

# 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(10) 5313–6024 (2015)



### Cover

See Dominic J. Hare, Philip A. Doble *et al.*, pp. 5383–5393. Image reproduced by permission of Dominic J. Hare from *Chem. Sci.*, 2015, 6, 5383.



### Inside cover

See Hayato Tsurugi, Kazushi Mashima *et al.*, pp. 5394–5399. Image reproduced by permission of Kazushi Mashima from *Chem. Sci.*, 2015, 6, 5394.

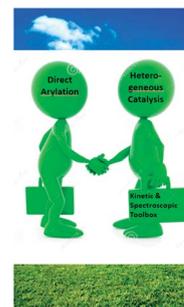
## PERSPECTIVE

5338

### Direct arylation and heterogeneous catalysis; ever the twain shall meet

Rafael Cano, Alexander F. Schmidt\* and Gerard P. McGlacken\*

We bring together the mature, yet poorly-understood, subject of heterogeneous catalysis with the rapidly expanding area of Direct Arylation, with a view towards the acceleration of catalyst design and the understanding of catalyst behaviour.



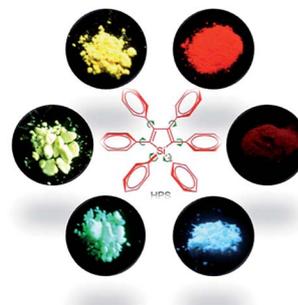
## MINIREVIEWS

5347

### Aggregation-induced emission of siloles

Zujin Zhao,\* Bairong He and Ben Zhong Tang\*

Recent advances in the structure–property relationship decipherment and luminescent functional materials development of AIE-active siloles are reviewed.



## Editorial staff

### Executive editor

May Copsey

### Deputy editor

Jeanne Andres

### Editorial production manager

Catherine Bacon

### Development editor

Mina Roussenova

### 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](mailto:chemicalscience@rsc.org)

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

E-mail [chemicalscience-rsc@rsc.org](mailto: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](mailto: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](mailto:orders@rsc.org)

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

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

For marketing opportunities relating to this journal, contact [marketing@rsc.org](mailto:marketing@rsc.org)

# Chemical Science

[www.rsc.org/chemicalscience](http://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

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.



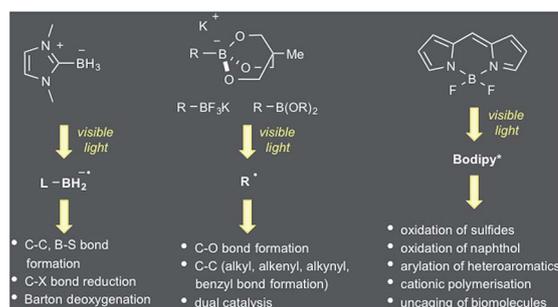
## MINIREVIEWS

5366

## Boron chemistry in a new light

Guillaume Duret, Robert Quinlan, Philippe Bissret\* and Nicolas Blanchard\*

Activation of stable boron species with visible-light allows the creation of boryl and/or carbon radicals through single electron- or energy transfer.



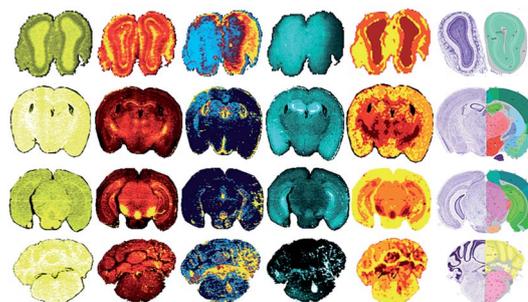
## EDGE ARTICLES

5383

## Visualising mouse neuroanatomy and function by metal distribution using laser ablation-inductively coupled plasma-mass spectrometry imaging

Bence Paul, Dominic J. Hare,\* David P. Bishop, Chad Paton, Van Tran Nguyen, Nerida Cole, Megan M. Niedwiecki, Erica Andreozzi, Angela Vais, Jessica L. Billings, Lisa Bray, Ashley I. Bush, Gawain McColl, Blaine R. Roberts, Paul A. Adlard, David I. Finkelstein, John Hellstrom, Janet M. Hergt, Jon D. Woodhead and Philip A. Doble\*

Studying the neuroanatomy of the mouse brain using imaging mass spectrometry and chemometric analysis.

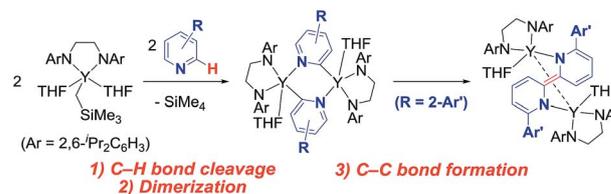


5394

## 2,2'-Bipyridyl formation from 2-arylpyridines through bimetallic diyttrium intermediate

Yu Shibata, Haruki Nagae, Shiki Sumiya, Raphaël Rochat, Hayato Tsurugi\* and Kazushi Mashima\*

Formation of dianionic 2,2'-bipyridyl-bridged dinuclear yttrium complexes proceeded upon treatment of  $(\text{ArNCH}_2\text{CH}_2\text{NAr})\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$  with 2-arylpyridine, in which mononuclear (2-pyridylphenyl)yttrium complexes were detected as key intermediates.

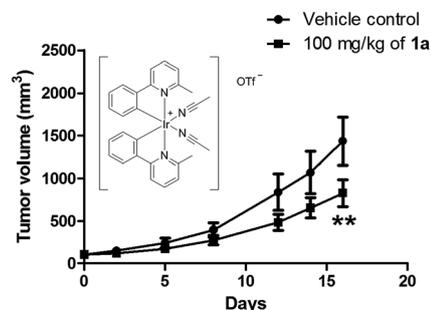


5400

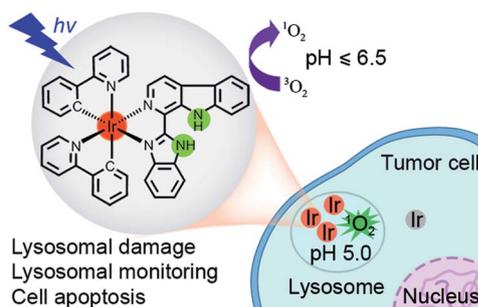
## An iridium(III)-based irreversible protein-protein interaction inhibitor of BRD4 as a potent anticancer agent

Hai-Jing Zhong, Lihua Lu, Ka-Ho Leung, Catherine C. L. Wong, Chao Peng, Siu-Cheong Yan, Dik-Lung Ma,\* Zongwei Cai,\* Hui-Min David Wang\* and Chung-Hang Leung\*

This is the first report of a metal complex that targets the BRD4-acylated histone protein-protein interaction (PPI).



5409

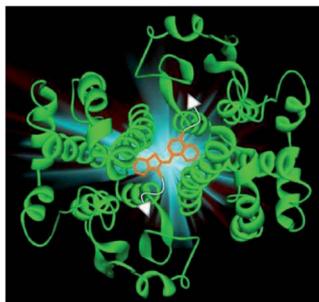


### Cyclometalated iridium(III) complexes as lysosome-targeted photodynamic anticancer and real-time tracking agents

Liang He, Yi Li, Cai-Ping Tan,\* Rui-Rong Ye, Mu-He Chen, Jian-Jun Cao, Liang-Nian Ji and Zong-Wan Mao\*

We report the rational design and photodynamic anticancer mechanism studies of iridium(III) complexes with pH-responsive singlet oxygen ( $^1\text{O}_2$ ) production and lysosome-specific imaging properties.

5419

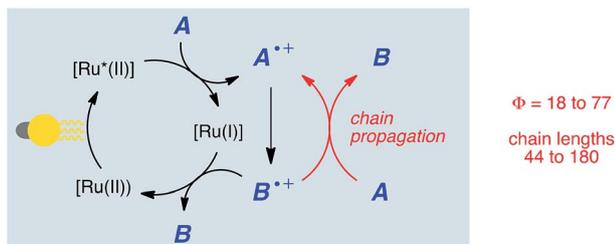


### Protein recognition by bivalent, 'turn-on' fluorescent molecular probes

Linor Unger-Angel, Bhimsen Rout, Tal Ilani, Miriam Eisenstein, Leila Motiei and David Margulies\*

The selective and sensitive identification of different proteins becomes possible by modifying the known intercalating dye, thiazole orange, with two protein binders. These 'turn-on' fluorescence probes enable the identification of acetylcholinesterase, glutathione-s-transferases and avidin with high affinity, specificity, and high signal-to-noise ratio.

5426

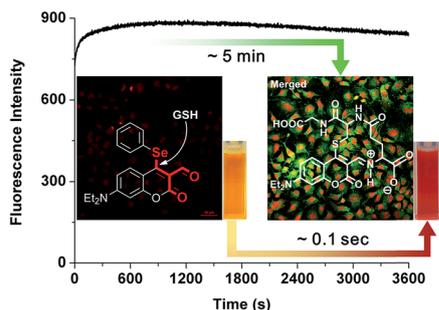


### Characterizing chain processes in visible light photoredox catalysis

Megan A. Cismesia and Tehshik P. Yoon\*

The combination of quantum yield and luminescence quenching measurements provides a method to rapidly characterize the occurrence of chain processes in a variety of photoredox reactions.

