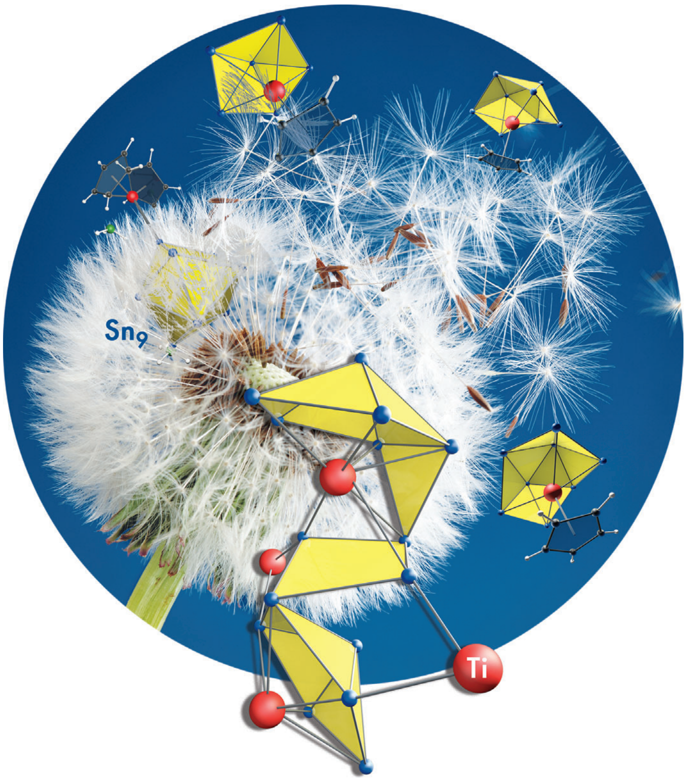
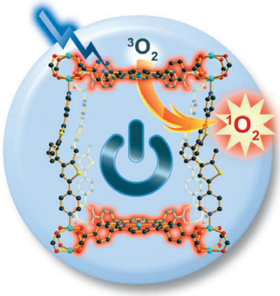
Like the seeds of a blowball ...

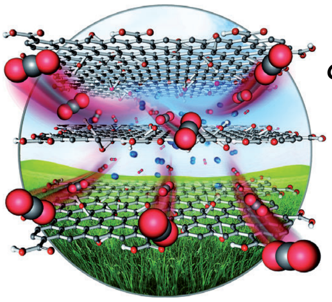


... are distributed in the air, fragments of transition-metal tin-cluster complexes are dispersed in solution. In their Communication on page 522 ff., T. F. Fässler and co-workers report on the versatile reactivity of [Cp_2TiCl_2] in liquid ammonia toward nonastannide Zintl anions and their relevance for the formation of large titanium–tin clusters. Depending on the reaction conditions, clusters of eight and nine Sn atoms are captured and stabilized by Ti atoms. The largest isolated cluster contains one Ti atom that exclusively binds to ten Sn atoms. Cover art designed by D. Marchand Fässler.

Photochromism

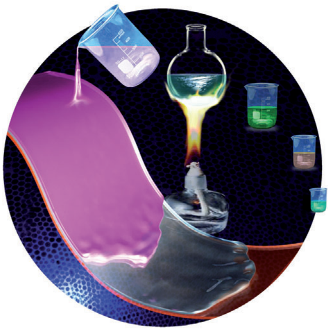
In their Communication on page 430 ff., H.-C. Zhou et al. report two photochromic metal–organic frameworks, one of which can be used for the reversible control of singlet oxygen generation.





Gas Transport

W. Jin et al. show in their Communication on page 578 ff. that a membrane formed from layers of graphene oxide has excellent CO_2 transport and separation properties.



Transparent Conducting Oxides

The preparation of transparent-conducting-oxide nanocrystal inks with high crystallinity, uniform morphology, monodispersity, and high stability is described by H. B. Zeng et al. in their Communication on page 462 ff.

How to contact us:

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

Reprints, E-Prints, Posters, Calendars:
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Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
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Courier Services:
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Spotlight on Angewandte's Sister Journals **388 – 391**

Author Profile

"My motto is 'the journey is as important as the destination'.
The secret of being a successful scientist is recruit co-workers smarter than yourself …"
This and more about Michael S. Sherburn can be found on page 392.

Michael S. Sherburn **392**

News

J. Lloret-Fillol

E. Fernández

J. Forniés

C. Jacob

Grupo Especializado de Química Organometálica Prizes 2014: J. Lloret-Fillol, E. Fernández, and J. Forniés **393**

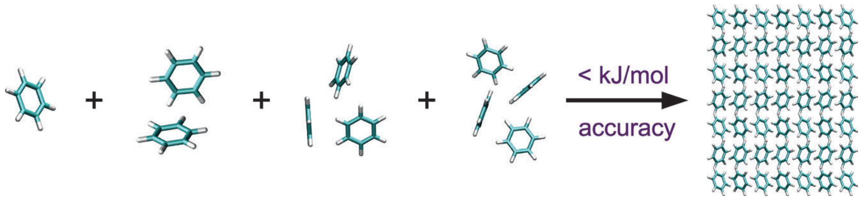
Hans G. A. Hellmann Prize: C. Jacob **393**

Highlights

Polymorphism

G. J. O. Beran* ______ **396–398**

A New Era for ab initio Molecular Crystal Lattice Energy Prediction



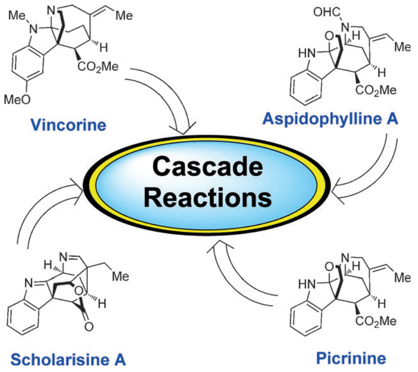
From first principles: In recent studies the lattice energy of crystalline benzene was predicted with sub-kilojoule per mole accuracy. Fundamental to this success was the combination of a fragment approach with state-of-the-art electronic structure methods.

Minireviews

Natural Products

J. M. Smith, J. Moreno, B. W. Boal, N. K. Garg* ______ **400–412**

Cascade Reactions: A Driving Force in Akuammiline Alkaloid Total Synthesis



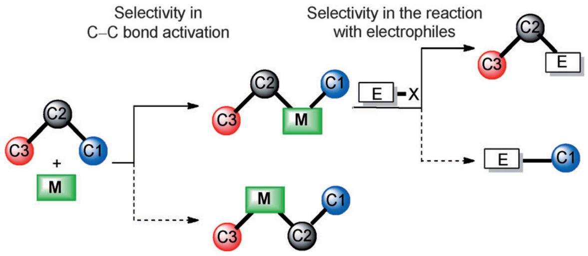
The akuammiline alkaloids are a family of terrestrial natural products which have a rich history and display promising therapeutic potential. Until recently, syntheses of these natural products have remained elusive. This Minireview describes several recently completed synthetic efforts, and illustrates how the akuammilines have provided inspiration for the discovery of novel cascade processes.

Reviews

C–C Activation

I. Marek,* A. Masarwa, P.-O. Delaye, M. Leibeling ______ **414–429**

Selective Carbon–Carbon Bond Cleavage for the Stereoselective Synthesis of Acyclic Systems



Open, sesame! The creation of new bonds has dominated the field of organic synthesis; however, selective C–C cleavage (see scheme) is an important alternative for the construction of interesting molecular frameworks. This Review examines approaches to the synthesis of challenging acyclic molecular skeletons by the regio-, diastereo-, or enantioselective cleavage of carbon–carbon bonds, with a focus on the ring opening of small rings.

