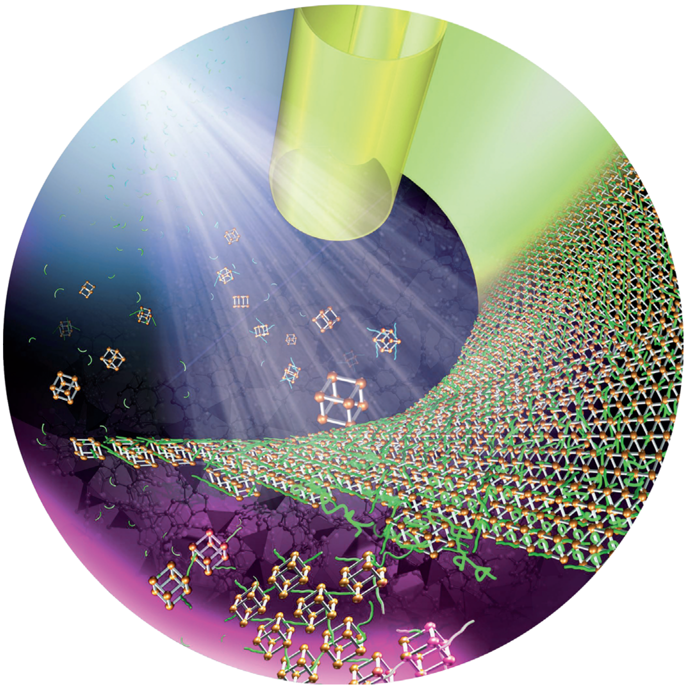
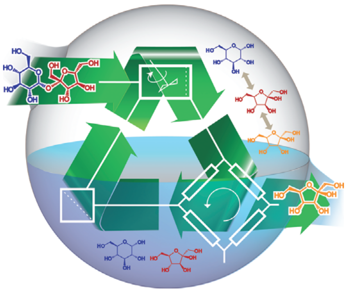
The processability of metal–organic frameworks …

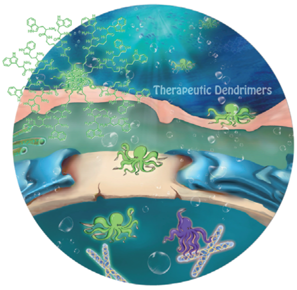


… presents a major challenge in their further application. In their Communication on page 4259 ff., X. Feng, Bo Wang, and co-workers introduce a photoinduced postsynthetic polymerization (PSP) strategy to covalently link crystals of metal–organic frameworks (MOFs) by polymer chains. The PSP approach is a facile and mild method to prepare flexible and stand-alone MOF-based membranes.

Biocatalysis

S. Panke et al. describe in their Communication on page 4182 ff. how integration of continuous chromatography into a multienzyme cascade reaction allows thermodynamic constraints to be overcome to form pure D-psicose from sucrose in high yield.



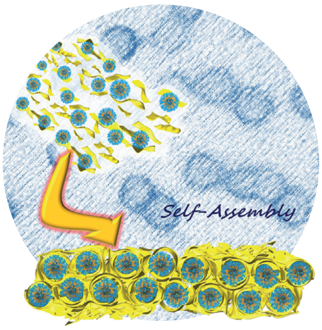


Peptide Drugs

In their Communication on page 4289 ff., X. Xu, Z. Gu, et al. describe the supramolecular interactions between bioinspired therapeutic dendrimers that are used for efficient tumor therapy and nucleic acids via the tryptophan residues.

Mesoporous Materials

In their Communication on page 4222 ff., Y. Yamauchi et al. show that electrostatic interactions between negatively charged nanosheets and positively charged polymeric micelles make possible the formation of composite micelles.



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Author Profile

"My favorite author (fiction) is V. S. Naipaul (A House for Mr. Biswas).
I would have liked to have discovered the zipper—brilliant, flexible, versatile, and essential. Simple, yet intricate …"
This and more about Varinder K. Aggarwal can be found on page 4150.

News


A. Zaban


R. Neumann


E. Lifshitz


S. Magdassi


D. Gelman


E. Narevicius


D. Stalke


P. A. Schwerdtfeger


S. L. Buchwald

Books

Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools

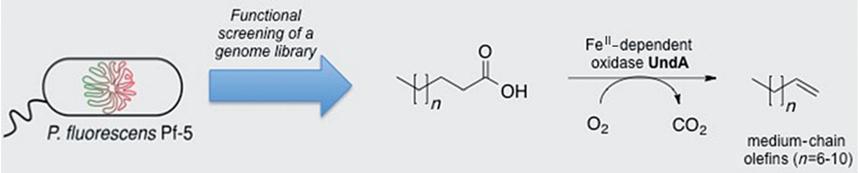
reviewed by P. H. M. Budzelaar ____ **4154**

Highlights

Enzymatic Synthesis

R. Kourist* ____ **4156 – 4158**

A New Class of Enzymes Discovered: A Non-Heme Oxidase Produces Medium-Chain 1-Alkenes



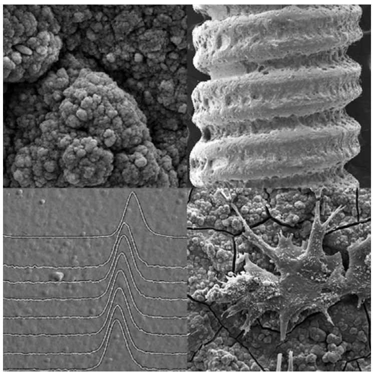
The recently discovered non-heme oxidase UndA catalyzes the conversion of lauric acid into 1-undecene. For the discovery, an impressive number of 6000 bacterial clones bearing a genome library of *Pseudomonas fluorescens* had to be screened by gas chromatography. The discovery of UndA is a breakthrough, as it paves the way towards the biotechnological production of medium-chain 1-alkenes from renewable materials.

Reviews

Bioactive Glasses

D. S. Brauer* ____ **4160 – 4181**

Bioactive Glasses—Structure and Properties



Boning up: Bioactive glasses are successfully used for bone regeneration, as they bond to bone, degrade over time, release ions, and stimulate bone healing. This Review discusses how the glass structure controls their properties, and shows how a structure-based design may pave the way towards new bioactive glass implants for bone regeneration.

For the USA and Canada:
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Communications

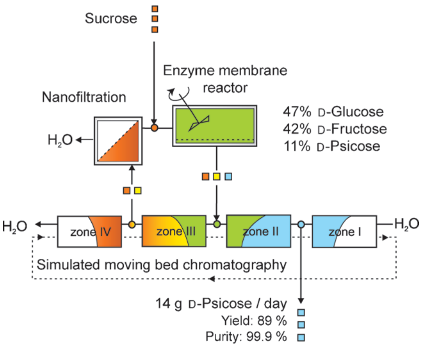
Biocatalysis

N. Wagner, A. Bosshart, J. Failmezger, M. Bechtold, S. Panke* ____ 4182 – 4186

A Separation-Integrated Cascade Reaction to Overcome Thermodynamic Limitations in Rare-Sugar Synthesis

Frontispiece

Bed of sugars: A multienzyme cascade reaction was integrated with continuous chromatography, realized as simulated moving-bed chromatography to overcome an intrinsic yield limitation. Efficient production in a three-step cascade reaction yielded pure D-psicose from sucrose with high yields and high enzyme efficiency.

