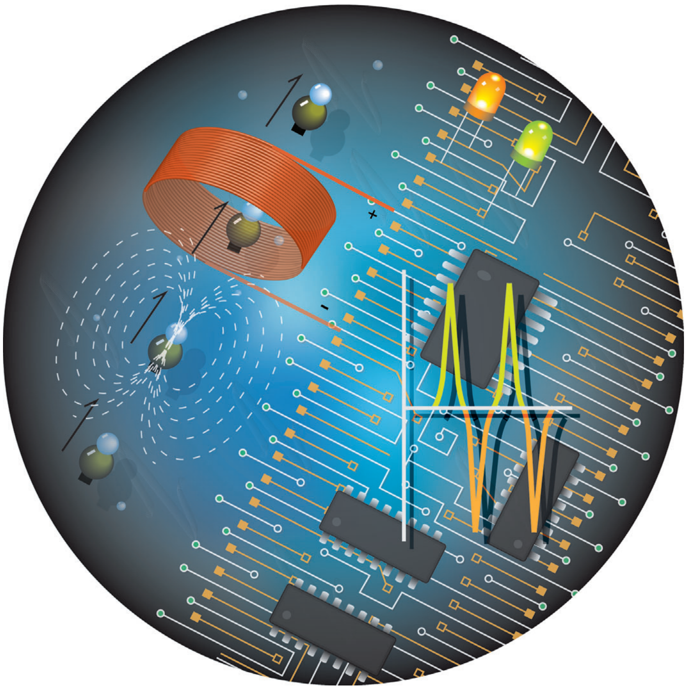
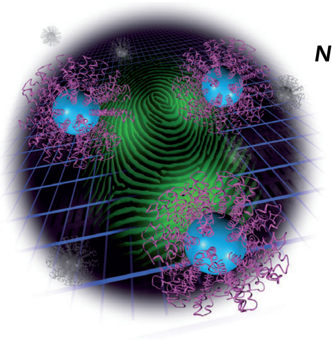
A magnetic microbot ...

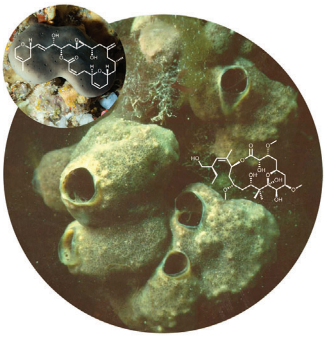


… travels autonomously in an aqueous medium powered by the catalytic decomposition of H_2O_2. In their Communication on page 1521 ff., A. Chattopadhyay and S. K. Sailapu relate how passage of the bot through a Faraday coil generates electricity which can be used for LED illumination. The self-propelled power-generating unit is a model for an autonomous bot with secondary function.

Porphyrinoids
In their Communication on page 1506 ff., D. Kim, T. Iwamoto, H. Shinokubo et al. demonstrate that silylenes regioselectively insert into the C–C bonds of an antiaromatic norcorrole Ni^{II} complex to provide ring-expansion products.



Nanoparticles
Q. Yuan and co-workers describe in their Communication on page 1616 ff. a general technique based on near-infrared-light-mediated imaging and molecular recognition for the detection of latent fingerprints.



Drug Discovery
M. O. Steinmetz et al. describe the crystal structures of laulimalide and peloruside A bound to tubulin and explain their mechanism of action in their Communication on page 1621 ff.

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Service

Author Profile

"My motto is 'If it were easy, someone would have already done it.'
I advise my students to work hard and play hard …"
This and more about Mark J. MacLachlan can be found on page 1478.

News


B. F. Cravatt


K. Itami


A. Kirschning


G. A. Molander


C. D. Vanderwal


N. Cramer

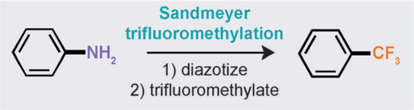

D. Rauh

Books

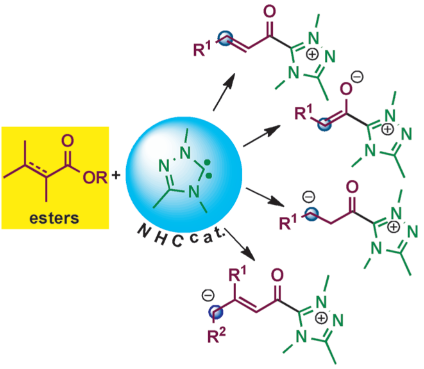
Highlights

Synthetic Methods

A means to trifluoromethylate: The beneficial properties imparted by the trifluoromethylation of aromatic compounds continue to drive the discovery of novel reagents and reactions for the late-stage introduction of such moieties. Highlighted here is the recently discovered Sandmeyer trifluoromethylation approach, which now permits aromatic amines to be substrates in a direct trifluoromethylation strategy.



NHC Organocatalysis

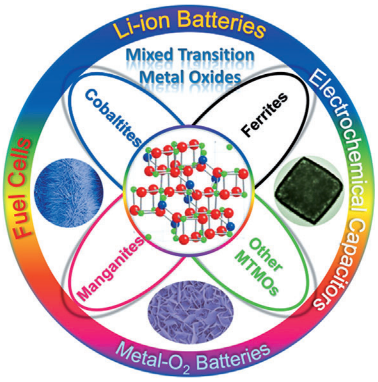


Esters—what else! A new strategy in NHC organocatalysis allows the α-, β- and γ-activation of saturated and unsaturated esters. The resulting acyl azolium intermediates efficiently participate in domino reactions with suitable substrates to generate synthetically valuable carbo- and heterocycles with very good diastereo- and excellent enantioselectivities.

Reviews

Mixed Metal Oxides

Full of energy: Recent advances in the rational design and synthesis of mixed transition-metal oxides (MTMOs, designated as $A_xB_{3-x}O_4$) with controllable compositions and structures and their applications in various electrochemical energy storage/conversion technologies are summarized and discussed (see picture). Future trends and prospects for their further development are also discussed.



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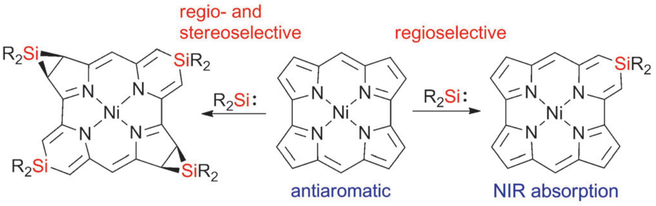
Communications

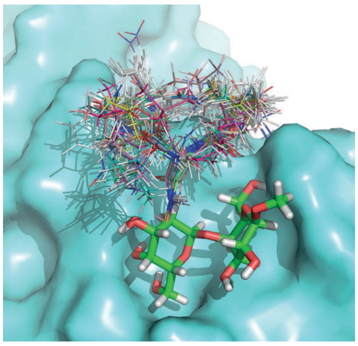
Porphyrinoids



This looks like a good spot for Si: The treatment of an antiaromatic norcorrole Ni^{II} complex with a kinetically stabilized silylene provided ring-expansion products in excellent yields by highly regioselective insertion into the β-β pyrrolic C–C bonds. The absorption spectrum of the resulting silicon-containing Ni^{II} porphyrinoid is substantially red-shifted into the near-infrared region.