For the USA and Canada:
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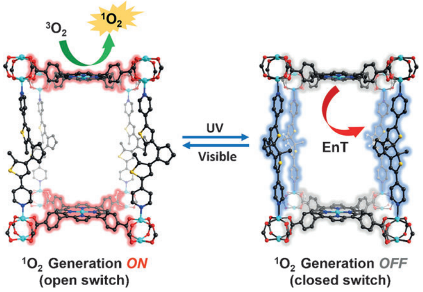
Photochromism

J. Park, D. Feng, S. Yuan, H.-C. Zhou* —— **430 – 435**

Photochromic Metal–Organic Frameworks: Reversible Control of Singlet Oxygen Generation



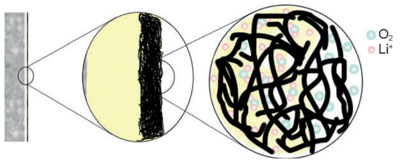
Back and forth: Through a classical pillar-layer structure constructed with mixed linkers, two photochromic metal–organic frameworks, PC-PCN and SO-PCN, have been developed. SO-PCN integrates a photochromic switch and photosensitizer, and has demonstrated reversible control of $^1O_2$ generation (see figure).

Frontispiece

Lithium–Oxygen Batteries

M. Balaish, E. Peled, D. Golodnitsky, Y. Ein-Eli* —— **436 – 440**

Liquid-Free Lithium–Oxygen Batteries

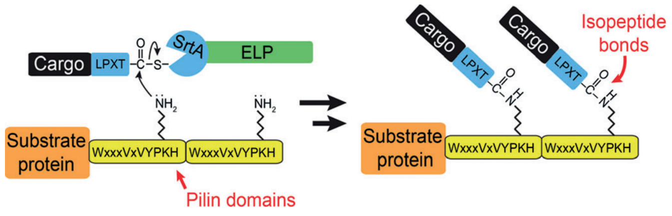


A polymer-based system: Rechargeable lithium–oxygen cells based on a solid polymer electrolyte (SPE) were operated at a temperature higher than the melting point of the polymer electrolyte. The proposed SPE-based Li-O_2 cells showed a stable cycling, possessing a higher cell discharge voltage and a drastically lower charge voltage.

Site-Specific Bioconjugation

J. J. Bellucci, J. Bhattacharyya, A. Chilkoti* —— **441 – 445**

A Noncanonical Function of Sortase Enables Site-Specific Conjugation of Small Molecules to Lysine Residues in Proteins

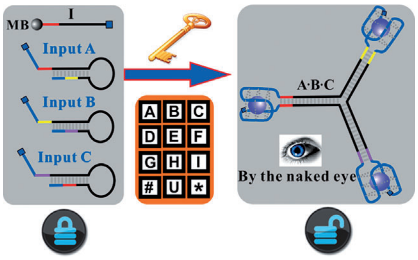


Branching out: A noncanonical function of the sortase A enzyme was used to conjugate small molecules exclusively to the side chains of one or more lysine residues within a specific sequence element engineered into a protein substrate. This isopeptide ligation reaction offers a mechanism to site-specifically functionalize proteins with multiple moieties in a manner orthogonal to available methods.

Biocomputing

J. H. Chen, S. G. Zhou,* J. L. Wen —— **446 – 450**

Concatenated Logic Circuits Based on a Three-Way DNA Junction: A Keypad-Lock Security System with Visible Readout and an Automatic Reset Function

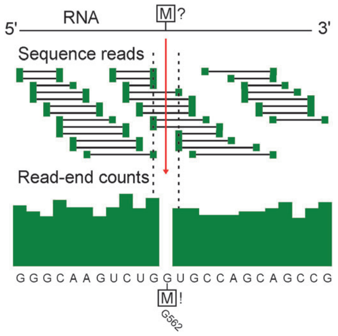


Safe as houses: Concatenated logic circuits operating as a biocomputing keypad-lock security system with an automatic reset function were successfully constructed on the basis of toehold-mediated strand displacement and three-way-DNA-junction architecture. By the use of a split-G-quadruplex DNAzyme as the signal reporter, the output of the keypad lock was clearly recognized by the naked eye (see picture; MB = magnetic bead).

RNA Modifications

U. Birkedal, M. Christensen-Dalsgaard, N. Krogh, R. Sabarinathan, J. Gorodkin, H. Nielsen* ______ **451 – 455**

Profiling of Ribose Methylations in RNA by High-Throughput Sequencing

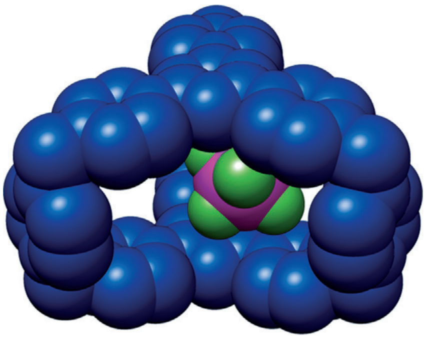


Composed of RNA and protein, ribosomes are the sites of protein synthesis in the cell. The RNA component is chemically modified at many residues close to the active site. A new sequencing method maps the most prominent modification, ribose methylation, across the entire ribosomal RNA in a single experiment. This method should aid in the study of fundamental aspects of ribosome function.

Host–Guest Complexes

N. Hafezi, J. M. Holcroft, K. J. Hartlieb, E. J. Dale, N. A. Vermeulen, C. L. Stern, A. A. Sarjeant, J. F. Stoddart* _ **456 – 461**

Modulating the Binding of Polycyclic Aromatic Hydrocarbons Inside a Hexacationic Cage by Anion–π Interactions



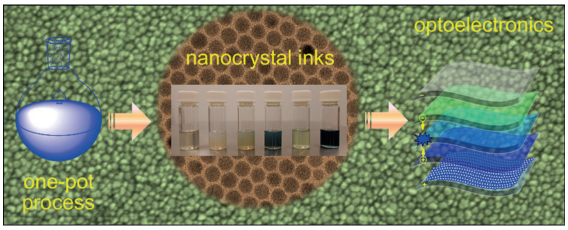
The ins and outs: A hexacationic macrobicyclic receptor comprised of pyridinium units fused together by electron-poor triazine rings has been shown to be a good receptor for polycyclic aromatic hydrocarbons. The lower than expected association constant for the PF_6^- salt with pyrene is attributed to the PF_6^- counterions fleetingly occupying the cavity. X-ray crystallography confirmed the presence of a PF_6^- ion in its cavity.

Transparent Conducting Oxides

J. Z. Song, S. A. Kulinich, J. H. Li, Y. L. Liu, H. B. Zeng* ______ **462 – 466**

A General One-Pot Strategy for the Synthesis of High-Performance Transparent-Conducting-Oxide Nanocrystal Inks for All-Solution-Processed Devices

Back Cover



Nanocrystal inks: A series of transparent conducting oxide nanocrystals were prepared by a simple, generic, and easily scalable one-pot method. The formed NCs are of high crystallinity, uniform morphology, monodispersity, and high stability and could be employed for the assembly of high-quality electrodes.

Molecular Dynamics

A. Arcella, J. Dreyer, E. Ippoliti, I. Ivani, G. Portella, V. Gabelica, P. Carloni, M. Orozco* ______ **467 – 471**

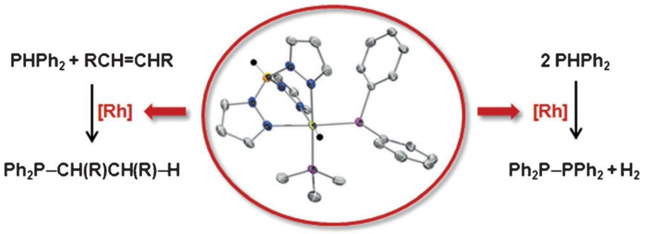
Structure and Dynamics of Oligonucleotides in the Gas Phase

Molecular dynamics calculations and mass spectrometry are combined to obtain an atomistic description of DNA under vacuum after electrospray vaporization under mild ionization conditions. After vaporization, gas-phase ions with different mass/charge (*m*/*z*) ratios are produced and for the most abundant charge state, the structure preserves a memory of the native conformation.

Rhodium Complexes

A. M. Geer, Á. L. Serrano, B. de Bruin, M. A. Ciriano, C. Tejel* ______ **472 – 475**

Terminal Phosphanido Rhodium Complexes Mediating Catalytic P–P and P–C Bond Formation

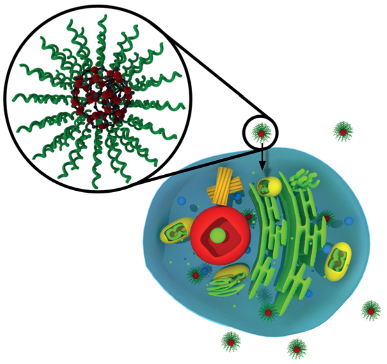


Oxidative addition of secondary phosphanes to a rhodium ethylene complex has led to mononuclear phosphanido rhodium complexes, which have been fully characterized (see picture). The terminal phosphanides are active catalysts for the “green synthesis” of phosphanes and diphosphanes under mild conditions through phosphane dehydrocoupling and olefin hydrophosphination reactions.

