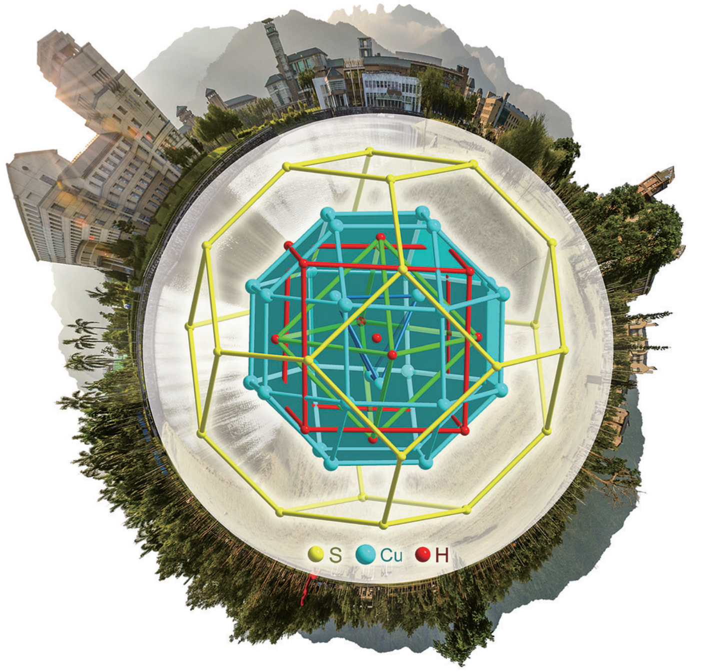
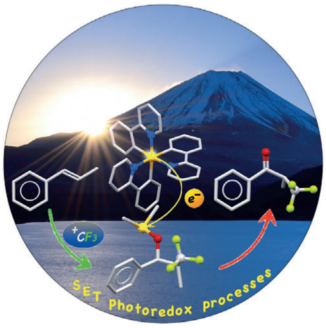
Dithiolato-protected copper hydride nanoclusters …



… that evolve hydrogen under sunlight irradiation were prepared. As C. W. Liu and co-workers describe in their Communication on page 7214 ff., these nanoclusters were structurally characterized by various spectroscopic methods, including single-crystal neutron diffraction. The onion-like structure displays a geometric entity that is reminiscent of a Chinese puzzle ball.

Keto-Trifluoromethylation

In their Communication on page 7144 ff., T. Koike, M. Akita et al. describe the synthesis of valuable α-CF_3-substituted ketones from aromatic alkenes by combining photoredox-catalyzed trifluoromethylation and oxidation with DMSO.

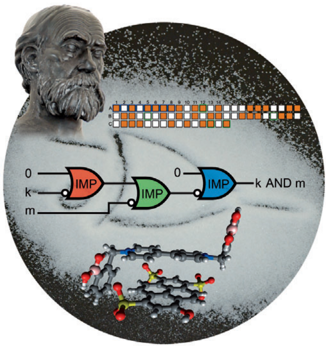


Density Functional Calculations

Y. Li, Y. Liao, and Z. Chen report in their Communication on page 7248 ff. a new inorganic two-dimensional material, namely the Be_2C monolayer, which was designed by density functional calculations.

Molecular Computing

In their Communication on page 7339 ff., A. Schiller and co-workers present a method to integrate an (in principle) unlimited number of molecular logic gates to construct complex circuits on microtiter plates.



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Service

Author Profile

“My biggest motivation is the best is yet to come! If I were not a scientist, I would be a writer or actor—or maybe a bishop …”
This and more about Nazario Martín can be found on page 7116.

News

O. Daugulis

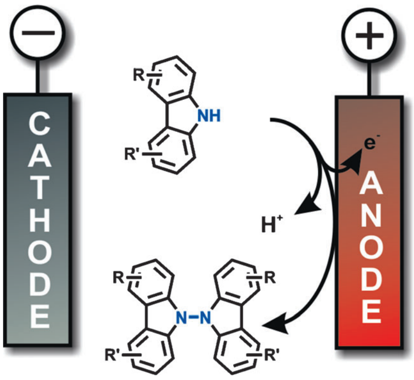
J. N. Johnston

G. E. Keck

H.-w. Liu

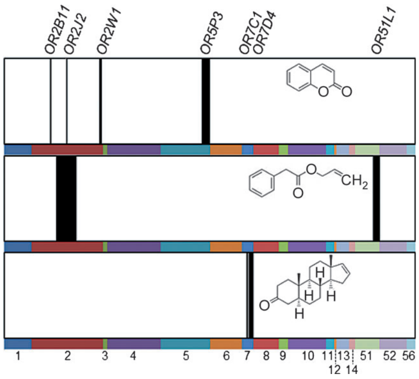
Books

Highlights



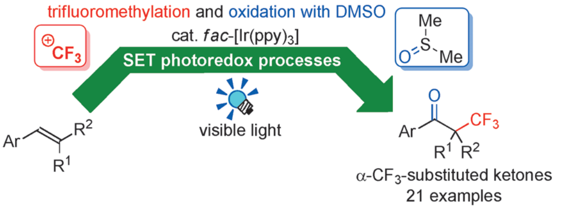
Current affairs: Efficient N,N dimerization by using an electric current is a recent powerful example of preparative electrosynthesis where conventional reagents fail. The general and practical nature of this method as well as other applications will breathe new life into the electroorganic synthesis of complex molecules.

Reviews



The sheer unlimited variation in biologically relevant chemosensory entities are defined by a "combinatorial odor code", which comprises a central group of up to 40 out of the circa 230 high impact odorants that have been identified. This suggests the foodborne stimulus space to have co-evolved with, and roughly match our circa 400 olfactory receptors (see picture: odor-specific receptor activity pattern; OR = olfactory receptor).

Communications



Valuable α-CF_3-substituted ketones can be synthesized from aromatic alkenes by combining photoredox-catalyzed trifluoromethylation and oxidation with DMSO. The iridium photocatalyst *fac*-[Ir(ppy)$_3$] (ppy = 2-phenylpyridine) plays key roles in this keto-trifluoromethylation. SET = single electron transfer.

Frontispiece

For the USA and Canada:
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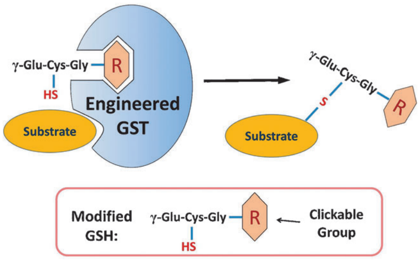
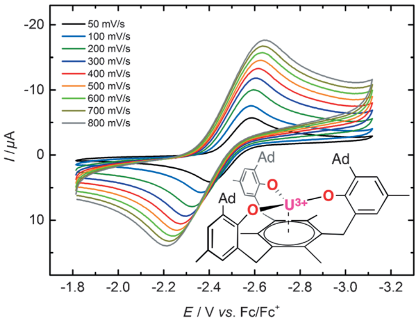


Click bait: An enzymatic system involving a clickable probe was developed for profiling the small-molecule substrates of glutathione S-transferases (GSTs). The GST mutant was paired with a clickable glutathione analogue to give a highly efficient enzyme–cofactor pair for labeling GST substrates. The conjugated GST substrates can then be biotinylated through click chemistry and subsequently enriched and then analyzed by LC–MS/MS.