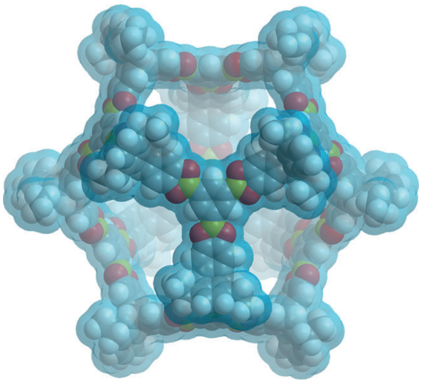
Frontispiece

Glycoarrays



Target the toxin: An array of modified ligands was generated after coating microtiter plates with a common precursor containing a reactive functionality. Physically adsorbed ligand–polymer conjugates tolerate a variety of reaction conditions and support instant evaluation of the library by ELISA, as well as subsequent iterative cycles of modification and evaluation. High-affinity ligands for *E. coli* Shiga toxin type 2 were discovered by using this method.

Porous Organic Cage Compounds



Big boronic ester cages: A shape-persistent cuboctahedron can be almost quantitatively formed by a 48-fold one-pot condensation of 12 molecules of a triptycene tetrol with 8 molecules of triboronic acid. The desolvated crystalline material of this cage has a specific surface area of 3758 $m^2 g^{-1}$ and a maximum pore size of 2.3 nm, thus making it mesoporous by the IUPAC definition.

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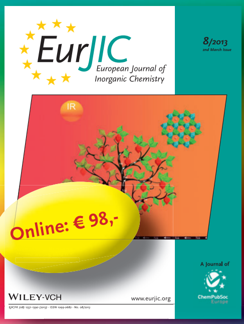

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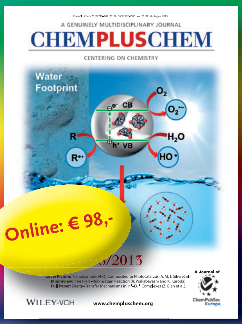

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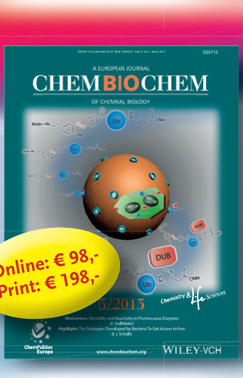

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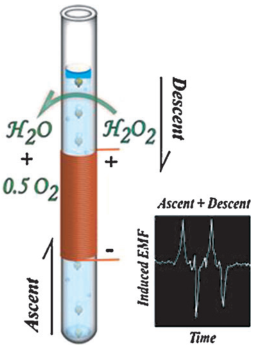
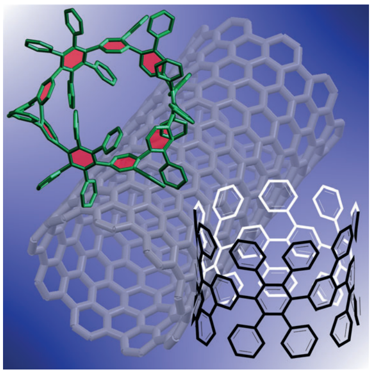
PSJ-13-59145_gu

The ups and downs: A magnetic chemical locomotor decorated with Pd nanoparticles catalytically decomposes H_2O_2. The bubbles of O_2 generated lend the bot buoyancy and the micromagnet induces an electromotive force (EMF) in a copper coil in its vicinity.



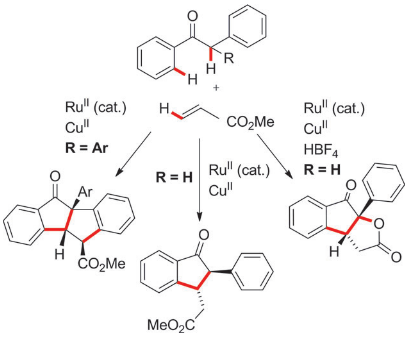
Generation of Electricity

Front Cover



Tube design: Polyphenylene cylinders that resemble precursors of carbon nanotubes (CNTs) have been synthesized and characterized by X-ray crystallography. The oxidative cyclodehydrogenation was investigated for ring-strained molecules as a final step towards a bottom-up synthesis of CNT segments, and revealed strain relief through a 1,2-phenyl shift.

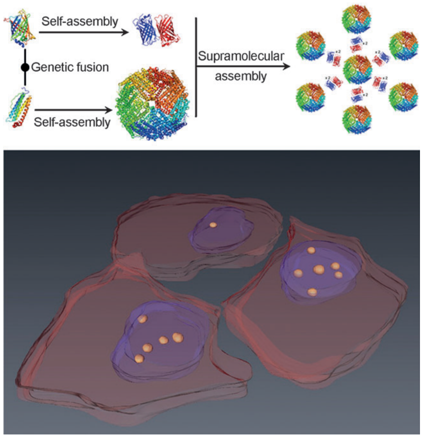
Carbon Nanostructures



Carbon coupling cascade: Arylacetophenones react with Michael acceptors under ruthenium catalysis to set up triple and quadruple C–H functionalization pathways. Through choice of reaction conditions, novel indanone carbacycles, indeno indene carbacycles, and indeno furanone heterocycles can each be accessed in a single step.

Cascade Reaction

The fluorescent protein citrine and the H subunits of human ferritin were genetically fused to combine their self-assembly properties. As a result, a three-dimensional network of interactions was established to form extended, fluorescent, and crystalline supramolecular protein assemblies (SMPAs) in live HeLa cells. With the addition of a genetically encoded nuclear localization signal, SMPA formation was targeted exclusively to the cell nucleus.

