The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

*H. Ishikawa, M. Honma, Y. Hayashi**
One-Pot Synthesis of a DPP4 Inhibitor by a Four-Component Coupling Reaction Mediated by Diphenylprolinol Silyl Ether

*A. V. Zabula, S. N. Spisak, A. S. Filatov, A. Y. Rogachev, M. A. Petrukhina**
Strain-Releasing Trap for Highly Reactive Electrophiles: Structural Characterization of Bowl-Shaped Arenium Carbocations

*F. E. Zilly, J. P. Acevedo, W. Augustyniak, A. Deege, U. W. Häusig, M. T. Reetz**
Tuning a P450 Enzyme for Methane Oxidation

*H. C. S. Chan, J. Kendrick, F. J. J. Leusen**
The Tale of Molecule VI, a Benchmark Sulfonimide for Crystal-Structure Prediction: Are Its Polymorphs Predictable?

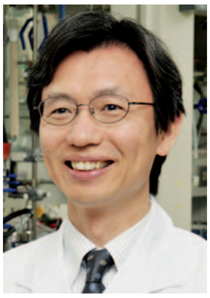
*A. Nagy, J. Fulara, I. Garkusha, J. P. Maier**
On the Benzylium/Tropylium-Ion Dichotomy: Electronic Absorption Spectra in Neon Matrices

*R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott, V. K. Aggarwal**
Enantioselective Construction of Quaternary Stereogenic Centers from Tertiary Boronic Esters: Methodology and Applications

X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao**
Selective Formation of Imines by Aerobic Photocatalytic Oxidation of Amines on TiO_2

*K. Press, Ad Cohen, I. Goldberg, V. Venditto, M. Mazzeo, M. Kol**
Salalen–Titanium Complexes for the Highly Isospecific Polymerization of 1-Hexene and Propylene

Author Profile



“When I wake up I do some simple stretching exercises for a little while before having breakfast. A good work day begins with a ‘good morning’ …”
This and more about Zhaomin Hou can be found on page 2430.

Obituaries

Dudley H. Williams

Books

C–H Activation

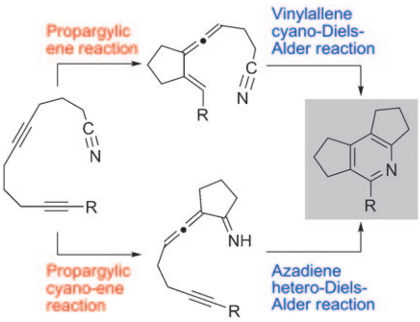
Jin-Quan Yu, Zhangjie Shi

Highlights

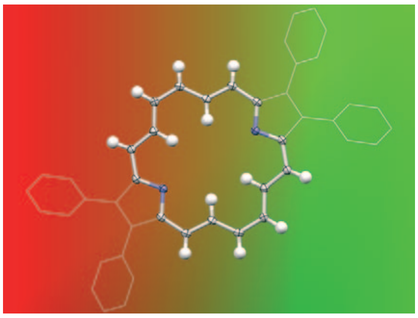
[2+2+2] Cycloaddition

Metal-Free Cyclotrimerization for the De Novo Synthesis of Pyridines

Two routes, one destination: The metal-free, uncatalyzed [2+2+2] cycloaddition of cyanodiynes can proceed through two different reaction cascades, both yielding pyridines as products (see scheme). The unactivated cyano group can act either as an enophile in Alder–ene or as a dienophile in hetero-Diels–Alder reactions—both of which are rather uncommon for this well-known functional group.



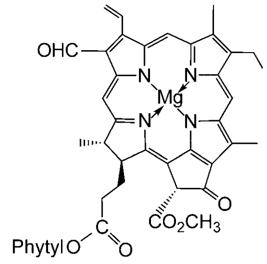
Porphyrinoids



“**Porphyrins really are the [18]annulenes of nature**”—This is the title of a report dealing with a new macrocycle (see structure; gray C, white H, blue N), which can be considered as either a porphyrin or an [18]annulene. The spectroscopic data prove the aromatic and porphyrinoid character of the new compound, and support the simple concept of a $(4n+2)\pi$ main conjugation pathway as a key criterion for porphyrinoid Hückel aromaticity.

Chlorophyll

A bacterium sees red: Chlorophyll f (Chl f), a tetrapyrrole displaying unprecedented red-shifted absorption bands, was discovered in cyanobacteria and its structure was deduced by spectroscopic means. The new chromophore of Chl f is likely a result of biological adaptation and biochemical optimization in bacteria in their struggle for survival. It is a sign of life’s constant demand for energy obtained from sunlight through photosynthesis.

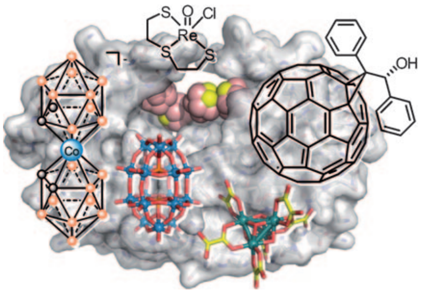


Chl f

Minireviews

Enzyme Inhibitors

Creativity in demand: Enzyme inhibitor scaffolds ranging from typical small organic molecules to inorganic clusters and even to polymers demonstrate that the whole repertoire of organic, inorganic, and macromolecular chemistry can be used to meet the challenge of specific molecular recognition in complex biological systems.



For the USA and Canada:
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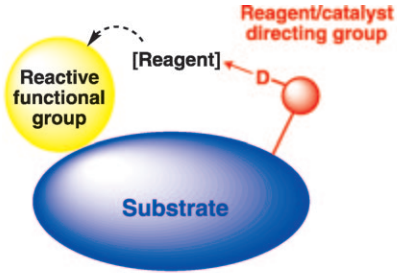
Reviews

Directed Reactions

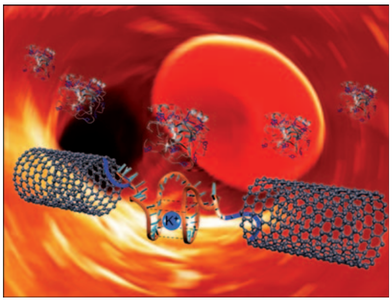
Controlling the outcome: Directing groups have been widely used in recent years to control chemical reactions. In cases when the existing functional group within a substrate is unsuited to achieve an efficient intramolecular reagent/catalyst delivery, the specific introduction of an appropriately designed removable reagent-directing group can be used to address this problem (see scheme).