5435



### Exceptional time response, stability and selectivity in doubly-activated phenyl selenium-based glutathione-selective platform

Youngsam Kim, Sandip V. Mulay, Minsuk Choi, Seungyoon B. Yu, Sangyong Jon and David G. Churchill\*

Outstanding glutathione chemosensing selectivity with a new coumarin-based probe is reported and discussed in the context of live cell experiments; the point of attack is flanked by two proximal carbonyl groups.

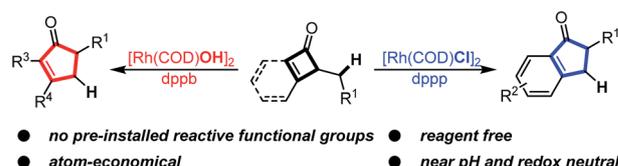


5440

### Rh-catalyzed reagent-free ring expansion of cyclobutenones and benzocyclobutenones

Peng-hao Chen, Joshua Sieber, Chris H. Senanayake and Guangbin Dong\*

A reagent-free Rh-catalyzed ring-expansion reaction via C–C cleavage of cyclobutenones and benzocyclobutenones is reported.

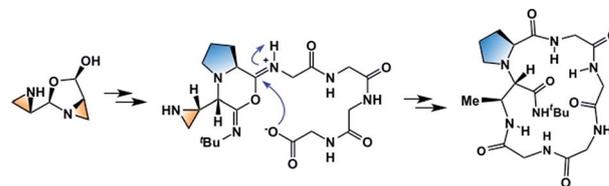


5446

### Mechanistic investigation of aziridine aldehyde-driven peptide macrocyclization: the imidoanhydride pathway

Serge Zaretsky, Jennifer L. Hickey, Joanne Tan, Dmitry Pichugin, Megan A. St. Denis, Spencer Ler, Benjamin K. W. Chung, Conor C. G. Scully and Andrei K. Yudin\*

Aziridine aldehydes participate in a multicomponent reaction with  $\alpha$ -amino amides and isocyanides to generate reactive imidoanhydride intermediates.

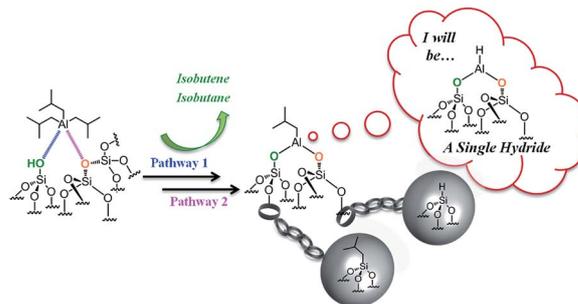


5456

### Well-defined silica supported aluminum hydride: another step towards the utopian single site dream?

Baraa Werghi, Anissa Bendjeriou-Sedjerari, Julien Sofack-Kreutzer, Abdesslem Jedidi, Edy Abou-Hamad, Luigi Cavallo\* and Jean-Marie Basset\*

Reaction of triisobutylaluminum with SBA15<sub>700</sub> at room temperature occurs by two parallel pathways involving either silanol or siloxane bridges.

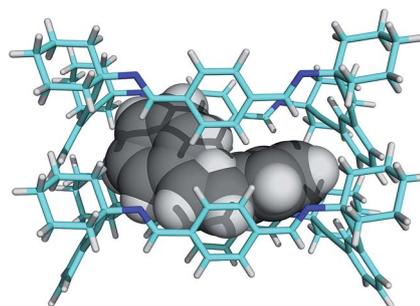


5466

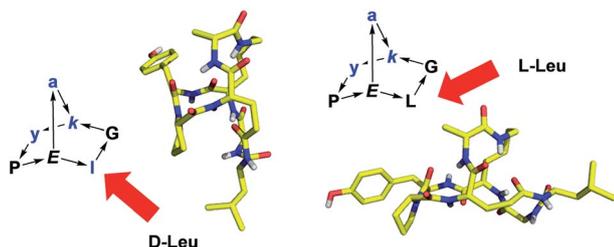
### A crystalline sponge based on dispersive forces suitable for X-ray structure determination of included molecular guests

Elena Sanna, Eduardo C. Escudero-Adán, Antonio Bauzá, Pablo Ballester, Antonio Frontera, Carmen Rotger and Antonio Costa\*

A new organic material assembled by dispersive forces exhibits stable one-dimensional channels suitable as the solid support in X-ray structural studies by the crystalline sponge method.



5473

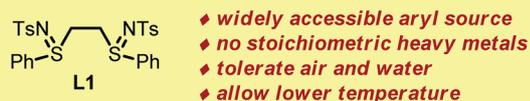
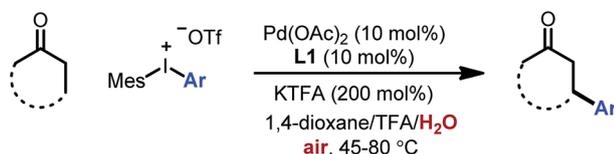


### Bridged bicyclic peptides as potential drug scaffolds: synthesis, structure, protein binding and stability

Marco Bartoloni, Xian Jin, Maria José Marcaida, João Banha, Ivan Dibonaventura, Swathi Bongoni, Kathrin Bartho, Olivia Gräbner, Michael Sefkow, Tamis Darbre and Jean-Louis Reymond\*

Diastereomeric norbornapeptides represent globular scaffolds with geometries determined by the chirality of amino acid residues and sharing structural features of  $\beta$ -turns and  $\alpha$ -helices.

5491

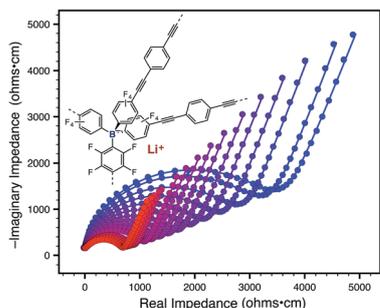


### Palladium-catalyzed direct $\beta$ -arylation of ketones with diaryliodonium salts: a stoichiometric heavy metal-free and user-friendly approach

Zhongxing Huang, Quynh P. Sam and Guangbin Dong\*

A user-friendly protocol for the Pd-catalyzed direct  $\beta$ -arylation of ketones is described, which avoids the use of stoichiometric heavy metals.

5499

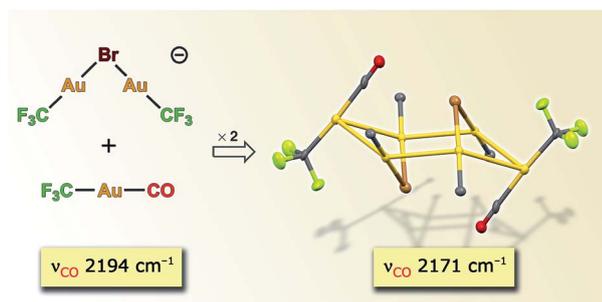


### Tetraarylborate polymer networks as single-ion conducting solid electrolytes

Jeffrey F. Van Humbeck, Michael L. Aubrey, Alaaeddin Alsaiee, Rob Ameloot, Geoffrey W. Coates, William R. Dichtel and Jeffrey R. Long\*

A new family of solid polymer electrolytes based upon anionic tetrakis(phenyl)borate tetrahedral nodes and linear bis-alkyne linkers is reported.

5506



### A hexanuclear gold carbonyl cluster

Sonia Martínez-Salvador, Larry R. Falvello, Antonio Martín and Babil Menjón\*

Aurophilic interactions are responsible for the spontaneous formation of a *cyclo*-Au<sub>6</sub> carbonyl cluster whereby significant  $\nu_{\text{CO}}$  lowering is observed.

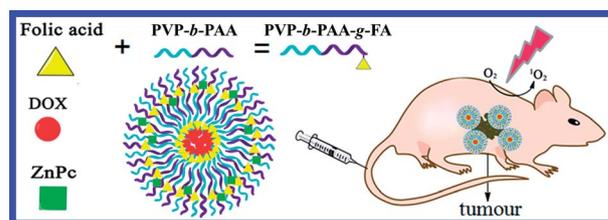


5511

### A supramolecular nanovehicle toward systematic, targeted cancer and tumor therapy

Ruizheng Liang, Shusen You, Lina Ma, Chunyang Li, Rui Tian, Min Wei,\* Dan Yan,\* Meizhen Yin,\* Wantai Yang, David G. Evans and Xue Duan

A supramolecular nanovehicle (denoted as SNV) was fabricated by encapsulating zinc phthalocyanine (ZnPc) and doxorubicin (DOX) into a copolymer (PVP-*b*-PAA-*g*-FA), so as to achieve systematic and targeted tumor imaging and therapy.