DNA Nanostructures

C. M. Calabrese, T. J. Merkel, W. E. Briley, P. S. Randeria, S. P. Narayan, J. L. Rouge, D. A. Walker, A. W. Scott, C. A. Mirkin* ______ **476 – 480**

Biocompatible Infinite-Coordination-Polymer Nanoparticle–Nucleic-Acid Conjugates for Antisense Gene Regulation

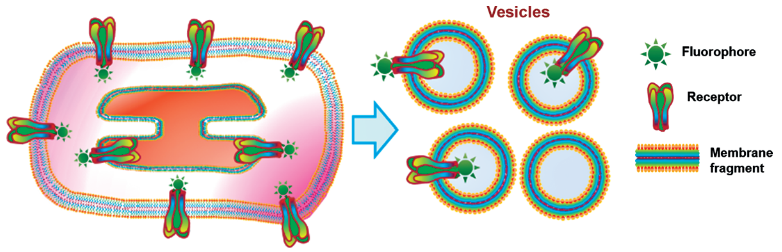


Iron it out: DNA-modified infinite-coordination-polymer (ICP) nanoparticles were constructed by a facile method to afford biocompatible gene-regulation agents. The iron(III)-based ICP nanoparticles were synthesized in water and conjugated directly to oligonucleotides by a copper-free click reaction. The resulting conjugates were capable of entering cells and effecting antisense gene regulation without transfection agents (see picture).

Transmembrane Proteins

F. H. Moonschi, A. K. Effinger, X. Zhang, W. E. Martin, A. M. Fox, D. K. Heidary, J. E. DeRouchey, C. I. Richards* ______ **481 – 484**

Cell-Derived Vesicles for Single-Molecule Imaging of Membrane Proteins



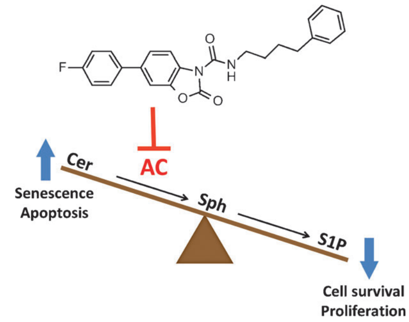
Solubility solution: Vesicles derived from cell membranes were used to isolate individual receptors for single-molecule imaging. This approach maintains receptors in their physiological membrane. Fluorescently labeled receptors embedded in vesicles were used for ligand binding studies in solution and immobilized on a glass substrate for single-molecule determination of nicotinic receptor stoichiometry.

Enzyme Inhibition

D. Pizzirani, A. Bach, N. Realini,
A. Armirotti, L. Mengatto, I. Bauer,
S. Girotto, C. Pagliuca, M. De Vivo,
M. Summa, A. Ribeiro,
D. Piomelli* ______ 485–489

Benzoxazolone Carboxamides: Potent and Systemically Active Inhibitors of Intracellular Acid Ceramidase

Inside Cover



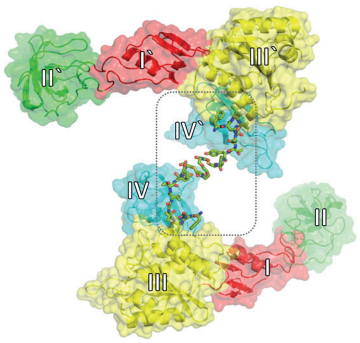
A key regulator of the sphingolipid metabolism is acid ceramidase (AC), which offers a molecular target in disorders such as cancer and inflammation, in which sphingolipid signaling might be dysfunctional. The shown compound is metabolically stable, inhibits AC activity both in vitro and in vivo, and can thus be used as a potent chemical probe to investigate the roles of ceramides in physiology and pathology.

Medicinal Chemistry

H. M. Maric, V. B. Kasaragod,
L. Haugaard-Kedström, T. J. Hausrat,
M. Kneussel, H. Schindelin,
K. Strømgaard* ______ 490–494

Design and Synthesis of High-Affinity Dimeric Inhibitors Targeting the Interactions between Gephyrin and Inhibitory Neurotransmitter Receptors

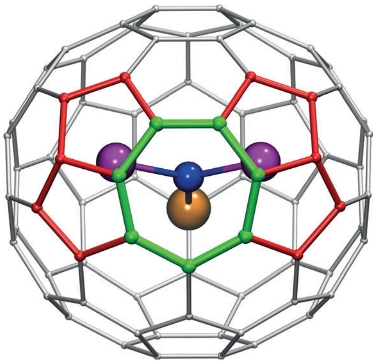
Double-teaming: Dimeric peptide ligands were developed that target gephyrin, the central scaffolding protein for inhibitory neurotransmitter receptors in the brain, with unprecedented high affinity. Dimerization also substantially improved the serum stability, thus providing compounds with great promise for further studies of gephyrin–receptor interactions. The X-ray structure shows one of these peptides in complex with two monomers of the gephyrin E domain.



Fullerenes

Y. Zhang, K. B. Ghiassi, Q. Deng,
N. A. Samoylova, M. M. Olmstead,*
A. L. Balch,* A. A. Popov* ______ 495–499

Synthesis and Structure of $LaSc_2N@C_s$(hept)-C_{80} with One Heptagon and Thirteen Pentagons



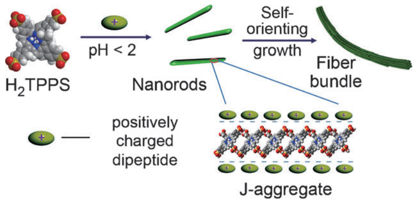
An unanticipated discovery: The isomer of $LaSc_2N@C_{80}$ with a heptagonal ring and two pairs of adjacent pentagons has been isolated and characterized by single-crystal X-ray diffraction. Sc magenta, La orange, N blue.

Ordered Porphyrin Assemblies

K. Liu, R. Xing, C. Chen, G. Shen, L. Yan,
Q. Zou, G. H. Ma, H. Möhwald,
X. Yan* ______ 500–505

Peptide-Induced Hierarchical Long-Range Order and Photocatalytic Activity of Porphyrin Assemblies

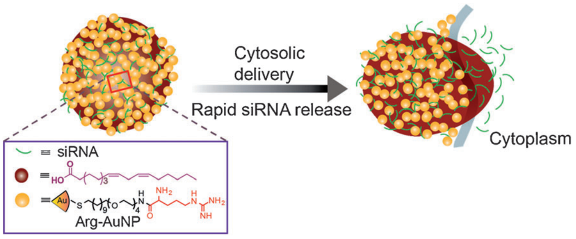
Get organized, be effective! Dipeptide-adjusted porphyrin self-assembly resulted in the formation of fiber bundles with hierarchical long-range order by a thermodynamically driven pathway based on the competitive interplay of multiple weak interactions (see picture). The long-range alignment of the fibers led to anisotropic birefringence, a large Stokes shift, amplified chirality, excellent photostability, and sustainable photocatalytic activity.



Antitumor Agents

Y. Jiang, R. Tang, B. Duncan, Z. W. Jiang, B. Yan, R. Mout, V. M. Rotello* **506 – 510**

Direct Cytosolic Delivery of siRNA Using Nanoparticle-Stabilized Nanocapsules

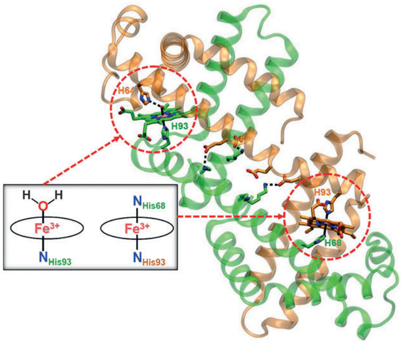


Special delivery: Nanoparticle-stabilized capsules (NPSCs) rapidly deliver small interfering RNA (siRNA) into the cytosol of a cell in a cholesterol-dependent manner, and the siRNA enters cells by membrane fusion. Such a platform effectively silenced model gene expression up to 90%, thus highlighting NPSC-facilitated direct cytosolic siRNA delivery as a powerful tool for gene regulation and disease treatment.

