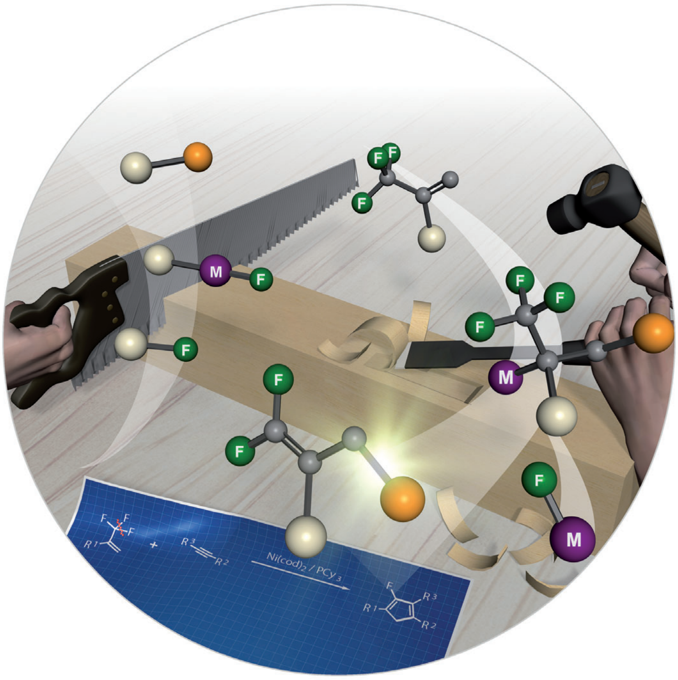
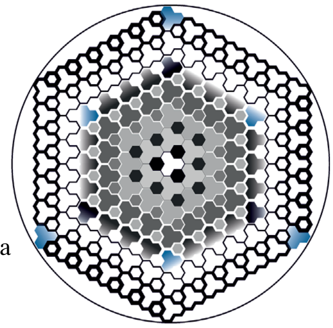
The carbon–fluorine bond ...

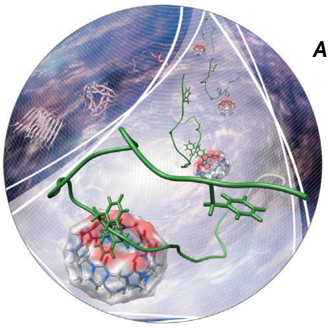


... is known as one of the strongest chemical bonds. It is typically difficult to cleave, however, this cleavage can be achieved by a metal-mediated approach involving oxidative addition. In their Communication on page 7564 ff., J. Ichikawa and co-workers demonstrate a new method for C–F bond cleavage that utilizes β-fluorine elimination for a nickel-mediated [3+2] cycloaddition. The cover image illustrates two different tools for processing wood—a metal saw (oxidative addition) and a chisel (β-elimination)—as an analogy to the methods for metal-mediated C–F bond cleavage.



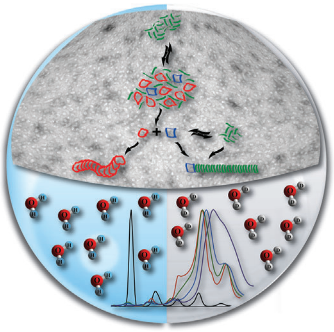
Graphitic Carbon Nitride

In their Communication on page 7450 ff., A. I. Cooper, M. J. Bojdys, et al. report crystalline thin films of triazine-based graphitic carbon nitride (TGCN). TGCN is structurally similar to graphite but it is a semiconductor, and the thin films display a direct bandgap between 1.6 and 2.0 eV.



Amyloids

In their Communication on page 7461 ff., K. Kim, H. I. Kim, and co-workers demonstrate that cucurbit[7]uril inhibits the fibrillation of insulin and β-amyloid by capturing crucial phenylalanine residues through host–guest interactions.



Protein Aggregation

In their Communication on page 7560 ff., D. Otsen, T. J. D. Jørgensen, and co-workers reveal that for α-synuclein oligomers, which are widely accepted to be cytotoxic species in Parkinson's disease, two different types are formed.

How to contact us:

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

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Telephone: (+49) 6201–606-280

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Service

Author Profile

"My favorite saying is "the devil is in the detail". The principal aspects of my personality are modesty and optimism …"
This and more about Yi Xie can be found on page 7396.

News

A. K. Cheetham

J. A. Reimer

T. M. Swager

T. Sasamori

M. Weck

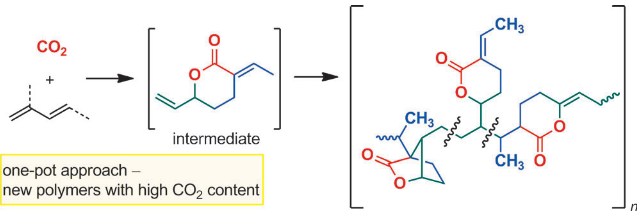
Books

Highlights

CO_2 Copolymers

G. Fiorani, A. W. Kleij* ______ **7402 – 7404**

Preparation of CO_2/Diene Copolymers: Advancing Carbon Dioxide Based Materials



CO_2-based materials: Metastable CO_2/diene-based lactones, which were prepared by the palladium-catalyzed telomerization of CO_2 and dienes, easily undergo aerobic radical homo-polymerization to give novel CO_2-rich polymers. This two-step reaction set-up expands the potential applications of CO_2-based copolymers by adding innovative compositions, structures, and properties.

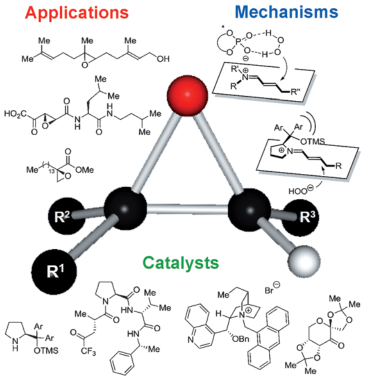
Minireviews

Synthetic Methods

R. L. Davis, J. Stiller, T. Naicker, H. Jiang, K. A. Jørgensen* ______ **7406 – 7426**

Asymmetric Organocatalytic Epoxidations: Reactions, Scope, Mechanisms, and Applications

Pick your type: In the past several decades, highly useful epoxidation protocols have been developed with a variety of activation modes using a wide range of asymmetric organocatalysts. This review documents the rapid and expansive development in this area, thus providing a clear overview of the various catalyst types available for asymmetric organocatalytic epoxidations, as well as their mechanisms and applications.

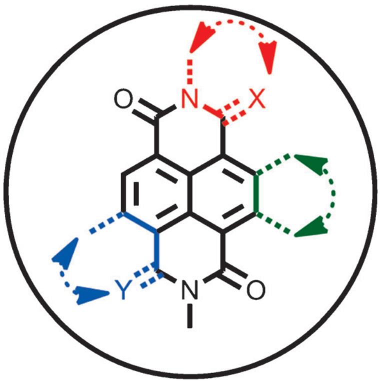


Reviews

Dyes/Pigments

S.-L. Suraru, F. Würthner* __ **7428 – 7448**

Strategies for the Synthesis of Functional Naphthalene Diimides



Core competence: The structural modification of naphthalene diimides has undergone significant development in the last few years, which has culminated in a broad range of new derivatives with different adjustable electronic properties. This Review describes the synthetic strategies towards core-substituted as well as core-expanded naphthalene diimides.

