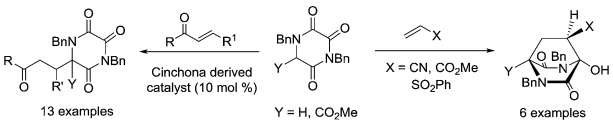
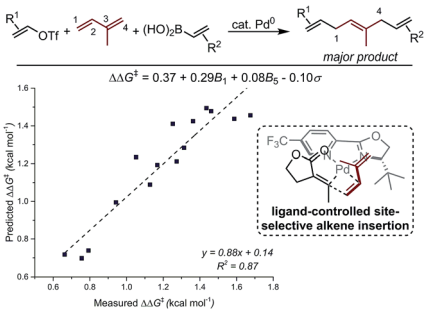






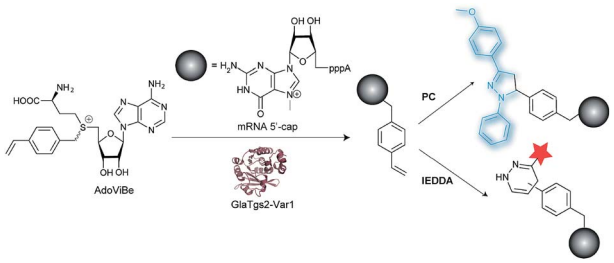




Development and investigation of a site selective palladium-catalyzed 1,4-difunctionalization of isoprene using pyridine–oxazoline ligands

Matthew S. McCammant and Matthew S. Sigman*

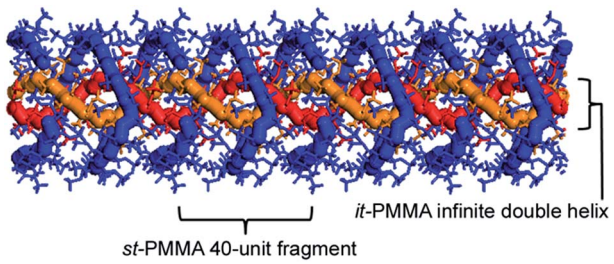
Palladium-catalyzed 1,4-difunctionalizations of isoprene that produce skipped polyenes are reported.



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*

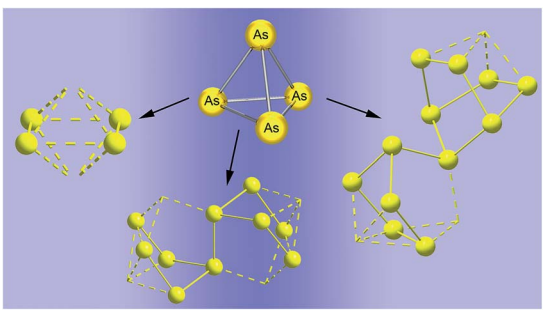
Enzymatic transfer of 4-vinylbenzyl to the mRNA 5′-cap gives access to the fluorogenic photoclick and the inverse electron-demand Diels–Alder reaction.



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.



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 As_4 moieties of yellow arsenic to built-up the to-date largest known As_n ligands.

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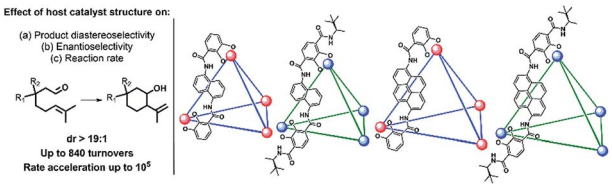
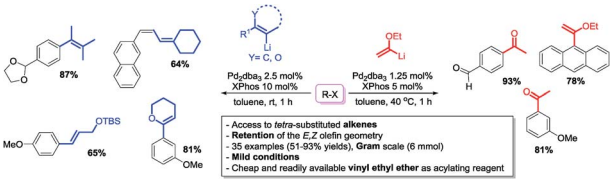
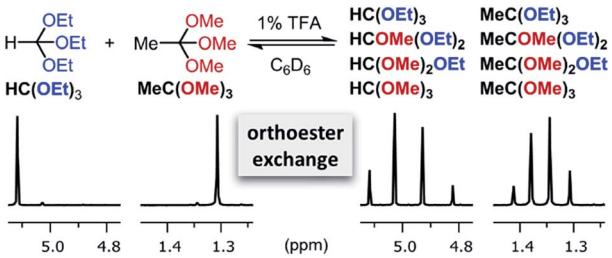
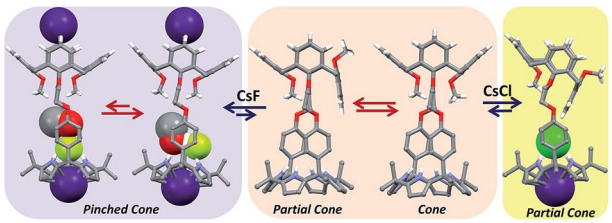
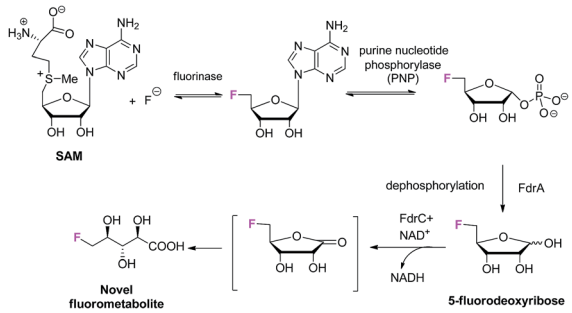