Communications

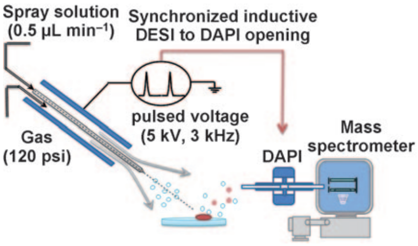
Biosensors

Filling in the gap: Label-free, real-time electrical detection of proteins is achieved with high selectivity and real single-molecule sensitivity by using aptamer-functionalized molecular electronic devices with single-walled carbon nanotubes as point contacts.



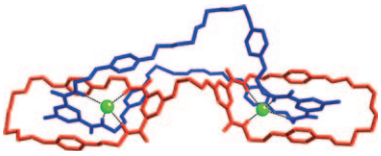
Mass Spectrometry

Well-orchestrated: A new mass spectrometry protocol (see picture) synchronizes microdroplet creation, nebulizing gas pulsing, and DAPI interface opening. A number of advances result: 100-fold improved detection limit, simultaneous positive and negative ion spectra, and decreased spray volumes in desorption electrospray ionization (DESI).



Catenanes

Chloride, you're nicked! A novel handcuff catenane was prepared by anion templation and π–π stacking interactions. In addition, the first crystal structure determination of such a catenane is reported (see picture).

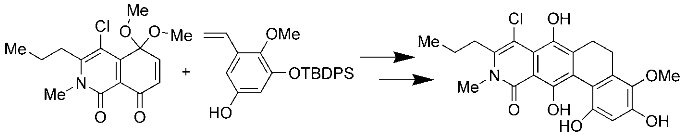


Contents

Natural Product Synthesis

D. L. Sloman, B. Mitasev, S. S. Scully, J. A. Beutler, J. A. Porco, Jr.* **2511 – 2515**

Synthesis and Biological Evaluation of ABCD Ring Fragments of the Kibdelones



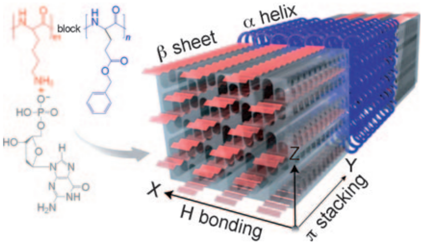
Arylation goes platinum: The synthesis of the ABCD ring fragments of the kibdelones has been achieved through a novel Pt^{IV}-catalyzed arylation of a quinone monoketal followed by photocyclization (see scheme). Biological evaluation in the NCI 60-cell screen revealed that the kibdelone ABCD ring analogues were about 2000 times less active than kibdelones B and C, suggesting that the tetrahydroxanthone structure of the kibdelones is crucial for cytotoxicity.

Supramolecular Chemistry

N. Houbenov,* J. S. Haataja, H. Iatrou, N. Hadjichristidis, J. Ruokolainen, C. F. J. Faul,* O. Ikkala* **2516 – 2520**

Self-Assembled Polymeric Supramolecular Frameworks

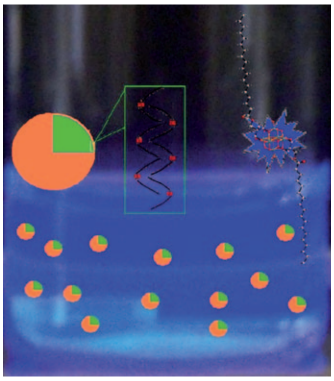
Within the framework: Ionic complexation of diblock copolypeptide poly(γ-benzyl-L-glutamate)-*block*-poly(L-lysine) (PBLG-*b*-PLL) with 2′-deoxyguanosine 5′-monophosphate (dGMP, gray) generates a polymeric supramolecular framework solid with self-assembled cages based on two orthogonal shape-persistent motifs: PBLG α helices (blue) and PLL β sheets (red), which in turn are held together by shape-persistent hydrogen-bonded G-ribbons.



Polyoxometalates

P. Yin, P. Wu, Z. Xiao, D. Li, E. Bitterlich, J. Zhang, P. Cheng, D. V. Vezenov, T. Liu,* Y. Wei* **2521 – 2525**

A Double-Tailed Fluorescent Surfactant with a Hexavanadate Cluster as the Head Group



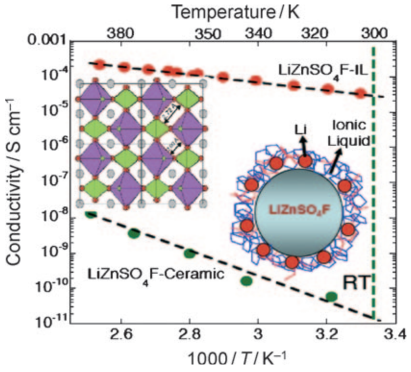
Blue rinse: A hybrid surfactant that comprises a hexavanadate cluster and two C_{18} alkyl chains shows unexpected blue luminescence (see picture). The luminescence arises from the interaction between the counterions and the hexavanadate clusters, and varies with the type of counterions. This behavior was confirmed by studying the self-assembly of the hybrids with various counterions in different solvents.

