



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:

M. A. Newton, M. Di Michiel, A. Kubacka, A. Iglesias-Juez, M. Fernández-García
Observing Oxygen Storage and Release at Work under Cycling Redox Conditions: Synergies between Noble Metal and Oxide Promoter

P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux, M. Leclerc*
Synthesis of 5-Alkyl[3,4-c]thienopyrrole-4,6-dione-Based Polymers through Direct Heteroarylation

J. Zeng, C. Zhu, J. Tao, M. Jin, H. Zhang, Z.-Y. Li, Y. Zhu, Y. Xia*
Controlling the Nucleation and Growth of Silver on Palladium Nanocubes by Manipulating the Reaction Kinetics

C. A. DeForest, K. S. Anseth*
Photoreversible Patterning of Biomolecules within Click-Based Hydrogels

T. A. Nigst, J. Ammer, H. Mayr*
Ambident Reactivities of Methylhydrazines

M. Nazaré,* H. Matter,* D. W. Will, M. Wagner, M. Urmann, J. Czech, H. Schreuder, A. Bauer, K. Ritter, V. Wehner
Fragment Deconstruction of Small, Potent Factor Xa Inhibitors: Exploring the Superadditivity Energetics of Fragment Linking in Protein–Ligand Complexes

G. J. L. Bernardes, G. Casi, S. Trüssel, I. Hartmann, K. Schwager, J. Scheuermann, D. Neri*
A Traceless Vascular Targeting Antibody–Drug Conjugate for Cancer Therapy

H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori*
Enhancement of Proton Mobility in Extended Nanospace Channels

Author Profile



*“If I won the lottery, I would wonder how on earth my name appeared on the ticket.
The greatest scientific advance in the next decade will be the discovery of a second habitable earth ...”*
This and more about Nicolai Cramer can be found on page 302.

Nicolai Cramer _____ 302

News

New Academicians of the Chinese
Academy of Sciences _____ 303 – 304



Y. Li



Z. Liu



H. Tian



C.-H. Yan



X. Yang



J. Zhao



R. Noyori

Books

Privileged Chiral Ligands and Catalysts Qi-Lin Zhou

reviewed by C. Mazet _____ 305

Modern Inorganic Synthetic Chemistry Ruren Xu, Wenqin Pang, Qisheng Huo

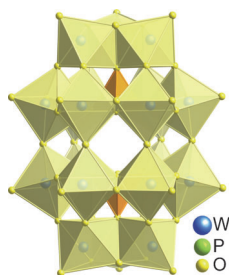
reviewed by W. Bensch _____ 305

Highlights

Polyoxometalates

E. Ahmed, M. Ruck* — 308–309

Ionothermal Synthesis of
Polyoxometalates



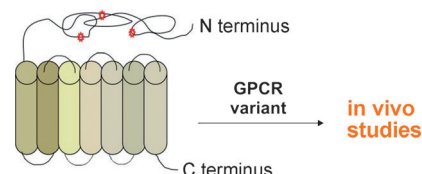
An emerging approach: In the ionothermal synthesis of transition-metal-oxide clusters an ionic liquid acts as a solvent, structure-directing agent, and charge-compensating species. The method may open new convenient routes for the synthesis of polyoxometalate-based materials.

Genetic Code

A. G. Beck-Sickinger,*
N. Budisa* — 310–312

Genetically Encoded Photocrosslinkers as
Molecular Probes To Study G-Protein-
Coupled Receptors (GPCRs)

The genetic code was expanded with orthogonal pairs to introduce photoactivatable amino acids into G-protein-coupled receptors (GPCRs) in a noninvasive manner. In this way the receptor surface could be mapped by searching for specific ligand interaction sites and the complex dynamics could be studied. This method is also useful for probing the structure of GPCR complexes in living cells.



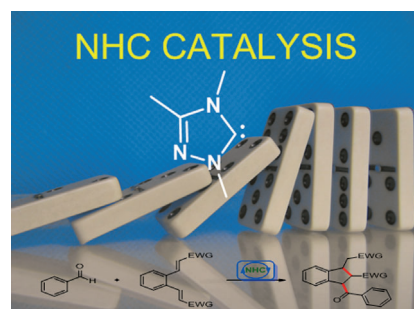
Minireviews

Domino Reactions

A. Grossmann, D. Enders* — 314–325

N-Heterocyclic Carbene Catalyzed
Domino Reactions

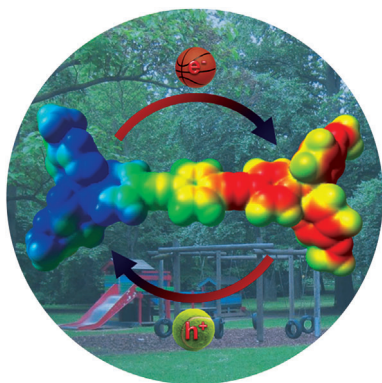
Every Jack will find his Jill: Uniting unique activation modes of N-heterocyclic carbene (NHC) catalysts with the concept of domino reactions (see picture, EWG = electron-withdrawing group), a new fast-growing field came into the spotlight in last three years. The state of the art of this field is presented and the definition of the domino reactions for the NHC catalysis is re-considered.



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sales tax.



Mix and match: Organic mixed-valence compounds are excellent model systems to study fundamental electron- and charge-transfer phenomena, as well as offering numerous perspectives for application. Particularly attractive is the possibility to systematically change the properties, since such compounds can be synthesized with a number of different redox centers and bridging units.

