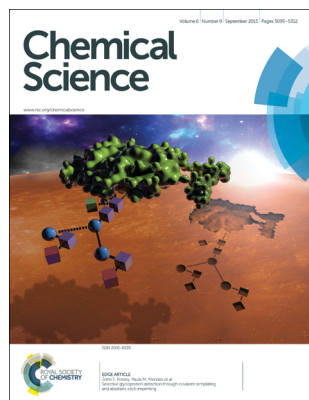


IN THIS ISSUE

ISSN 2041-6539 CODEN CSHCBM 6(9) 5095–5312 (2015)



Cover
See John S. Fossey,
Paula M. Mendes *et al.*,
pp. 5114–5119.
Image reproduced by
permission of Paula M. Mendes
from *Chem. Sci.*, 2015, **6**, 5114.



Inside cover
See Ian F. Hermans,
Gavin F. Painter *et al.*,
pp. 5120–5127.
Image reproduced by
permission of Gavin F. Painter
from *Chem. Sci.*, 2015, **6**, 5120.

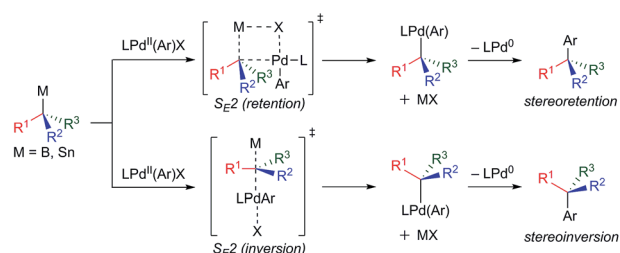
MINIREVIEW

5105

Configurationaly stable, enantioenriched organometallic nucleophiles in stereospecific Pd-catalyzed cross-coupling reactions: an alternative approach to asymmetric synthesis

Chao-Yuan Wang, Joseph Derosa and Mark R. Biscoe*

Several research groups have recently developed methods to employ configurationally stable, enantioenriched organometallic nucleophiles in stereospecific Pd-catalyzed cross-coupling reactions.



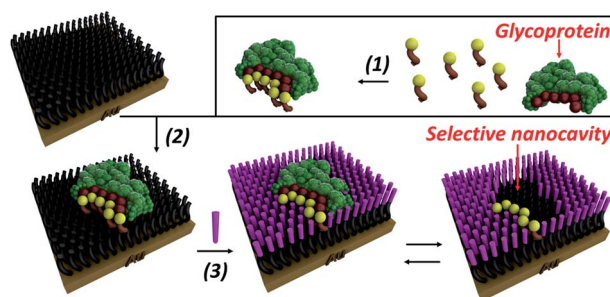
EDGE ARTICLES

5114

Selective glycoprotein detection through covalent templating and allosteric click-imprinting

Alexander Stephenson-Brown, Aaron L. Acton,
Jon A. Preece, John S. Fossey* and Paula M. Mendes*

A hierarchical bottom-up route exploiting reversible covalent interactions with boronic acids and so-called click chemistry for selective glycoprotein detection is described. The self-assembled and imprinted surfaces confer high binding affinities, nanomolar sensitivity, exceptional glycoprotein specificity and selectivity.



Editorial staff

Executive editor

May Copsey

Deputy editor

Jeanne Andres

Editorial production manager

Catherine Bacon

Development editors

Mina Roussanova

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

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

Information for authors

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

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

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

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

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

© The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Registered Charity No. 207890.

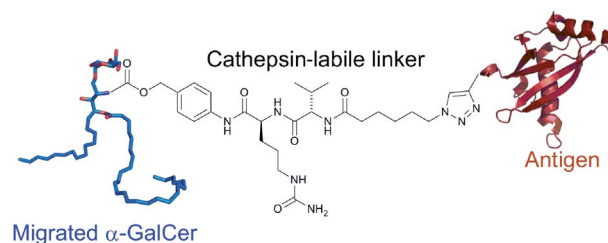


5120

NKT cell-dependent glycolipid–peptide vaccines with potent anti-tumour activity

Regan J. Anderson, Benjamin J. Compton, Ching-wen Tang, Astrid Authier-Hall, Colin M. Hayman, Gene W. Swinerd, Renata Kowalczyk, Paul Harris, Margaret A. Brimble, David S. Larsen, Olivier Gasser, Robert Weinkove, Ian F. Hermans* and Gavin F. Painter*

Glycolipid–peptide conjugates designed to release vaccine components within target cells ensuring potent CD1d dependent T cell responses.