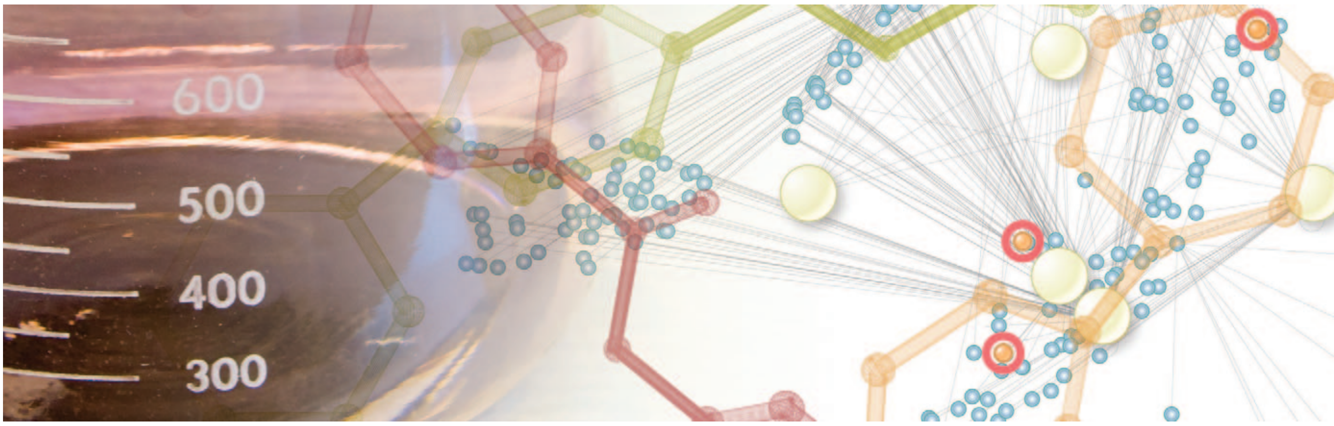
Solid Electrolytes

P. Barpanda, J.-N. Chotard, C. Delacourt, M. Reynaud, Y. Filinchuk, M. Armand, M. Deschamps, J.-M. Tarascon* **2526 – 2531**

$LiZnSO_4F$ Made in an Ionic Liquid: A Ceramic Electrolyte Composite for Solid-State Lithium Batteries

Wrapped in IL: Solid electrolytes are key for safer lithium batteries. The novel $LiZnSO_4F$ fluorosulfate prepared by an ionic-liquid-assisted synthesis delivers high ionic conductivity at room temperature (see picture). The lithium-containing ionic-liquid layer tailors the ionic conductivity of inorganic composites by a surface effect. This finding can be useful in designing solid electrolytes with high ionic conductivity.





Call for nominations 2011

Novartis Early Career Award in Organic Chemistry

The Novartis Early Career Award in Organic Chemistry was created to mark Novartis' commitment to science and innovation in chemistry. The award is presented annually to outstanding scientists who are active in the areas of organic or bioorganic chemistry in the broadest sense, and is intended to provide support for investigators early in their career. We are now seeking nominations of candidates who began their independent academic career in or after 2001, from all academic institutions. The nominations will be assessed by Novartis senior scientists together with leading external experts in the field. Two winners will be identified, each of whom will receive an unrestricted research grant. Deadline for the submission of nominations, including a letter of recommendation and a curriculum vitae, is April 30, 2011.*

Past Awardees: Karl Gademann, University of Basel (2010); Jin-Quan Yu, The Scripps Research Institute (2010); Magnus Rueping, RWTH Aachen University (2009); Christopher J. Chang, University of California, Berkeley (2009); Matthew J. Gaunt, University of Cambridge (2008); Jeffrey S. Johnson, University of North Carolina at Chapel Hill (2008); Lukas J. Goossen, Technische Universität Kaiserslautern (2007); Anna K. Mapp, University of Michigan Ann Arbor (2007); Armido Studer, University of Münster (2006); F Dean Toste, University of California Berkeley (2006); Benjamin List, Max-Planck-Institute Mülheim an der Ruhr (2005); Dirk Trauner, University of California Berkeley (2005); J Stephen Clark, University of Nottingham (2004); Jonathan P Clayden, University of Manchester (2004); Thorsten Bach, Technical University of Munich (2003); Bernhard Breit, University of Freiburg (2002); Thomas Carell, University of Munich (2002).

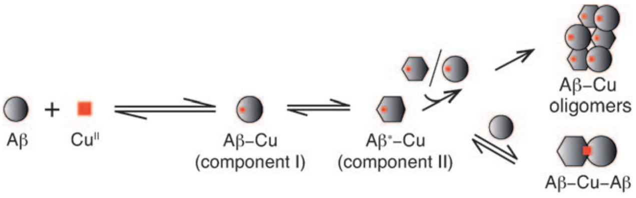
*Nominations should be sent to Dr. Gurdip Bhalay, Novartis Institutes for Biomedical Research, Horsham Research Centre, Horsham, West Sussex, UK; e-mail: gurdip.bhalay@novartis.com.

NOVARTIS

Amyloid β Peptides

J. T. Pedersen, K. Teilum,
N. H. H. Heegaard, J. Østergaard,
H.-W. Adolph,
L. Hemmingsen* ——— **2532 – 2535**

Rapid Formation of a Preoligomeric Peptide–Metal–Peptide Complex Following Copper(II) Binding to Amyloid β Peptides



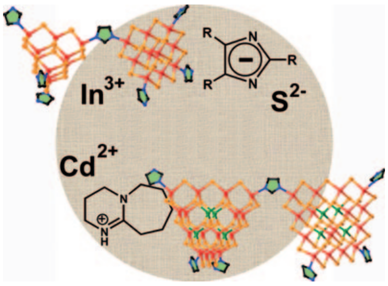
Cu^{II} connects peptides: The mechanism of binding of Cu^{II} to amyloid β peptides (Aβ) implicated in Alzheimer's disease was elucidated by stopped-flow spectroscopy, NMR relaxation, and simulation of the kinetics on the millisecond timescale. Two monomeric Cu–Aβ species and a dimeric Aβ–Cu–Aβ species were identified (see picture). Aberrant aggregation apparently occurs from the monomeric species.

3D Covalent Arrays

T. Wu, R. Khazhakyan, L. Wang, X. Bu,
S.-T. Zheng, V. Chau,
P. Feng* ——— **2536 – 2539**

Three-Dimensional Covalent Co-Assembly between Inorganic Supertetrahedral Clusters and Imidazolates

An unlikely marriage between chalcogenide clusters and imidazolates leads to a family of 3D covalent arrays of supertetrahedral chalcogenide clusters and imidazolate ligands (see picture). These are the first examples of supertetrahedral clusters being assembled with anionic ligands.