Enzyme Substrates

S. Feng, L. Zhang, G. Adilijiang, J. Liu,
M. Luo, H. Deng* ________ **7149 – 7153**

Substrate Profiling of Glutathione S-transferase with Engineered Enzymes and Matched Glutathione Analogues

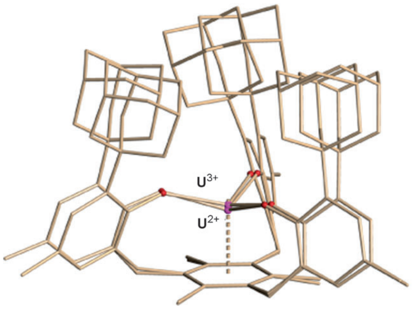


U2 bites: Cyclic voltammetry scans of the uranium(III) complex $[\{(^{\mathrm{Ad,Me}}\mathrm{ArO})_3\mathrm{Mes}\}\mathrm{U}]$ (**1**) revealed a reversible reduction at −2.495 V—the first electrochemical evidence for a formally divalent molecular uranium complex. Chemical reduction of **1** initiates redox isomerization and coordination to form a uranium hydride, and, upon addition of a crown ether, hydride insertion into the coordinated arene occurs.

Low-Valent Uranium (1)

H. S. La Pierre, H. Kameo, D. P. Halter,
F. W. Heinemann,
K. Meyer* ________ **7154 – 7157**

Coordination and Redox Isomerization in the Reduction of a Uranium(III) Monoarene Complex



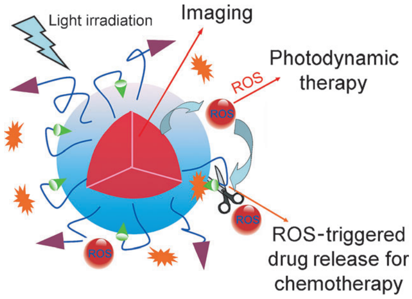
U2 rocks: The molecular and electronic structure of a uranium(II) monoarene complex with a $5f^4$ electronic configuration supported by δ backbonding was established experimentally by single-crystal X-ray diffraction, variable-temperature ^{1}H NMR and X-band EPR spectroscopy, solution-state and solid-state magnetism studies, and optical absorption spectroscopy. The electronic structure of the complex was further investigated by DFT calculations.

Low-Valent Uranium (2)

H. S. La Pierre, A. Scheurer,
F. W. Heinemann, W. Hieringer,
K. Meyer* ________ **7158 – 7162**

Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding

Three in one: A theranostic nanoplatform based on a conjugated polyelectrolyte covalently linked to an anticancer drug (orange) through a linker (green) cleaved by reactive oxygen species (ROS) had functionalities for image, therapy, and on-demand drug release (see picture). An enhanced therapeutic effect was possible through combined photodynamic therapy and chemotherapy with ROS-triggered drug release upon illumination with a single light switch.

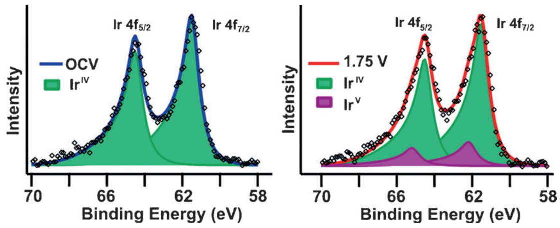


Cancer Nanotechnology

Y. Yuan, J. Liu, B. Liu* ________ **7163 – 7168**

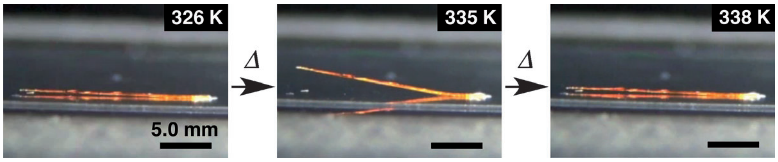
Conjugated-Polyelectrolyte-Based Polyprodrug: Targeted and Image-Guided Photodynamic and Chemotherapy with On-Demand Drug Release upon Irradiation with a Single Light Source

Electrocatalysis



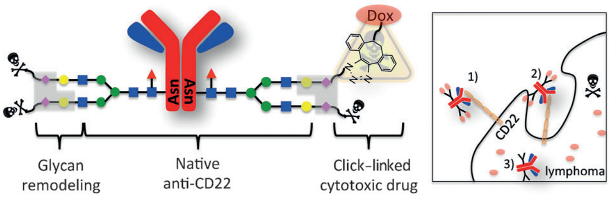
The surface species of an iridium oxide electrocatalyst under oxygen evolution reaction (OER) conditions were probed by ambient-pressure X-ray photoelectron spectroscopy (APXPS). Under OER conditions, iridium undergoes a change in oxidation state from Ir^{IV} to Ir^{V} predominantly at the catalyst surface, indicating that the OER on iridium oxide occurs on a single iridium site, suggesting an OOH-mediated mechanism.

Polymorphism



A rigorous workout: An amphiphile composed of two tetra(ethylene glycol) chains connecting π–π-stacking rigid aromatic units showed a reversible thermally driven single-crystal-to-single-crystal transition involving a bending and straightening motion on a macroscopic scale (see picture). The single-crystal motion occurs as a result of changes in the conformation and alignment of the molecules rather than bond formation/cleavage.

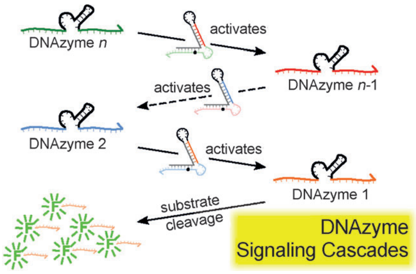
Drug Design



Dressed to kill: Enzymatic remodeling of the glycans of cancer-targeting antibodies to include a sialic acid moiety modified with an azido function enables the site-specific attachment of cytotoxic drugs by strain-promoted azide–alkyne cycloaddition. An anti-CD22 antibody modified with doxorubicin (Dox) is shown to selectively target and kill lymphoma cells.

Signaling Cascades

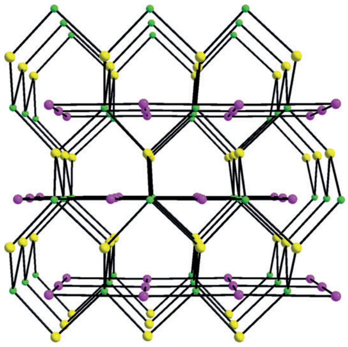
Signaling between DNAzymes was achieved using a structured chimeric substrate (SCS) that releases a downstream activator after cleavage by an upstream DNAzyme. The SCS molecule can be activated by various upstream DNAzymes and coupled to DNA strand-displacement devices, and it is highly resistant to interference from background DNA. This work enables the rational design of synthetic regulatory networks, with potential applications in biodetection and theranostics.