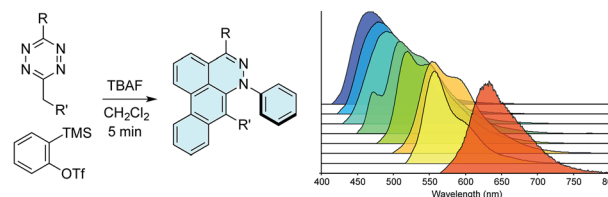


5128

Triple aryne–tetrazine reaction enabling rapid access to a new class of polyaromatic heterocycles

Sung-Eun Suh, Stephanie A. Barros and David M. Chenoweth*

We report the triple aryne–tetrazine reaction for rapid access to a new class of dibenzocinnoline heteroaromatics.

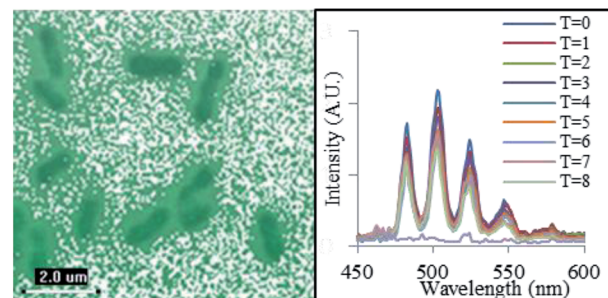


5133

Fluorescence spectroscopy and microscopy as tools for monitoring redox transformations of uranium in biological systems

Debbie L. Jones, Michael B. Andrews, Adam N. Swinburne, Stanley W. Botchway, Andrew D. Ward, Jonathan R. Lloyd and Louise S. Natrajan*

Luminescence spectroscopy, microscopy and lifetime image mapping offers new insights into the bioreduction of *Geobacter sulfurreducens* with uranyl.

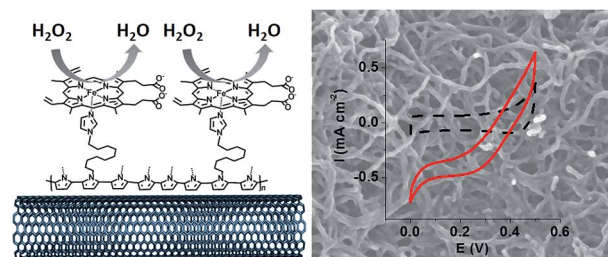


5139

Biomimetic versus enzymatic high-potential electrocatalytic reduction of hydrogen peroxide on a functionalized carbon nanotube electrode

Bertrand Reuillard, Solène Gentil, Marie Carrière, Alan Le Goff* and Serge Cosnier

We report the non-covalent functionalization of a multi-walled carbon nanotube (MWCNT) electrode with a biomimetic model of the horseradish peroxidase (HRP) active site.



5144

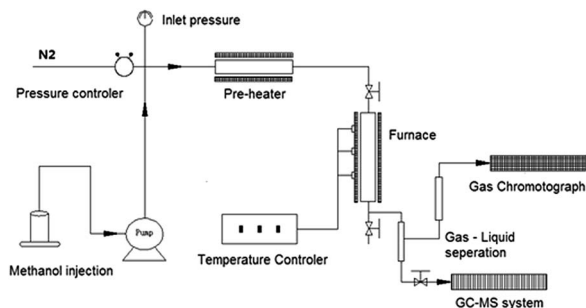


Enhancing electron affinity and tuning band gap in donor–acceptor organic semiconductors by benzothiadiazole directed C–H borylation

D. L. Crossley, I. A. Cade, E. R. Clark, A. Escande, M. J. Humphries, S. M. King, I. Vitorica-Yrezabal, M. J. Ingleson* and M. L. Turner*

Electrophilic borylation using BCl_3 and benzothiadiazole to direct the C–H functionalisation of an adjacent aromatic unit produces fused boracyclic materials with minimally changed HOMO energies but significantly reduced LUMO energies.