Dimeric Proteins

Y.-W. Lin, S. Nagao, M. Zhang, Y. Shomura, Y. Higuchi, S. Hirota* **511 – 515**

Rational Design of Heterodimeric Protein using Domain Swapping for Myoglobin

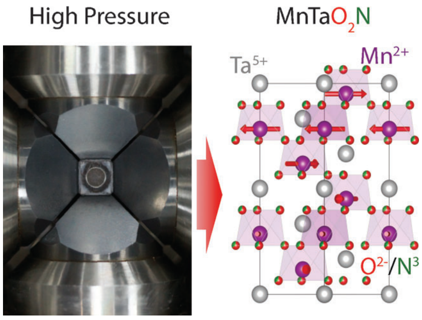


Designer proteins: Protein design is a useful method for creating novel artificial proteins. An artificial heterodimeric protein with two different heme active sites [a bis(histidine)-coordinated heme and a H_2O/histidine-coordinated heme] was developed using domain swapping for horse myoglobin (see figure). The developed method is useful for designing artificial multiheme proteins.

$LiNbO_3$-type Magnetic Oxynitride

C. Tassel, Y. Kuno, Y. Goto, T. Yamamoto, C. M. Brown, J. Hester, K. Fujita, M. Higashi, R. Abe, K. Tanaka, Y. Kobayashi, H. Kageyama* **516 – 521**

$MnTaO_2N$: Polar $LiNbO_3$-type Oxynitride with a Helical Spin Order



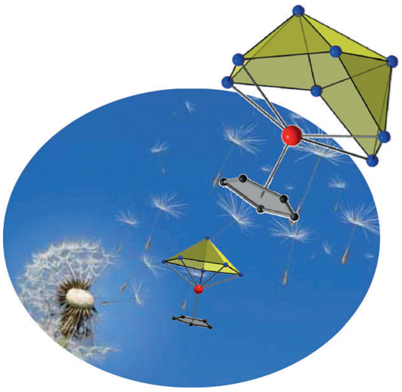
Under pressure: The first $LiNbO_3$-type oxynitride, $MnTaO_2N$, has been synthesized using a high-pressure technique (see picture). Contrary to conventional ammonolysis reaction, this approach allows to obtain an oxynitride with a middle-to-late transition metal. $MnTaO_2N$ is non-centrosymmetric unlike most oxynitrides and exhibits a nontrivial helical spin ordering below 25 K.

Zintl Cluster Compounds

C. B. Benda, M. Waibel, T. F. Fässler* **522 – 526**

On the Formation of Intermetalloid Clusters: Titanocene(III)diammin as a Versatile Reactant Toward Nonastannide Zintl Clusters

Front Cover



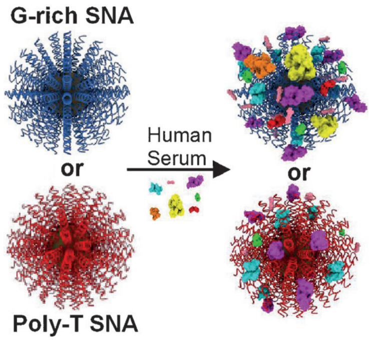
MSn_8—Like the seeds of a blowball: In the presence of Zintl anions, titanocene(IV) dichloride is reduced in liquid ammonia, and a titanocene(III) diammin complex is formed. Stepwise ligand exchange reactions lead to a variety of intermediate Ti_nSn_m clusters that give insight into the formation of larger intermetalloid clusters.

Protein Binding to Nanoparticles

A. B. Chinen, C. M. Guan, C. A. Mirkin* 527–531

Spherical Nucleic Acid Nanoparticle Conjugates Enhance G-Quadruplex Formation and Increase Serum Protein Interactions

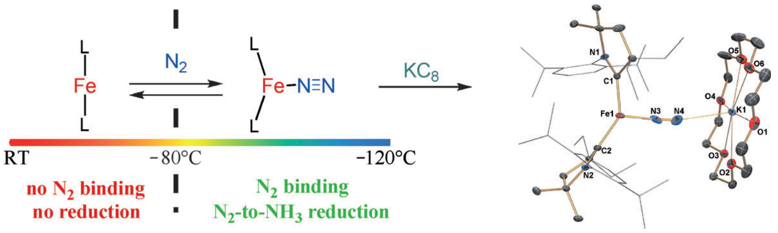
Structure determines binding: Spherical nucleic acid nanoparticles (SNAs) adsorb proteins in a sequence-dependent fashion. G-rich SNAs adsorb more types and more total protein than poly-T SNAs, leading to increased macrophage uptake. This demonstrates that tertiary DNA structures can dictate nanoparticle protein corona formation, providing guidelines for the design of more efficacious therapeutic nucleic acid-based nanomaterials.



Nitrogen Fixation

G. Ung, J. C. Peters* 532–535

Low-Temperature N_2 Binding to Two-Coordinate L_2Fe^0 Enables Reductive Trapping of $L_2FeN_2^-$ and NH_3 Generation

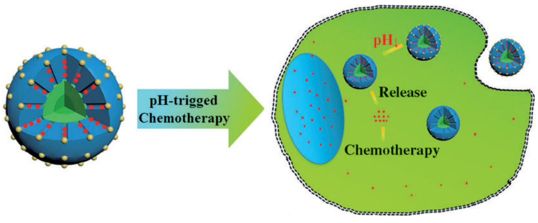


An N_2 fix: The title complex facilitates the conversion of N_2 (1 atm) into NH_3, but only at temperatures below −78 °C. The best yield (170% relative to $[L_2Fe]$) was measured at −95 °C. N_2 binding becomes thermodynamically more favored at low temperature such that a sufficiently high concentration of $[L_2Fe(N_2)]$ forms below −80 °C. This N_2 binding event enables trapping and isolation (as a K^+ adduct) of the reactive anionic three-coordinate complex $[L_2Fe^{-I}(N_2)]^-$.

Theranostics

Y. H. Wang, S. Y. Song, J. H. Liu, D. P. Liu,* H. J. Zhang* 536–540

ZnO-Functionalized Upconverting Nanotheranostic Agent: Multi-Modality Imaging-Guided Chemotherapy with On-Demand Drug Release Triggered by pH

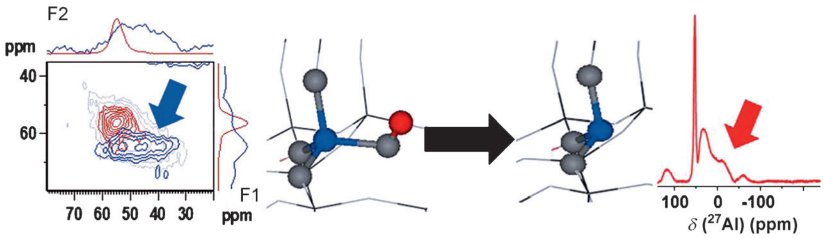


A nanotheranostic agent: A ZnO-functionalized upconverting nanotheranostic platform for multi-modality bioimaging (UCL/CT/MRI) and pH-triggered on-demand drug release has been successfully fabricated (see picture). Nontoxic ZnO can play the role of a “gatekeeper” to block the drug in the mesopores of the as-prepared agents until ZnO is dissolved in the acidic environment around tumors.

Zeolites

J. Brus, L. Kobera, W. Schoefberger, M. Urbanová, P. Klein, P. Sazama, E. Tabor, S. Sklenak, A. V. Fishchuk, J. Dědeček* ______ **541 – 545**

Structure of Framework Aluminum Lewis Sites and Perturbed Aluminum Atoms in Zeolites as Determined by $^{27}Al\{^1H\}$ REDOR (3Q) MAS NMR Spectroscopy and DFT/Molecular Mechanics

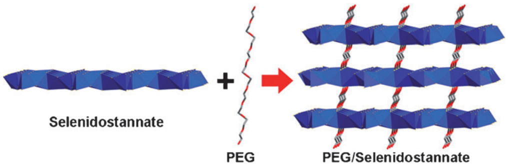


Here's where all the action is: The title studies indicate that tricoordinated framework (FR) $(SiO)_3Al$ atoms serve as electron-pair-acceptor Al_{FR} Lewis sites in zeolites with the CHA and FER topology. These sites can be formed by the dehydroxylation of AlOH atoms tricoordinated to the framework (see picture). Both AlOH and Al_{FR} Lewis species have broad ^{27}Al NMR resonances, but they can be differentiated on the basis of their δ_i, C_Q, and η values.

