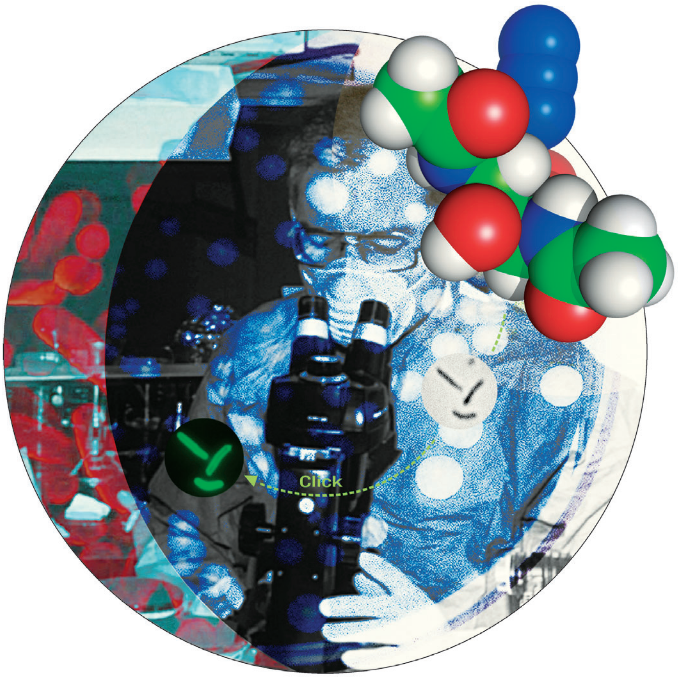
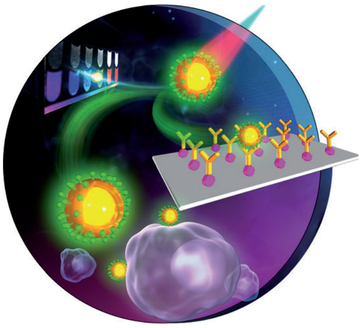
Legionella pneumophila …

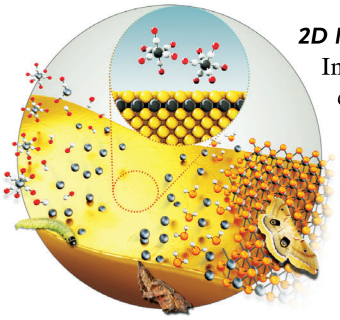


… is a deadly pathogen that was discovered after an outbreak in 1976 at the convention of the American Legion in Philadelphia. In their Communication on page 1275 ff., S. Dukan, B. Vauzeilles, and co-workers describe a simple strategy to detect and identify living *Legionella pneumophila* by metabolic incorporation of a modified carbohydrate into their lipopolysaccharides, followed by further conjugation using click chemistry. Picture of Dr. Feely: CDC/Stafford Smith. Cover artwork: David Garino.

Upconversion Nano-Bioprobes

Nano-bioprobes based on lanthanide-doped $LiLuF_4$ core/shell architectures are sensitive for the detection of β-hCG, and exhibit high upconversion quantum yields, as X. Y. Chen et al. show in their Communication on page 1252 ff.



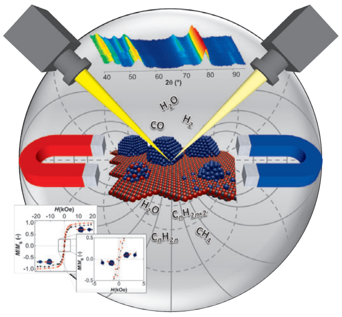


2D Nanomaterials

In their Communication on page 1266 ff., H. C. Choi et al. present patternable growth of large-scale MoS_2 atomic layers from vaporized $[Mo(CO)_6]$ on gold that reacts with H_2S. Atomic layers of MoS_2 are specifically formed, which can be isolated by means of etching.

Heterogeneous Catalysis

Magnetometry and X-ray diffraction are used in combination with specially designed reaction chambers by M. Claeys et al. in their Communication on page 1342 ff., to reveal the size-dependent oxidation of an industrially relevant cobalt Fischer–Tropsch catalyst under working conditions.



How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
Gesellschaft
Deutscher Chemiker

Service

Spotlight on Angewandte's Sister Journals *1190 – 1193*

Author Profile

"My biggest motivation is to be the best in whatever I do. I lose track of time when I start brainstorming for a new idea. …"
This and more about Teck-Peng Loh can be found on page 1194.

Teck-Peng Loh **1194**

News

P. M. Pinto

D. Vocadlo

M. Ciufolini

M. MacLachlan

A. Woolley

A. R. Wheeler

M. Lautens

J. Pawliszyn

Y. Zhao

Canadian Society of Chemistry and Chemical Institute of Canada Awards **1195 – 1196**

Books

Gold Nanoparticles for Physics, Chemistry, and Biology — Catherine Louis, Olivier Pluchery — *reviewed by P. K. Jain* **1197**

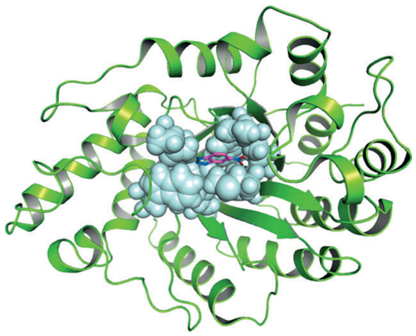
Highlights

Protein Engineering

M. Höhne,
U. T. Bornscheuer* ________ 1200 – 1202

Protein Engineering from “Scratch” Is Maturing

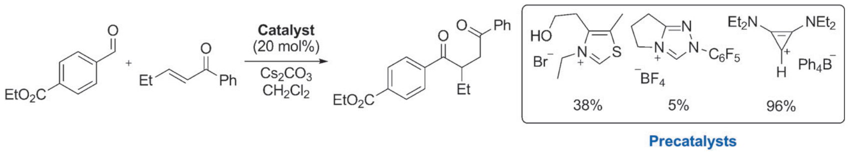
Precisely tuning the active site by protein engineering has led to the development of a highly efficient Kemp eliminase (see structure with substrate in the binding pocket). The starting protein scaffold with only low activity originated from computational design, as no natural enzyme with this activity was known. This is a breakthrough in protein design, as novel catalytic activities are now in reach that match those of natural enzymes.



Homogeneous Catalysis

S. J. Connon* ________ 1203 – 1205

Diaminocyclopropenylidene Organocatalysts: Beyond N-Heterocyclic Carbenes



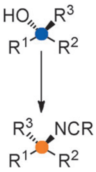
Cyclopropenylidene carbenes have been found to be efficient catalysts for the intermolecular Stetter reaction between aromatic aldehydes and α,β-unsaturated ketones. In this transformation, the cyclopropenylidene proved superior to more traditional thiazolium- and triazolium-derived carbenes. Preparation and evaluation of a chiral analogue have also been reported.

Stereoinversion

A. F. B. Räder,
K. Tiefenbacher* ________ 1206 – 1207

Tertiary Alcohols as Substrates for S_N2-Like Stereoinversion

Rewrite the textbooks! The stereospecific bimolecular substitution reaction (S_N2) is usually limited to primary and secondary electrophiles. The Shenvi group has developed a method in which tertiary alcohol substrates are converted into isocyanides with configurational inversion. Intriguingly, tertiary hydroxy groups react selectively in the presence of unprotected primary and secondary hydroxy groups.