5152

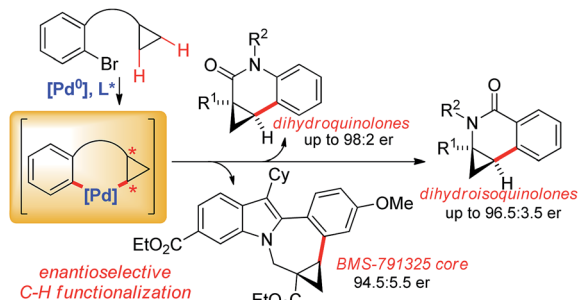


Methanol-to-hydrocarbons conversion over $\text{MoO}_3/\text{H-ZSM-5}$ catalysts prepared via lower temperature calcination: a route to tailor the distribution and evolution of promoter Mo species, and their corresponding catalytic properties

B. Liu, L. France, C. Wu, Z. Jiang, V. L. Kuznetsov, H. A. Al-Megren, M. Al-Kinany, S. A. Aldrees, T. Xiao* and P. P. Edwards*

A series of $\text{MoO}_3/\text{H-ZSM-5}$ catalysts were prepared via calcination at a lower-than-usual temperature and evaluated.

5164

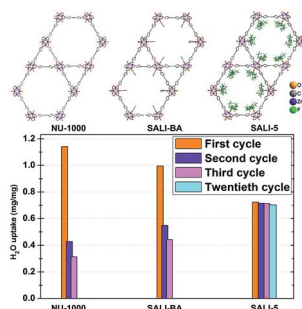


Enantioselective palladium(0)-catalyzed intramolecular cyclopropane functionalization: access to dihydroquinolones, dihydroisoquinolones and the BMS-791325 ring system

J. Pedroni, T. Saget, P. A. Donets and N. Cramer*

Enantioselective palladium(0)-catalyzed C–H arylations of cyclopropanes provide efficient access to dihydroquinolones, dihydroisoquinolones and the BMS-791325 indolobenzazepine core.

5172



Water stabilization of Zr_6 -based metal–organic frameworks via solvent-assisted ligand incorporation

Pravas Deria, Yongchul G. Chung, Randall Q. Snurr, Joseph T. Hupp* and Omar K. Farha*

Water stability in metal–organic frameworks (MOFs) is critical for several practical applications; we report here fundamental understanding how capillary forces induce damage to MOFs and highlight that metal node functionalization as a strategy to create vapor-stable and recyclable MOFs.

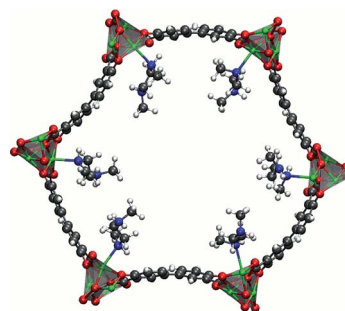


5177

CO₂ induced phase transitions in diamine-appended metal–organic frameworks

Bess Vlasisavljevich, Samuel O. Odoh, Sondre K. Schnell, Allison L. Dzubak, Kyuho Lee, Nora Planas, Jeffrey B. Neaton, Laura Gagliardi* and Berend Smit*

Using a combination of density functional theory and lattice models, we study the effect of CO₂ adsorption in an amine functionalized metal–organic framework.