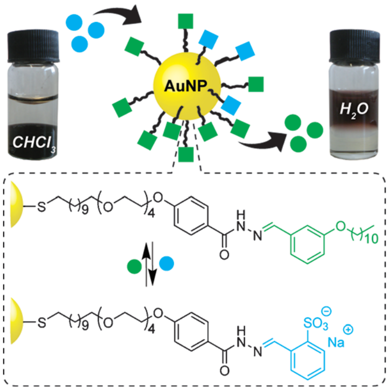


Supramolecular Chemistry

F. della Sala, E. R. Kay* ____ 4187 – 4191

Reversible Control of Nanoparticle Functionalization and Physicochemical Properties by Dynamic Covalent Exchange

Ligand swap shop: Dynamic covalent hydrazone exchange within a homogeneous monolayer bound to the surface of gold nanoparticles is tracked in real time. The introduction of appropriately functionalized aldehyde exchange units allows reversible tuning of nanoparticle solvophilicity and presents a generalizable covalent approach to postsynthetic modification of nanoparticle functionalization and properties.

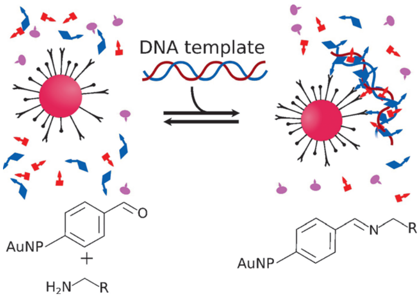


Dynamic Combinatorial Chemistry

P. Nowak, V. Saggiomo, F. Salehian, M. Colomb-Delsuc, Y. Han, S. Otto* ____ 4192 – 4197

Localized Template-Driven Functionalization of Nanoparticles by Dynamic Combinatorial Chemistry

On target: By combining imine-based dynamic combinatorial chemistry and DNA templates, amines capable of interacting with the target were grafted on aldehyde-functionalized nanoparticles only if and where the nanoparticles (NPs) interacted with the templates. The method opens up new opportunities for synthesizing multivalent, nanoparticle-based receptors for biomacromolecules.

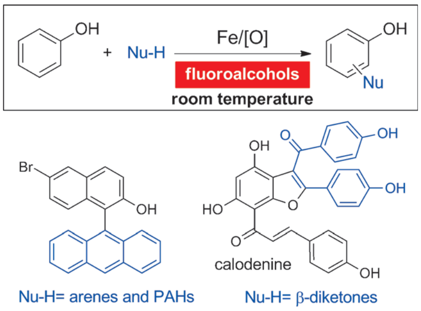


Oxidative Cross-Coupling

E. Gaster, Y. Vainer, A. Regev, S. Narute, K. Sudheendran, A. Werbeloff, H. Shalit, D. Pappo* ____ 4198 – 4202

Significant Enhancement in the Efficiency and Selectivity of Iron-Catalyzed Oxidative Cross-Coupling of Phenols by Fluoroalcohols

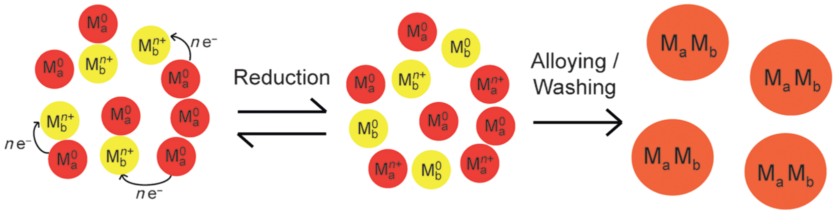
Not just a solvent: The use of fluorinated solvents leads to a significant rate acceleration and enhancement of the chemoselectivity of the iron-catalyzed oxidative coupling of phenols. This method was used for the synthesis of 2‴-dehydroxycalodenin B.



Nanostructures

A. Kirkeminde, S. Spurlin, L. Draxler-Sixta,
J. Cooper, S. Ren* ________ **4203 – 4207**

Metal Redox Processes for the Controlled Synthesis of Metal Alloy Nanoparticles

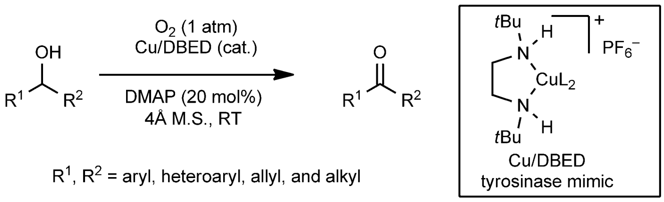


A metal redox method makes use of spontaneous oxidation–reduction processes to grow a variety of nanocrystalline alloys from zerovalent metal precursors and salts of a suitable second metal in an oxidized state. The compositional stoichiometry of the final nanoparticles can be controlled by adjusting the temperature of the alloying reactions.

Biomimetic Catalysis

B. Xu, J.-P. Lumb,*
B. A. Arndtsen* ________ **4208 – 4211**

A TEMPO-Free Copper-Catalyzed Aerobic Oxidation of Alcohols

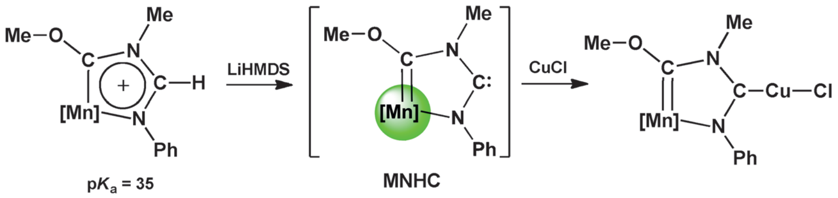


That's (non)radical: The employment of a tyrosinase-based biomimetic catalyst led to the efficient oxidation of various alcohols (including secondary aliphatic ones) at ambient temperature, without the use of a radical co-oxidant. The unique catalyst system provides complementary selectivity to previously described Cu-based systems. DMAP = dimethylaminopyridine.

N-Heterocyclic Carbenes

J. Ruiz,* L. García, M. Vivanco, Á. Berros,
J. F. Van der Maelen ________ **4212 – 4216**

Generating and Trapping Metalla-N-Heterocyclic Carbenes

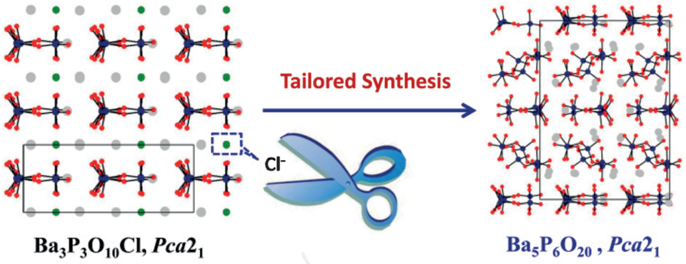


Caught in a trap: Metalla-imidazolium salts have been prepared and are used in the generation of highly nucleophilic singlet metalla-N-heterocyclic carbenes (MNHCs). MNHCs were trapped by addition of transition-metal fragments, such as CuCl. [Mn] = [Mn(bipy)(CO)$_2$]; LiHDMS = lithium hexamethyldisilazide.