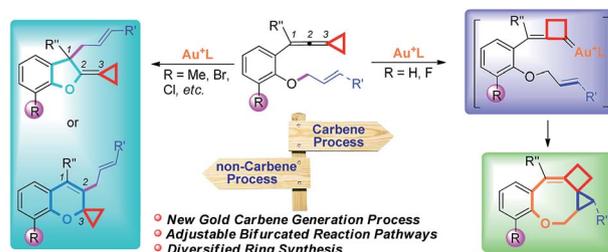


5519

### Gold(I)-catalyzed cycloisomerization of vinylidenecyclopropane-enes via carbene or non-carbene processes

De-Yao Li, Yin Wei, Ilan Marek, Xiang-Ying Tang\* and Min Shi\*

Gold catalyzed cycloisomerization of aromatic ring tethered vinylidenecyclopropane-enes provides a divergent synthetic protocol for the construction of O-containing fused heterocycles through controllable carbene or non-carbene related processes.

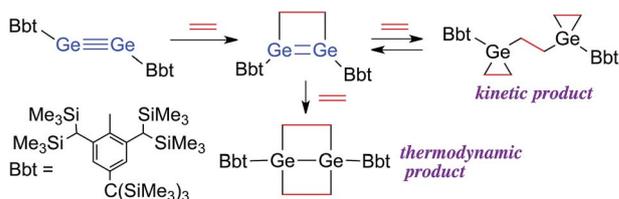


5526

### Reaction of a diaryldigermine with ethylene

Takahiro Sasamori,\* Tomohiro Sugahara, Tomohiro Agou, Koh Sugamata, Jing-Dong Guo, Shigeru Nagase and Norihiro Tokitoh\*

Reaction of a stable digermine with ethylene afforded the corresponding 1,2-digermacyclobutene. Depending on the reaction conditions applied, further reaction of this 1,2-digermacyclobutene with ethylene furnished two different reaction products: a 1,4-digerma-bicyclo[2.2.0]hexane or a bis(germiranyl)ethane.

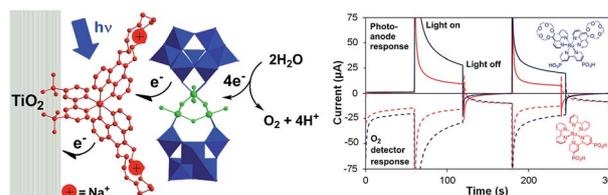


5531

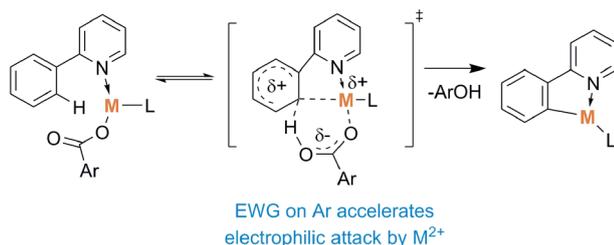
### Water splitting with polyoxometalate-treated photoanodes: enhancing performance through sensitizer design

John Fielden,\* Jordan M. Sumliner, Nannan Han, Yurii V. Geletii, Xu Xiang, Djamaladdin G. Musaev,\* Tianquan Lian\* and Craig L. Hill\*

Improved sensitizer design dramatically enhances visible light-driven water oxidation from dye-sensitized TiO<sub>2</sub> photoanodes treated with polyoxometalate water oxidation catalyst [(Ru<sub>4</sub>O<sub>4</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](γ-SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]<sup>10-</sup>.



5544

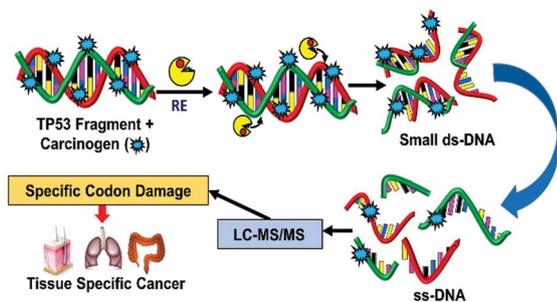


### Carboxylate-assisted C–H activation of phenylpyridines with copper, palladium and ruthenium: a mass spectrometry and DFT study

A. Gray, A. Tsybizova and J. Roithova\*

The transition state of metal carboxylate mediated C–H activation is associated with carbon–metal bond formation supported by electron-poor carboxylates.

5554

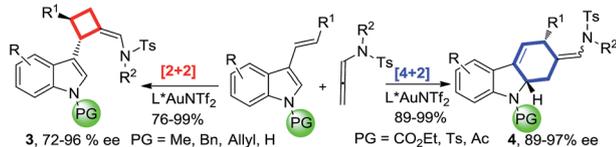


### Chemical selectivity of nucleobase adduction relative to *in vivo* mutation sites on exon 7 fragment of p53 tumor suppressor gene

Spundana Malla, Karteek Kadimisetty, You-Jun Fu, Dharamainder Choudhary, Ingela Jansson, John B. Schenkman and James F. Rusling\*

A 32-bp fragment of P53 gene reacted with benzo[a]pyrene metabolite BPDE was analyzed by LC-MS/MS. Chemically reactive sites were similar to frequently mutated codons in tumors.

5564

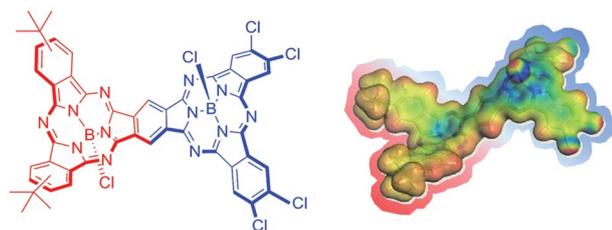


### Enantioselective gold-catalyzed intermolecular [2+2] versus [4+2]-cycloadditions of 3-styrylindoles with *N*-allenamides: observation of interesting substituent effects

Yidong Wang, Peichao Zhang, Yuan Liu, Fei Xia\* and Junliang Zhang\*

The cycloaddition mode ([2+2] vs. [4+2]) can be unexpectedly switched by the simple modification of the *N*-substituent of the 3-styrylindoles.

5571



### A push–pull unsymmetrical subphthalocyanine dimer

Germán Zango, Johannes Zirzmeier, Christian G. Claessens, Timothy Clark,\* M. Victoria Martínez-Díaz,\* Dirk M. Guldi\* and Tomás Torres\*

Unsymmetrical subphthalocyanine fused dimers have been prepared, resulting in unprecedented push–pull  $\pi$ -extended curved aromatic macrocycles.

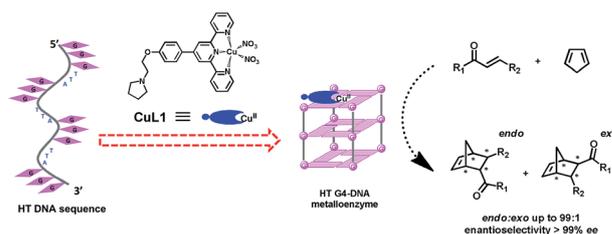


5578

### Terpyridine–Cu(II) targeting human telomeric DNA to produce highly stereospecific G-quadruplex DNA metalloenzyme

Yinghao Li, Mingpan Cheng, Jingya Hao, Changhao Wang, Guoqing Jia\* and Can Li\*

A highly stereospecific G-quadruplex DNA metalloenzyme was found by exploring the G-quadruplex targeting ligand pool.

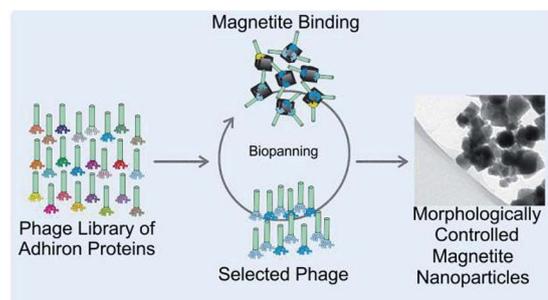


5586

### Phage display selected magnetite interacting Adhirons for shape controlled nanoparticle synthesis

Andrea E. Rawlings, Jonathan P. Bramble, Anna A. S. Tang, Lori A. Somner, Amy E. Monnington, David J. Cooke, Michael J. McPherson, Darren C. Tomlinson and Sarah S. Staniland\*

Biopanning was used to generate novel artificial binding proteins which are able to control the formation of synthetic cubic nanoparticles of magnetite.

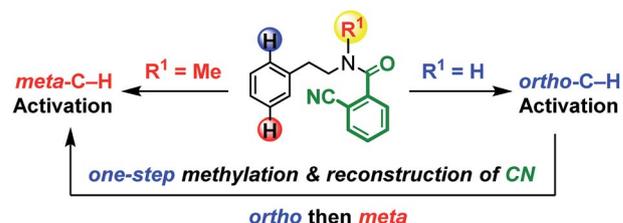


5595

### Pd(II)-catalyzed remote regiodivergent *ortho*- and *meta*-C–H functionalizations of phenylethylamines

Shangda Li, Huafang Ji, Lei Cai and Gang Li\*

A methylation switches the remote regioselectivity of C–H functionalizations of phenylethylamines.

