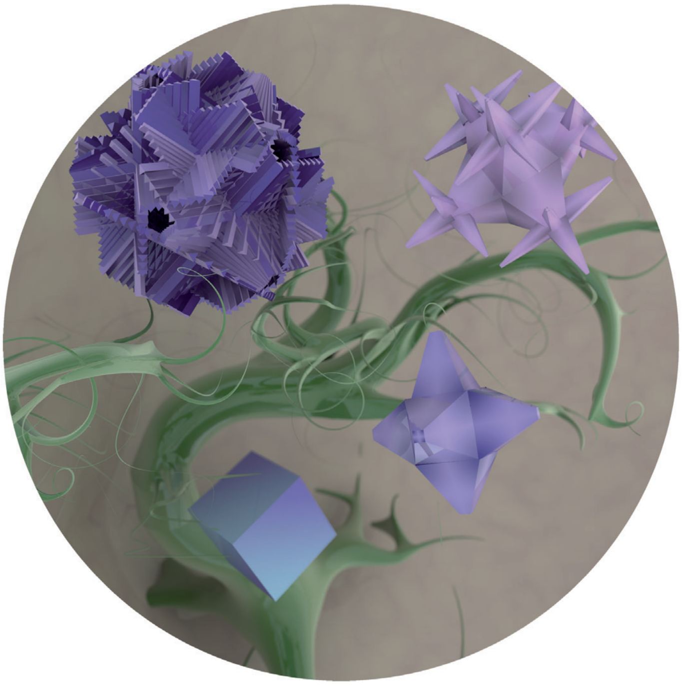
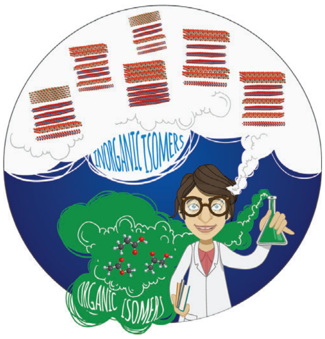
Nature seeds pathways ...



… to hierarchical structures, which scientists strive to emulate through the synthesis of advanced nanostructures. In their Communication on page 1181 ff., R. G. Weiner and S. E. Skrabalak describe the synthesis of hierarchically stellated nanocrystals by sequential seed-directed overgrowth. These structures are analogous to organic dendrimers, but seed symmetry, rather than molecular connectivity, directs the multi-level branching (Image designed by Ella Marushchenko, Scientific Illustrations).

Inorganic Isomers

In their Communication on page 1130 ff., D. C. Johnson et al. describe the preparation of structural inorganic isomers with $NbSe_2$ trilayers and PbSe bilayers from designed precursors.



Green Chemistry

In their Communication on page 1159 ff., M. P. Sibi, D. C. Webster, J. Sivaguru, et al. report polymeric materials derived from biomass with built-in phototriggers that degrade back to the monomers under irradiation of UV light.

Insect Pheromones

A bed bug aggregation pheromone that consists of six components and is effective at luring bed bugs into traps in infested premises is described by R. Britton, G. Gries, et al. in their Communication on page 1135 ff.

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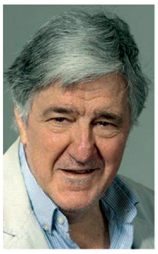
News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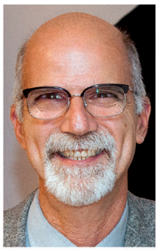
G. Bellussi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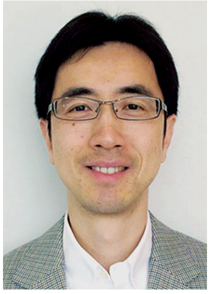


"In a spare hour, I exercise on the treadmill. My motto is 'be low-key, work high-key' ..."
This and more about Zhiqun Lin can be found on page 1072.

Correspondence

Crystal-Field Analysis

M. Karbowiak,* J. Cichos,
C. Rudowicz ______ 1074 – 1076

Comment on the Crystal-Field Analysis Underlying “Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped $NaYF_4$ Crystals”

The crystal-field (CF) analysis and energy-level fittings for Eu^{3+} ions in α- and β-$NaYF_4$ by Tu et al. is critically assessed. It is argued that the method used for CF parameter fittings by Tu et al. is inappropriate, thus leading to incorrect numerical results and erroneous interpretation of experimental data.

Crystal-Field Analysis

D. T. Tu, W. Zheng,
X. Y. Chen* ______ 1077 – 1078

Reply to Comment on “Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped $NaYF_4$ Crystals”

In this reply, the authors of the Communication “Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped $NaYF_4$ Crystals” respond to the comment by Karbowiak et al., who criticized the crystal-field (CF) analysis of Eu^{3+} in disordered $NaYF_4$. The authors clarify their interpretations of the issues raised.

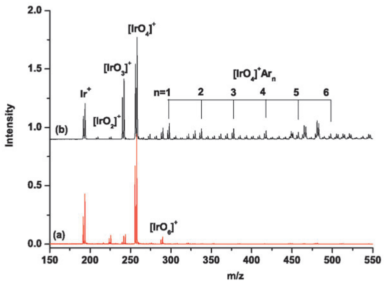
Highlights

Oxidation States

P. Pyykkö,* W.-H. Xu ______ 1080 – 1081

The Formal Oxidation States of Iridium Now Run from −III to +IX

Rarer than a new element: Recently Wang et al. produced the $[(Ir^{+IX})O_4]^+$ ion by a pulsed laser vaporization/thermal expansion method and studied it by IR photodissociation spectroscopy. The oxidation state of +IX had been unknown previously. The picture shows the mass spectra for the argon-tagged iridium oxide species.

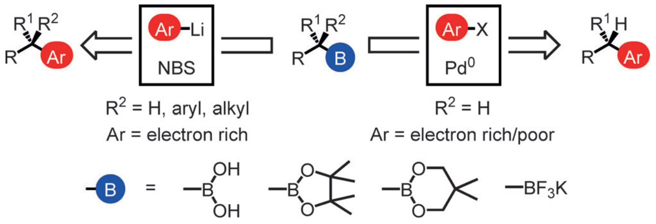


Minireviews

Cross-Coupling

D. Leonori,*
V. K. Aggarwal* ______ 1082 – 1096

Stereospecific Couplings of Secondary and Tertiary Boronic Esters



Just couple it: In the past decade, highly efficient protocols have been developed to allow the stereospecific arylation of chiral organoborons. This Minireview documents the rapid development of this area, thus providing a clear overview of the various processes available together with mechanisms, as well as their scope and limitations.

For the USA and Canada:
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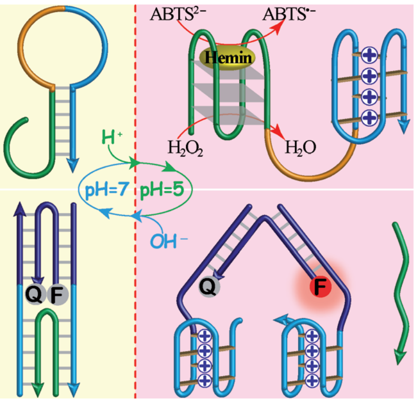
Reviews

DNA Nanotechnology

F. Wang, X. Liu, I. Willner* **1098 – 1129**

DNA Switches: From Principles to Applications



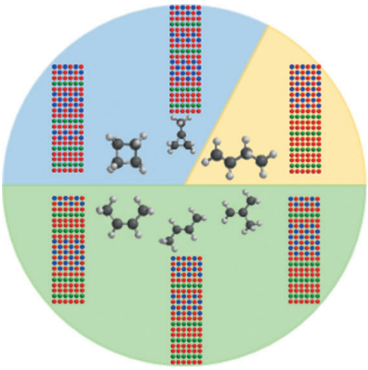
Switched on: The stimuli-triggered reversible reconfiguration of i-motifs, G-quadruplexes, and duplex DNA structures, and of DNA devices, such as tweezers, nanosprings or walkers, are the basis for DNA switches that can be triggered by changes in pH values, metal ions/ligands, and photonic or electrochemical signals. Applications of DNA switches include controlled drug delivery, opening/closure of pores, and switchable catalysis.

