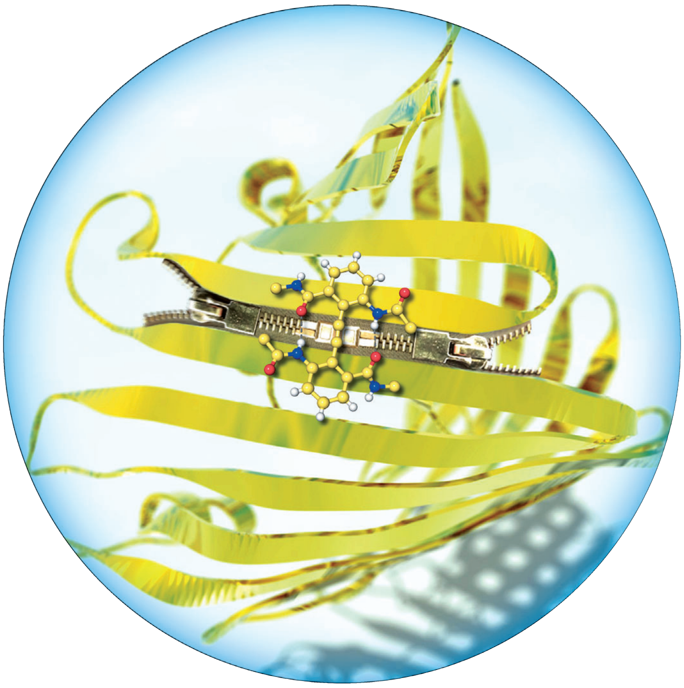
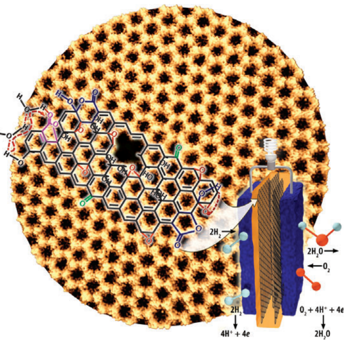
β-Sheets, key secondary structural elements ...

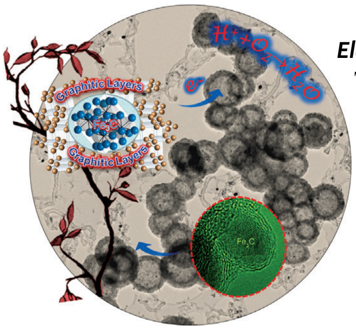


… of folded proteins, are commonly involved in therapeutically important protein–protein interactions and are a critical constituent of amyloid deposits in many neurodegenerative conditions. In their Communication on page 3650 ff., A. D. Hamilton, S. Thompson, et al. reveal a strategy for mediating these interactions through the use of a tetrasubstituted diphenylacetylene to induce the formation of β-sheet structures in two directions (illustration by Dr. Karl Harrison).

Graphene Oxides

In their Communication on page 3588 ff., A. M. Dattelbaum, P. Zelenay et al. describe the reaction of graphene oxide with ozone, which results in a significantly improved ionic (protonic) conductivity (cover artwork: Andrew Sproles).



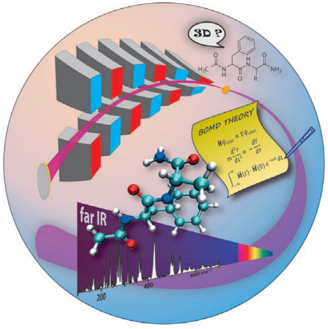


Electrocatalysis

The synthesis of hollow spheres comprising uniform iron carbide nanoparticles encased by graphitic layers is described by W. Xing, Q. F. Li et al. in the Communication on page 3675 ff. The spheres show excellent electrocatalytic activity.

Far-IR Spectroscopy

M.-P. Gaigeot, A. M. Rijs et al. show in their Communication on page 3663 ff. that far-IR spectroscopy combined with Born–Oppenheimer molecular dynamics simulations can be used to study the conformational structure of peptides.



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Service

Author Profile

"In a spare hour, I like to watch TV.
My favorite way to spend a holiday is to go fishing …"
This and more about Xiong Wen (David) Lou can be found on page 3544.