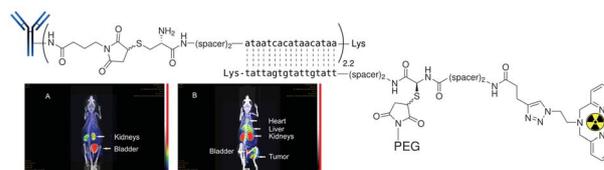


5601

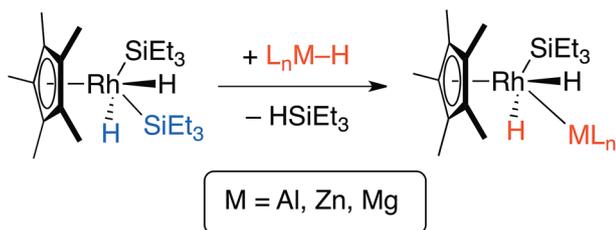
### *In vivo* demonstration of an active tumor pretargeting approach with peptide nucleic acid bioconjugates as complementary system

Anna Leonidova, Christian Foerster, Kristof Zarschler, Maik Schubert, Hans-Jürgen Pietzsch, Jörg Steinbach, Ralf Bergmann, Nils Metzler-Nolte, Holger Stephan\* and Gilles Gasser\*

The first successful application of a pretargeting approach using a PNA-modified epidermal growth factor receptor specific antibody and a complementary <sup>99m</sup>Tc-labeled PNA is presented.



5617

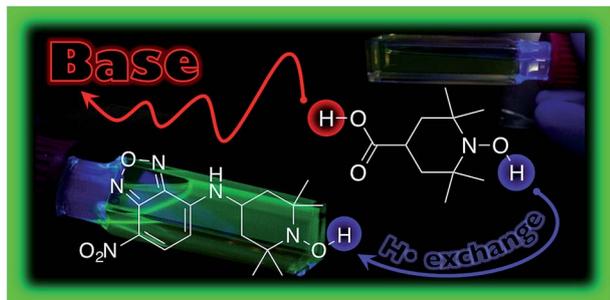


### Addition of aluminium, zinc and magnesium hydrides to rhodium(III)

Olga Ekkert, Andrew J. P. White, Harold Toms and Mark R. Crimmin\*

We report the addition of M–H bonds (M = Al, Zn, Mg) to a Rh(III) intermediate generated from the reductive elimination of triethylsilane from  $[\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2]$ .

5623

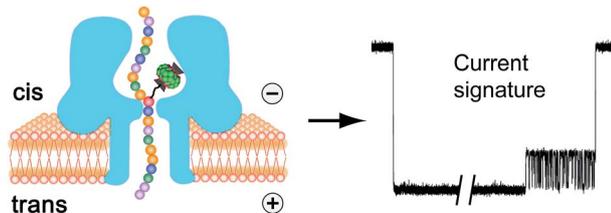


### Experimental demonstration of pH-dependent electrostatic catalysis of radical reactions

Marta Klinska, Leesa M. Smith, Ganna Gryn'ova, Martin G. Banwell and Michelle L. Coote\*

Fluorescence spectroscopy demonstrated pH-dependent electrostatic effects on the kinetics and thermodynamics of hydrogen atom transfer between 1-hydroxy-2,2,6,6-tetramethyl-4-piperidinecarboxylic acid and {2,2,6,6-tetramethyl-4-[(7-nitro-2,1,3-benzoxadiazol-4-yl)amino]-1-piperidinyloxydanyl radical in dichloromethane.

5628

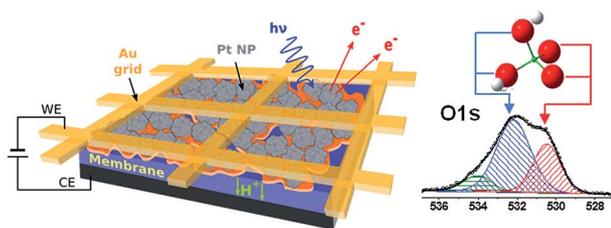


### Detection of 5-methylcytosine and 5-hydroxymethylcytosine in DNA via host-guest interactions inside $\alpha$ -hemolysin nanopores

Tao Zeng, Lei Liu, Ting Li, Yuru Li, Juan Gao, Yuliang Zhao\* and Hai-Chen Wu\*

After selective modification with a host-guest complex, 5-methylcytosine and 5-hydroxymethylcytosine in ssDNA can be unambiguously detected by the generation of characteristic current events during the translocation of the modified DNA through  $\alpha$ -hemolysin nanopores.

5635



### In situ investigation of dissociation and migration phenomena at the Pt/electrolyte interface of an electrochemical cell

Yeuk Ting Law, Spyridon Zafeiratos, Stylianos G. Neophytides, Alin Orfanidi, Dominique Costa, Thierry Dintzer, Rosa Arrigo, Axel Knop-Gericke, Robert Schlögl and Elena R. Savinova\*

Using near ambient pressure X-ray photoelectron spectroscopy we probe *in situ* the double layer at the Pt/liquid electrolyte interface.

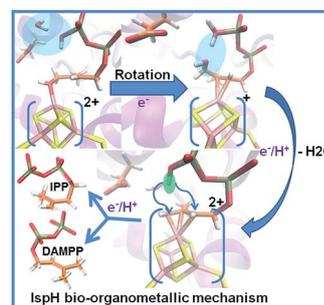


5643

### Mechanistic insights into the reductive dehydroxylation pathway for the biosynthesis of isoprenoids promoted by the IspH enzyme

Safwat Abdel-Azeim, Abdesslem Jedidi, Jorg Eppinger and Luigi Cavallo\*

We report an integrated QM/MM study of the bio-organometallic reaction pathway of the reductive dehydroxylation of (*E*)-4-hydroxy-3-methylbut-2-enyl pyrophosphate (HMBPP).

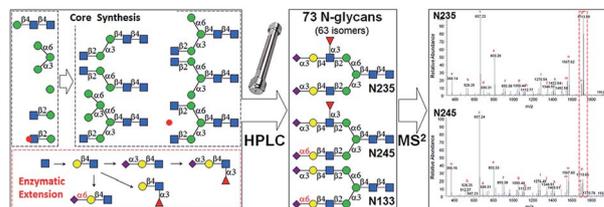


5652

### Efficient chemoenzymatic synthesis of an N-glycan isomer library

Lei Li, Yunpeng Liu, Cheng Ma, Jingyao Qu, Angie D. Calderon, Baolin Wu, Na Wei, Xuan Wang, Yuxi Guo, Zhongying Xiao, Jing Song, Go Sugiarto, Yanhong Li, Hai Yu, Xi Chen and Peng George Wang\*

An efficient chemoenzymatic synthesis strategy and a HILIC-based purification approach enabled rapid access to an N-glycan isomer library.

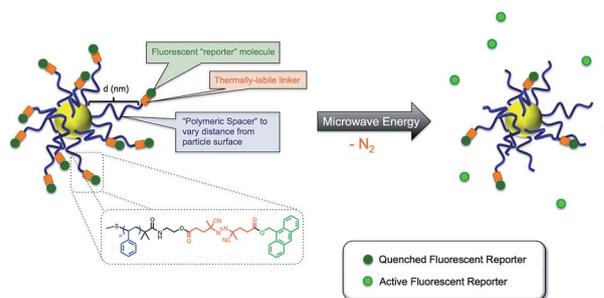


5662

### Probing the surface-localized hyperthermia of gold nanoparticles in a microwave field using polymeric thermometers

Christopher P. Kabb, R. Nicholas Carmean and Brent S. Sumerlin\*

Gold nanoparticles decorated with "polymeric thermometers," consisting of a polymeric spacer, thermally-labile azo linker, and fluorescent tag, were used to quantify the extent of localized hyperthermia under microwave irradiation.

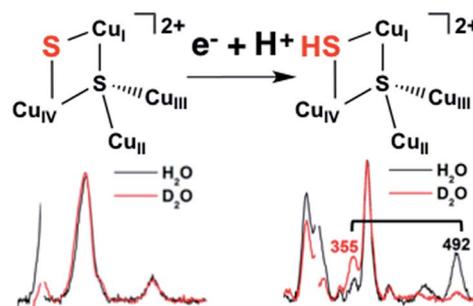


5670

### Protonation state of the Cu<sub>4</sub>S<sub>2</sub> Cu<sub>Z</sub> site in nitrous oxide reductase: redox dependence and insight into reactivity

Esther M. Johnston, Simone Dell'Acqua, Sofia R. Pauleta, Isabel Moura and Edward I. Solomon\*

The edge ligand in the Cu<sub>4</sub>S<sub>2</sub> Cu<sub>Z</sub> form of nitrous oxide reductase is a μ<sub>2</sub>-thiolate in the 1-hole and a μ<sub>2</sub>-sulfide in the 2-hole redox state, leading to proton-coupled electron transfer reactivity.



5680

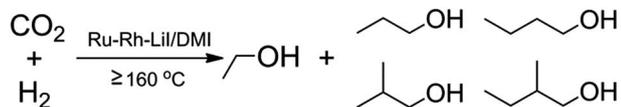


### Detection and remediation of organophosphorus compounds by oximate containing organogels

Jennifer R. Hiscock, Mark R. Sambrook, Neil J. Wells and Philip A. Gale\*

A series of supramolecular diamide organogels containing a reactive compound for the remediation of organophosphorus (OP) species, in particular OP chemical warfare agents (CWAs), has been prepared in DMSO.

