

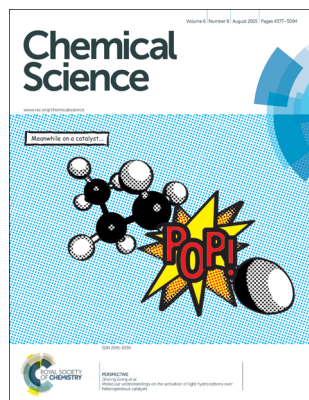
Chemical Science

www.rsc.org/chemicalscience

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

IN THIS ISSUE

ISSN 2041-6539 CODEN CSHCBM 6(8) 4377–5094 (2015)



Cover
See Jinlong Gong *et al.*,
pp. 4403–4425.
Image reproduced by
permission of Jinlong Gong
from *Chem. Sci.*,
2015, 6, 4403.



Inside cover
See Jean-François
Nierengarten, Dirk M. Guldi,
Enrique Ortí, Nazario Martín
et al., pp. 4426–4432.
Image reproduced by
permission of Nazario Martín
from *Chem. Sci.*,
2015, 6, 4426.

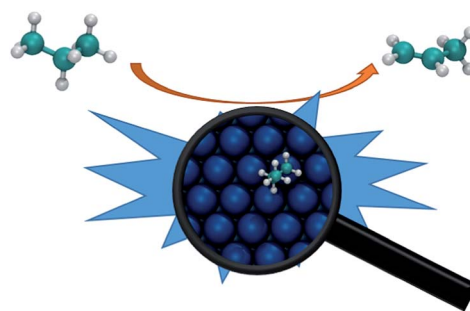
PERSPECTIVE

4403

Molecular understandings on the activation of light hydrocarbons over heterogeneous catalysts

Zhi-Jian Zhao, Cheng-chau Chiu and Jinlong Gong*

This review describes recent progress on mechanistic understanding of heterogeneous catalytic dehydrogenation reactions of light alkanes.



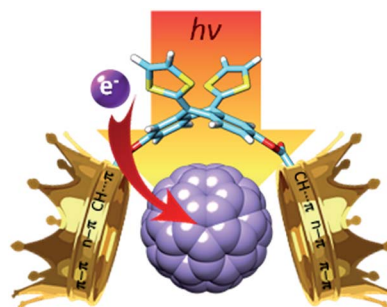
EDGE ARTICLES

4426

Unveiling the nature of supramolecular crown ether–C₆₀ interactions

L. Moreira, J. Calbo, R. M. Krick Calderon, J. Santos, B. M. Illescas, J. Aragón, J.-F. Nierengarten,* D. M. Guldi,* E. Ortí* and N. Martín*

Preparation of exTTF-(crown ether)₂ receptors, which host C₆₀, to understand the nature of the fullerene–crown ether interaction. A combination of experimental and *in silico* studies suggest that it results from the interplay of donor–acceptor, π – π , n – π and CH \cdots π interactions.



Editorial staff

Executive editor

May Copsey

Deputy editor

Jeanne Andres

Editorial production manager

Catherine Bacon

Development editors

Alessia Millemaggi

Cesar Palmero

Publishing editors

Nelly Berg, Matthew Bown, Sage Bowser,
Hugh Cowley, Alan Holder, Samantha Ivell,
James Moore, Liisa Niitsoo, Victoria Richards,
Susan Weatherby, Rachel Wood

Publishing assistants

Natalie Ford, Bethany Johnson, Rebecca Wojturska

Publisher

Jamie Humphrey

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

For pre-submission queries please contact May Copsey, Executive editor.

E-mail chemicalscience-rsc@rsc.org

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

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

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

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

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

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

Chemical Science

www.rsc.org/chemicalscience

Editorial board

Editor-in-chief

Daniel G. Nocera, Harvard University

Associate editors

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

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

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

Advisory board

Takuzo Aida, University of Tokyo
Markus Antonietti, Max Planck Institute of Colloids and Interfaces
Polly Arnold, University of Edinburgh
Xinhe Bao, Dalian Institute of Chemical Physics
Guy Bertrand, University of California, Los Angeles
Jeffrey Bode, Swiss Federal Institute of Technology Zurich
Christopher Chang, University of California, Berkeley
Chi-Ming Che, University of Hong Kong
Jason Chin, Medical Research Council Laboratory of Molecular Biology
Daniel Chiu, University of Washington
Graham Cooks, Purdue University
Eugenio Coronado, University of Valencia
Lee Cronin, University of Glasgow
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 Hseih-Wilson, California Institute of Technology
Eric Jacobsen, Harvard University
Takashi Kato, University of Tokyo
Seong Keun Kim, Seoul National University
Jerome Lacour, University of Geneva
James Leighton, Columbia University
Steve Ley, University of Cambridge
Chao-Jun Li, McGill University
Wenbin Lin, University of North Carolina
Watson Loh, Instituto de Quimica
Julie Macpherson, University of Warwick
Stephen Mann, University of Bristol
Bert Meijer, Eindhoven University of Technology
Nils Metzler-Nolte, Ruhr University Bochum
Scott Miller, Yale University
Daniel Mindiola, Indiana University
Mohammad Movassaghi, Massachusetts Institute of Technology
Jonathan Nitschke, University of Cambridge
Kyoko Nozaki, University of Tokyo
Takashi Ooi, Nagoya University
Rachel O'Reilly, University of Warwick
Michel Orrit, Leiden University
Oleg Ozerov, Texas A&M University
Hongkun Park, Harvard University

Rasmata 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.

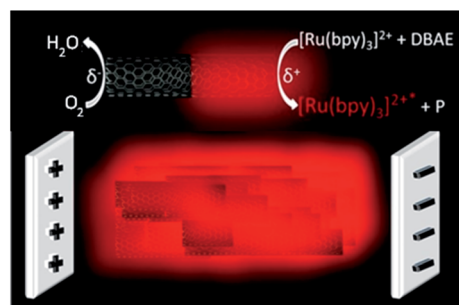


4433

3D electrogenerated chemiluminescence: from surface-confined reactions to bulk emission

Milica Sentic, Stéphane Arbault, Laurent Bouffier, Dragan Manojlovic, Alexander Kuhn* and Neso Sojic*

Electrogenerated chemiluminescence is extended to the 3D by generating light at the level of millions of micro-emitters addressed remotely by bipolar electrochemistry.

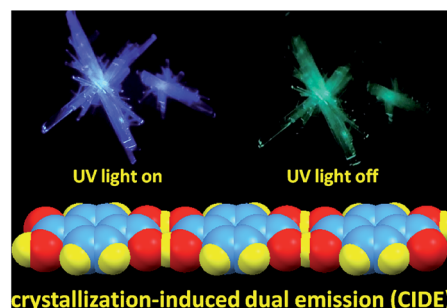


4438

Crystallization-induced dual emission from metal- and heavy atom-free aromatic acids and esters

Yongyang Gong, Lifang Zhao, Qian Peng, Di Fan, Wang Zhang Yuan,* Yongming Zhang* and Ben Zhong Tang

Crystallization-induced dual emission (fluorescence and phosphorescence) is observed in a group of pure organic aromatic acids and esters.

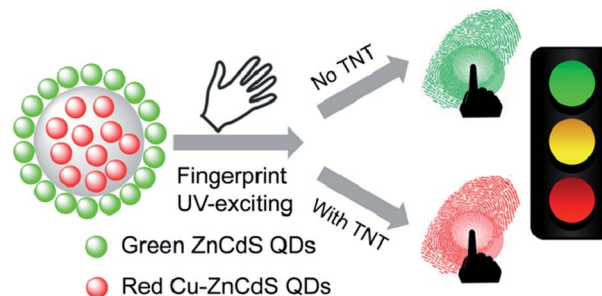


4445

Dual-emitting quantum dot nanohybrid for imaging of latent fingerprints: simultaneous identification of individuals and traffic light-type visualization of TNT

Peng Wu, Chaoying Xu, Xiandeng Hou, Jing-Juan Xu* and Hong-Yuan Chen*

A nanohybrid was employed for fingerprint imaging that was capable of simultaneous identification of individuals and TNT visualization in a "traffic-light" manner.

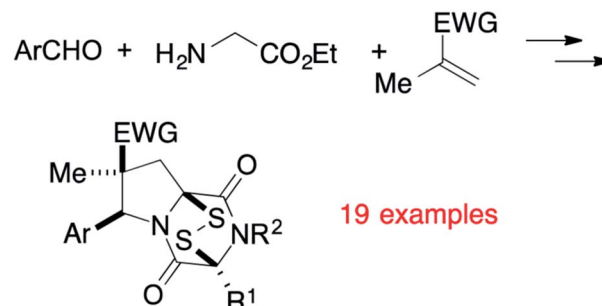


4451

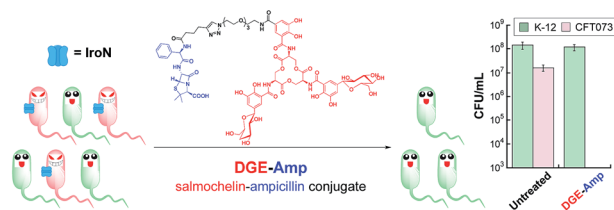
Tricyclic analogues of epidithiodioxopiperazine alkaloids with promising *in vitro* and *in vivo* antitumor activity

Marcus Baumann, André P. Dieskau, Brad M. Loertscher, Mary C. Walton, Sangkil Nam, Jun Xie, David Horne* and Larry E. Overman*

A short synthesis of 1,4-dioxohexahydro-6*H*-3,8*a*-epidithiopyrrolo[1,2-*a*]pyrazines will enable future mechanistic and translational studies of these structurally novel and promising clinical antitumor candidates.



4458



Targeting virulence: salmochelin modification tunes the antibacterial activity spectrum of β -lactams for pathogen-selective killing of *Escherichia coli*

Phoom Chairatana, Tengfei Zheng and Elizabeth M. Nolan*

New antibiotics are required to treat bacterial infections and counteract the emergence of antibiotic resistance.