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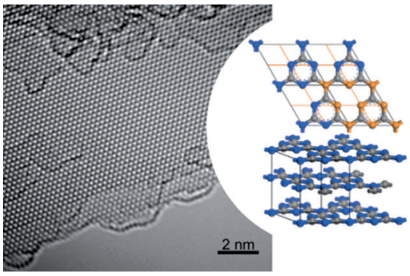
Communications

Carbon Nitride

G. Algara-Siller, N. Severin, S. Y. Chong, T. Björkman, R. G. Palgrave, A. Laybourn, M. Antonietti, Y. Z. Khimyak, A. V. Krasheninnikov, J. P. Rabe, U. Kaiser, A. I. Cooper,* A. Thomas, M. J. Bojdys* ——— **7450 – 7455**

Triazine-Based Graphitic Carbon Nitride: a Two-Dimensional Semiconductor

Frontispiece



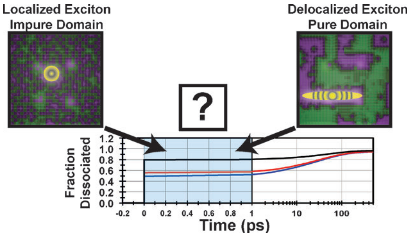
Only five non-metallic materials of the graphene family were known up to date: graphene, hBN, BCN, fluorographene, and graphene oxide. For the first time, crystalline thin films of triazine-based graphitic carbon nitride (TGCN) are now presented. TGCN is structurally similar to graphite but it is a semiconductor. The thin films are a few to several hundreds of atomic layers thick and display a direct bandgap between 1.6 and 2.0 eV.

Exciton Dissociation

H. M. Heitzer, B. M. Savoie, T. J. Marks,* M. A. Ratner* ——— **7456 – 7460**

Organic Photovoltaics: Elucidating the Ultra-Fast Exciton Dissociation Mechanism in Disordered Materials

Inside Cover



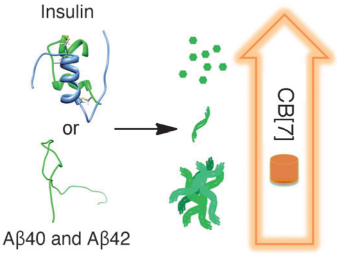
An exciting model: An exciton dissociation model that captures both ultra-fast and diffusion-limited behavior in bulk-heterojunction organic photovoltaic (OPV) systems is proposed. The model examines the disparate mechanisms for ultra-fast exciton delocalization: exciton delocalization and impure domains.

Amyloids

H. H. Lee, T. S. Choi, S. J. C. Lee, J. W. Lee, J. Park, Y. H. Ko, W. J. Kim, K. Kim,* H. I. Kim* ——— **7461 – 7465**

Supramolecular Inhibition of Amyloid Fibrillation by Cucurbit[7]uril

Inside Back Cover

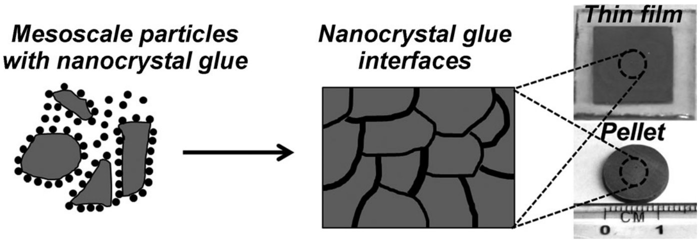


Supramolecular strategy: Amyloid fibrillation of insulin and β-amyloid was modulated by using cucurbit[7]uril (CB[7]). CB[7] exhibits high binding affinity for phenylalanine residues, which are crucial to the hydrophobic interactions formed during amyloid fibrillation. This supramolecular strategy based on a residue-specific interaction has potential for the development of a therapeutic agent for amyloidosis.

Inorganic Interfaces

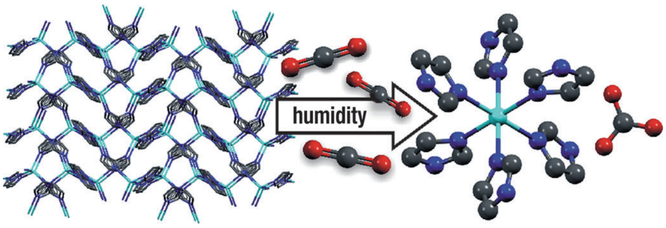
J. S. Son, H. Zhang, J. Jang, B. Poudel, A. Waring, L. Nally, D. V. Talapin* ——— **7466 – 7470**

All-Inorganic Nanocrystals as a Glue for BiSbTe Grains: Design of Interfaces in Mesostructured Thermoelectric Materials



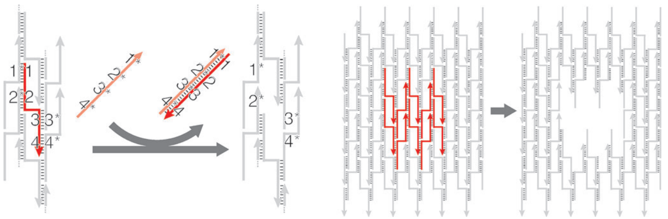
The interfaces in thermoelectric materials can be formed by using bismuth nanocrystals (NCs) capped with $(N_2H_5)_4Sb_2Te_7$ ligands that serve as a "glue" for mesoscopic grains, which are joined in hot-pressed pellets or solution-processed thin films. The design of the NC glue allows selective enhancement or decrease of the majority-carrier concentration near the grain boundaries.

Materials for Carbon Sequestration



ZIF today, carbonate tomorrow: The sensitivity of zeolitic imidazolate frameworks (ZIFs) to CO_2 in humid environments, which was previously not recognized, leads to degradation of porous and nonporous Zn-, Co-, and Cd-based ZIFs into complex carbonates. Only one of the five tested ZIFs was resistant to chemical attack by CO_2.

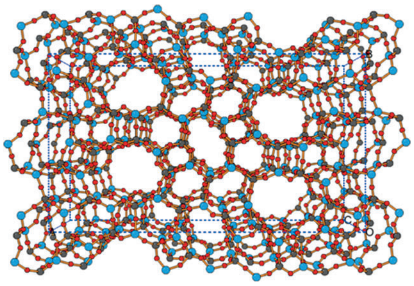
DNA Architectures



Carving out a shape-changing strategy: The modularly interconnected architecture of single-stranded DNA tile and brick structures was used to develop a general method for structural reconfiguration. The removal of one component strand (see picture) revealed a newly exposed toehold on a neighboring strand, thus enabling the removal of regions of connected component strands without the need to modify the strands with predesigned external toeholds.