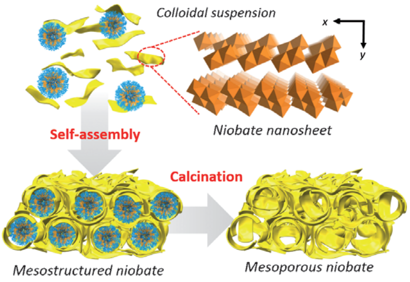
Structure–Property Relationships

S. Zhao, P. Gong, S. Luo, L. Bai, Z. Lin,*
Y. Tang, Y. Zhou, M. Hong,
J. Luo* ________ **4217 – 4221**

Tailored Synthesis of a Nonlinear Optical Phosphate with a Short Absorption Edge



Next generation: A deep-UV nonlinear optical material $Ba_5P_6O_{20}$ based on flexible $[P_3O_{10}]^{5-}$ building units has been synthesized. $Ba_5P_6O_{20}$ inherits the structural features of $Ba_3P_3O_{10}Cl$, one of the first deep-UV NLO phosphates, but exhibits a markedly shortened absorption edge of $\lambda = 167$ nm.



Mesoporous architectures were obtained through evaporation-induced assembly of polymeric micelles with crystalline nanosheets. The electrostatic interactions between negatively charged nanosheets and positively charged polymeric micelles make possible the formation of composite micelles. Removal of the micelles by calcination results in mesoporous oxides with the original crystalline structure.

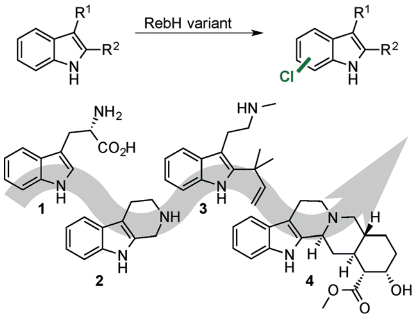
Mesoporous Materials

B. P. Bastakoti, Y. Li, M. Imura,
N. Miyamoto, T. Nakato, T. Sasaki,
Y. Yamauchi* ______ **4222 – 4225**

Polymeric Micelle Assembly with Inorganic Nanosheets for Construction of Mesoporous Architectures with Crystallized Walls

Back Cover

Halogenase variants capable of site-selective halogenation of large biologically active compounds (e.g., **2**–**4**) were obtained through directed evolution. The substrate scope of the halogenase RebH is limited primarily to compounds similar in size to tryptophan (**1**). RebH was engineered to accept a range of large indoles and carbazoles, including tryptoline (**2**), yohimbine (**4**), and carvedilol, with levels of conversion sufficient for preparative-scale reactions.



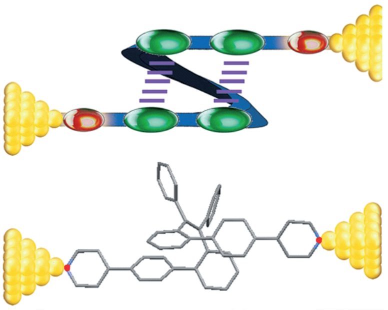
Biocatalysis

J. T. Payne, C. B. Poor,
J. C. Lewis* ______ **4226 – 4230**

Directed Evolution of RebH for Site-Selective Halogenation of Large Biologically Active Molecules

---

Single-molecule junctions with simultaneous through-bond and trough-space conducting channels are achieved based on the folded molecules that contain a pair of π–π stacked biphenyls. They were investigated by the scanning tunneling microscope based break-junction technique and theoretical calculations.



Charge Transport

L. Chen, Y.-H. Wang, B. He, H. Nie, R. Hu,
F. Huang, A. Qin, X.-S. Zhou,* Z. Zhao,*
B. Z. Tang* ______ **4231 – 4235**

Multichannel Conductance of Folded Single-Molecule Wires Aided by Through-Space Conjugation

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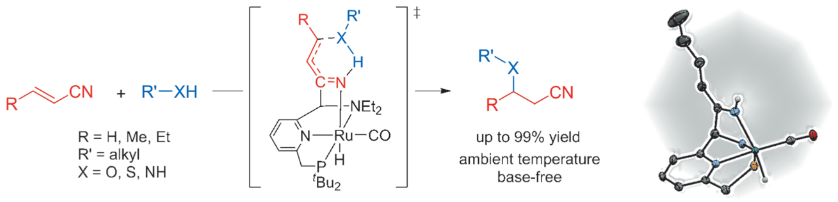


It all adds up: A novel pathway for oxa-Michael addition to challenging β-substituted unsaturated nitrile substrates is described based on a dearomatized ruthenium PNN pincer catalyst (see picture). Metal–ligand cooperative activation of the nitrile is key to the observed reactivity.

Oxa-Michael Additions

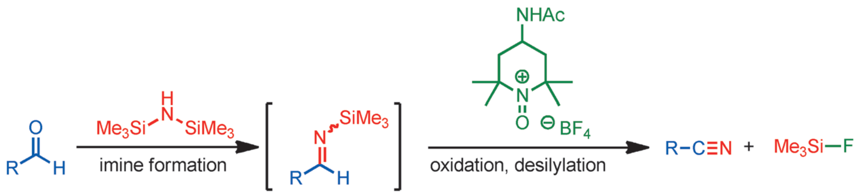
S. Perdriau, D. S. Zijlstra, H. J. Heeres,
J. G. de Vries,* E. Otten* ______ **4236 – 4240**

A Metal–Ligand Cooperative Pathway for Intermolecular Oxa-Michael Additions to Unsaturated Nitriles

Synthetic Methods

C. B. Kelly, K. M. Lambert,
M. A. Mercadante, J. M. Ovian,
W. F. Bailey,*
N. E. Leadbeater* ———— **4241 – 4245**

Access to Nitriles from Aldehydes Mediated by an Oxoammonium Salt



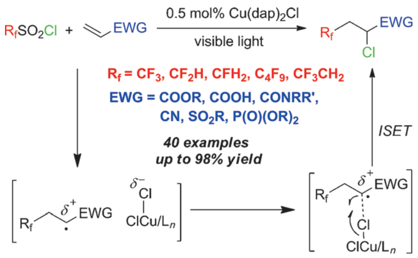
A serendipitous find: The scalable and high yielding title reaction is mediated by 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate and hexamethyldisilazane (HMDS). The reaction likely involves reversible silylimine formation between HMDS and an aldehyde, and subsequent oxidation and desilylation. The spent oxidant can be easily recycled.