Reviews

Mixed-Valence Compounds

A. Heckmann, C. Lambert* — 326–392

Organic Mixed-Valence Compounds: A Playground for Electrons and Holes

Communications

Asymmetric Hydroamination

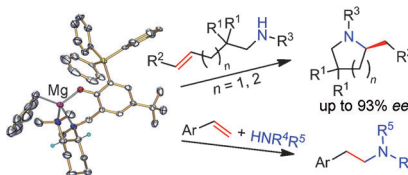


X. Zhang, T. J. Emge,
K. C. Hultzsich* — 394–398

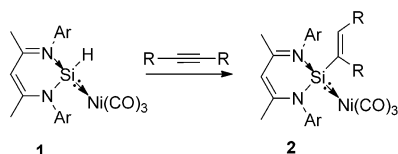
A Chiral Phenoxyamine Magnesium Catalyst for the Enantioselective Hydroamination/Cyclization of Aminoalkenes and Intermolecular Hydroamination of Vinyl Arenes



If Grignard had only known! A chiral magnesium complex catalyzes the intramolecular hydroamination/cyclization of aminoalkenes with high efficiency at temperatures as low as -20°C and enantioselectivities as high as 93 % *ee*. The high activity of this system also allows the catalytic intermolecular anti-Markovnikov addition of pyrrolidine and benzylamine to vinyl arenes.



Frontispiece



Not copy and paste: Although β -diketiminato ligands have been employed for the stabilization of Ge^{II} and Sn^{II} hydrides, the corresponding Si^{II} hydride is not accessible. However, coordination of silicon(II) to a $\{\text{Ni}(\text{CO})_3\}$ fragment allowed

the isolation of the first Si^{II} hydride metal complex **1**. This complex was used for the first silicon(II)-based and Ni^0 -mediated, stereoselective hydrosilylation of alkynes. R = phenyl, tolyl.

Hydrosilylation with Silicon(II)

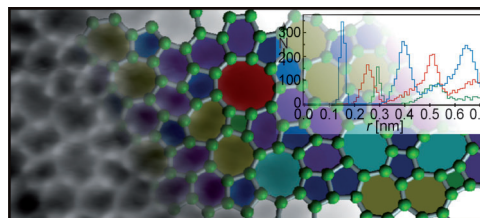
M. Stoelzel, C. Präsang, S. Inoue,
S. Enthaler, M. Driess* — 399–403

Hydrosilylation of Alkynes by $\text{Ni}(\text{CO})_3$ -Stabilized Silicon(II) Hydride



Thin Oxide Films

L. Lichtenstein, C. Büchner, B. Yang,
S. Shaikhutdinov, M. Heyde,* M. Sierka,
R. Włodarczyk, J. Sauer,
H.-J. Freund ————— 404–407



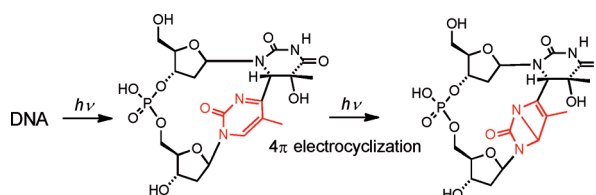
The Atomic Structure of a Metal-Supported Vitreous Thin Silica Film

Clear as glass: The atomic structure of a metal-supported vitreous thin silica film was resolved using low-temperature scanning tunneling microscopy (STM). Based on the STM image, a model was constructed and the atomic arrangement

of the thin silica glass determined (see picture). The total pair correlation function of the structural model shows good agreement with diffraction experiments performed on vitreous silica.

DNA Lesions

K. Haiser, B. P. Fingerhut, K. Heil, A. Glas,
T. T. Herzog, B. M. Pillés, W. J. Schreier,
W. Zinth,* R. de Vivie-Riedle,*
T. Carell* ————— 408–411



Mechanism of UV-Induced Formation of Dewar Lesions in DNA

The importance of a backbone: The mechanism of formation of Dewar lesions (see scheme) has been investigated by using femtosecond IR spectroscopy and ab initio calculations of the excited state.

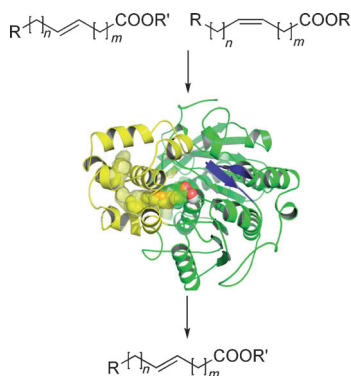
The 4π electrocyclic ring closure is rather slow, occurs with an unusual high quantum yield, and—surprisingly—is controlled by the phosphate backbone.

Protein Engineering

H. B. Brundiek, A. S. Evitt, R. Kourist,
U. T. Bornscheuer* ————— 412–414



Creation of a Lipase Highly Selective for *trans* Fatty Acids by Protein Engineering



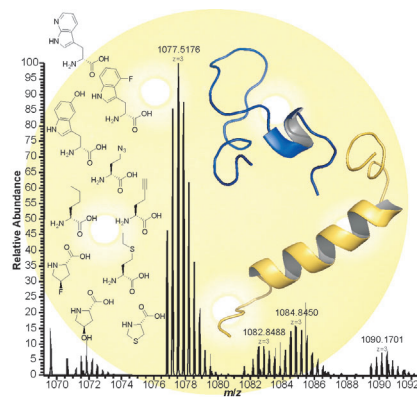
Sorting out: Protein engineering of lipase CAL-A led to the discovery of mutants with excellent chemoselectivity for the removal of *trans* and saturated fatty acids from partially hydrogenated vegetable oil. These fatty acids, identified as a major risk factor for human health, can now be removed by enzyme catalysis.