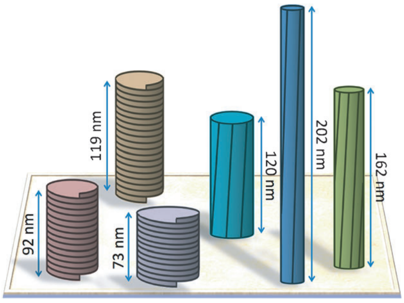
Zeolite Structures

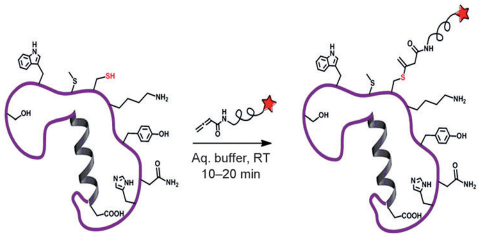
Structure elucidation: The structure of the new medium-pore aluminophosphate molecular sieve PST-6 (see picture) with 36 crystallographically distinct tetrahedral sites and thus with the most complex zeolite structure known to date, has been solved by combining X-ray diffraction, electron crystallography, and computer modeling.



DNA Nanostructure

Tubular structures were constructed in a size-controlled fashion by a new DNA origami method and analyzed by atomic force microscopy. The formation of unexpectedly long tubes with different helical properties was observed in addition to that of the expected short ones. Analysis of the content of short and long tubes allows an estimation of the folding pathways.





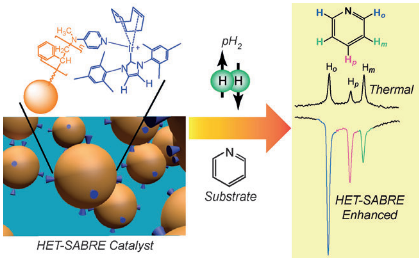
Tagged: Allenamides add selectively to the thiol group of cysteine and does not react with the other functional groups on the unprotected peptide or protein under physiological conditions.

Protein Modifications

A. Abbas, B. Xing,*
T. P. Loh* ________ **7491 – 7494**

Allenamides as Orthogonal Handles for Selective Modification of Cysteine in Peptides and Proteins

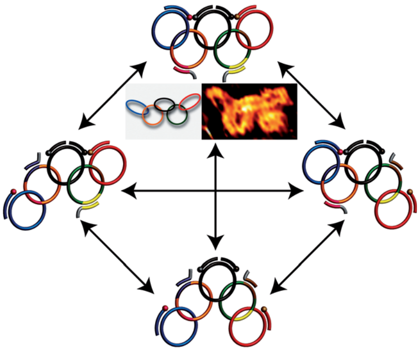
Sending a signal: A novel variant of an iridium-based organometallic catalyst was synthesized and immobilized on polymer microbeads. Upon administration of para-hydrogen (pH_2) gas to a solution containing the catalyst and pyridine, up to a fivefold enhancement is observed in the ^1H NMR spectra owing to the title process (HET-SABRE). The catalyst is easy to recycle and holds potential for applications varying from spectroscopic studies of catalysis to imaging metabolites.



NMR Spectroscopy

F. Shi, A. M. Coffey, K. W. Waddell,
E. Y. Chekmenev,
B. M. Goodson* ________ **7495 – 7498**

Heterogeneous Solution NMR Signal Amplification by Reversible Exchange

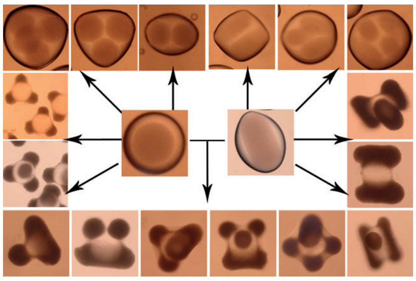


A feat worthy of a medal: A five-ring interlocked DNA catenane underwent programmed and switchable reconfiguration across four states (see picture). The dynamics of transitions between the states were monitored by fluorescence spectroscopy. By the tethering of gold nanoparticles to the five-ring catenane scaffold, reconfiguration of the nanoparticles was demonstrated.

DNA Machines

C. H. Lu, X. J. Qi, A. Cecconello,
S.-S. Jester, M. Famulok,
I. Willner* ________ **7499 – 7503**

Switchable Reconfiguration of an Interlocked DNA Olympiadane Nanostructure



Mix and match: Emulsions of nonspherical multicore PAM/PEG droplets and hierarchical PAM/PEG hydrogel microarchitectures (see figure) are prepared by combining polymerization-induced phase separation with droplet coalescence in microdevices. This enables the fine-tuning of their morphology and inner structure.

Microfluidics

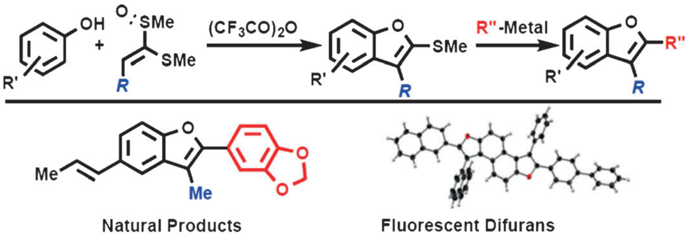
S. Guo, T. Yao, X. B. Ji, C. F. Zeng,
C. Q. Wang, L. X. Zhang* ___ **7504 – 7509**

Versatile Preparation of Nonspherical Multiple Hydrogel Core PAM/PEG Emulsions and Hierarchical Hydrogel Microarchitectures

Synthetic Methods

K. Murakami, H. Yorimitsu,*
A. Osuka ________ 7510–7513

Practical, Modular, and General Synthesis of Benzofurans through Extended Pummerer Annulation/Cross-Coupling Strategy

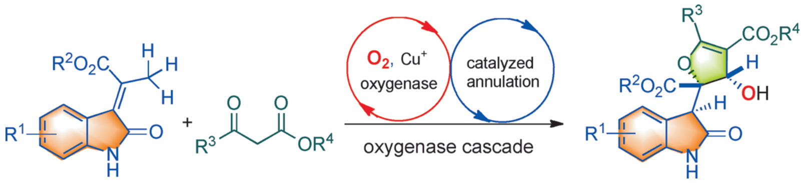


It's simple: Operationally simple, efficient, and widely applicable Pummerer annulations of simple phenols with ketene dithioacetal monoxides provide a variety of benzofurans with a methylthio group at the 2-position. Subsequent nickel-catalyzed arylation culminates in diversity-oriented synthesis of multisubstituted benzofurans. The title sequence was used in the synthesis of biologically active natural products and highly fluorescent benzofurans.

Reaction Cascades

Y. Wang, J. O. Bauer, C. Strohmann,
K. Kumar* ________ 7514–7518

A Bioinspired Catalytic Oxygenase Cascade to Generate Complex Oxindoles

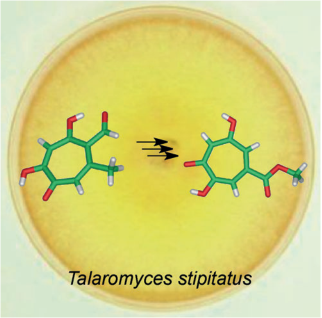


O_2 cascades: The first one-pot oxygenase cascade is presented, wherein a copper-catalyzed oxygenase reaction transforms the allylic CH_3 of 3-methylidene oxindole into an aldehyde, which then undergoes an aldol–oxa-Michael addition reaction with β-ketoesters to give dihydrofuran-bearing oxindoles.