Communications

Layered Compounds

M. Esters, M. B. Alemayehu, Z. Jones,
N. T. Nguyen, M. D. Anderson, C. Grosse,
S. F. Fischer,
D. C. Johnson* **1130 – 1134**

Synthesis of Inorganic Structural Isomers By Diffusion-Constrained Self-Assembly of Designed Precursors: A Novel Type of Isomerism



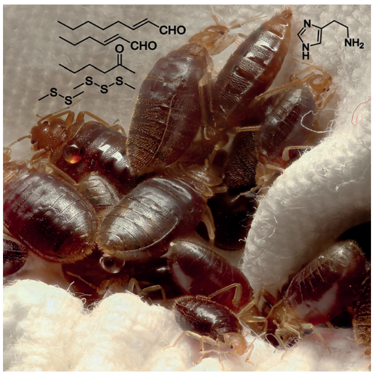
Just as organic molecules have isomers resulting from different interconnectivity (as shown for C_4H_8), layered compounds have similar structural isomers. The six possible structural isomers containing four Se-Nb-Se trilayers and four bilayers of PbSe were synthesized from designed precursors. Thus, thousands of new compounds may be selectively prepared from fragments of known compounds.

Frontispiece

Insect Pheromones

R. Gries, R. Britton,* M. Holmes, H. Zhai,
J. Draper, G. Gries* **1135 – 1138**

Bed Bug Aggregation Pheromone Finally Identified



Sleep tight! Bed bugs rely on chemical cues to locate and arrest in safe shelters. This aggregation pheromone comprises five volatile components (dimethyl disulfide and dimethyl trisulfide, (E)-2-hexenal, (E)-2-octenal, 2-hexanone) that attract bed bugs, and one less-volatile component (histamine) that causes their arrestment upon contact. This blend is highly effective at luring bed bugs into traps in infested premises.

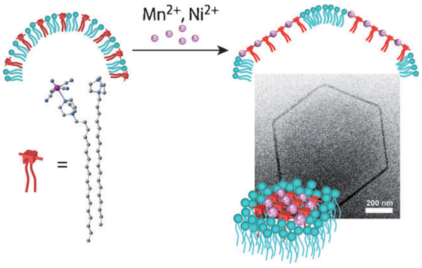
Back Cover

Lipid Membranes

R. Ohtani, M. Inukai, Y. Hijikata, T. Ogawa,
M. Takenaka, M. Ohba,*
S. Kitagawa* ______ 1139 – 1143

Sequential Synthesis of Coordination Polymersomes

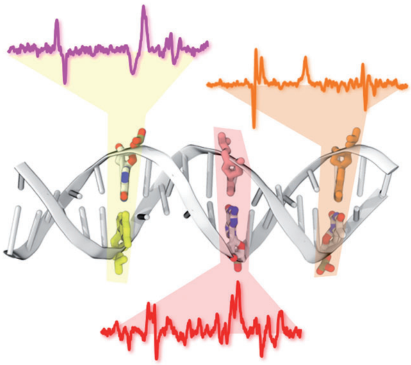
The sequential synthesis of coordination polymers on lipid bilayers provides novel organic–inorganic hybrid liposomes, so-called coordination polymersomes (CPsomes), which formed unilamellar faceted spheres with plain coordination polymer raft domains that consist of cyanide-bridged linkages based on a lipophilic building unit. This is a novel approach for the construction of artificial raft domains and for creating composite soft materials.



High-Throughput Screening

L. Guerrini,* Ž. Krpetić, D. van Lierop,
R. A. Alvarez-Puebla,
D. Graham ______ 1144 – 1148

Direct Surface-Enhanced Raman Scattering Analysis of DNA Duplexes

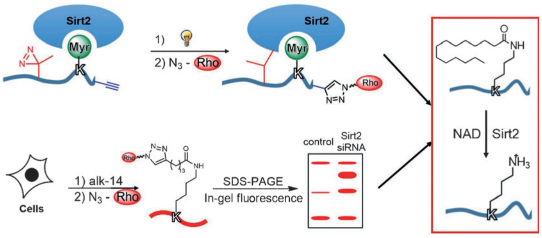


Accessing genomic information: A fast and affordable high-throughput screening method based on surface-enhanced Raman spectroscopy (SERS) is a low-cost and ultrasensitive genotyping strategy for gaining detailed genomic information on DNA duplexes. This method allows recognition of hybridization events, single-base mismatches, and base methylation.

Peptides

Z. Liu, T. Yang, X. Li, T. Peng, H. C. Hang,
X. D. Li* ______ 1149 – 1152

Integrative Chemical Biology Approaches for Identification and Characterization of "Erasers" for Fatty-Acid-Acylated Lysine Residues within Proteins



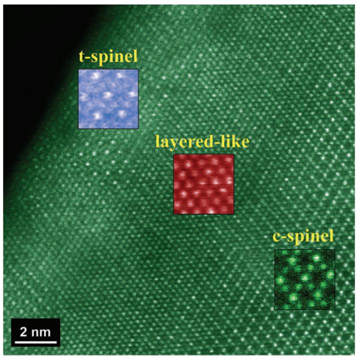
Chewing the fat: The use of integrative chemical biology approaches to examine human sirtuins as de-fatty-acid acylases in vitro and in cells is demonstrated. Photo-crosslinking chemistry is used to investigate enzymes which recognize fatty-acid-acylated lysine. Human Sirt2 was identified as a robust lysine de-fatty-acid acylase in vitro. The results also show that Sirt2 can regulate acylation of lysine residues by fatty acids within cells.

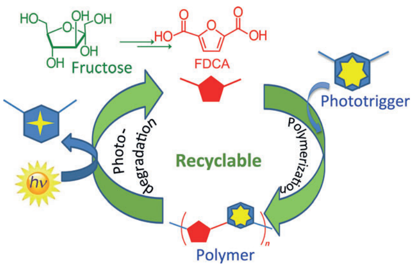
Lithium-Ion Batteries

S. Lee, G. Yoon, M. Jeong, M. Lee,
K. Kang,* J. Cho* ______ 1153 – 1158

Hierarchical Surface Atomic Structure of a Manganese-Based Spinel Cathode for Lithium-Ion Batteries

A coat for best: The coating of stoichiometric $LiMn_2O_4$ with highly doped spinels introduced a surface hierarchical atomic structure without the formation of an interfacial phase. The resulting materials (see HAADF-STEM image; t and c stand for tetragonal and cubic) exhibited significantly improved electrochemical performance at high temperatures, including rate capability and cyclability, with no significant reduction in capacity.





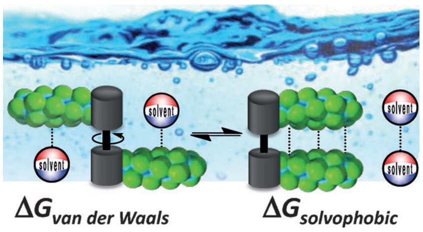
Biodegradable and recyclable: Renewable polymeric materials derived from biomass with built-in phototriggers were synthesized and evaluated for degradation under irradiation by UV light (see picture). Complete decomposition of the polymeric materials was observed with recovery of the monomer that was used to resynthesize the polymers.

Green Chemistry

S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi,* D. C. Webster,* J. Sivaguru* **1159–1163**

Programmed Photodegradation of Polymeric/Oligomeric Materials Derived from Renewable Bioresources

Inside Back Cover

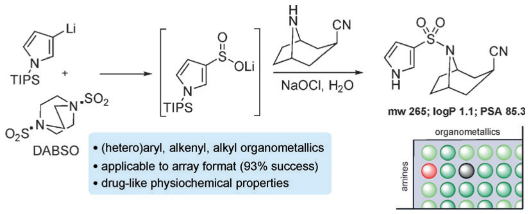


In full force: The balance of solvophobic and van der Waals dispersion forces on the self-association of perfluoroalkyl and alkyl chains is examined in solution. The contributions of dispersion interactions in apolar cohesion were strongly attenuated in solution compared to the gas phase. In contrast, solvophobic effects were dominant in driving the association of apolar chains in aqueous solution.