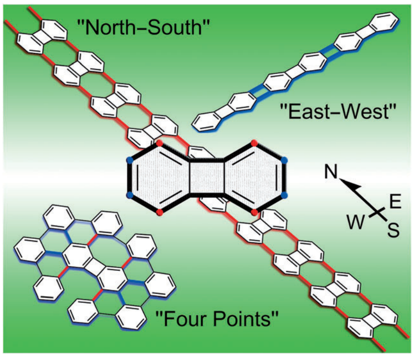


Protein–Protein Interactions

Graphene

F. Schlütter, T. Nishiuchi, V. Enkelmann,
K. Müllen* ________ **1538 – 1542**

Octafunctionalized Biphenylenes: Molecular Precursors for Isomeric Graphene Nanostructures



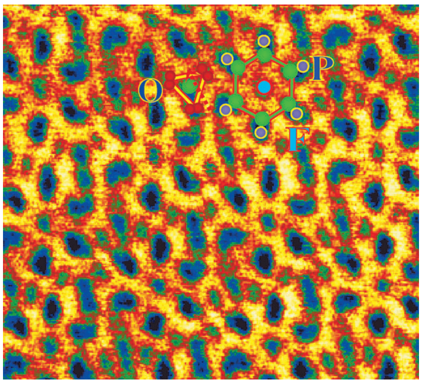
Carbon allotropes: A straightforward method for the octafunctionalization of biphenylene based on the [2+2]-cycloaddition of an aryne intermediate has been developed. This enabled the synthesis of isomeric graphene nanoribbons, [*n*]phenylenes, and nanographenes with even-membered rings embedded in a hexagonal lattice.

Electron Microscopy

C. L. Chen, Z. C. Wang,* M. Saito, T. Tohei,
Y. Takano, Y. Ikuhara ______ **1543 – 1547**

Fluorine in Shark Teeth: Its Direct Atomic-Resolution Imaging and Strengthening Function

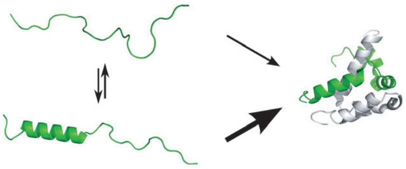
Smile! Aberration-corrected electron microscopy allows the spatial resolution of every individual atomic column in the complex fluorapatite structure of shark tooth enameloid. With the support of ab initio calculations, fluorine atoms are shown to be covalently bound to the surrounding calcium atoms, which improves understanding of their caries-reducing effects in shark teeth.



Ligand Binding

V. Iešmantavičius, J. Dogan, P. Jemth,
K. Teilum, M. Kjaergaard* __ **1548 – 1551**

Helical Propensity in an Intrinsically Disordered Protein Accelerates Ligand Binding

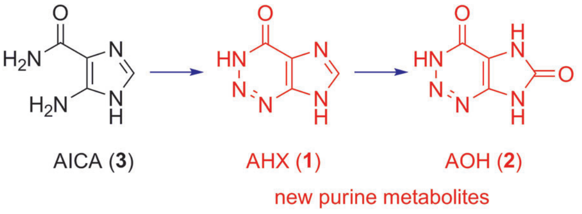


Binding kinetics: Intrinsically disordered proteins frequently display transient secondary structure. But, the role of this secondary structure for the binding process is not well understood. By modulating the helical propensity of an intrinsically disordered protein domain and monitoring the structural and kinetic changes by NMR spectroscopy and stopped-flow methods, the effects on ligand binding can be deduced.

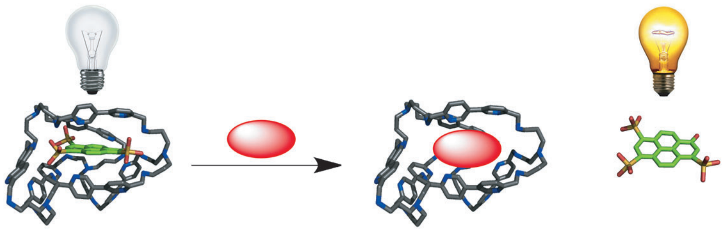
Natural Products

J.-H. Choi, T. Ohnishi, Y. Yamakawa,
S. Takeda, S. Sekiguchi, W. Maruyama,
K. Yamashita, T. Suzuki, A. Morita, T. Ikka,
R. Motohashi, Y. Kiriiwa, H. Tobina,
T. Asai, S. Tokuyama, H. Hirai, N. Yasuda,
K. Noguchi, T. Asakawa, S. Sugiyama,
T. Kan, H. Kawagishi* ______ **1552 – 1555**

The Source of "Fairy Rings": 2-Azahypoxanthine and its Metabolite Found in a Novel Purine Metabolic Pathway in Plants



The fairy of the rings: The common metabolite, 2-aza-8-oxohypoxanthine (**2**), of the "fairy", 2-azahypoxanthine (**1**), was isolated from rice, thus supporting the existence of endogenous **1** and **2** in plants. Compound **1** is synthesized from **3** by treatment with $NaNO_2$ and then NH_3; **1** can then be converted into **2** by xanthine oxidase. The new purine pathway to form the compounds occurs in rice and *Arabidopsis* through a route similar to the chemical synthesis.

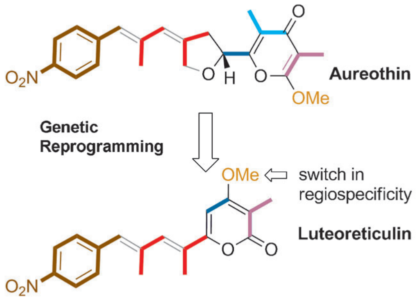


Self-assembled precursors could be reduced and demetalated in high yields to generate two new covalent architectures. These organic molecules display high aqueous solubility, and the larger cage strongly binds aromatic polyanions in water, including the fluorescent dye molecule pyranine (with nanomolar affinity), thus allowing for the design of an indicator-displacement assay.

Container Molecules

J. Mosquera, S. Zarra,
J. R. Nitschke* ________ 1556 – 1559

Aqueous Anion Receptors through Reduction of Subcomponent Self-Assembled Structures



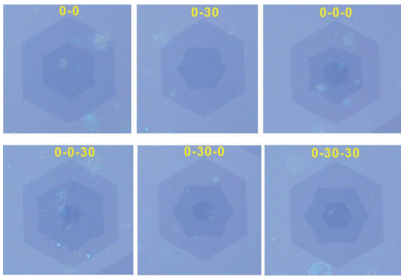
Transformers: Through genetic reprogramming, the aureothin pathway was gradually morphed into an assembly line for luteoreticulin. The first rational conversion of a complex polyketide into another natural product emulates a probable evolutionary scenario. This study also reveals the unprecedented iterative use of an acyl transferase domain and a context-dependent switch in the regioselectivity of a pyrone methyltransferase.