Natural Product Biosynthesis

A. al Fahad, A. Abood, T. J. Simpson,
R. J. Cox* ________ 7519–7523

The Biosynthesis and Catabolism of the Maleic Anhydride Moiety of Stipitatonic Acid

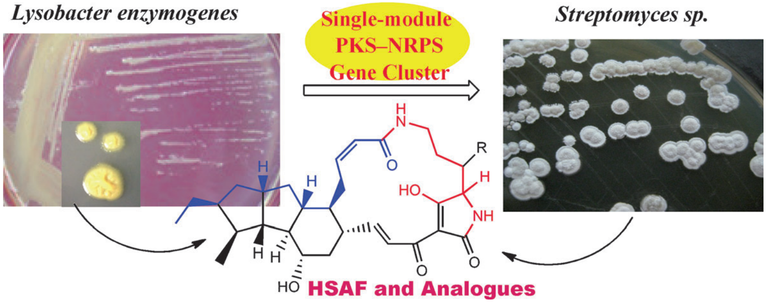


Building and demolition: The biochemical steps leading from the first-formed tropolone of the stipitatic acid pathway in the fungus *Talaromyces stipitatus* via the maleic anhydride containing stipitatonic acid have been determined by coordinated gene knockout and in vitro assays. The formation of shunt products including cordytropolone and talaroditropolone sheds light on the metabolism in other fungal organisms.

Natural Products

Y. Li, H. Chen, Y. Ding, Y. Xie, H. Wang,
R. L. Cerny, Y. Shen,* L. Du* 7524–7530

Iterative Assembly of Two Separate Polyketide Chains by the Same Single-Module Bacterial Polyketide Synthase in the Biosynthesis of HSAF

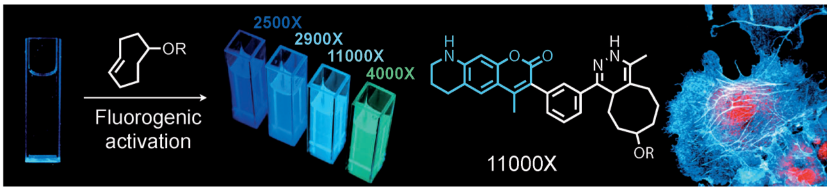


Only a single-module hybrid polyketide synthase–nonribosomal peptide synthetase (PKS-NRPS) is found in the biosynthetic gene cluster of the broad-spectrum antifungal polycyclic tetramate macrolactam HSAF (see picture), although two separate hexaketide chains are required to assemble the HSAF skeleton. Heterologous production and in vitro reconstitution by using purified PKS and NRPS demonstrated the iterative polyketide biosynthetic mechanism.

Fluorogenic Probes

L. G. Meimetis, J. C. T. Carlson, R. J. Giedt, R. H. Kohler, R. Weissleder* **7531 – 7534**

Ultrafluorogenic Coumarin–Tetrazine Probes for Real-Time Biological Imaging

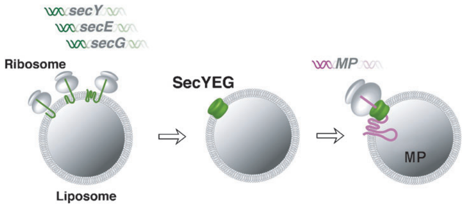


Fiercely fluorogenic: Brightness enhancement of greater than 10000-fold is detected in a series of coumarin–tetrazine probes, the largest to date of any bioorthogonal fluorogenic platform. This enhancement is achieved by the logical use of through-bond energy transfer (TBET) in molecular design. High-spatial-resolution "no-wash" images of extra- and intracellular targets were obtained with negligible background signal.

Artificial Cells

H. Matsubayashi, Y. Kuruma, T. Ueda* **7535 – 7538**

In Vitro Synthesis of the *E. coli* Sec Translocon from DNA



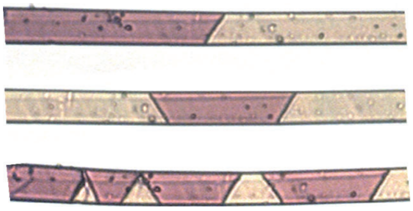
Cell free: The *E.coli* Sec translocon, which mediates the insertion of membrane proteins into the plasma membrane, was successfully reconstructed by synthesizing its component proteins in vitro. The synthesized SecYEG components were spontaneously inserted into a liposome membrane and formed a functional complex. The synthesized Sec translocon was able to mediate the membrane translocation of single- and multi-span membrane proteins (MPs).

Spin Crossover

M. Sy, F. Varret,* K. Boukheddaden,* G. Bouchez, J. Marrot, S. Kawata, S. Kaizaki **7539 – 7542**

Structure-Driven Orientation of the High-Spin–Low-Spin Interface in a Spin-Crossover Single Crystal

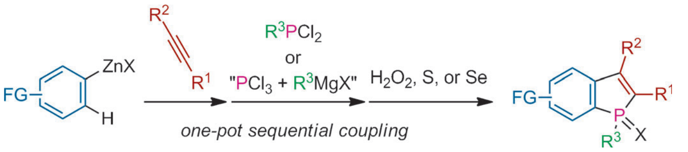
Elastic interfaces: The orientations of high-spin–low-spin (HS–LS) interfaces at the thermal transition of thin Fe(NCSe) spin-crossover crystals, observed by optical microscopy (see picture) are explained by considering the structural mismatch between the LS and HS phases in 2D models. The orientations correspond to mismatch-free situations which also explain the resilience of the crystals upon repeated switching.



Multicomponent Coupling

B. Wu, M. Santra, N. Yoshikai* **7543 – 7546**

A Highly Modular One-Pot Multicomponent Approach to Functionalized Benzo[*b*]phosphole Derivatives

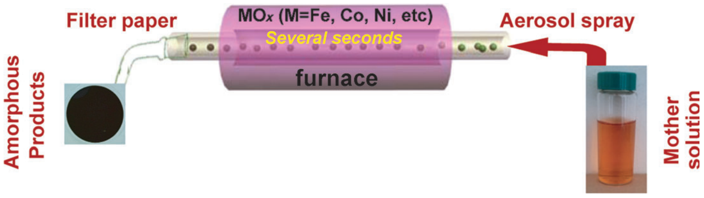


All the pieces in one pot: A novel one-pot sequential coupling of readily available reaction components allows the construction of a library of benzo[*b*]phosphole derivatives. The method employs an arylzinc reagent, an alkyne, dichlorophenylphosphine (or phosphorus trichloride and a Grignard reagent), and an oxidant, and features the cobalt-catalyzed migratory arylzincation of the alkyne and electrophilic phosphacyclization as key steps.