4472

Object Image

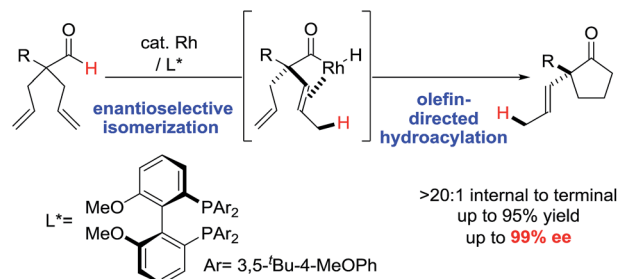


Small molecular logic systems can draw the outlines of objects via edge visualization

Jue Ling, Gaowa Naren, Jessica Kelly, David B. Fox and A. Prasanna de Silva

Like a child with a crayon, logical molecules produce outline drawings from a template.

4479

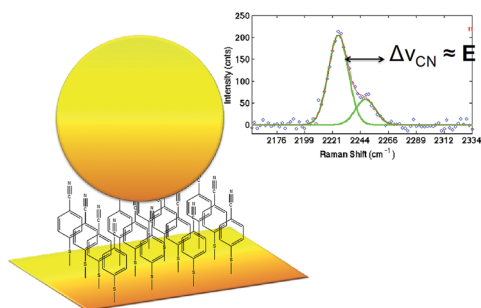


Rh-catalyzed desymmetrization of α -quaternary centers by isomerization-hydroacylation

Jung-Woo Park, Kevin G. M. Kou, Daniel K. Kim and Vy M. Dong*

A Rh-catalyzed desymmetrization of α,α -bis(allyl)aldehydes occurs by enantioselective isomerization followed by olefin-directed hydroacylation.

4484



Alkyl-nitrile adlayers as probes of plasmonically induced electric fields

Daniel T. Kwasnieski, Hao Wang and Zachary D. Schultz*

Adsorbed mercaptoalkylnitriles show Stark shifts on plasmonic surfaces that provide a direct measurement of the induced electric field.

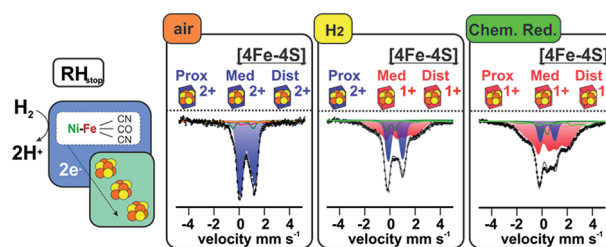


4495

Cofactor composition and function of a H₂-sensing regulatory hydrogenase as revealed by Mössbauer and EPR spectroscopy

Federico Roncaroli, Eckhard Bill,* Bärbel Friedrich, Oliver Lenz, Wolfgang Lubitz* and Maria-Eirini Pandelia*

A regulatory hydrogenase is characterised by Mössbauer, EPR and FTIR yielding insight into structure and function of this dihydrogen sensor.

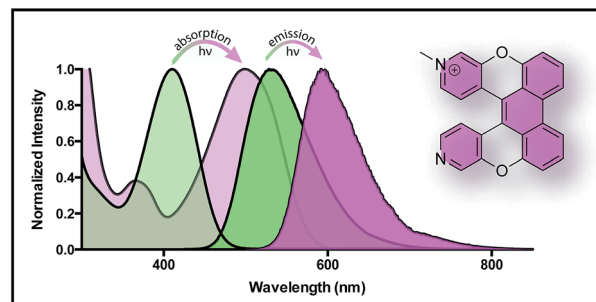


4508

Synthesis and properties of lysosome-specific photoactivatable probes for live-cell imaging

Mai N. Tran, Robert-André F. Rarig and David M. Chenoweth*

We describe the synthesis and application of a new class of large Stokes shift lysosome-specific photoactivatable probes for live-cell imaging.

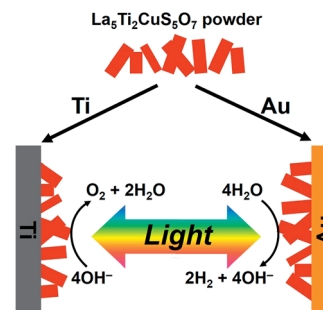


4513

Photoanodic and photocathodic behaviour of La₅Ti₂CuS₅O₇ electrodes in the water splitting reaction

Guijun Ma, Yohichi Suzuki, Rupashree Balia Singh, Aki Iwanaga, Yosuke Moriya, Tsutomu Minegishi, Jingyuan Liu, Takashi Hisatomi, Hiroshi Nishiyama, Masao Katayama, Kazuhiko Seki, Akihiro Furube, Taro Yamada and Kazunari Domen*

La₅Ti₂CuS₅O₇ embedded into the surface of Au and Ti substrates shows a photocurrent attributable to HER and OER.

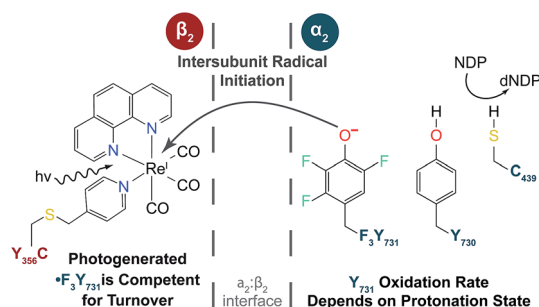


4519

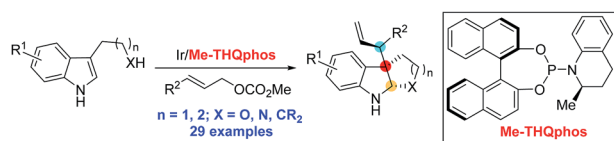
Direct interfacial Y₇₃₁ oxidation in α₂ by a photoβ₂ subunit of *E. coli* class Ia ribonucleotide reductase

David Y. Song, Arturo A. Pizano, Patrick G. Holder, JoAnne Stubbe* and Daniel G. Nocera*

Proton-coupled electron transfer (PCET) is a fundamental mechanism important in a wide range of biological processes including the universal reaction catalysed by ribonucleotide reductases (RNRs) in making *de novo*, the building blocks required for DNA replication and repair.



4525



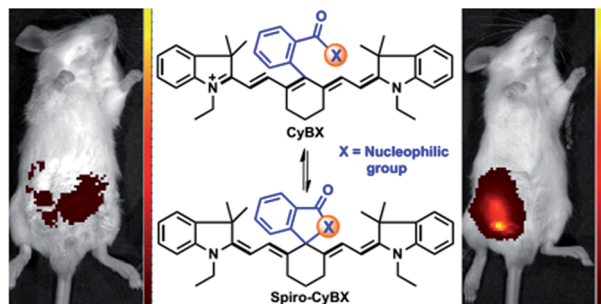
- one step, three contiguous stereocenters
- diverse chiral indoline building blocks
- high functional group tolerance
- good C3 siteselectivity
- excellent regioselectivity
- up to 99% ee, >20/1 dr

Ligand-enabled Ir-catalyzed intermolecular diastereoselective and enantioselective allylic alkylation of 3-substituted indoles

Xiao Zhang, Wen-Bo Liu, Hang-Fei Tu and Shu-Li You*

A ligand-enabled Ir-catalyzed diastereoselective and enantioselective allylic alkylation of 3-substituted indoles is reported, providing indoline products containing three contiguous stereocenters in one step with high site-, regio-, diastereo- and enantioselectivities from a wide range of readily available starting materials.

4530

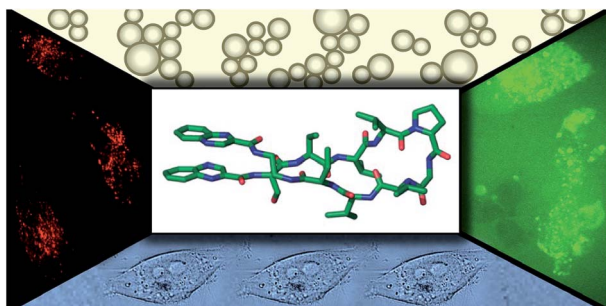


A simple and effective "capping" approach to readily tune the fluorescence of near-infrared cyanines

Longwei He, Weiyang Lin,* Qiuyan Xu, Mingguang Ren, Haipeng Wei and Jian-Yong Wang

A simple and effective capping approach was introduced to readily tune the fluorescence of NIR cyanines.

4537

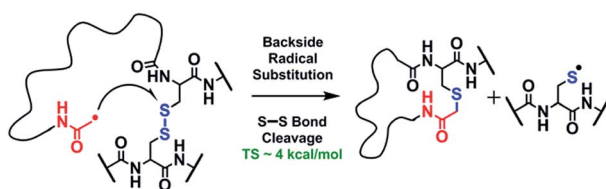


A new quinoxaline-containing peptide induces apoptosis in cancer cells by autophagy modulation

Rubí Zamudio-Vázquez, Saška Ivanova, Miguel Moreno, María Isabel Hernández-Alvarez, Ernest Giralt, Axel Bidon-Chanal, Antonio Zorzano,* Fernando Albericio* and Judit Tulla-Puche*

The most cytotoxic compound from a library of quinoxaline-containing peptides is endocytosed into HeLa cells, accumulates in acidic compartments, and blocks autophagy by altering lysosomal function, leading to apoptosis activation.

4550



Mechanisms and energetics of free radical initiated disulfide bond cleavage in model peptides and insulin by mass spectrometry

Chang Ho Sohn, Jinshan Gao, Daniel A. Thomas, Tae-Young Kim, William A. Goddard III and J. L. Beauchamp*

Direct radical substitution at sulfur initiates disulfide bond cleavage by hydrogen-deficient radicals in peptides and proteins.

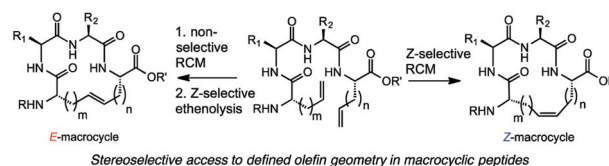


4561

Stereoselective synthesis of macrocyclic peptides via a dual olefin metathesis and ethenolysis approach

Shane L. Mangold and Robert H. Grubbs*

A metathesis strategy for controlling olefin geometry within macrocyclic peptides has been achieved using catalyst-directed RCM and ethenolysis.