Organic–Inorganic Hybrid Composites

W.-W. Xiong, J.-W. Miao, K.-Q. Ye, Y. Wang, B. Liu, Q.-C. Zhang* ______ **546 – 550**

Threading Chalcogenide Layers with Polymer Chains

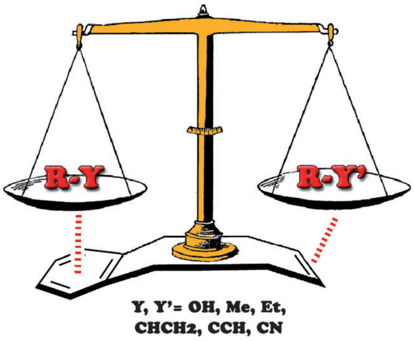


Common thread: Inserting a polymer into a crystalline inorganic matrix to understand its structure, position, and the structure–property relationships of the resulting composites is important for designing new inorganic–organic materials and tuning their properties. Single crystals of polymer-chalcogenide composites were isolated by trapping polyethyleneglycol within a selenidostannate matrix under surfactant-thermal conditions.

Noncovalent π Interactions

A. E. Aliev,* J. R. T. Arendorf, I. Pavlakos, R. B. Moreno, M. J. Porter, H. S. Rzepa, W. B. Motherwell* ______ **551 – 555**

Surfing π Clouds for Noncovalent Interactions: Arenes versus Alkenes



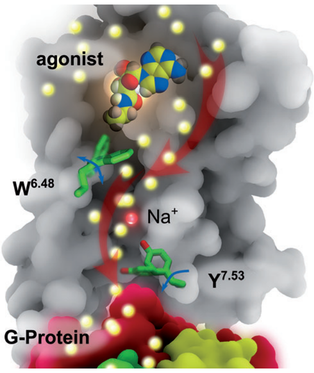
Where do their affinities lie? In studies using molecular balances, noncovalent interactions with an arene dominated over those with an alkene, and a π-facial hydrogen bond from a hydroxy group to an arene was favored by about 1.2 kJ mol^{-1}. Data for $Y = CH_2CH_3$, $CHCH_2$, CCH, and CN groups indicated a long-range electrostatic C⋯π interaction between the Y substituent and the π system. The strongest interaction observed was with the cyano group.

Structural Biology

S. Yuan,* Z. Hu, S. Filipek, H. Vogel* ______ **556 – 559**

W246$^{6.48}$ Opens a Gate for a Continuous Intrinsic Water Pathway during Activation of the Adenosine A_{2A} Receptor

Water logged: Activation of G-protein-coupled receptors depends on the presence of water molecules inside the receptor. Microsecond molecular dynamics simulations revealed that agonist binding leads to structural fluctuations of the residue W$^{6.48}$ inducing water influx and creation of a continuous water pathway (yellow dots, see structure) across the receptor.

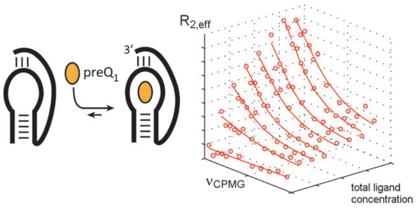


NMR Spectroscopy

T. Moschen, C. H. Wunderlich, R. Spitzer, J. Levic, R. Micura, M. Tollinger,* C. Kreutz* 560 – 563

Ligand-Detected Relaxation Dispersion NMR Spectroscopy: Dynamics of $preQ_1$–RNA Binding

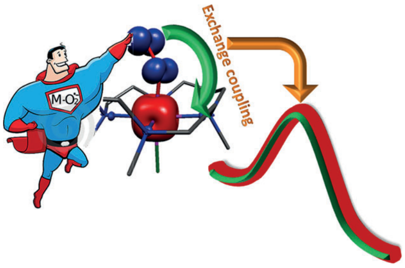
Close interactions: Described is an NMR approach which gives access to two parameters of a ligand–receptor interaction. The off rate and the population of the small molecular–receptor complex can be determined. Ligand-detected NMR relaxation dispersion experiments represent a diagnostic tool for the characterization of binding mechanisms.



Reaction Mechanisms

A. Ansari, P. Jayapal, G. Rajaraman* 564 – 568

C–H Bond Activation by Metal–Superoxo Species: What Drives High Reactivity?



Superoxoman: The title reaction was investigated and the calculations reveal that Mn–$O_2^{\bullet-}$ and Fe–$O_2^{\bullet-}$ are stronger oxidants compared to either Cr–$O_2^{\bullet-}$ or Cu–$O_2^{\bullet-}$, and the oxidative abilities are found to be correlated to the magnetic exchange parameter J. These findings have direct relevance to the functions of several metalloenzymes.

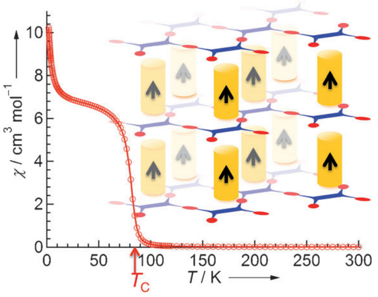
Magnets

VIP

H. Fukunaga, H. Miyasaka* 569 – 573

Magnet Design by Integration of Layer and Chain Magnetic Systems in a π-Stacked Pillared Layer Framework

A pillared layer framework (PLF) was used to rationally design and fabricate a long-range ordered magnet with a phase transition temperature (T_c) of 82 K by integrating two low-dimensional magnetic materials, namely a layer magnetic system and a one-dimensional columnar magnetic system. Furthermore, T_c increased linearly with the applied pressure.

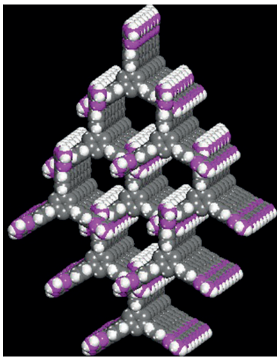


Porous Materials

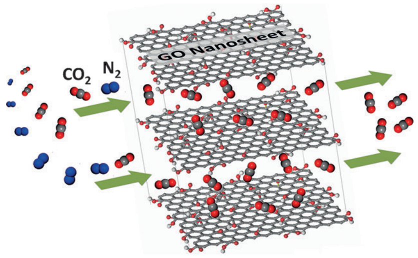
P. Li, Y. He, Y. Zhao, L. Weng, H. Wang, R. Krishna, H. Wu, W. Zhou, M. O'Keeffe, Y. Han, B. Chen* 574 – 577

A Rod-Packing Microporous Hydrogen-Bonded Organic Framework for Highly Selective Separation of C_2H_2/CO_2 at Room Temperature

A 3D microporous rod-packing hydrogen-bonded organic framework was constructed from a trigonal building subunit with diaminotriazine functional groups. This framework exhibits highly selective separation of C_2H_2/CO_2 at ambient temperature and pressure.



Between the sheets: Assembled graphene oxide laminates featuring molecular-sieving interlayer spaces and straight diffusion pathways afford fast and selective channels for gas transport through the membrane. The membrane shows excellent preferential CO_2 permeation from gas mixtures.