Molecular Recognition

C. Adam, L. Yang, S. L. Cockroft* **1164–1167**

Partitioning Solvophobic and Dispersion Forces in Alkyl and Perfluoroalkyl Cohesion

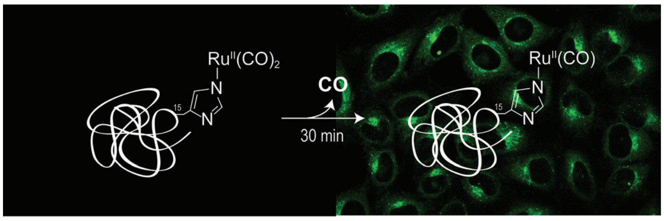


Array array: A simple aqueous solution of an amine and bleach, added to in situ-generated metal sulfinates, allows the effective preparation of a varied range of sulfonamides. The sulfinate intermediates are formed by organometallic addition to the solid SO_2 surrogate DABSO. A 70-compound array was prepared to demonstrate the utility of the method, with an emphasis on delivering molecules with drug-like physiochemical properties.

Sulfonamide Synthesis

A. S. Deeming, C. J. Russell, M. C. Willis* **1168–1171**

Combining Organometallic Reagents, the Sulfur Dioxide Surrogate DABSO, and Amines: A One-Pot Preparation of Sulfonamides, Amenable to Array Synthesis



Artificial metalloproteins release carbon monoxide spontaneously in aqueous solution, cells, and mice. The $Ru^{II}(CO)_2$–protein complexes were formed from the reaction of the hydrolytic decomposition products of CO-releasing molecule 3 (CORM-3) with histidine residues exposed on the surface of proteins.

CO Release

M. Chaves-Ferreira, I. S. Albuquerque, D. Matak-Vinkovic, A. C. Coelho, S. M. Carvalho, L. M. Saraiva, C. C. Romão, G. J. L. Bernardes* **1172–1175**

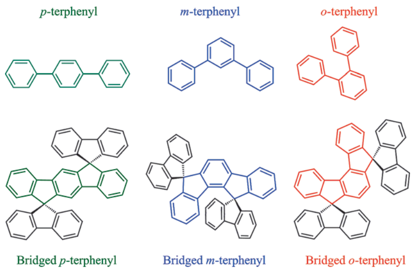
Spontaneous CO Release from $Ru^{II}(CO)_2$–Protein Complexes in Aqueous Solution, Cells, and Mice

Organic Semiconductors

M. Romain, S. Thiery, A. Shirinskaya, C. Declairieux, D. Tondelier, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel* ______ 1176 – 1180

ortho-, *meta*-, and *para*-Dihydroindenofluorene Derivatives as Host Materials for Phosphorescent OLEDs

Bridging, strain, and electronics: The rigidification of terphenyls by the introduction of spiro bridges, leading to *ortho* [2,1-*c*]-, *meta* [1,2-*a*]-, and *para* [1,2-*b*]-dihydroindenofluorenes, affects their electronic properties. The [1,2-*a*] isomer possessing a high triplet state energy level is the first example of a dihydroindenofluorene used as the host in a sky-blue phosphorescent organic LED.

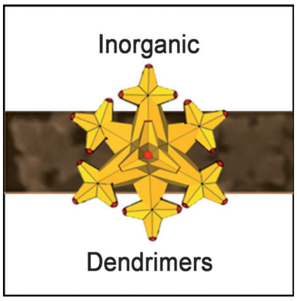


Nanocrystals

R. G. Weiner, S. E. Skrabalak* ______ 1181 – 1184

Metal Dendrimers: Synthesis of Hierarchically Stellated Nanocrystals by Sequential Seed-Directed Overgrowth

Front Cover



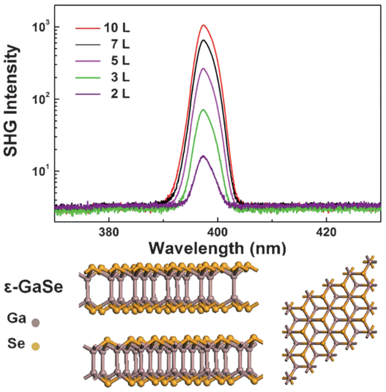
Building connections: Sequential seed-directed overgrowth provides a route to metal dendrimers, which are hierarchically branched nanocrystals analogous to molecular dendrimers. By manipulating the seed shape, the number of branches is readily controlled. By repeating the seed-mediated co-reduction process, iterative chain growth with concentric branching is possible.

Optics in Nanosheets

W. Jie, X. Chen, D. Li, L. Xie, Y. Y. Hui, S. P. Lau, X. D. Cui, J. H. Hao* ______ 1185 – 1189

Layer-Dependent Nonlinear Optical Properties and Stability of Non-Centrosymmetric Modification in Few-Layer GaSe Sheets

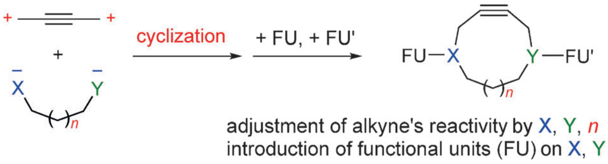
2D materials: Layer-dependent second-order optical nonlinearity has been observed in few-layer (L) gallium selenide sheets, which is the first observation of second harmonic generation (SHG; see picture) on two-dimensional GaSe nanosheets because of the absence of the inversion symmetric center for ε-GaSe. Two-photon excited fluorescence has also been found in the few-layer GaSe sheets.



Strained Molecules

R. Ni, N. Mitsuda, T. Kashiwagi, K. Igawa,* K. Tomooka* ______ 1190 – 1194

Heteroatom-embedded Medium-Sized Cycloalkynes: Concise Synthesis, Structural Analysis, and Reactions

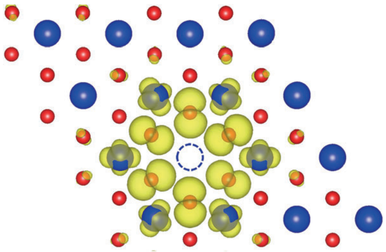


Bent out of shape: A variety of medium-sized cycloalkynes were efficiently synthesized by the cyclization of a dicationic 2-butyne unit and dianionic bis(hetero)substituted acyclic alkynes. The alkyne moiety of the cycloalkyne has a unique bent structure and high reactivity toward cycloaddition reactions. Furthermore, preparation of multifunctionalized alkynes was achieved by embedding medium-sized cycloalkyne within a peptide chain.

Defect Engineering

H. Wang, J. J. Zhang, X. Hang, X. D. Zhang,* J. F. Xie, B. C. Pan, Y. Xie* ———— **1195 – 1199**

Half-Metallicity in Single-Layered Manganese Dioxide Nanosheets by Defect Engineering

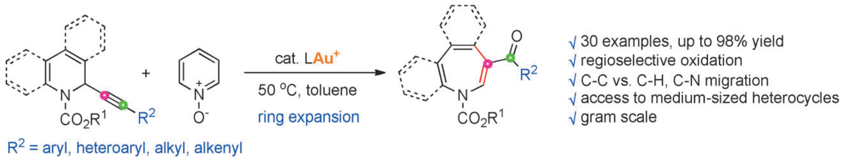


A manganese dioxide monolayer was rendered half-metallic by a defect engineering strategy, which was confirmed by calculations. These theoretical studies showed that the half-metallicity of a single-layered MnO_2 nanosheet can be observed for a wide range of vacancy concentrations and even in the presence of both Mn and O vacancies.