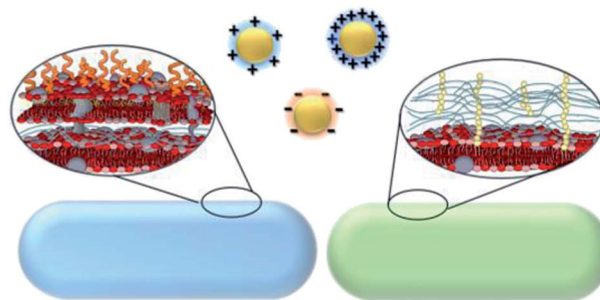


5186

Impacts of gold nanoparticle charge and ligand type on surface binding and toxicity to Gram-negative and Gram-positive bacteria

Z. Vivian Feng,* Ian L. Gunsolus, Tian A. Qiu, Katie R. Hurley, Lyle H. Nyberg, Hilena Frew, Kyle P. Johnson, Ariane M. Vartanian, Lisa M. Jacob, Samuel E. Lohse, Marco D. Torelli, Robert J. Hamers, Catherine J. Murphy and Christy L. Haynes*

Higher cationic charge density on nanoparticles is correlated with higher toxicity to bacteria.

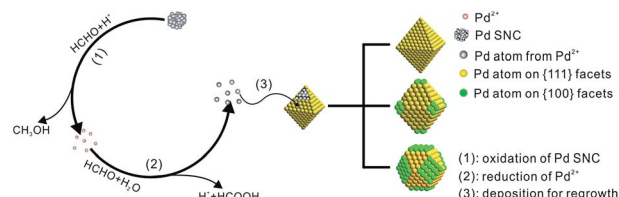


5197

Redox reaction induced Ostwald ripening for size- and shape-focusing of palladium nanocrystals

Zhaorui Zhang, Zhenni Wang, Shengnan He, Chaoqi Wang, Mingshang Jin* and Yadong Yin*

Size- and shape-focusing of palladium nanocrystals have been successfully achieved through the Ostwald ripening process induced by a redox reaction.

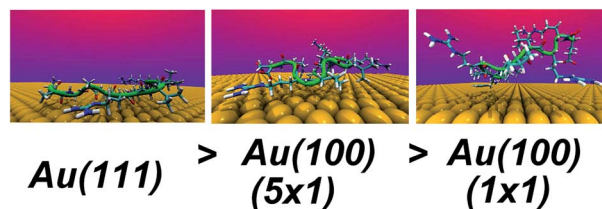


5204

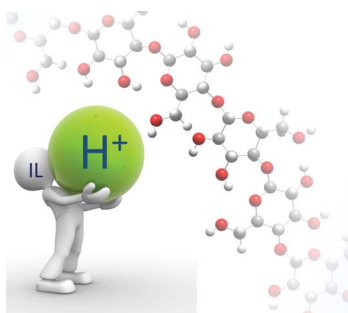
Facet selectivity in gold binding peptides: exploiting interfacial water structure

Louise B. Wright, J. Pablo Palafox-Hernandez, P. Mark Rodger,* Stefano Corni* and Tiffany R. Walsh*

We demonstrate that surface hydration is a key factor in dictating the free energy of non-covalent peptide-materials recognition.



5215



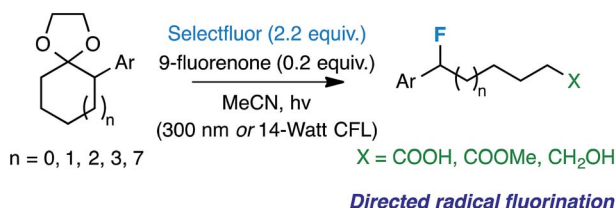
Beyond a solvent: the roles of 1-butyl-3-methylimidazolium chloride in the acid-catalysis for cellulose depolymerisation

Heitor Fernando Nunes de Oliveira, Christophe Farès and Roberto Rinaldi*

1-Butyl-3-methylimidazolium chloride plays other roles in the acid-catalysed depolymerisation of cellulose rather than being 'merely' a solvent for the biopolymer. The ionic liquid species enhances the Hammett acidity of the catalyst, thus improving the kinetics of cellulose depolymerisation.