5685

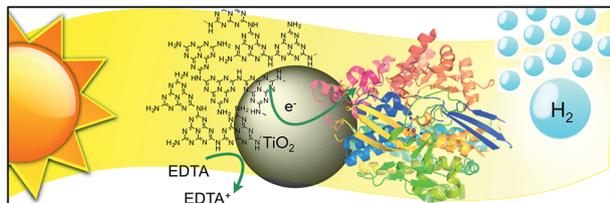


### Highly selective hydrogenation of CO<sub>2</sub> into C<sub>2+</sub> alcohols by homogeneous catalysis

Qingli Qian,\* Meng Cui, Zhenhong He, Congyi Wu, Qinggong Zhu, Zhaofu Zhang, Jun Ma, Guanying Yang, Jingjing Zhang and Buxing Han\*

Methanol, ethanol, propanol, 2-methyl propanol, butanol, and 2-methyl butanol were produced in homogeneous CO<sub>2</sub> hydrogenation with a selectivity for C<sub>2+</sub> alcohols of 96.4%.

5690

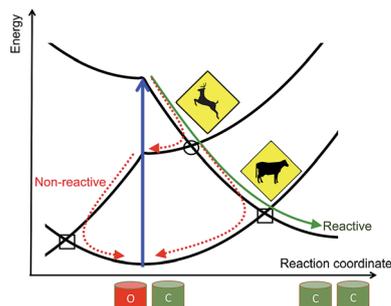


### Carbon nitride–TiO<sub>2</sub> hybrid modified with hydrogenase for visible light driven hydrogen production

Christine A. Caputo, Lidong Wang, Radim Beranek and Erwin Reisner\*

Solar light driven hydrogen production with a heterogenised hydrogenase on a carbon nitride–TiO<sub>2</sub> hybrid is reported that sets a new benchmark for photo-H<sub>2</sub> production.

5695



### A curve-crossing model to rationalize and optimize diarylethene dyads

Benjamin Lasorne,\* Arnaud Fihey, David Mendive-Tapia and Denis Jacquemin\*

Extra crossing points play a key role in the photochemistry of diarylethene dyads.

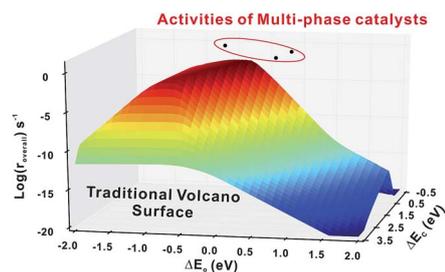


5703

## Possibility of designing catalysts beyond the traditional volcano curve: a theoretical framework for multi-phase surfaces

Ziyun Wang, Hai-Feng Wang and P. Hu\*

The current theory of catalyst activity in heterogeneous catalysis is mainly obtained from the study of catalysts with mono-phases, while most catalysts in real systems consist of multi-phases, the understanding of which is far short of chemists' expectation.



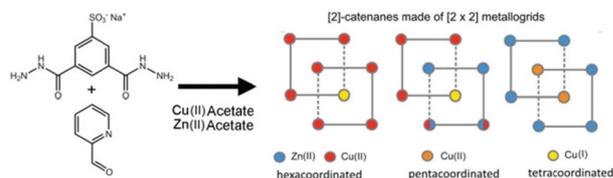
Multi-phase catalysts VS. Mono-phase catalysts

5712

## Mixed valence mono- and hetero-metallic grid catenanes

Chandan Giri, Filip Topić, Massimo Cametti\* and Kari Rissanen\*

Multicomponent self-assembly was employed to obtain, in the solid state, a series of mixed valence mono- and hetero-metallic grid catenanes, which were characterized by single crystal X-ray diffraction.



5719

## Rational synthesis of normal, abnormal and anionic NHC–gallium alkyl complexes: structural, stability and isomerization insights

Marina Uzelac, Alberto Hernán-Gómez, David R. Armstrong, Alan R. Kennedy and Eva Hevia\*

Using two alternative methodologies, new light has been shed on the stability and rational formation of abnormal NHC–gallium complexes.

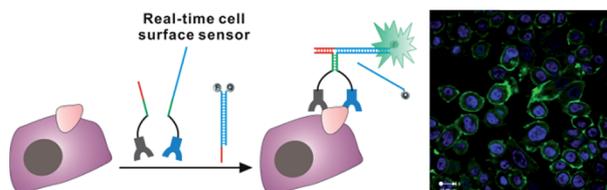


5729

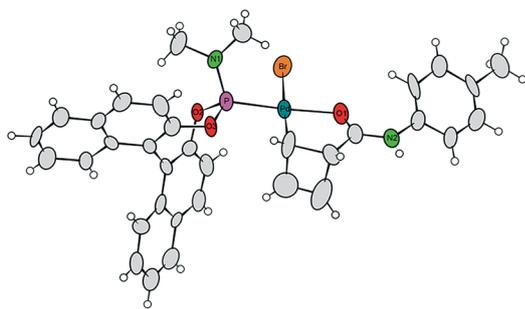
## Constructing real-time, wash-free, and reiterative sensors for cell surface proteins using binding-induced dynamic DNA assembly

Yanan Tang, Zhixin Wang, Xiaolong Yang, Junbo Chen, Linan Liu, Weian Zhao, X. Chris Le and Feng Li\*

A real-time, wash-free, and reiterative sensor is constructed for monitoring cell surface proteins using the principle of binding-induced DNA dynamic assembly.



5734

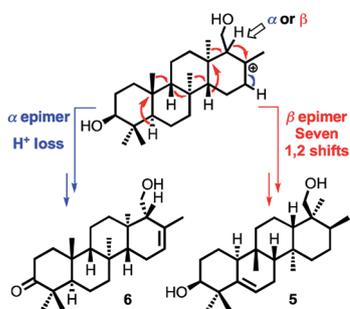


### Dynamic behaviour of monohaptoallylpalladium species: internal coordination as a driving force in allylic alkylation chemistry

Lan-Gui Xie, Viktor Bagutski, Davide Audisio, Larry M. Wolf, Volker Schmidts, Kathrin Hofmann, Cornelia Wirtz, Walter Thiel, Christina M. Thiele\* and Nuno Maulide\*

Structural and reactivity studies of internally coordinated monohaptoallylpalladium(II) complexes.

5740

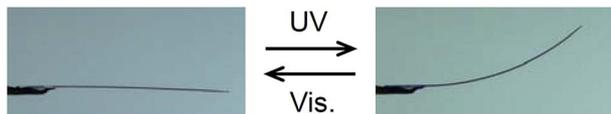


### Biosynthetic insights provided by unusual sesterterpenes from the medicinal herb *Aletris farinosa*

Victoria L. Challinor, Ryne C. Johnston, Paul V. Bernhardt, Reginald P. Lehmann, Elizabeth H. Krenske and James J. De Voss\*

Configuration of a single stereocenter determines if a key carbocation in sesterterpene biosynthesis undergoes simple elimination or a cascade of seven 1,2-methyl and hydride migrations.

5746

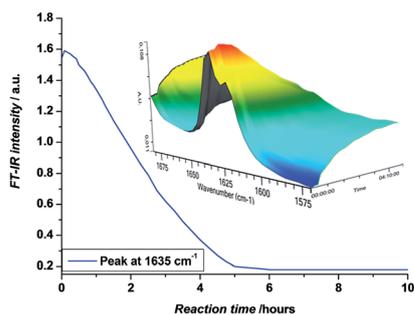


### Light-driven bending of diarylethene mixed crystals

Satoko Ohshima, Masakazu Morimoto and Masahiro Irie\*

The bending response of mixed crystals by selective photoisomerization revealed that the local shape change of each molecule is additively linked to the macroscopic deformation of the crystals.

5753



### Synthesis of sequence-defined acrylate oligomers via photo-induced copper-mediated radical monomer insertions

Joke Vandenberg, Gunter Reekmans, Peter Adriaensens and Tanja Junkers\*

Photo-induced copper-mediated radical polymerization is used to synthesize monodisperse sequence defined acrylate oligomers via consecutive single unit monomer insertion reactions and intermediate purification of the compounds by column or preparative recycling size exclusion chromatography.

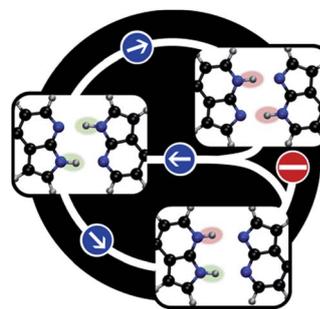


5762

### Stepwise double excited-state proton transfer is not possible in 7-azaindole dimer

Rachel Crespo-Otero,<sup>\*</sup> Nawee Kungwan<sup>\*</sup> and Mario Barbatti<sup>\*</sup>

Topographical analysis of the dimer's excited state shows that internal conversion after first proton transfer blocks the stepwise process.

