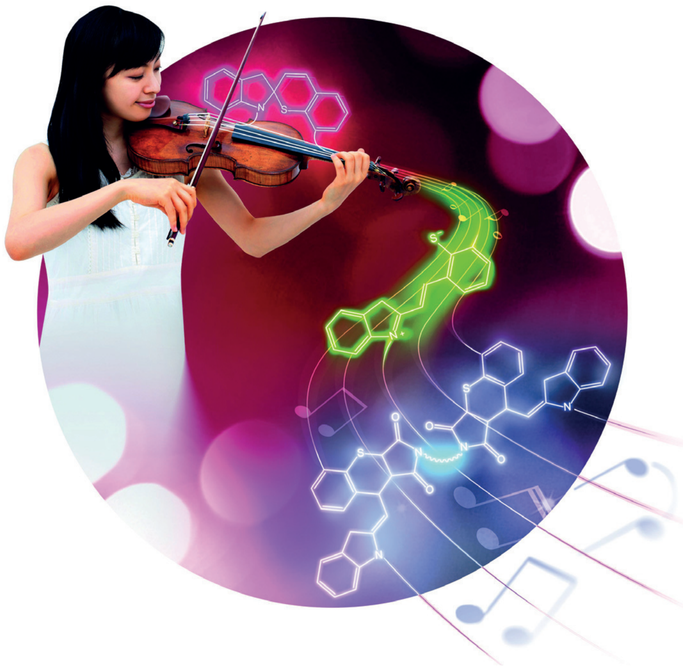
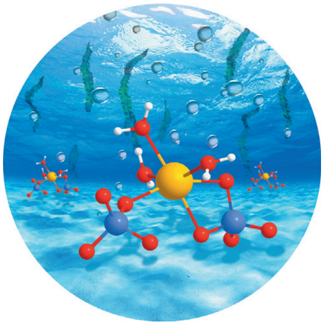
Just as mechanical force ...

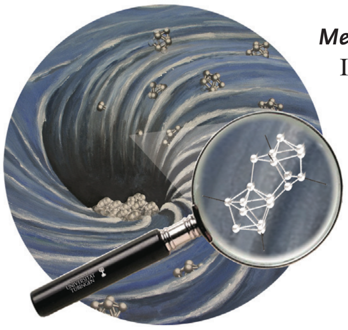


… applied to the strings of a violin produces beautiful sounds, mechanical stress acting on polymers leads to interesting chemical reactions. In their Communication on page 3040 ff., W. Weng et al. show that when mechanically loaded, a spirothiopyran-containing polymer turns bright green and undergoes cross-linking. Two distinct chemical responses to a mechanical load are combined in a single reactive site.



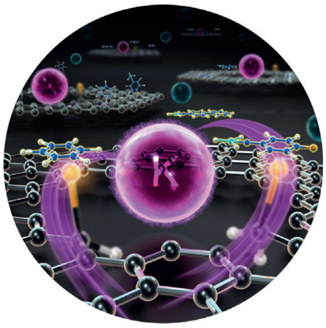
Oxygen Evolution

K.-C. Lau, T.-C. Lau, and co-workers show in their Communication on page 3012 ff. that the FeO_4^{2-} ion can be activated by Ca^{2+} to give oxygen evolution at pH 9–10.



Metalloid Clusters

In their Communication on page 3216 ff., A. Schnepf et al. show that the oxidation of $[Ge_9(Hyp)_3]^-$ ($Hyp = Si(SiMe_3)_3$) with an Fe^{II} salt leads to $Ge_{18}(Hyp)_6$, the largest metalloid Group 14 cluster that has been structurally characterized to date.



Graphene Oxide

A heterogeneous, inexpensive, and environmentally friendly graphene oxide catalyst is used for the synthesis of biaryl compounds by benzene C–H arylation by J. Wang, D. Ma, and co-workers in their Communication on page 3124 ff.

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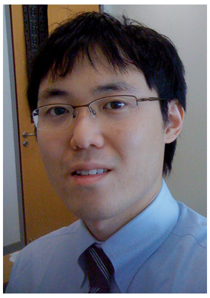


"My favorite author (fiction) is Jeffery Deaver.
My favorite saying is 'God is in the detail' …"
This and more about Naohiko Yoshikai can be found on page 2972.

News

P. Hegemann

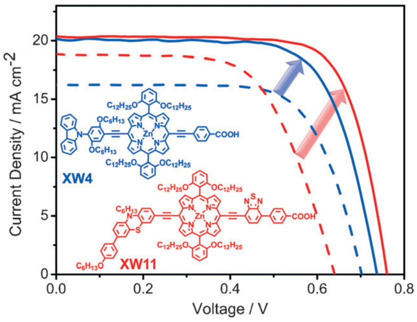
R. L. Melen

B. L. Feringa

K. Kohse-Höinghaus

Highlights

Solar Cells



Here comes the sun: By using a combined strategy of molecular engineering and cosensitization, impressively high J_{sc} and V_{oc} values were achieved for porphyrin dyes, resulting in high photovoltaic efficiencies up to 11.5 %, a record for non-ruthenium dye-sensitized solar cells (DSSCs) with the I^-/I_3^- electrolyte. The results provide insight into furthering the development of efficient DSSCs through synergistically enhanced photovoltage and photocurrent.

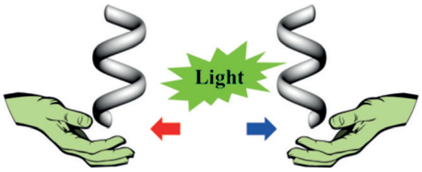
Minireviews

ESI Mass Spectrometry

Periscope depth: Electrospray mass spectrometry (ESI-MS) is a powerful tool for studying reaction mechanisms. The reverse-periscope concept is proposed to exemplify the potential of ESI-MS to analyze the gas/liquid interface and identify reaction intermediates present in solution. Mechanisms of complex reactions, such as multicomponent reactions, organocatalyzed reactions, and homogeneous metal catalysis, can be studied in detail.

Reviews

Liquid Crystals



Photoisomerizable chiral molecular switches or motors as guests induce chirality into achiral nematic liquid crystals and enable light-driven chirality inversion of the resulting cholesteric liquid crystals (CLCs). This Review describes the recent developments in the rational design of chiral guests with the capability for light-directed chirality inversion of CLCs.