Zeotype Frameworks

L. Wei, Q. Wei, Z.-E. Lin,* Q. Meng, H. He, B.-F. Yang, G.-Y. Yang* ____ **7188 – 7191**

A 3D Aluminoborate Open Framework Interpenetrated by 2D Zinc–Amine Coordination-Polymer Networks in Its 11-Ring Channels

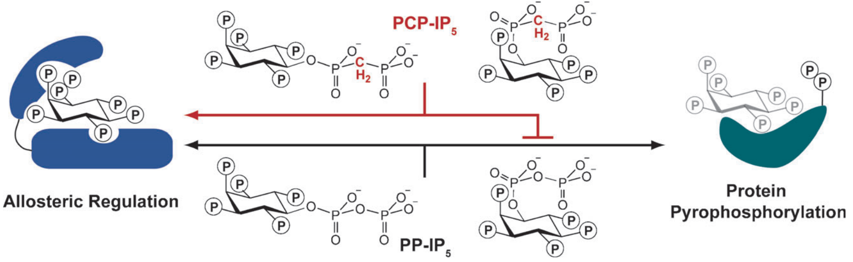


A union grounded in independence: An inorganic–organic hybrid solid, $[\mathrm{Zn(NH_2C_3H_6NH_2)_2}][\mathrm{AlB_5O_{10}}]$, combining the structural features of 3D open-framework inorganic solids and 2D zinc–amine coordination polymers was synthesized under solvothermal conditions with the coordination polymer in the pores of the aluminoborate (Zn purple, Al yellow, B_5O_{10} green). The hybrid showed extensive luminescence and moderate second-harmonic-generation efficiency.

Second Messenger Signaling

M. Wu, L. S. Chong, S. Capolicchio, H. J. Jessen, A. C. Resnick, D. Fiedler* ____ **7192 – 7197**

Elucidating Diphosphoinositol Polyphosphate Function with Nonhydrolyzable Analogues

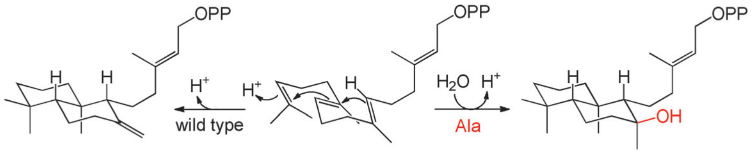


Stable analogues of high-energy messengers: Bisphosphonate analogues of the diphosphoinositol polyphosphate (PP-IP) messengers are resistant to chemical and biochemical degradation. The compounds mimic the natural counterparts well when proteins are regulated allosterically by PP-IPs, but have an opposing effect in protein pyrophosphorylation. Thus, the compounds can be used to elucidate PP-IP signaling properties.

Enzyme Catalysis

K. Potter, J. Criswell, J. Zi, A. Stubbs, R. J. Peters* ____ **7198 – 7202**

Novel Product Chemistry from Mechanistic Analysis of *ent*-Copalyl Diphosphate Synthases from Plant Hormone Biosynthesis

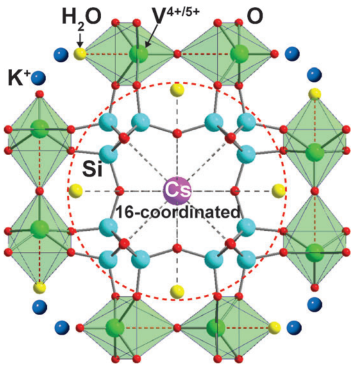


Getting active: An active-site water molecule, coordinated by histidine and asparagine residues, serves as the catalytic base in all *ent*-copalyl diphosphate synthases (CPSs). When these residues are substituted by alanine, the mutant CPSs produce stereochemically novel *ent*-8-hydroxy-CPP. Given the requisite presence of CPSs in all land plants for gibberellin phytohormone biosynthesis, such plasticity presumably underlies the observed diversification of the resulting labdane-related diterpenoids.

Cs$^+$ Removal

S. J. Datta, W. K. Moon, D. Y. Choi, I. C. Hwang, K. B. Yoon* ____ **7203 – 7208**

A Novel Vanadosilicate with Hexadeca-Coordinated Cs$^+$ Ions as a Highly Effective Cs$^+$ Remover



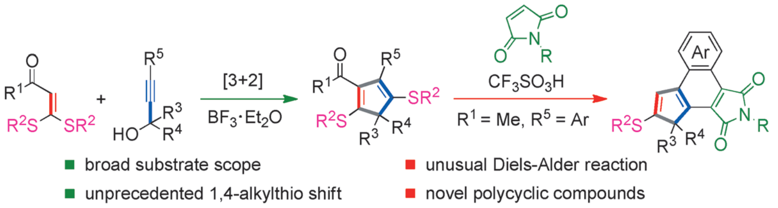
A novel vanadosilicate is an excellent remover of Cs$^+$ ions from groundwater, seawater, and highly acidic or basic nuclear waste solutions. This material can therefore be used for the removal of radioactive ^{137}Cs$^+$ ions from contaminated water.

[3+2] Cycloaddition

Z. Fang, J. Liu, Q. Liu, X. Bi* **7209 – 7213**

[3+2] Cycloaddition of Propargylic Alcohols and α-Oxo Ketene Dithioacetals: Synthesis of Functionalized Cyclopentadienes and Further Application in a Diels–Alder Reaction

Inside Cover



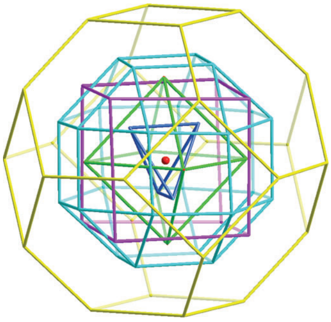
2,5-Dialkylthio cyclopentadienes were prepared by the BF$_3$·Et$_2$O catalyzed regiospecific [3+2] cycloaddition of propargylic alcohols and α-oxo ketene dithioacetals in good to excellent yields. Furthermore, an unusual dethiolating Diels–Alder reaction of these cyclopentadienes with maleimides was discovered, which yielded novel fluorescent polycyclic compounds.

Copper Hydrides

A. J. Edwards, R. S. Dhayal, P.-K. Liao, J.-H. Liao, M.-H. Chiang, R. O. Piltz, S. Kahlal, J.-Y. Saillard, C. W. Liu* **7214 – 7218**

Chinese Puzzle Molecule: A 15 Hydride, 28 Copper Atom Nanoball

Front Cover

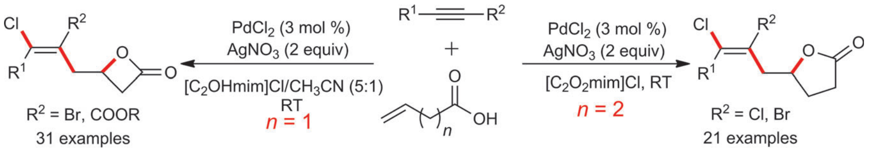


Rhombicuboctahedral nanoclusters: Two isostructural and concentric clusters [Cu$_{28}$(H)$_{15}$(S$_2$CNR)$_{12}$]PF$_6$ (NR = N^{n}Pr$_2$, aza-15-crown-5) are air- and moisture-stable and were prepared through a one-pot synthesis. The presence of capping, truncating, and interstitial hydrides within the metal framework was confirmed by single-crystal neutron diffraction and reproduced by DFT calculations.