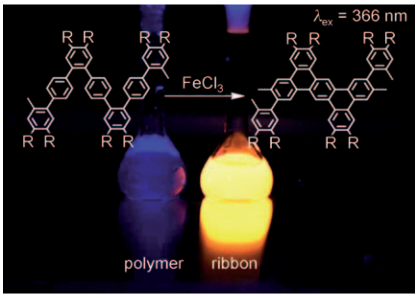


Nanoribbon Synthesis

L. Dössel, L. Gherghel, X. Feng,
K. Müllen* ——— **2540 – 2543**

Graphene Nanoribbons by Chemists: Nanometer-Sized, Soluble, and Defect-Free

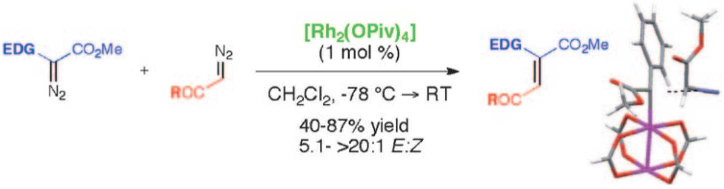
Closing the zipper: A method for the bottom-up organic synthesis of defect-free graphene nanoribbons in solution has been developed. Polyphenylene precursors with a unique kinked backbone enabled full cyclodehydrogenation in a single reaction step by an intramolecular Scholl reaction with $FeCl_3$ (see scheme).



Diazo Cross-Coupling

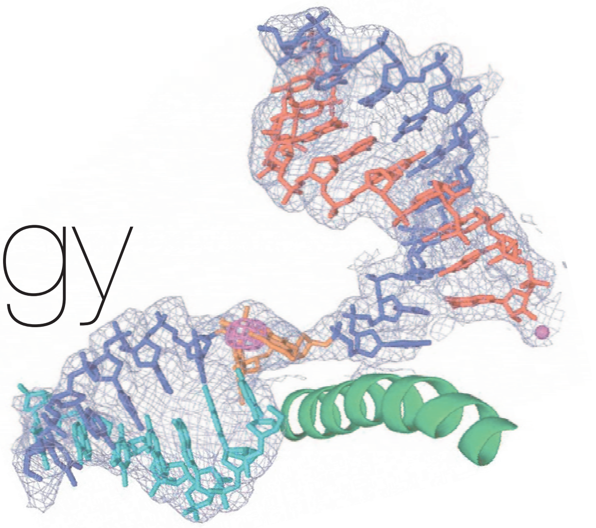
J. H. Hansen, B. T. Parr, P. Pelphrey,
Q. Jin, J. Autschbach,
H. M. L. Davies* ——— **2544 – 2548**

Rhodium(II)-Catalyzed Cross-Coupling of Diazo Compounds



Nothing left to chance: A convenient protocol for selective cross-coupling of diazo compounds for the convergent synthesis of alkenes was developed (see scheme; EDG = aryl, heteroaryl, vinyl; R = O-alkyl, aryl). The selectivity control elements were identified by ReactIR and DFT calculations and provide a framework for the design of viable diazo coupling reactions.

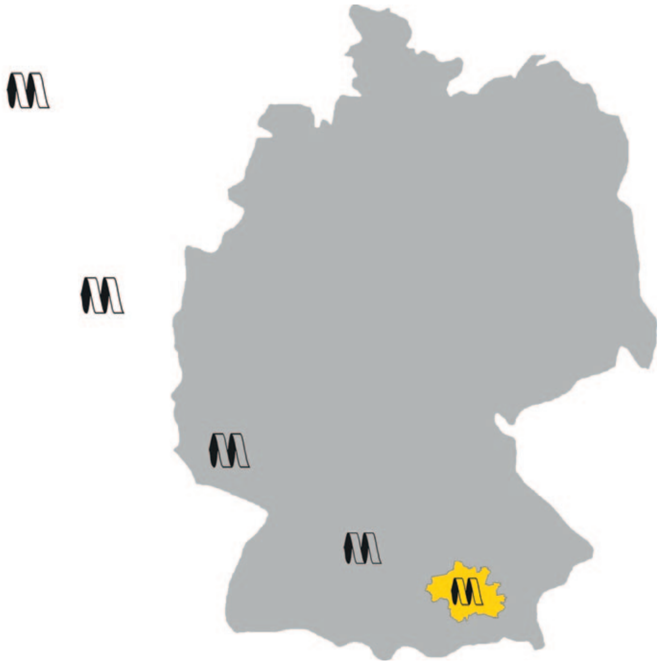
CIPS^M-Fest of Chemical Biology



Munich, Germany,
September 15th to 16th 2011

Confirmed Speakers:

Shankar Balasubramanian,	Dept. of Chemistry, Uni. of Cambridge UK
Chris Chang,	Dept. of Chemistry, UC Berkeley
Jon Clardy,	Dept. of Chemistry & Chem. Biology, Harvard Med. School, Broad Inst., Harvard Uni.
Benjamin F. Cravatt III,	Dept. of Chemical Physiology, The Skaggs Inst., The Scripps Res. Inst.
François Diederich,	ETH Zürich, Lab. of Organic Chemistry
Wilfred A. van der Donk,	The Dept. of Chemistry, Uni. of Illinois at Urbana-Champaign
Michael Famulok,	Rheinische Friedrich-Wilhelms-Uni. Bonn, Lab. of Chemical Biology
Itaru Hamachi,	Dept. of Synthetic Chemistry and Biological Chemistry, Kyoto Uni.
Julius Rebek,	The Skaggs Inst. for Chemical Biology, The Scripps La Jolla
Brian L. Roth,	Pharmacology Dept., Uni. North Carolina at Chapel Hill
Peter G. Schultz,	The Scripps Research Inst., La Jolla
Mitsuhiko Shionoya,	Dept. Chemical Biology, Uni. of Tokyo
Hiroshi Sugiyama,	Dept. Chemical Biology, Kyoto Uni.
Christopher T. Walsh,	Harvard Medical School, Dept. Chemistry & Chemical Biology, Harvard Uni.