Polyketides

Y. Sugimoto, L. Ding, K. Ishida,
C. Hertweck* ________ 1560 – 1564

Rational Design of Modular Polyketide Synthases: Morphing the Aureothin Pathway into a Luteoreticulin Assembly Line

Carbon materials: The synthesis of 100 μm pyramid-like bi- and trilayer graphene domains deposited on copper foils with hexagonal shape is reported (see picture). The produced graphene domains show almost exclusively either 0° or 30° interlayer rotations. First-principle calculations show that the rotations can originate from the graphene nucleation at a copper step.

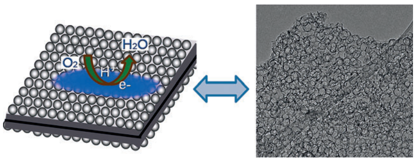


Graphene Pyramids

Z. Yan, Y. Liu, L. Ju, Z. Peng, J. Lin,
G. Wang, H. Zhou, C. Xiang,
E. L. G. Samuel, C. Kittrell, V. I. Artyukhov,
F. Wang,* B. I. Yakobson,*
J. M. Tour* ________ 1565 – 1569

Large Hexagonal Bi- and Trilayer Graphene Single Crystals with Varied Interlayer Rotations

Nitrogen doping: Mesoporous nitrogen-doped carbon nanosheets with defined mesopore size of 22 nm exhibits outstanding oxygen reduction reaction performance comparable to that of the Pt/C catalyst in alkaline medium (see picture), pronounced activity, and long-term stability under acidic conditions.



Porous Carbon Catalysts

W. Wei, H. Liang, K. Parvez, X. Zhuang,
X. Feng,* K. Müllen* ________ 1570 – 1574

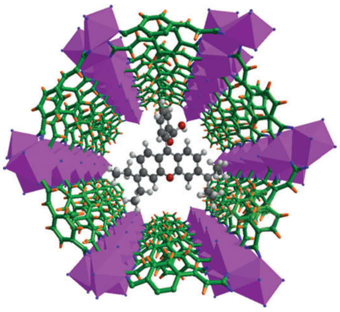
Nitrogen-Doped Carbon Nanosheets with Size-Defined Mesopores as Highly Efficient Metal-Free Catalyst for the Oxygen Reduction Reaction

Luminescent Metal–Organic Sensors

M.-J. Dong, M. Zhao, S. Ou, C. Zou,
C.-D. Wu* ______ **1575 – 1579**

A Luminescent Dye@MOF Platform: Emission Fingerprint Relationships of Volatile Organic Molecules

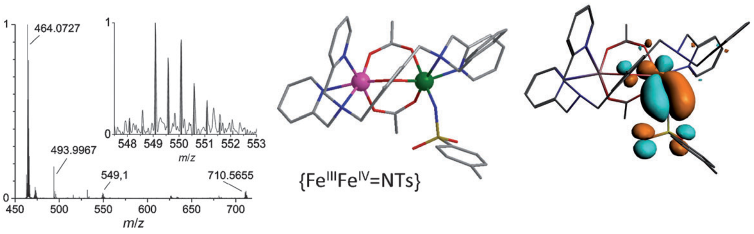
Got the glow: A 3D coordination network with large hexagonal nanotube channels based on 1D infinite rod-shaped metal-carboxylate chains is reported. This material can absorb Rhodamine B dye into its pores to form a luminescent platform for visually probing different small molecules.



Nitrene Transfer

E. Gouré, F. Avenier, P. Dubourdeaux,
O. Sénèque, F. Albrieux, C. Lebrun,
M. Clémancey, P. Maldivi,*
J.-M. Latour* ______ **1580 – 1584**

A Diiron(III,IV) Imido Species Very Active in Nitrene-Transfer Reactions

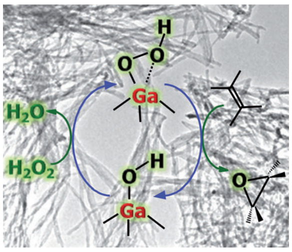


Nitrene transfer: An Fe^{III}Fe^{IV} imido intermediate is identified in nitrene-transfer reactions by desorption electrospray ionization mass spectrometry (DESI-MS). DFT calculations show that low-lying Fe^{III}Fe^{III}-•N-tosyl configurations play a major role in the high reactivity of the intermediate.

Heterogeneous Catalysis

W. Lueangchaichaweng, N. R. Brooks,
S. Fiorilli, E. Gobechiya, K. Lin, L. Li,
S. Parres-Esclapez, E. Javon, S. Bals,
G. Van Tendeloo, J. A. Martens,
C. E. A. Kirschhock, P. A. Jacobs,
P. P. Pescarmona* ______ **1585 – 1589**

Gallium Oxide Nanorods: Novel, Template-Free Synthesis and High Catalytic Activity in Epoxidation Reactions

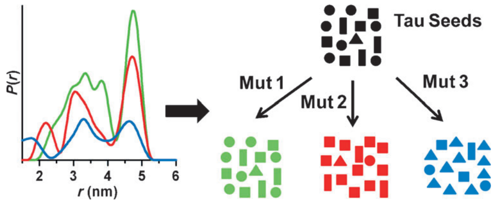


Selective epoxidation: Gallium oxide nanorods with unprecedented small dimensions (20–80 nm length and 3–5 nm width) were prepared using a novel, template-free synthesis method. The nanorods are much superior to conventional gallium oxide both in terms of specific surface area and number of acid sites and display excellent performance as epoxidation catalyst with H_2O_2 as the oxidant (see picture).

Proteins

V. Meyer, P. D. Dinkel, Y. Luo, X. Yu,
G. Wei, J. Zheng, G. R. Eaton, B. Ma,
R. Nussinov, S. S. Eaton,
M. Margittai* ______ **1590 – 1593**

Single Mutations in Tau Modulate the Populations of Fibril Conformers through Seed Selection

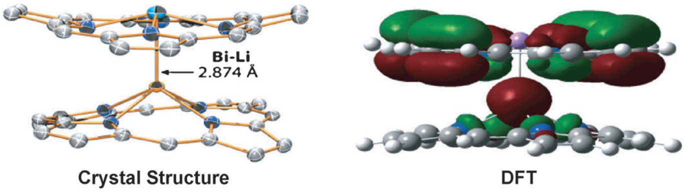


It takes only one mutation: The conformational ensembles of four-repeat tau fibrils, formed after templated growth, have been determined by double electron-electron resonance spectroscopy through the measurement of distances between two spin labels. The results indicate that single mutations in tau can alter the populations of fibril conformers based on the selection of structurally compatible seeds.