For the USA and Canada:
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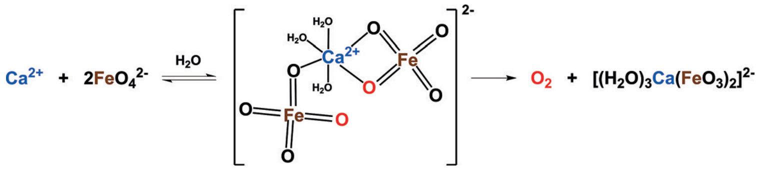
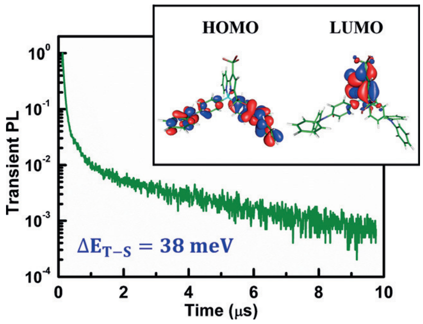
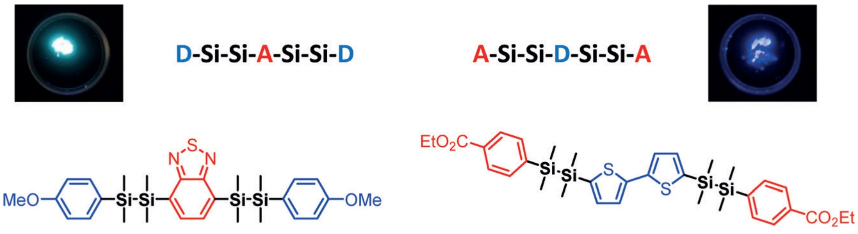
Communications



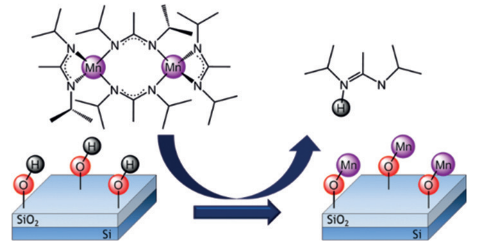
Calcium can: Although the FeO_4^{2-} ion is stable in water at pH 9–10, it can be readily activated by Ca^{2+} ions to generate O_2. Similar activating effects are also observed with Mg^{2+} and Sr^{2+}.

Reducing the gap: Using a boron atom as the spiro linker between an electron-deficient pyridyl pyrrolide and an electron-donating phenylcarbazolyl or triphenylamine fragment, boron complexes with a narrow HOMO–LUMO orbital overlap, small singlet–triplet energy gap (down to 38 meV), and strong thermally activated delayed fluorescence (TADF) were prepared. For the first time boron-complex-based OLEDs show a significant TADF contribution.





Disilane-bridged donor–acceptor–donor (D-Si-Si-A-Si-Si-D) molecules and acceptor–donor–acceptor (A-Si-Si-D-Si-Si-A) compounds display strong solid-state emission (see picture) and aggregation-induced emission (AIE). X-ray diffraction reveals there is no π–π stacking in crystals to suppress intermolecular interaction.

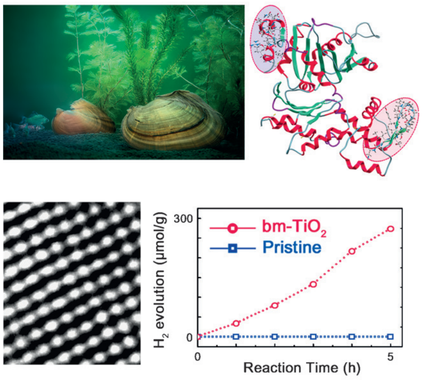


Wet Mn deposition: The deposition of high-purity manganese oxide layers on a silica surface was achieved by solution layer deposition: a solution chemistry route to form functional oxide layers. The mechanism taking place on the surface was determined by coupling ^{29}Si MAS NMR, XPS, and HRTEM analyses.

Bioprocess-Inspired Synthesis

J. J. Xie, H. Xie, B.-L. Su, Y. B. Cheng,
X. D. Du, H. Zeng, Wang, W. M. Wang,
H. Wang, Z. Y. Fu* ________ **3031 – 3035**

Mussel-Directed Synthesis of Nitrogen-Doped Anatase TiO_2

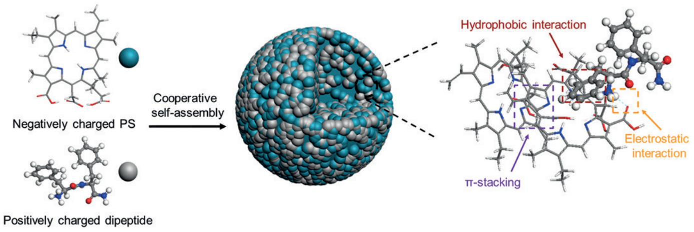


The pearl is the oyster's autobiography: Based on a natural pearl culture process, hierarchically meso/macroporous nitrogen-doped TiO_2 is obtained directly in living *Cristaria plicata* at ambient temperature, demonstrating enhanced visible-light photocatalytic activity in both chemical waste remediation and hydrogen generation. Intracellular proteins are found to be involved in the formation of TiO_2.

Assembled Nanodrugs

K. Liu, R. Xing, Q. Zou, G. Ma,
H. Möhwald, X. Yan* ______ **3036 – 3039**

Simple Peptide-Tuned Self-Assembly of Photosensitizers towards Anticancer Photodynamic Therapy



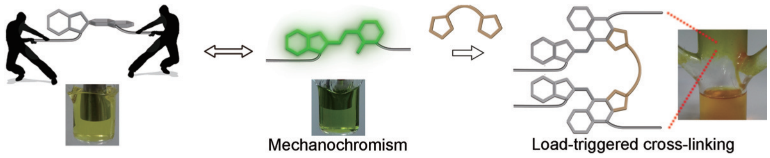
Simple but effective: Amphiphilic dipeptides or amino acids can tune the self-assembly of photosensitizers (PS) towards anticancer photodynamic therapy. Simple components to realize the nanofabrication of therapeutic agents based on cooperative self-assembly represent a versatile and robust approach towards anticancer therapy.

Polymer Mechanochemistry

H. Zhang, F. Gao, X. Cao, Y. Li, Y. Xu,
W. Weng,* R. Boulatov ______ **3040 – 3044**

Mechanochromism and Mechanical-Force-Triggered Cross-Linking from a Single Reactive Moiety Incorporated into Polymer Chains

Front Cover

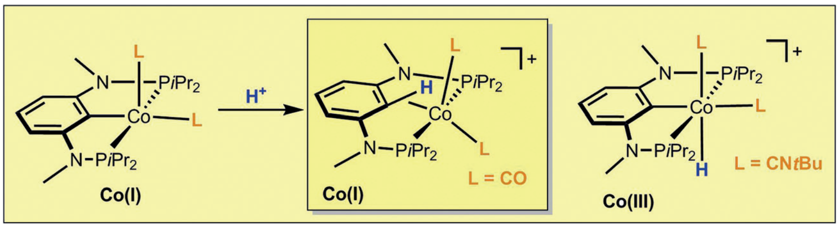


A dual mechanoresponsive moiety: A novel spirothiopyran-based mechanophore showed mechanochromism and underwent load-triggered thiol–ene click reactions (see picture). This versatile mechanophore opens a new avenue towards stress sensing and mechanochemical modification techniques, such as grafting, strengthening by stress, and self-healing.