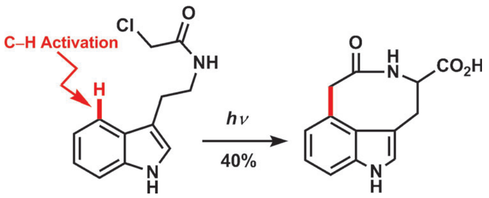
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Minireviews

Natural Products

P. J. Gritsch, C. Leitner, M. Pfaffenbach,
T. Gaich* ________ **1208 – 1217**

The Witkop Cyclization: A Photoinduced C–H Activation of the Indole System



To wit: The title reaction resembles a photoinduced electron-transfer process, and allows the direct formation of medium-sized lactams by C–H activation of the indole nucleus. Therefore it is a versatile tool for the construction of polycyclic indole alkaloid scaffolds.

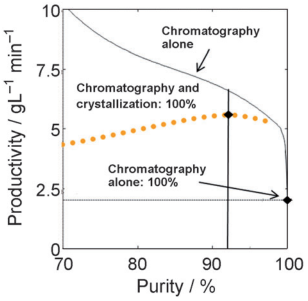
Reviews

Enantiomer Separation

H. Lorenz,
A. Seidel-Morgenstern* ____ **1218 – 1250**

Processes To Separate Enantiomers

Crystallization, chromatography, or both? Processes for the separation of enantiomers are discussed, with a focus on enantioselective crystallization and preparative chromatography, both individually and combined. The application of the phase diagrams and the incorporation of racemization steps are also considered.



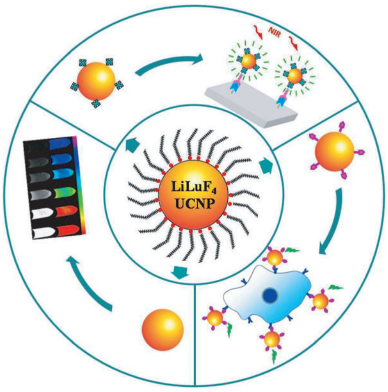
Communications

Upconversion Nano-Bioprobe

P. Huang, W. Zheng, S. Y. Zhou, D. T. Tu,
Z. Chen, H. M. Zhu, R. F. Li, E. Ma,
M. D. Huang, X. Y. Chen* __ **1252 – 1257**

Lanthanide-Doped LiLuF4 Upconversion Nanoprobes for the Detection of Disease Biomarkers

A small but sensitive biosensor: Successive injection of shell precursors enabled the synthesis of novel and highly emissive LiLuF$_4$:Ln^{3+} core/shell upconversion nanoparticles that were effective as sensitive upconversion luminescent probes for the detection of β-hCG (an important disease marker). The nanoprobes were also used successfully in proof-of-concept computed tomography and upconversion luminescence dual-mode bioimaging.



Frontispiece

Highly attractive 2014 Rates*

for members of ChemPubSoc Europe societies

*(without local VAT)

ChemPubSoc Europe

Online: € 98,-
Print: € 398,-

IF 2012: 5.831

Online: € 98,-
Print: € 398,-

IF 2012: 3.344

Online: € 98,-

IF 2012: 3.120

Online: € 98,-

NEW to the family

first society owned open-access chemistry journal

Open-Access Journal

Online: € 98,-
Print: € 198,-

IF 2012: 3.740

Online: € 98,-
Print: € 198,-

IF 2012: 2.835

Online: € 98,-

IF 2012: 7.475

Online: € 98,-

IF 2012: 5.181

Online: € 98,-
Print: € 198,-

IF 2012: 3.349

Online: € 98,-

New! Starting 2014

Online ordering:

Simply visit the journal's homepage at

www.onlinelibrary.wiley.com

Choose

GET ACCESS
Subscribe / Renew

on the left-hand menu and complete your order.

SVENSKA KEMISTSAMFUNDET

KNCV

GDCh
GESELLSCHAFT DEUTSCHER CHEMIKER

SCG Schweizerische Chemische Gesellschaft
SSC Société Suisse de Chimie
SCS Swiss Chemical Society

Société Chimique de France

GÖCH
GESELLSCHAFT ÖSTERREICHISCHER CHEMIKER

MKE

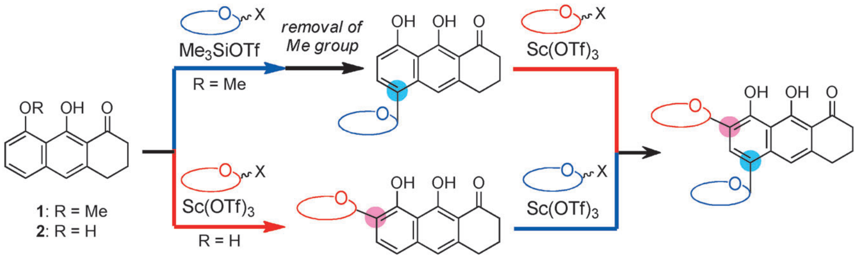
SOCIEDADE PORTUGUESA DE QUÍMICA

Real Sociedad Española de Química

Association of Greek Chemists

www.chempubsoc.eu

PSJ-13-59145_gu



The stage is set... The two anthrones **1** and **2** enabled bis-C-glycosylation (see scheme; Tf = trifluoromethanesulfonyl) to provide advanced platforms for the synthesis of the pluramycin class of antitumor antibiotics. These two efficient methods overcome the challenge of the regio- and stereoselective installation of two different *C*-glycosides.

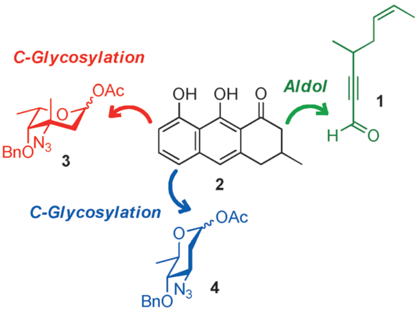
C-Glycosylation

K. Kitamura, Y. Ando, T. Matsumoto,*
K. Suzuki* ———— **1258 – 1261**

Synthesis of the Pluramycins 1: Two Designed Anthrones as Enabling Platforms for Flexible Bis-C-Glycosylation

---

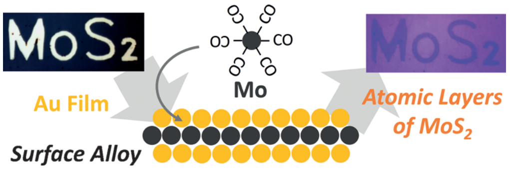
... for a speedy synthesis: In a brief, highly convergent total synthesis of saptomycin B, the target compound was efficiently assembled from the four building blocks **1**–**4** (see scheme; Bn = benzyl) by exploiting anthrone **2** as a platform. A member of the pluramycin class of antibiotics, saptomycin B was obtained in 10 steps and 15 % overall yield.



Natural Products Synthesis

K. Kitamura, Y. Maezawa, Y. Ando,
T. Kusumi, T. Matsumoto,*
K. Suzuki* ———— **1262 – 1265**

Synthesis of the Pluramycins 2: Total Synthesis and Structure Assignment of Saptomycin B



When a gold surface reacts with vaporized [Mo(CO)$_6$] at 300 °C, a surface alloy forms, which in turn becomes an ideal large-scale atom-thick Mo reservoir. When this alloy further reacts with H_2S, atomic layers of MoS_2 are specifically formed on Au, which can be isolated by means of etching.