Location: Buchner Lecture Hall,
Department of Chemistry,
Ludwig Maximilians University Munich,
Feodor-Lynen-Str.,
81377 Munich

Registration and further details under: www.cipsm.de/fest

CIPSM CENTER FOR INTEGRATED PROTEIN SCIENCE MUNICH

in cooperation with

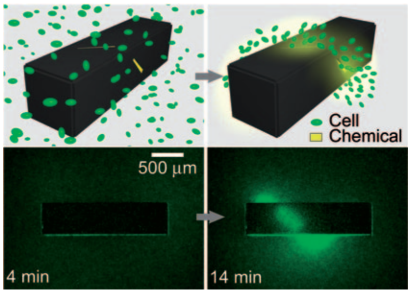
Bayer HealthCare

3D Chemical Scaffolds

Y. V. Kalinin, J. S. Randhawa,
D. H. Gracias* ______ 2549 – 2553

Three-Dimensional Chemical Patterns for Cellular Self-Organization

Falling into line: A method for the precise generation of durable 3D chemical patterns within stationary media was used to direct the chemotactic self-organization of living cells. A container with carefully positioned slits, through which a chemoattractant (yellow) can diffuse, controls the self-organization of *Escherichia coli* cells (green ellipsoids) expressing green fluorescent protein into a helical pattern (see fluorescence images).

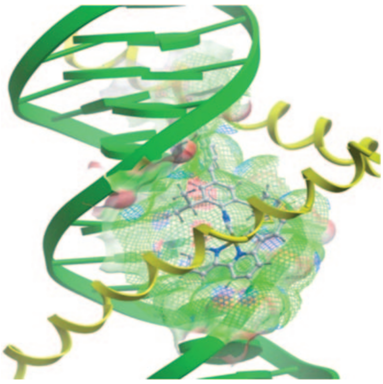


DNA Recognition

P. Wang, C.-H. Leung, D.-L. Ma,
R. W.-Y. Sun, S.-C. Yan,
Q.-S. Chen, C.-M. Che* ______ 2554 – 2558

Specific Blocking of CREB/DNA Binding by Cyclometalated Platinum(II) Complexes

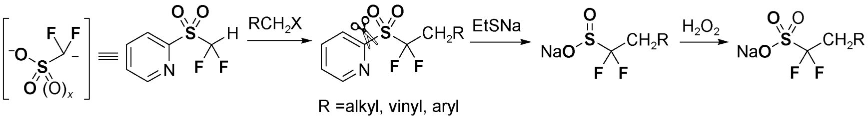
In the groove: The unique major-groove-binding properties of a Pt^{II} complex can be used to block the interaction between the transcription factor CREB and DNA (see picture). Variation of the ligands around the Pt^{II} center changes the DNA binding mode and results in specific gene regulators with superior potency and selectivity.



Fluorinated Sulfonates

G. K. S. Prakash,* C. Ni, F. Wang, J. Hu,
G. A. Olah* ______ 2559 – 2563

From Difluoromethyl 2-Pyridyl Sulfone to Difluorinated Sulfonates: A Protocol for Nucleophilic Difluoro(sulfonato)methylation

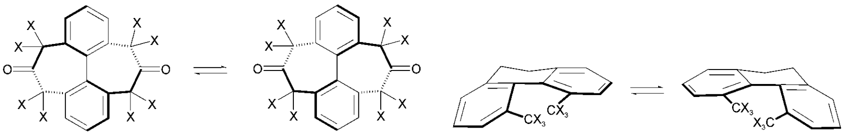


An efficient method for the synthesis of alkyl α,α-difluorosulfonates has been developed. The selection of the 2-pyridyl group as the aryl substituent on the sulfone is critically important for the success of this transformation (see scheme). The synthetic application of fluorinated sulfones is extended and a unique solution is provided for a long-standing challenge in nucleophilic difluoro(sulfonato)methylation reactions.

Deuterium Isotope Effects

D. J. O'Leary,* P. R. Rablen,
M. P. Meyer* ______ 2564 – 2567

On the Origin of Conformational Kinetic Isotope Effects

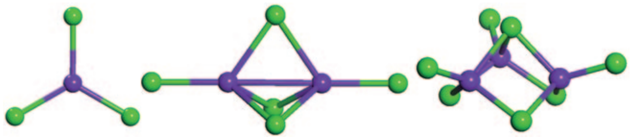


1: k_H/k_D controlled by vibrational entropy and enthalpy

2: k_H/k_D controlled by zero-point energy

Neatly dissected: The computed conformational kinetic isotope effects (KIEs) for biphenyls **1** and **2** (X = D or H) are in good agreement with experimental values and have been partitioned according to the Bigeleisen–Mayer and $\Delta H/\Delta S$ approaches. In [D$_8$]-**1** the KIE is dominated by a normal entropic contribution which overshadows an enthalpic contribution determined by H_{vib} and not H_{ZPE}. The inverse isotope effect in [D$_6$]-**2** is governed by an enthalpic zero-point energy term (H_{ZPE}) working against a normal entropic contribution.

Magnetic Superhalogens

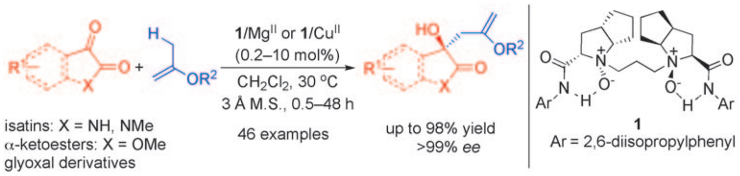


Magnetic superoxidizers: A series of magnetic superhalogens formed of $(Mn_xCl_{2x+1})^-$ units has been discovered (see picture; Mn violet, Cl green). The series was characterized by photoelectron spectroscopy, mass spectrometry, and theoretical studies.

M. M. Wu, H. Wang, Y. J. Ko, Q. Wang, Q. Sun, B. Kiran, A. K. Kandalam, K. H. Bowen,* P. Jena* ____ **2568 – 2572**

Manganese-Based Magnetic Superhalogens

Asymmetric Catalysis



A familiar ring: An efficient catalytic asymmetric hetero-ene reaction of 1,2-dicarbonyl compounds (including isatins, α-ketoesters, and glyoxal derivatives) is described. The catalyst system derived from **1** can be used for a broad substrate scope and the corresponding products were obtained in good yield and excellent enantioselectivity. M.S. = molecular sieves.