Pincer Ligands

S. Murugesan, B. Stöger, E. Pittenauer,
G. Allmaier, L. F. Veiros,
K. Kirchner* ______________ **3045 – 3048**

A Cobalt(I) Pincer Complex with an η^2-C_{aryl}—H Agostic Bond: Facile C—H Bond Cleavage through Deprotonation, Radical Abstraction, and Oxidative Addition

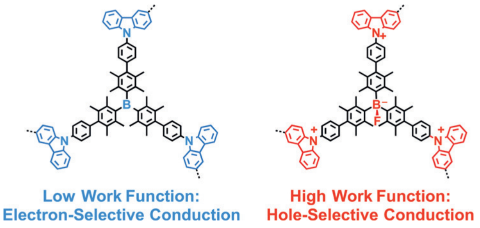


Protonation of $[Co(PCP^{NMe}\text{-}iPr)(CO)_2]$ yields the Co^I pincer complex $[Co(\kappa^3 P,CH,P\text{-}P(CH)P^{NMe}\text{-}iPr)(CO)_2]^+$ featuring an η^2-C_{aryl}—H agostic bond. This bond can be cleaved easily by deprotonation, radical abstraction with oxygen or TEMPO to afford the paramagnetic Co^{II} PCP complex $[Co(PCP^{NMe}\text{-}iPr)(CO)_2]^+$, or by CN*t*Bu promoted oxidative addition to give Co^{III} PCP hydride complexes.

Semiconducting Films

C. Gu, N. Huang, Y. Chen, H. Zhang, S. Zhang, F. Li, Y. Ma, D. Jiang* ———— **3049 – 3053**

Porous Organic Polymer Films with Tunable Work Functions and Selective Hole and Electron Flows for Energy Conversions

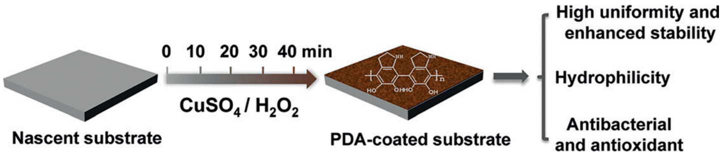


Nanofilters for electrons and holes: Porous organic polymer films were designed to have tunable work functions, and were used to control selective hole and electron flows to achieve high-efficiency energy conversions, including solar cells and light-emitting diodes.

Membrane Surfaces

C. Zhang, Y. Ou, W. X. Lei, L. S. Wan, J. Ji, Z.-K. Xu* ———— **3054 – 3057**

$CuSO_4/H_2O_2$-Induced Rapid Deposition of Polydopamine Coatings with High Uniformity and Enhanced Stability

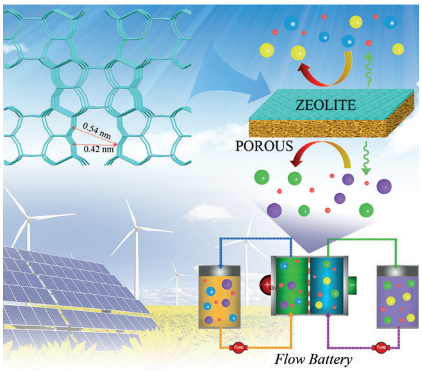


Mussel-inspired surfaces: A facile and robust approach to rapidly construct polydopamine (PDA) coatings on various substrates is presented. The $CuSO_4/H_2O_2$-triggered PDA coatings show high uniformity, enhanced stability, excellent hydrophilicity, antioxidant ability, and antibacterial performance.

Flow Batteries

Z. Yuan, X. Zhu, M. Li, W. Lu, X. Li,* H. Zhang* ———— **3058 – 3062**

A Highly Ion-Selective Zeolite Flake Layer on Porous Membranes for Flow Battery Applications

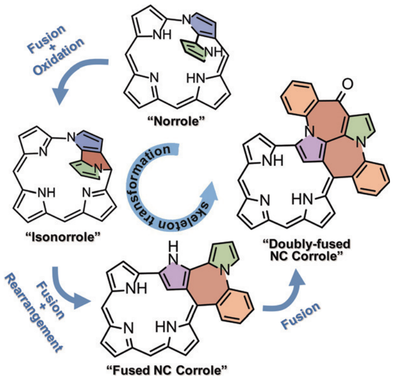


Go with the flow: For the first time, a zeolite-coated membrane that can perfectly separate ions of different sizes was fabricated for use in flow battery applications. See picture; large and small spheres are redox-active and non-reaction ions, respectively.

Porphyrinoids

M. Li, P. C. Wei, M. Ishida, X. Li, M. Savage, R. Guo, Z. P. Ou, S. H. Yang, H. Furuta,* Y. S. Xie* ———— **3063 – 3067**

Macrocyclic Transformations from Norrole to Isonorrole and an N-Confused Corrole with a Fused Hexacyclic Ring System Triggered by a Pyrrole Substituent



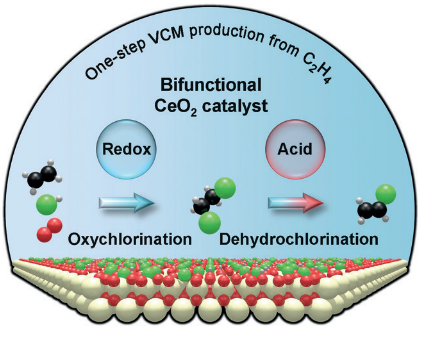
Confusing corroles: The pyrrole-substituted corrole isomer norrole underwent an oxidative fusion reaction to afford a unique N-C_{meso}-fused isonorrole. The isonorrole was subsequently converted into singly and doubly N-C_{Ar}-fused N-confused corroles with unprecedented fused [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic structures, respectively.

Ceria Catalysis

M. Scharfe, P. A. Lira-Parada, V. Paunović, M. Moser, A. P. Amrute, J. Pérez-Ramírez* ——— **3068 – 3072**

Oxychlorination–Dehydrochlorination Chemistry on Bifunctional Ceria Catalysts for Intensified Vinyl Chloride Production

One material, two functions: Ceria is used as the catalyst to produce the vinyl chloride monomer (VCM) from C_2H_4 in one step and in high yield, enabling redox-catalyzed oxychlorination and acid-catalyzed dehydrochlorination on the same material. The bifunctional character of CeO_2 intensifies the current two-step process for polyvinyl chloride manufacture and brings great stability advantages with respect to the archetypical $CuCl_2$ oxychlorination catalyst.