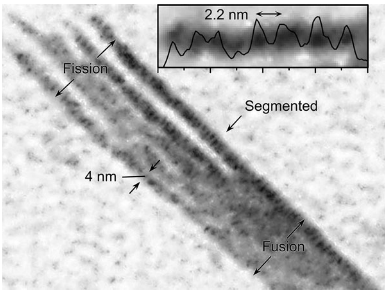
2D Nanomaterials

I. Song, C. Park, M. Hong, J. Baik,
H.-J. Shin, H. C. Choi* ——— **1266 – 1269**

Patternable Large-Scale Molybdenium Disulfide Atomic Layers Grown by Gold-Assisted Chemical Vapor Deposition

Inside Back Cover

Seeing is believing: Amphiphilic perylene bisimide aggregates were visualized by transmission electron microscopy and the self-assembly of dye aggregates from small nanorods to large nanoribbons in water was observed on the molecular level. The fluorescence properties of these dye aggregates were enhanced for the higher order nanostructures.



Dye Aggregates in Water

X. Zhang, D. Görl, V. Stepanenko,
F. Würthner* ———— **1270 – 1274**

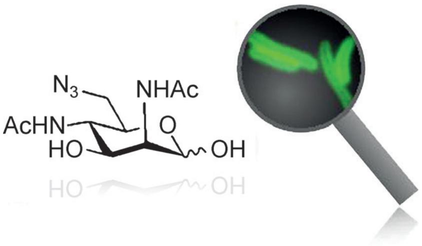
Hierarchical Growth of Fluorescent Dye Aggregates in Water by Fusion of Segmented Nanostructures

Carbohydrates

J. Mas Pons, A. Dumont, G. Sautejeau,
E. Fugier, A. Baron, S. Dukan,*
B. Vauzeilles* ———— **1275–1278**

Identification of Living *Legionella pneumophila* Using Species-Specific Metabolic Lipopolysaccharide Labeling

Front Cover

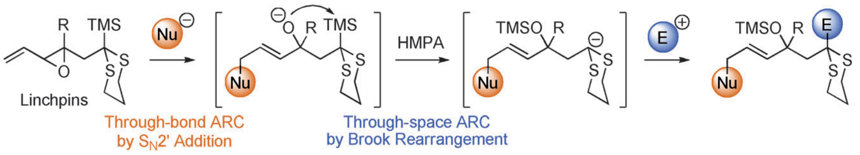


Tracking a killer: Almost 40 years after its first identified outbreak in Philadelphia, *Legionella pneumophila* remains difficult to track. Metabolic lipopolysaccharide labeling with a specific monosaccharide allows detection and identification of living representatives of this dangerous pathogen. Notably other *Legionella* species are not labeled using this method.

Synthetic Methods

M. Z. Chen, O. Gutierrez,
A. B. Smith, III* ———— **1279–1282**

Through-Bond/Through-Space Anion Relay Chemistry Exploiting Vinylepoxides as Bifunctional Linchpins

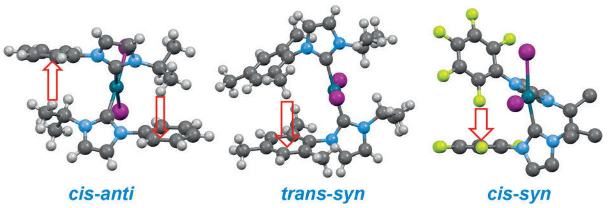


Anion relay chemistry: The design, synthesis, and validation of three vinylepoxide linchpins for through-bond/through-space anion relay chemistry (ARC) have been achieved. For negative charge migration, this class of bifunctional linchpins employs through-bond ARC by an S_N2' reaction, followed by through-space ARC exploiting a 1,4-Brook rearrangement (HMPA = hexamethylphosphoramide, TMS = trimethylsilyl).

Conformation Analysis

X. Xu, B. Pooi, H. Hirao,*
S. H. Hong* ———— **1283–1287**

CH–π and CF–π Interactions Lead to Structural Changes of N-Heterocyclic Carbene Palladium Complexes



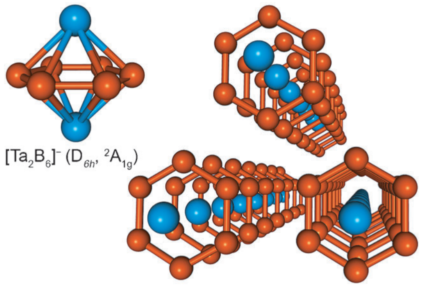
Doing the twist: The roles of CH–π and CF–π interactions in determining the structure of the title complexes were studied. The CH–π interactions led to the *cis-anti* isomers in 1-aryl-3-isopropylimidazol-2-ylidene-based complexes, while CF–π interactions led to the exclusive formation of the *cis-syn* isomer of diiodobis(3-isopropyl-1-pentafluorophenylimidazol-2-ylidene)palladium(II). C gray, N violet, Pd turquoise, F yellow, I purple.

B_6 ring building blocks

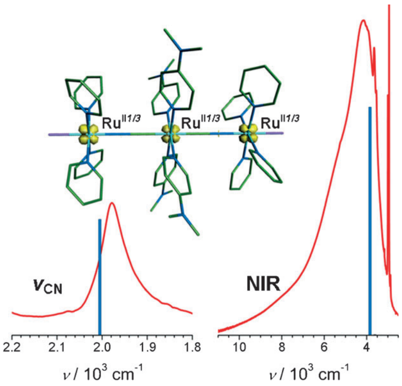
W. L. Li, L. Xie, T. Jian, C. Romanescu,
X. Huang,* L.-S. Wang* ———— **1288–1292**

Hexagonal Bipyramidal $[Ta_2B_6]^{-/0}$ Clusters: B_6 Rings as Structural Motifs

B ring it on: Photoelectron spectroscopic and theoretical investigations show that the $[Ta_2B_6]^{-/0}$ clusters have bipyramidal structures with a planar B_6 ring capped by two Ta atoms (see picture, Ta blue, B orange). These gaseous clusters have similar structures to motifs in solid materials suggesting that new boron structural motifs may be discovered by studying boride clusters.



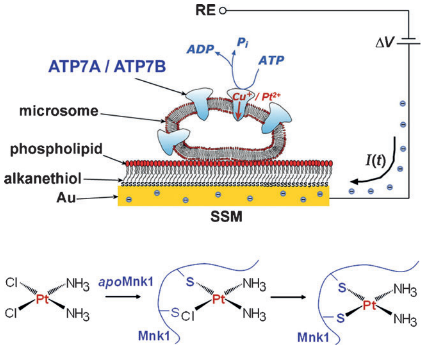
A class upgrade: The presence of a set of 4-dimethylaminopyrine (dmap) ligands in the linear mixed-valence complex *trans*-$[Ru(dmap)_4\{(\mu\text{-}CN)Ru(py)_4Cl\}_2]^{3+}$ (py = pyridine) results in a complex with a symmetrical class III delocalized ground state, according to its IR and NIR spectra. The predicted spectra from (TD)DFT calculations are in close agreement with the experimental data, thus supporting the assignment.



Class III Delocalization

G. E. Pieslinger, P. Alborés, L. D. Slep, L. M. Baraldo* ________ **1293 – 1296**

Class III Delocalization in a Cyanide-Bridged Trimetallic Mixed-Valence Complex

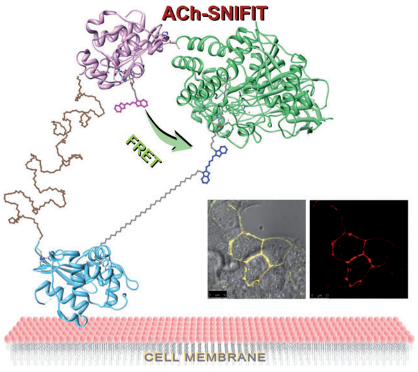


Charge measurements, in the presence of cisplatin or oxaliplatin, on COS-1 microsomes enriched with Cu-ATPases, show vectorial displacement of a charged Pt species upon ATP addition. Co-administration of a Pt drug and Cu inhibits charge translocation. ESI-MS and NMR experiments demonstrate formation of monodentate Pt drug adducts, that evolve into stable and unreactive chelate adducts with CXXC motifs.