Gold Catalysis

M. Chen, Y.-F. Chen, N. Sun, J.-D. Zhao, Y.-H. Liu,* Y.-X. Li* ———— **1200 – 1204**

Gold-Catalyzed Oxidative Ring Expansion of 2-Alkynyl-1,2-Dihydropyridines or -quinolines: Highly Efficient Synthesis of Functionalized Azepine or Benzazepine Scaffolds

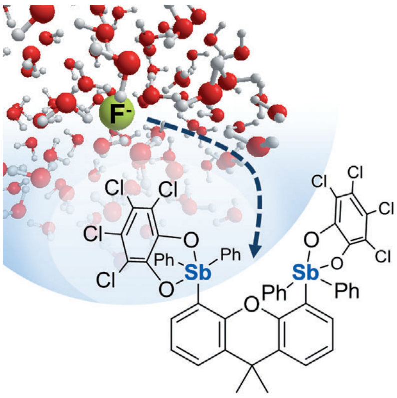


Ring expansion: A gold-catalyzed highly regio- and chemoselective oxidative ring expansion of 2-alkynyl-1,2-dihydropyridine and its analogues was achieved using pyridine-*N*-oxide as the oxidant. Thereby, medium-sized azepine derivative can be obtained with a broad functional group tolerance. DFT studies indicate that the reaction proceeds through the formation of a cyclopropyl gold intermediate.

Hypervalent Compounds

M. Hirai, F. P. Gabbaï* ———— **1205 – 1209**

Squeezing Fluoride out of Water with a Neutral Bidentate Antimony(V) Lewis Acid

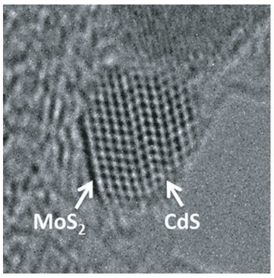


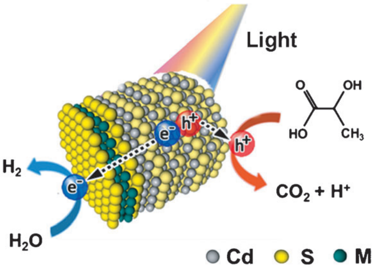
Fluoride sponge: Due to hydration, fluoride anions are weakly basic and reluctant to bind with neutral Lewis acids in water. A bifunctional Lewis acid containing two stiboranes as Lewis acidic units forms an anionic fluoride complex stabilized by a Sb-F-Sb chelate motif. A monofunctional analogue shows that the bidentate Sb_2 system is more acidic by at least two orders of magnitude.

Photocatalysis

J. Chen, X.-J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue, H. Zhang* ———— **1210 – 1214**

One-pot Synthesis of CdS Nanocrystals Hybridized with Single-Layer Transition-Metal Dichalcogenide Nanosheets for Efficient Photocatalytic Hydrogen Evolution





A single layer makes the difference: MS_2–CdS (M = W or Mo) nanohybrids with single-layer MS_2 nanosheets selectively grown on the Cd-rich (0001) surface of wurtzite CdS nanocrystals (see picture) are synthesized by a facile one-pot wet-chemical method. The MS_2–CdS nanohybrids showed excellent photocatalytic activity towards the hydrogen evolution reaction and good stability.

Chiral Polymers

F. Auriemma,* C. De Rosa,
M. R. Di Caprio, R. Di Girolamo,
W. C. Ellis, G. W. Coates* **1215 – 1218**

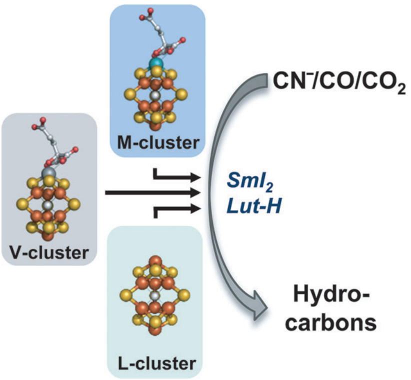
Stereocomplexed Poly(Limonene Carbonate): A Unique Example of the Cocrystallization of Amorphous Enantiomeric Polymers

When life gives you lemons, make a stereocomplex! Enantiomerically pure isotactic poly(limonene carbonate), derived from citrus oil and CO_2, is an amorphous polymeric material in spite of its regular constitution and configuration. However, upon mixing together both enantiomers, a "zippering" interaction between chains of opposite configuration occurs, resulting in an overall semi-crystalline ensemble.

Enzyme Catalysis

C. C. Lee, Y. Hu,*
M. W. Ribbe* **1219 – 1222**

Catalytic Reduction of CN^-, CO, and CO_2 by Nitrogenase Cofactors in Lanthanide-Driven Reactions

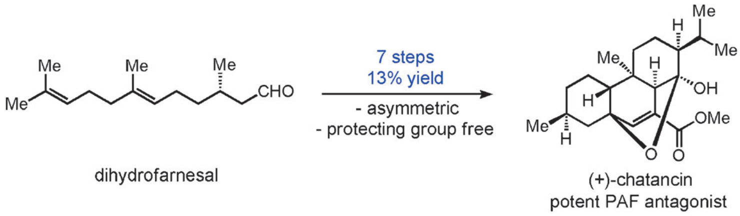


Extracted nitrogenase cofactors (M-, V-, and L-clusters) catalyzed the reductions of cyanide (CN^-), carbon monoxide (CO), and carbon dioxide (CO_2) to hydrocarbons in organic solvents. In these reactions, samarium(II) iodide (SmI_2) and 2,6-lutidinium triflate (Lut-H) were employed as a reductant and a proton source, respectively.

Natural Product Synthesis

Y.-M. Zhao, T. J. Maimone* **1223 – 1226**

Short, Enantioselective Total Synthesis of Chatancin

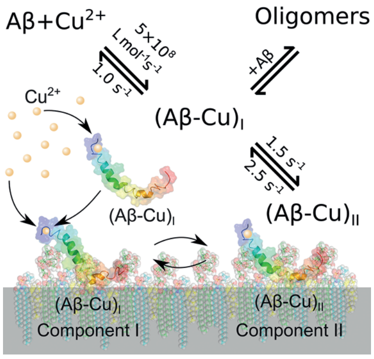


New orchestration: The synthetic route to the polycyclic diterpene (+)-chatancin does not rely on a macrocyclization step, avoids protecting-group manipulations, and appears to be suitable for the straightforward construction of analogues. Adaptations to the general strategy should serve in synthesis of other cembrane-derived natural products.

Amyloid β Peptides

T. Branch, P. Girvan, M. Barahona,
L. Ying* **1227 – 1230**

Introduction of a Fluorescent Probe to Amyloid-β to Reveal Kinetic Insights into Its Interactions with Copper(II)



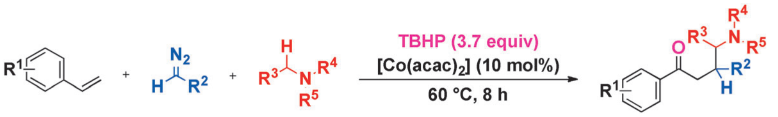
The interactions of Aβ with Cu^{2+} have been elucidated using a highly sensitive fluorescent probe. The timescales of association, dissociation, dimerization, and switching between the two major Aβ–Cu^{2+} coordination modes were determined. The kinetic method is capable of determining the efficacy of ligands at sequestering coordinated Cu^{2+} from Aβ. This method may be applicable to other Cu^{2+} binding proteins.

One-Pot Processes

J. Zhang, J. Jiang, D. Xu, Q. Luo, H. Wang, J. Chen, H. Li, Y. Wang, X. Wan* ______ 1231 – 1235

Interception of Cobalt-Based Carbene Radicals with α-Aminoalkyl Radicals: A Tandem Reaction for the Construction of β-Ester-γ-amino Ketones

Inside Cover

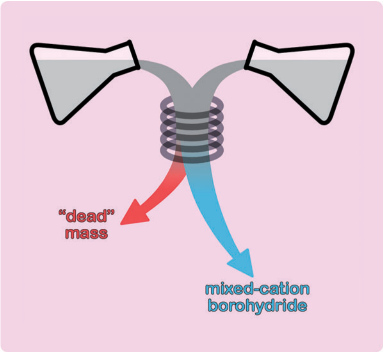


Radical combination: The interception of cobalt-based carbene radicals with α-aminoalkyl radicals in combination with a Kornblum–DeLaMare reaction leads to β-ester-γ-amino ketones, which are otherwise difficult to obtain with high chemoselectivity. The transformation features a wide substrate scope and is highly efficient and insensitive to moisture and air.