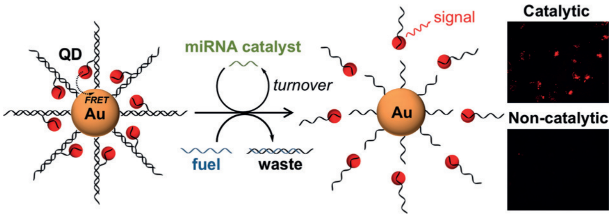


Molecular Imaging

X. He, T. Zeng, Z. Li, G. Wang, N. Ma* ——— **3073 – 3076**

Catalytic Molecular Imaging of MicroRNA in Living Cells by DNA-Programmed Nanoparticle Disassembly

Inside Cover

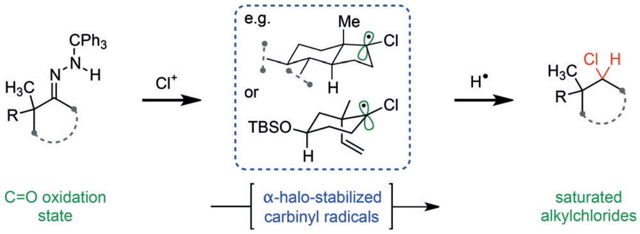


Break it up! High-sensitivity molecular imaging of microRNA in living cells is realized by DNA-programmed catalytic disassembly of gold nanoparticles and quantum dots (QDs).

Halogenation

J. R. Reyes, V. H. Rawal* ——— **3077 – 3080**

Reductive Chlorination and Bromination of Ketones via Trityl Hydrazones

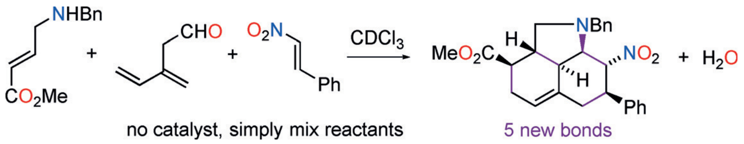


Halogen before hydrogen: Trityl hydrazones may be transformed, by action of halonium ion sources, into α-chloro and α-bromo carbinyl radicals, reduction of which affords the corresponding alkyl chlorides and alkyl bromides. Notably, this unique transformation efficiently constructs homoallylic and neopentyl chlorides, and provides a reductive hydrazone halogenation complementary to Barton's redox-neutral vinyl halide synthesis. TBS = *tert*-butyldimethylsilyl.

Domino Reactions

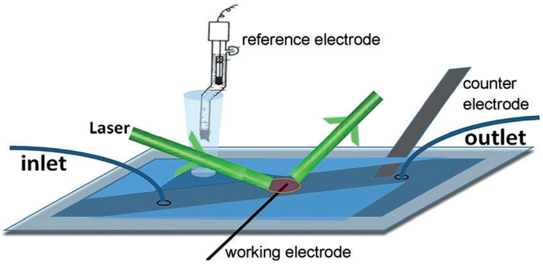
S. M. Tan, A. C. Willis, M. N. Paddon-Row,* M. S. Sherburn* ——— **3081 – 3085**

Multicomponent Diene-Transmissive Diels–Alder Sequences Featuring Aminodendralenes



Amine way to make polycycles: Multicyclic amine-containing systems are accessible in one-pot sequences from a skipped dienal, an amine, and two dienophiles. This stereoselective and atom-economical method delivers five new covalent bonds, and is brought about simply by mixing the precursors.

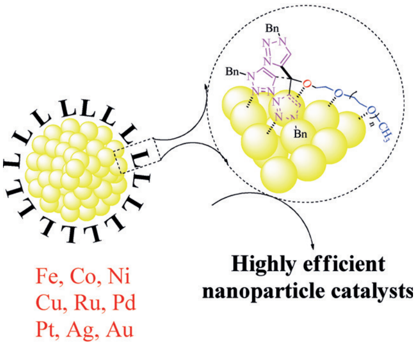
Single-Molecule Nanocatalysis



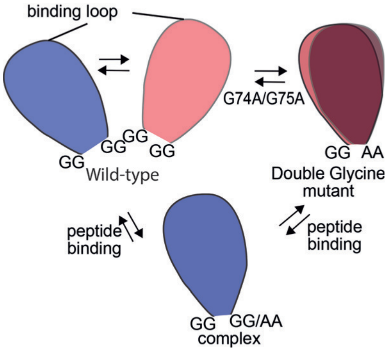
Catalyst deactivation: By combining single-molecule nanocatalysis with traditional electrochemical methods, the kinetics of the deactivation of a Pt/C electrocatalyst at the single-particle level were studied during electrocatalytic hydrogen oxidation. A correlation between stability and deactivation of the PT/C catalyst was shown.

Nanocatalysts

A tip of the cap: A water-soluble tris(triazolyl)-polyethylene glycol amphiphilic ligand encapsulates and stabilizes transition metal nanoparticle catalysts. The capping ligands allow for highly efficient nitro-arene reduction, click, Suzuki–Miyaura, and transfer hydrogenation reactions.



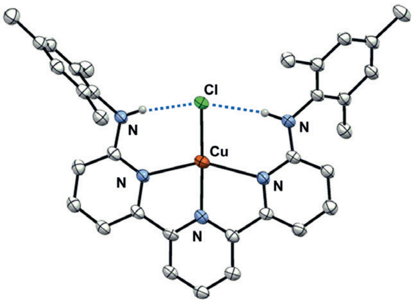
Enzyme Selectivity



In the loop: Modification of flexible loops induces structural equilibrium redistribution of an enzyme active site. A ligand-selective change of binding affinity to the active site of cyclophilin is achieved by tuning of the dynamics of a highly flexible loop. This system may serve as a model system for studying the effects of various time scales of loop motion on protein function tuned by mutations.

Copper Complexes

Entatic state: Hydrogen bonds constrain the geometry of Cu^{I} and Cu^{II} complexes. A highly unusual square-planar geometry about Cu^{I} (see structure) is shown to be nearly isostructural to the Cu^{II} core. The minimal reorganization energy between redox states allows for extremely rapid Cu^{I}/Cu^{II} electron-transfer self-exchange rates.

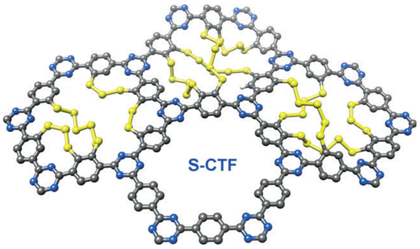


Lithium–Sulfur Batteries

S. N. Talapaneni, T. H. Hwang, S. H. Je, O. Buyukcakir, J. W. Choi,* A. Coskun* ———— **3106 – 3111**

Elemental-Sulfur-Mediated Facile Synthesis of a Covalent Triazine Framework for High-Performance Lithium–Sulfur Batteries

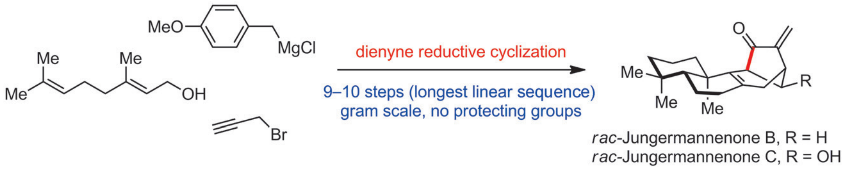
Elemental stabilization: A covalent triazine framework (CTF) with chemically embedded polymeric sulfur (S-CTF) was synthesized under catalyst- and solvent-free reaction conditions from 1,4-dicyanobenzene and elemental sulfur. This material was used as a robust cathode for high-performance lithium–sulfur batteries with very good cycling stabilities.