Vectorial Displacement

F. Tadini-Buoninsegni, G. Bartolommei, M. R. Moncelli, G. Inesi, A. Galliani, M. Sinisi, M. Losacco, G. Natile, F. Arnesano* ________ **1297 – 1301**

Translocation of Platinum Anticancer Drugs by Human Copper ATPases ATP7A and ATP7B

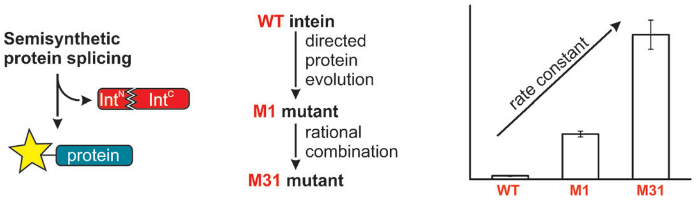


A semisynthetic fluorescence-based probe (ACh-SNIFIT) for the direct, real-time detection of acetylcholine and anticholinesterase compounds such as drugs and nerve agents is introduced. The probe possesses good sensitivity, tunable detection range, and can be selectively targeted to cell surfaces, thereby making it an attractive tool for applications in analytical chemistry and quantitative biology.

Fluorescent Probes

A. Schena, K. Johnsson* ____ **1302 – 1305**

Sensing Acetylcholine and Anticholinesterase Compounds



Supernatural splicing: The first naturally occurring, atypically split intein was identified and characterized. The short N-terminal fragment of the AceL-TerL intein consists of only 25 amino acids and was therefore amenable to chemical synthesis. Mutants with up to 50-fold improved splicing rates were obtained by directed protein evolution and showed unprecedented utility for labeling diverse proteins by semisynthetic protein trans-splicing.

Protein Ligation

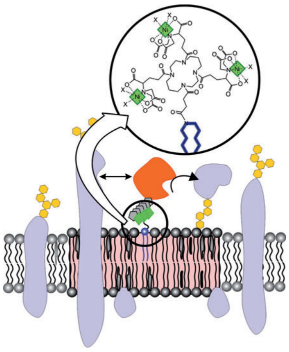
I. V. Thiel, G. Volkmann, S. Pietrokovski,* H. D. Mootz* ________ **1306 – 1310**

An Atypical Naturally Split Intein Engineered for Highly Efficient Protein Labeling

Plasma Membrane Organization

O. Beutel, J. Nikolaus, O. Birkholz, C. You,
T. Schmidt, A. Herrmann,
J. Piehler* ———— 1311 – 1315

High-Fidelity Protein Targeting into Membrane Lipid Microdomains in Living Cells

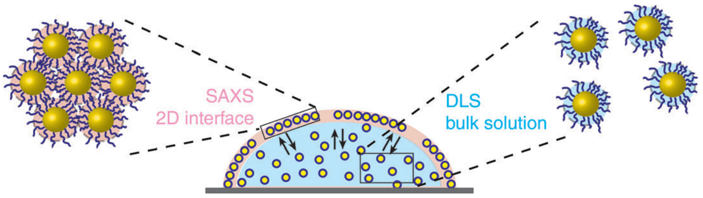


Rapid rafting: Lipid analogues with multivalent chelator head groups allow the tethering of proteins to membrane liquid-ordered and liquid-disordered lipid phases. His-tagged proteins can thus be stably and specifically targeted into lipid microdomains within the plasma membrane of living cells.

DNA Nanotechnology

S. J. Tan,* J. S. Kahn, T. L. Derrien,
M. J. Campolongo, M. Zhao,
D.-M. Smilgies, D. Luo* ———— 1316 – 1319

Crystallization of DNA-Capped Gold Nanoparticles in High-Concentration, Divalent Salt Environments

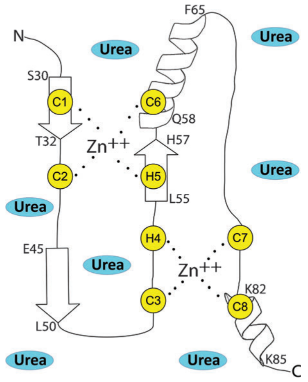


DNA hybridization: Parallel small-angle X-ray scattering (parSAXS; DLS = dynamic light scattering) shows that two-dimensional DNA–gold nanoparticle crystals can be obtained at extremely high salt concentrations using a non-base-pairing DNA model ligand. The interparticle spacings in the crystals can be engineered and further tuned by ligand length and ionic strength.

Molten Globules

M. J. Walczak, B. Samatanga,
F. van Drogen, M. Peter, I. Jelesarov,
G. Wider* ———— 1320 – 1323

The RING Domain of the Scaffold Protein Ste5 Adopts a Molten Globular Character with High Thermal and Chemical Stability

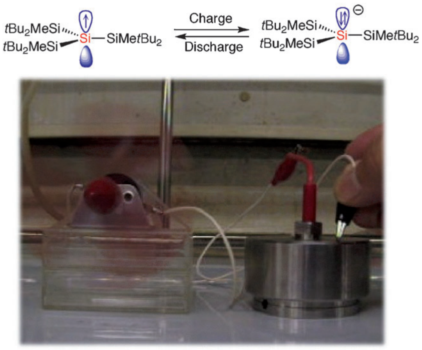


Infusible molten globule: Biophysical experiments show that the RING-H2 domain of the yeast scaffold protein Ste5 exhibits a molten globule fold of high stability. Upon binding of the physiological Gβ/γ ligand, this domain adopts a better-defined globular structure that provides novel insights into the mechanism of recruiting binding partners, which may well be a feature of other RING domains.

Electrochemistry

H. Maruyama, H. Nakano,*
M. Nakamoto,
A. Sekiguchi* ———— 1324 – 1328

High-Power Electrochemical Energy Storage System Employing Stable Radical Pseudocapacitors

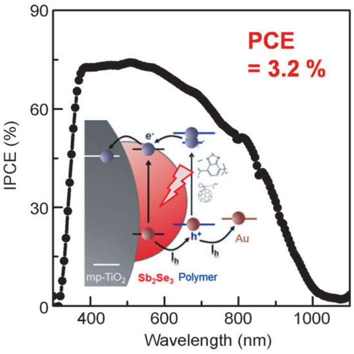


Radical batteries: A lithium-free energy storage system using stable radicals of the heavy Group 14 elements as the anode and graphite as the cathode has been designed (see picture) that delivers a larger energy density than the dual carbon cell and electrochemical capacitor. This energy storage system employing stable-radical pseudocapacitors showed remarkable cycle stability without significant loss of power density.

Solar Cells

Y. C. Choi, T. N. Mandal, W. S. Yang, Y. H. Lee, S. H. Im, J. H. Noh, S. I. Seok* — 1329 – 1333

Sb_2Se_3-Sensitized Inorganic–Organic Heterojunction Solar Cells Fabricated Using a Single-Source Precursor

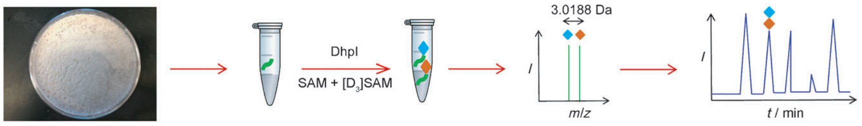


Sb_2Se_3 as a light sensitizer: Sb_2Se_3 was deposited on mesoporous TiO_2 (mp-TiO_2) by a simple solution-based method that employs a single-source precursor. A solar cell that is based on Sb_2Se_3 as the light sensitizer exhibited outstanding light harvesting that covered the near-IR region with a power conversion efficiency (PCE) of approximately 3.2% (IPCE = incident photon to current efficiency).