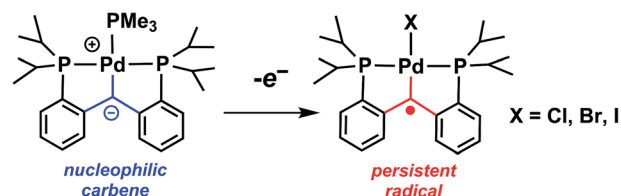


4570

Palladium carbene complexes as persistent radicals

C. C. Comanescu, M. Vyushkova and V. M. Iluc*

A series of palladium(II) persistent radical carbene complexes, $[PC(sp^2)P]PdX$ ($X = Cl, Br, I$), was synthesized from the nucleophilic carbene $[PC(sp^2)P]PdPMe_3$.

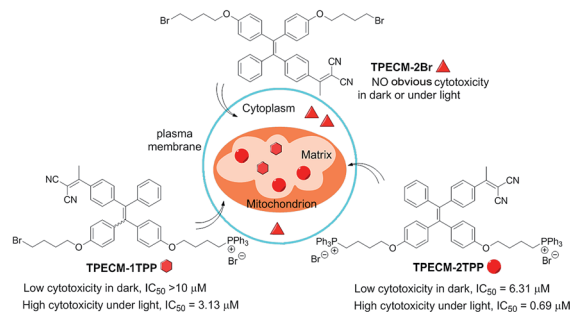


4580

Image-guided combination chemotherapy and photodynamic therapy using a mitochondria-targeted molecular probe with aggregation-induced emission characteristics

Chong-Jing Zhang, Qinglian Hu, Guangxue Feng, Ruoyu Zhang, Youyong Yuan, Xianmao Lu and Bin Liu*

Mitochondria-targeted AIE photosensitizers show multifunctions of targeted and image-guided combination chemotherapy and photodynamic therapy.

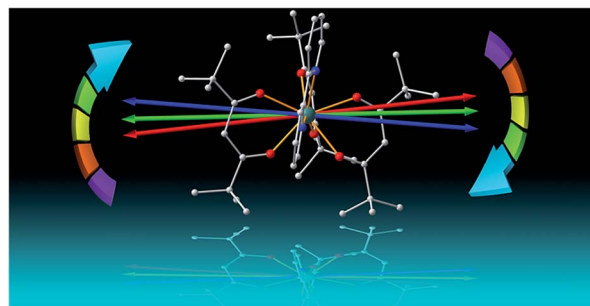


4587

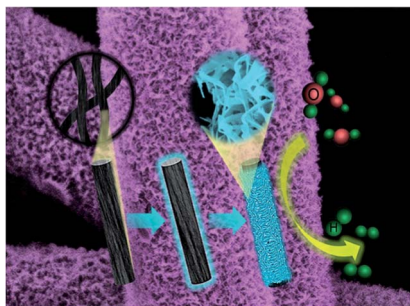
Does the thermal evolution of molecular structures critically affect the magnetic anisotropy?

Kang Qian, José J. Baldoví, Shang-Da Jiang,* Alejandro Gaita-Ariño,* Yi-Quan Zhang, Jacob Overgaard, Bing-Wu Wang, Eugenio Coronado* and Song Gao*

In the absence of a critical phase transition, one can safely use the crystal structure information determined at liquid nitrogen temperature in magnetic anisotropy research.



4594

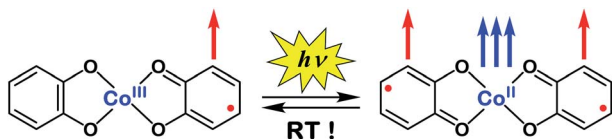


Cobalt diselenide nanobelts grafted on carbon fiber felt: an efficient and robust 3D cathode for hydrogen production

Ya-Rong Zheng, Min-Rui Gao, Zi-You Yu, Qiang Gao, Huai-Ling Gao and Shu-Hong Yu*

An easily scaled-up 3D CoSe₂/CFF hierarchical electrode has been developed as a highly active and stable hydrogen evolution reaction cathode.

4599



Bidirectional photoswitching of magnetic properties at room temperature: ligand-driven light-induced valence tautomerism

Alexander Witt, Frank W. Heinemann and Marat M. Khusniyarov*

A unique molecular switch – a cobalt dioxolene complex featuring photoisomerizable ligands – allows unprecedented control of magnetic properties with light at room temperature.

4610

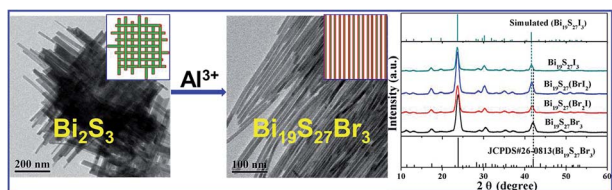


Oxalyl amide assisted palladium-catalyzed synthesis of pyrrolidones via carbonylation of γ -C(sp³)-H bonds of aliphatic amine substrates

Chao Wang, Li Zhang, Changpeng Chen, Jian Han, Yingming Yao* and Yingsheng Zhao*

The first Pd-catalyzed regioselective γ -carbonylation of oxalyl amide protected aliphatic amines with carbon monoxide leading to synthesis of pyrrolidones has been developed.

4615



Shape and composition control of Bi₁₉S₂₇(Br_{3-x}I_x) alloyed nanowires: the role of metal ions

Yihui Wu, Huanhuan Pan, Xin Zhou, Mingrun Li, Bin Zhou, Chi Yang, Wen-Hua Zhang,* Jiansheng Jie* and Can Li*

Highly uniform single-crystalline Bi₁₉S₂₇(Br_{3-x}I_x) alloyed nanowires (NWs) (0 ≤ x ≤ 3) were achieved for the first time. The NWs show a composition-independent band gap and have great application potential in optoelectronic devices.

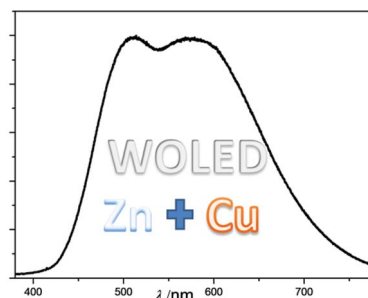


4623

Luminescent zinc(II) and copper(I) complexes for high-performance solution-processed monochromic and white organic light-emitting devices

G. Cheng, G. K.-M. So, W.-P. To, Y. Chen, C.-C. Kwok, C. Ma, X. Guan, X. Chang, W.-M. Kwok and C.-M. Che*

High performance orange (EQE up to 15.64%) and white (EQE up to 6.88%) solution processed OLEDs fabricated solely with emitters of non-platinum group metals were reported. The white device has CIE coordinates of (0.42, 0.44) and CRI of 81.

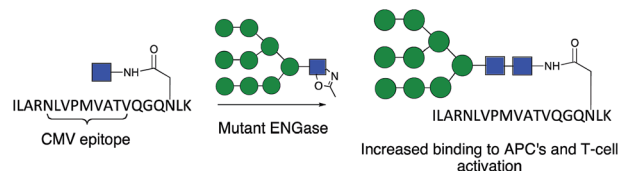


4636

Convergent chemo-enzymatic synthesis of mannosylated glycopeptides; targeting of putative vaccine candidates to antigen presenting cells

Julie D. McIntosh, Margaret A. Brimble,* Anna E. S. Brooks, P. Rod Dunbar,* Renata Kowalczyk, Yusuke Tomabechi and Antony J. Fairbanks*

Convergent chemo-enzymatic synthesis of mannosylated glycopeptides enhances uptake by human antigen presenting cells whilst preserving the immunogenicity of peptide epitopes.

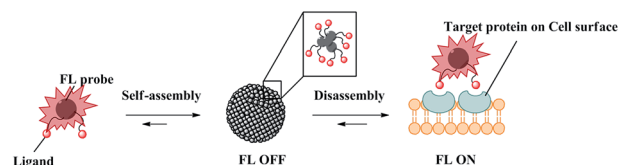


4643

Near-infrared fluorescence activation probes based on disassembly-induced emission cyanine dye

Tai-Cheng Hou, Ying-Yi Wu, Po-Yi Chiang and Kui-Thong Tan*

In the presence of target analyte, bright fluorescence in the near-IR region is emitted through the recognition-induced disassembly of the probe aggregate.

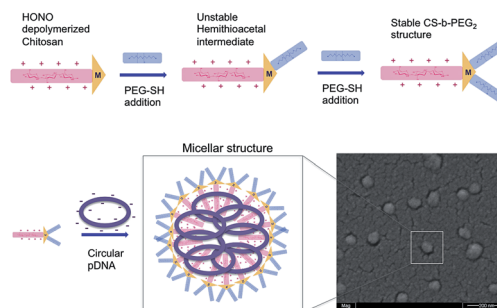


4650

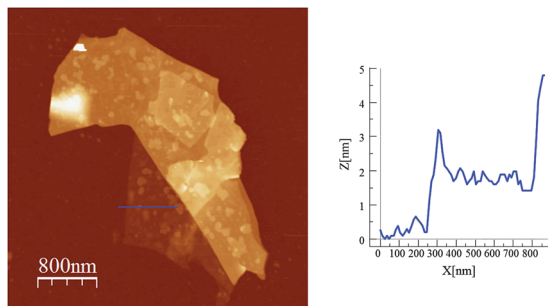
Regioselective thioacetylation of chitosan end-groups for nanoparticle gene delivery systems

V. D. Pickenhahn, V. Darras, F. Dziopa, K. Biniński, G. De Crescenzo, M. Lavertu* and M. D. Buschmann*

We present a novel, aqueous thiol-based conjugation strategy that constitutes an alternative to the oxime-click pathway for generating a reactive end-group on chitosan (CS), which could also be applicable to other polymers.



4665

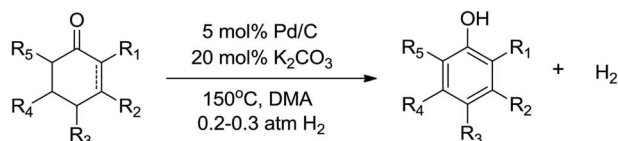


Graphene related magnetic materials: micromechanical exfoliation of 2D layered magnets based on bimetallic anilate complexes with inserted $[\text{Fe}^{\text{III}}(\text{acac}_2\text{-trien})]^+$ and $[\text{Fe}^{\text{III}}(\text{sal}_2\text{-trien})]^+$ molecules

Alexandre Abhervé, Samuel Mañas-Valero, Miguel Clemente-León* and Eugenio Coronado*

The Scotch tape method has been used for the exfoliation of layered coordination compounds formed by a 2D bimetallic anilate-based anionic network and $\text{Fe}(\text{III})$ cationic complexes placed between or within the layers.