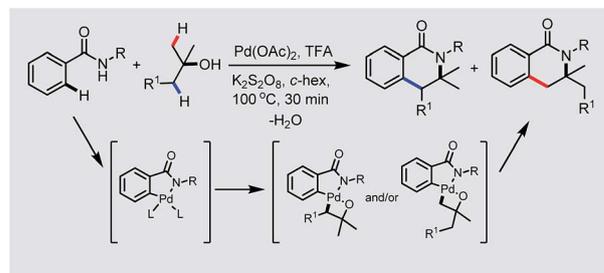


5768

### Modular synthesis of dihydro-isoquinolines: palladium-catalyzed sequential C(sp<sup>2</sup>)-H and C(sp<sup>3</sup>)-H bond activation

Weidong Liu, Qingzhen Yu, Le'an Hu, Zenghua Chen and Jianhui Huang<sup>\*</sup>

An efficient synthesis of dihydro-isoquinolines *via* a Pd-catalyzed double C-H bond activation/annulation featuring a short reaction time, high atom economy and the formation of a sterically less favoured tertiary C-N bond.

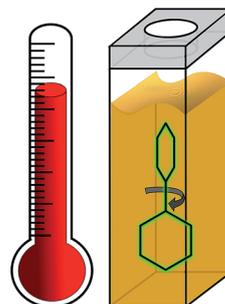


5773

### Unravelling the effect of temperature on viscosity-sensitive fluorescent molecular rotors

Aurimas Vyšniauskas, Maryam Qurashi, Nathaniel Gallop, Milan Balaz, Harry L. Anderson and Marina K. Kuimova<sup>\*</sup>

We examine the effect of temperature on three viscosity-sensitive fluorophores termed 'molecular rotors'. In the case of the conjugated porphyrin dimer, it can be used for measuring both viscosity and temperature concurrently.



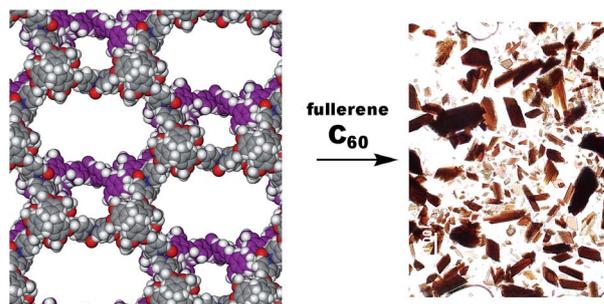
Molecular sensors	$\eta$	T
BODIPY	✓	✗
Kiton Red	✓ or ✗	✓
Porphyrin dimer	✓	✓

5779

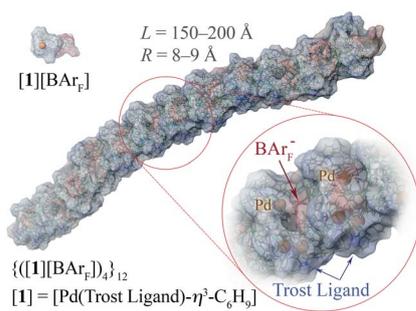
### Copper coordination polymers from cavitand ligands: hierarchical spaces from cage and capsule motifs, and other topologies

Flora L. Thorp-Greenwood, Tanya K. Ronson and Michael J. Hardie<sup>\*</sup>

Copper coordination polymers from cavitand ligands are reported including networked cage-motif structures, one of which takes up C<sub>60</sub> from solution.



5793

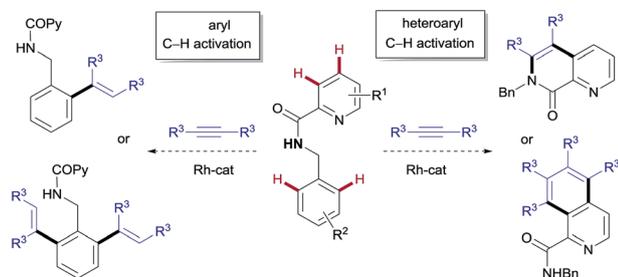


### Pd- $\eta^3$ -C<sub>6</sub>H<sub>9</sub> complexes of the Trost modular ligand: high nuclearity columnar aggregation controlled by concentration, solvent and counterion

Daugirdas Tomas Racys, Julian Eastoe, Per-Ola Norrby, Isabelle Grillo, Sarah E. Rogers and Guy C. Lloyd-Jones\*

Pd- $\eta^3$ -C<sub>6</sub>H<sub>9</sub> cations bearing the Trost ligand (2) undergo two-stage oligomerisation-aggregation to form high nuclearity aggregates (up to 56 Pd centres), with aggregation strongly modulated by concentration, solvent and counter-anion.

5802

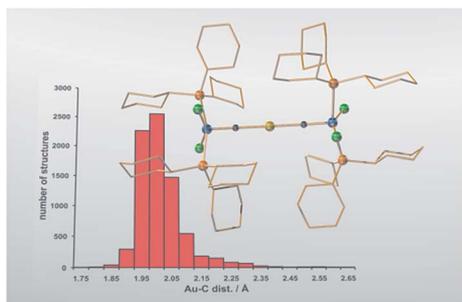


### Rh/Rh<sup>III</sup> catalyst-controlled divergent aryl/heteroaryl C-H bond functionalization of picolinamides with alkynes

Ángel Manu Martínez, Javier Echavarren, Inés Alonso, Nuria Rodríguez,\* Ramón Gómez Arrayás\* and Juan C. Carretero\*

Switchable site-selectivity through catalyst control is achieved in the direct functionalization of picolinamides that contain two distinct C-H sites to construct diverse scaffolds from the same starting material.

5815

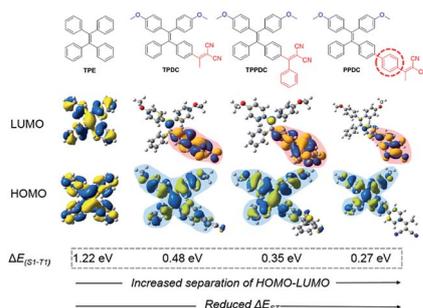


### Carbide complexes as $\pi$ -acceptor ligands

Anders Reinholdt, Johan E. Vibenholt, Thorbjørn J. Morsing, Magnus Schau-Magnussen, Nini E. A. Reeler and Jesper Bendix\*

A terminal carbide complex binds as a  $\pi$ -acceptor towards electron-rich metal centers, mirroring CO, and provides the first homoleptic, carbide-ligated complex.

5824



### Tuning the singlet-triplet energy gap: a unique approach to efficient photosensitizers with aggregation-induced emission (AIE) characteristics

Shidang Xu, Youyong Yuan, Xiaolei Cai, Chong-Jing Zhang, Fang Hu, Jing Liang, Guanxin Zhang, Deqing Zhang and Bin Liu\*

The efficiency of the intersystem crossing process can be improved by reducing the energy gap between the singlet and triplet excited states ( $\Delta E_{S^1-T^1}$ ), which offers the opportunity to improve the yield of the triplet excited state.

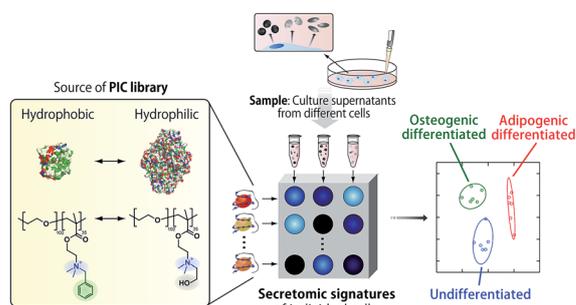


5831

### A polyion complex sensor array for markerless and noninvasive identification of differentiated mesenchymal stem cells from human adipose tissue

Shunsuke Tomita,\* Miho Sakao, Ryoji Kurita, Osamu Niwa and Keitaro Yoshimoto\*

A sensor array of cross-reactive polyion complexes enabled markerless and noninvasive identification of osteogenic and adipogenic differentiation of human mesenchymal stem cells.

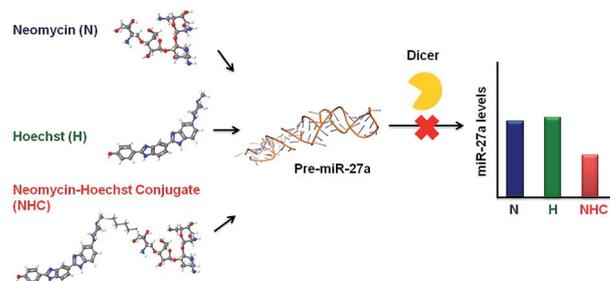


5837

### Potent inhibition of miR-27a by neomycin-bisbenzimidazole conjugates

Smita Nahar, Nihar Ranjan, Arjun Ray, Dev P. Arya\* and Souvik Maiti\*

Potent downregulation of oncogenic miRNA is obtained by conjugation of neomycin and bisbenzimidazoles.