Synthetic Methods

J. Li, W. Yang, S. Yang,* L. Huang, W. Wu, Y. Sun, H. Jiang* **7219 – 7222**

Palladium-Catalyzed Cascade Annulation To Construct Functionalized β- and γ-Lactones in Ionic Liquids

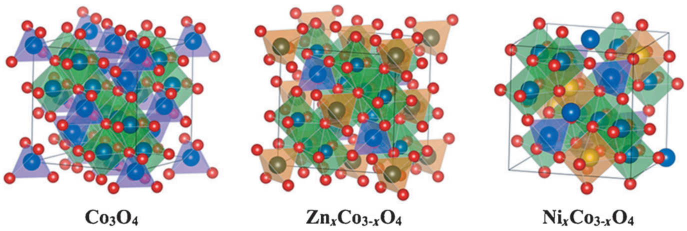


Four in one: A highly efficient and mild palladium-catalyzed, one-pot, four-step cascade annulation has been developed to afford the title compounds in moderate to good yields with high regio- and diastereoselectivities in ionic liquids, thus making the transformation green and practical. In particular, this reaction provides a novel and convenient methodology for the construction of naturally occurring biologically active β- and γ-lactones.

Nanoarray Catalysts

Z. Ren, V. Botu, S. Wang, Y. Meng, W. Song, Y. Guo, R. Ramprasad, S. L. Suib, P.-X. Gao* **7223 – 7227**

Monolithically Integrated Spinel M$_x$Co$_{3-x}$O$_4$ (M = Co, Ni, Zn) Nanoarray Catalysts: Scalable Synthesis and Cation Manipulation for Tunable Low-Temperature CH$_4$ and CO Oxidation

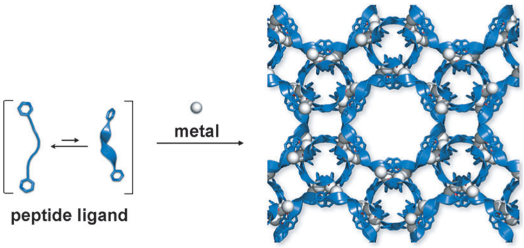

Co$_3$O$_4$ Zn$_x$Co$_{3-x}$O$_4$ Ni$_x$Co$_{3-x}$O$_4$

Industrial-scale fabrication of spinel nanoarray monolithic catalysts is presented. The catalytic performance is tunable towards different low-temperature catalytic oxidation by rationally manipulated cation occupancy and concentration, which lead to controlled gas adsorption–desorption behavior and adjusted surface-oxygen defect population.

Peptide Folding and Assembly

T. Sawada,* A. Matsumoto,
M. Fujita* ______ **7228 – 7232**

Coordination-Driven Folding and Assembly of a Short Peptide into a Protein-like Two-Nanometer-Sized Channel

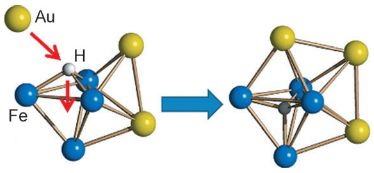


Silver(I) coordination induces the folding and assembly processes of a short peptide ligand containing the Gly-Pro-Pro sequence in aqueous alcohol, giving rise to a single crystal composed of polyproline II helices. This peptide-folded porous crystal possesses two-nanometer-sized helical nanochannels, which efficiently take up anions, organic chiral molecules, and bio-oligomers.

Metal Hydride Clusters

M. Bortoluzzi, I. Ciabatti, C. Femoni,
M. Hayatifar, M. C. Iapalucci, G. Longoni,
S. Zacchini* ______ **7233 – 7237**

Hydride Migration from a Triangular Face to a Tetrahedral Cavity in Tetranuclear Iron Carbonyl Clusters upon Coordination of $[AuPPh_3]^+$ Fragments

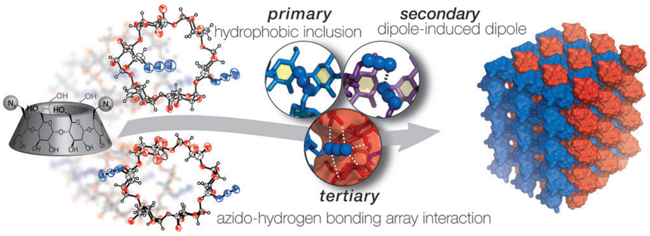


Caught in a trap: The first low-valent molecular metal cluster containing an interstitial four-coordinate hydride ion in a tetrahedral site has been obtained and fully characterized. Its formation proceeds via hydride migration from the surface to the tetrahedral cavity of the tetra-iron cage after addition of a $[AuPPh_3]^+$ fragment.

Azido Interactions

M. Ménand,* S. Adam de Beaumais,
L.-M. Chamoreau, E. Derat, S. Blanchard,
Y. Zhang, L. Bouteiller,
M. Sollogoub* ______ **7238 – 7242**

Solid-State Hierarchical Cyclodextrin-Based Supramolecular Polymer Constructed by Primary, Secondary, and Tertiary Azido Interactions

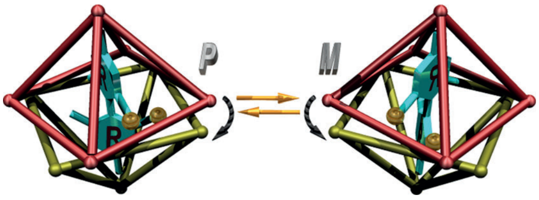


Self-assembled polymer: The crystallization of a di-azido-α-cyclodextrin revealed a polymeric self-assembly involving a variety of azido-type interactions. The crystal arrangement relies on the cooperativity of a primary azido inclusion, a secondary azido–azido interaction involving an unprecedented distribution of canonical forms, and a tertiary azido–hydrogen bonding array located in the groove of a CD-based polymeric helix.

Supramolecular Chirality

Y. Tsunoda, K. Fukuta, T. Imamura,
R. Sekiya, T. Furuyama, N. Kobayashi,
T. Haino* ______ **7243 – 7247**

High Diastereoselection of a Dissymmetric Capsule by Chiral Guest Complexation



Guests in a twist: Coordination-driven self-assembly of an achiral cavitand produced a dissymmetric capsule. Interconversion of the *P* and *M* helicities of the capsule was biased by the encapsulation of a chiral guest with remarkable diastereoselectivity. The absolute helicity of the diastereomeric complex was determined based on CD exciton coupling theory and DFT calculations.