Peptide Synthesis

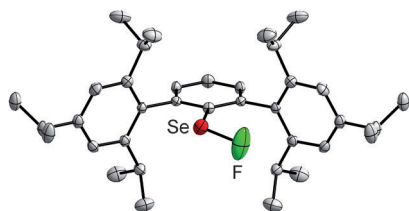
F. Oldach, R. Al Toma, A. Kuthning,
T. Caetano, S. Mendo, N. Budisa,*
R. D. Süßmuth* ————— 415–418



Congeneric Lantibiotics from Ribosomal In Vivo Peptide Synthesis with Noncanonical Amino Acids



Expanded repertoire: Synthetic amino acids translated into propeptides dramatically increase the chemical diversity of the two-component lantibiotic lichenicidin. This opens new routes towards novel and unique peptide antibiotic sequences, which could display features important for medical applications.



Joining the stable: The first examples of the highly unstable selenenyl fluorides $RSeF$ are prepared from the reaction on the tin selenide $RSeSnMe_3$ with XeF_2 . Through the use of extremely large protecting groups (*m*-terphenyl ligands) which stabilizes the $RSeF$ units against disproportionation, the compounds could be isolated and characterized by NMR spectroscopy and single-crystal structure analysis (see structure).

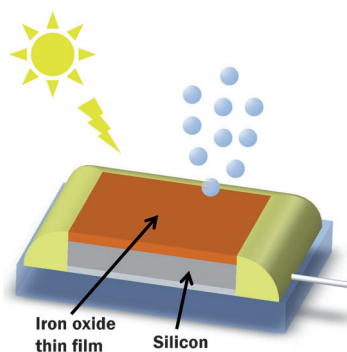
Selenenyl Fluorides

H. Poleschner,* S. Ellrodt,
M. Malischewski, J.-y. Nakatsuji,
C. Rohner, K. Seppelt — 419–422

$Trip_2C_6H_3SeF$: The First Isolated Selenenyl Fluoride



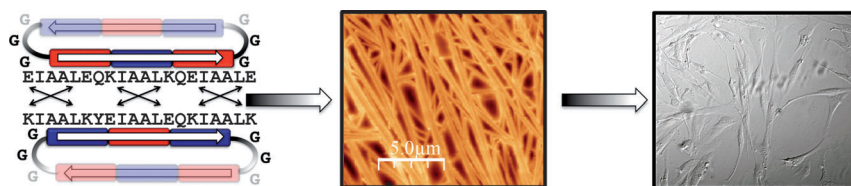
Silicon splits: The application of silicon to water oxidation is limited due to unfavorable interface properties. However, these can be circumvented by using a high-performance silicon photoanode with a catalytically active iron oxide thin film (see picture). This approach results in photocurrents as high as 17 mAcm^{-2} under 1 sun and zero overpotential conditions.



Water Oxidation

K. Jun, Y. S. Lee, T. Buonassisi,
J. M. Jacobson* — 423–427

High Photocurrent in Silicon Photoanodes Catalyzed by Iron Oxide Thin Films for Water Oxidation



Two faces for one matrix: A single bifaceted cyclopeptide block forms highly branched, porous, and intricate fibrillar networks, which span microscopic dimensions and mimic the extracellular matrix to support cell growth and proliferation (see picture). The peptide block has two domains connected with triglycine linkers (GGG); the domains consist of positively (blue) and negatively (red) charged heptads that provide interactions between different blocks.

eration (see picture). The peptide block has two domains connected with triglycine linkers (GGG); the domains consist of positively (blue) and negatively (red) charged heptads that provide interactions between different blocks.

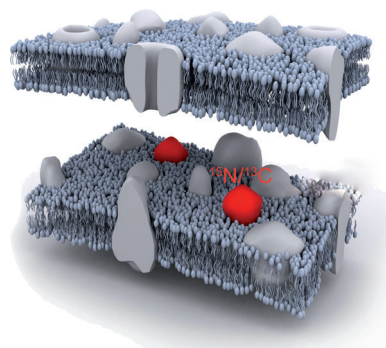
Tissue Engineering

A. Bella, S. Ray, M. Shaw,
M. G. Ryadnov* — 428–431

Arbitrary Self-Assembly of Peptide Extracellular Microscopic Matrices



Membrane proteins in their native cellular membranes are accessible by dynamic nuclear polarization magic angle spinning solid-state NMR spectroscopy without the need of purification and reconstitution (see picture). Dynamic nuclear polarization is essential to achieve the required gain in sensitivity to observe the membrane protein of interest.



Solid-State NMR Spectroscopy

T. Jacso, W. T. Franks, H. Rose, U. Fink,
J. Broecker, S. Keller, H. Oschkinat,
B. Reif* — 432–435

Characterization of Membrane Proteins in Isolated Native Cellular Membranes by Dynamic Nuclear Polarization Solid-State NMR Spectroscopy without Purification and Reconstitution

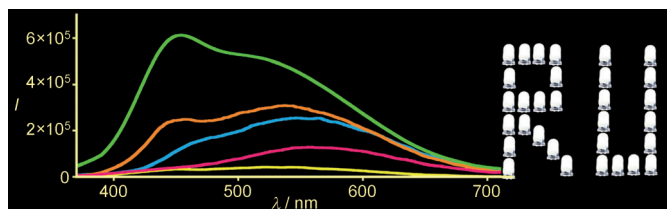


White-Light Emitters

M. Roushan, X. Zhang, J. Li* — 436–439



Solution-Processable White-Light-Emitting Hybrid Semiconductor Bulk Materials with High Photoluminescence Quantum Efficiency



Glowing white: Bulk hybrid semiconductor materials built from periodic nanostructured 2D layers of ZnS emit bright white light. Their emission intensity, quantum efficiency, and color quality can

be systematically tuned by varying the composition of both the inorganic and organic components. The materials show great promise as a new type of single-phase white-light-emitting phosphors.