4674

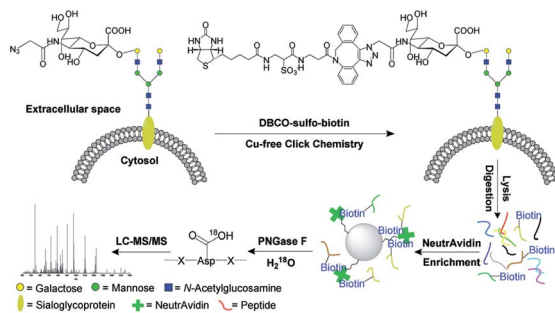


Reaction-activated palladium catalyst for dehydrogenation of substituted cyclohexanones to phenols and H_2 without oxidants and hydrogen acceptors

Jingwu Zhang, Qiangqiang Jiang, Dejun Yang, Xiaomei Zhao, Yanli Dong and Renhua Liu*

A combination of Pd/C and H_2 is found to dehydrogenate a wide range of substituted cyclohexanones and 2-cyclohexenones to their corresponding phenols with high isolated yields, with H_2 as the only byproduct.

4681

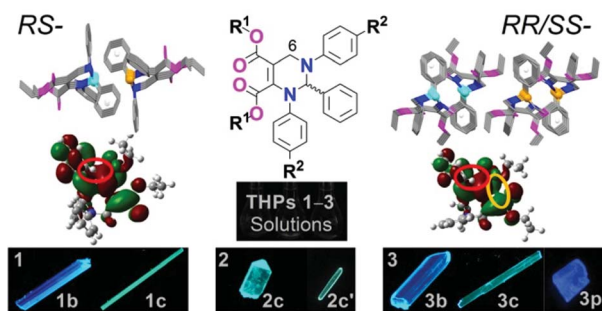


Systematic and site-specific analysis of *N*-sialoglycosylated proteins on the cell surface by integrating click chemistry and MS-based proteomics

Weixuan Chen, Johanna M. Smeekens and Ronghu Wu*

A method integrating metabolic labeling, copper-free click chemistry and MS-based proteomics is effective to globally and site-specifically analyze surface *N*-sialoglycoproteins.

4690



Insight into the strong aggregation-induced emission of low-conjugated racemic C6-unsubstituted tetrahydropyrimidines through crystal-structure–property relationship of polymorphs

Qihua Zhu, Yilin Zhang, Han Nie, Zujin Zhao, Shuwen Liu,* Kam Sing Wong* and Ben Zhong Tang*

Racemic low-conjugated non-emissive THPs 1–3 can form highly emissive *RS*- and *RR/SS*-packing polymorphs with mixed through-bond and through-space conjugation.

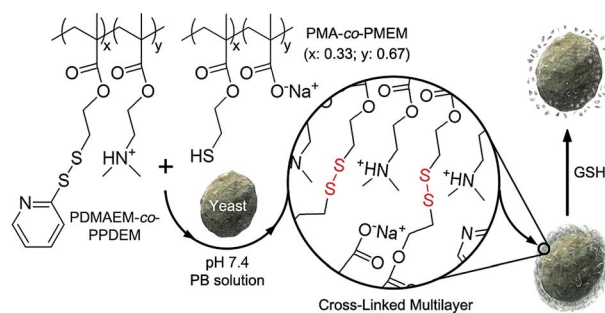


4698

Cytocompatible *in situ* cross-linking of degradable LbL films based on thiol–exchange reaction

Sung Ho Yang,* Jinsu Choi, L. Palanikumar, Eun Seong Choi, Juno Lee, Juan Kim, Insung S. Choi* and Ja-Hyoung Ryu*

A highly cytotocompatible LbL process was developed, based on the thiol–exchange reaction, for forming *in situ* cross-linked and degradable films under physiologically mild conditions.

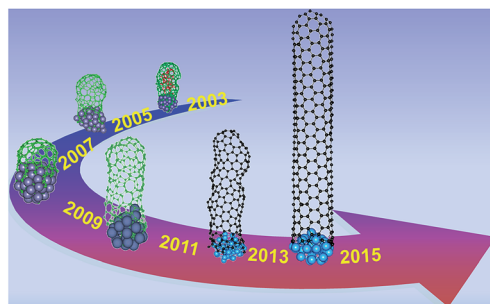


4704

Atomistic simulation of the growth of defect-free carbon nanotubes

Ziwei Xu, Tianying Yan* and Feng Ding*

The atomistic simulation of defect-free SWCNT growth is realized for the first time after 12 years of continuous effort.

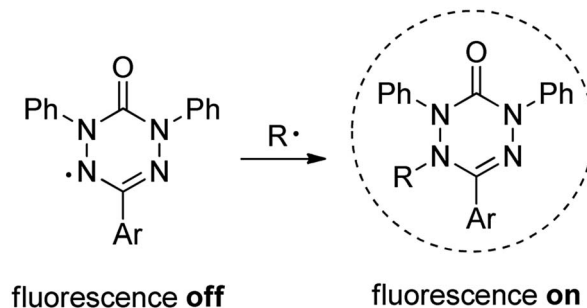


4712

Profluorescent verdazyl radicals – synthesis and characterization

David Matuschek, Steffen Eusterwiemann, Linda Stegemann, Carsten Doerenkamp, Birgit Wibbeling, Constantin G. Daniliuc, Nikos L. Doltsinis,* Cristian A. Strassert,* Hellmut Eckert* and Armido Studer*

The synthesis and characterization of various 6-oxo-verdazyl radicals and their diamagnetic styryl radical trapping products are presented.

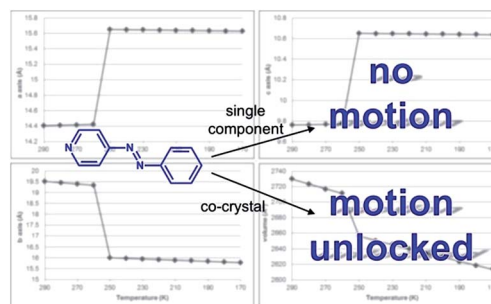


4717

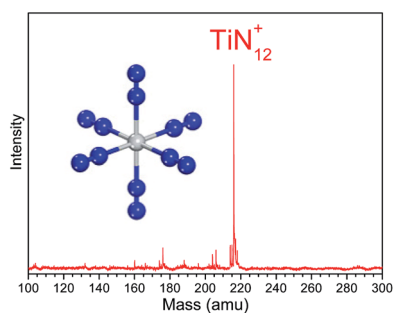
Achieving dynamic behaviour and thermal expansion in the organic solid state *via* co-crystallization

Kristin M. Hutchins, Ryan H. Groeneman, Eric W. Reinheimer, Dale C. Swenson and Leonard R. MacGillivray*

Molecular motion of an azo functional group is 'unlocked' *via* co-crystallizations.



4723

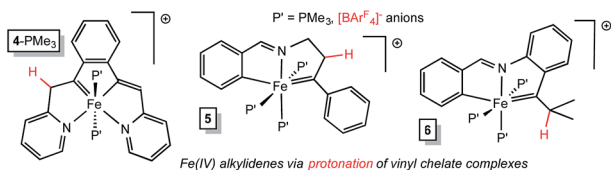


Experimental observation of TiN_{12}^+ cluster and theoretical investigation of its stable and metastable isomers

Ke-Wei Ding, Xiao-Wei Li, Hong-Guang Xu, Tao-Qi Li,*
Zhong-Xue Ge,* Qian Wang* and Wei-Jun Zheng*

In the O_h symmetric structure of TiN_{12}^+ , the interaction between Ti and N_2 weakens the N–N bond significantly.

4730

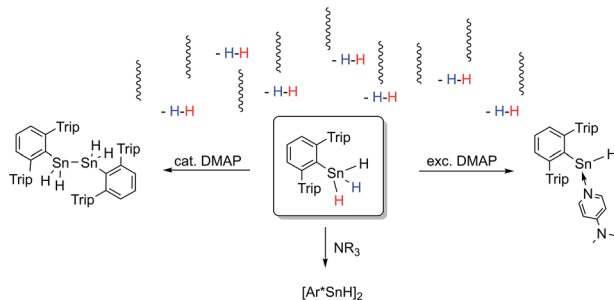


Fe(IV) alkylidenes via protonation of Fe(II) vinyl chelates and a comparative Mössbauer spectroscopic study

Brian M. Lindley, Ala'aeddeen Swidan, Emil B. Lobkovsky,
Peter T. Wolczanski,* Mario Adelhardt, Jörg Sutter
and Karsten Meyer

Fe(IV) alkylidenes are produced via protonation of Fe(II) vinyl chelate complexes.

4737

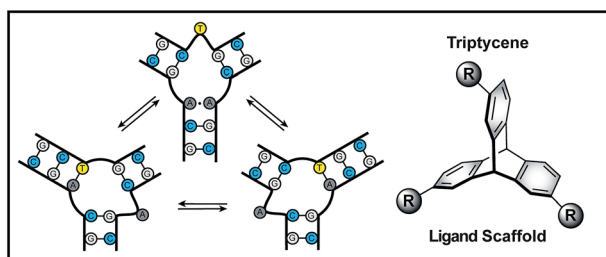


A nitrogen-base catalyzed generation of organotin(II) hydride from an organotin trihydride under reductive dihydrogen elimination

Christian P. Sindlinger, Andreas Stasch, Holger F. Bettinger
and Lars Wesemann*

Amine bases are shown to induce reductive elimination of dihydrogen from NR_3 from triphenyltin trihydride.

4752



Triptycene-based small molecules modulate (CAG)·(CTG) repeat junctions

Stephanie A. Barros and David M. Chenoweth*

A triptycene-based scaffold is used to develop a new class of ligands for modulating the structure of junction forming trinucleotide repeat expansion sequences.