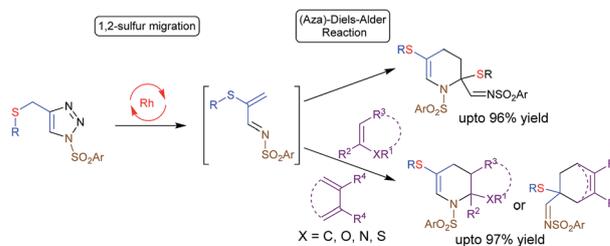


5847

### Tandem 1,2-sulfur migration and (aza)-Diels-Alder reaction of $\beta$ -thio- $\alpha$ -diazoimines: rhodium catalyzed synthesis of (fused)-polyhydropyridines, and cyclohexenes

Dongari Yadagiri and Pazhamalai Anbarasan\*

Rhodium catalyzed synthesis of substituted tetrahydropyridines was accomplished from readily accessible thio-tethered *N*-sulfonyl-1,2,3-triazoles.

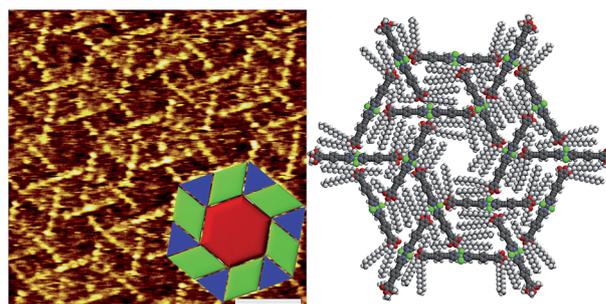


5853

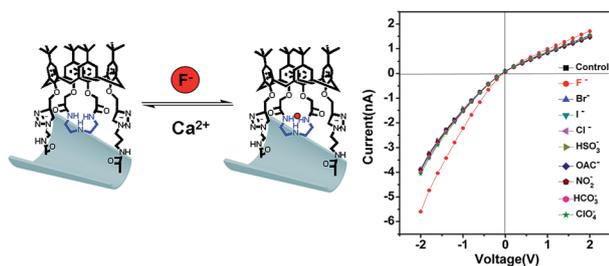
### Concentration-dependent rhombitrihexagonal tiling patterns at the liquid/solid interface

Vladimir Stepanenko, Ramesh Kandanelli, Shinobu Uemura, Frank Würthner\* and Gustavo Fernández\*

A self-assembling Pd(II) complex forms sophisticated concentration-dependent Archimedean tiling patterns composed of three types of polygons at the liquid/solid interface.



5859

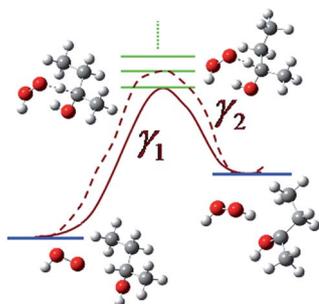


### Fluoride responsive single nanochannel: click fabrication and highly selective sensing in aqueous solution

Guanrong Nie, Yue Sun, Fan Zhang, Miaomiao Song, Demei Tian, Lei Jiang and Haibing Li\*

A  $F^-$  responsive nanochannel based on hydrogen-bonding interactions was designed to accomplish highly selective sensing in aqueous solution.

5866

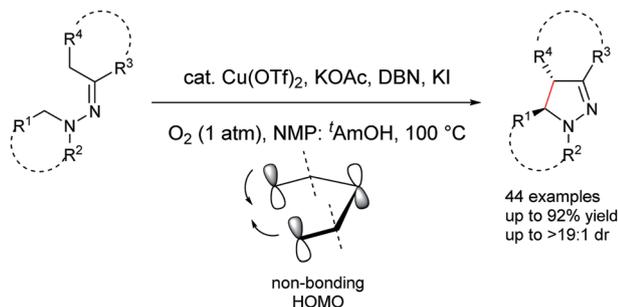


### Multi-path variational transition state theory for chiral molecules: the site-dependent kinetics for abstraction of hydrogen from 2-butanol by hydroperoxyl radical, analysis of hydrogen bonding in the transition state, and dramatic temperature dependence of the activation energy

Junwei Lucas Bao, Rubén Meana-Pañeda and Donald G. Truhlar\*

A hydrogen bond at the transition state can lower the enthalpy of activation, but raise the free energy of activation.

5882

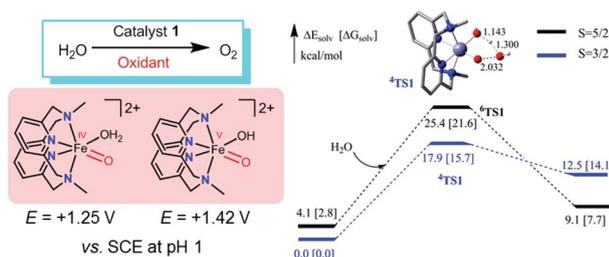


### Copper-catalyzed diastereoselective aerobic intramolecular dehydrogenative coupling of hydrazones via $sp^3$ C–H functionalization

Xuesong Wu, Mian Wang, Guangwu Zhang, Yan Zhao, Jianyi Wang\* and Haibo Ge\*

Diastereoselective aerobic dehydrogenative cyclization of hydrazones is described via a copper-catalyzed  $sp^3$  C–H functionalization process.

5891



### Water oxidation catalysed by iron complex of *N,N'*-dimethyl-2,11-diaza[3,3](2,6)pyridinophane. Spectroscopy of iron–oxo intermediates and density functional theory calculations

Wai-Pong To, Toby Wai-Shan Chow, Chun-Wai Tse, Xiangguo Guan,\* Jie-Sheng Huang and Chi-Ming Che\*

$Fe^{IV}=O$  and/or  $Fe^V=O$  intermediates are suggested to be involved in water oxidation with  $[NH_4]_2[Ce^{IV}(NO_3)_6]$ ,  $NaO_4$ , or Oxone catalyzed by  $[Fe^{III}(L1)Cl_2]^+$  (**1**) on the basis of spectroscopic measurements and DFT calculations.

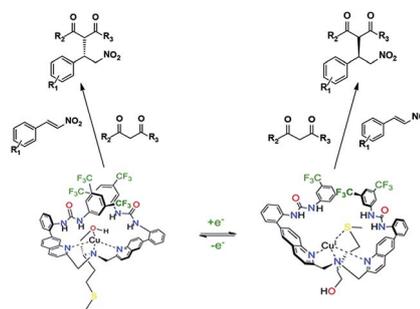


5904

### Redox-configurable ambidextrous catalysis: structural and mechanistic insight

Shahab Mortezaei, Noelle R. Catarineu, Xueyou Duan, Chunhua Hu and James W. Canary\*

A helically chiral copper complex is used as a switchable asymmetric catalyst capable of delivering either enantiomer of a Michael addition reaction.

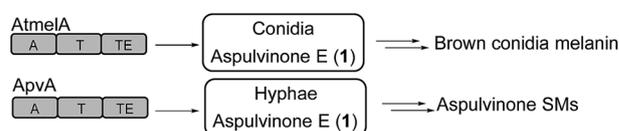


5913

### Spatial regulation of a common precursor from two distinct genes generates metabolite diversity

Chun-Jun Guo, Wei-Wen Sun, Kenneth S. Bruno, Berl R. Oakley, Nancy P. Keller and Clay C. C. Wang\*

We have demonstrated that spatial regulation of the same product from two distinct genes generates metabolite diversity.

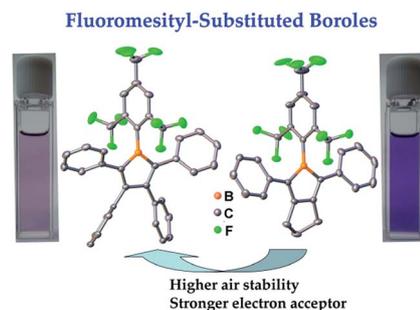


5922

### Taming the beast: fluoromesityl groups induce a dramatic stability enhancement in boroles

Zuolun Zhang, Robert M. Edkins, Martin Haehnel, Marius Wehner, Antonius Eichhorn, Lisa Mailänder, Michael Meier, Johannes Brand, Franziska Brede, Klaus Müller-Buschbaum, Holger Braunschweig and Todd B. Marder\*

Boroles with a fluoromesityl group on the B atom have greatly improved air stability compared to their mesityl analogues.

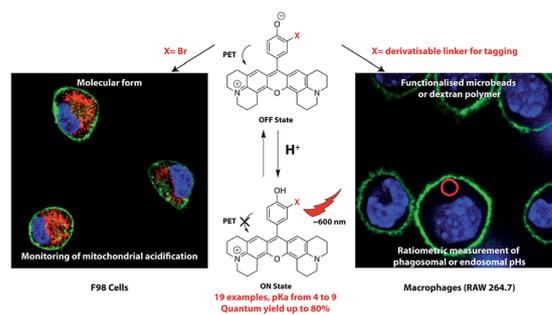


5928

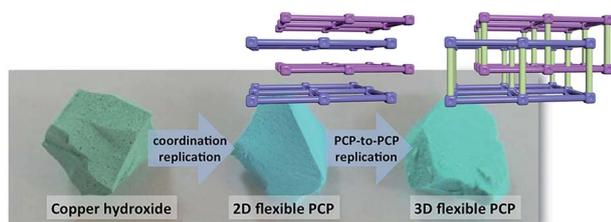
### H-Rubies, a new family of red emitting fluorescent pH sensors for living cells

Guillaume Despras, Alsu I. Zamaleeva, Lucie Dardevet, Céline Tisseyre, Joao Gamelas Magalhaes, Charlotte Garner, Michel De Waard, Sebastian Amigorena, Anne Feltz, Jean-Maurice Mallet and Mayeul Collot\*

H-Rubies is a family of pH probes that display a bright red fluorescence upon acidification. They have been used as molecular form to monitor mitochondrial acidification and as functionalised forms to provide ratiometric systems to measure phagosomal and endosomal pH in macrophages.