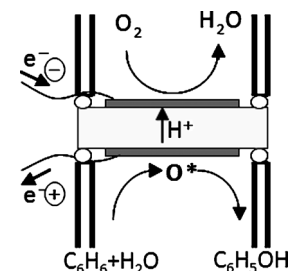
Benzene Hydroxylation

B. Lee, H. Naito, T. Hibino* — 440–444



Electrochemical Oxidation of Benzene to Phenol

Gas-phase electrochemistry: The direct hydroxylation of benzene to phenol was investigated using an electrochemical cell. The production of phenol over a VO_x anode was found to be significant at 50 °C. The resultant current efficiency for phenol production and selectivity toward phenol reached 76.5 and 94.7%, respectively.



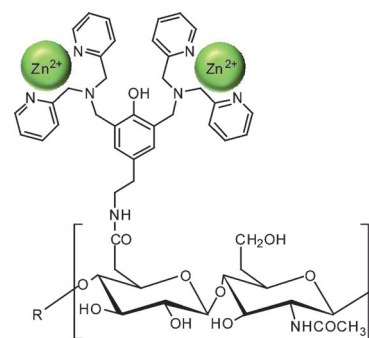
Drug Delivery

G. Liu, K. Y. Choi, A. Bhirde, M. Swierczewska, J. Yin, S. W. Lee, J. H. Park, J. I. Hong, J. Xie, G. Niu, D. O. Kiesewetter, S. Lee,* X. Chen* — 445–449



Sticky Nanoparticles: A Platform for siRNA Delivery by a Bis(zinc(II) dipicolylamine)-Functionalized, Self-Assembled Nanoconjugate

Delivering the goods: Multifunctional, self-assembled, polymeric nanoparticles for the simultaneous delivery of small-molecule drugs and siRNA have been synthesized. The nanoparticles are composed of biodegradable hyaluronic acid, for tumor targeting and cellular delivery, and a high siRNA binding affinity is provided by a Zn^{II} -dipicolylamine analogue as an artificial phosphate-binding receptor (see scheme).



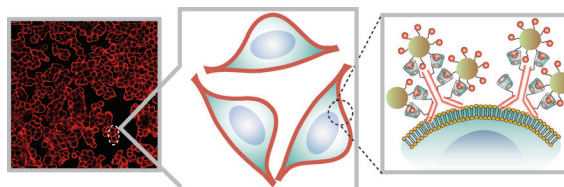
Back Cover

Cell Labeling

S. S. Agasti, M. Liong, C. Tassa, H. J. Chung, S. Y. Shaw, H. Lee,* R. Weissleder* — 450–454

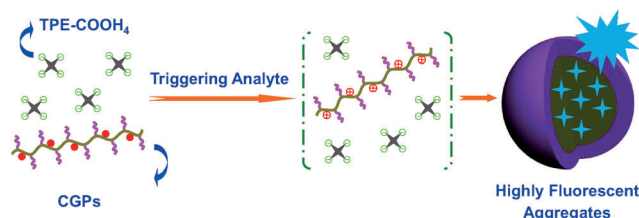


Supramolecular Host–Guest Interaction for Labeling and Detection of Cellular Biomarkers



Be my guest: A supramolecular host–guest interaction is utilized for highly efficient bioorthogonal labeling of cellular targets. Antibodies labeled with a cyclodextrin host molecule bind to adamantane-labeled magnetofluorescent nano-

particles (see picture) and provide an amplifiable strategy for biomarker detection that can be adapted to different diagnostic techniques such as molecular profiling or magnetic cell sorting.



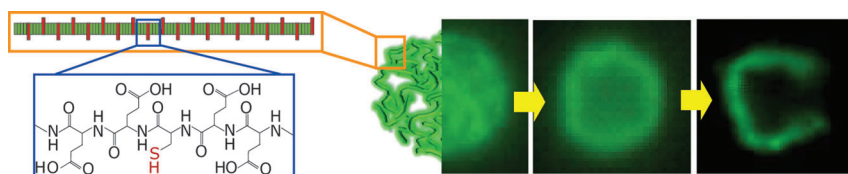
Trip the light of plastic: An aqueous fluorogenic sensing system consisting of selective and specific analyte-triggerable charge-generation polymers (CGPs) and a negatively charged aggregation-induced emission active fluorogen (TPE-COOH₄)

is presented. In the presence of a triggering analyte of interest, the CGPs undergo electrostatic complexation with TPE-COOH₄ leading to intense fluorescence emission due to the aggregation of TPE-COOH₄.

Sensors

C. Li, T. Wu, C. Hong, G. Zhang,*
S. Liu* 455–459

A General Strategy To Construct Fluorogenic Probes from Charge-Generation Polymers (CGPs) and AIE-Active Fluorogens through Triggered Complexation



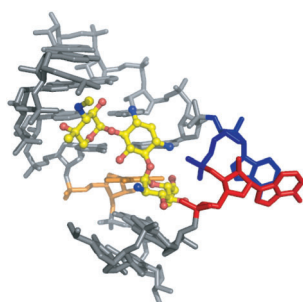
In nature, the sequence of amino acids in a protein is determined by the genetic code. Biosynthesis of polypeptides by bacteria can be used to exploit this natural process to afford exact control over properties such as molecular weight, chemical

functionality, and structure. It is demonstrated how control over the positioning of functional groups can be used to tune the degradation of assembled polypeptide particles (see scheme).