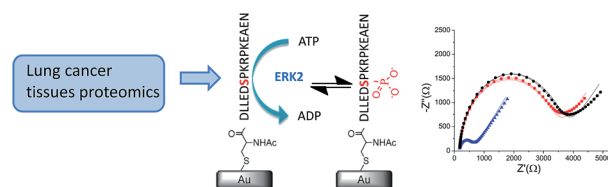


4756

Integrating proteomics with electrochemistry for identifying kinase biomarkers

Einav Amit, Rofeamor Obena, Yi-Ting Wang, Roman Zhuravel, Aaron James F. Reyes, Shir Elbaz, Dvir Rotem, Danny Porath, Assaf Friedler,* Yu-Ju Chen* and Shlomo Yitzchaik*

We present an integrated approach for highly sensitive identification and validation of substrate-specific kinases as cancer biomarkers.

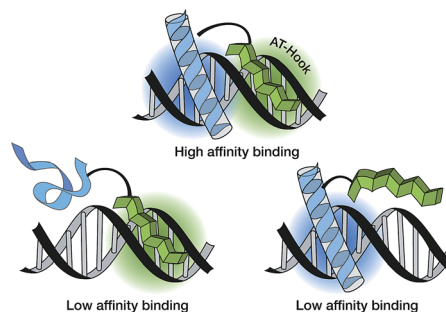


4767

The AT-Hook motif as a versatile minor groove anchor for promoting DNA binding of transcription factor fragments

Jéssica Rodríguez, Jesús Mosquera, Jose R. Couceiro, M. Eugenio Vázquez* and José L. Mascareñas*

We report the development of chimeric DNA binding peptides comprising a DNA binding fragment of natural transcription factors (the basic region of a bZIP protein or a monomeric zinc finger module) and an AT-Hook peptide motif.

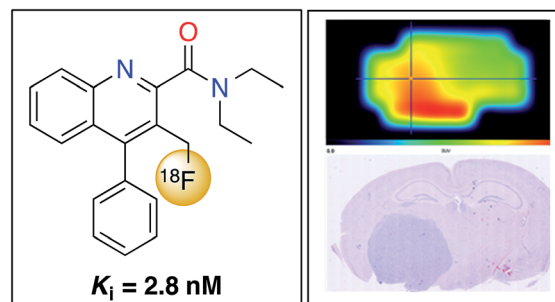


4772

A novel ¹⁸F-labelled high affinity agent for PET imaging of the translocator protein

Adele Blair, Filip Zmuda, Gaurav Malviya, Adriana A. S. Tavares, Gilles D. Tamagnan, Anthony J. Chalmers, Deborah Dewar, Sally L. Pimlott and Andrew Sutherland*

A novel ¹⁸F-labelled quinoline-2-carboxamide has been characterised as a novel PET imaging agent for the translocator protein.

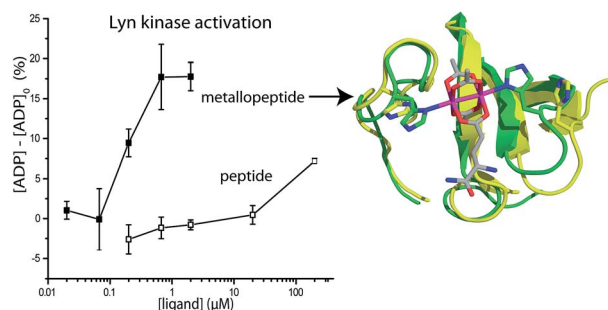


4778

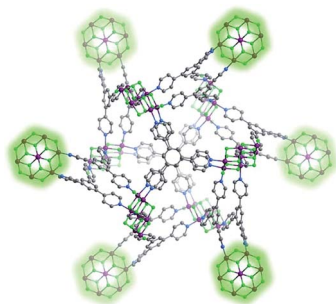
Potent and selective inhibition of SH3 domains with dirhodium metalloinhibitors

Farrukh Vohidov, Sarah E. Knudsen, Paul G. Leonard, Jun Ohata, Michael J. Wheadon, Brian V. Popp, John E. Ladbury and Zachary T. Ball*

Specific, designed histidine–rhodium interactions allow a metallopeptide to bind Lyn kinase with nanomolar affinity and to activate kinase activity.



4784

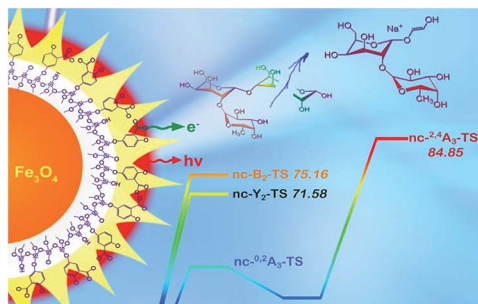


Double-walled pyr topology networks from a novel fluoride-bridged heptanuclear metal cluster

Kai-Jie Chen, John J. Perry IV, Hayley S. Scott, Qing-Yuan Yang and Michael J. Zaworotko*

Two isostructural networks with double-walled pyr topology comprised of novel fluoride-bridged heptanuclear metal clusters and 3-connected ligands have been synthesized and characterized by X-ray diffraction, thermogravimetric analysis, and gas sorption experiments.

4790

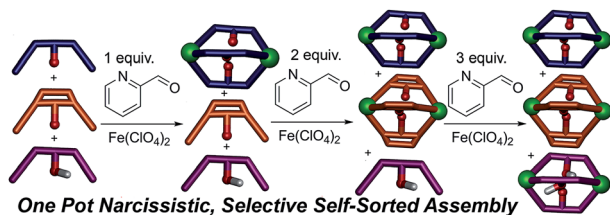


UV-activated multilayer nanomatrix provides one-step tunable carbohydrate structural characterization in MALDI-MS

Rofeamor P. Obena, Mei-Chun Tseng, Indah Primadona, Jun Hsiao, I-Che Li, Rey Y. Capangpangan, Hsiu-Fong Lu, Wan-Sheung Li, Ito Chao, Chun-Cheng Lin and Yu-Ju Chen*

Our work highlights DHB@MNP-induced pseudo-MS/MS for oligosaccharide characterization, with some insights on this nanoparticle-mediated energy transfer dynamics.

4801

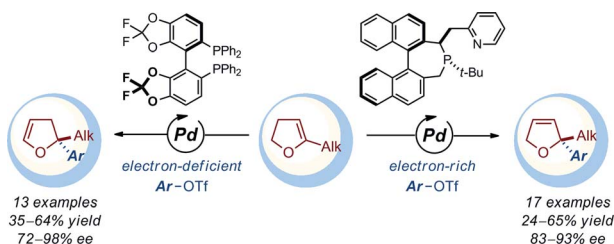


High fidelity sorting of remarkably similar components via metal-mediated assembly

Lauren R. Holloway, Michael C. Young, Gregory J. O. Beran and Richard J. Hooley*

Subtle differences in coordination angle and rigidity lead to narcissistic self-sorting between highly similar individual components upon metal-mediated assembly.

4807



Access to enantioenriched 2,3- and 2,5-dihydrofurans with a fully substituted C2 stereocenter by Pd-catalyzed asymmetric intermolecular Heck reaction

Gustavo M. Borrajo-Calleja, Vincent Bizet, Thomas Bürgi and Clément Mazet*

A palladium catalyzed intermolecular asymmetric Heck reaction provides access to valuable 2,3- and 2,5-dihydrofurans with a fully substituted C2 stereocenter with high levels of regio- and enantiocontrol.

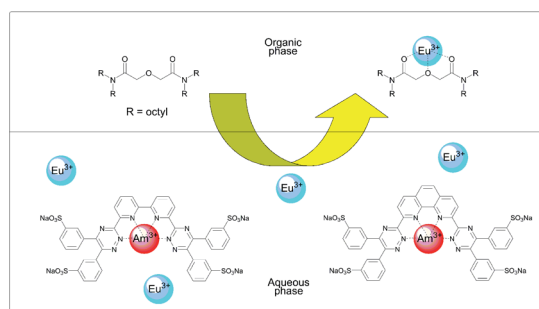


4812

Hydrophilic sulfonated bis-1,2,4-triazine ligands are highly effective reagents for separating actinides(III) from lanthanides(III) via selective formation of aqueous actinide complexes

Frank W. Lewis,* Laurence M. Harwood,* Michael J. Hudson, Andreas Geist, Valery N. Kozhevnikov, Petr Distler and Jan John

Tetrasulfonated bis-1,2,4-triazine ligands can selectively complex and separate actinides from lanthanides in aqueous nitric acid with very high selectivities.

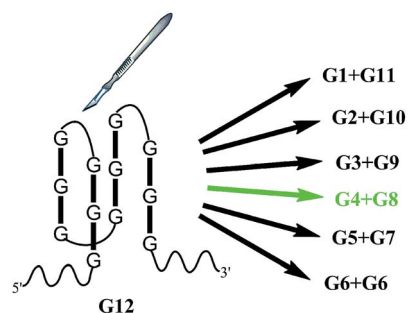


4822

How to split a G-quadruplex for DNA detection: new insight into the formation of DNA split G-quadruplex

Jinbo Zhu, Libing Zhang, Shaojun Dong and Erkang Wang*

A magic "law of 4 : 8" to split the G-quadruplex for DNA detection has been found.

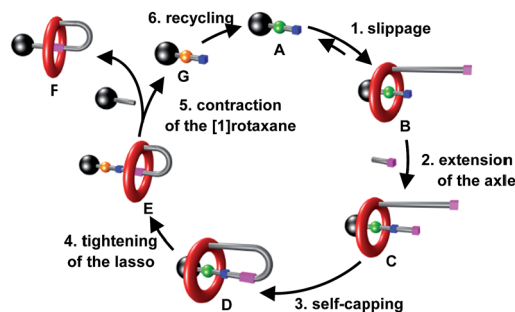


4828

Synthesis of triazolium-based mono- and tris-branched [1]rotaxanes using a molecular transporter of dibenzo-24-crown-8

P. Waelès, C. Clavel, K. Fournel-Marotte and F. Coutrot*

A general synthesis to mono- and multi-branched [1]rotaxanes that are devoid of any efficient template is reported.