Metal Oxide Catalysts

L. Kuai, J. Geng, C. Chen, E. Kan, Y. Liu, Q. Wang, B. Geng* ______ 7547 – 7551

A Reliable Aerosol-Spray-Assisted Approach to Produce and Optimize Amorphous Metal Oxide Catalysts for Electrochemical Water Splitting

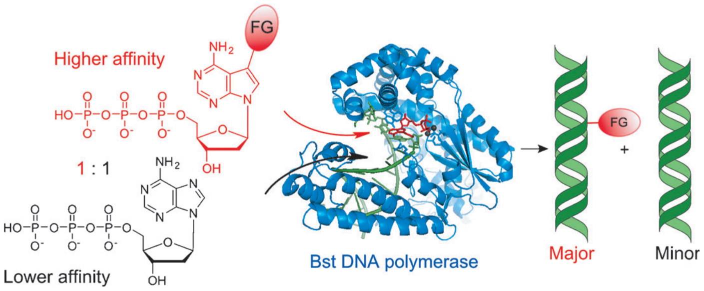


Spraying out catalysts: An aerosol-spray-assisted route with metal salts is a reliable route to identify amorphous metal oxide catalysts for electrochemical water splitting. The composition of the products can be precisely controlled from the precursor solution. The catalysts can be continuously collected at a rate of about 0.1 g h^{-1} from a single home-made device, and this method is thus scalable and suitable for industrial applications.

Functionalized DNA

P. Kielkowski, J. Fanfrlík, M. Hocek* ______ 7552 – 7555

7-Aryl-7-deazaadenine 2′-Deoxyribonucleoside Triphosphates (dNTPs): Better Substrates for DNA Polymerases than dATP in Competitive Incorporations

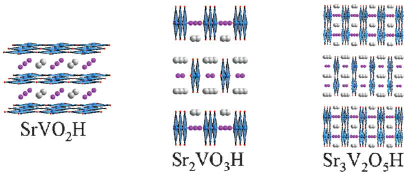


More is more! Bulky functionalized 7-aryl-7-deazaadenine 2′-deoxyribonucleoside triphosphates (dNTPs) are better substrates than their natural counterparts in competitive primer extensions with DNA polymerases (see picture). This ability is important for the possible in vivo enzymatic synthesis of functionalized DNA.

Oxide–Hydrides

F. Denis Romero, A. Leach, J. S. Möller, F. Foronda, S. J. Blundell, M. A. Hayward* ______ 7556 – 7559

Strontium Vanadium Oxide–Hydrides: “Square-Planar” Two-Electron Phases



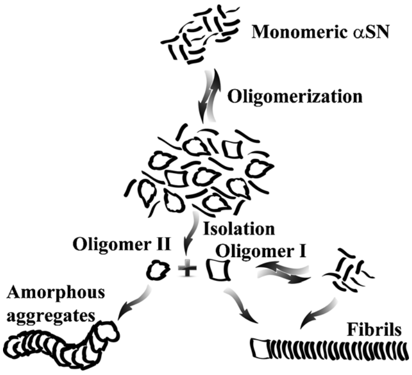
Exchanging anions makes vanadium square: Reaction with CaH$_2$ leads to oxide-for-hydride ion exchange in Sr$_{n+1}$V$_n$O$_{3n+1}$ ($n=\infty$, 1, 2) strontium vanadium oxides. The resulting oxide–hydride phases, SrVO$_2$H, Sr$_2$VO$_3$H, and Sr$_3$V$_2$O$_5$H$_2$, contain arrays of apex-linked V^{3+}O$_4$ squares stacked with SrH layers/chains, such that SrVO$_2$H can be considered to be analogous to infinite-layer oxide phases but with a d^2 electron count.

Protein Aggregation

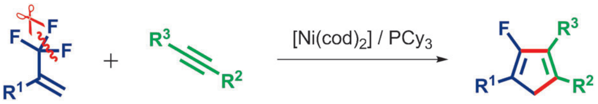
W. Paslawski, S. Mysling, K. Thomsen, T. J. D. Jørgensen,* D. E. Otzen* ______ 7560 – 7563

Co-existence of Two Different α-Synuclein Oligomers with Different Core Structures Determined by Hydrogen/Deuterium Exchange Mass Spectrometry

On-pathway or off-pathway? α-Synuclein oligomers are widely accepted to be cytotoxic species in Parkinson’s disease. There is debate as to whether they are intermediate species of fibril formation or the distinct end product of aggregation. Data indicate that both are correct and two different types of α-synuclein oligomers are formed: one that can be elongated by monomers and form fibrils and a second that stacks together to form more amorphous structures.



Back Cover



Clear-cut: The nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes afforded fluorine-containing multi-substituted cyclopentadienes. This reaction involves the consecutive and regioselective double C–F bond cleavage of a trifluoromethyl and a pentafluoroethyl group by β-fluorine elimination.

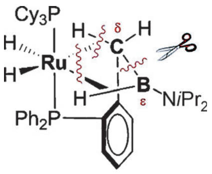
C–F Bond Activation

T. Ichitsuka, T. Fujita, T. Arita,
J. Ichikawa* ______________ **7564 – 7568**

Double C–F Bond Activation through β-Fluorine Elimination: Nickel-Mediated [3+2] Cycloaddition of 2-Trifluoromethyl-1-alkenes with Alkynes

Front Cover

Bond activity: A new phosphinoborane ruthenium complex was isolated. This complex exhibits two adjacent δ-C_{sp3}–H and ε-B_{sp2}–H agostic interactions involving directly connected σ-bonds of different polarity, which can either be displaced or lead selectively to B–C or C–H bond cleavage, depending on the experimental conditions.



Ligand Design

A. Cassen, Y. Gloaguen, L. Vendier,
C. Duhayon, A. Poblador-Bahamonde,
C. Raynaud, E. Clot, G. Alcaraz,*
S. Sabo-Etienne* __________ **7569 – 7573**

B–H, C–H, and B–C Bond Activation: The Role of Two Adjacent Agostic Interactions

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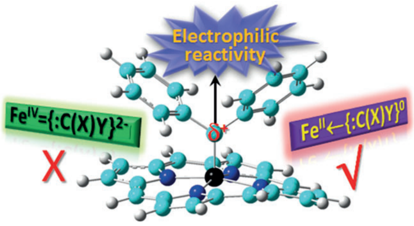

Doubled up: This work describes the first accurate predictions of the Mössbauer and ^{13}C NMR spectra, local geometries, and Fe–C bonding of iron porphyrin carbenes (IPCs). Unlike the previously assumed picture of a double bond between iron and carbon [Fe^{IV}={C(X)Y}$^{2-}$], analogous to the catalytic intermediates in conventional P450 reactions (Fe^{IV}=O^{2-}), IPC complexes are best described as Fe^{II}←{:C(X)Y}^{0}.

Structure Elucidation

R. L. Khade, W. Fan, Y. Ling, L. Yang,
E. Oldfield, Y. Zhang* _____ **7574 – 7578**

Iron Porphyrin Carbenes as Catalytic Intermediates: Structures, Mössbauer and NMR Spectroscopic Properties, and Bonding

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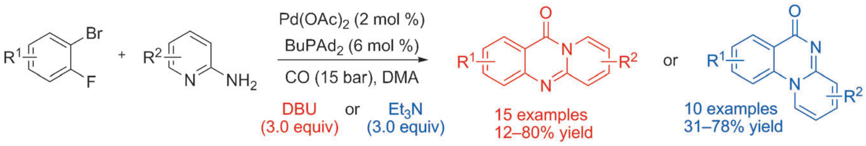


First base, second base... home run! A base-controlled palladium-catalyzed carbonylation/intramolecular nucleophilic aromatic substitution reaction gave linear and angular fused pyridoquinazolones: 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) yielded the linear products, whereas NEt_3 gave the angular derivatives (see scheme; Ad = adamantyl, DMA = dimethylacetamide). A light-induced Diels–Alder reaction of the product was also observed.