Borohydrides

T. Jaroń,* P. A. Orłowski, W. Wegner, K. J. Fijałkowski, P. J. Leszczyński, W. Grochala* ______ 1236 – 1239

Hydrogen Storage Materials: Room-Temperature Wet-Chemistry Approach toward Mixed-Metal Borohydrides

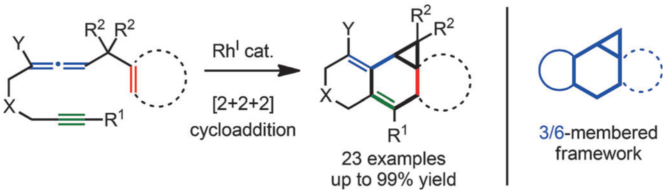


Avoiding "dead mass": Hydrogen-rich mixed-metal borohydrides, which are promising materials for the chemical storage of hydrogen, were prepared by a wet-chemistry approach. This method is based on a metathesis reaction, does not lead to a high percentage of "dead mass" (metal halides and coordinated solvents), and was exemplified for a series of MZn(BH_4) borohydrides (M = Li, Na, K).

Synthetic Methods

Y. Ohta, S. Yasuda, Y. Yokogawa, K. Kurokawa, C. Mukai* ______ 1240 – 1244

Stereospecific and Stereoselective Rhodium(I)-Catalyzed Intramolecular [2+2+2] Cycloaddition of Allene-Ene-Ynes: Construction of Bicyclo[4.1.0]heptenes

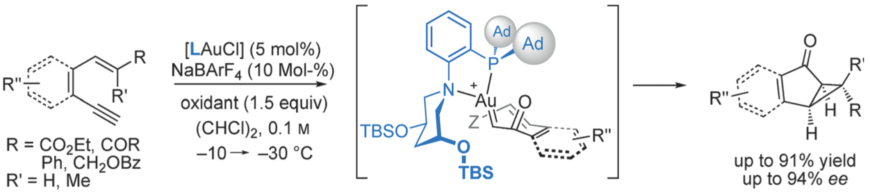


Two by three: Treatment of allene-ene-yne substrates with [{RhCl(CO)$_2$}$_2$] effected the intramolecular [2+2+2]-type ring-closing reaction to produce various of tri- and tetracyclic derivatives containing a cyclopropane ring. The reaction is highly stereoselective as well as stereospecific with good to excellent yields.

Asymmetric Catalysis

K. Ji, Z. Zheng, Z. Wang, L. Zhang* ______ 1245 – 1249

Enantioselective Oxidative Gold Catalysis Enabled by a Designed Chiral P,N-Bidentate Ligand

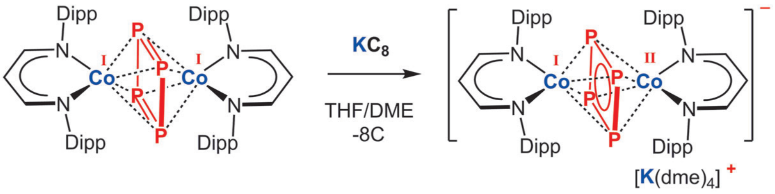


Giving gold a new shine: A chiral P,N-bidentate ligand containing a C_2-symmetric piperidine ring enabled enantioselective intramolecular cyclopropanation by an α-oxo gold carbene intermediate generated in situ (see scheme; Ad = adamantyl). The ligand design is based on the well-organized triscoordinated gold center in a previously proposed structure of the carbene intermediate in the presence of a P,N-bidentate ligand.

Coordination Chemistry

S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue,
T. Szilvási, M. Adelhardt, J. Sutter,
K. Meyer, M. Driess* ______ **1250 – 1254**

A Neutral Tetraphosphacyclobutadiene
Ligand in Cobalt(I) Complexes



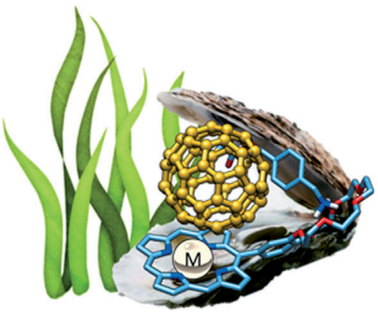
Rectangular goes square: The rectangular neutral tetraphosphacyclobutadiene ligand has been coordinatively stabilized for the first time by reacting β-diketiminato cobalt(I) complexes with white phosphorus. Surprisingly, the one-electron reduction of the title complexes with C_8K leads to the corresponding mixed-valent cobalt(I,II) complexes with the square-planar cyclo-P_4^{2-} ligand.

Supramolecular Interactions

L. Moreira, J. Calbo, B. M. Illescas,
J. Aragó, I. Nierengarten,
B. Delavaux-Nicot, E. Ortí,* N. Martín,*
J.-F. Nierengarten* ______ **1255 – 1260**

Metal-Atom Impact on the Self-Assembly
of Cup-and-Ball Metalloporphyrin–
Fullerene Conjugates

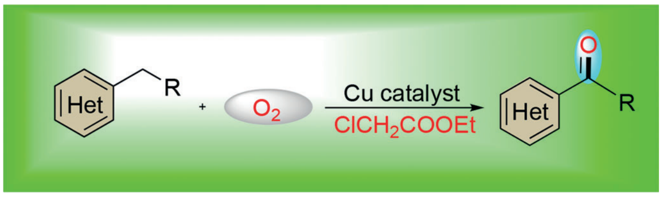
The pearl in the oyster: The influence of the metal atom in the overall stability of a series of cup-and-ball complexes formed by a crown porphyrin and a fullerene ammonium derivative is evaluated. The combination of experimental and in silico studies provides a deep insight into the nature of the porphyrin–fullerene interaction.



Selective Oxidations

J. Liu, X. Zhang, H. Yi, C. Liu, R. Liu,
H. Zhang, K. Zhuo,* A. Lei* **1261 – 1265**

Chloroacetate-Promoted Selective
Oxidation of Heterobenzylic Methylenes
under Copper Catalysis

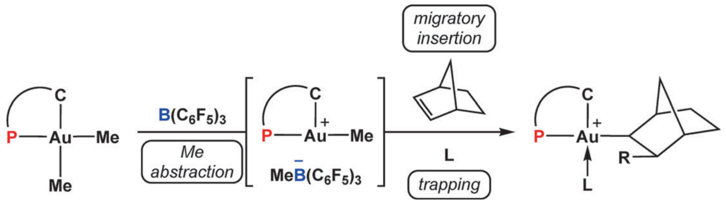


Molecular oxygen can be used for the selective oxidation of C–H bonds of N-heterocyclic compounds to the corresponding ketones with a copper catalyst and ethyl chloroacetate as a promoter. In this transformation, various substituted N-heterocyclic compounds were well tolerated. Preliminary mechanistic investigations indicated that organic radical species were involved in the overall process.

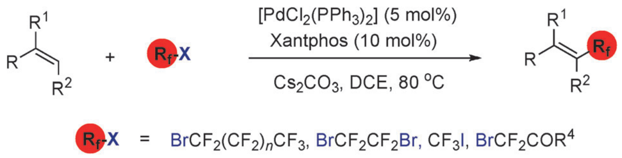
Migratory Insertion at Gold

F. Rekhroukh, R. Brousses, A. Amgoune,*
D. Bourissou* ______ **1266 – 1269**

Cationic Gold(III) Alkyl Complexes:
Generation, Trapping, and Insertion of
Norbornene



Migratory insertion of alkenes into gold–carbon bonds, a key yet unprecedented organometallic reaction, is observed. Methide abstraction from a (P,C) cyclometalated gold(III) dimethyl complex with $B(C_6F_5)_3$ generates a highly reactive cationic Au^{III} complex. In the presence of norbornene, migratory insertion into the Au–C bond proceeds at low temperature. The resulting norbornyl complex was trapped with pyridines and chloride.

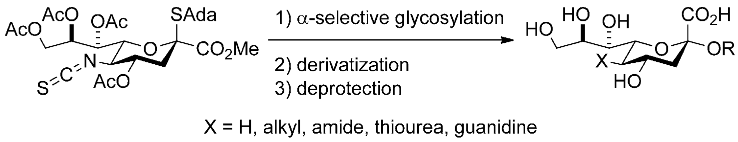


Simplicity is beauty: The title reaction features a broad substrate scope and excellent functional-group compatibility. Mechanistic studies reveal that the free fluoroalkyl radicals initiated by [Pd^0L_n] through a single-electron transfer pathway is involved in the Heck-type catalytic cycle.