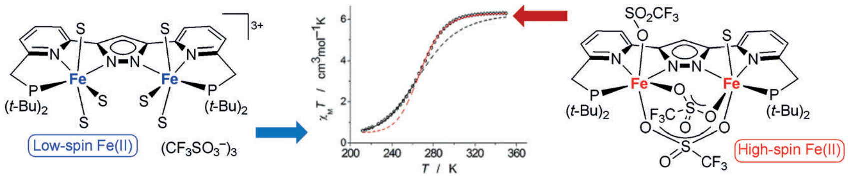


Membranes

J. Shen, G. Liu, K. Huang, W. Jin,* K. Lee, N. Xu ______ **578 – 582**

Membranes with Fast and Selective Gas-Transport Channels of Laminar Graphene Oxide for Efficient CO_2 Capture

Inside Back Cover



A pyrazolate-bridged ligand with two {PNN} pincer-type compartments has been developed. Its diiron(II) complex $LFe_2(OTf)_3(NCMe)$ shows a sequential, reversible, and complete spin state switching between the all-high-spin and all-low-spin states in solution, which correlates with a rapid multistep triflate/MeCN ligand exchange equilibrium. The spin transition temperature can be continuously tuned by varying the triflate concentration.

Spin Switching

S. Samanta, S. Demesko, S. Dechert, F. Meyer* ______ **583 – 587**

A Two-in-one Pincer Ligand and its Diiron(II) Complex Showing Spin State Switching in Solution through Reversible Ligand Exchange

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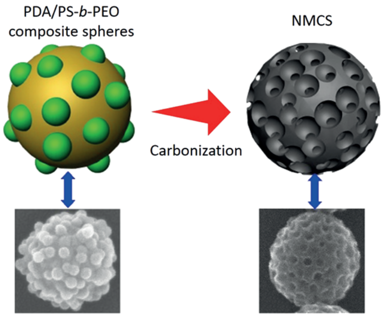
Mesoporous materials: Nitrogen-doped mesoporous carbon spheres (NMCS) with extra-large pores were synthesized through assembly of diblock copolymer micelles. Polymerized dopamine (DA)/polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) composite spheres formed by self-polymerization of DA and spontaneous co-assembly with PS-*b*-PEO micelles. After carbonization and removal of the template, NMCS with large mesopores (up to 16 nm) were obtained.



Mesoporous Carbon Spheres

J. Tang, J. Liu,* C. Li, Y. Li, M. O. Tade, S. Dai,* Y. Yamauchi* ______ **588 – 593**

Synthesis of Nitrogen-Doped Mesoporous Carbon Spheres with Extra-Large Pores through Assembly of Diblock Copolymer Micelles

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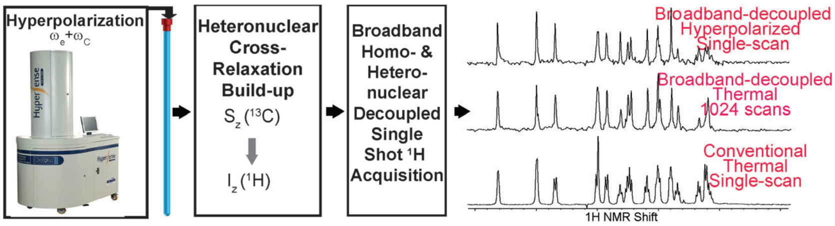


HyperBIRD: An approach to acquire ^1H NMR spectra with enhanced sensitivity and resolution is presented. It is based on polarizing ex situ the ^{13}C nuclei, letting this polarization spontaneously enhance the C-bonded ^1H nuclei, and detecting solely the latter using a single-scan BIRD sequence that delivers homo- and heter-decoupled ^1H spectra.

NMR Spectroscopy

K. J. Donovan, L. Frydman* ______ **594 – 598**

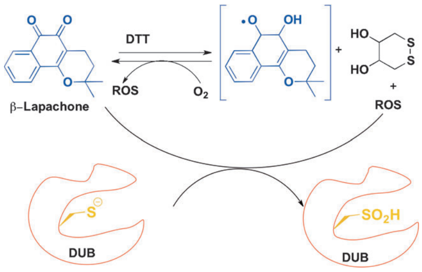
HyperBIRD: A Sensitivity-Enhanced Approach to Collecting Homonuclear-Decoupled Proton NMR Spectra

Quinones and Deubiquitinases

S. Ohayon, M. Refua, A. Hendler,
A. Aharoni,* A. Brik* ______ **599 – 603**

Harnessing the Oxidation Susceptibility of Deubiquitinases for Inhibition with Small Molecules

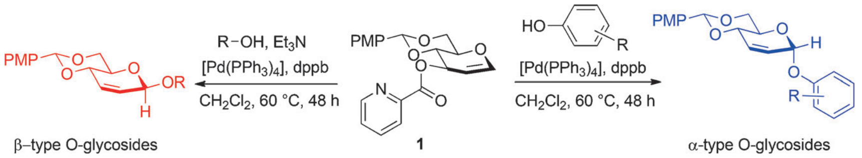
Rub a DUB style: Reactive oxygen species generated by small molecules such as *ortho* quinones rapidly deactivate deubiquitinases (DUBs) by selective and irreversible oxidation of the catalytic cysteine residue. DTT = dithiothreitol.



Nucleophilicity

S. Xiang, K. L. M. Hoang, J. He, Y. J. Tan,
X.-W. Liu* ______ **604 – 607**

Reversing the Stereoselectivity of a Palladium-Catalyzed O-Glycosylation through an Inner-Sphere or Outer-Sphere Pathway

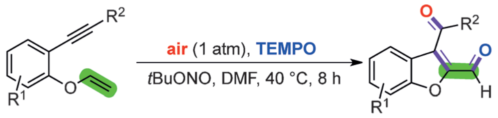


A soft touch: An efficient and concise method for the construction of various O-glycosidic bonds by a palladium-catalyzed reaction with **1** has been developed. The stereochemistry of the anomeric center derives from either an inner-sphere or outer-sphere pathway. Harder nucleophiles such as aliphatic alcohols and sodium phenoxides gave β products, and α products were resulted from softer nucleophiles such as phenol. dppb = 1,4-bis(diphenylphosphino)butane, PMP = *para*-methoxyphenyl.

Heterocycle Synthesis

M. Hu, R.-J. Song, J.-H. Li* ______ **608 – 612**

Metal-Free Radical *5-exo*-dig Cyclizations of Phenol-Linked 1,6-Enynes for the Synthesis of Carbonylated Benzofurans



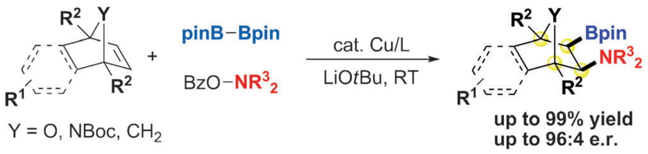
- Real enyne *5-exo*-dig cyclization
- Metal-free
- Radical process
- Dioxygen activation
- 24 examples, up to 84% yield, 1 gram scale

Benzofurans are obtained by the *t*BuONO-initiated radical *5-exo*-dig cyclization of enynes under mild and metal-free conditions. The two oxygen atoms that constitute the newly formed carbonyl groups of the benzofuran system originate from O_2 and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), respectively.

Synthetic Methods

R. Sakae, K. Hirano,* T. Satoh,
M. Miura* ______ **613 – 617**

Copper-Catalyzed Stereoselective Aminoboration of Bicyclic Alkenes

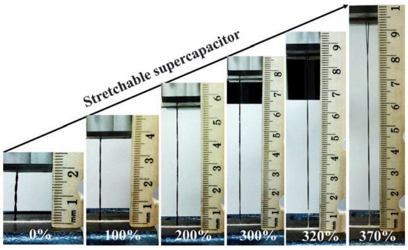


Have a nice ring: A copper-catalyzed aminoboration of bicyclic alkenes with diboron reagents and hydroxylamines has been developed. Subsequent oxidative transformations of the boryl group provide access to oxygen- and nitrogen-rich cyclic molecules. With a chiral bisphosphine ligand, (*R*,*R*)-Ph-BPE, the aminoboration could be conducted in an enantioselective fashion.

Conductive Materials

T. Chen, R. Hao, H. Peng, L. Dai* **618 – 622**

High-Performance, Stretchable, Wire-Shaped Supercapacitors

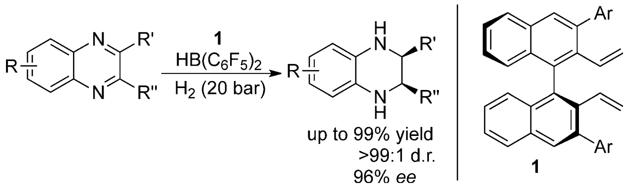


Stretching out: Wire-shaped supercapacitors with more than 350% elasticity have been developed by twisting two carbon-nanotube-wrapped elastic wires together with a polymer electrolyte between them. These newly developed wire devices exhibited high performance with a stability lasting for multiple stretching cycles.