News

C.-H. Wong

A. Fürstner

D. Nicewicz

H. Waldmann

Obituaries

Bild von Philippa Cornforth

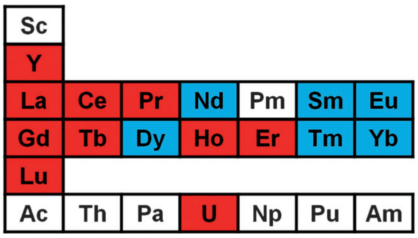
With the death of the remarkable organic chemist Sir John Warcup Cornforth, winner of the 1975 Nobel Prize in Chemistry, an era of biological chemistry has ended. His scientific achievements ranged across quite diverse areas, especially the elucidation of the stereochemistry of cholesterol biosynthesis.

Books

Highlights

Divalent Lanthanides and Uranium

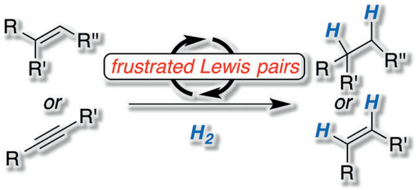
It takes two to tango: The “reduced”, divalent lanthanides M^{2+} have electronic ground-state configurations of either $4f^{n+1}5d^0$ (blue) or $4f^n5d^1$ (red). The latter may be incorporated in the spacious anions $[M(Cp')_3]^-$ and thus the single d^1 trapped in a z^2 like SOMO. This chemistry has now been transcribed to U^{2+} ($5f^36d^1$), a much sought-after species.



Minireviews

Synthetic Methods

Recent metal-free approaches to the hydrogenation of nonpolar double and triple bonds using molecular hydrogen are described. Despite transition-metal-based methodologies for these fundamental chemical transformations, metal-free alternatives are highly desirable. Such technology has only been recently introduced with the aid of frustrated Lewis pairs.



Reviews

Electrochemistry

Revealing electrochemistry: Key issues related to the electrochemistry of nanoparticles are being uncovered through innovative techniques capable of relating activity and structure, ultimately at the level of a single nanoparticle. Recent advances in experimental approaches are discussed and assessed, with particular emphasis on those that enhance the fundamental understanding of electrocatalysis and nanoscale electrochemistry.

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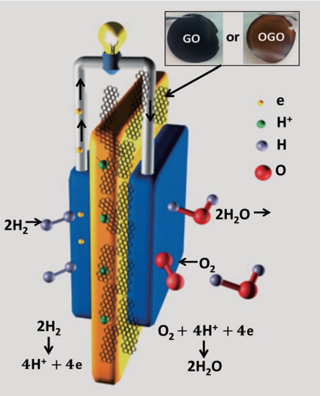
Communications



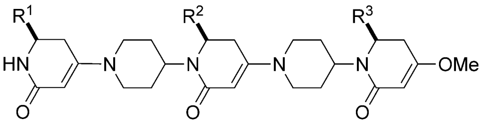
Oxidized: The reaction of graphene oxide (GO) with ozone results in a high level of oxidation that leads to a significantly improved ionic (protonic) conductivity of GO. This effect originates from enhanced proton hopping, which is due to the higher content of oxygenated functional groups in the basal planes and edges of the ozonated GO as well as the morphology changes that are caused by the ozonation.

Graphene Oxides

W. Gao, G. Wu, M. T. Janicke, D. A. Cullen, R. Mukundan, J. K. Baldwin, E. L. Brosha, C. Galande, P. M. Ajayan, K. L. More, A. M. Dattelbaum,* P. Zelenay* ______ **3588 – 3593**

Ozonated Graphene Oxide Film as a Proton-Exchange Membrane

Frontispiece



Do we know, when designing a new peptidomimetic scaffold like the one shown, how it can resemble secondary structures? Design and modular synthesis of this elongated mimic is reported, and the structure is related to ideal and real structures at PPI interfaces.