Synthetic Methods

Z. Feng, Q.-Q. Min, H.-Y. Zhao, J.-W. Gu, X. Zhang* ——— **1270 – 1274**

A General Synthesis of Fluoroalkylated Alkenes by Palladium-Catalyzed Heck-Type Reaction of Fluoroalkyl Bromides

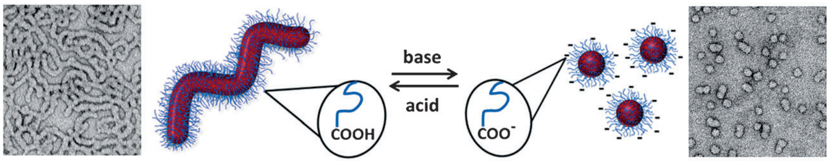


Very high α-selectivity is found in the coupling reactions of a readily prepared crystalline isothiocyanate-protected sialyl donor with typical carbohydrate alcohols (Ada = 1-adamantanyl). The isothiocyanate group is subsequently transformed into a number of functional groups including C—H and C—C bonds, amides, and thioureas, all in one step. A guanidino function is also accessible.

Cumulative Coupling

A. R. Mandhapati, S. Rajender, J. Shaw, D. Crich* ——— **1275 – 1278**

The Isothiocyanato Moiety: An Ideal Protecting Group for the Stereoselective Synthesis of Sialic Acid Glycosides and Subsequent Diversification

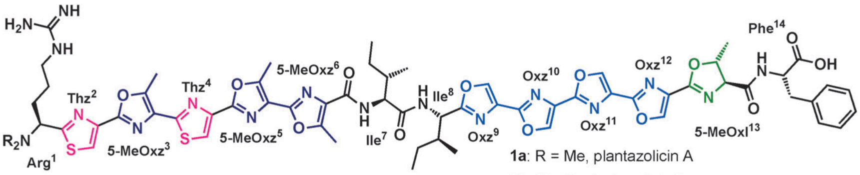


From worms to spheres: Ionization of a single terminal carboxylic acid on each stabilizer chain of gels containing non-ionic diblock copolymer worms confers unexpected pH-sensitivity; this subtle change in the packing parameter induces a reversible worm-to-sphere transformation with concomitant degelation.

Diblock Copolymers

J. R. Lovett, N. J. Warren, L. P. D. Ratcliffe, M. K. Kocik, S. P. Armes* ——— **1279 – 1283**

pH-Responsive Non-Ionic Diblock Copolymers: Ionization of Carboxylic Acid End-Groups Induces an Order–Order Morphological Transition



1a: R = Me, plantazolicin A
1b: R = H, plantazolicin B

The synthesis of plantazolicin A, which exhibits desirable selective activity against the causative agent of anthrax toxicity, and its biosynthetic precursor plantazolicin B is reported. The syntheses were achieved through an efficient, unified, and highly convergent route featuring dicyclizations to form 2,4-concatenated oxazoles, and the mild synthesis of thiazoles from natural amino acids.

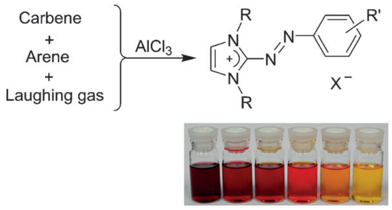
Natural Products

Z. E. Wilson, S. Fenner, S. V. Ley* ——— **1284 – 1288**

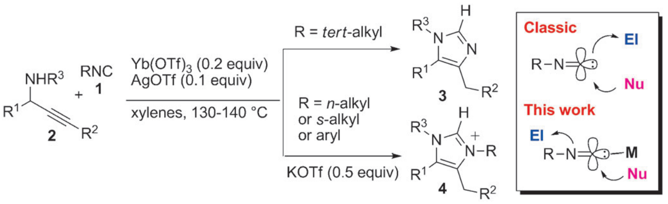
Total Syntheses of Linear Polythiazole/Oxazole Plantazolicin A and Its Biosynthetic Precursor Plantazolicin B

Nitrous Oxide

Dyes from laughing gas: Azoimidazolium dyes can be obtained by a simple coupling reaction of N-heterocyclic carbenes with nitrous oxide and arenes. This shows that N_2O can be used as an efficient N_2 donor in synthetic organic chemistry.

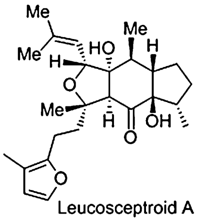


Synthetic Methods

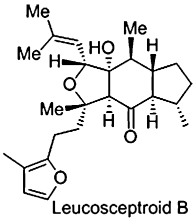


Salty stuff: The reaction of propargylamines with *tert*-butylisonitrile in the presence of a catalytic amount of $Yb(OTf)_3$ and AgOTf afforded 1,4,5-trisubstituted imidazoles, whereas the same reaction with primary and secondary alkylisonitriles, as well as arylisonitriles, in the presence of $Yb(OTf)_3$/AgOTf/KOTf afforded 1,3,4,5-tetrasubstituted imidazolium salts in excellent yields. Tf = trifluoromethanesulfonyl.

Terpenoids



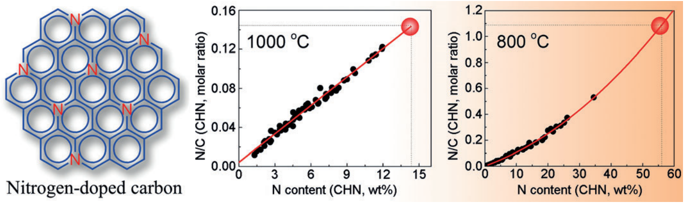
Leucosceptroid A



Leucosceptroid B

The sesterterpenoids leucosceptroids A and B are plant secondary metabolites with potent antifeedant and antifungal activities. A convergent and scalable synthesis of leucosceptroids A and B was achieved by employing an aldol reaction and an SmI_2-mediated intramolecular ketyl–olefin radical cyclization as the key steps.

Carbon Materials

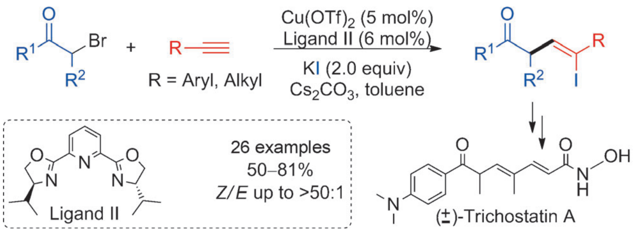


Doping control: The relationship between the nitrogen/carbon molar ratio and nitrogen content in nitrogen-doped carbon materials (NDCs) has been found to depend only on the carbonization temperature, being irrespective of the precursor, carbon type, and preparation conditions. The upper limit for the nitrogen content was explained by an energetically favorable graphitic N-doping configuration.

Synthetic Methods

T. Xu, X. L. Hu* ________ **1307 – 1311**

Copper-Catalyzed 1,2-Addition of α-Carbonyl Iodides to Alkynes

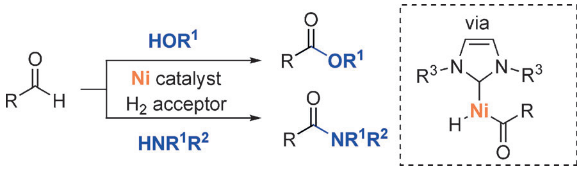


A versatile method: Copper catalysis is employed in the synthesis of β,γ-unsaturated ketones through the 1,2-addition of α-carbonyl iodides to alkynes. The reactions exhibit wide substrate scope and high functional group tolerance. The method was applied for the formal synthesis of (±)-trichostatin A, a histone deacetylase inhibitor.