Asymmetric Catalysis

Z. Zhang, H. Du* **623 – 626**

A Highly *cis*-Selective and Enantioselective Metal-Free Hydrogenation of 2,3-Disubstituted Quinoxalines

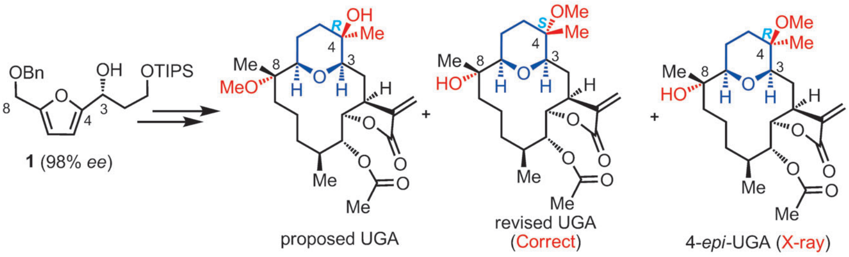


At the core: A highly *cis*-selective and enantioselective metal-free hydrogenation of the title compounds was achieved using in situ generated chiral borane catalysts. The catalyst shown was generated from the chiral diene **1**. The resulting tetrahydroquinoxalines products can be found as core structures for biologically active compounds.

Total Synthesis

L. Zhu, Y. Liu, R. Ma, R. Tong* **627 – 632**

Total Synthesis and Structural Revision of (+)-Uprolide G Acetate

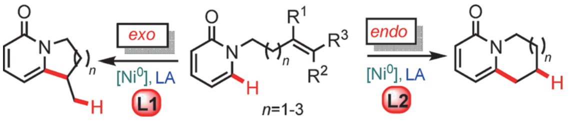


Three tries: The first, asymmetric total synthesis of the proposed structure of (+)-uprolide G acetate (UGA) has been achieved, but its spectral properties clearly differed from those reported for natural UGA. Two possible structures for the natural UGA were proposed and their total syntheses were achieved, thus leading to identification and confirmation of the correct structure and absolute configuration of the natural UGA.

C–H Activation

P. A. Donets, N. Cramer* **633 – 637**

Ligand-Controlled Regiodivergent Nickel-Catalyzed Annulation of Pyridones

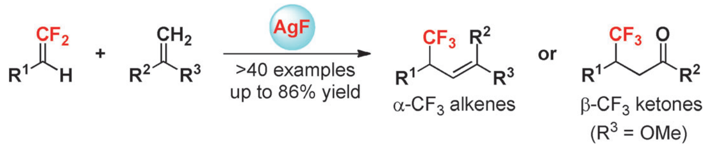


Nickeled and dimed: Nickel(0)-catalyzed C–H functionalization of 2-pyridones and subsequent ligand-controlled regioselective cyclization affords 1,6-annulated 2-pyridones. Cyclooctadiene (**L1**) selectively leads to *exo* cyclization, whereas the addition of a bulky N-heterocyclic carbene ligand (**L2**) switches to the *endo* mode. The method was applied in the synthesis of the lupin alkaloid (±)-cytisine. LA = Lewis acid.

Fluorination

B. Gao, Y. Zhao, J. Hu* ______ **638 – 642**

AgF-Mediated Fluorinative Cross-Coupling of Two Olefins: Facile Access to α-CF_3 Alkenes and β-CF_3 Ketones

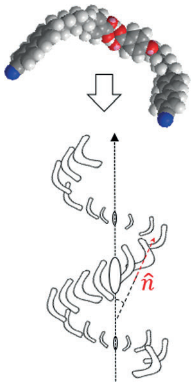


The in situ formation of a trifluoromethyl moiety and an intermolecular alkenyl C−H functionalization were combined in a single reaction system. This AgF-mediated fluorination with a subsequent cross-coupling reaction between *gem*-difluoroolefins and non-fluorinated alkenes provides facile access to both α-CF_3 alkenes and β-CF_3 ketones.

Liquid Crystals

S. M. Jansze, A. Martínez-Felipe, J. M. D. Storey, A. T. M. Marcelis, C. T. Imrie* ______ **643 – 646**

A Twist-Bend Nematic Phase Driven by Hydrogen Bonding

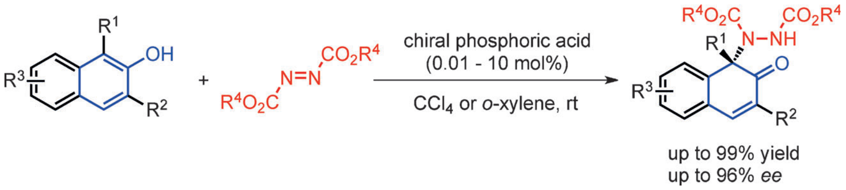


Intriguing interplay: When the benzoic acid units in 4-[6-(4′-cyanobiphenyl-4-yl)-hexyloxy]benzoic acid dimerize by hydrogen bonding (see picture), promesogenic liquid crystal trimers form. These supramolecular complexes show an enantiotropic nematic phase, which on cooling transforms into the twist-bend nematic phase in which the bent, achiral complexes spontaneously form helical structures.

Asymmetric Dearomatization

S.-G. Wang, Q. Yin, C.-X. Zhuo, S.-L. You* ______ **647 – 650**

Asymmetric Dearomatization of β-Naphthols through an Amination Reaction Catalyzed by a Chiral Phosphoric Acid

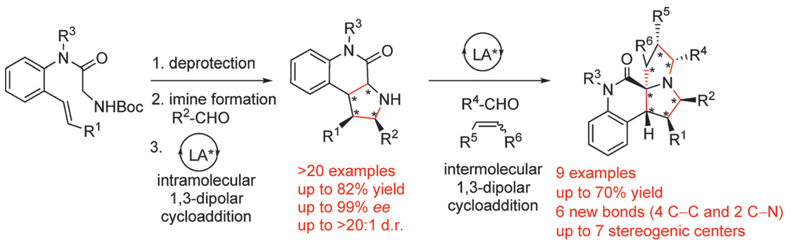


Useful skeletons: An electrophilic amination reaction catalyzed by chiral phosphoric acid is the basis for a highly efficient asymmetric dearomatization of naphthols. This protocol provides functionalized β-naphthalenone compounds with a chiral quaternary carbon center in excellent yields and enantioselectivity. These motifs are found in various biologically active natural products and therapeutic reagents.

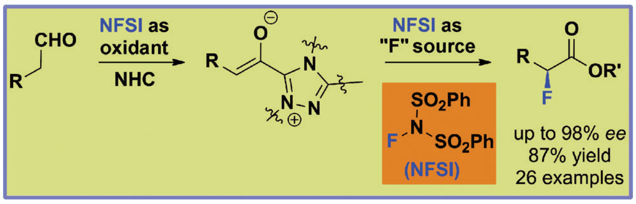
Cycloaddition

S. R. Vidadala, C. Golz, C. Strohmann, C.-G. Daniliuc, H. Waldmann* **651 – 655**

Highly Enantioselective Intramolecular 1,3-Dipolar Cycloaddition: A Route to Piperidino-Pyrrolizidines



So selective: A highly enantioselective intramolecular 1,3-dipolar cycloaddition alone or in tandem with a highly diastereoselective intermolecular 1,3-dipolar cycloaddition provides efficient access to complex natural-product-inspired polycyclic scaffolds. Piperidino-pyrrolizidines with up to seven contiguous stereocenters were thus obtained.



A dual role: The title reaction proceeds in the presence of NFSI, which serves as an oxidant and as a "F" source. The C–F bond formation occurs directly at the α position of simple aliphatic aldehydes, thus overcoming nontrivial challenges, such as competitive difluorination and nonfluorination, and proceeds with high to excellent enantioselectivities.