Heterocycle Synthesis

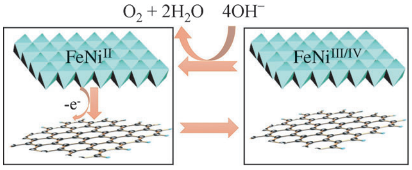
J. Chen, K. Natte, A. Spannenberg,
H. Neumann, P. Langer, M. Beller,*
X.-F. Wu* ________________ **7579 – 7583**

Base-Controlled Selectivity in the Synthesis of Linear and Angular Fused Quinazolinones by a Palladium-Catalyzed Carbonylation/Nucleophilic Aromatic Substitution Sequence

Oxygen Evolution Catalysts

X. Long, J. Li, S. Xiao, K. Yan, Z. Wang,
H. Chen, S. Yang* ———— **7584 – 7588**

A Strongly Coupled Graphene and FeNi Double Hydroxide Hybrid as an Excellent Electrocatalyst for the Oxygen Evolution Reaction

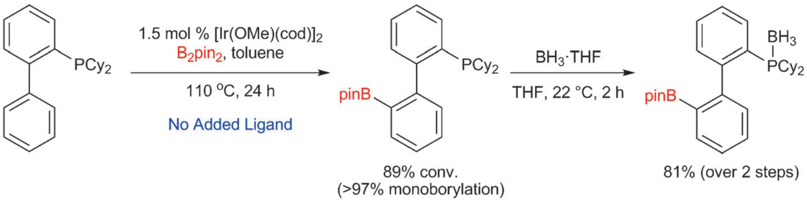


A low-cost and highly active electrochemical catalyst for the oxygen evolution reaction is created by alternatively stacking FeNi double hydroxide cation layers with GO anionic sheets. The advanced performance of the catalyst stems from the intrinsic catalytic activity of the layered FeNi double hydroxide and is boosted by the high electric conductivity of the adjoining graphene sheets.

C–H Borylation

K. M. Crawford, T. R. Ramseyer,
C. J. A. Daley, T. B. Clark* —— **7589 – 7593**

Phosphine-Directed C–H Borylation Reactions: Facile and Selective Access to Ambiphilic Phosphine Boronate Esters

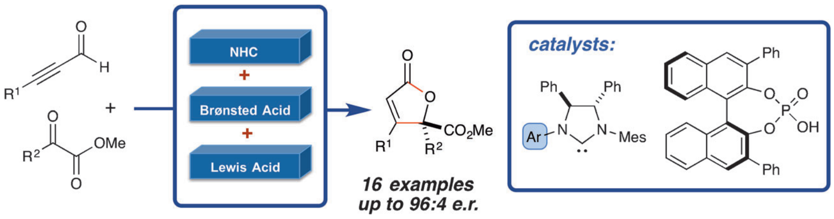


Directed borylation: Ambiphilic phosphine boronate esters are accessed by a phosphine-directed C–H borylation reaction. The Lewis basic phosphine directs the borylation to the adjacent C–H bond, providing access to intriguing ligand and catalyst scaffolds.

Asymmetric Catalysis

A. Lee, K. A. Scheidt* ———— **7594 – 7598**

A Cooperative N-Heterocyclic Carbene/Chiral Phosphate Catalysis System for Allenolate Annulations



Cooperation: A highly enantioselective NHC-catalyzed [3+2] annulation of α,β-alkynals and α-ketoesters generates the desired γ-crotonolactones in high yields. The reaction is based on the cooperative catalysis of a chiral Brønsted acid and a precatalyst consisting of a C_1-symmetric biaryl and a saturated imidazolium moiety.

Metallopeptide Design

L. Zheng, A. Marcozzi, J. Y. Gerasimov,
A. Herrmann* ———— **7599 – 7603**

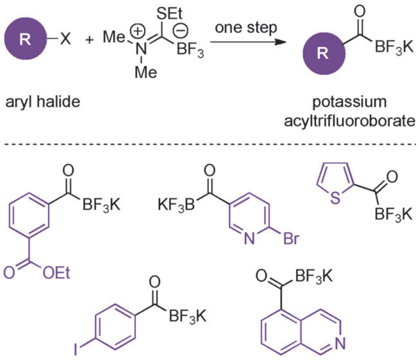
Conformationally Constrained Cyclic Peptides: Powerful Scaffolds for Asymmetric Catalysis

Ligand development: A cyclic peptide, containing only natural amino acids along with an intramolecular disulfide bridge, was identified as a simple and versatile coordination sphere for asymmetric catalysis. “Alanine scanning” provided mechanistic insights and assisted in systematic optimizations for the peptide ligands.

Acyltrifluoroborate Reagents

G. Erős, Y. Kushida,
J. W. Bode* ________ 7604 – 7607

A Reagent for the One-Step Preparation of Potassium Acyltrifluoroborates (KATs) from Aryl- and Heteroarylhalides

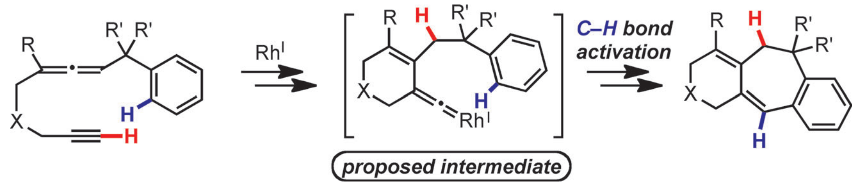


Bring it on! The challenge of forming acyl boranes by trapping acyl anion equivalents is avoided by the design and development of an electrophilic source of the acyltrifluoroborate group. This novel reagent makes possible the one-step transformation of aryl and heteroaryl halides into the corresponding potassium acyltrifluoroborates via organolithium intermediates.

Cyclization

Y. Kawaguchi, S. Yasuda, A. Kaneko,
Y. Oura, C. Mukai* ________ 7608 – 7612

Rhodium(I)-Catalyzed Cycloisomerization of Benzylallene-Alkynes through C–H Activation

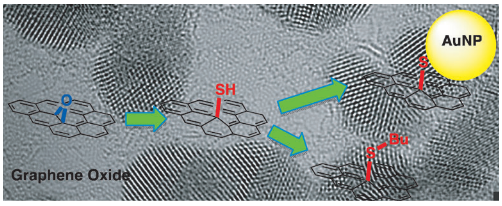


Vinylidene complex: An efficient Rh^I-catalyzed cycloisomerization of benzylallene-alkynes produced the tricyclo$[9.4.0.0^{3,8}]$pentadecapentaene skeleton through C_{sp^2}–H bond activation. Based on deuteration and competition experiments, a reaction mechanism was proposed, which proceeds via a vinylidenecarbene–Rh^I intermediate.