Photoredox Catalysis

X.-J. Tang,
W. R. Dolbier, Jr.* ———— **4246 – 4249**

Efficient Cu-catalyzed Atom Transfer Radical Addition Reactions of Fluoroalkylsulfonyl Chlorides with Electron-deficient Alkenes Induced by Visible Light

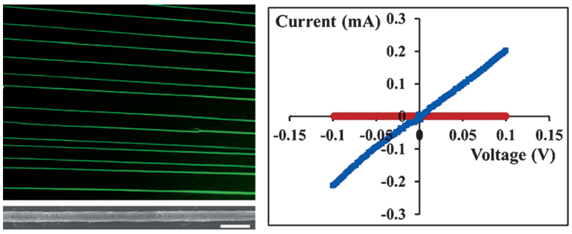
Fluorinated radicals are generated under Cu catalysis from R_fSO_2Cl. They are used for atom transfer radical addition reactions with electron-deficient alkenes such as α,β-unsaturated ketones, amides, esters, carboxylic acids, sulfone, and phosphonate. ISET = inner single electron transfer.



Nanowires

B. Li, C. Zhang, B. Jiang, W. Han,
Z. Lin* ———— **4250 – 4254**

Flow-Enabled Self-Assembly of Large-Scale Aligned Nanowires

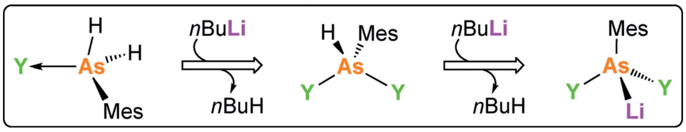


Metallic nanowires are obtained by using highly oriented DNA nanowires as templates. A swelling-induced transfer printing technique is employed to transfer the ultralong DNA nanowires onto a desirable substrate; metallic nanowires are then generated by exposing the DNA nanowires preloaded with metal salts to an oxygen plasma.

Yttrium–Arsenic Complexes

T. Pugh, A. Kerridge,
R. A. Layfield* ———— **4255 – 4258**

Yttrium Complexes of Arsine, Arsenide, and Arsinidene Ligands



As to why: Deprotonation of the yttrium–arsine complex [$Cp'_3YAs(H)_2Mes$] (Cp′ = η^5-C_5H_4Me, Mes = mesityl) yields the μ-arsenide complex [$\{Cp'_2Y[\mu\text{-}As(H)Mes]\}_3$]. Deprotonation of the arsenide complex by *n*BuLi produces [$Li(thf)_4]_2[\{Cp'_2Y(\mu\text{-}AsMes)\}_3Li$], which contains the first example of an arsinidene ligand in rare-earth metal chemistry. The structures and bonding characteristic of each complex are described.

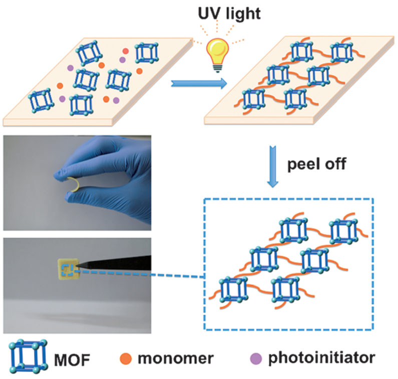
Metal–Organic Frameworks

Y. Zhang, X. Feng,* H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang, B. Wang* **4259 – 4263**

Photoinduced Postsynthetic Polymerization of a Metal–Organic Framework toward a Flexible Stand-Alone Membrane

Front Cover

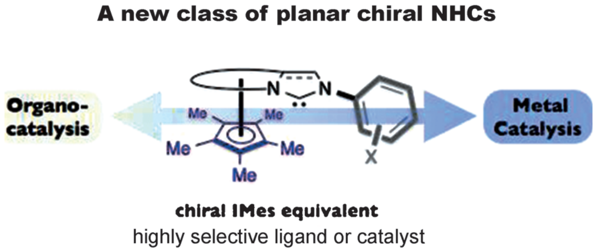
Link-up: A UV-light-induced postsynthetic polymerization (PSP) was employed to covalently link crystals of metal–organic frameworks (MOFs) by flexible polymer chains. The obtained MOF-based membranes are homogeneously structured and show very good separation capacities for the removal of Cr^{VI} ions from water.



Asymmetric Catalysis

C. T. Check, K. P. Jang, C. B. Schwamb, A. S. Wong, M. H. Wang, K. A. Scheidt* ———— **4264 – 4268**

Ferrocene-Based Planar Chiral Imidazopyridinium Salts for Catalysis



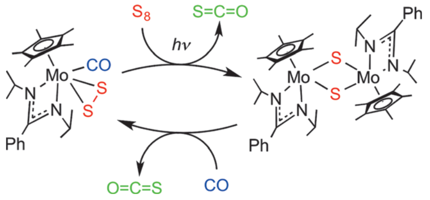
Planar chiral azolium salts that incorporate a sterically demanding iron sandwich complex are synthesized. These new N-heterocyclic carbenes can be employed both as organocatalysts and as ligands for transition-metal catalysis, which demonstrates their unprecedented versatility and potential broad utility in asymmetric catalysis.

Sulfur Atom Transfer

W. S. Farrell, P. Y. Zavalij, L. R. Sita* ———— **4269 – 4273**

Metal-Catalyzed "On-Demand" Production of Carbonyl Sulfide from Carbon Monoxide and Elemental Sulfur

BeCOS: Carbonyl sulfide (COS) is conveniently generated in situ in high yield and chemical purity directly from CO and S_8 in solution and under near-ambient conditions upon photolysis of the precatalyst [Cp*Mo{N(*i*Pr)C(Ph)N(*i*Pr)}(CO)$_2$]. The tolerance of this catalytic process to protic substrates supports the facile synthesis of more complex organic products through the "on-demand" production of COS.

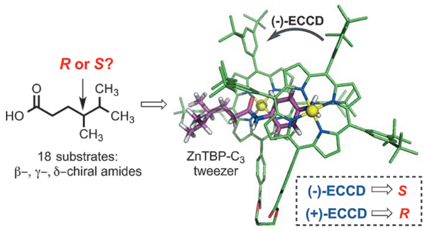


Host–Guest Systems

M. Tanasova, M. Anyika, B. Borhan* ———— **4274 – 4278**

Sensing Remote Chirality: Stereochemical Determination of β-, γ-, and δ-Chiral Carboxylic Acids

Binding of bis(porphyrin) tweezers to β-, γ-, or δ-chiral carboxylic amides yields chiral helical complexes which generate a bisignate Cotton Effect (ECCD) to enable the unambiguous determination of the chirality for remote stereocenters. The sign of the observed ECCD curve can be related to the absolute stereochemistry of the bound chiral substrate in a predictable manner.