Natural Product Purification

J. Gao, K. Ju, X. Yu, J. E. Velásquez, S. Mukherjee, J. Lee, C. Zhao, B. S. Evans, J. R. Doroghazi, W. W. Metcalf,* W. A. van der Donk* — 1334 – 1337

Use of a Phosphonate Methyltransferase in the Identification of the Fosfazinomycin Biosynthetic Gene Cluster

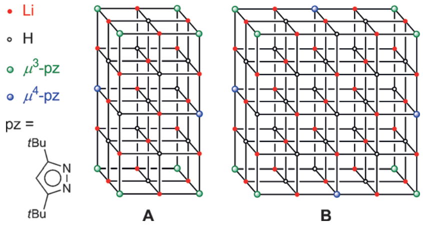


Catching fosfazinomycin: The phosphonate methyltransferase DhpI was used with a mixture of unlabeled and labeled *S*-adenosyl methionine (SAM) to purify phosphonates from crude spent medium. Its use to locate the fosfazinomycin biosynthetic gene cluster is demonstrated.

Ionic Hydrides

A. Stasch* — 1338 – 1341

Well-Defined, Nanometer-Sized LiH Cluster Compounds Stabilized by Pyrazolate Ligands



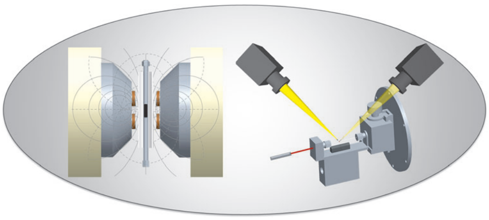
Masterpieces of cubism: A series of pyrazolate-stabilized LiH clusters have been prepared in hydrocarbon solution in a bottom-up approach and structurally characterized. The clusters are based on the cubic lattice cutout structures **A** and **B** (see picture), consist of up to 37 Li^+ ions and 26 H^- ligands, and can contain significantly more hydride than pyrazolate ligands.

Heterogeneous Catalysis

N. Fischer, B. Clapham, T. Feltes, E. van Steen, M. Claeys* — 1342 – 1345

Size-Dependent Phase Transformation of Catalytically Active Nanoparticles Captured In Situ

Back Cover

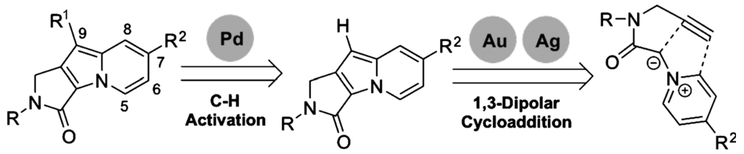


Size does matter: Using magnetometry and X-ray diffraction in combination with novel designed reaction chambers (see picture), the size-dependent oxidation of an industrially relevant cobalt Fischer–Tropsch catalyst is revealed under working conditions.

Fluorophore Design

E. J. Choi, E. Kim, Y. Lee, A. Jo,
S. B. Park* ______________ **1346 – 1350**

Rational Perturbation of the Fluorescence Quantum Yield in Emission-Tunable and Predictable Fluorophores (Seoul-Fluors) by a Facile Synthetic Method Involving C–H Activation



It's all in the design: Seoul-Fluors with predictable photophysical properties, including a fluorescent reactive-oxygen-species sensor that was not previously accessible, were synthesized efficiently by coinage-metal-catalyzed intramolecular 1,3-dipolar cycloaddition and subsequent palladium-mediated C–H activation (see scheme). The quantum yield of the products could be controlled systematically by altering the electronic nature of the substituents.

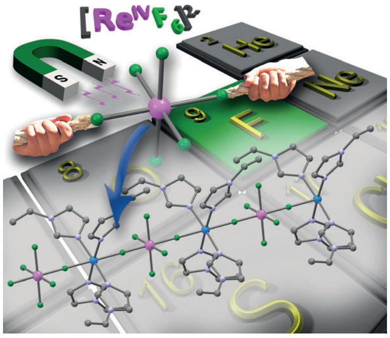
Magnetic Modules

K. S. Pedersen,* M. Sigrist,
M. A. Sørensen, A.-L. Barra,
T. Weyhermüller, S. Piligkos,
C. Aa. Thuesen, M. G. Vinum, H. Mutka,
H. Weihe, R. Clérac,*
J. Bendix* ______________ **1351 – 1354**

$[ReF_6]^{2-}$: A Robust Module for the Design of Molecule-Based Magnetic Materials

Inside Cover

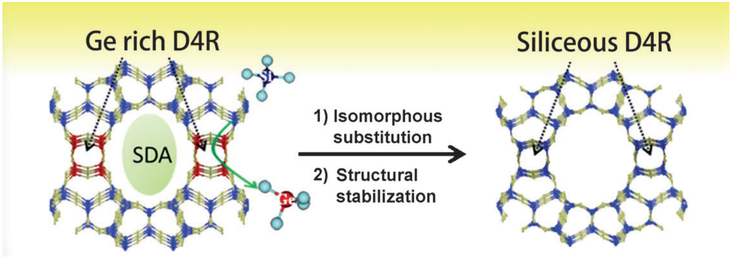
Fluoride gaining weight: An axial perturbation of the octahedral $[ReF_6]^{2-}$ ion gives rise to a strong magnetic anisotropy and slow relaxation of the magnetization. The robust character of $[ReF_6]^{2-}$ facilitates its use as a structure-directing magnetic building block for extended systems. The 1D coordination polymers $[M(viz)_4(ReF_6)]_\infty$ (viz = 1-vinylimidazole, M = Zn, Ni) are prepared and have pronounced magnetic interactions through the fluoride bridges.



Zeolites

H. Xu, J. Jiang, B. Yang, L. Zhang, M. He,
P. Wu* ______________ **1355 – 1359**

Post-Synthesis Treatment gives Highly Stable Siliceous Zeolites through the Isomorphous Substitution of Silicon for Germanium in Germanosilicates

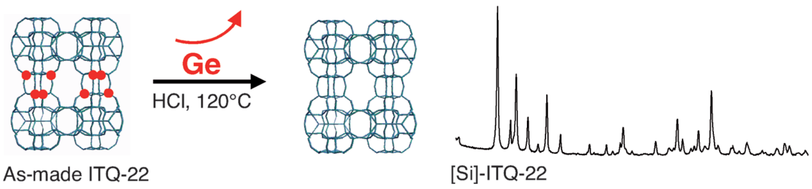


A straight swap: The pores and crystalline structures of germanosilicates can be stabilized by treating as-synthesized samples under acidic conditions. The resulting substitution of Ge by Si gives highly siliceous zeolites, analogous to the germanosilicates, but highly stable against harsh acid treatment and calcination.

Zeolites

L. Burel, N. Kasian, A. Tuel* **1360 – 1363**

Quasi All-Silica Zeolite Obtained by Isomorphous Degermanation of an As-Made Germanium-Containing Precursor



Ge out: Treating ITQ-22 precursors with concentrated HCl removes templating molecules from the pores and extracts most of the Ge species from the framework. The degermanation does not modify the framework topology, and the resulting Ge-free [Si]-ITQ-22 is highly mesoporous, stable, and the possibility to incorporate aluminum makes it potentially interesting in acid catalysis.