1414

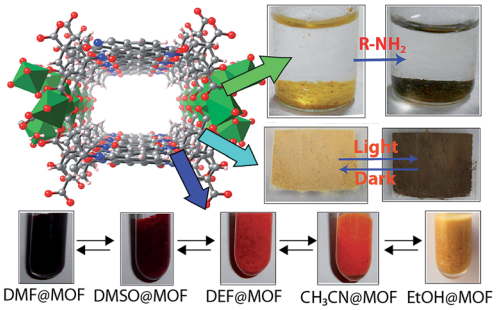


Identification of a fluorometabolite from *Streptomyces* sp. MA37: (2*R*3*S*4*S*)-5-fluoro-2,3,4-trihydroxypentanoic acid

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

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

1420

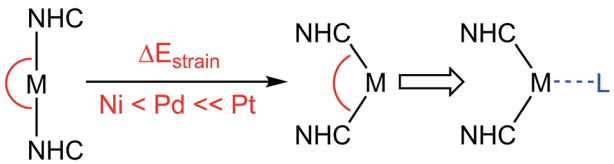


Solid state organic amine detection in a photochromic porous metal organic framework

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

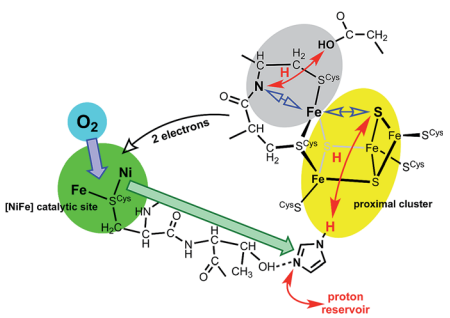


Bite-angle bending as a key for understanding group-10 metal reactivity of d^{10}-[M(NHC)$_2$] complexes with sterically modest NHC ligands

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

Experimental and theoretical investigations on the novel 14 VE complexes [M^0(iPr$_2$Im)$_2$] (M = Pd **3**, Pt **4**; iPr$_2$Im = 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 d^{10}-[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 O_2.

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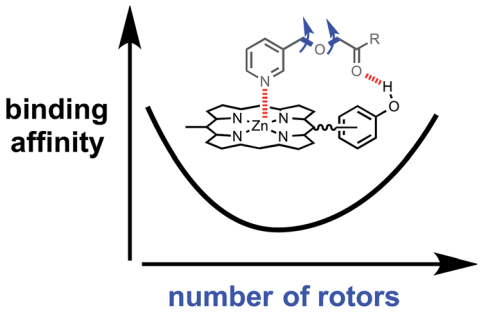