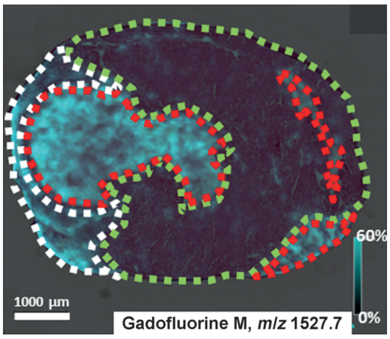


Imaging Agents

M. Aichler, K. Huber, F. Schilling,
F. Lohöfer, K. Kosanke, R. Meier,
E. J. Rummeny, A. Walch,*
M. Wildgruber ______ **4279 – 4283**

Spatially Resolved Quantification of Gadolinium(III)-Based Magnetic Resonance Agents in Tissue by MALDI Imaging Mass Spectrometry after In Vivo MRI

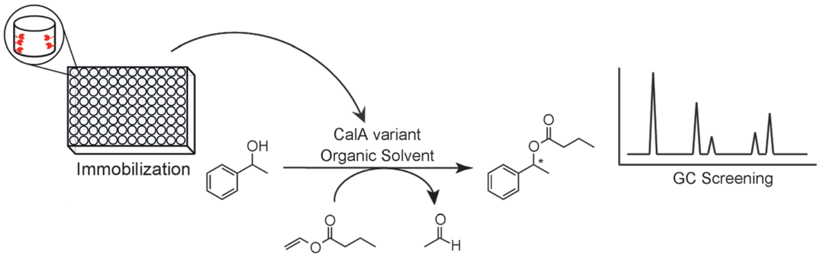
Contrast agents: As a consequence of nonlinear correlation between the contrast agent concentration in tissue and the MRI signal obtained in vivo, quantification of certain biological or pathophysiological processes by MRI remains a challenge. MALDI imaging is a valuable tool for corroborating the in vivo imaging MRI signals. This method enabled in situ quantification of the contrast agent directly in tissue with high spatial resolution.



Biocatalysis

Y. Wikmark, M. Svedendahl Humble,*
J.-E. Bäckvall* ______ **4284 – 4288**

Combinatorial Library Based Engineering of *Candida antarctica* Lipase A for Enantioselective Transacylation of *sec*-Alcohols in Organic Solvent



Try the library: A method is reported for screening lipase libraries for the enantioselective transacylation of *sec*-alcohols in organic solvents. This could be useful for creating enantioselective lipase variants for synthetic applications such as the dynamic kinetic resolution of alcohols and amines. The method could also be applied to other His_6-tagged enzymes and other reactions.

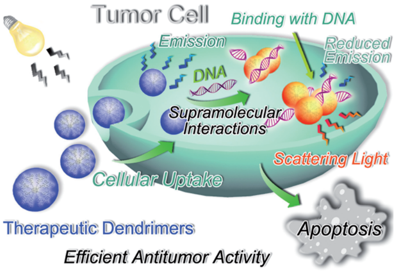
Peptide Drugs

X. Zhang, Z. Zhang, X. Xu,* Y. Li, Y. Li,
Y. Jian, Z. Gu* ______ **4289 – 4294**

Bioinspired Therapeutic Dendrimers as Efficient Peptide Drugs Based on Supramolecular Interactions for Tumor Inhibition

Inside Back Cover

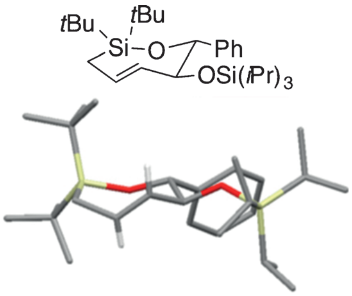
Tryptophan-rich peptide dendrimers (TRPDs) with a precise molecular structure were developed as a new type of dendritic peptide drug for efficient tumor therapy. The significant supramolecular interactions between the therapeutic dendrimers and DNA were extensively studied, and experimental results indicate that TRPDs are efficient antitumor agents both in vitro and in vivo.



Medium-Ring Compounds

B. Hurlocker, C. Hu,
K. A. Woerpel* ______ **4295 – 4298**

Structure and Reactivity of an Isolable Seven-Membered-Ring *trans*-Alkene

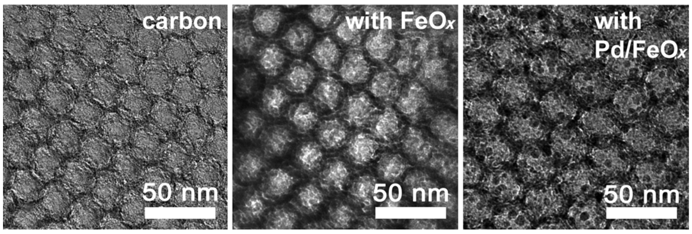


Feeling the strain: A seven-membered-ring *trans*-alkene was isolated in 72% yield from a one-flask, two-step reaction. X-ray crystallographic analysis shows that the double bond is twisted out of coplanarity by 54°, and the C atoms are pyramidalized by 31° from the ideal trigonal-planar geometry. Hyperconjugative interactions with the C–Si bond and the proximity of the O atom to the double bond are consistent with the observed reactivity.

Li–O_2 Batteries

J. Xie, X. Yao, Q. Cheng, I. P. Madden,
P. Dornath, C.-C. Chang, W. Fan,*
D. Wang* **4299 – 4303**

Three Dimensionally Ordered Mesoporous Carbon as a Stable, High-Performance Li–O_2 Battery Cathode



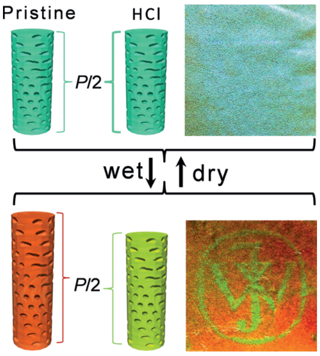
Concealed: To address the issue of carbon-support instability in Li–O_2 batteries, a layer of FeO_x grown on the carbon surface by atomic layer deposition (ALD) is used to physically separate a three dimensionally ordered mesoporous carbon support from the electrolyte. When the FeO_x surface is decorated with ALD-grown Pd nanoparticles, the cyclability of the cathode is significantly enhanced.

Photonic Patterns

M. K. Khan, A. Bsoul, K. Walus,
W. Y. Hamad,
M. J. MacLachlan* **4304 – 4308**

Photonic Patterns Printed in Chiral Nematic Mesoporous Resins

Printing photonic patterns made easy: Using chemical "inks", latent photonic patterns were written onto chiral nematic mesoporous-resin films. The patterns are invisible in the dry films, but emerge upon swelling. Inkjet printing of the resin films afforded high-resolution photonic patterns that can be revealed upon swelling and erased by drying, making them suitable for anti-counterfeiting applications.