Therapeutic Carriers

D. H. C. Chang, A. P. R. Johnston,
K. L. Wark, K. Breheney,
F. Caruso* 460–464

Engineered Bacterially Expressed Polypeptides: Assembly into Polymer Particles with Tailored Degradation Profiles

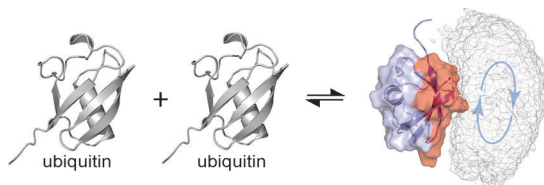


Resistance explained: The crystal structures of the ribosomal decoding A site with an A1408G antibiotic-resistance mutation were solved in the presence and absence of the aminoglycoside geneticin (see structure, geneticin carbon framework in yellow). These structures show how bacteria acquire high-level resistance against aminoglycosides by the mutation.

Antibiotic Resistance

J. Kondo* 465–468

A Structural Basis for the Antibiotic Resistance Conferred by an A1408G Mutation in 16S rRNA and for the Antiprotozoal Activity of Aminoglycosides



Another kind of dynamics: Ubiquitin noncovalently dimerizes with a dissociation constant of approximately 5 mM. The two subunits adopt an array of relative orientations, utilizing an interface also for binding to other proteins (see picture).

Quaternary fluctuation among members of the dimer ensemble constitutes a different kind of dynamics that complements the tertiary dynamics of each ubiquitin subunit.

Protein Dynamics

Z. Liu, W. P. Zhang, Q. Xing, X. Ren,
M. Liu, C. Tang* 469–472

Noncovalent Dimerization of Ubiquitin

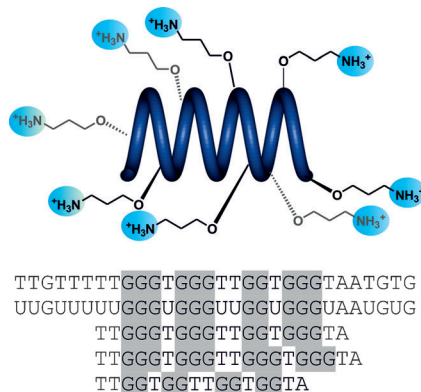


Foldamer–DNA Recognition

L. Delaurière, Z. Dong, K. Laxmi-Reddy,
F. Godde, J.-J. Toulmé,*
I. Huc* ————— 473–477



Deciphering Aromatic Oligoamide
Foldamer–DNA Interactions



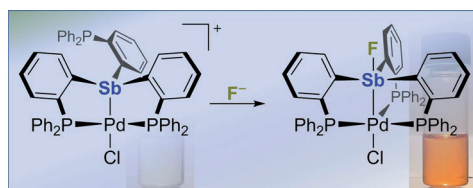
Finest selection: Side-chain selective, end-group selective, diastereoselective, and RNA- vs. DNA-selective interactions have been revealed between multiturn helical aromatic amide foldamers having cationic side chains and G-quadruplex aptamers.

Lewis Acids

C. R. Wade, I.-S. Ke,
F. P. Gabbaï* ————— 478–481



Sensing of Aqueous Fluoride Anions by
Cationic Stibine–Palladium Complexes



Turn on the lantern! The stibine donor ligand of a cationic palladium complex acts as a Lewis acid and reacts with a fluoride anion to afford the corresponding fluorostiboranyl–palladium species (see

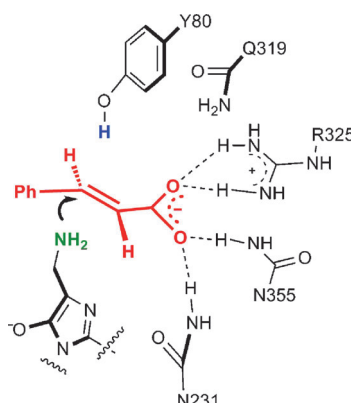
scheme). Binding of the fluoride anion to the antimony center induces a change in denticity of the triphosphine unit and leads to a bright-orange trigonal-bipyramidal d⁸ lantern complex.

Enzyme Catalysis

B. Wu, W. Szymański, G. G. Wybenga,
M. M. Heberling, S. Bartsch,
S. de Wildeman, G. J. Poelarends,
B. L. Feringa, B. W. Dijkstra,
D. B. Janssen* ————— 482–486



Mechanism-Inspired Engineering of
Phenylalanine Aminomutase for
Enhanced β -Regioselective Asymmetric
Amination of Cinnamates



Turn to switch: A mutant of phenylalanine aminomutase was engineered that can catalyze the regioselective amination of cinnamate derivatives (see scheme, red) to, for example, β -amino acids. This regioselectivity, along with the X-ray crystal structures, suggests two distinct carboxylate binding modes differentiated by C _{β} –C_{ipso} bond rotation, which determines if β - (see scheme) or α -addition takes place.