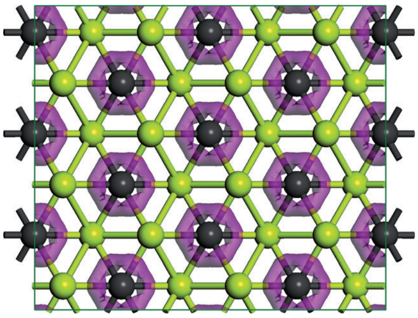
Planar Hexacoordinate Carbon

Y. Li,* Y. Liao, Z. Chen* ____ **7248 – 7252**

Be$_2$C Monolayer with Quasi-Planar Hexacoordinate Carbons: A Global Minimum Structure

Inside Back Cover

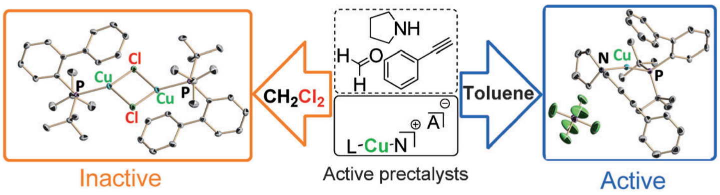
Promising material: In the two-dimensional Be$_2$C monolayer, each carbon atom binds to six Be atoms forming a quasi-planar hexacoordinate carbon moiety (see structure; C black, Be green). Be$_2$C monolayer has good stability and is the global minimum structure in 2D space. Further, it is semiconducting with a moderate direct band gap.



Homogeneous Catalysis

A. Grirrane,* E. Álvarez, H. García,*
A. Corma* ____ **7253 – 7258**

Deactivation of Cationic Cu^{I} and Au^{I} Catalysts for A^3 Coupling by CH$_2$Cl$_2$: Mechanistic Implications of the Formation of Neutral Cu^{I} and Au^{I} Chlorides



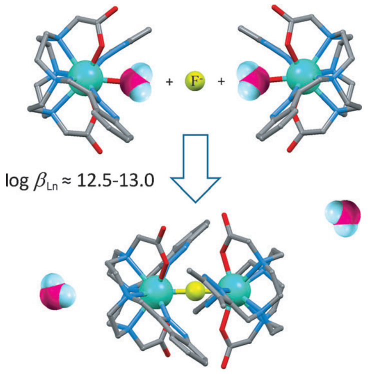
Proceed with caution! Care should be exercised when using CH$_2$Cl$_2$ as a solvent for reactions in which amines are a reagent, since undesirable deactivation of cationic Cu^{I} and Au^{I} catalysts to form the corresponding inactive neutral chloride complexes [LMCl] (M = Cu or Au) can occur as a result of the generation of hydrogen chloride in the medium. This phenomenon was studied on the basis of a Mannich three-component coupling reaction (see scheme).

Supramolecular Sensors

T. Liu, A. Nonat, M. Beyler,
M. Regueiro-Figueroa, K. Nchimi Nono,
O. Jeannin, F. Camerel, F. Debaene,
S. Cianférani-Sanglier, R. Tripier,*
C. Platas-Iglesias,*
L. J. Charbonnière* ____ **7259 – 7263**

Supramolecular Luminescent Lanthanide Dimers for Fluoride Sequestering and Sensing

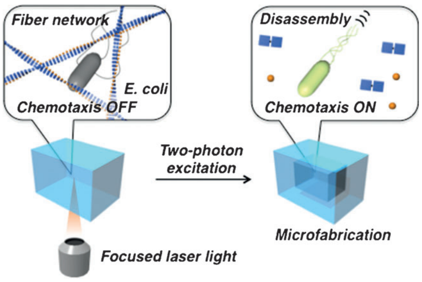
Fluoride anions can be detected at the nanomolar level in aqueous solution with a luminescent europium complex that forms dimeric supramolecular assemblies. The fluoride-containing complexes are stabilized by a bridging Eu–F–Eu coordination mode, π–π stacking interactions, and a hydrogen-bonding network, which control the assembly of the two europium complexes around the fluoride anion.



Supramolecular Hydrogels

T. Yoshii, M. Ikeda,
I. Hamachi* ____ **7264 – 7267**

Two-Photon-Responsive Supramolecular Hydrogel for Controlling Materials Motion in Micrometer Space

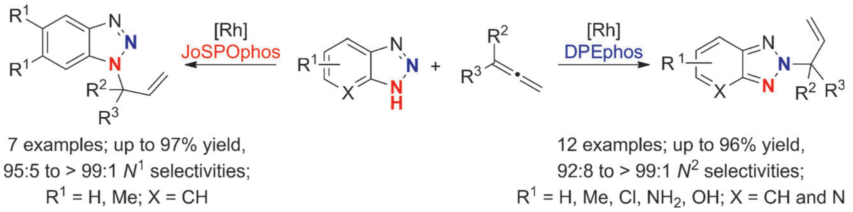


Exciting developments: Fluidity inside a supramolecular hydrogel consisting of a nanofiber network has been controlled in a spatiotemporal manner by two-photon excitation. The off–on switching of the Brownian motion of nanobeads and the chemotaxis of bacteria by two-photon excitation was successfully demonstrated (see picture).

Heterocycles

K. Xu, N. Thieme, B. Breit* **7268 – 7271**

Unlocking the N^2 Selectivity of Benzotriazoles: Regiodivergent and Highly Selective Coupling of Benzotriazoles with Allenes

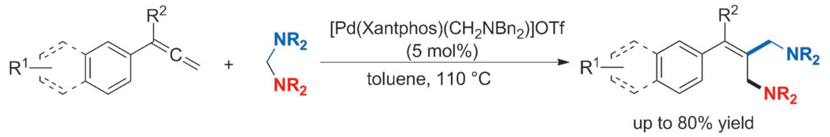


Ligand control: Exceptionally high N^2 and N^1 selectivities have been achieved in the rhodium-catalyzed coupling of benzotriazoles with allenes by using DPEphos and JoSPOphos, respectively (see scheme). This method permits the atom-economic synthesis of valuable branched N^2- and N^1-allylated benzotriazole derivatives.

C–N Activation

J. Hu, Y. Xie, H. Huang* **7272 – 7276**

Palladium-Catalyzed Insertion of an Allene into an Aminal: Aminomethylamination of Allenes by C–N Bond Activation

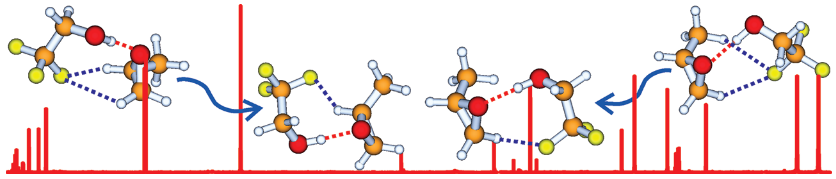


Break to link: The direct insertion of an allene into the C–N bond of an aminal in the presence of a palladium catalyst is described. This new method is concise and operationally simple and can be used for the atom-economic synthesis of a broad range of 1,3-diamines. The reaction involves cleavage of the C–N bond, formation of a π-allylpalladium intermediate, and nucleophilic addition.