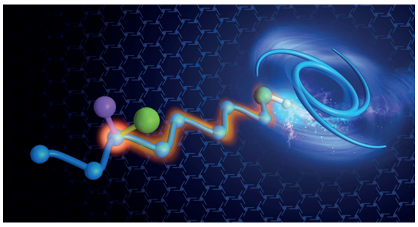


Surface Chirality

T. Chen, S.-Y. Li, D. Wang,* M. Yao,
L.-J. Wan* **4309 – 4314**

Remote Chiral Communication in Coadsorber-Induced Enantioselective 2D Supramolecular Assembly at a Liquid/Solid Interface

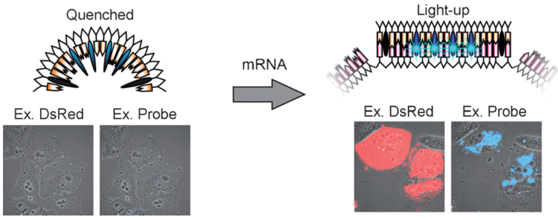
Getting the message across: The transmission of stereochemical information through a long flexible spacer of up to five methylene groups and noncovalent hydrogen bonds was observed in 2D supramolecular assembly at a liquid/solid interface. The confinement effect during 2D crystallization and specific noncovalent interactions between the chiral coadsorber and the achiral building blocks play an important role in efficient chiral communication.



RNA Detection

H. Asanuma,* M. Akahane, R. Niwa,
H. Kashida, Y. Kamiya **4315 – 4319**

Highly Sensitive and Robust Linear Probe for Detection of mRNA in Cells

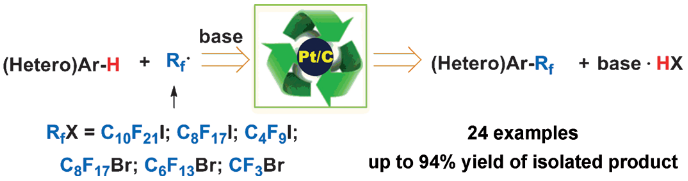


A linear probe robustly detects mRNA in cells with high sensitivity. The probe was modified with base surrogates prepared from D-threoninol, with anthraquinone moieties near the 5′- and 3′-termini, and with perylene moieties. In cells, a probe designed to target DsRed resulted in distinct blue fluorescence only in cells transfected with plasmid encoding DsRed.

Perfluoroalkylation

L. He, K. Natte, J. Rabeah, C. Taeschler,
H. Neumann, A. Brückner,
M. Beller* ———— 4320 – 4324

Heterogeneous Platinum-Catalyzed C–H Perfluoroalkylation of Arenes and Heteroarenes



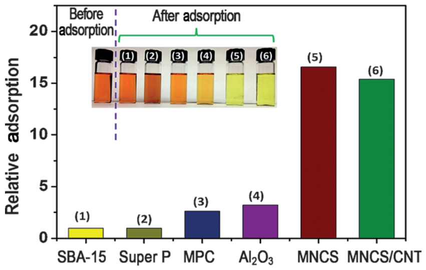
Platinum level: The efficient and versatile title reaction is based on the radical reactivity of perfluoroalkyl halides. The ready availability of the starting materials, the excellent substrate tolerance, and the reusability of catalyst make this protocol attractive for the economic synthesis of perfluoroalkyl-group-substituted aromatic compounds.

Electrochemistry

J. X. Song, M. L. Gordin, T. Xu, S. R. Chen,
Z. X. Yu, H. Sohn, J. Lu, Y. Ren, Y. H. Duan,
D. H. Wang* ———— 4325 – 4329

Strong Lithium Polysulfide Chemisorption on Electroactive Sites of Nitrogen-Doped Carbon Composites For High-Performance Lithium–Sulfur Battery Cathodes

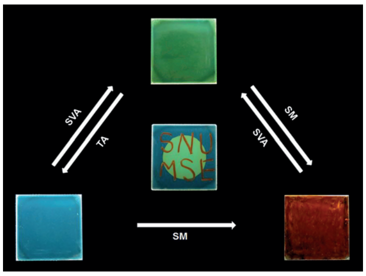
A composite that consists of carbon-nanotube-interpenetrated mesoporous nitrogen-doped carbon spheres (MNCS/CNT) can strongly chemisorb polysulfides and was used as a cathode material for lithium–sulfur batteries. Moreover, the highly conductive nitrogen-doped carbon material enables direct and easy redox reactions of the adsorbed polysulfides, which leads to good electrode kinetics.



Supramolecular Chemistry

H.-J. Kim, D. R. Whang, J. Gierschner,
C. H. Lee, S. Y. Park* ———— 4330 – 4333

High-Contrast Red–Green–Blue Tricolor Fluorescence Switching in Bicomponent Molecular Film

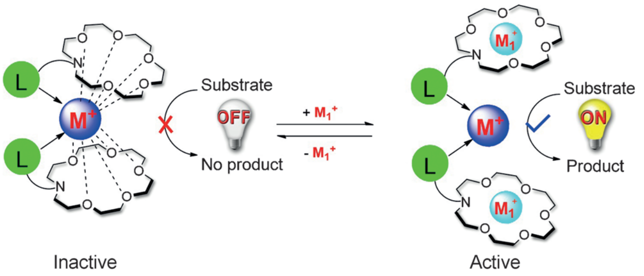


Reversible red–green–blue luminescence switching with a high ratiometric color contrast ($\lambda_{em}=594$, 527, 458 nm for red, green, and blue, respectively) was realized by different external stimuli such as heat, solvent-vapor exposure, and mechanical force. It was shown that Förster resonance energy transfer in a bicomponent mixture could be efficiently switched on and off through supramolecular control.

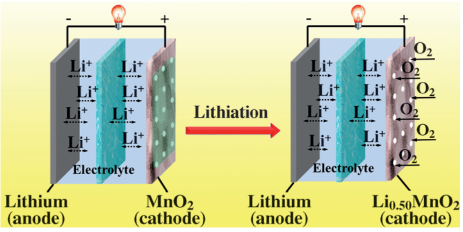
Asymmetric Catalysis

G.-H. Ouyang, Y.-M. He, Y. Li, J.-F. Xiang,
Q.-H. Fan* ———— 4334 – 4337

Cation-Triggered Switchable Asymmetric Catalysis with Chiral Aza-CrownPhos



Quick on the trigger: A new kind of phosphoramidite ligand, modified by an aza-crown ether, has been designed and synthesized. The activity of its rhodium catalyst can be reversibly switched "ON" and "OFF" in the asymmetric hydrogenation of dehydroamino acid esters by modulations derived from host–guest interactions.



Never say die: Depleted Li–MnO$_2$ batteries could be further utilized as rechargeable Li–O$_2$ batteries with admitted oxygen. Thus, when the manganese oxide electrode was lithiated in situ and exposed to air (see picture), the resulting battery showed superior performance, including high capacity, a low overpotential, high rate capability, and high cycling stability.