Coordination Chemistry

V. Balasanthiran, M. H. Chisholm,*
C. B. Durr ——— **1594 – 1597**

On the Molecular Structure and Bonding in a Lithium Bismuth Porphyrin Complex: LiBi(TPP)$_2$

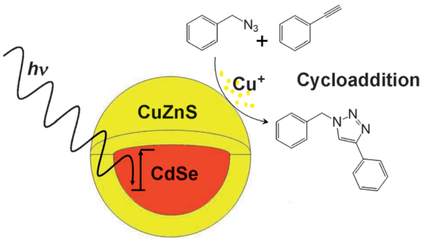


Strong bonding interaction: The dark green crystalline LiBi(TPP)$_2$ shows a remarkably short Bi–Li interaction in the solid state of 2.874 Å (TPP = tetraphenylporphyrin; see picture). The molecule was shown to remain intact in the solution phase and through use of DFT calculations it appears to involve a dative bond from the cationic Bi(TPP) moiety to the anionic Li(TPP) moiety.

Core–Shell Materials

J. C. Bear, N. Hollingsworth,*
P. D. McNaughter, A. G. Mayes,
M. B. Ward, T. Nann, G. Hogarth,
I. P. Parkin* ——— **1598 – 1601**

Copper-Doped CdSe/ZnS Quantum Dots: Controllable Photoactivated Copper(I) Cation Storage and Release Vectors for Catalysis

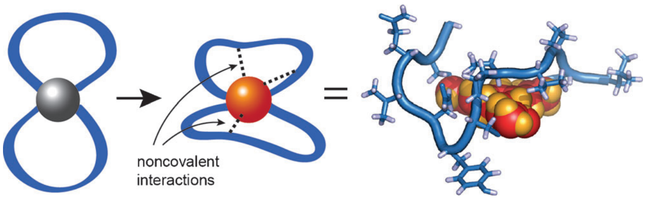


Copper catalysis: Core–shell nanoparticles made of CdSeZnS quantum dots (QDs) with a copper-doped shell have been prepared. Doping copper ions in the ZnS QD shell provides an alternate decay pathway for photoexcited CdSe affording a vector for the release of metal ions for catalysis.

Structured Peptides

S. Chen, D. Bertoldo, A. Angelini, F. Pojer,
C. Heinis* ——— **1602 – 1606**

Peptide Ligands Stabilized by Small Molecules



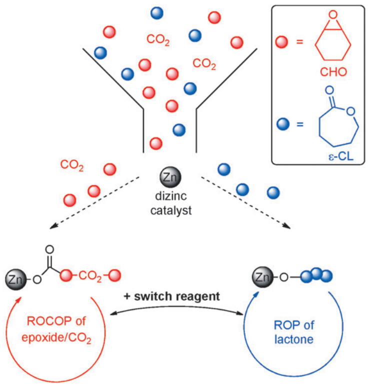
Bicyclic peptide ligands provide an attractive format for the development of therapeutics based on antibody-mimicking structures but their flexible conformation limits binding affinity. Small hydrophilic molecules at the center of bicyclic peptides were found to form noncovalent interactions with amino acids in the peptides and thus stabilize their conformation and strengthen the binding interaction.

Ring-Opening Polymerization

C. Romain, C. K. Williams* **1607 – 1610**

Chemoselective Polymerization Control: From Mixed-Monomer Feedstock to Copolymers

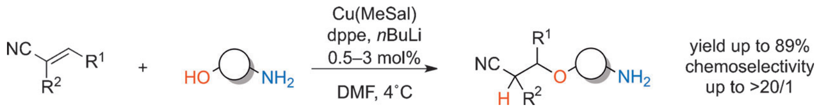
It's under control: A novel chemoselective ring-opening polymerization yields predictable polymer/copolymer compositions from a mixture of monomers. The selectivity depends on the nature of the zinc–oxygen functionality at the growing polymer chain end, and can be controlled by the addition of exogenous switch reagents.



Synthetic Methods

S. Uesugi, Z. Li, R. Yazaki,*
T. Ohshima* ______________ **1611 – 1615**

Chemoselective Catalytic Conjugate Addition of Alcohols over Amines



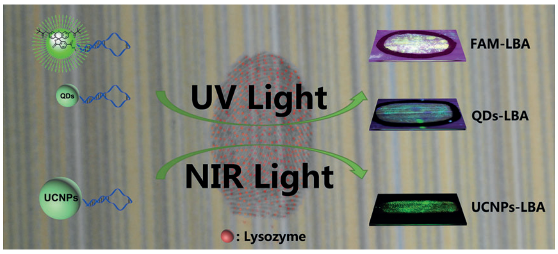
The cooperative nature of a copper catalyst enabled the highly chemoselective activation of alcohols in the presence of amines and thus the conjugate addition of the hydroxy group to soft Lewis basic α,β-unsaturated nitriles. The presented method proceeds under proton-transfer conditions, reverses the innate reactivity of the OH and NH groups, and does not require protecting groups. dppe = 1,2-bis(diphenylphosphino)ethane, MeSal = 3-methylsalicylate.

Nanoparticles

J. Wang, T. Wei, X. Li, B. Zhang, J. Wang,
C. Huang, Q. Yuan* _______ **1616 – 1620**

Near-Infrared-Light-Mediated Imaging of Latent Fingerprints based on Molecular Recognition

Inside Back Cover



Caught! A general strategy for imaging latent fingerprints takes advantage of the background fluorescence suppressing ability of upconversion nanomaterials (UCNPs) and the specific recognition function of DNA aptamers for a target compound in fingerprint ridges. This strategy simultaneously meets the selectivity and generality criteria in photoluminescence approaches and does not suffer from background fluorescence.

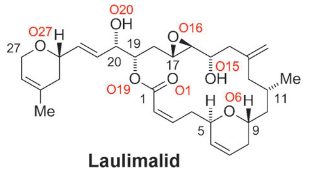
Drug Discovery

A. E. Prota, K. Bargsten, P. T. Northcote,
M. Marsh, K.-H. Altmann, J. H. Miller,
J. F. Díaz, M. O. Steinmetz* **1621 – 1625**

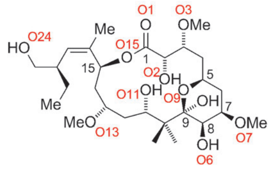
Structural Basis of Microtubule Stabilization by Laulimalide and Peloruside A

Back Cover

Microtubule-stabilizing agents: Laulimalide and peloruside A are attractive next-generation microtubule-stabilizing agents for use in combination chemotherapy with taxane-site drugs. X-ray crystallography shows that both compounds bind to a unique site on β-tubulin. The data define the mechanism of action of laulimalide and peloruside on tubulin and microtubules.