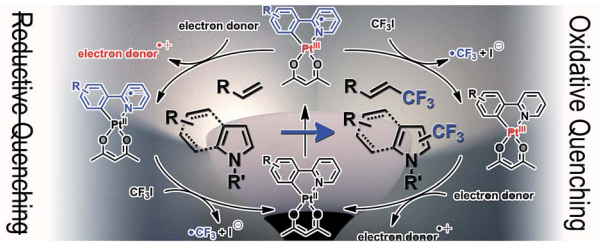

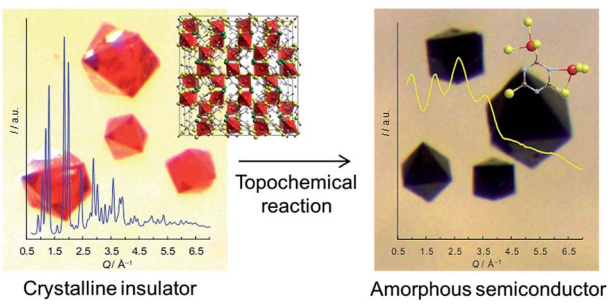

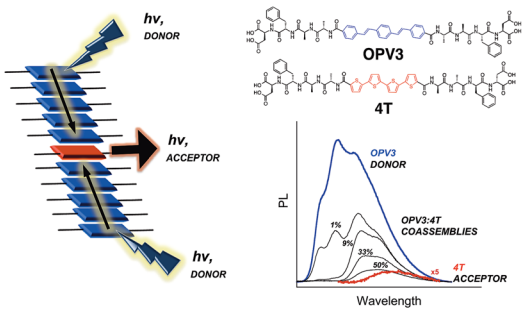

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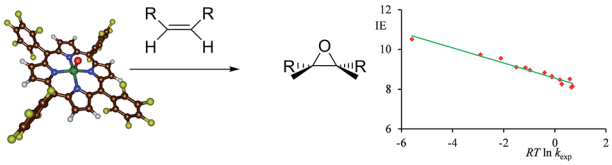

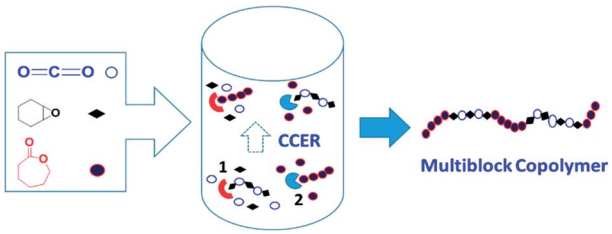

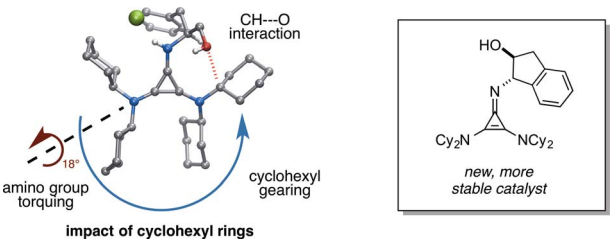

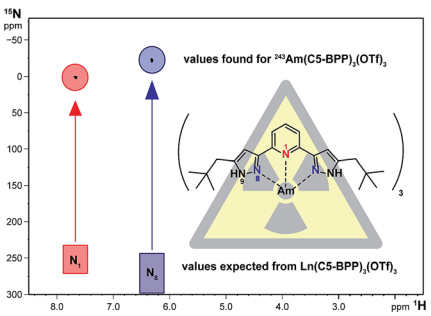

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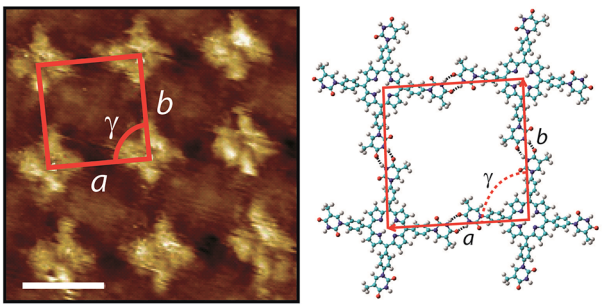
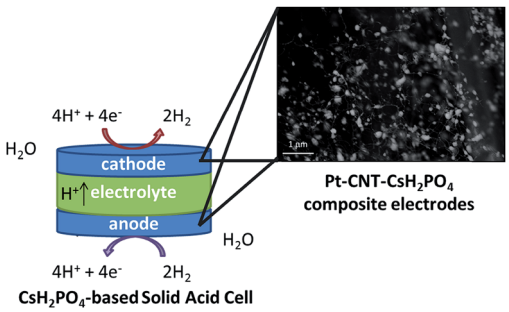


Thymine functionalised porphyrins, synthesis and heteromolecular surface-based self-assembly

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

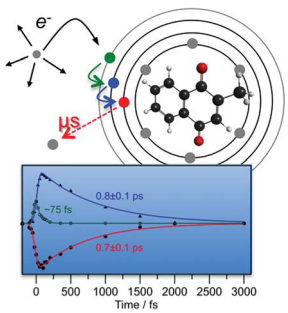
The synthesis and surface-based self-assembly of thymine-functionalised porphyrins is described.



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.



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

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

Robert Eagling