Electrocatalysis

Y. Hu, T. Zhang, F. Cheng,* Q. Zhao, X. Han, J. Chen* ________ **4338 – 4343**

Recycling Application of Li–MnO$_2$ Batteries as Rechargeable Lithium–Air Batteries

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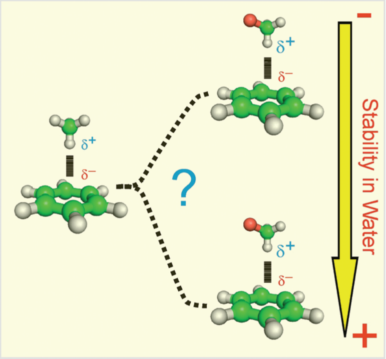
Electrostatic and charge-transfer contributions to CH–π complexes can be modulated by attaching electron-withdrawing substituents to the carbon atom. Although they have a clearly stabilizing effect in the gas phase, the influence of this chemical modification for the behavior in water is more difficult to predict. Dynamic combinatorial chemistry is used to provide a definitive and quantitative answer to this question.



Polarizing CH–π bonds

E. Jiménez-Moreno, A. M. Gómez, A. Bastida, F. Corzana, G. Jiménez-Oses, J. Jiménez-Barbero, J. L. Asensio* ________ **4344 – 4348**

Modulating Weak Interactions for Molecular Recognition: A Dynamic Combinatorial Analysis for Assessing the Contribution of Electrostatics to the Stability of CH–π Bonds in Water

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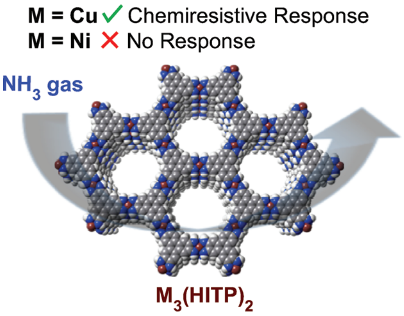

A MOF with a nose: Previous efforts to use metal–organic frameworks (MOFs) for chemical sensing have been hindered by poor signal transduction due to a lack of electrical conductivity. A new conductive 2D MOF can be used for the chemiresistive sensing of ammonia. It is shown that the sensing response can be varied by the choice of the metal node.

Metal–Organic Frameworks

M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager, M. Dincă* ____ **4349 – 4352**

Cu$_3$(hexaiminotriphenylene)$_2$: An Electrically Conductive 2D Metal–Organic Framework for Chemiresistive Sensing

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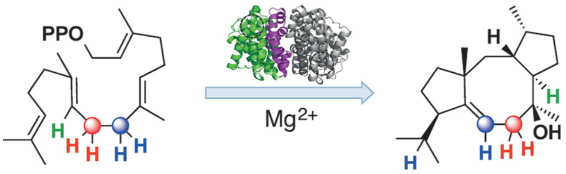


Biosynthetic virtuosity: Cyclooctat-9-en-7-ol synthase (CotB2) catalyzes the synthesis of an unusual 5-8-5 fused-ring structure with six chiral centers from the achiral C$_{20}$ substrate geranylgeranyl diphosphate. By combining in vivo studies with in vitro reactions, an unusual cyclization mechanism was elucidated, which involves a carbon–carbon backbone rearrangement and three long-range hydride shifts. OPP = pyrophosphate.

Biosynthesis

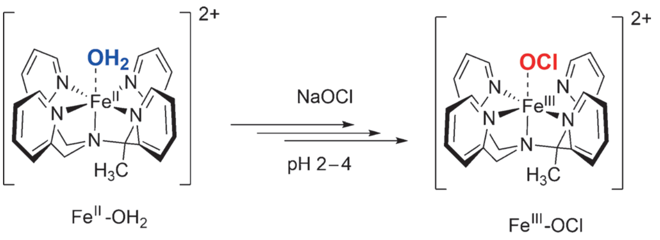
A. Meguro, Y. Motoyoshi, K. Teramoto, S. Ueda, Y. Totsuka, Y. Ando, T. Tomita, S.-Y. Kim, T. Kimura, M. Igarashi, R. Sawa, T. Shinada, M. Nishiyama, T. Kuzuyama* ________ **4353 – 4356**

An Unusual Terpene Cyclization Mechanism Involving a Carbon–Carbon Bond Rearrangement

Bioinorganic Chemistry

A. Draksharapu, D. Angelone,
M. G. Quesne, S. K. Padamati, L. Gómez,
R. Hage, M. Costas, W. R. Browne,*
S. P. de Visser* **4357 – 4361**

Identification and Spectroscopic Characterization of Nonheme Iron(III) Hypochlorite Intermediates

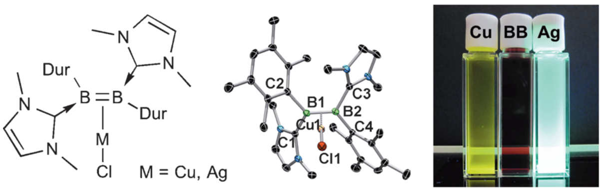


Understanding metalloenzymes: A synthetic Fe^{III}-OCl complex has been generated and spectroscopically characterized at room temperature. Such nonheme iron(III) hypohalite intermediates have been implicated in biological halogenation reactions and may offer clues to understanding the activity of iron halogenases.

π-Diborene Complexes

P. Bissinger, A. Steffen,* A. Vargas,
R. D. Dewhurst, A. Damme,
H. Braunschweig* **4362 – 4366**

Unexpected Luminescence Behavior of Coinage Metal π-Diborene Complexes



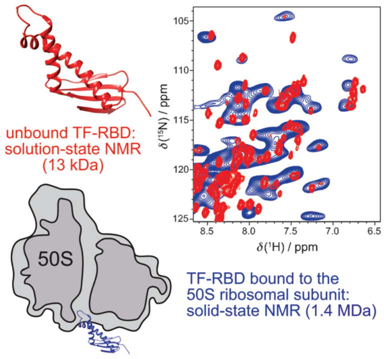
Boron illuminates: Unprecedented photophysical properties were observed for luminescent π-diborene complexes of Cu and Ag, including unusually high fluorescence quantum yields in solution. This indicates that little to no intersystem crossing between S_1 and T_n occurs despite the strong spin–orbit coupling of the metal atoms. The replacement of carbon with boron thus yields luminescent isolobal analogues of otherwise non-emissive olefin complexes of Cu and Ag.

Protein NMR Spectroscopy

E. Barbet-Massin, C.-T. Huang, V. Daebel,
S.-T. D. Hsu, B. Reif* **4367 – 4369**

Site-Specific Solid-State NMR Studies of "Trigger Factor" in Complex with the Large Ribosomal Subunit 50S

NMR beyond 1 MDa: Magic-angle spinning (MAS) solid-state NMR experiments of the ribosome binding domain of the trigger factor (TF-RBD) in complex with the 50S ribosome yield defined chemical shift changes for α2 in TF-RBD. The combined use of proton detection and high MAS frequencies (60 kHz) enables the investigation of approximately 20 μg quantities of labeled protein.