Graphene Oxide

H. R. Thomas, A. J. Marsden, M. Walker,
N. R. Wilson,* J. P. Rourke* 7613 – 7618

Sulfur-Functionalized Graphene Oxide by Epoxide Ring-Opening

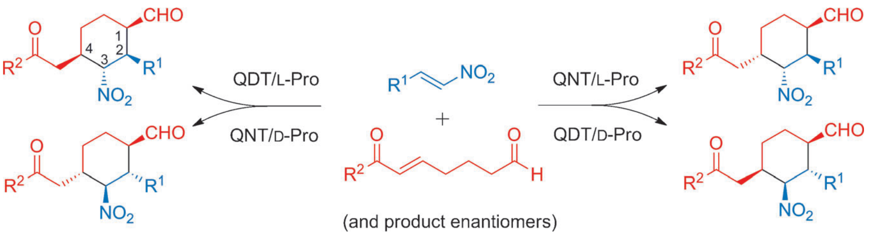


GO for gold: Potassium thioacetate was used to selectively open the epoxides present on a graphene oxide (GO) surface. This new route into functionalization of GO was exploited to attach gold nanoparticles on a GO surface (see picture).

Carbocycle Synthesis

N. K. Rana, H. Huang,
J. C.-G. Zhao* ________ 7619 – 7623

Highly Diastereodivergent Synthesis of Tetrasubstituted Cyclohexanes Catalyzed by Modularly Designed Organocatalysts

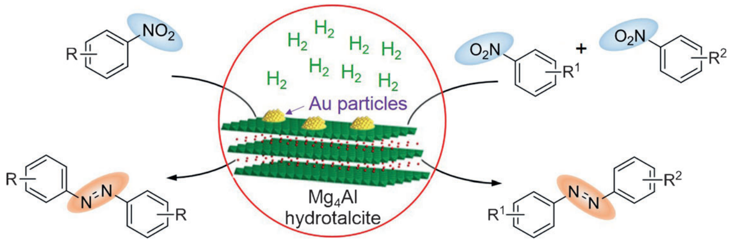


Stereoisomer made to order: Diastereodivergence is realized through controlling the stereoselectivity of the individual steps of a tandem Michael/Michael reaction. Up to 8 of the 16 possible stereoisomers have been successfully obtained in high enantio- and diastereoselectivities using modularly designed organocatalysts for the tandem reaction and an ensuing epimerization. QDT = quinidine thiourea, QNT = quinine thiourea.

Supported Catalysts

X. Liu, H. Q. Li, S. Ye, Y. M. Liu, H. Y. He, Y. Cao* ________ **7624 – 7628**

Gold-Catalyzed Direct Hydrogenative Coupling of Nitroarenes To Synthesize Aromatic Azo Compounds

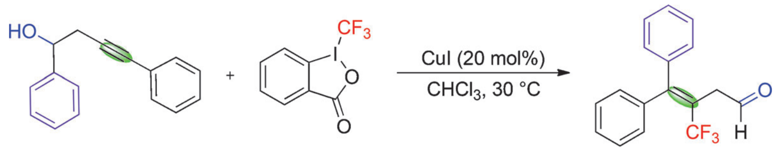


Game of rates: A general approach for the chemoselective hydrogenative coupling of nitroarenes to give the corresponding azo compounds, using a heterogeneous gold catalyst, has been developed. As a result of the remarkable synergy between the metal and support, a facile condensation of transient nitroso and hydroxylamine intermediates proceeds. The desired transformation is highly selective under mild reaction conditions.

Trifluoromethylation

P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu,* Y.-M. Liang* ________ **7629 – 7633**

Copper-Catalyzed One-Pot Trifluoromethylation/Aryl Migration/Carbonyl Formation with Homopropargylic Alcohols

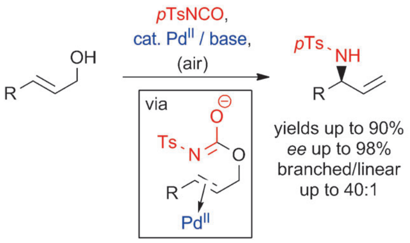


A copper-catalyzed one-pot reaction of homopropargylic alcohols involves trifluoromethylation, aryl migration, and formation of a carbonyl group. A series of 3-butenal and 3-buten-1-one derivatives with a trifluoromethyl-substituted olefin were obtained in moderate to good yields with high regioselectivity. The mechanism is proposed to involve a 5-*ipso* cyclization.

Cascade Reactions

J. M. Bauer, W. Frey, R. Peters* ________ **7634 – 7638**

Asymmetric Cascade Reaction to Allylic Sulfonamides from Allylic Alcohols by Palladium(II)/Base-Catalyzed Rearrangement of Allylic Carbamates

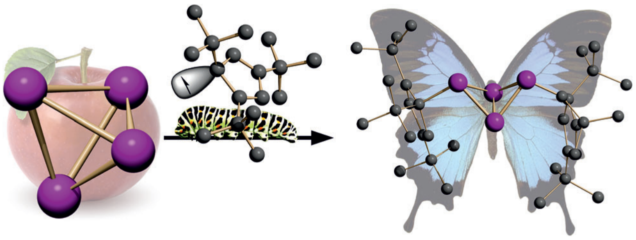


Going through changes: Highly enantioenriched allylic amines have been prepared by a cascade reaction capable of transforming allylic alcohols into chiral sulfonyl-protected allylic amines. This process is catalyzed by the combination of a chiral palladacycle and a tertiary amine base and merges high step-economy with operational simplicity. Mechanistic studies suggest that the key step is a [3,3] rearrangement of a deprotonated *N*-sulfonylcarbamate.

Phosphorus Activation

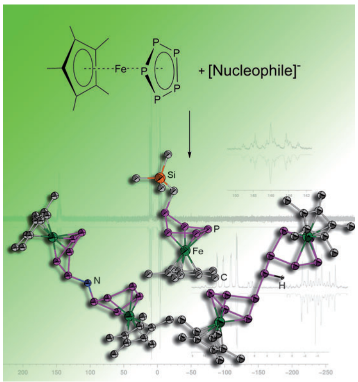
S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner, M. Scheer* ________ **7639 – 7642**

Selective Functionalization of P_4 by Metal-Mediated C–P Bond Formation



New wings for the P_4 butterfly: Using two methods starting from white phosphorus, the carbon-substituted bicyclic P_4 butterfly compounds $Cp^R{}_2P_4$ ($Cp^R = C_5(4\text{-}n\text{Bu}C_6H_4)_5$, $C_5H_2t\text{Bu}_3$, C_5Me_5, $C_5Hi\text{Pr}_4$) were generated. The methods involve the intermediary formation of $\{Cp^R\}$ radicals that selectively open one P–P bond of the P_4 tetrahedron. The simple procedures and the broad variety of suitable Cp^R substituents open new ways in the carbon-based P_4 activation.

Pentaphosphaferrocene [Cp*Fe(η^5-P_5)] reacts with different nucleophiles, leading to the formation of unprecedented mono-, di-, or trianionic species. These compounds show a dissimilarity to its carbonaceous relative ferrocene.