Natural Product Synthesis

W. Liu, H. Li, P.-J. Cai, Z. Wang, Z.-X. Yu, X. Lei* ———— **3112 – 3116**

Scalable Total Synthesis of *rac*-Jungermannenones B and C



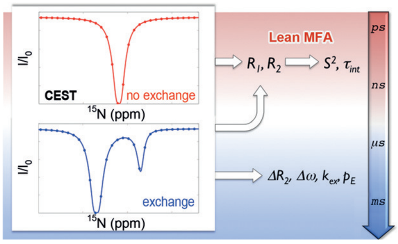
A *rac* to the finish: A 1,6-dienyne reductive cyclization reaction has been developed for the first scalable and protecting-group-free synthesis of *rac*-jungermannenones B and C. Preliminary mechanistic studies support a vinyl radical cyclization/allylic radical isomerization mechanism. DFT calculations explain the high regioselectivity observed in the 1,6-dienyne reductive radical cyclization.

NMR Spectroscopy

Y. Gu, A. L. Hansen, Y. Peng, R. Brüschweiler* ———— **3117 – 3119**

Rapid Determination of Fast Protein Dynamics from NMR Chemical Exchange Saturation Transfer Data

An integrated protocol is reported for the rapid measurement of longitudinal and transverse spin relaxation parameters of proteins using chemical exchange saturation transfer experiments (CEST; see picture). The experiments are suitable for quantitative interpretation by a lean model-free approach (Lean MFA).

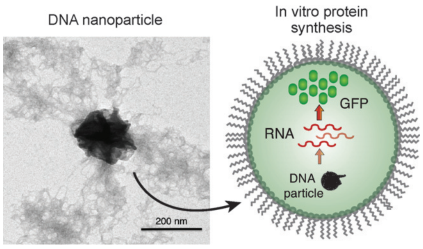


DNA Nanoparticles

R. Galinis, G. Stonyte, V. Kiseliovas, R. Zilionis, S. Studer, D. Hilvert, A. Janulaitis, L. Mazutis* ———— **3120 – 3123**

DNA Nanoparticles for Improved Protein Synthesis In Vitro

Express yourself: Using an isothermal DNA amplification reaction, single DNA molecules were converted into DNA nanoparticles. DNA condensation was triggered by inorganic pyrophosphate and magnesium ions. The resulting DNA nanoparticles were used as templates for high-yield in vitro protein synthesis. GFP = green fluorescent protein.



Graphene Oxide

Y. Gao, P. Tang, H. Zhou, W. Zhang, H. Yang, N. Yan, G. Hu, D. Mei, J. Wang,* D. Ma* ———— 3124 – 3128

Graphene Oxide Catalyzed C—H Bond Activation: The Importance of Oxygen Functional Groups for Biaryl Construction

Back Cover

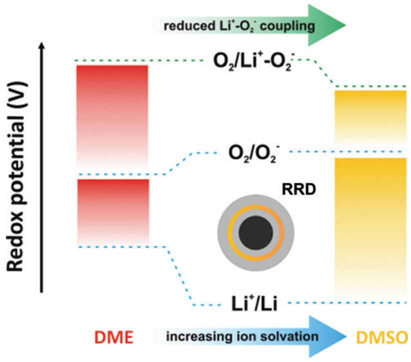
A heterogeneous, inexpensive, and environmentally friendly graphene oxide (GO) catalytic system for the C—H bond arylation of benzene enables the formation of biaryl compounds in the presence of aryl iodides. The oxygen functional groups in these GO sheets and the addition of KO*t*Bu are essential for the observed catalytic activity.

Oxygen Electrochemistry

D. G. Kwabi, V. S. Bryantsev, T. P. Batcho, D. M. Itkis, C. V. Thompson, Y. Shao-Horn* ———— 3129 – 3134

Experimental and Computational Analysis of the Solvent-Dependent $O_2/Li^+\text{-}O_2^-$ Redox Couple: Standard Potentials, Coupling Strength, and Implications for Lithium–Oxygen Batteries

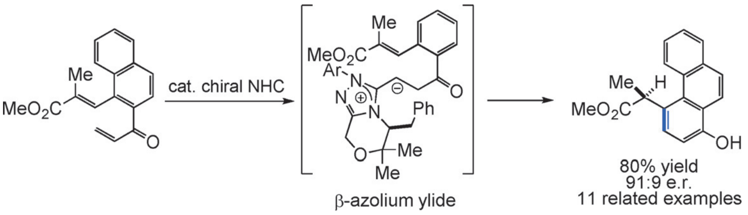
The free-energy landscape of reactions involved in the Li oxygen reduction reaction (ORR) were obtained by rotating ring disk (RRD) measurements and calculations. Differences in redox potentials of O_2/O_2^- and $O_2/Li^+\text{-}O_2^-$ couples vs. Li^+/Li in dimethoxyethane (DME) and dimethylsulfoxide (DMSO) reflect the influence of increasing solvation on the free energy of O_2^- formation vs. Li^+/Li and $Li^+\text{-}O_2^-$ coupling.



NHC Catalysis

Y. Nakano, D. W. Lupton* ———— 3135 – 3139

Enantioselective N-Heterocyclic Carbene Catalysis by the Umpolung of α,β-Unsaturated Ketones



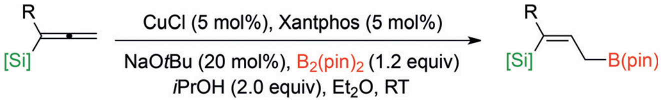
β-azolium ylide

One for addition: The 1,4-addition of N-heterocyclic carbenes (NHCs) into conjugate acceptors followed by tautomerization provides the β-azolium ylide. This intermediate provides access to a range of enantioenriched 2-aryl propionates. The reaction was possible using electron-rich N-substituted triazolium catalysts in the presence of hexafluoroisopropanol (HFIP).

Allylic Compounds

W. Yuan, L. Song, S. Ma* ———— 3140 – 3143

Copper-Catalyzed Borylcupration of Allenylsilanes

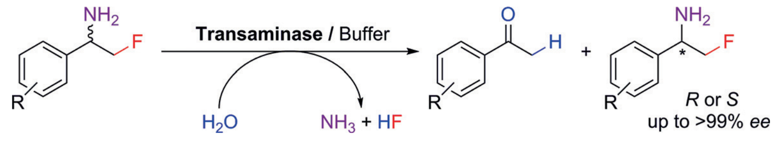


Do a (dis)favor: A new highly selective copper-catalyzed borylcupration of allenylsilanes for the synthesis of thermodynamically disfavored 3-silylalk-2(*Z*)-enylboronates was developed. Such stereodefined allylic boronates containing an extra alkenyl silane moiety are useful organodimetallic reagents for organic synthesis.