5938

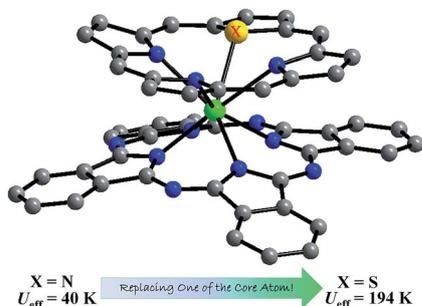


### Mesoscopic superstructures of flexible porous coordination polymers synthesized *via* coordination replication

Kenji Sumida, Nirmalya Moitra, Julien Reboul, Shotaro Fukumoto, Kazuki Nakanishi, Kazuyoshi Kanamori, Shuhei Furukawa\* and Susumu Kitagawa\*

Monolithic superstructures of two- and three-dimensional flexible frameworks are prepared *via* coordination replication from a copper hydroxide parent phase.

5947

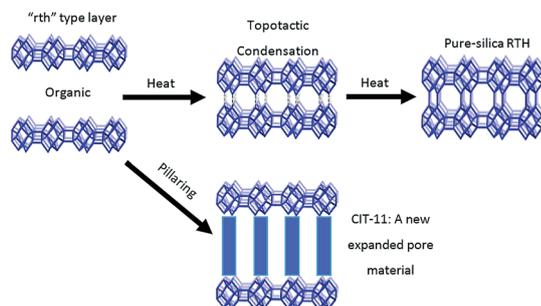


### Rational enhancement of the energy barrier of bis(tetrapyrrole) dysprosium SMMs *via* replacing atom of porphyrin core

Wei Cao, Chen Gao, Yi-Quan Zhang, Dongdong Qi, Tao Liu,\* Kang Wang, Chunying Duan, Song Gao\* and Jianzhuang Jiang\*

Replacing a porphyrin N atom induces higher electrostatic environment anisotropy around the Dy center, giving the highest energy barrier among bis(tetrapyrrole) Dy SMMs.

5955

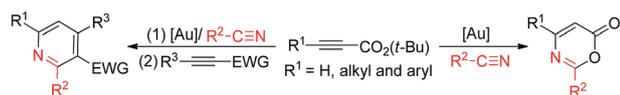


### Synthesis of the RTH-type layer: the first small-pore, two dimensional layered zeolite precursor

Joel E. Schmidt, Dan Xie and Mark E. Davis\*

The "rth" type layer is the first porous 2D zeolite layer; it forms zeolite RTH *via* topotactic condensation or can be pillared to create a thermally stable, expanded pore material.

5964



### Gold-catalyzed formal $[4\pi + 2\pi]$ -cycloadditions of propiolate derivatives with unactivated nitriles

Somnath Narayan Karad, Wei-Kang Chung and Rai-Shung Liu\*

Gold-catalyzed hetero- $[4\pi + 2\pi]$ -cycloadditions of *tert*-butyl propiolates with unactivated nitriles are described. This new finding enables a one-pot gold-catalyzed synthesis of highly substituted pyridines.

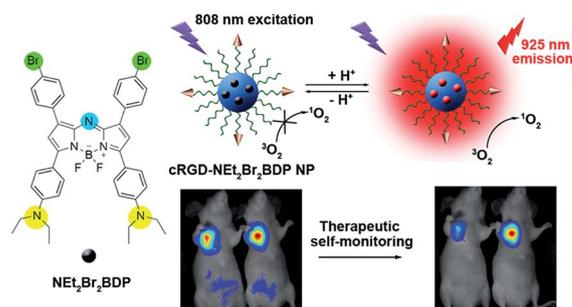


5969

### A pH-activatable and aniline-substituted photosensitizer for near-infrared cancer theranostics

Jiangwei Tian, Jinfeng Zhou, Zhen Shen, Lin Ding, Jun-Sheng Yu and Huangxian Ju\*

A trifunctional photosensitizer was designed to achieve highly selective near-infrared tumor imaging, efficient photodynamic therapy and therapeutic self-monitoring.

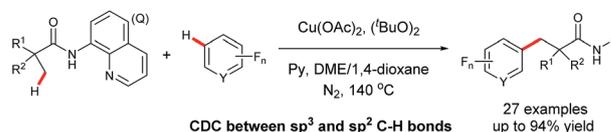


5978

### Pyridine-enabled copper-promoted cross dehydrogenative coupling of C(sp<sup>2</sup>)-H and unactivated C(sp<sup>3</sup>)-H bonds

Xuesong Wu, Yan Zhao and Haibo Ge\*

Pyridine-enabled cross dehydrogenative coupling of sp<sup>2</sup> C-H bonds of polyfluoroarenes and unactivated sp<sup>3</sup> C-H bonds of amides was achieved.

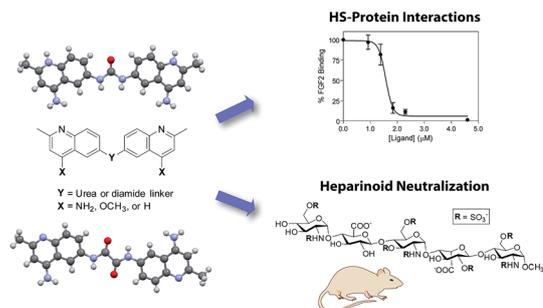


5984

### Small molecule antagonists of cell-surface heparan sulfate and heparin-protein interactions

Ryan J. Weiss, Philip L. S. M. Gordts, Dzung Le, Ding Xu, Jeffrey D. Esko and Yitzhak Tor\*

A series of rationally designed surfen analogs were synthesized and utilized as antagonists of glycosaminoglycan-protein interactions, including the neutralization of the anticoagulant activity of fondaparinux, a synthetic pentasaccharide analog of heparin.

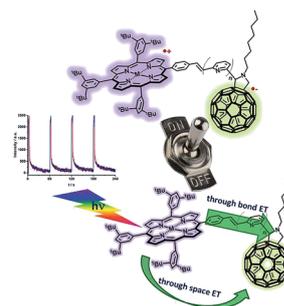


5994

### On-off switch of charge-separated states of pyridine-vinylene-linked porphyrin-C<sub>60</sub> conjugates detected by EPR

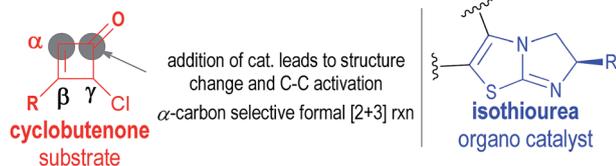
S. V. Kirner, D. Arteaga, C. Henkel, J. T. Margraf, N. Alegret, K. Ohkubo, B. Insuasty, A. Ortiz,\* N. Martin, L. Echegoyen,\* S. Fukuzumi,\* T. Clark and D. M. Guldi\*

The on-off switch of charge separated states in a new series of pyridine-vinylene linked porphyrin-C<sub>60</sub> conjugates was detected by EPR at 77 K.



## EDGE ARTICLES

6008

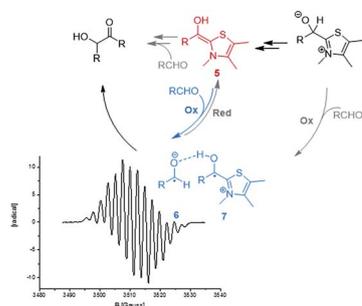


### Cycloaddition of cyclobutenone and azomethine imine enabled by chiral isothiourea organic catalysts

Bao-Sheng Li, Yuhuang Wang, Zhichao Jin and Yonggui Robin Chi\*

An organocatalytic carbon–carbon bond activation of  $\gamma$ -mono-chlorine substituted cyclobutenone provides an  $\alpha$ -carbon selective cycloadduct with excellent stereoselectivities.

6013



### NHC-catalysed benzoin condensation – is it all down to the Breslow intermediate?

Julia Rehbein,\* Stephanie-M. Ruser and Jenny Phan

The NHC-catalysed benzoin condensation has been studied mechanistically by a combination of experimental and computational chemistry. The presented EPR-spectroscopic and computational data provide evidence for a radical pair as a potential second key-intermediate that is derived from the Breslow-intermediate *via* an SET process.

## CORRECTIONS

6019

### Correction: Characterizing chain processes in visible light photoredox catalysis

Megan A. Cismesia and Tehshik P. Yoon\*

6020

### Correction: Fluorescent carbon dot–molecular salt hydrogels

Angelina Cayuela, Stuart R. Kennedy, M. Laura Soriano, Christopher D. Jones, Miguel Valcárcel\* and Jonathan W. Steed\*



6021

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

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