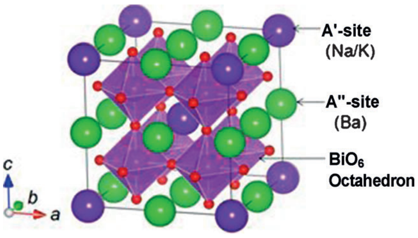
Protein–Protein Interactions

D. Xin, L. M. Perez, T. R. Ioerger, K. Burgess* ______ **3594 – 3598**

A Multifaceted Secondary Structure Mimic Based On Piperidine-piperidinones

---

A double helping: The title compound was prepared by hydrothermal reaction of $NaBiO_3 \cdot nH_2O$, $Ba(OH)_2 \cdot 8H_2O$, and KOH at 220 °C. The structure of the double perovskite was determined to be $(Na_{0.25}K_{0.45})(Ba_{1.00})_3(Bi_{1.00})_4O_{12}$, and thermally decomposed to a simple perovskite structure above 400 °C. The synthesized compounds exhibit superconductive diamagnetism, and zero resistivity below 8 K.



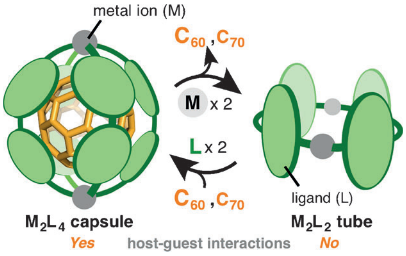
Superconductors

M. H. K. Rubel, A. Miura, T. Takei, N. Kumada,* M. Mozahar Ali, M. Nagao, S. Watauchi, I. Tanaka, K. Oka, M. Azuma, E. Magome, C. Moriyoshi, Y. Kuroiwa, A. K. M. Azharul Islam ______ **3599 – 3603**

Superconducting Double Perovskite Bismuth Oxide Prepared by a Low-Temperature Hydrothermal Reaction

---

Varying degrees of hospitality: An M_2L_4 coordination capsule and an M_2L_2 coordination tube formed from Hg^{II} hinges and bent bispyridine ligands underwent reversible interconversion at room temperature in response to changes in the metal-to-ligand ratio (see picture). Only the capsule accommodated large spherical molecules, fullerenes C_{60} and C_{70}, and the bound guests were released upon transformation into the tube by the addition of metal ions.



Transformable Capsules

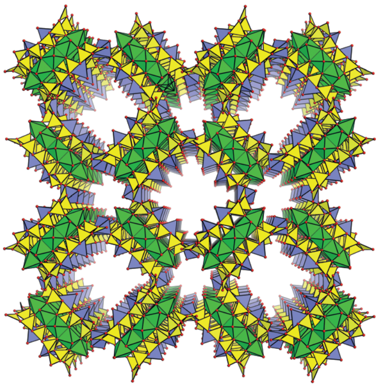
N. Kishi, M. Akita, M. Yoshizawa* ______ **3604 – 3607**

Selective Host–Guest Interactions of a Transformable Coordination Capsule/Tube with Fullerenes

Mesoporous Vanadoborates

H. Chen, Z. B. Yu, Z. Bacsik, H. Zhao,
Q. Yao, J. Sun* ______ **3608 – 3611**

Construction of Mesoporous Frameworks with Vanadoborate Clusters

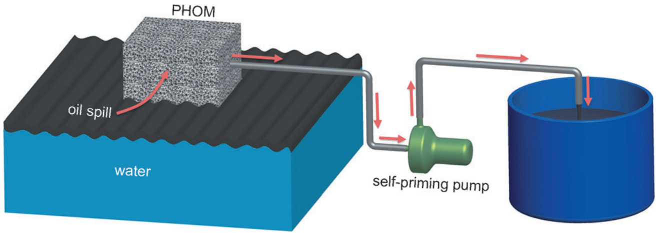


Pores for thought: A vanadoborate with a 38 × 38 × 20-ring channel system and a mesoporous pore size (24.7 × 12.7 Å) has been assembled from zinc-containing elliptical vanadoborate clusters and Zn polyhedra (see picture). CO_2 adsorption studies confirmed the porosity of the as-synthesized material. This structure demonstrates the possibility of constructing 3D ordered mesopores from inorganic cluster compounds.