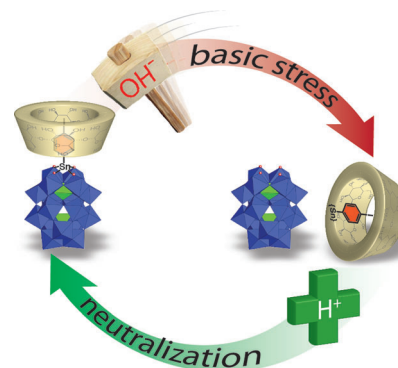
Polyoxometalate–cyclodextrin assembly

G. Izzet,* M. Ménand,* B. Matt,
S. Renaudineau, L.-M. Chamoreau,
M. Sollogoub,* A. Proust* — 487–490

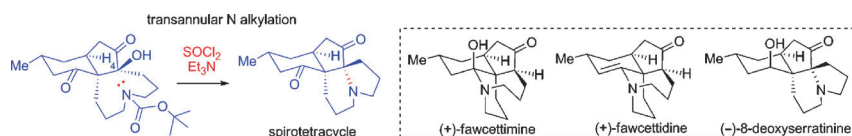


Cyclodextrin-Induced Auto-Healing of
Hybrid Polyoxometalates

You'll never walk alone: An auto-healing process of the first host–guest complex involving a polyoxometalate hybrid and a cyclodextrin is reported. Indeed, this inclusion complex allows the complete restoration of the anchored organic moiety released by a basic stress, a process otherwise not fully reversible.



Inside Back Cover



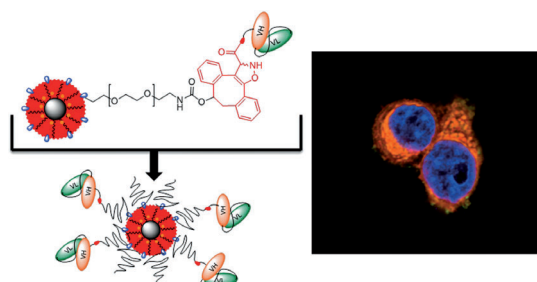
A shared story: Three fawcettimine- and serratinine-type *Lycopodium* alkaloids are prepared from a common tetracyclic spiroidiketone intermediate in concise total syntheses (see scheme). The intermediate

was constructed by a remarkable biosynthesis-inspired transannular N–C bond formation to the spiro-configured carbon center and a hydroxy-directed pinacol coupling promoted by SmI_2 .

Natural Product Synthesis

H. Li, X. Wang, X. Lei* — 491–495

Total Syntheses of *Lycopodium* Alkaloids
(+)-Fawcettimine, (+)-Fawcettidine, and
(–)-8-Deoxyserratinine



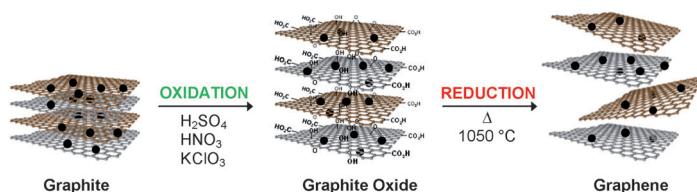
Particularly suitable: An N-terminal serine mutant of anti-HER2 scFv antibody was conjugated to polymer-coated magnetofluorescent nanoparticles by strain-promoted

alkyne–nitron cycloaddition. The resulting nanoparticles (see scheme) proved effective in targeting and labeling HER2-positive breast cancer cells.

Protein Nanoconjugation

M. Colombo, S. Sommaruga,
S. Mazzucchi, L. Polito, P. Verderio,
P. Galeffi, F. Corsi, P. Tortora,
D. Prosperi* — 496–499

Site-Specific Conjugation of ScFvs
Antibodies to Nanoparticles by
Bioorthogonal Strain-Promoted Alkyne–
Nitron Cycloaddition



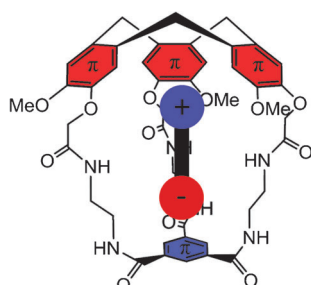
All at C? Graphenes prepared by the top-down exfoliation of graphite are shown to contain metallic impurities (see scheme, metal impurities shown as black dots).

These impurities may dominate their properties and can have a negative influence on their potential applications.

Impure Graphene

A. Ambrosi, S. Y. Chee, B. Khezri,
R. D. Webster, Z. Sofer,
M. Pumera* — 500–503

Metallic Impurities in Graphenes
Prepared from Graphite Can Dramatically
Influence Their Properties



Brothers and enemies: Anion– π and cation– π interactions act in a synergistic way when gathered in the molecular cavity of a hemicyptophane host, affording an efficient contribution (-170 kJ mol^{-1}) in zwitterion recognition. NMR titration experiments and calculations reveal the positioning of the guest in the cavity of the heteroditopic receptor. This study emphasizes the importance of anion– π bonds in host–guest chemistry.

Supramolecular Chemistry

O. Perraud, V. Robert, H. Gornitzka,
A. Martinez,* J.-P. Dutasta* — 504–508

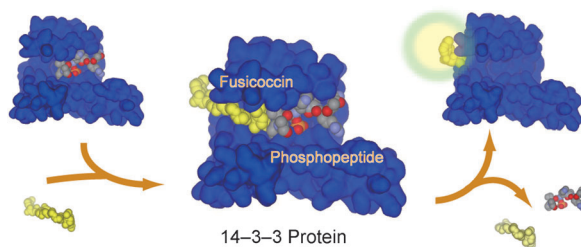
Combined Cation– π and Anion– π
Interactions for Zwitterion Recognition

Protein–Protein Interactions

M. Takahashi, A. Kawamura, N. Kato,
T. Nishi, I. Hamachi,
J. Ohkanda* ————— 509–512



Phosphopeptide-Dependent Labeling of
14–3–3 ζ Proteins by Fusicoccin-Based
Fluorescent Probes



Fluorescent combination: Cell-penetrating probes derived from the diterpene fusicoccin can form ternary complexes with 14–3–3 proteins and phosphopeptide

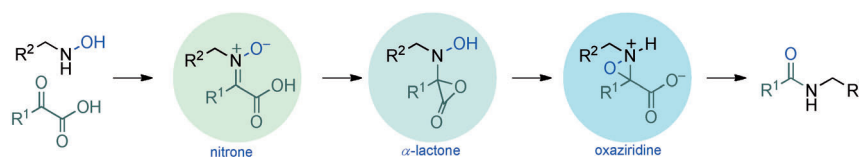
ligands, whereupon the probes site-specifically attach a fluorescent tag onto the surface of the 14–3–3 proteins.