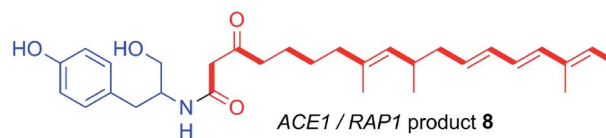


4837

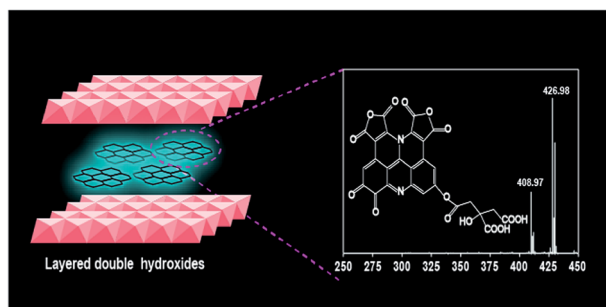
Heterologous expression of the avirulence gene ACE1 from the fungal rice pathogen Magnaporthe oryzae

Z. Song, W. Bakeer, J. W. Marshall, A. A. Yakasai, R. M. Khalid, J. Collemare, E. Skellam, D. Tharreau, M.-H. Lebrun, C. M. Lazarus, A. M. Bailey, T. J. Simpson and R. J. Cox*

Heterologous expression of key components of the *Magnaporthe grisea* ACE1 gene cluster produces a potential precursor of cryptic avirulence signalling compounds that induce resistance to *M. grisea* in rice.



4846

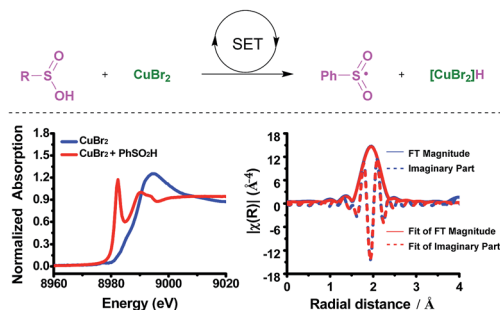


Structure observation of graphene quantum dots by single-layered formation in layered confinement space

Liqing Song, Jingjing Shi, Jun Lu and Chao Lu*

We observe the structure of single-layered graphene quantum dots prepared in the 2D confined space of layered double hydroxides.

4851

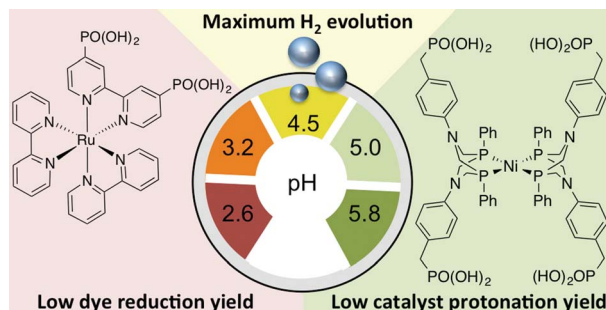


Operando X-ray absorption and EPR evidence for a single electron redox process in copper catalysis

Qingquan Lu, Jian Zhang, Pan Peng, Guanghui Zhang, Zhiliang Huang, Hong Yi, Jeffrey T. Miller and Aiwen Lei*

A single electron redox process between Cu(II) and a sulfinic acid, and characterization of the formed Cu(I) are clearly shown using *operando* X-ray absorption and EPR evidence.

4855

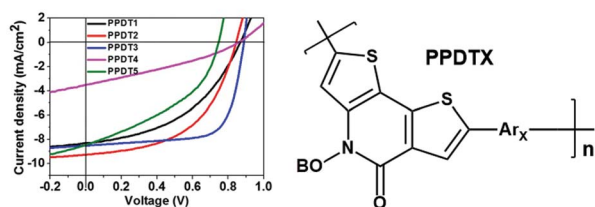


Unravelling the pH-dependence of a molecular photocatalytic system for hydrogen production

Anna Reynal,* Ernest Pastor, Manuela A. Gross, Shababa Selim, Erwin Reisner* and James R. Durrant*

The electron-donating ability of the sacrificial agent and the protonation of the catalyst determine the optimum pH for hydrogen production.

4860



Wide bandgap OPV polymers based on pyridinonedithiophene unit with efficiency >5%

Alexander M. Schneider, Luyao Lu, Eric F. Manley, Tianyue Zheng, Valerii Sharapov, Tao Xu, Tobin J. Marks, Lin X. Chen* and Luping Yu*

We report the properties of a new series of wide band gap photovoltaic polymers based on the *N*-alkyl 2-pyridone dithiophene (PDT) unit.

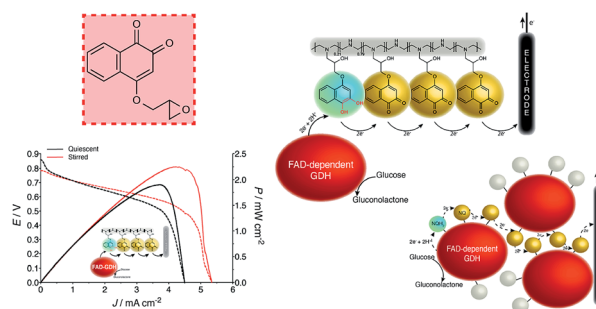


4867

Rational design of quinones for high power density biofuel cells

Ross D. Milton, David P. Hickey, Sofiene Abdellaoui, Koun Lim, Fei Wu, Boxuan Tan and Shelley D. Minteer*

Rationally designing quinones to label GDH and create a redox hydrogel that delivers high OCP, current and power densities.

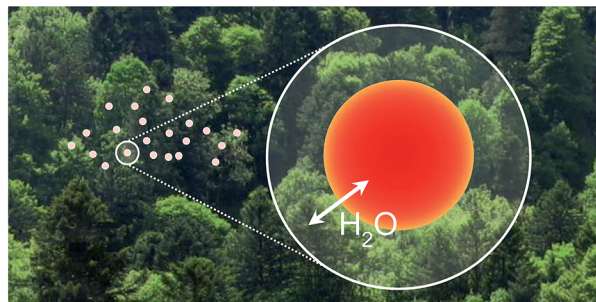


4876

Water diffusion in atmospherically relevant α -pinene secondary organic material

Hannah C. Price,* Johan Mattsson, Yue Zhang, Allan K. Bertram, James F. Davies, James W. Grayson, Scot T. Martin, Daniel O'Sullivan, Jonathan P. Reid, Andrew M. J. Rickards and Benjamin J. Murray*

We report the first direct measurements of water diffusion coefficients in secondary organic aerosol.

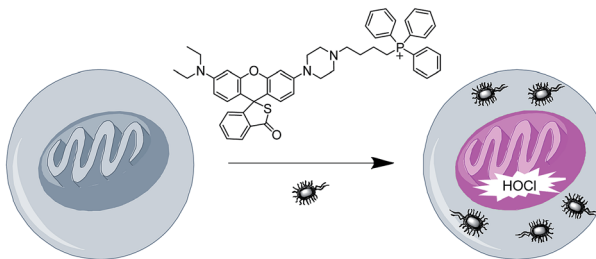


4884

HOCl can appear in the mitochondria of macrophages during bacterial infection as revealed by a sensitive mitochondrial-targeting fluorescent probe

Jin Zhou, Lihong Li, Wen Shi,* Xinghui Gao, Xiaohua Li and Huimin Ma*

HOCl can appear in the mitochondria of macrophages during bacterial infection as revealed by a new sensitive mitochondrial-targeting fluorescent probe.

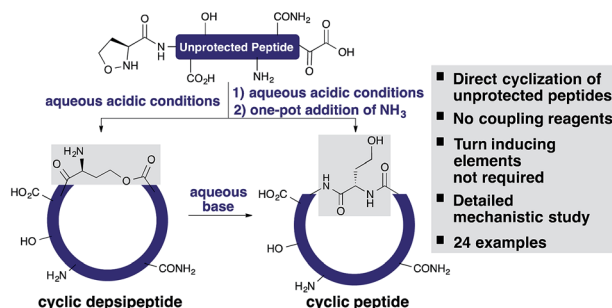


4889

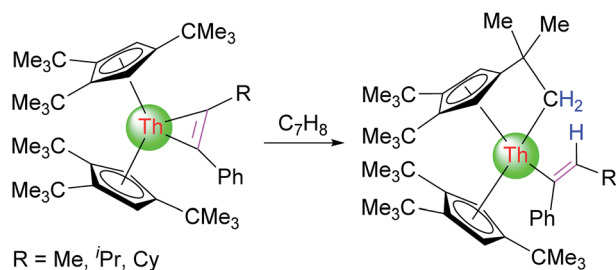
Spontaneous head-to-tail cyclization of unprotected linear peptides with the KAHA ligation

Florian Rohrbacher, Gildas Deniau, Anatol Luther and Jeffrey W. Bode*

The α -ketoacid–hydroxylamine (KAHA) ligation enables the direct cyclization of unprotected peptides upon cleavage, without coupling reagents or purification of precursors. We report the synthesis of a library of 24 cyclic peptides and a detailed mechanistic study.



4897

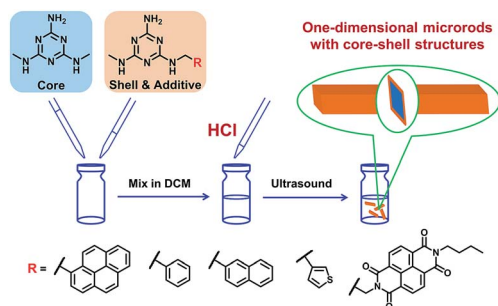


C–H bond activation induced by thorium metallacyclopropene complexes: a combined experimental and computational study

Bo Fang, Lei Zhang, Guohua Hou, Guofu Zi,^{*} De-Cai Fang^{*} and Marc D. Walter^{*}

Thorium metallacyclopropenes derived from phenyl(alkyl)acetylenes are very reactive complexes that undergo selective intramolecular C–H bond activation.