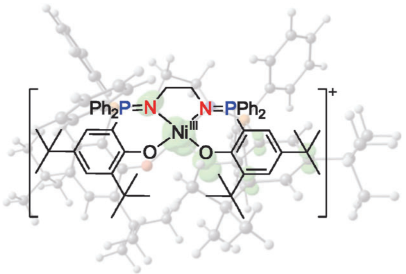
The coupling reaction of *N*-phenoxyacetamides with *N*-tosylhydrazones or diazoesters proceeds through Rh^{III}-catalyzed C—H bond activation. *ortho*-Alkenyl phenols are obtained in good yields and with excellent regio- and stereoselectivity.

Synthetic Methods

F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang, J. Wang* **1364 – 1367**

Rhodium(III)-Catalyzed *ortho* Alkenylation of *N*-Phenoxyacetamides with *N*-Tosylhydrazones or Diazoesters through C—H Activation

---

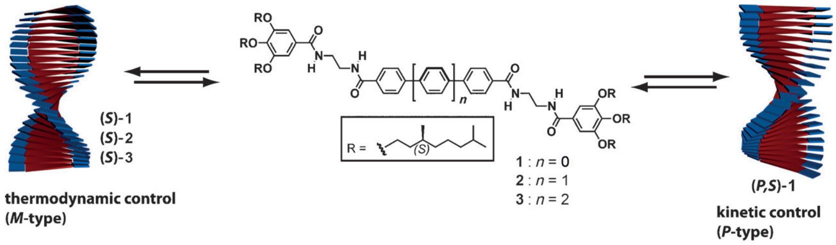


P = N does not equal C = N: A rare tetracoordinated Ni^{III} complex is obtained in the one-electron oxidation of a nickel(II) complex containing a novel phosphasalen ligand. The metal center as the oxidation site, and not the ligand as is the case for nickel salen complexes, is demonstrated by various techniques such as X-ray diffraction, EPR spectrocopy, and DFT calculations (see picture).

Nickel(III) Complexes

T.-P.-A. Cao, G. Nocton, L. Ricard, X. F. Le Goff, A. Auffrant* **1368 – 1372**

A Tetracoordinated Phosphasalen Nickel(III) Complex



Twist of fate: The helical organization of oligo-*p*-phenylene-based organogelators has been investigated spectroscopically. Whilst OPPs **2** and **3** self-assemble into left-handed helices, an inversion of the supramolecular helicity of **1** occurs depending on the formation conditions because of the atropisomerism of the biphenyl central unit.

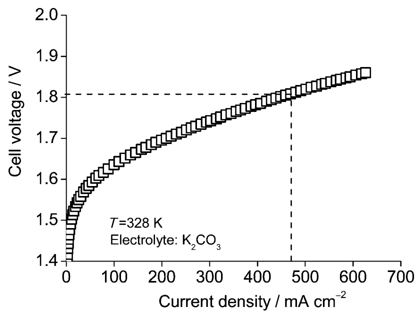
Helical Structures

F. Aparicio, B. Nieto-Ortega, F. Nájera, F. J. Ramírez, J. T. López Navarrete,* J. Casado,* L. Sánchez* **1373 – 1377**

Inversion of Supramolecular Helicity in Oligo-*p*-phenylene-Based Supramolecular Polymers: Influence of Molecular Atropisomerism

---

Relieving the precious of work: An alkaline membrane water electrolysis system containing low-cost transition-metal catalysts and an anion exchange membrane has a cell potential of 1.81 V at 470 mA cm^{-2} and 328 K in K_2CO_3, similar to that with platinum-group-metal catalysts. This system is durable and very efficient during transitory regimes allowing production of hydrogen from renewable sources.



Hydrogen Production

C. C. Pavel, F. Cecconi, C. Emiliani, S. Santiccioli, A. Scaffidi, S. Catanorchi, M. Comotti* **1378 – 1381**

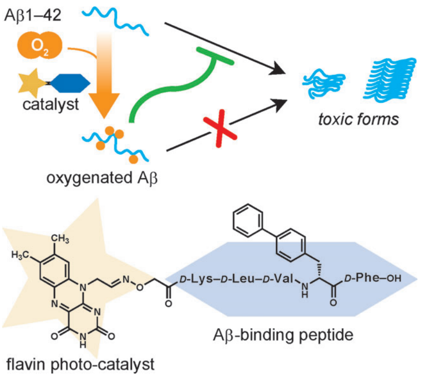
Highly Efficient Platinum Group Metal Free Based Membrane-Electrode Assembly for Anion Exchange Membrane Water Electrolysis

Alzheimer's Disease

A. Taniguchi, D. Sasaki, A. Shiohara, T. Iwatsubo, T. Tomita, Y. Sohma,* M. Kanai* **1382 – 1385**

Attenuation of the Aggregation and Neurotoxicity of Amyloid-β Peptides by Catalytic Photooxygenation

Light makes right: Riboflavin-catalyzed photooxygenation of amyloid-β peptide (Aβ) 1–42 occurred in well-defined positions under physiologically relevant conditions. Selective, cell-compatible photooxygenation of Aβ1–42 by the flavin catalyst attached to an Aβ-binding peptide markedly decreased aggregation and neurotoxicity of Aβ; the native Aβ was even switched from a pathogen to an aggregation inhibitor.

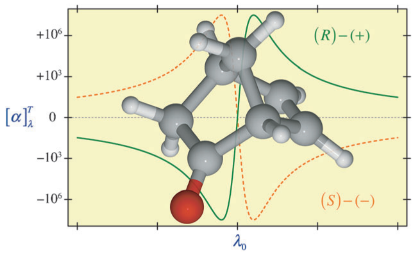


Chiroptical Effects

P. Lahiri, K. B. Wiberg, P. H. Vaccaro,* M. Caricato, T. D. Crawford **1386 – 1389**

Large Solvation Effect in the Optical Rotatory Dispersion of Norbornenone

Solvation and dispersive optical activity: The particularly large specific optical rotation of (1*R*,4*R*)-norbornenone has been probed under solvated and isolated (vapor-phase) conditions. The pronounced influence that solvent degrees of freedom exert upon intrinsic chiroptical properties could therefore be documented.



DOI: 10.1002/anie.201310367

Flashback: 50 Years Ago . . .

Defensive substances was the topic of a Review by H. Schildknecht. In this case, the substances were the compounds used for defensive secretion by arthropods, including beetles, earwigs, and millipedes. Analysis of the defensive substances showed them to contain quinones, carboxylic acids, and aromatic aldehydes.

Rolf Huisgen reported his latest results on 1,3-dipolar cycloaddition reactions in two Communications, including the reactions of either azlactones (oxazolones) or mesoionic compounds as 1,3-dipoles in the synthesis of functionalized pyrroles. He also summarized kinetic investigations into the valence tautomerism of cyclooctatetraene in a Review.

Ernst Otto Fischer, who shared the 1973 Nobel Prize in Chemistry with Geoffrey Wilkinson, also published two Communications—on the topic of dicyclopentadienyl complexes. The first report was on the synthesis of dicyclopentadienyleuropium by reacting metallic europium with cycopentadiene in liquid ammonia, and the second dealt with the reaction of $[C_5H_5MoC_6H_6(CO)]PF_6$ with hydride ions to form the π complex $C_5H_5MoC_6H_5$. For an account of the history of sandwich complexes, see *Angew. Chem. Int. Ed.* **2012**, *124*, 6052–6058.

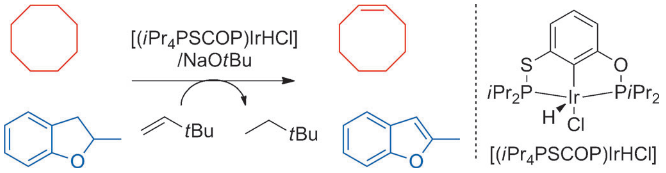
Heinz Staab reported the synthesis of the hitherto elusive formyl chloride on a preparative scale by the reaction of 1-formylimidazole with HCl at −60°C in chloroform. The synthesis is particularly practical as the imidazolium chloride byproduct precipitates from the solution and can be removed by filtration.