Biocatalysis

A. Cuetos, M. García-Ramos,
E.-M. Fischereder, A. Díaz-Rodríguez,
G. Grogan, V. Gotor,* W. Kroutil,*
I. Lavandera* ______________ **3144 – 3147**

Catalytic Promiscuity of Transaminases: Preparation of Enantioenriched β-Fluoroamines by Formal Tandem Hydrodefluorination/Deamination

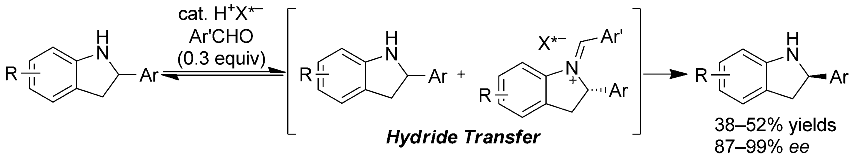


A night out for TAs: Transaminases (TAs) are shown to react with aromatic β-fluoroamines, thus leading to enantioselective dehalogenation and deamination to form the corresponding acetophenone derivatives. Racemic β-fluoroamines are resolved in a kinetic resolution by tandem hydrodefluorination/deamination, thus giving the corresponding amines with up to greater than 99 % *ee*. This method exploits the catalytic promiscuity of TAs as a tool for novel transformations.

Kinetic Resolution

K. Saito, T. Akiyama* ________ **3148 – 3152**

Chiral Phosphoric Acid Catalyzed Kinetic Resolution of Indolines Based on a Self-Redox Reaction

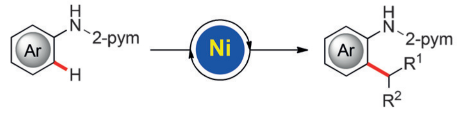


The asymmetric synthesis of indolines was achieved by oxidative kinetic resolution of the indoline racemate, involving the formation and reduction of an iminium intermediate using a chiral phosphoric acid catalyst and a salicylaldehyde derivative. This method was applicable to various racemic indolines and the corresponding products were obtained in good yields with excellent enantioselectivities.

C—H Activation

Z. Ruan, S. Lackner,
L. Ackermann* ______________ **3153 – 3157**

A General Strategy for the Nickel-Catalyzed C—H Alkylation of Anilines



Unified Strategy:
- primary and secondary alkyl halides
- monodentate pyrimidyl (pym) DG
- via a six-membered nickelacycle
- electron-rich anilines
- inexpensive nickel catalyst
- removable DG

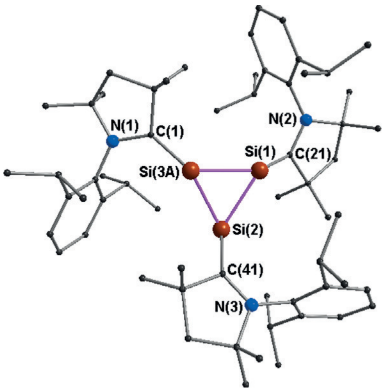
One for all: An inexpensive nickel catalyst enables the C—H alkylation of pyrimidyl anilines with both primary and secondary alkyl halides. The directing group (DG) could be easily removed in a traceless fashion, and the products contain key structural motifs of important anticancer drugs.

Carbenes

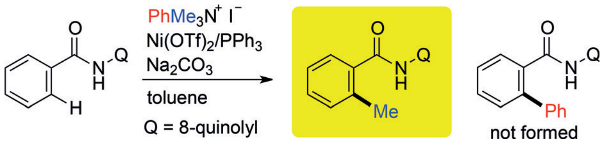
K. C. Mondal,* S. Roy, B. Dittrich,*
D. M. Andrada, G. Frenking,*
H. W. Roesky* ______________ **3158 – 3161**

A Triatomic Silicon(0) Cluster Stabilized by a Cyclic Alkyl(amino) Carbene

Three-sided: Reaction of potassium graphite with a cyclic alkyl(amino) carbene tetrachlorosilane adduct results in the formation of a stable and isolable carbene-stabilized triatomic silicon(0) cluster (see figure). The triangular compound was characterized by single crystal X-ray structural crystallography, and its bonding and electron density distributions were studied by quantum chemical calculations.

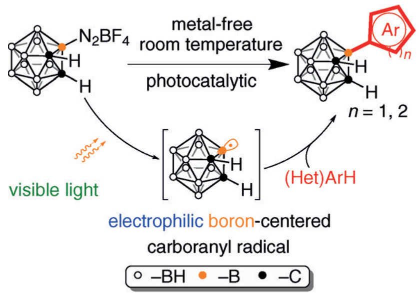


C–H Activation



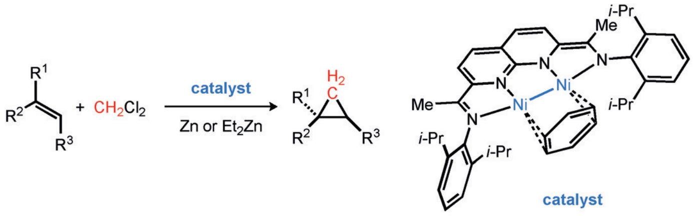
Its all about Me! The methylation of C(sp^2)–H bonds was achieved through the Ni^{II}-catalyzed reaction of benzamides with phenyltrimethylammonium bromide or iodide as the source of the methyl group. The reaction has a broad scope and shows high functional-group compatibility. The reaction is also applicable to the methylation of C(sp^3)–H bonds in aliphatic amides.

Photocatalysis



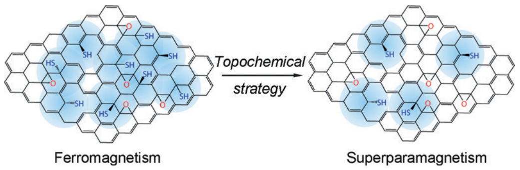
Dye away: A photocatalytic boron arylation of *o*-carborane has been achieved. In the presence of visible light and an organic dye (photocatalyst), a boron-centered carboranyl radical was efficiently produced from 3-diazonium-*o*-carborane tetrafluoroborate. This reactive intermediate can undergo electrophilic substitution reactions with a wide range of (hetero)arenes under very mild reaction conditions.

Carbene Transfer Reactions



Nickel interplay: Dinuclear nickel complexes (see scheme) catalyze the reductive cyclopropanation of alkenes with CH_2Cl_2 as the methylene source and Zn or Et_2Zn as the terminal reductant. Diverse alkenes bearing common functional groups are tolerated under the mildly reducing reaction conditions.