Rotational Spectroscopy

J. Thomas, W. Jäger, Y. Xu* **7277 – 7280**

Chirality Induction and Amplification in the 2,2,2-Trifluoroethanol···Propylene Oxide Adduct

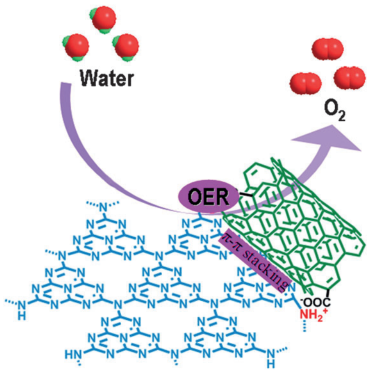


In the open: A broadband rotational spectroscopic investigation reveals that 2,2,2-trifluoroethanol (TFE)···propylene oxide (PO) exhibits noticeable chirality amplification: *g*+ TFE···*S*-PO was found to be favored over that of *g*− TFE···*S*-PO by a factor of 2.8 at 60 K. All the observed TFE··PO conformers take on the open geometry, in contrast to 2-fluoroethanol···PO which prefers the closed form. Perfluorination at CH_3 increases the binding energy of TFE···PO by 70% over its ethanol counterpart.

Oxygen Evolution

T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao* **7281 – 7285**

Graphitic Carbon Nitride Nanosheet–Carbon Nanotube Three-Dimensional Porous Composites as High-Performance Oxygen Evolution Electrocatalysts

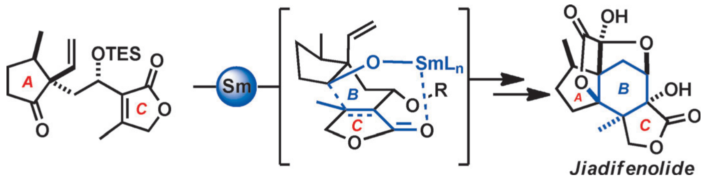


Combining C and N to make O: 3D porous graphitic carbon nitride nanosheet–carbon nanotube composites have been synthesized through a spontaneous assembly process. The high nitrogen content, enhanced electron conductivity, and improved mass transport result in excellent catalytic oxygen evolution activity and strong durability, superior to those reported for other nonmetal catalysts and noble-metal catalysts (see figure; OER: oxygen evolution reaction).

Natural Product Synthesis

I. Paterson,* M. Xuan,
S. M. Dalby* ______________ 7286 – 7289

Total Synthesis of Jiadifenolide



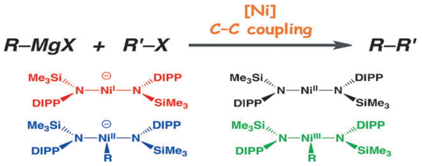
Synthetic adventure: The total synthesis of the pentacyclic sesquiterpenoid jiadifenolide, a potent neurite outgrowth promoter, is reported. The synthesis showcases an adventurous samarium-mediated cyclization reaction to establish the ABC-tricyclic core and adjacent quaternary stereocenters. Late-stage oxidation of a pendant vinyl group completes the highly stereocontrolled assembly of this intricate structure.

Ni-Catalyzed C–C Coupling

M. I. Lipschutz, T. D. Tilley* 7290 – 7294

Carbon–Carbon Cross-Coupling Reactions Catalyzed by a Two-Coordinate Nickel(II)–Bis(amido) Complex via Observable Ni^{I}, Ni^{II}, and Ni^{III} Intermediates

Cross-examination: The C–C coupling of aryl halides with Grignard reagents in the presence of a two-coordinate nickel complex has been identified and evaluated mechanistically. A Ni^{III}–alkyl species was isolated and fully characterized and compelling experimental evidence was found of the role played by this species as well as those of other key Ni^{I} and Ni^{II} intermediates in the catalytic cycle (see scheme, DIPP = 2,6-diisopropylphenyl).

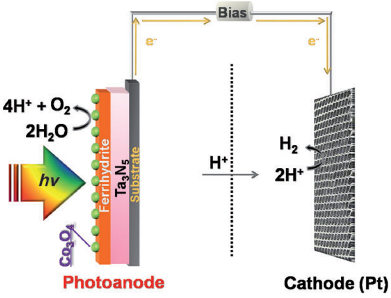


Photoelectrochemistry

G. Liu, J. Shi, F. Zhang, Z. Chen, J. Han, C. Ding, S. Chen, Z. Wang, H. Han, C. Li* ______________ 7295 – 7299

A Tantalum Nitride Photoanode Modified with a Hole-Storage Layer for Highly Stable Solar Water Splitting

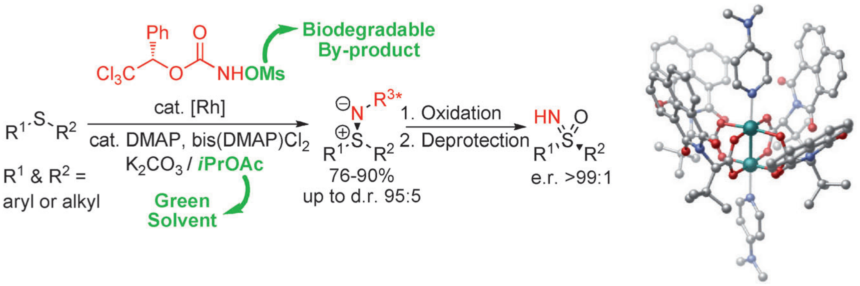
The presence of a ferrihydrite layer allows stable water oxidation at the Co_3O_4/ferrihydrite/Ta_3N_5 photoanode for at least 6 h. This is the Ta_3N_5-based photoanode that is the most durable against photocorrosion reported to date. The role of the ferrihydrite layer is a hole-storage layer, increasing the hole-storage capacity and suppressing photocorrosion of Ta_3N_5 electrode.



Chiral Sulfilimines

H. Lebel,* H. Piras,
J. Bartholoméüs ______________ 7300 – 7304

Rhodium-Catalyzed Stereoselective Amination of Thioethers with *N*-Mesyloxycarbamates: DMAP and Bis(DMAP)CH_2Cl_2 as Key Additives



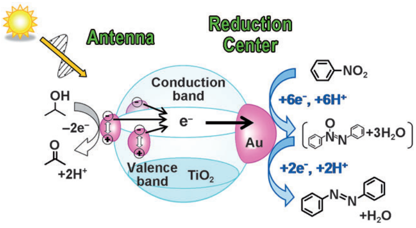
The select committee: A mixture of 4-dimethylaminopyridine (DMAP) and bis(DMAP)CH_2Cl_2 proved pivotal in achieving high selectivity in the Rh-catalyzed intermolecular amination of thioethers with a readily available chiral *N*-mesyloxycarbamate to produce sulfilimines in excellent yields. Mechanistic studies suggest a Rh^{II}-Rh^{III} complex to be the catalytically active species.