Read more in Issue 2/1964.

Iridium Catalysis

W. Yao, Y. Zhang, X. Jia, Z. Huang* ________ 1390 – 1394

Selective Catalytic Transfer Dehydrogenation of Alkanes and Heterocycles by an Iridium Pincer Complex

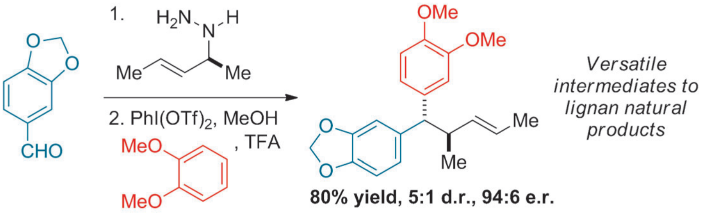


With just a pinch of iridium: A new PSCOP-pincer Ir complex exhibits unprecedented activity for the catalytic transfer dehydrogenation of cyclic and linear alkanes. The system effects regioselective dehydrogenation of linear alkanes to α-olefins under rather mild conditions. The Ir complex can be used in the selective catalytic dehydrogenation of a wide range of O- and N-heterocycles.

Natural Product Synthesis

J. C. T. Reddel, K. E. Lutz, A. B. Diagne, R. J. Thomson* ________ 1395 – 1398

Stereocontrolled Syntheses of Tetralone- and Naphthyl-Type Lignans by a One-Pot Oxidative [3,3] Rearrangement/Friedel–Crafts Arylation

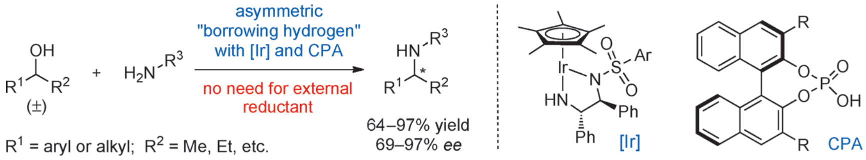


Cascade process: A two-step three-component cascade process that consists of an oxidative [3,3] sigmatropic rearrangement and a Friedel–Crafts arylation has been developed. This stereoselective fragment-coupling cascade sequence provides benzhydryl-type products that are versatile intermediates for the stereocontrolled synthesis of lignan natural products. Tf = trifluoromethylsulfonyl, TFA = trifluoroacetic acid.

Asymmetric Catalysis

Y. Zhang, C.-S. Lim, D. S. B. Sim, H.-J. Pan, Y. Zhao* ________ 1399 – 1403

Catalytic Enantioselective Amination of Alcohols by the Use of Borrowing Hydrogen Methodology: Cooperative Catalysis by Iridium and a Chiral Phosphoric Acid



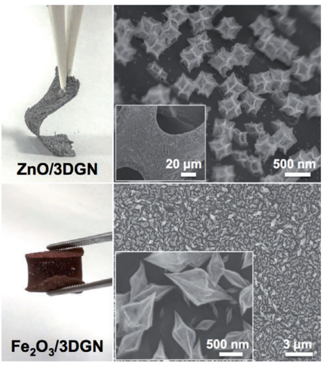
Donation to a good cause: A wide range of chiral amines were obtained in high yield with good enantioselectivity by the catalytic amination of alcohols without the use of an external reductant (the alcohol substrate served as the H_2 donor; see scheme). Cooperative catalysis by an iridium complex and a chiral phosphoric acid proved key to the high reactivity and selectivity of this system.

Graphene Composites

X. Cao, B. Zheng, X. Rui, W. Shi, Q. Yan, H. Zhang* ________ 1404 – 1409

Metal Oxide-Coated Three-Dimensional Graphene Prepared by the Use of Metal–Organic Frameworks as Precursors

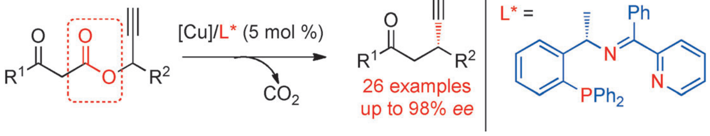
Flexible method, flexible materials: In a simple method for the preparation of metal-oxide-coated 3D graphene composites, metal–organic frameworks that served as precursors of the metal oxides were synthesized on 3D graphene networks (3DGNs), and the metal oxide/3DGN composites were then obtained by a two-step annealing process. ZnO/3DGN and Fe_2O_3/3DGN (see picture) were tested successfully in a photocatalytic reaction and a lithium-ion battery.



Synthetic Methods

F.-L. Zhu, Y. Zou, D.-Y. Zhang, Y.-H. Wang,
X.-H. Hu, S. Chen, J. Xu,*
X.-P. Hu* ———————— **1410 – 1414**

Enantioselective Copper-Catalyzed Decarboxylative Propargylic Alkylation of Propargyl β-Ketoesters with a Chiral Ketimine P,N,N-Ligand

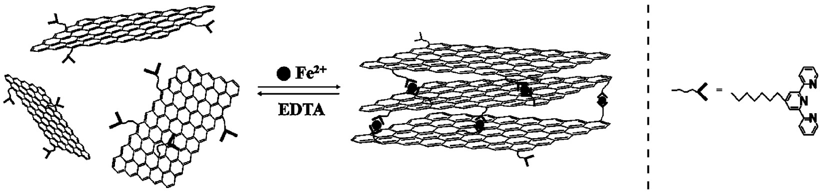


Treatment of propargyl β-ketoesters with a catalyst, prepared in situ from $[Cu(CH_3CN)_4]BF_4$ and a newly developed chiral tridentate ketimine P,N,N-ligand under mild reaction conditions, generates β-ethynyl ketones in good yields and with high enantioselectivities. Pregeneration of ketone enolates is not required and thus the reaction represents the first enantioselective copper-catalyzed decarboxylative propargylic alkylation.

Electrode Materials

S. Song, Y. Xue, L. Feng,* H. Elbatal,
P. Wang, C. N. Moorefield,
G. R. Newkome, L. Dai* —— **1415 – 1419**

Reversible Self-Assembly of Terpyridine-Functionalized Graphene Oxide for Energy Conversion

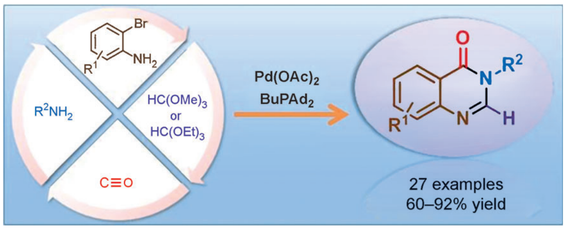


Held together by (cleavable) iron chains: Terpyridine-functionalized graphene oxide was prepared for self-assembly into 3D architectures with various metal ions (see picture; EDTA = ethylenediaminetetraacetic acid). The assemblies showed significantly improved electroactivities for energy conversion and storage, in particular as electrode materials for the oxygen reduction reaction (ORR), photocurrent generation, and supercapacitance.