Magnetic Materials

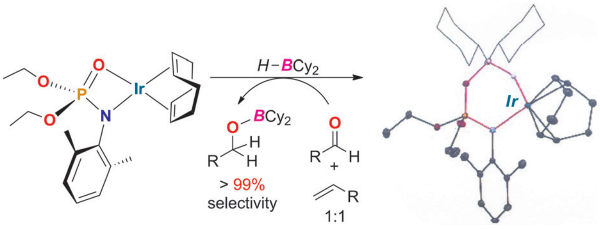


Beneath the surface: Modification of graphene oxide with thiol groups results in ferromagnetic reduced graphene oxide; subsequent mild oxidation and partial thiol group removal produces superparamagnetic reduced graphene oxide. The magnetic domains are reduced to a critical size and the number of unpaired spins decreased to result in a superparamagnetic structure. This material shows large negative low-field magnetoresistance at ambient temperature.

B–H Activation

M. W. Drover, L. L. Schafer,*
J. A. Love* ———————— **3181 – 3186**

Capturing $HBCy_2$: Using N,O-Chelated Complexes of Rhodium(I) and Iridium(I) for Chemoselective Hydroboration

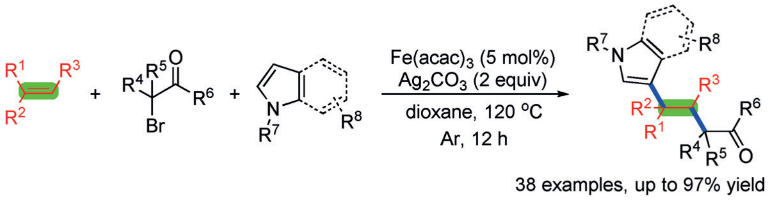


Cooperative activation of $HBCy_2$ provided six-membered genuine rhoda- and iridacycles containing a δ-[M]⋯H–B agostic interaction. The treatment of these Shimoi-type borane adducts with an aldehyde and an alkene resulted in chemoselective aldehyde hydroboration and reformation of the 1,3-N,O-chelated starting material (see scheme). In contrast, free $HBCy_2$ is selective for alkene hydroboration.

Synthetic Methods

X.-H. Ouyang, R.-J. Song, M. Hu, Y. Yang,
J.-H. Li* ———————— **3187 – 3191**

Silver-Mediated Intermolecular 1,2-Alkylarylation of Styrenes with α-Carbonyl Alkyl Bromides and Indoles

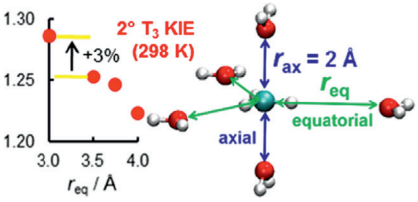


Bridging alkene: An intermolecular arene $C(sp^2)$–H functionalization strategy is established for the radical 1,2-alkylarylation of styrenes with α-carbonyl alkyl bromides and indoles using iron as the catalyst and silver as the promotor. This method enables the formation of two C–C bonds in a single reaction. acac = acetylacetonate.

Computational Chemistry

P. B. Wilson,
I. H. Williams* ———————— **3192 – 3195**

Influence of Equatorial CH⋯O Interactions on Secondary Kinetic Isotope Effects for Methyl Transfer

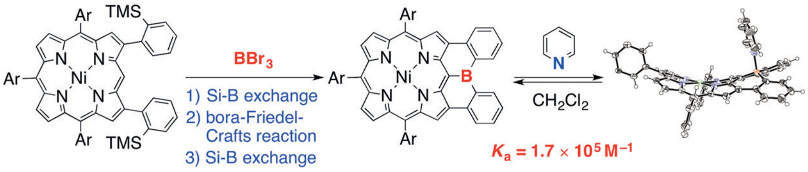


Behavior in confinement: $k(CH_3)/k(CT_3)$ for methyl transfer in a constrained cage of water molecules was found to be sensitive to CH⋯O hydrogen-bonding interactions: It increased by 3% as the equatorial distance r_{eq} decreased from 3.5 to 3.0 Å for a constant axial distance r_{ax} = 2.0 Å (see graph), thus suggesting that factors other than axial compression may contribute to isotope-effect variations for methyltransferase and its mutant structures.

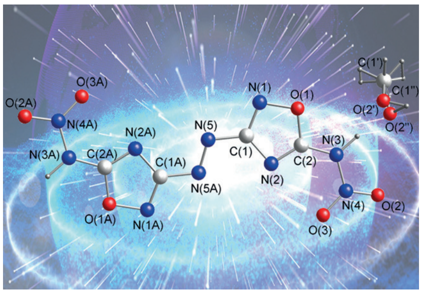
Porphyrins

K. Fujimoto, J. Oh, H. Yorimitsu,*
D. Kim,* A. Osuka* ———— **3196 – 3199**

Directly Diphenylborane-Fused Porphyrins



A clear expansive π: Diphenylborane-fused porphyrins were synthesized from the corresponding β-(2-trimethylsilylphenyl)-substituted porphyrins. The porphyrin π-system interacts with the vacant p-orbital of the boron. Pyridine adds at the boron center erasing the electronic interaction.

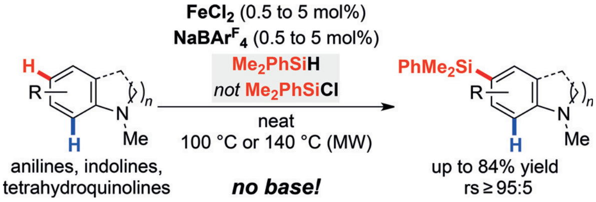


Just plane dense and full of energy: A dense compound with a planar structure, 5,5′-dinitramino-3,3′-azo-1,2,4-oxadiazole, has been synthesized, as have its energetic salts. Some of them were found to have potential applications as energetic compounds.

Energetic Materials

Y. Tang, H. Gao,* L. A. Mitchell, D. A. Parrish, J. M. Shreeve* **3200 – 3203**

Syntheses and Promising Properties of Dense Energetic 5,5′-Dinitramino-3,3′-azo-1,2,4-oxadiazole and Its Salts

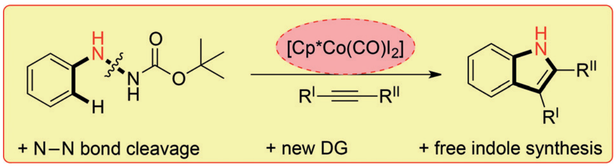


So simple: Combining a base-metal salt and $NaBAr^F_4$ generates a Lewis acid that promotes the C–H silylation of electron-rich arenes with hydrosilanes. The more obvious choice, chlorosilanes, do not participate in this electrophilic aromatic substitution. No base is required to absorb the protons released, so this process resembles a typical Friedel–Crafts reaction. Ar^F = 3,5-bis(trifluoromethyl)phenyl.