Cross-Coupling

A. M. Whittaker,
V. M. Dong* ________ **1312 – 1315**

Nickel-Catalyzed Dehydrogenative Cross-Coupling: Direct Transformation of Aldehydes into Esters and Amides



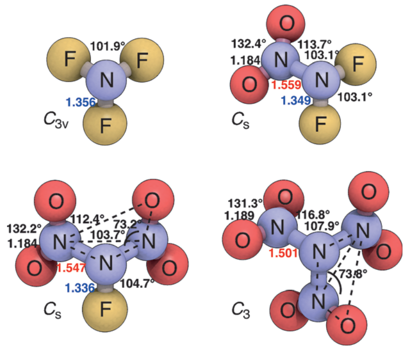
Nickel for a change: By exploring a new mode of nickel-catalyzed cross-coupling, both aromatic and aliphatic aldehydes can be directly transformed into either esters or amides. The success of this oxidative coupling depends on the appropriate choice of catalyst and organic oxidant (α,α,α-trifluoroacetophenone or benzaldehyde). Mechanistic data supports a catalytic cycle involving oxidative addition into the aldehyde C—H bond.

Energetic Materials

K. O. Christe,* W. W. Wilson,
G. Bélanger-Chabot, R. Haiges,
J. A. Boatz, M. Rahm, G. K. S. Prakash,
T. Saal, M. Hopfinger ________ **1316 – 1320**

Synthesis and Characterization of Fluorodinitroamine, FN(NO$_2$)$_2$

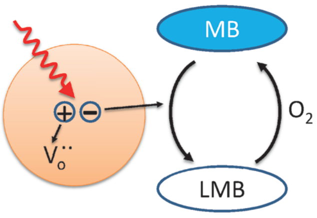
A missing link: FN(NO$_2$)$_2$, a fluoronitroamine, is a thermally unstable compound that decomposes at about −20 °C. It is shown that fluorine substitution further weakens the N—N bonds in N(NO$_2$)$_3$, and the yet unknown F$_2$N(NO$_2$) molecule is thus predicted to be even less stable than FN(NO$_2$)$_2$.



Color Switching

W. Wang, Y. Ye, J. Feng, M. Chi, J. Guo,
Y. Yin* ________ **1321 – 1326**

Enhanced Photoreversible Color Switching of Redox Dyes Catalyzed by Barium-Doped TiO$_2$ Nanocrystals

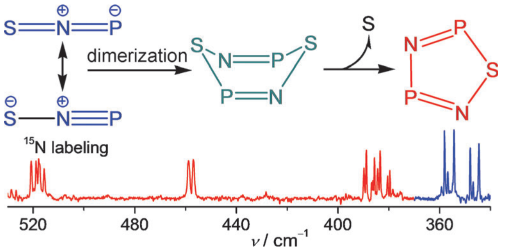


Rewritable paper: Barium-doped TiO$_2$ nanocrystals enable the highly reversible light-responsive color switching of redox dyes. Oxygen vacancies that result from the Ba doping serve as sacrificial electron donors to scavenge the holes generated in the TiO$_2$ nanocrystals under UV irradiation and subsequently promote the reduction of methylene blue (MB) to its colorless leuco form (LMB).

Main-Group-Element Heterocycles

X. Q. Zeng,* H. M. Li, H. L. Sun,
H. Beckers,* H. Willner,
H. F. Schaefer, III* ———— **1327 – 1330**

SN_2P_2: A Neutral Five-Membered Sulfur–Pnictogen(III) Ring

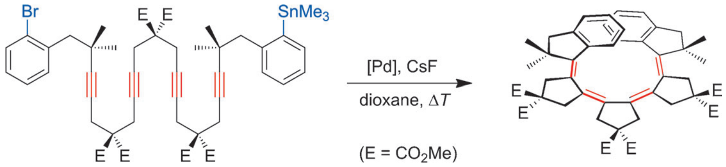


Give me five: A neutral five-membered sulfur–pnictogen(III) ring compound with 6π electrons, 2,4-diphospha-3,5-diazathiole (SN_2P_2), was identified among the products of the flash pyrolysis of $SP(N_3)_3$. It is formed in the gas phase by head-to-tail dimerization of 1,3-dipolar SNP and the subsequent elimination of sulfur from the unstable six-membered-ring intermediate $S_2N_2P_2$ is described.

Helicenes

B. Milde, M. Leibeling, M. Pawliczek,
J. Grunenberg, P. G. Jones,
D. B. Werz* ———— **1331 – 1335**

π-Helicenes Truncated to a Minimum: Access Through a Domino Approach Involving Multiple Carbopalladations and a Stille Coupling



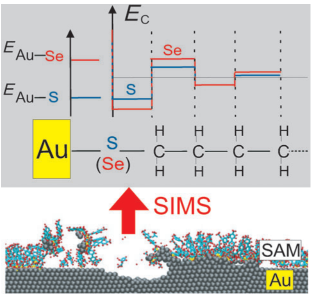
Maximal domino, minimal helicene: An approach involving multiple carbopalladations and a Stille coupling, starting from a linear oligoyne chain, gives access to helicenes with π-systems that are truncated to an oligoene chain. Structural and chiroptical properties were evaluated by X-ray crystallography and CD spectroscopy.

Chemical Bonding

J. Ossowski, J. Rysz, M. Krawiec,
D. Maciazek, Z. Postawa, A. Terfort,
P. Cyganik* ———— **1336 – 1340**

Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption

Pass it on: The strength of a chemical bond does not only influence the strength of its immediate neighbors, but the effect penetrates further along a molecule. Studying ordered surface monolayers by TOF-SI mass spectrometry provides an opportunity to look at this influence on all the bonds in a species at once.

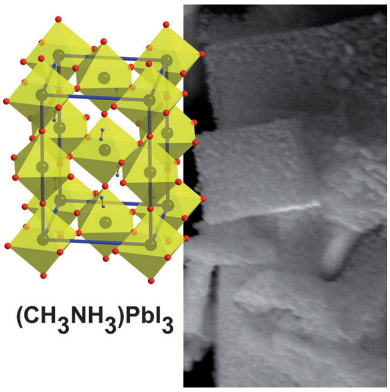


Porous Materials

T. Kollek, D. Gruber, J. Gehring,
E. Zimmermann, L. Schmidt-Mende,
S. Polarz* ———— **1341 – 1346**

Porous and Shape-Anisotropic Single Crystals of the Semiconductor Perovskite $CH_3NH_3PbI_3$ from a Single-Source Precursor

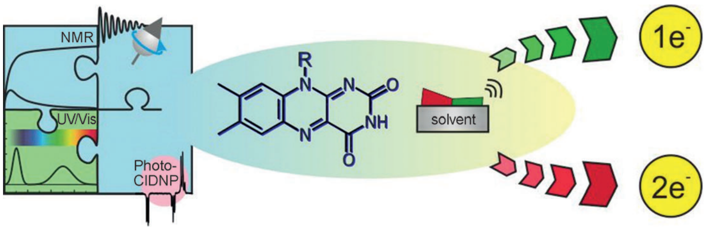
A crystal-to-crystal transition provides the perovskite semiconductor $CH_3NH_3PbI_3$ from a chain-like precursor. Porosity was generated by a spinodal phase separation mechanism. Furthermore, the particle shape of the perovskite nanocrystals could be tuned with a colloidal capper.



Photocatalysis

C. Feldmeier, H. Bartling, K. Magerl,
R. M. Gschwind* **1347 – 1351**

LED-Illuminated NMR Studies of Flavin-Catalyzed Photooxidations Reveal Solvent Control of the Electron-Transfer Mechanism

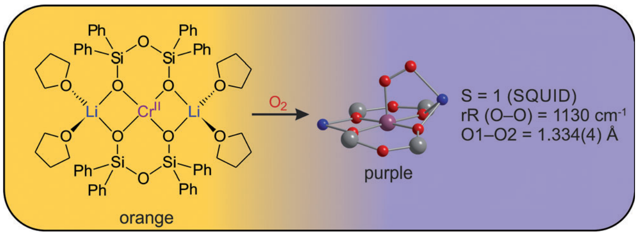


Lighting up: LED illumination setups make it possible to determine NMR reaction profiles and CIDNP studies of photocatalytic reactions. Combined NMR and UV/Vis studies on flavin-catalyzed photooxidations revealed that even without a protein shell flavin can act as either a one- or two-electron mediator depending on the solvent.