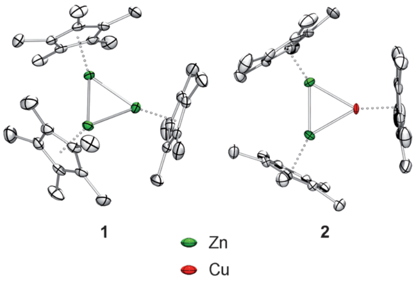


σ-Aromaticity

K. Freitag, C. Gemel, P. Jerabek,
I. M. Oppel, R. W. Seidel, G. Frenking,*
H. Banh, K. Dilchert,
R. A. Fischer* **4370 – 4374**

The σ-Aromatic Clusters $[Zn_3]^+$ and $[Zn_2Cu]$: Embryonic Brass

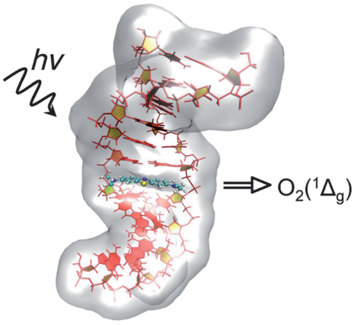
Bold as brass: The bonding situations of the Cp* ligand-protected clusters $[Zn_3]^+$ (**1**) and $[Zn_2Cu]$ (**2**) were investigated by quantum chemical calculations revealing a high degree of σ-aromaticity similar to the trihydrogen ion $[H_3]^+$. The new species serve as molecular building units of Cu_nZn_m nanobrass clusters as indicated by liquid-injection field desorption ionization (LIFDI) mass spectrometry.



Methylene Blue Photophysics

J. J. Nogueira,* M. Oppel,
L. González* ________ 4375 – 4378

Enhancing Intersystem Crossing in Phenotiazinium Dyes by Intercalation into DNA

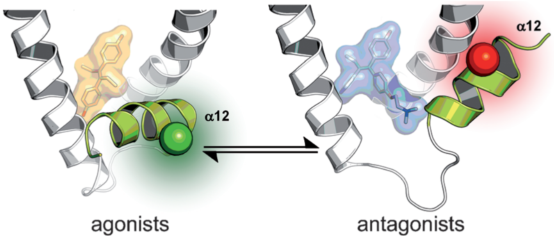


Intercalation of methylene blue into DNA protects the dye from hydrogen bonding with external water molecules. This activates an intersystem crossing pathway mediated by electronic spin–orbit coupling, which is inactive in aqueous solution. Thus, the photodynamic therapy efficacy of methylene blue is enhanced upon binding to DNA.

Receptor Ligands

S. C. Mayer-Wrangowski,
D. Rauh* ________ 4379 – 4382

Monitoring Ligand-Induced Conformational Changes for the Identification of Estrogen Receptor Agonists and Antagonists



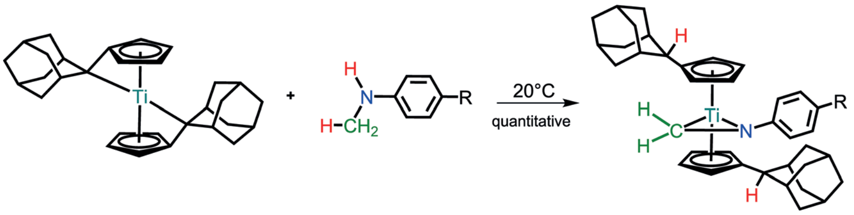
Agonistic and antagonistic small-molecule regulators induce distinct conformational changes within the ligand-binding domain of the estrogen receptor, thereby altering the receptor's activity. A direct binding assay for the detection of estrogen receptor ligands was developed that distinguishes between different binding modes and is suitable for high-throughput screening.

C–H Activation

M. Manßen, N. Lauterbach, J. Dörfler,
M. Schmidtmann, W. Saak, S. Doye,*
R. Beckhaus* ________ 4383 – 4387

Efficient Access to Titanaaziridines by C–H Activation of *N*-Methylanilines at Ambient Temperature

Inside Cover

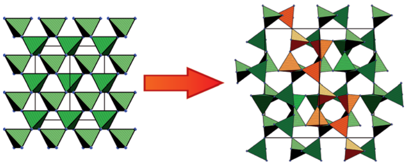


Killing two birds with one stone: A bis(η^5,η^1-pentafulvene)titanium complex reacts with secondary *N*-methylamines resulting in simultaneous N–H and C–H activation and formation of titanaaziridines. These reactions can even be performed below room temperature und generate three-membered titanacycles. The first molecular structure of a titanium methyleneaniline complex is determined.

Phosphorus Nitrides

D. Baumann, R. Niklaus,
W. Schnick* ________ 4388 – 4391

A High-Pressure Polymorph of Phosphorus Oxonitride with the Coesite Structure



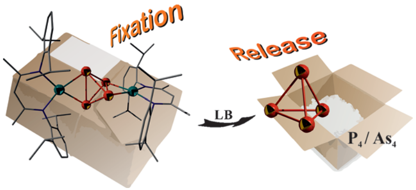
Under pressure: The coesite structure type was observed in a high-pressure polymorph of phosphorus oxonitride (PON). This is the first example of this structure occurring outside of SiO_2. This result represents a major step towards the synthesis of a stishovite-type polymorph of PON.

Intact P_4 and As_4 Complexes

F. Spitzer, M. Sierka, M. Latronico,
P. Mastrorilli, A. V. Virovets,
M. Scheer* ———— 4392 – 4396

Fixation and Release of Intact E_4 Tetrahedra (E = P, As)

Too fragile? Just wrap it! Sensitive P_4 and As_4 can be stabilized in $[(\mathrm{NacnacCu})_2(\mu,\eta^{2:2}\text{-}E_4)]$ (E = P, As), which serves as storage material. The E_4 tetrahedra are intact, which was confirmed by calculations and experimentally by liberation with a Lewis base (LB). $[\mathrm{NacnacCu}(\eta^2\text{-}P_4)]$ was also isolated, which contains an intact, side-on coordinated P_4 entity. Its dynamic behavior was examined by different NMR techniques.

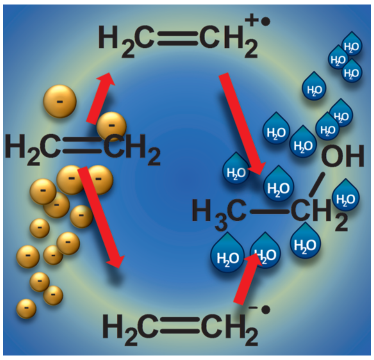


Electron-Induced Ethanol Synthesis

J. Warneke, Z. Wang, P. Swiderek,
J. H. Bredehöft* ———— 4397 – 4400

Electron-Induced Hydration of an Alkene: Alternative Reaction Pathways

Going soft: Post-irradiation thermal desorption spectrometry (TDS) has shown that electron-induced reactions in condensed mixtures of ethylene and water lead to the synthesis of ethanol. This synthesis is not only induced by soft electron impact ionization but also by electron attachment to ethylene and a subsequent acid/base reaction with water.



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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