Lewis Acid Catalysis

Q. Yin, H. F. T. Klare, M. Oestreich* **3204 – 3207**

Friedel–Crafts-Type Intermolecular C–H Silylation of Electron-Rich Arenes Initiated by Base-Metal Salts

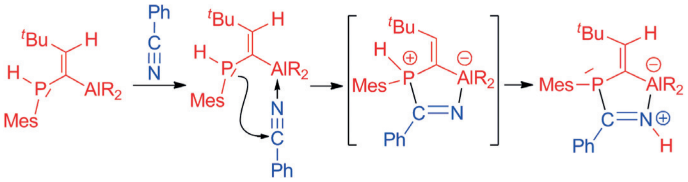


This is aN-Nulation! A redox-neutral cobalt(III)-catalyzed synthesis of free indoles featuring an N–N bond cleavage has been achieved. An increase of reactivity could be observed on tuning the directing group (DG) at the hydrazine-β-nitrogen atom, which turned out to be the crucial factor for the reaction.

C–H Activation

A. Lerchen, S. Vásquez-Céspedes, F. Glorius* **3208 – 3211**

Cobalt(III)-Catalyzed Redox-Neutral Synthesis of Unprotected Indoles Featuring an N–N Bond Cleavage



Cooperative activation and hydrogen shift is observed as a new reactivity pattern upon treatment of a P–H functionalized Al/P frustrated Lewis pair with various unsaturated substrates. Unusual highly functionalized phosphorus compounds were obtained, such as a phosphinyltriazene or phosphaurea. With benzonitrile, the sequence adduct formation, activation, and H-shift gives an iminophosphine (see scheme).

Frustrated Lewis Pairs

L. Keweloh, H. Klöcker, E.-U. Würthwein, W. Uhl* **3212 – 3215**

A P–H Functionalized Al/P Frustrated Lewis Pair: Substrate Activation and Selective Hydrogen Transfer

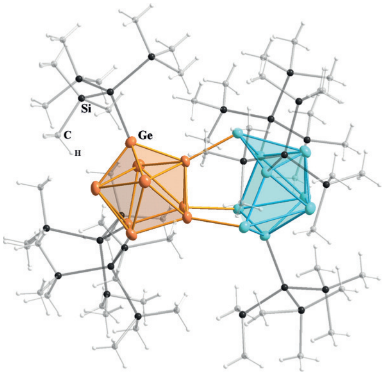
Metalloid Clusters

O. Kysliak, C. Schrenk,
A. Schnepf* ______ **3216 – 3219**

The Largest Metalloid Group 14 Cluster, $Ge_{18}[Si(SiMe_3)_3]_6$: An Intermediate on the Way to Elemental Germanium

Inside Back Cover

Germanium snapshot: The oxidation of $[Ge_9(Hyp)_3]^-$ (Hyp = $Si(SiMe_3)_3$) with an iron(II) salt leads to $Ge_{18}(Hyp)_6$ (**1**), the largest metalloid Group 14 cluster that has been structurally characterized to date. **1** can be regarded as a trapped first intermediate of the formation of the elemental phase Ge(*cF*136), providing first insights into the principles of the formation of elemental germanium from molecular precursors.

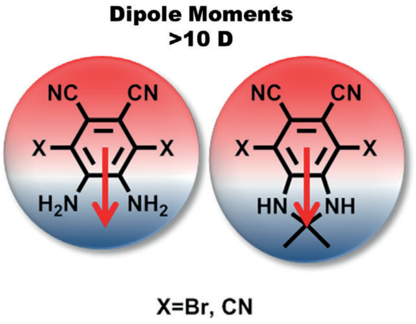


High Dipole Moments

J. Wudarczyk, G. Papamokos,
V. Margaritis, D. Schollmeyer, F. Hinkel,
M. Baumgarten, G. Floudas,
K. Müllen* ______ **3220 – 3223**

Hexasubstituted Benzenes with Ultrastrong Dipole Moments

Just a moment: Molecules with high dipole moments are desirable materials for organic electronic applications such as nonlinear optics and ferroelectrics. Hexasubstitution of benzene and a novel method to synthesize dihydrobenzimidazoles has allowed charge-free compounds to be generated with dipole moments above 10 debye.

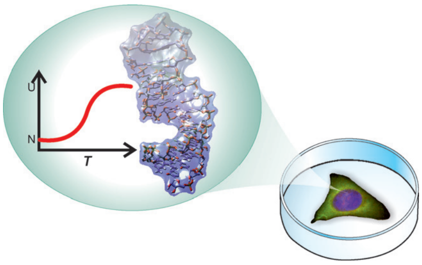


RNA Folding Stability

M. Gao, D. Gnutt, A. Orban, B. Appel,
F. Righetti, R. Winter, F. Narberhaus,
S. Müller, S. Ebbinghaus* ______ **3224 – 3228**

RNA Hairpin Folding in the Crowded Cell

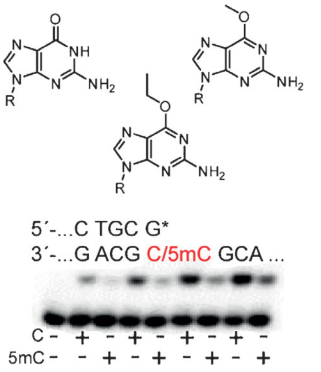
From the test tube to the cell: In-cell folding experiments spatio-temporally resolve RNA hairpin stability in the living cell. The folding stability inside cells is found to be comparable to that in dilute physiological buffer.



Epigenetics

J. von Watzdorf, K. Leitner,
A. Marx* ______ **3229 – 3232**

Modified Nucleotides for Discrimination between Cytosine and the Epigenetic Marker 5-Methylcytosine



The most common epigenetic marker in eukaryotic cells—5-methyl-2′-deoxycytosine (5mC)—plays a key role in gene regulation. Therefore, 5mC can serve as an important biomarker for diagnostics. Direct detection of 5mC can be achieved by either incorporation of modified nucleotides or extension of 3′-modified primers by employing thermostable polymerases.

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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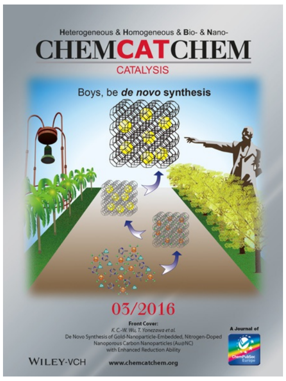

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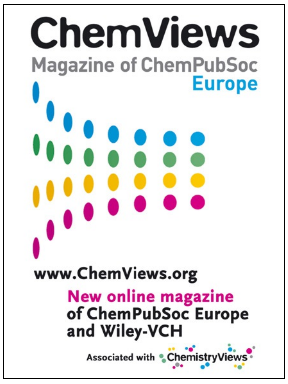

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