Chromium Complexes

F. Schax, S. Suhr, E. Bill, B. Braun,
C. Herwig, C. Limberg* **1352 – 1356**

A Heterobimetallic Superoxide Complex formed through O_2 Activation between Chromium(II) and a Lithium Cation



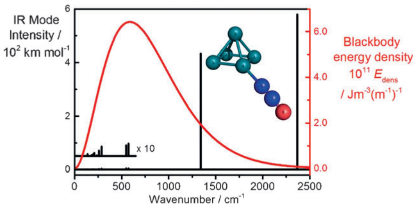
A superoxide in an oxide environment: A heterobimetallic superoxide was accessed by reaction of a mononuclear lithium siloxido chromate(II) with O_2 at low temperatures to yield a mononuclear chromium(III) superoxide complex. The crystal-structure and spectroscopic data reveal that the superoxido ligand interacts with an adjacent lithium cation, which may have aided the O_2 activation.

Metal Clusters

I. S. Parry, A. Kartouzian, S. M. Hamilton,
O. P. Balaj, M. K. Beyer,*
S. R. Mackenzie* **1357 – 1360**

Chemical Reactivity on Gas-Phase Metal Clusters Driven by Blackbody Infrared Radiation

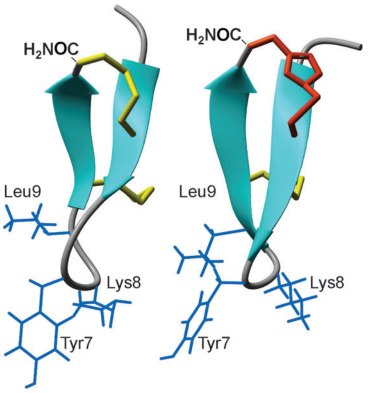
Gently does it: A nascent blackbody radiation field provides enough excitation to drive the decomposition of nitrous oxide on the surface of isolated rhodium clusters. This gentlest of all photoexcitation techniques, similar in many respects to blackbody infrared radiative dissociation (BIRD), provides unique information on the entrance-channel barriers for this important catalytic process.



Peptidomimetics

A. Gori, C. Wang, P. J. Harvey,
K. J. Rosengren, R. F. Bhola, M. L. Gelmi,
R. Longhi, M. J. Christie, R. J. Lewis,
P. F. Alewood,* A. Brust* **1361 – 1364**

Stabilization of the Cysteine-Rich Conotoxin MrIA by Using a 1,2,3-Triazole as a Disulfide Bond Mimetic



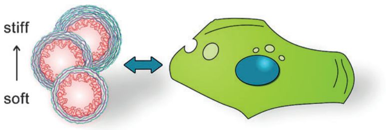
Click fix: Disulfide bond engineering of a χ-conopeptide (left) delivered selectively formed bioactive 1,2,3-triazole–disulfide hybrids (right) with vastly improved stability and function in a neuropathic pain model. The structural implications and broad impact of this selective folding and disulfide mimetic strategy for the stabilization of disulfide-rich peptides is discussed.

Endocytosis

R. Hartmann, M. Weidenbach,
M. Neubauer, A. Fery,
W. J. Parak* ______ **1365 – 1368**

Stiffness-Dependent In Vitro Uptake and Lysosomal Acidification of Colloidal Particles

Stiffness matters: The properties of colloidal particles determine their uptake into cells. Only the mechanical stiffness of microparticles was varied, whereas other parameters were kept constant. The uptake was monitored in situ by analyzing individual particle trajectories including the progress of endocytosis. Soft particles with low stiffness are transported faster to lysosomes than stiffer ones.



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

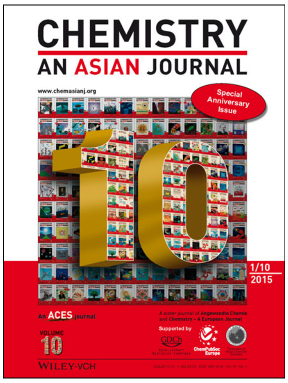
A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

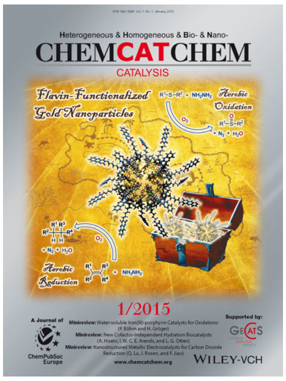
This article is available online free of charge (Open Access).

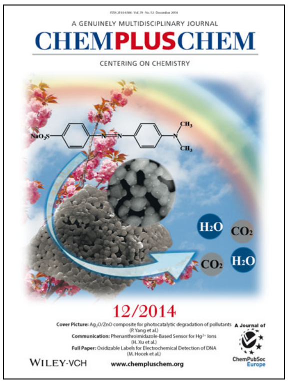
This article is accompanied by a cover picture (front or back cover, and inside or outside).

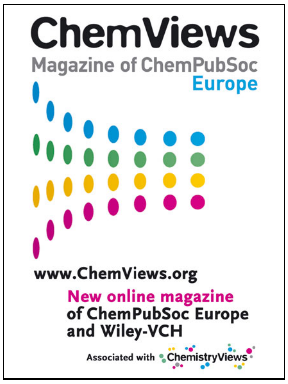
The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

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.



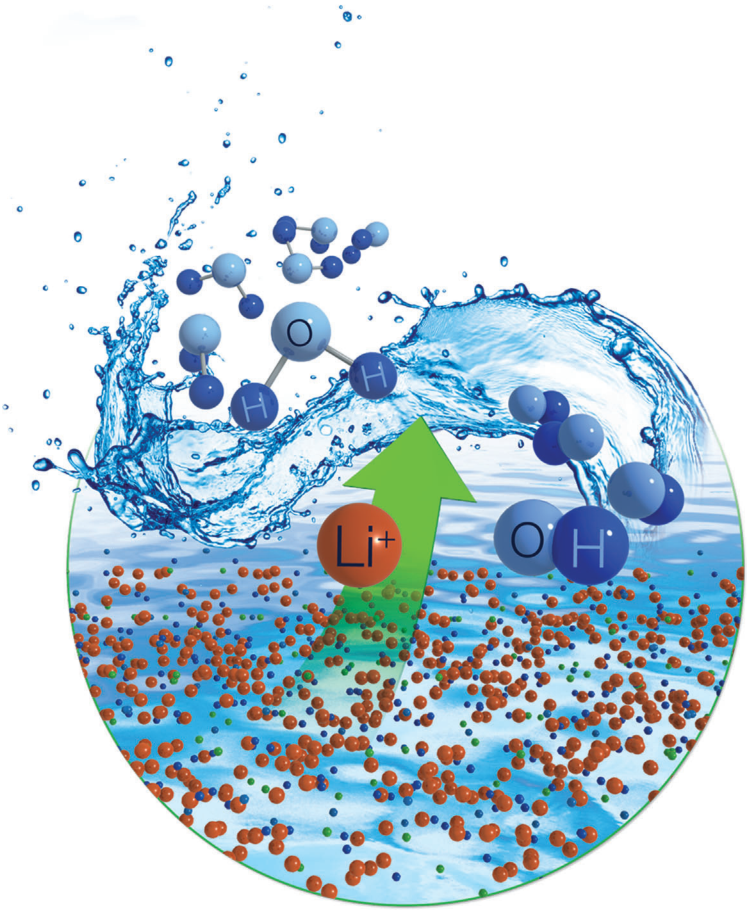






Angewandte Corrigendum

The cover picture of issue 1/2015 contains a mistake that was only noticed after printing. The wrong picture has been replaced in the online version, and the correct version is shown below.
The editorial office of *Angewandte Chemie* apologizes for this mistake.



Excellent Stability of a Lithium-Ion-Conducting Solid Electrolyte upon Reversible Li^+/H^+ Exchange in Aqueous Solutions

C. Ma,* E. Rangasamy, C. Liang,
J. Sakamoto, K. L. More, M. Chi* __ **129**

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