Photocatalysis

S. Naya, T. Niwa, T. Kume, H. Tada* ——— 7305 – 7309

Visible-Light-Induced Electron Transport from Small to Large Nanoparticles in Bimodal Gold Nanoparticle-Loaded Titanium(IV) Oxide

Visible-light-induced electron transport: Visible-light irradiation of TiO_2-supported gold nanoparticles (NPs) with a bimodal size distribution (BM-Au/TiO_2) gives rise to long-range electron transport from about 14 small NPs to one large Au NP through the conduction band of TiO_2. As a result of the enhancement of the charge separation, BM-Au/TiO_2 exhibits a high level of visible-light activity for the synthesis of azobenzenes (see picture) from nitrobenzenes.

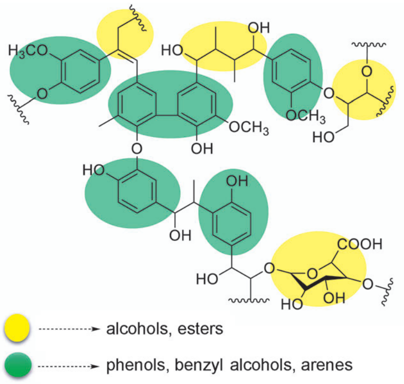


Biomass Conversion

R. Ma, W. Y. Hao, X. L. Ma, Y. Tian, Y. D. Li* ——— 7310 – 7315

Catalytic Ethanolysis of Kraft Lignin into High-Value Small-Molecular Chemicals over a Nanostructured α-Molybdenum Carbide Catalyst

Krafty upgrade of a waste product: Kraft lignin was fully depolymerized into C_6–C_{10} liquid products (see scheme) over a nanostructured α-molybdenum carbide catalyst in supercritical ethanol. In this process, which can be regarded as a fundamental finding for the upgrade of Kraft lignin to bio-oils under mild conditions, lignin fragments are rapidly stabilized with ethanol on the surface of the catalyst.

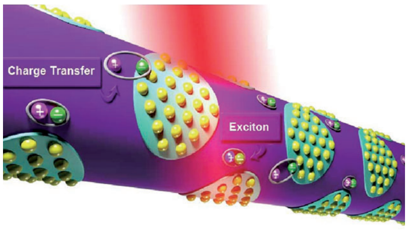


Nanocluster

W. Qin, J. Lohrman, S. Ren* 7316 – 7319

Magnetic and Optoelectronic Properties of Gold Nanocluster–Thiophene Assembly

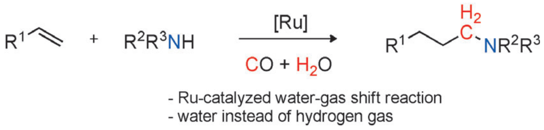
Nanohybrids consisting of Au nanocluster and polythiophene nanowire assemblies (see picture) exhibit unique thermal-responsive optical behaviors and charge-transfer controlled magnetic and optoelectronic properties. The Au nanoclusters enhance photoabsorption and conductivity, leading to an increase of power conversion efficiency by 14%.



Amine Synthesis

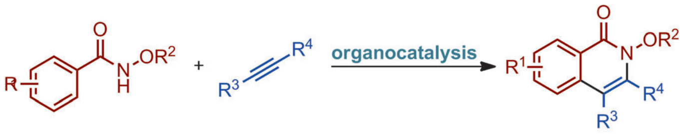
S. Gülak, L. Wu, Q. Liu, R. Franke, R. Jackstell, M. Beller* ——— 7320 – 7323

Phosphine- and Hydrogen-Free: Highly Regioselective Ruthenium-Catalyzed Hydroaminomethylation of Olefins



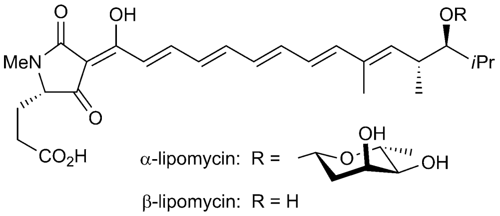
HAM it up: A highly regioselective ruthenium-catalyzed synthesis of amines, through hydroaminomethylation (HAM), is reported. This novel procedure is practical (P-ligand-free, one pot) and economic (low catalyst loading and inexpensive metal). Bulk industrial as well as functionalized olefins give the corresponding tertiary amines in high yields (up to 92%) with excellent regioselectivities (*n*/*iso* > 99:1) and full chemoselectivity.

Organocatalysis



Annulation without hesitation: *N*-alkoxybenzamides convert into isoquinolones smoothly and rapidly under organocatalytic conditions. The annulation of unsymmetrical diarylacetylenes proceeds with a high regioselectivity. The transformation is based on the hypervalent-iodine mediated generation of nitrenium ions.

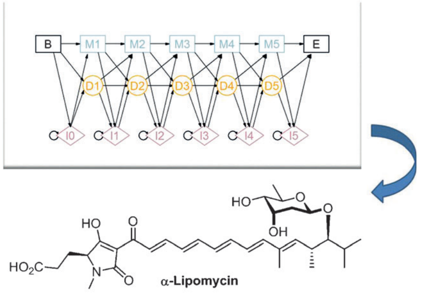
Natural Product Synthesis



Making doubly sure: 40 years ago the structures of α-lipomycin and its aglycon β-lipomycin were determined except for the configurations of the side-chain stereocenters. All of the relevant β-lipomycin candidates have now been synthesized. The optical rotation of the (12*R*,13*S*) isomer matched that of the natural product. The (12*R*,13*S*)-configured D-digitoxide was synthesized too and identified as α-lipomycin.

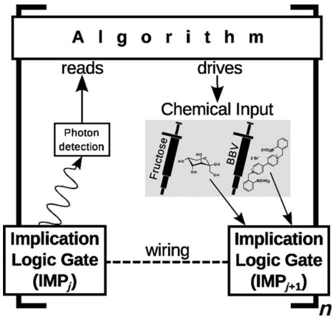
Natural Product Structures

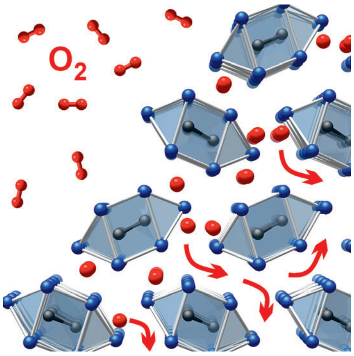
Peekaboo with stereocenters: The hidden configuration of natural products can be uncovered using a statistical model to deduce unknown configurations from amino acid sequences of ketoreductases. The synthesis of β-lipomycin finally confirms the validity of this method in particular for chiral centers in α-position.



Molecular Computing

Logic gates with sugar and light: A molecular IMP (implication function) gate can be constructed with a boronic acid sugar probe which gives a fluorescent signal as an output. An external wiring algorithm translates the fluorescent output from one gate into a chemical input for the next gate on microtiter plates. This process is demonstrated on a four-bit full adder.