Reaction Mechanisms

I. Pusterla, J. W. Bode* ————— 513–516



The Mechanism of the α -Ketoacid–
Hydroxylamine Amide-Forming Ligation



Three-ring circus! Surprisingly complex molecular acrobatics are observed in the mechanism of the α -ketoacid–hydroxylamine amide-forming ligation. Although this remarkable reaction can already be used for the chemoselective

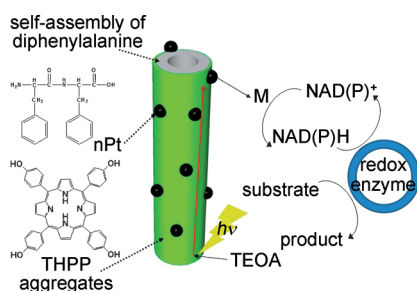
union of large, unprotected peptide fragments the elucidated mechanism provides important clues to extending its application to larger and more complex biological targets.

Artificial Photosynthesis

J. H. Kim, M. Lee, J. S. Lee,
C. B. Park* ————— 517–520



Self-Assembled Light-Harvesting Peptide
Nanotubes for Mimicking Natural
Photosynthesis



Light-harvesting peptide nanotubes are synthesized by the self-assembly of diphenylalanine with THPP and platinum nanoparticles (nPt; see picture; TEOA = triethanolamine). The light-harvesting peptide nanotubes are suitable for mimicking photosynthesis because of their structure and electrochemical properties that are similar to the ones of photosystem I in natural photosynthesis.

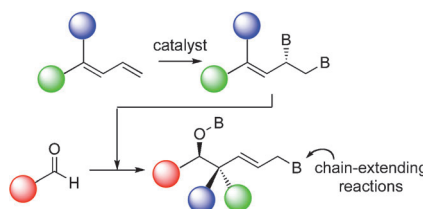
Front Cover

Asymmetric Catalysis

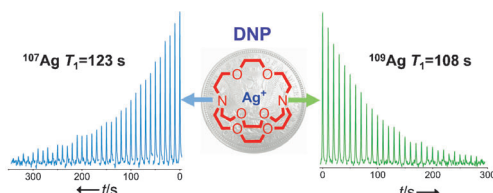
L. T. Kliman, S. N. Mlynarski, G. E. Ferris,
J. P. Morken* ————— 521–524



Catalytic Enantioselective 1,2-Diboration
of 1,3-Dienes: Versatile Reagents for
Stereoselective Allylation



More with boron: The development of catalytic enantioselective 1,2-diboration of 1,3-dienes enables a new strategy for enantioselective carbonyl allylation reactions (see scheme). These reactions occur with outstanding levels of stereoselection and can be applied to both monosubstituted and 1,1-disubstituted dienes. The carbonyl allylation reactions provide enantiomerically enriched functionalized homoallylic alcohol products.



Both isotopes of silver, ^{107}Ag and ^{109}Ag , were simultaneously polarized by dynamic nuclear polarization (DNP), thus allowing large signal enhancements and the NMR characterization of Ag complexes in the millimolar concentration range. Since

both isotopes have long relaxation times T_1 , the hyperpolarized NMR signal of one isotope could still be observed even after the magnetization of the other isotope had been destroyed by radio-frequency pulses.

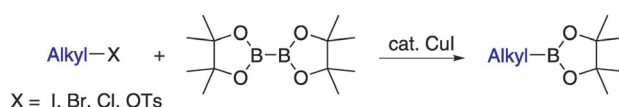
Silver NMR Spectroscopy

L. Lumata, M. E. Merritt, Z. Hashami, S. J. Ratnakar, Z. Kovacs* — 525–527

Production and NMR Characterization of Hyperpolarized $^{107,109}\text{Ag}$ Complexes



Inside Cover



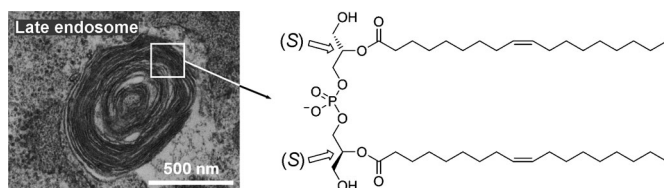
Easy access: An unprecedented copper-catalyzed cross-coupling reaction of the title compounds with diboron reagents is described (see scheme; Ts = 4-toluenesulfonyl). This reaction can be used to

prepare both primary and secondary alkylboronic esters having diverse structures and functional groups. The resulting products would be difficult to access by other means.

Cross-Coupling

C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel,* T. B. Marder,* L. Liu* — 528–532

Alkylboronic Esters from Copper-Catalyzed Borylation of Primary and Secondary Alkyl Halides and Pseudohalides



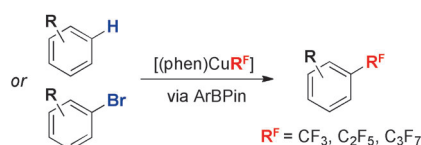
At a glance: The stereochemical configuration of the diglycerophosphate backbone of the endosome-specific lipid bis(monoacylglycero)phosphate (BMP, see picture) was determined by ^1H NMR spectroscopy. Enantiomeric discrimina-

tion was facilitated by introduction of D-camphor ketals as chiral shift reagents, and enantiopure synthetic BMP analogues were prepared as reference materials. Natural BMP exhibited the unusual *sn*-1,1' diglycerophosphate backbone.