Phosphaferrocenes

E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer* **7643 – 7646**

Functionalization of a *cyclo*-P_5 Ligand by Main-Group Element Nucleophiles

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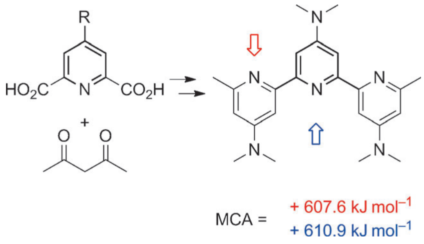
Super Lewis bases! The hitherto unknown 4,4′′-bis(dimethylamino)- and 4,4′,4′′-tris(dimethylamino)terpyridines have been prepared by a simple and flexible synthesis. Nonafloxy-substituted terpyridine intermediates allow smooth introduction of dimethylamino groups or palladium-catalyzed coupling reactions. The calculated methyl cation affinities of the novel terpyridines promise unprecedented high Lewis basicities and excellent ligand properties.



Functionalized Terpyridines

P. Hommes, C. Fischer, C. Lindner, H. Zipse,* H.-U. Reissig* **7647 – 7651**

Unprecedented Strong Lewis Bases—Synthesis and Methyl Cation Affinities of Dimethylamino-Substituted Terpyridines

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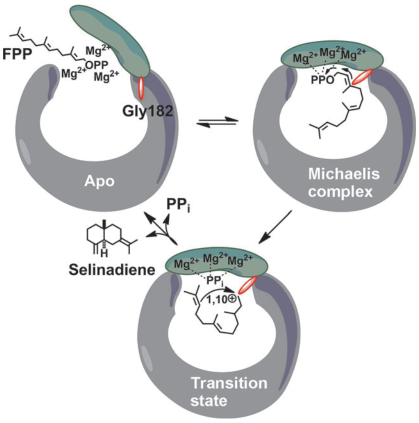
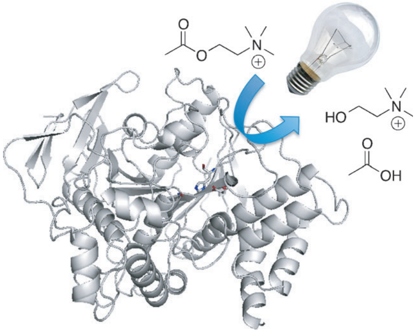


A class act: The open and closed (ligand-bound) conformations of selinadiene synthase reveal an induced-fit mechanism, and give insights into carbocation formation and regulation in class I terpene cyclases. The substrate turnover is accomplished by an effector triad on the G1 helix, comprising the pyrophosphate sensor Arg178, the linker Asp181, and the effector Gly182. This structural motif is strictly conserved in all class I terpene cyclases.

Enzyme Models

P. Baer, P. Rabe, K. Fischer, C. A. Citron, T. A. Klapschinski, M. Groll,* J. S. Dickschat* **7652 – 7656**

Induced-Fit Mechanism in Class I Terpene Cyclases



Taming an enzyme with light: Acetylcholinesterase (AChE) is one of the most active enzymes and an essential component of synaptic transmission in cholinergic systems. Based on the well-known drug tacrine, a photoswitchable inhibitor that can optically control the enzymatic activity of AChE was developed, and its inhibitory effect was shown by tracheal tensometry. The molecule is a weak inhibitor in the dark, but gains full activity when irradiated with UV light.

Photopharmacology

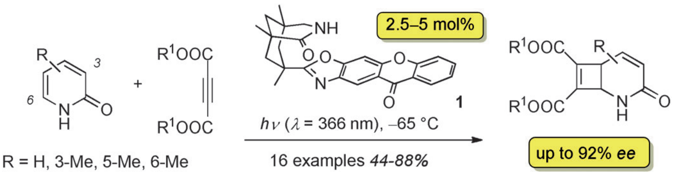
J. Broichhagen, I. Jurastow, K. Iwan, W. Kummer, D. Trauner* **7657 – 7660**

Optical Control of Acetylcholinesterase with a Tacrine Switch

Photochemistry

M. M. Maturi, T. Bach* ____ 7661 – 7664

Enantioselective Catalysis of the Intermolecular [2+2] Photocycloaddition between 2-Pyridones and Acetylenedicarboxylates



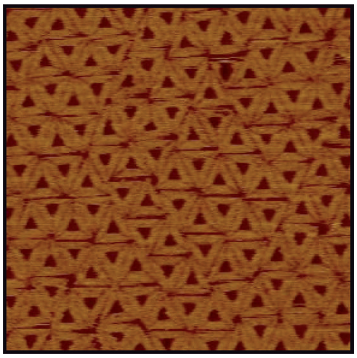
Unprecedented heights: Although the triplet state of pyridones (which is populated through sensitizer **1**) lies more than 250 kJ mol⁻¹ above the ground state, the enantioselective control of an intermolecular [2+2] photocycloaddition has been achieved for the first time, using only low catalyst loadings.

DNA Nanotechnology

A. Aghebat Rafat, T. Pirzer, M. B. Scheible, A. Kostina, F. C. Simmel* __ 7665 – 7668

Surface-Assisted Large-Scale Ordering of DNA Origami Tiles

Molecular tessellation: Electrostatic control of adhesion and mobility of DNA origami structures on mica surfaces using monovalent cations facilitates formation of large, ordered 2D arrays of origami tiles. The lattices can be formed either by close-packing of symmetric, non-interacting DNA origami structures, or by utilizing blunt-end stacking interactions between the origami units. The resulting crystalline lattices are readily utilized as templates for the ordered arrangement of proteins.

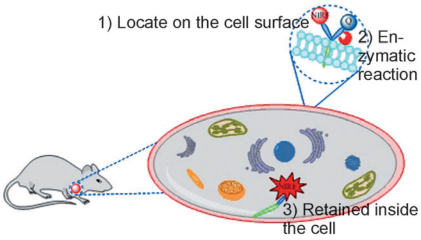


Tumor Diagnosis

H.-Y. Hu, D. Vats, M. Vizovisek, L. Kramer, C. Germanier, K. U. Wendt, M. Rudin, B. Turk,* O. Plettenburg,* C. Schultz* ________ 7669 – 7673

In Vivo Imaging of Mouse Tumors by a Lipidated Cathepsin S Substrate

Lipidated protease FRET probes were previously shown to be internalized by target cells releasing the protease of interest. A lipidated, non-peptidic FRET probe is presented for cathepsin S, a protease secreted by macrophages in the tumor environment. In cultured cells and in a grafted tumor mouse model, the probe is successfully cleaved and in the mouse is accumulated in the tumor tissue with little signal in organs such as liver and lung.



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).

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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

One-Pot Semisynthesis of Exon 1 of the Huntingtin Protein: New Tools for Elucidating the Role of Posttranslational Modifications in the Pathogenesis of Huntington's Disease

A. Ansaloni, Z. M. Wang, J. S. Jeong, F. S. Ruggeri, G. Dietler, H. A. Lashuel* ——— **1928–1933**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201307510

The authors of this Communication sincerely regret failing to cite the paper "Synthesis of pathological and nonpathological human exon 1 huntingtin" by Zauner et al.,[1] reporting the first chemical synthesis of exon 1 of the huntingtin protein containing 22 or 42 Q using solid-phase peptide synthesis.

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[1] D. Singer, T. Zauner, M. Genz, R. Hoffmann, T. Zuchner, *J. Pept. Sci.* **2010**, *16*, 358–363.