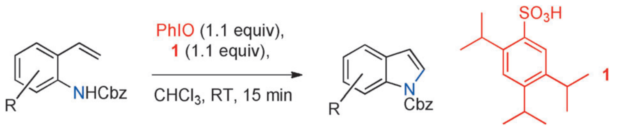


Oxygen topochemistry: Nanoparticles of Bi_3Ir, a hitherto uncharacterized intermetallic compound, reversibly intercalate oxygen from air at room temperature. In the resulting metallic suboxide, the intermetallic building units are preserved. The activation energy for oxide diffusion is one order of magnitude smaller than that in any known material. Bi_3IrO_x is the first metallic oxide ion conductor and also the first that operates at room temperature.

Oxide Ion Conductor

M. Heise, B. Rasche, A. Isaeva,
A. I. Baranov, M. Ruck,* K. Schäfer,
R. Pöttgen, J.-P. Eufinger,
J. Janek ______ **7344–7348**

A Metallic Room-Temperature Oxide Ion Conductor

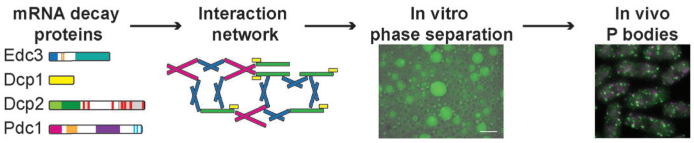


Convenient route to indole: A fast, productive, and operationally simple indole synthesis was developed. The oxidative cyclization of 2-vinyl anilines with iodosobenzene and the sterically congested aryl sulfonic acid **1** provides an efficient and convenient access to the indole core (see scheme; Cbz = benzyloxycarbonyl).

Indole Synthesis

L. Fra, A. Millán, J. A. Souto,
K. Muñiz* ______ **7349–7353**

Indole Synthesis Based On A Modified Koser Reagent



In phase: In vivo, components of the mRNA decay machinery can undergo a phase transition to form P-bodies. This spontaneous cellular clustering process was reconstituted using purified proteins. Intermolecular contacts between the Edc3 LSm domain and helical leucine-rich motifs in Dcp2 and Pdc1 form the backbone of the interaction network.

Protein–Protein Interactions

S. A. Fromm, J. Kamenz, E. R. Nöldeke,
A. Neu, G. Zocher,
R. Sprangers* ______ **7354–7359**

In Vitro Reconstitution of a Cellular Phase-Transition Process that Involves the mRNA Decapping Machinery

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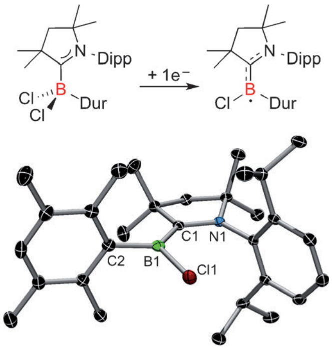


Neutral boron radicals: Reduction of dihaloborane adducts stabilized by a cyclic (alkyl)(amino)carbene leads to the isolation of neutral radicals with a boryl unit. The structure of a duryl derivative was elucidated by X-ray analysis (see picture; duryl = 2,3,5,6-tetramethylphenyl) and this radical was found to be highly stable. DFT calculations revealed that the species showed the largest spin density at boron compared to other isolated boryl radicals.

Neutral Boron Radicals

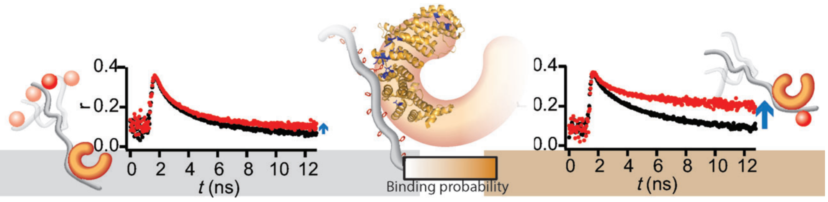
P. Bissinger, H. Braunschweig,*
A. Damme, I. Krummenacher,
A. K. Phukan, K. Radacki,
S. Sugawara ______ **7360–7363**

Isolation of a Neutral Boron-Containing Radical Stabilized by a Cyclic (Alkyl)(Amino)Carbene

Intrinsically Disordered Proteins

S. Milles, E. A. Lemke* ____ **7364 – 7367**

Mapping Multivalency and Differential Affinities within Large Intrinsically Disordered Protein Complexes with Segmental Motion Analysis



Flexible backbones: A combined fluorescence correlation and time-resolved polarization spectroscopy approach was used to study differential binding within large and disordered protein complexes with multivalent interactions. The differential segmental backbone mobility of a disordered nucleoporin in complex with transport receptors was detected. Local binding preferences were identified within the disordered protein which range over several orders of magnitude.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Regio- and Chemoselective C—H Chlorination/Bromination of Electron-Deficient Arenes by Weak Coordination and Study of Relative Directing-Group Abilities

X. Sun, G. Shan, Y. Sun,
Y. Rao* ________________ **4440–4444**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: DOI: 10.1002/anie.201300176

In Table 2 of this Communication, a couple of heteroarene structures including furan derivatives **22a** and **22b**, thiophene derivatives **23a** and **23b**, and pyrrole derivative **18** have been misassigned. Those products are not the proposed 3-halogenated compounds but they should be the 5-halogenated regioisomers. The results indicate that the electrophilic aromatic halogenation will dominate the regioselectivity in reactions of such heteroarenes under the reported conditions.

Angewandte Corrigendum

In the bottom part of Figure 2b of this Communication, the scale of the vertical axis is wrong. The correct Figure is shown here.

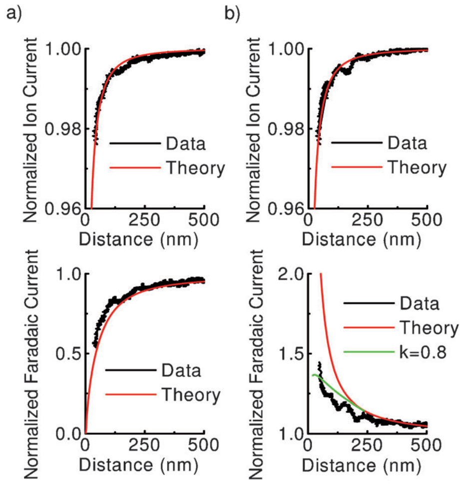

Figure 2. Approach curves of a DBCNP for simultaneous ion current (top) and electrochemical (bottom) measurements on an insulating (a) and conductive (b) substrate in 1.0 mm $FcCH_2OH$+PBS. The SECM and SICM electrodes were held at 500 and 200 mV versus a reference Ag/AgCl electrode, respectively. The RG value used for the theoretical curves was 1.5.

Multifunctional Nanoprobes for Nanoscale Chemical Imaging and Localized Chemical Delivery at Surfaces and Interfaces

Y. Takahashi, A. I. Shevchuk, P. Novak, Y. Zhang, N. Ebejer, J. V. Macpherson, P. R. Unwin, A. J. Pollard, D. Roy, C. A. Clifford, H. Shiku, T. Matsue, D. Klenerman, Y. E. Korchev* ______ **9638–9642**

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201102796