4907

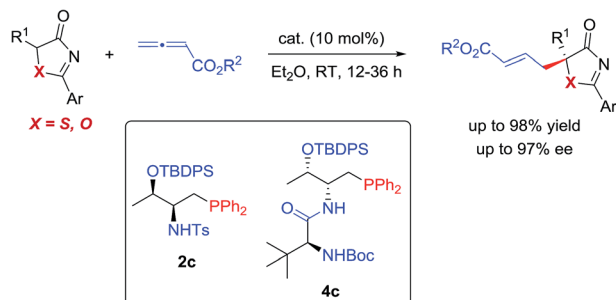


Self-assembling 1D core/shell microrods by the introduction of additives: a one-pot and shell-tunable method

Jun Xu, Hongde Yu, Liulin Yang, Guanglu Wu, Zhiqiang Wang, Dong Wang and Xi Zhang^{*}

A one-pot method for the fabrication of 1D core/shell microrods with tunable shell compositions by the introduction of additives.

4912

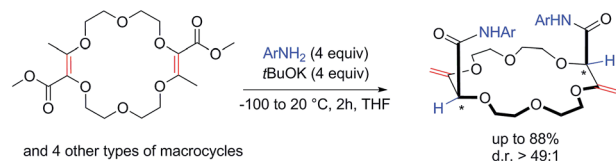


Highly enantioselective construction of tertiary thioethers and alcohols *via* phosphine-catalyzed asymmetric γ -addition reactions of 5H-thiazol-4-ones and 5H-oxazol-4-ones: scope and mechanistic understandings

Tianli Wang, Zhaoyuan Yu, Ding Long Hoon, Kuo-Wei Huang, Yu Lan^{*} and Yixin Lu^{*}

A new method for facile access to enantioenriched tertiary thioethers/alcohols.

4923



Remote stereoselective deconjugation of α,β -unsaturated esters by simple amidation reactions

Mahesh Vishe, Radim Hrdina, Amalia I. Poblador-Bahamonde, Céline Besnard, Laure Guénée, Thomas Bürgi and Jérôme Lacour^{*}

The amidation of macrocyclic conjugated esters affords in one-pot single (chiral) β,γ -unsaturated diastereomers *via* effective remote stereocontrol.

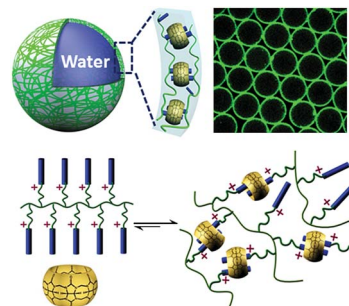


4929

Supramolecular hydrogel microcapsules *via* cucurbit [8]uril host–guest interactions with triggered and UV-controlled molecular permeability

Ziyi Yu, Jing Zhang, Roger J. Coulston, Richard M. Parker, Frank Biedermann, Xin Liu, Oren A. Scherman* and Chris Abell*

Host–guest assembly at the interface of microfluidic droplets offers a versatile strategy to construct supramolecular hydrogel microcapsules with “smart” cargo release.

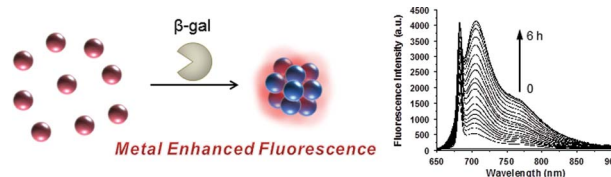


4934

An enzyme-responsive metal-enhanced near-infrared fluorescence sensor based on functionalized gold nanoparticles

Zhanghua Zeng, Shin Mizukami, Katsumasa Fujita and Kazuya Kikuchi*

An enzyme-responsive NIR nanosystem based on MEF was fabricated by surface functionalization of gold nanoparticles. Sensors based on this strategy are promising for enzyme detection in early diagnostic imaging and *in vivo* applications.

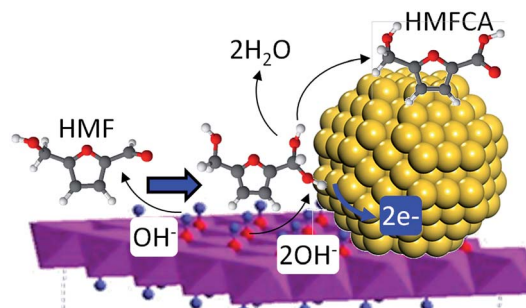


4940

Solid base catalysed 5-HMF oxidation to 2,5-FDCA over Au/hydrotalcites: fact or fiction?

Leandro Ardemani, Giannantonio Cibin, Andrew J. Dent, Mark A. Isaacs, Georgios Kyriakou, Adam F. Lee,* Christopher M. A. Parlett, Stephen A. Parry and Karen Wilson*

Synergistic effects between alkali-free hydrotalcites and gold nanoparticles afford efficient heterogeneous catalysts for the cascade oxidation of 5-HMF to 2,5-FDCA.

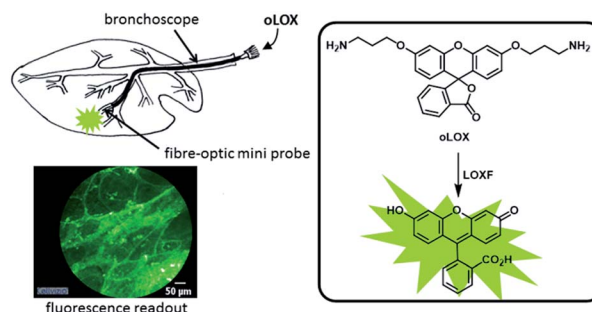


4946

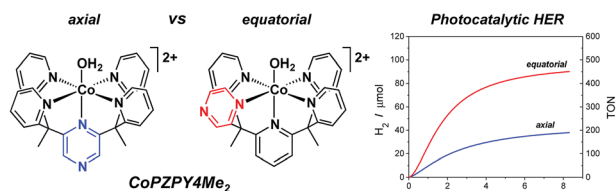
Optical molecular imaging of lysyl oxidase activity – detection of active fibrogenesis in human lung tissue

Tashfeen Aslam, Amy Miele, Sunay V. Chankeshwara, Alicia Megia-Fernandez, Chesney Michels, Ahsan R. Akram, Neil McDonald, Nik Hirani, Chris Haslett, Mark Bradley* and Kevin Dhaliwal*

A fluorogenic probe provides real-time measurement of lysyl oxidase activity in *ex vivo* asinine and human lung tissue.



4954

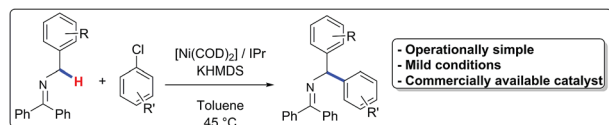


Bioinspired design of redox-active ligands for multielectron catalysis: effects of positioning pyrazine reservoirs on cobalt for electro- and photocatalytic generation of hydrogen from water

Jonah W. Jurss, Rony S. Khnayzer, Julien A. Panetier, Karim A. El Roz, Eva M. Nichols, Martin Head-Gordon,^{*} Jeffrey R. Long,^{*} Felix N. Castellano^{*} and Christopher J. Chang^{*}

We report the effects of installing redox-active pyrazines at distinct positions in a series of isostructural Co catalysts.

4973

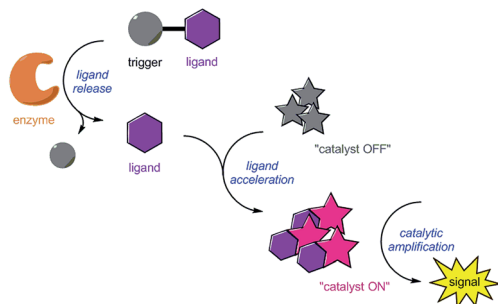


Synthesis of (diarylmethyl)amines using Ni-catalyzed arylation of C(sp³)-H bonds

José A. Fernández-Salas, Enrico Marelli and Steven P. Nolan^{*}

The first nickel catalyzed deprotonative cross coupling between C(sp³)-H bonds and aryl chlorides is reported, allowing the challenging arylation of benzylimines in the absence of directing group or stoichiometric metal activation.

4978

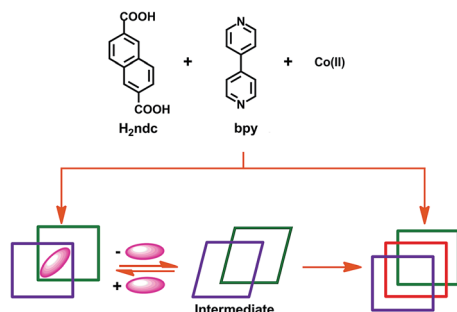


Signal transduction and amplification through enzyme-triggered ligand release and accelerated catalysis

Sean Goggins, Barrie J. Marsh, Anneke T. Lubben and Christopher G. Frost^{*}

An enzyme-triggered catalytic signal amplification cascade is described through the design of a novel enzyme substrate that selectively activates an organometallic transfer hydrogenation catalyst once triggered.

4986



Isolation of a structural intermediate during switching of degree of interpenetration in a metal-organic framework

Himanshu Aggarwal, Raj Kumar Das, Prashant M. Bhatt and Leonard J. Barbour^{*}

A structural intermediate has been isolated for the first time during switching of interpenetration from twofold to threefold in the MOF [Co₂(ndc)₂(bpy)].

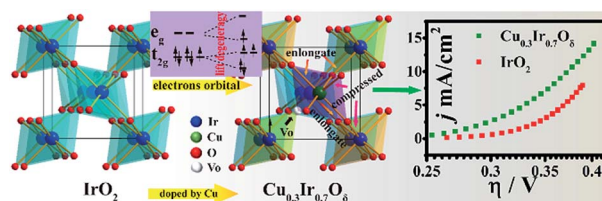


4993

An efficiently tuned d-orbital occupation of IrO₂ by doping with Cu for enhancing the oxygen evolution reaction activity

Wei Sun, Ya Song, Xue-Qing Gong,* Li-mei Cao and Ji Yang*

Tuning Ir d-orbital occupation *via* doping Cu into the IrO₂ lattice to prepare a highly efficient oxygen evolution reaction catalyst, Cu_{0.3}Ir_{0.7}O₆.