K. Zheng, C. K. Yin, X. H. Liu, L. L. Lin, X. M. Feng* ____ **2573 – 2577**

Catalytic Asymmetric Addition of Alkyl Enol Ethers to 1,2-Dicarbonyl Compounds: Highly Enantioselective Synthesis of Substituted 3-Alkyl-3-Hydroxyoxindoles

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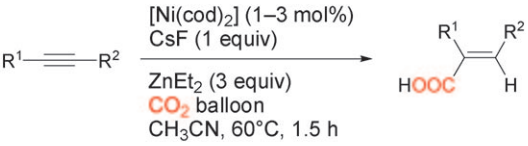
CO_2 Activation



Hydrocarboxylation of alkynes: The first example of nickel-catalyzed hydrozincation of alkynes that form stereodefined hydrocarboxylation products is presented (see scheme; cod = cycloocta-1,5-diene). This catalytic system is efficient for the activation of CO_2 and the three-component reaction produces products that could be converted into important oxindole or γ-butyrolactam derivatives.

S. Li, W. Yuan, S. Ma* ____ **2578 – 2582**

Highly Regio- and Stereoselective Three-Component Nickel-Catalyzed *syn*-Hydrocarboxylation of Alkynes with Diethyl Zinc and Carbon Dioxide

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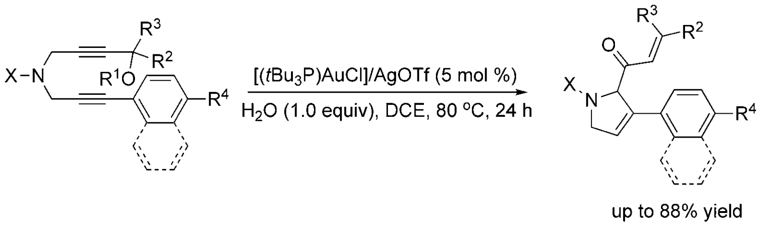
Gold Catalysis



A novel synthetic protocol for the preparation of the title compounds has been developed from a gold-catalyzed cycloisomerization of 1,6-diynes containing propargylic ester and arene–yne units. The corresponding nitrogen-containing five-membered heterocyclic compounds have been obtained in moderate to good yields (see scheme; DCE = 1,2-dichloroethane, Tf = triflate). A plausible reaction mechanism has been proposed on the basis of deuterium labeling experiments.

D.-H. Zhang, L.-F. Yao, Y. Wei, M. Shi* ____ **2583 – 2587**

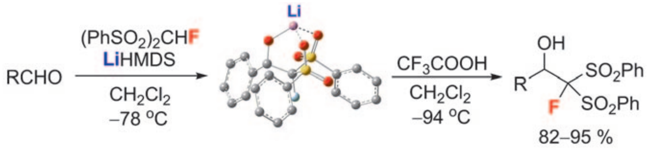
Gold(I)-Catalyzed Cycloisomerization of 1,6-Diynes: Synthesis of 2,3-Disubstituted 3-Pyrroline Derivatives

Contents

Fluoromethylation

X. Shen, L. Zhang, Y. Zhao, L. Zhu, G. Li, J. Hu* ______________ **2588 – 2592**

Nucleophilic Fluoromethylation of Aldehydes with Fluorobis(phenylsulfonyl)methane: The Importance of Strong Li–O Coordination and Fluorine Substitution for C–C Bond Formation

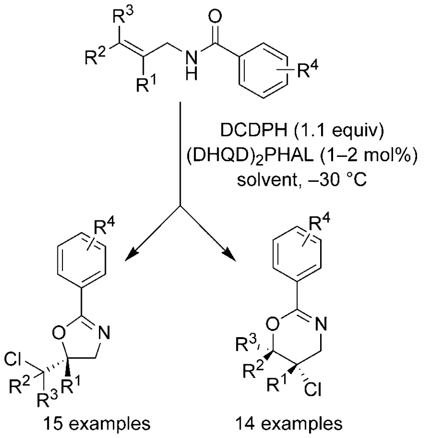


The tighter, the better! Fluorobis(phenylsulfonyl)methane reacts readily with aldehydes to give addition products in excellent yields (see scheme; LiHMDS = lithium hexamethyldisilazide), which is in sharp contrast to previous findings. Both strong Li–O coordination at low temperature and fluorine substitution play important roles in successful C–C bond formation.

Asymmetric Synthesis

A. Jaganathan, A. Garzan, D. C. Whitehead, R. J. Staples, B. Borhan* ______________ **2593 – 2596**

A Catalytic Asymmetric Chlorocyclization of Unsaturated Amides



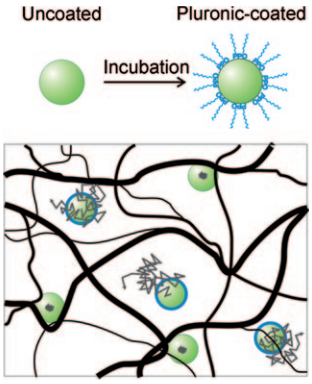
The asymmetric chlorocyclization of unsaturated amides catalyzed by $(DHQD)_2PHAL$ yields oxazoline and dihydrooxazine derivatives (see scheme). The reaction is operationally simple and employs 1–2 mol% of the commercially available $(DHQD)_2PHAL$ (hydroquinidine 1,4-phthalazinediyl diether) catalyst. Different substitution patterns of the olefin as well as aromatic and aliphatic olefin substituents are well tolerated. DCDPH = *N*,*N*-dichloro-5,5-diphenylhydantoin.

Drug Delivery

M. Yang, S. K. Lai, Y.-Y. Wang, W. Zhong, C. Happe, M. Zhang, J. Fu, J. Hanes* ______________ **2597 – 2600**

Biodegradable Nanoparticles Composed Entirely of Safe Materials that Rapidly Penetrate Human Mucus

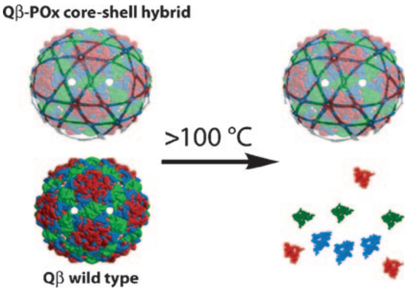
Slipping through: Pluronic molecules adsorb onto nanoparticle surfaces through their polypropylene oxide (PPO) segments with the flanking polyethylene glycol (PEG) segments forming a dense muco-inert brush (see picture; top). While uncoated particles are immobilized in mucus through adhesive interactions with mucus mesh elements, coated particles diffuse rapidly through spaces in the mucus mesh (bottom).