5225

Photosensitized unstrained C-C cleavage

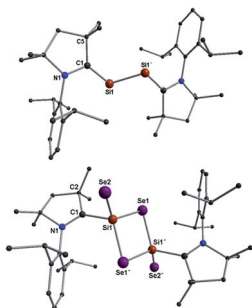


Unstrained C–C bond activation and directed fluorination through photocatalytically-generated radical cations

Cody Ross Pitts, Michelle Sheanne Bloom, Desta Doro Bume, Qinzhe Zhang and Thomas Lectka*

Unstrained C–C activation via putative radical cation formation promotes a directed radical fluorination event using Selectfluor, catalytic 9-fluorenone, and light.

5230

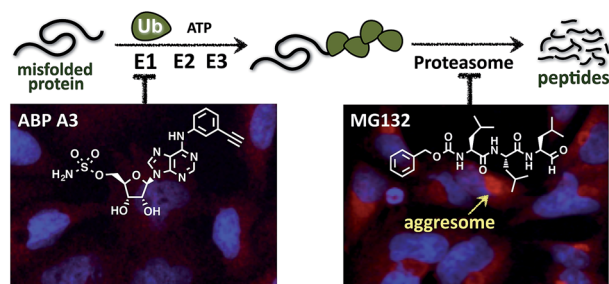


A soluble molecular variant of the semiconducting silcondiselenide

Kartik Chandra Mondal, Sudipta Roy, Birger Dittrich,* Bholanath Maity, Sayan Dutta, Debasis Koley,* Suresh Kumar Vasa, Rasmus Linser, Sebastian Dechert and Herbert W. Roesky*

Silcondiselenide is a semiconductor and exists as an insoluble polymer $(\text{SiSe}_2)_n$ which is prepared by reacting elemental silicon with selenium powder in the temperature range of 400–850 °C.

5235



An inhibitor of ubiquitin conjugation and aggresome formation

Heeseon An and Alexander V. Statsyuk*

An inhibitor of ubiquitin activating E1 enzyme inhibits ubiquitin conjugation and aggresome formation.

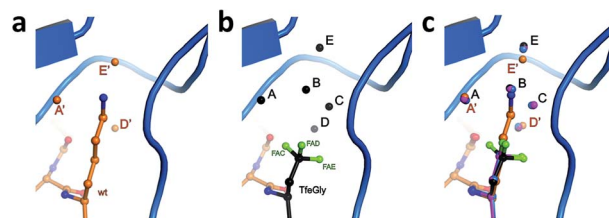


5246

Fluorine teams up with water to restore inhibitor activity to mutant BPTI

Shijie Ye, Bernhard Loll, Allison Ann Berger, Ulrike Mülow, Claudia Alings, Markus Christian Wahl and Beate Koks^{*}

Fluorinated derivatives of aminobutyric acid engage in unique interactions with structural waters within the BPTI/trypsin interface and restore inhibitor activity.

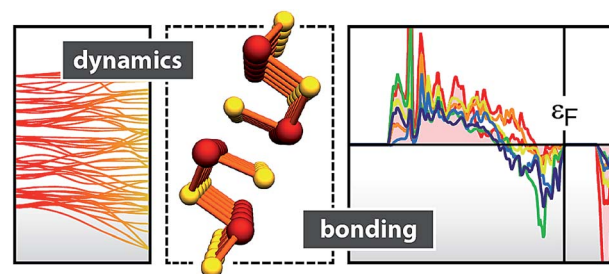


5255

Vibrational properties and bonding nature of Sb_2Se_3 and their implications for chalcogenide materials

Volker L. Deringer, Ralf P. Stoffel, Matthias Wuttig and Richard Dronskowski^{*}

There is more to chemical bonding in chalcogenides than the shortest, strongest bonds, as revealed by microscopic quantum-chemical descriptors.

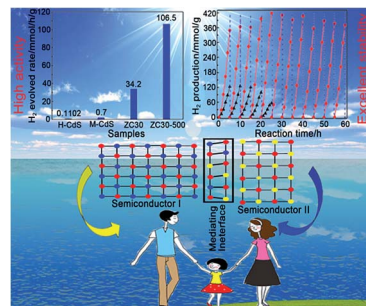


5263

Self-assembly of a mesoporous ZnS/mediating interface/CdS heterostructure with enhanced visible-light hydrogen-production activity and excellent stability

Kui Li, Rong Chen, Shun-Li Li, Min Han, Shuai-Lei Xie, Jian-Chun Bao,^{*} Zhi-Hui Dai and Ya-Qian Lan^{*}

We designed and successfully fabricated a ZnS/CdS 3D mesoporous heterostructure with a mediating $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ interface.