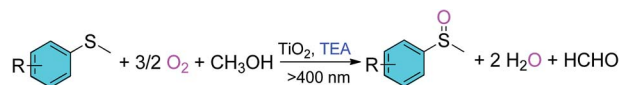


5000

Tertiary amine mediated aerobic oxidation of sulfides into sulfoxides by visible-light photoredox catalysis on TiO₂

Xianjun Lang, Wei Hao, Wan Ru Leow, Shuzhou Li,* Jincai Zhao and Xiaodong Chen*

The selective aerobic oxidation of sulfides into sulfoxides on TiO₂ under visible-light irradiation was accomplished through synergistic catalysis with triethylamine.

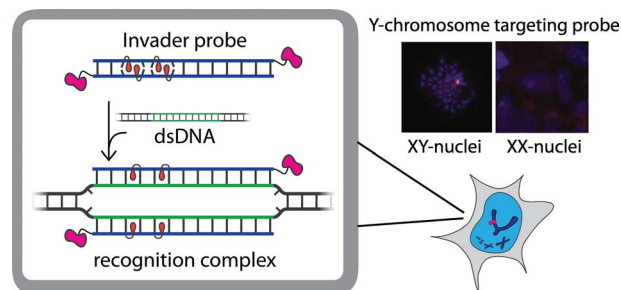


5006

Invader probes: harnessing the energy of intercalation to facilitate recognition of chromosomal DNA for diagnostic applications

Dale C. Guenther, Grace H. Anderson, Saswata Karmakar, Brooke A. Anderson, Bradley A. Didion, Wei Guo, John P. Versteegen and Patrick J. Hrdlicka*

Optimized Invader probes enable efficient ($C_{50} < 1 \mu\text{M}$), fast ($t_{50} < 3 \text{ h}$), kinetically stable (>24 h), and single nucleotide specific recognition of DNA targets.

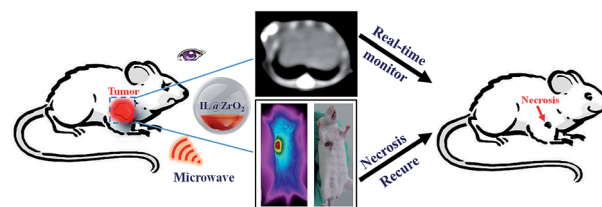


5016

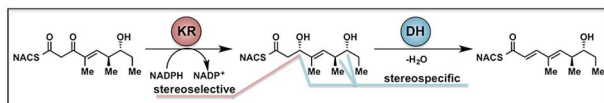
A smart all-in-one theranostic platform for CT imaging guided tumor microwave thermotherapy based on IL@ZrO₂ nanoparticles

Haitang Shi, Meng Niu, Longfei Tan, Tianlong Liu, Haibo Shao, Changhui Fu, Xiangling Ren, Tengchuang Ma, Jun Ren, Linlin Li, Huiyu Liu, Ke Xu,* Jianxin Wang, Fangqiong Tang and Xianwei Meng*

This paper develops a simple multifunctional theranostic platform using an IL@ZrO₂ nanostructure for CT imaging guided tumor microwave thermotherapy.



5027

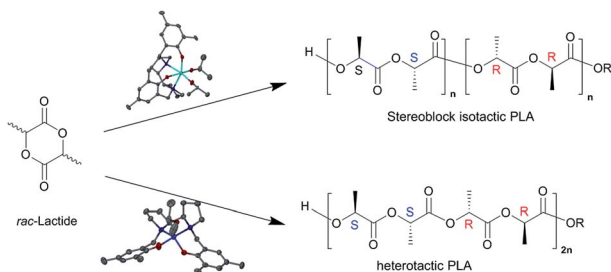


Tylosin polyketide synthase module 3: stereospecificity, stereoselectivity and steady-state kinetic analysis of β -processing domains via diffusible, synthetic substrates

William D. Fiers, Greg J. Dodge, Yang Li, Janet L. Smith, Robert A. Fecik* and Courtney C. Aldrich*

Natural and modified substrates coupled with LC-MS/MS analysis of products revealed the stereospecificity and stereoselectivity of a polyketide didomain.

5034

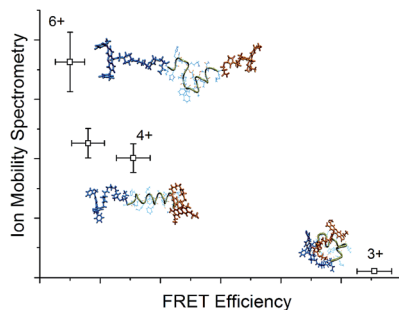


Metal influence on the iso- and hetero-selectivity of complexes of bipyrrrolidine derived salan ligands for the polymerisation of *rac*-lactide

Matthew D. Jones,* Lauren Brady, Paul McKeown, Antoine Buchard, Pascal M. Schäfer, Lynne H. Thomas, Mary F. Mahon, Timothy J. Woodman and John P. Lowe

A series complexes based on 2,2'-bipyrrrolidine based salan ligands have been prepared and either isotactic or heterotactic PLA have been prepared.

5040

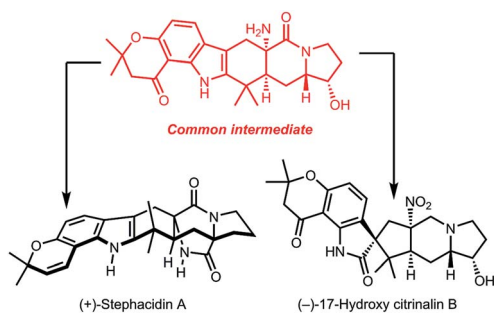


Conformational changes in amyloid-beta (12–28) alloforms studied using action-FRET, IMS and molecular dynamics simulations

Steven Daly, Alexander Kulesza, Frederic Poussigue, Anne-Laure Simon, Chang Min Choi, Geoffrey Knight, Fabien Chirot, Luke MacAleese, Rodolphe Antoine and Philippe Dugourd*

The gas phase conformations of two amyloid beta mutants are studied by multiple techniques to elucidate the origin of the different aggregation behaviour.

5048



Unified approach to prenylated indole alkaloids: total syntheses of (–)-17-hydroxy-citrinalin B, (+)-stephacidin A, and (+)-notoamide I

Eduardo V. Mercado-Marin and Richmond Sarpong*

The first strategy that provides reverse-prenylated indole alkaloids that bear a characteristic bicyclo[2.2.2]diazaoctane as well as those that lack this structural motif is reported.

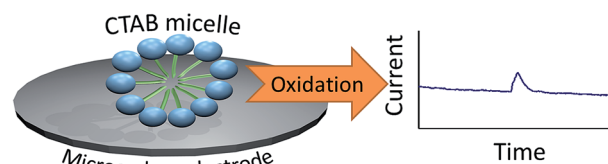


5053

Electrochemical detection of single micelles through 'nano-impacts'

H. S. Toh and R. G. Compton*

CTAB (cetyltrimethylammonium bromide) micelles are detected directly via the novel electrochemical method of 'nano-impacts' through oxidation of its bromide content.

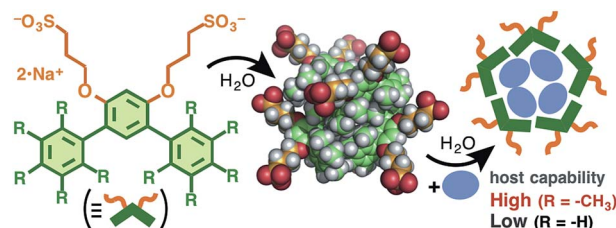


5059

Well-defined aqueous nanoassemblies from amphiphilic meta-terphenyls and their guest incorporation

Yusuke Okazawa, Kei Kondo, Munetaka Akita and Michito Yoshizawa*

Spherical molecular assemblies with diameters of ~ 2 nm were quantitatively formed in water from new amphiphilic meta-terphenyls and the nanoassembly with methyl groups provides superior host capability for fluorescent dyes.



5063

Site-selective formation of an iron(IV)–oxo species at the more electron-rich iron atom of heteroleptic μ -nitrido diiron phthalocyanines

Ümit İşci, Abayomi S. Faponle, Pavel Afanasiev, Florian Albrieux, Valérie Briois, Vefa Ahsen, Fabienne Dumoulin,* Alexander B. Sorokin* and Sam P. de Visser*

A combination of MS and computation on μ -nitrido bridged diiron complexes reveals H_2O_2 binding to the complex and generates an oxidant capable of oxidizing methane.

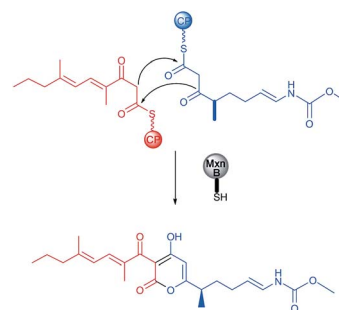


5076

In vitro reconstitution of α -pyrone ring formation in myxopyronin biosynthesis

H. Sucipto, J. H. Sahner, E. Prusov, S. C. Wenzel, R. W. Hartmann, J. Koehnke* and R. Müller*

α -Pyrone rings exist in many polyketide synthase (PKS) derived natural products. We report the first *in vitro* reconstitution of α -pyrone ring formation by a type I PKS using chemically synthesized substrates.



CORRECTIONS

5086

Correction: Pattern-based detection of anion pollutants in water with DNA polyfluorophores

Hyukin Kwon, Wei Jiang and Eric T. Kool*

5087

Correction: Assessing the exchange coupling in binuclear lanthanide(III) complexes and the slow relaxation of the magnetization in the antiferromagnetically coupled Dy₂ derivative

Chun Y. Chow, H el ene Bolvin, Victoria E. Campbell, R egis Guillot, Jeff W. Kampf, Wolfgang Wernsdorfer, Fr ed eric Gendron, Jochen Autschbach, Vincent L. Pecoraro* and Talal Mallah*

5088

Correction: A supramolecular strategy for tuning the energy level of naphthalenediimide: promoted formation of radical anions with extraordinary stability

Qiao Song, Fei Li, Zhiqiang Wang and Xi Zhang*

5090

Correction: Supramolecularly engineered phospholipids constructed by nucleobase molecular recognition: upgraded generation of phospholipids for drug delivery

Dali Wang, Chunlai Tu, Yue Su, Chuan Zhang, Udo Greiser, Xinyuan Zhu,* Deyue Yan and Wenxin Wang*