Stereochemical Elucidation

H.-H. Tan, A. Makino, K. Sudesh, P. Greimel,* T. Kobayashi* — 533–535

Spectroscopic Evidence for the Unusual Stereochemical Configuration of an Endosome-Specific Lipid



A versatile method for the synthesis of aryl perfluoroalkanes from arenes and aryl bromides is described. Substituted arenes or aryl bromides are converted in situ to an aryl boronate ester that readily undergoes perfluoroalkylation in air with $[(\text{phen})\text{CuR}^{\text{F}}]$. A broad range of aryl bromide substrates were perfluoroalkylated in good yield for the first time. $[(\text{phen})\text{CuCF}_3]$ is now commercially available and has been prepared on 20 g scale.

Trifluoromethylation

N. D. Litvinas, P. S. Fier, J. F. Hartwig* — 536–539

A General Strategy for the Perfluoroalkylation of Arenes and Arylbromides by Using Arylboronate Esters and $[(\text{phen})\text{CuR}^{\text{F}}]$



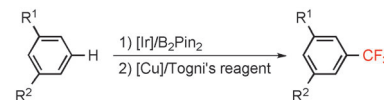
C–H Activation

T. Liu, X. Shao, Y. Wu,
Q. Shen* 540–543



Highly Selective Trifluoromethylation of 1,3-Disubstituted Arenes through Iridium-Catalyzed Arene Borylation

The old one two: A sequential iridium-catalyzed borylation and copper-catalyzed trifluoromethylation of arenes is described (see scheme; Pin = pinacol). The reaction is conducted under mild reaction conditions and tolerates a variety of functional groups. The advantages of this tandem procedure are demonstrated by the late-stage trifluoromethylation of a number of biologically active molecules.

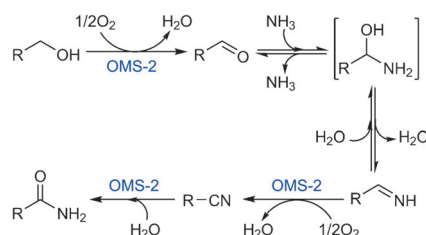


Catalytic Amide Synthesis

K. Yamaguchi, H. Kobayashi, T. Oishi,
N. Mizuno* 544–547



Heterogeneously Catalyzed Synthesis of Primary Amides Directly from Primary Alcohols and Aqueous Ammonia



In the presence of a manganese oxide based octahedral molecular sieve (OMS-2), a range of primary amides could be synthesized directly from primary alcohols and ammonia (see scheme). The observed catalysis was heterogeneous, and the recovered catalyst could be reused many times without an appreciable loss of its catalytic performance.

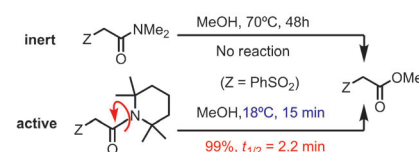
Amide Solvolysis

M. Hutchby, C. E. Houlden,
M. F. Haddow, S. N. G. Tyler,
G. C. Lloyd-Jones,*
K. I. Booker-Milburn* 548–551



Switching Pathways: Room-Temperature Neutral Solvolysis and Substitution of Amides

Stick or twist: By introducing steric hindrance at the nitrogen atom, stable linear amides bearing an electron-withdrawing α -substituent ($Z = \text{Ar}$, PhSO_2 , $\text{P}(\text{O})(\text{OR})_2$, CN , or CO_2R) can be induced to undergo solvolysis and substitution reactions through an elimination–addition mechanism (see picture). Key to this process is a low barrier to rotation around the amide bond and the α -substituent Z .

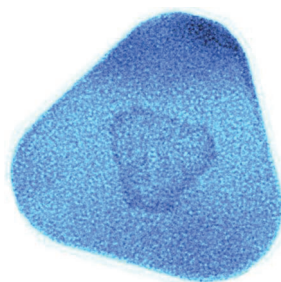


Nanoplates

J. Goebel, Q. Zhang, L. He,
Y. Yin* 552–555



Monitoring the Shape Evolution of Silver Nanoplates: A Marker Study



Out of the frame: A marker study using gold frames was designed to reveal that silver nanoplates undergo a shape transition during their seeded growth from triangular to circular to hexagonal plates before ultimately returning to triangular structures with an orientation 180° relative to that of the original triangular seeds (see picture, the original gold triangular frame is visible at the center of the silver nanoplate).



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



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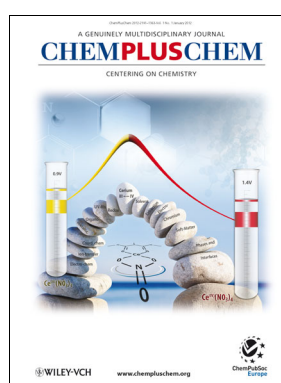
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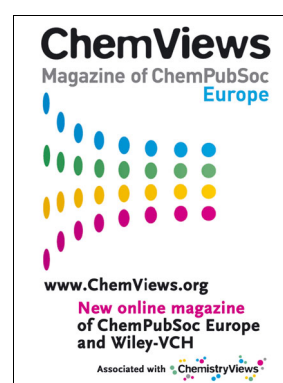
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