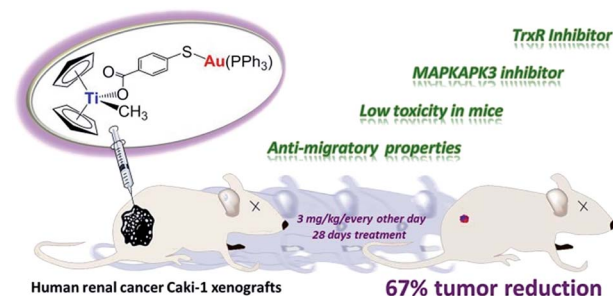


5269

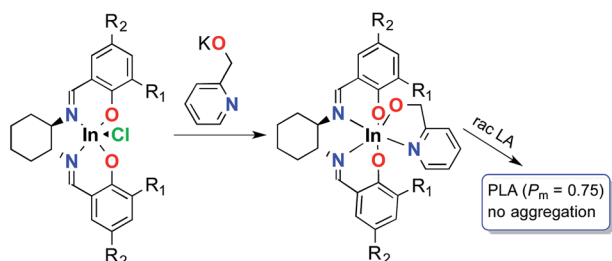
Heterometallic titanium–gold complexes inhibit renal cancer cells *in vitro* and *in vivo*

Jacob Fernández-Gallardo, Benelita T. Elie, Tanmoy Sadhukha, Swayam Prabha, Mercedes Sanaú, Susan A. Rotenberg, Joe W. Ramos^{*} and María Contel^{*}

Heterometallic compounds as anticancer agents demonstrating *in vivo* potential for the first time. Titanocene–gold derivatives: promising candidates for renal cancer.



5284

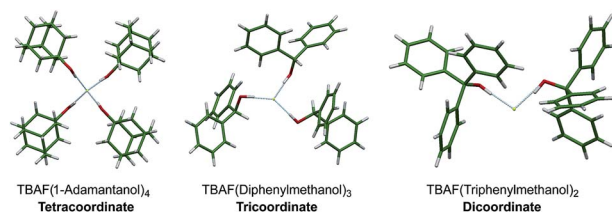


Overcoming aggregation in indium salen catalysts for isoselective lactide polymerization

D. C. Aluthge, J. M. Ahn and P. Mehrkhodavandi*

A methodology for controlling aggregation in highly active and isoselective indium catalysts for the ring opening polymerization of racemic lactide is reported.

5293

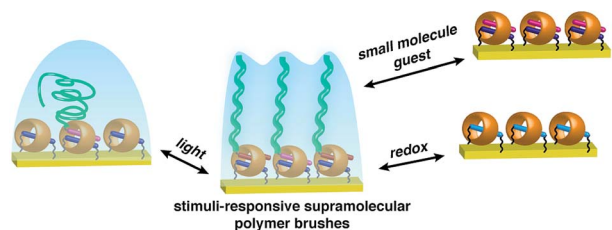


Coordination diversity in hydrogen-bonded homoleptic fluoride–alcohol complexes modulates reactivity

Keary M. Engle, Lukas Pfeifer, George W. Pidgeon, Guy T. Giuffredi, Amber L. Thompson, Robert S. Paton, John M. Brown and Véronique Gouverneur*

The X-ray structures of fourteen novel fluoride–alcohol complexes with tetrabutylammonium as the counterion show coordination diversity varying from four to two depending on the steric bulk of the alcohol.

5303



Cucurbit[8]uril directed stimuli-responsive supramolecular polymer brushes for dynamic surface engineering

Chi Hu, Feng Tian, Yu Zheng, Cindy Soo Yun Tan, Kevin R. West and Oren A. Scherman*

Dual stimuli-responsive supramolecular polymer brushes are attached to the surface with cucurbit[8]uril-rotaxanes for dynamic surface engineering.