Organocatalysis

F.-Y. Li, Z.-J. Wu, J. Wang* ____ **656 – 659**

Oxidative Enantioselective α-Fluorination of Aliphatic Aldehydes Enabled by N-Heterocyclic Carbene Catalysis

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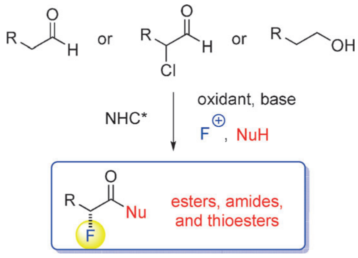
Two roles for NFSI: The N-heterocyclic carbene (NHC) catalyzed asymmetric fluorination of readily available simple aliphatic aldehydes, α-chloro aldehydes, and even alcohols proceeds via azolium enolates and yields a wide range of α-fluoro esters, amides, and thioesters with excellent enantioselectivity. *N*-Fluorobenzenesulfonimide (NFSI) acts as both a fluorinating reagent and an oxidant in this transformation.



Organocatalysis

X. Dong, W. Yang, W. Hu,
J. Sun* ____ **660 – 663**

N-Heterocyclic Carbene Catalyzed Enantioselective α-Fluorination of Aliphatic Aldehydes and α-Chloro Aldehydes: Synthesis of α-Fluoro Esters, Amides, and Thioesters

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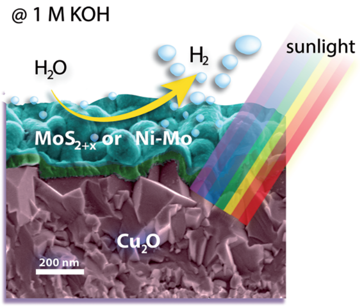
Amorphous molybdenum sulfide and nickel–molybdenum alloy efficiently catalyze the photoelectrochemical hydrogen evolution on a cuprous oxide photocathode in alkaline solutions.



Electrochemistry

C. G. Morales-Guio, L. Liardet,
M. T. Mayer, S. D. Tilley, M. Grätzel,
X. L. Hu* ____ **664 – 667**

Photoelectrochemical Hydrogen Production in Alkaline Solutions Using Cu_2O Coated with Earth-Abundant Hydrogen Evolution Catalysts

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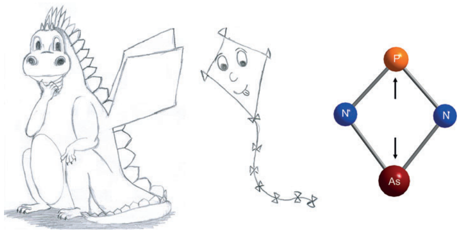


When you are two you cannot be too radical: The first biradicaloid with different radical centers, heteroatomic biradicaloid [P(μ-NR)$_2$As], was obtained by reducing the corresponding dichloroarsaphosphadiazane with magnesium. Structure elucidation revealed a kite-shaped planar four-membered N_2PAs ring with two equal P–N and As–N distances (see scheme, note in German the word for kite is Drachen, and dragon is Drache).

Biradicaloids

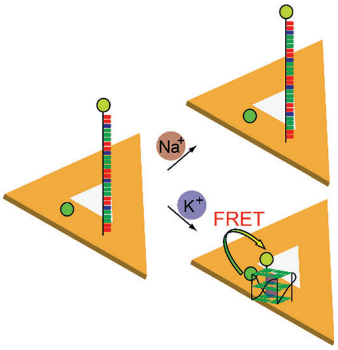
A. Hinz, A. Schulz,*
A. Villinger ____ **668 – 672**

A Mixed Arsenic–Phosphorus Centered Biradicaloid

DNA Nanotechnology

L. Olejko, P. J. Cywinski,*
I. Bald* ______ 673 – 677

Ion-Selective Formation of a Guanine Quadruplex on DNA Origami Structures



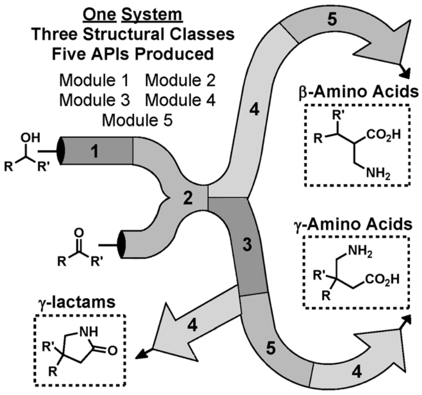
Right said FRET: Guanine (G) quadruplex structures are formed on DNA origami triangles in the presence of K$^+$ ions, whereas G-quadruplex formation is completely suppressed when Na$^+$ ions are present. This effect was studied with FRET measurements and ascribed to steric hindrance induced by the DNA origami platform. The systems may have potential for selective K$^+$ sensing.

Flow Chemistry

D. Ghislieri, K. Gilmore,
P. H. Seeberger* ______ 678 – 682

Chemical Assembly Systems: Layered Control for Divergent, Continuous, Multistep Syntheses of Active Pharmaceutical Ingredients

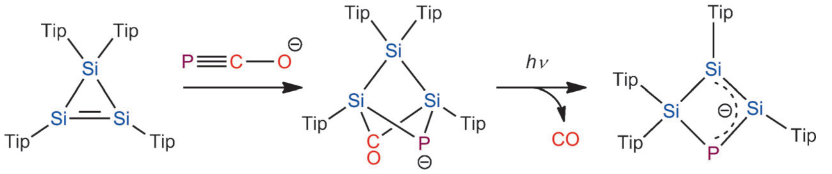
Single system, multiple medicines: A new paradigm in chemical synthesis is introduced, in which a systems-level approach to chemical synthesis allows access to a broad chemical space with a single process. The combination of five interchangeable reaction modules affords the continuous synthesis of β-amino acids, γ-lactams, and γ-amino acids, including the blockbuster drugs Gabapentin and Lyrica.



Si,P Heterocycles

T. P. Robinson, M. J. Cowley,
D. Scheschkewitz,*
J. M. Goicoechea* ______ 683 – 686

Phosphide Delivery to a Cyclotrisilene

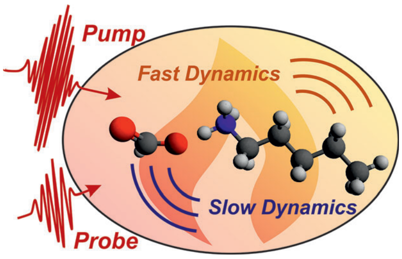


Addition of the 2-phosphoethynolate anion across the Si–Si double bond of a cyclic trisilene is presented. Photolysis of the resulting product affords a novel four-membered heterocycle exhibiting considerable allylic character. This latter species can be thought of as a congener of the cyclobutene anion.

Dynamic Heterogeneity

Z. Zheng, W. Fan, S. Roy, K. Mazur,
A. Nazet, R. Buchner, M. Bonn,
J. Hunger* ______ 687 – 690

Ionic Liquids: Not only Structurally but also Dynamically Heterogeneous

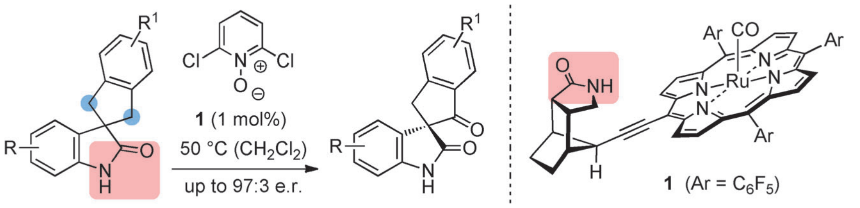


Size doesn’t matter: The equilibration of the ionic ammonium group in protic ionic liquids after an ultrafast temperature jump depends on the anion but not on the size of the hydrophobic side chain. This equilibration of the ionic domains is approximately two times slower than restructuring within the hydrophobic alkyl domains, which demonstrates the dynamic heterogeneity in ionic liquids.

Supramolecular Catalysis

J. R. Frost, S. M. Huber, S. Breitenlechner, C. Bannwarth, T. Bach* ______ 691 – 695

Enantiotopos-Selective C—H Oxygenation Catalyzed by a Supramolecular Ruthenium Complex



Correctly addressed: Catalyst **1** allows for a selective oxygenation of spirocyclic oxindoles at one of two enantiotopic positions (●). Evidence was collected that hydrogen bonding (■) is responsible for a perfect spatial overlap of the reactive centers in the transition state of the C—H activation reaction.

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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