Laulimalid

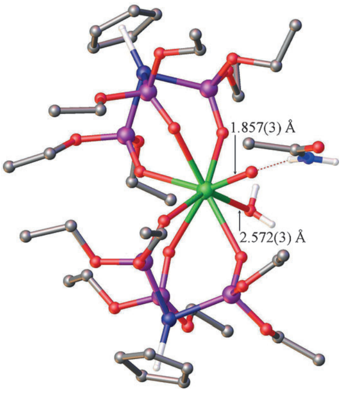


Pelorusid A

Lanthanide Oxo Complexes

Y.-M. So, G.-C. Wang, Y. Li, H. H.-Y. Sung,
I. D. Williams,* Z. Lin,*
W.-H. Leung* ______________ **1626 – 1629**

A Tetravalent Cerium Complex Containing a Ce═O Bond

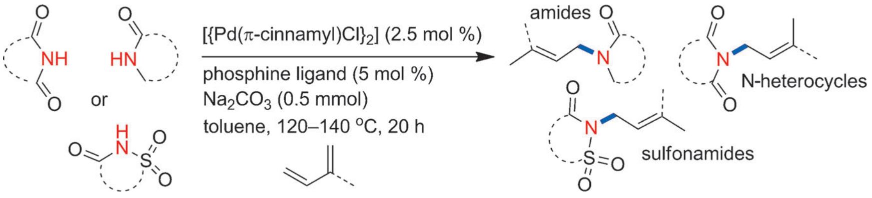


Bond, short bond: The Ce–oxo distance in the Ce^{IV} oxo aqua complex $[Ce{=}O(L_{OEt})_2(H_2O)]\cdot MeC(O)NH_2$ (**1**; $L_{OEt}^{-} = [Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^{-}$) is the shortest known, and is consistent with a multiple bond. DFT calculations reveal that the hydrogen bond to cocrystallized acetamide plays an important role in stabilizing the Ce═O moiety of **1** in the solid-state. The reactivity of **1** towards CO_2 and CO has also been studied.

C–N Bond formation

D. Banerjee, K. Junge,
M. Beller* ______ 1630 – 1635

A General Catalytic Hydroamidation of 1,3-Dienes: Atom-Efficient Synthesis of *N*-Allyl Heterocycles, Amides, and Sulfonamides

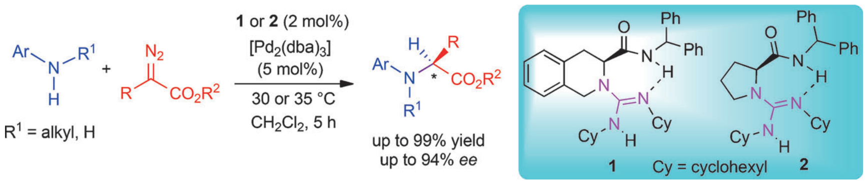


Give me an N bond: A general palladium-catalyzed intermolecular hydroamidation of 1,3-dienes with electron-deficient N-heterocycles, amides, and sulfonamides proceeded with high regioselectivity for 1,4-addition and excellent functional-group tolerance (see scheme). The practical utility of the method was demonstrated by the hydroamidation of functionalized biologically active substrates.

Asymmetric Catalysis

Y. Zhu, X. H. Liu,* S. X. Dong, Y. H. Zhou,
W. Li, L. L. Lin, X. M. Feng* 1636 – 1640

Asymmetric N–H Insertion of Secondary and Primary Anilines under the Catalysis of Palladium and Chiral Guanidine Derivatives

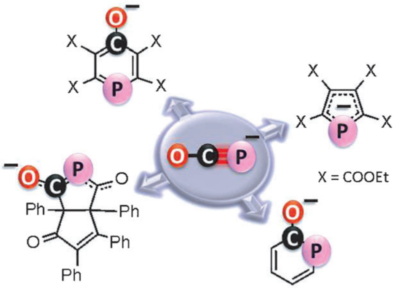


Hidden talents: Chiral guanidine derivatives were developed as useful ligands for the enantioselective insertion of carbenoids into the N–H bonds of secondary and primary anilines in combination with palladium(0), which was not previously known to promote asymmetric N–H insertion (see scheme; dba = dibenzylideneacetone). The N–H insertion mechanism was examined by kinetic isotope studies, control experiments, HRMS, and spectroscopic analysis.

Phosphorus Heterocycles

X. Chen, S. Alidori, F. F. Puschmann,
G. Santiso-Quinones, Z. Benkő,* Z. Li,
G. Becker, H.-F. Grützmacher,
H. Grützmacher* ______ 1641 – 1645

Sodium Phosphaethynolate as a Building Block for Heterocycles

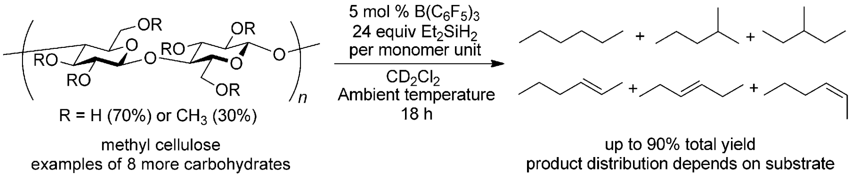


Small, but effective—such is the nature of the O–C≡P⁻ anion of the sodium phosphaethynolate salt. In atom-economic cycloadditions, several five- and six-membered phosphorus heterocycles are accessed, all of which are useful building blocks in their own right.

Biomass Deoxygenation

L. L. Adduci, M. P. McLaughlin,
T. A. Bender, J. J. Becker,
M. R. Gagné* ______ 1646 – 1649

Metal-Free Deoxygenation of Carbohydrates

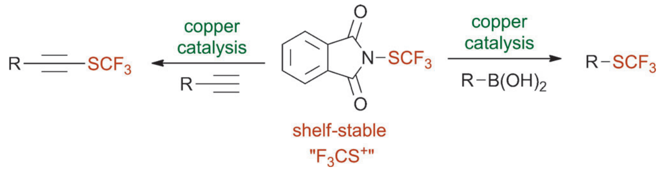


A spoonful of sugar: The Lewis acid $B(C_6F_5)_3$ catalyzes the complete deoxygenation of carbohydrates to give a mixture of hexane and hexene isomers, with diethylsilane (Et_2SiH_2) providing the hydride equivalent. A variety of carbohydrates including methyl cellulose can be deoxygenated by this metal-free method, and the system can be tuned for selective deoxygenation at certain sites.