Polymer-Encased Nanoparticles

F. Manzenrieder, R. Luxenhofer, M. Retzlaff, R. Jordan, M. G. Finn* ______________ **2601 – 2605**

Stabilization of Virus-like Particles with Poly(2-oxazoline)s

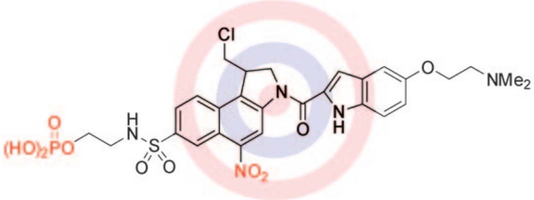


Wrap it up! Highly efficient copper-catalyzed click chemistry can cover virus-like particles with functionalized poly(2-oxazoline) chains without interparticle aggregation. The resulting core–shell structures are significantly more temperature-stable than the native protein particles.

Antitumor Agents

M. Tercel,* G. J. Atwell, S. Yang,
A. Ashoorzadeh, R. J. Stevenson,
K. J. Botting, Y. Gu, S. Y. Mehta,
W. A. Denny, W. R. Wilson,
F. B. Pruijn ______ **2606 – 2609**

Selective Treatment of Hypoxic Tumor Cells In Vivo: Phosphate Pre-Prodrugs of Nitro Analogues of the Duocarmycins

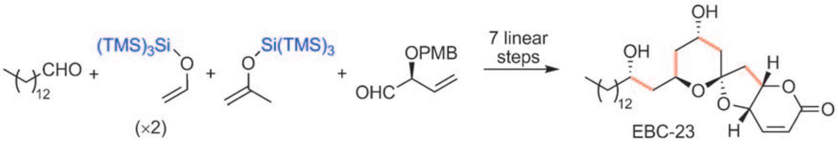


Hitting the hypoxic target: Combining a nitro prodrug with a water-soluble phosphate converts duocarmycin analogues from highly toxic DNA-alkylating agents to highly selective antitumor compounds. These prodrugs (see scheme) have outstanding activity against hypoxic tumor cells in vivo, cells which are usually considered the most resistant to conventional therapy.

Synthetic Methods

B. J. Albert, Y. Yamaoka,
H. Yamamoto* ______ **2610 – 2612**

Rapid Total Syntheses Utilizing "Supersilyl" Chemistry

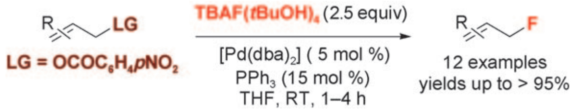


In short order: The shortest total syntheses of natural product EBC-23 (see scheme, PMB = *para*-methoxybenzyl, TMS = trimethylsilyl) and a polymethoxy-1-alkene to date have been accomplished in just ten total steps each from commercially available chemicals. The syntheses took advantage of highly diastereoselective supersilyl-directed cascade polyaldol reactions.

Catalytic Fluorination

C. Hollingworth, A. Hazari,
M. N. Hopkinson, M. Tredwell,
E. Benedetto, M. Huiban,
A. D. Gee, J. M. Brown,*
V. Gouverneur* ______ **2613 – 2617**

Palladium-Catalyzed Allylic Fluorination

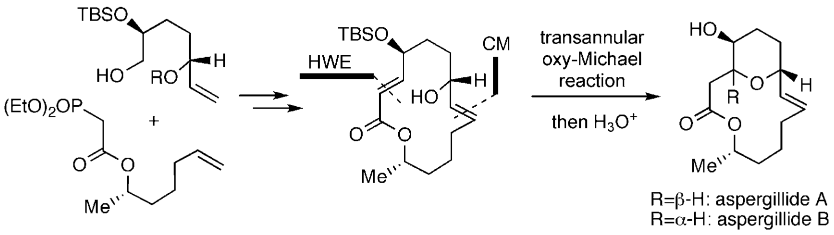


Mild and rapid: The title reaction is presented and its applicability to ^{18}F radiolabeling is demonstrated (see scheme; TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran, dba = dibenzylideneacetone). The use of *p*-nitrobenzoate as the leaving group is significant to the success of this catalytic organometallic fluorination process. A range of allylic fluorides were synthesized by this method.

Natural Product Synthesis

M. Kanematsu, M. Yoshida,
K. Shishido* ______ **2618 – 2620**

Total Synthesis of Aspergillide A and B Based on the Transannular Oxy-Michael Reaction



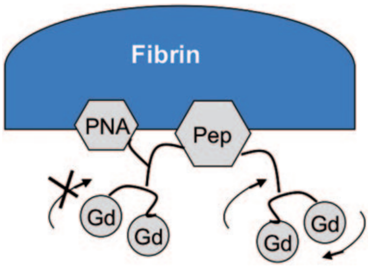
Keys to the kingdom: A highly efficient and diastereoselective transannular oxy-Michael reaction for the construction of the *syn*- and *anti*-tetrahydropyran units from a common 14-membered macrolactone is the key step for the total synthesis of aspergillide A and B (see scheme; CM = cross-metathesis, HWE = Horner–Wadsworth–Emmons, TBS = *tert*-butyldimethylsilyl).

Imaging Agents

Z. Zhang, A. F. Kolodziej, M. T. Greenfield,
P. Caravan* ______ 2621 – 2624

Heteroditopic Binding of Magnetic Resonance Contrast Agents for Increased Relaxivity

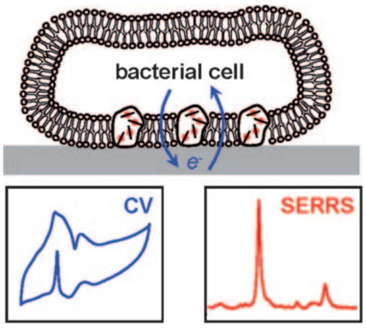
Kept within bounds: For peptide-targeted contrast agents, internal motion limits the relaxivity gain. A focused library approach identified an N-terminal thymine peptide nucleic acid (PNA) that reaches an additional binding pocket on the protein fibrin. The heteroditopic binding rigidifies the molecule upon binding, resulting in increased protein-bound relaxivity (see picture).