Multicomponent Reactions

L. He, H. Li, H. Neumann, M. Beller,*
X.-F. Wu* ———————— **1420 – 1424**

Highly Efficient Four-Component Synthesis of 4(3*H*)-Quinazolinones: Palladium-Catalyzed Carbonylative Coupling Reactions

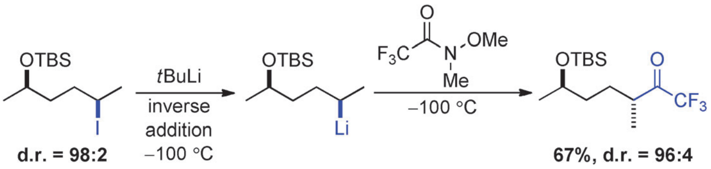


On all fours: A palladium-catalyzed four-component carbonylative coupling system for the synthesis of the title compounds in a concise and convergent fashion has been developed (see scheme). Notably, the process tolerates the presence of various reactive functional groups and is very selective for quinazolinones. The method was used in the successful synthesis of the precursor for the bioactive dihydrorutaempine.

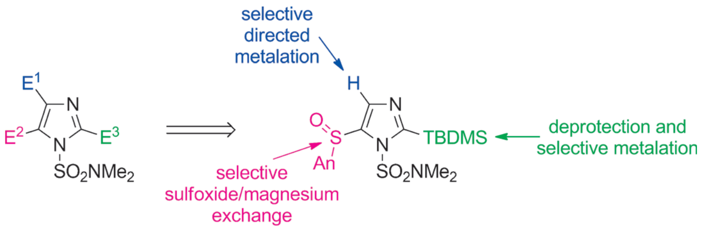
Chiral Alkyllithium Compounds

G. Dagousset, K. Moriya, R. Mose,
G. Berionni, K. Karaghiosoff,
P. Knochel* ———————— **1425 – 1429**

Diastereoselective Synthesis of Open-Chain Secondary Alkyllithium Compounds and Trapping Reactions with Electrophiles



Stereocontrol in acyclic systems: A practical stereoretentive iodine–lithium exchange served in the first general preparation of functionalized stereodefined acyclic secondary nonstabilized lithium reagents from the corresponding diastereomerically pure *syn* and *anti* alkyl iodides. Quenching with a range of electrophiles provides stereospecific access to both *syn* and *anti* acyclic alkyl derivatives with excellent diastereoselectivities (up to d.r. = 97:3).

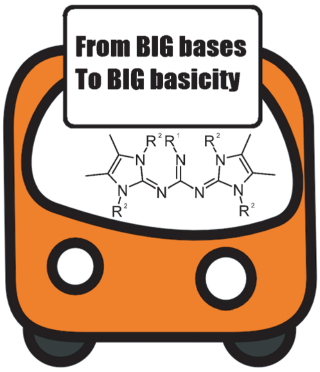


The successive regioselective functionalization of the imidazole scaffold can be realized by direct metalation with $\mathrm{TMPMgCl\cdot LiCl}$ and $\mathrm{TMP_2Zn\cdot 2\,MgCl\cdot 2\,LiCl}$ as well as by a sulfoxide/magnesium exchange triggered by $i\mathrm{PrMgCl\cdot LiCl}$ (see scheme, An = 4-methoxy-3,5-dimethylphenyl). The corresponding Mg and Zn intermediates have been quenched with a broad range of electrophiles, for example, aryl, alkenyl and allylic halides, acid chlorides, and aldehydes.

Heterocycle Functionalization

C. Sämann, E. Coya,
P. Knochel* ______ **1430 – 1434**

Full Functionalization of the Imidazole Scaffold by Selective Metalation and Sulfoxide/Magnesium Exchange

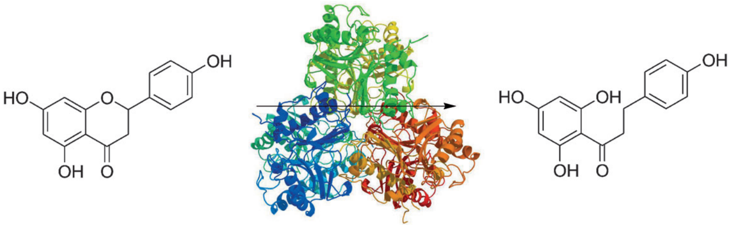


Think BIG: Probably the strongest organic non-phosphorus superbases, having $\mathrm{p}K_\alpha$ values of 26.1–29.3 in THF, are synthesized by combining imidazole and guanidine structural motifs to give *N*,*N*′-bis(imidazolyl)guanidine bases (termed BIG bases). Their basicity was determined in solution by UV/Vis spectroscopy and in the gas phase by computational methods. The innovative design opens possibilities for the broader application of organosuperbases.

Organosuperbases

K. Vazdar, R. Kunetskiy, J. Saame,
K. Kaupmees, I. Leito,*
U. Jahn* ______ **1435 – 1438**

Very Strong Organosuperbases Formed by Combining Imidazole and Guanidine Bases: Synthesis, Structure, and Basicity



The biocatalytic metabolic pathway for the degradation of flavonoids of *Eubacterium ramulus* was identified. A chalcone isomerase and an enoate reductase were successfully cloned, subsequently expressed in *E. coli*, and used under aerobic conditions, although *E. ramulus* is a strictly anaerobic bacterium. The engineered *E. coli* strain that expresses both enzymes was used for the conversion of several flavanones.

Biocatalysis

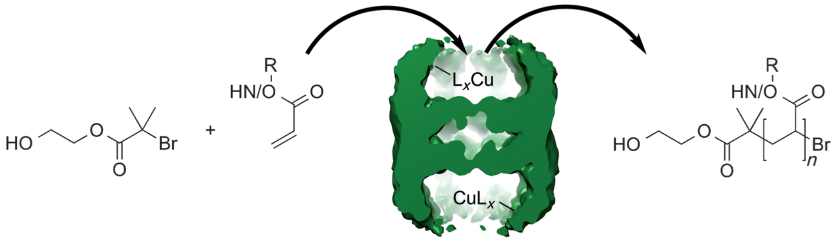
M. Gall, M. Thomsen, C. Peters,
I. V. Pavlidis, P. Jonczyk, P. P. Grünert,
S. Beutel, T. Scheper, E. Gross, M. Backes,
T. Geißler, J. P. Ley,* J.-M. Hilmer,
G. Krammer, G. J. Palm, W. Hinrichs,
U. T. Bornscheuer* ______ **1439 – 1442**

Enzymatic Conversion of Flavonoids using Bacterial Chalcone Isomerase and Enoate Reductase

Nanoreactor

K. Renggli, M. G. Nussbaumer, R. Urbani, T. Pfohl, N. Bruns* ———— **1443 – 1447**

A Chaperonin as Protein Nanoreactor for Atom-Transfer Radical Polymerization



Made in a protein: The group II chaperonin thermosome (THS) from the archaea *Thermoplasma acidophilum* is used as protein nanoreactor for atom-transfer radical polymerization. A copper catalyst was entrapped into the THS. The confined space within the nanoreactor favorably influences the polymerization of *N*-isopropyl acrylamide and poly(ethylene glycol) methyl ether acrylate.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

This article is available online free of charge (Open Access).

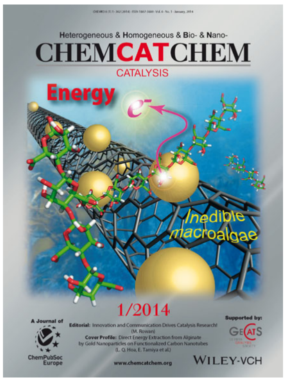
This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

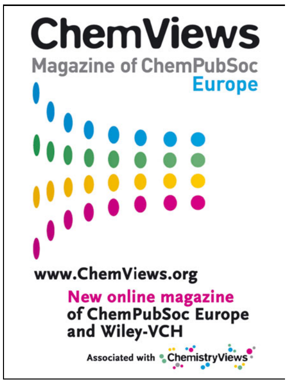
Check out these journals:

www.chemasianj.org



www.chemcatchem.org

www.chempluschem.org



www.chemviews.org