Synthetic Methods

R. Pluta, P. Nikolaienko,
M. Rueping* ______ 1650 – 1653

Direct Catalytic Trifluoromethylthiolation of Boronic Acids and Alkynes Employing Electrophilic Shelf-Stable *N*-(trifluoromethylthio)phthalimide

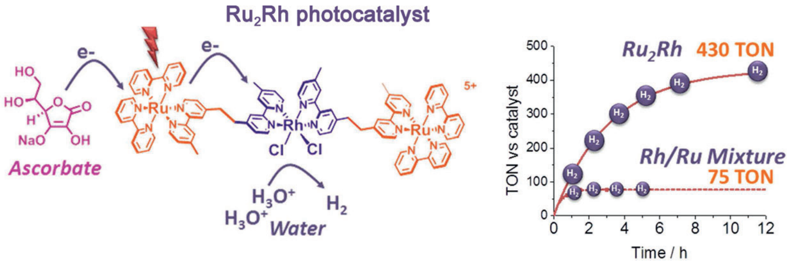


Shelf life: A new and safe method for the synthesis of *N*-(trifluoromethylthio)-phthalimide has been developed. It serves as a convenient and shelf-stable reagent for the direct copper-catalyzed trifluoromethylthiolation of readily available boronic acids and alkynes.

Hydrogen Evolution

T. Stoll, M. Gennari, J. Fortage,
C. E. Castillo, M. Rebarz, M. Sliwa,
O. Poizat, F. Odobel, A. Deronzier,*
M.-N. Collomb* ______ 1654 – 1658

An Efficient Ru^{II}–Rh^{III}–Ru^{II} Polypyridyl Photocatalyst for Visible-Light-Driven Hydrogen Production in Aqueous Solution

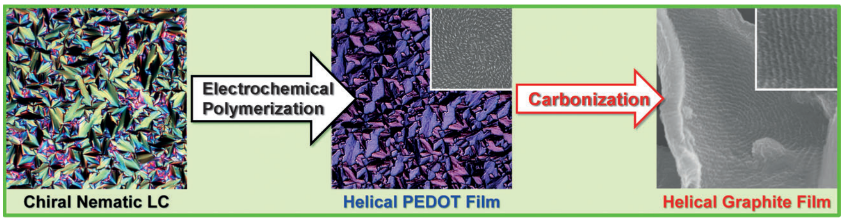


Hydrogen evolution in water: An efficient homogeneous single-component Ru_2Rh photocatalyst promoted H_2 evolution in fully aqueous solution in the presence of ascorbate as a sacrificial electron donor with turnover numbers (TONs) up to 430 (see picture). The catalytic performance of the linked system with a nonconjugated bridge was significantly improved as compared to that of a mixture of the separate components.

Carbon Materials

S. Matsushita, B. Yan, S. Yamamoto,
Y. S. Jeong, K. Akagi* ______ 1659 – 1663

Helical Carbon and Graphite Films Prepared from Helical Poly(3,4-ethylenedioxythiophene) Films Synthesized by Electrochemical Polymerization in Chiral Nematic Liquid Crystals

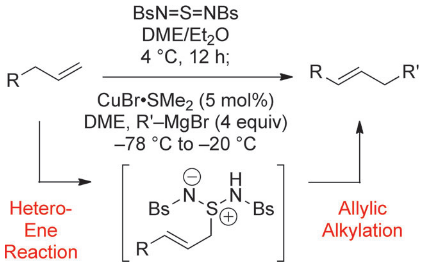


Helical carbon and graphite films are prepared from helical poly(3,4-ethylenedioxythiophene) films with a tunable helical sense and degree of helicity as precursors. The precursor polymer films are synthesized through asymmetric electrochemical polymerization in chiral nematic liquid-crystal (LC) fields. The spiral morphologies of the precursors are retained in the present graphite films.

C–C Coupling

H. Bao, L. Bayeh,
U. K. Tambar* ______ 1664 – 1668

Allylic Functionalization of Unactivated Olefins with Grignard Reagents

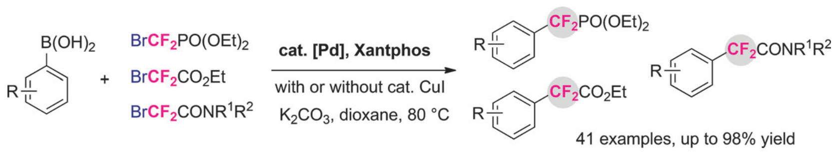


It all begins with olefins: Allylic functionalization with carbon nucleophiles is a powerful strategy for converting unactivated olefins into complex products. A general method for functionalizing olefins with aromatic, aliphatic, and vinyl Grignard reagents was developed. In a one-pot process, olefins are oxidized by a commercially available reagent to allylic electrophiles, which undergo selective copper-catalyzed allylic alkylation with Grignard reagents.

Difluoroalkylation

Z. Feng, Q.-Q. Min, Y.-L. Xiao, B. Zhang, X. Zhang* ——— 1669–1673

Palladium-Catalyzed Difluoroalkylation of Aryl Boronic Acids: A New Method for the Synthesis of Aryldifluoromethylated Phosphonates and Carboxylic Acid Derivatives

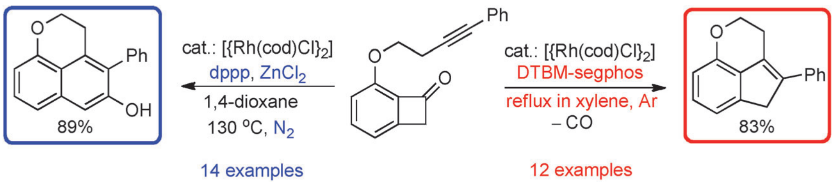


Palladium does it: The palladium-catalyzed difluoroalkylation of aryl boronic acids with bromodifluoromethylphosphonate, bromodifluoroacetate, and further derivatives has been developed (see scheme). Preliminary mechanistic studies reveal that a single electron transfer (SET) pathway may be involved in the catalytic cycle.

C–C Activation

P.-H. Chen, T. Xu, G. Dong* 1674–1678

Divergent Syntheses of Fused β-Naphthol and Indene Scaffolds by Rhodium-Catalyzed Direct and Decarbonylative Alkyne–Benzocyclobutenone Couplings

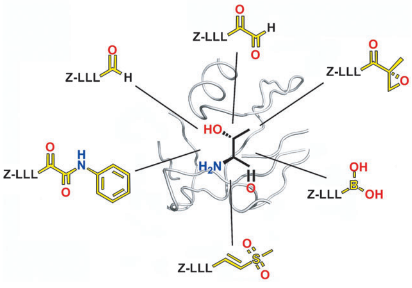


Cat. in control: A tunable rhodium-catalyzed intramolecular alkyne insertion reaction proceeding through C–C cleavage of benzocyclobutenones is described. Selective formation of either the direct or decarbonylative insertion product can be controlled by using different catalytic systems. A variety of fused β-naphthol and indene scaffolds were obtained in good yields with high functional-group tolerance.