Microbial Electron Transfer

D. Millo,* F. Harnisch,* S. A. Patil,
H. K. Ly, U. Schröder,
P. Hildebrandt ______ 2625 – 2627

In Situ Spectroelectrochemical Investigation of Electrocatalytic Microbial Biofilms by Surface-Enhanced Resonance Raman Spectroscopy



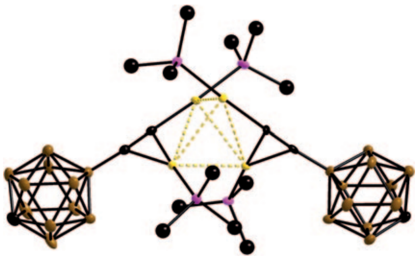
A mixed-culture-derived microbial biofilm, grown on silver electrodes, was studied in vivo with surface-enhanced resonance Raman scattering (SERRS) in combination with cyclic voltammetry. This experimental approach provides unprecedented structural information about the outer membrane cytochromes involved in the direct electron transfer across the bacterium–electrode interface.

Cluster Compounds

A. Himmelspach, M. Finze,*
S. Raub ______ 2628 – 2631

Tetrahedral Gold(I) Clusters with Carba-*closo*-dodecaboranylethynido Ligands: $[\{12\text{-}(\mathrm{R_3PAu})_2\mathrm{C{\equiv}C}\text{-}\mathit{closo}\text{-}1\text{-}\mathrm{CB_{11}H_{11}}\}_2]$

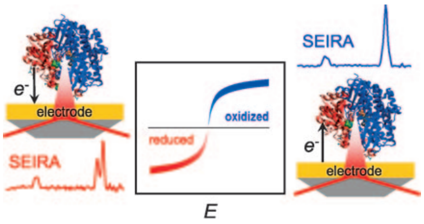
On golden bond: In both the solid state and in solution, the neutral dinuclear gold(I) complexes $[12\text{-}(\mathrm{R_3PAu})_2\mathrm{C{\equiv}C}\text{-}\mathit{closo}\text{-}1\text{-}\mathrm{CB_{11}H_{11}}]$ (R = Me, Et) dimerize to tetranuclear gold(I) clusters held together by aurophilic interactions. For the $\mathrm{Et_3P}$ complex, the dimer and the monomer exist in equilibrium in solution at 25 °C. In contrast, even at 75 °C only dimers ($\mathrm{Au^{I}_{4}}$ clusters), are observed for the $\mathrm{Me_3P}$ complex (see structure: C black, B brown, P pink, Au yellow).



Biocatalysis

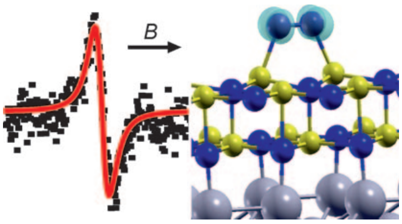
D. Millo, P. Hildebrandt, M.-E. Pandelia,
W. Lubitz, I. Zebger* ______ 2632 – 2634

SEIRA Spectroscopy of the Electrochemical Activation of an Immobilized [NiFe] Hydrogenase under Turnover and Non-Turnover Conditions

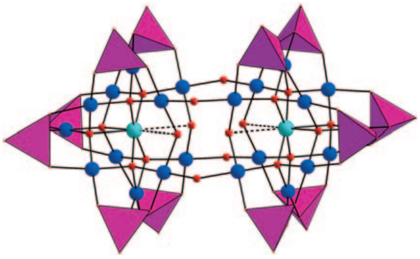


Effective and unaffected: An [NiFe] hydrogenase was immobilized on Au electrodes. Surface-enhanced infrared absorption (SEIRA) spectroscopy monitored structural changes of the active site as a function of the applied potential. The redox titration of the enzyme gave a formal potential ($E_{1/2}$) similar to that obtained for the enzyme in solution, demonstrating that the structure of the active site is not affected by the immobilization.

Distortion is the key: In situ EPR spectroscopy provides the first experimental confirmation that the adsorption of O_2 molecules on a stoichiometric ultrathin MgO(001) film on Mo(001) leads to the spontaneous formation of $O_2^{\bullet-}$ radicals. The results show that polaronic distortion of the MgO lattice (see picture; Mg yellow, O blue) stabilizes the radical, and this distortion is only possible in very thin films.



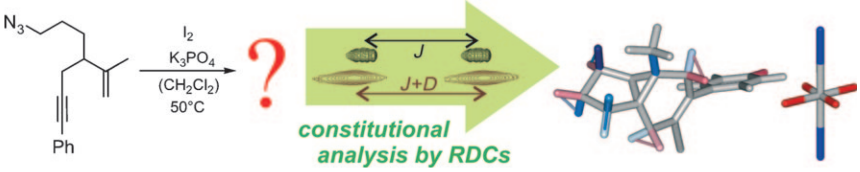
Heterogeneous Catalysis



A couple of coppers: Two Cu^{II} ions exhibit highly distorted cubic coordination and unexpectedly large magnetic exchange coupling in a discrete dicopper(II)-containing 22-palladate(II). The compound is isolated as the hydrated sodium salt $Na_{20}[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]\cdot 58\,H_2O$ (**1**) in which the polyanion (see structure: Cu turquoise, Pd blue, O red balls, $\{PO_4\}$ purple tetrahedra) is the largest noble metalate reported to date.

Noble Metalates

VIP



Analyze this! Residual dipolar couplings (RDCs) can be used to determine the constitution of a small molecule when traditional methods for structure elucidation fail. In a case study, a highly congested, tricyclic compound resulting from the electrophilic cyclization of an azide-containing 1,5-enyne was investigated.

Structure Elucidation

VIP

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

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