Proteasome Inhibition

M. L. Stein, H. Cui, P. Beck, C. Dubiella, C. Voss, A. Krüger, B. Schmidt, M. Groll* ——— 1679–1683

Systematic Comparison of Peptidic Proteasome Inhibitors Highlights the α-Ketoamide Electrophile as an Auspicious Reversible Lead Motif



A chemical leitmotif: Proteasome inhibitors featuring different electrophilic warheads were systematically compared. The results led to the introduction of the α-ketoamide unit as a promising reversible lead structure. The properties of the corresponding compounds in vitro and in vivo are comparable with those of the commercially available anticancer drugs Velcade and Kyprolis.

Tetraboride

A. Knappschneider, C. Litterscheid, N. C. George, J. Brgoch, N. Wagner, J. Beck, J. A. Kurzman, R. Seshadri, B. Albert* ——— 1684–1688

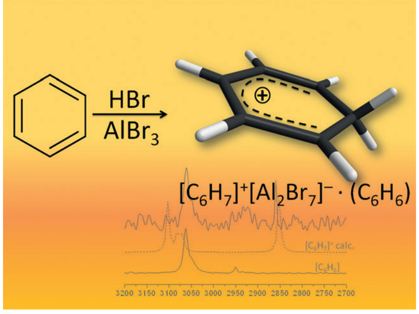
Peierls-Distorted Monoclinic MnB_4 with a Mn–Mn Bond

Now available as crystals: The structure of single crystals of MnB_4 (see picture) was solved using group-subgroup relationships and showed an unexpected short Mn–Mn bond caused by Peierls distortion. Calculations indicate Mn^I centers and paramagnetism, as confirmed by magnetic measurements. The tetraboride exhibits a pseudo-band gap and semiconducting behavior.

Superacids

F. Scholz, D. Himmel, L. Eisele, W. Unkrig, I. Krossing* —————— **1689 – 1692**

The Superacid HBr/AlBr$_3$: Protonation of Benzene and Ordered Crystal Structure of $[C_6H_7]^+[Al_2Br_7]^-$



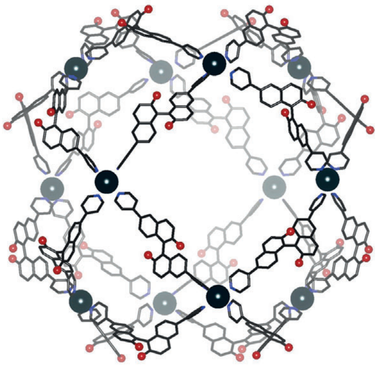
Benzene protonated: Crystalline and well-ordered protonated benzene as its $[C_6H_7]^+[Al_2Br_7]^- \cdot (C_6H_6)$ salt **1** is obtained by the combination of solid AlBr$_3$, benzene, and HBr gas. This unexpected simple and straight forward access shows that HBr/AlBr$_3$ is an underestimated superacid that should be used more frequently.

Metallosupramolecular Chemistry

C. Gütz, R. Hovorka, C. Klein, Q.-Q. Jiang, C. Bannwarth, M. Engeser, C. Schmuck, W. Assenmacher, W. Mader, F. Topić, K. Rissanen, S. Grimme, A. Lützen* —————— **1693 – 1698**

Enantiomerically Pure $[M_6L_{12}]$ or $[M_{12}L_{24}]$ Polyhedra from Flexible Bis(Pyridine) Ligands

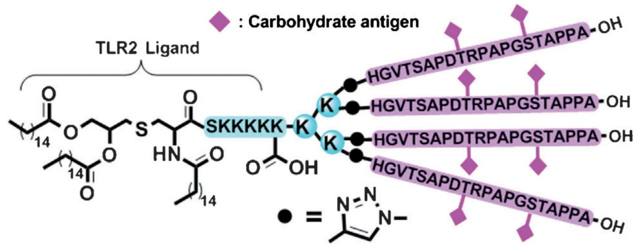
Make mine a sphere: BINOL-based bis(pyridine) ligands coordinate to Pd^{II} ions to form hexa- and dodecanuclear enantiomerically pure *endo*- and *exo*-functionalized metallosupramolecular spheres. Their chiral skeletons depend on the substitution pattern of the BINOL core. Despite the rotational freedom around the central aryl–aryl bond, the self-assembly is completely selective in a narcissistic self-recognition manner.


$[Pd_{12}\{(P)\text{-}\mathbf{2}\}_{24}]$

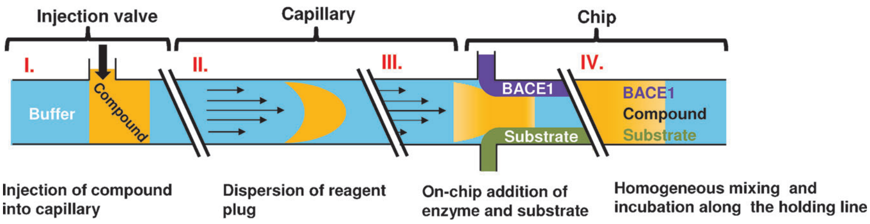
Multivalent Vaccines

H. Cai, Z.-Y. Sun, M.-S. Chen, Y.-F. Zhao, H. Kunz,* Y.-M. Li* ———— **1699 – 1703**

Synthetic Multivalent Glycopeptide-Lipopeptide Antitumor Vaccines: Impact of the Cluster Effect on the Killing of Tumor Cells



Multivalent vaccines containing a MUC1 glycopeptide bearing the STn antigen were chemically synthesized and immunologically evaluated. The induced immune responses in mice were dependent on the valence of the glycopeptide. The antisera exhibited strong binding to tumor cells which resulted in tumor cell death. This novel effect of clustered multivalent vaccines can be attributed to the altered pattern of the induced antibody isotypes.



Ready, steady, go! A flow-compatible dose–response screening assay was developed and seamlessly merged with chemical synthesis and analysis for investigation of structure–activity relationships (SAR) of β-secretase (BACE1) inhibitors. Yielding SAR data at a record-breaking cycle time this integrated platform may be a powerful method for the ever-accelerating drug discovery race.

Drug Discovery in Flow

M. Werner,* C. Kuratli, R. E. Martin,*
R. Hochstrasser, D. Wechsler, T. Enderle,
A. I. Alanine, H. Vogel ——— **1704 – 1708**

Seamless Integration of Dose-Response Screening and Flow Chemistry: Efficient Generation of Structure–Activity Relationship Data of β-Secretase (BACE1) Inhibitors

Inside Cover

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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