Porous Materials

J. Ge, Y. D. Ye, H. B. Yao, X. Zhu, X. Wang,
L. Wu, J. L. Wang, H. Ding, N. Yong,
L. H. He, S. H. Yu* ______ **3612 – 3616**

Pumping through Porous Hydrophobic/Oleophilic Materials: An Alternative Technology for Oil Spill Remediation

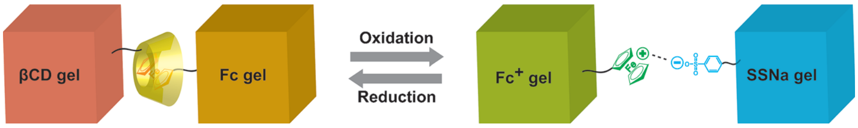


Thirsty, thirsty PHOMs: The continuous collection of oil spills in situ from the surface of water can be accomplished through external pumping on porous hydrophobic/oleophilic materials (PHOMs). Based on this novel design, oil/water separation and oil collection can be simultaneously achieved, and the oil sorption capacity is no longer limited to the volume and weight of the sorption material.

Hydrogel Self-Assembly

M. Nakahata, Y. Takashima,
A. Harada* ______ **3617 – 3621**

Redox-Responsive Macroscopic Gel Assembly Based on Discrete Dual Interactions



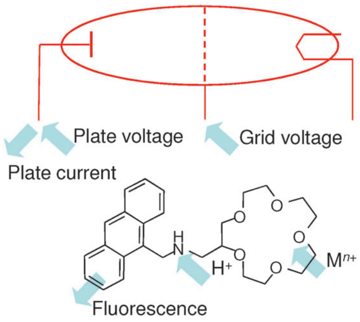
Changing partner on cue: The interaction between poly(acrylamide)-based hydrogels modified with β-cyclodextrin (βCD gel), ferrocene (Fc gel), and sodium *p*-styrenesulfonate (SSNa gel) was investigated. The βCD gel and the Fc gel selectively assembled with one another through a host–guest interaction (see picture). On the other hand, when Fc was oxidized to Fc^+, the Fc^+ gel selectively adhered to the SSNa gel through a cation–anion interaction.

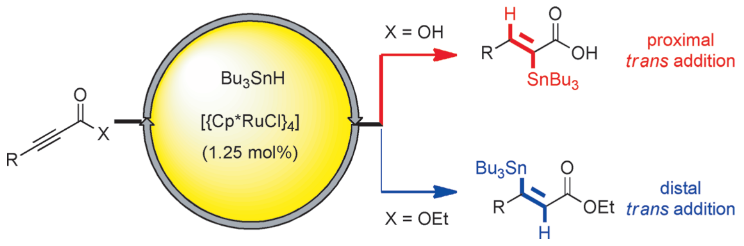
Molecular Devices

A. J. M. Huxley, M. Schroeder,
H. Q. Nimal Gunaratne,
A. Prasanna de Silva* ______ **3622 – 3625**

Modification of Fluorescent Photoinduced Electron Transfer (PET) Sensors/Switches To Produce Molecular Photo-Ionic Triode Action

Making the switch: A fluorophore-spacer$_1$-receptor$_1$-spacer$_2$-receptor$_2$ system has been developed that shows ionically tunable proton-induced off-on switching of fluorescence, reminiscent of thermionic triode behavior. The three-electrode concept of the triode is also followed in the photo-ionic system by the use of three active units within the structure (see picture).



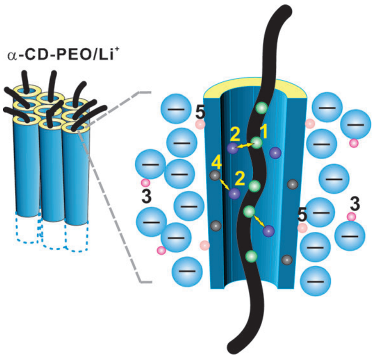


Unorthodox: Ruthenium catalysts allow stannanes to be added in a *trans* fashion across the triple bonds of terminal, internal, silylated, and chlorinated alkynes. This pattern violates the basic mechanism of transition-metal catalysis which otherwise secures high *cis* selectivity in hydrometalations. Cooperative effects between the ruthenium species and protic functionality render reactions of unsymmetrical substrates regioselective. $Cp^* = \eta^5$-C_5Me_5.

Reaction Mechanisms

S. M. Rummelt,
A. Fürstner* ________ **3626 – 3630**

Ruthenium-Catalyzed *trans*-Selective Hydrostannation of Alkynes

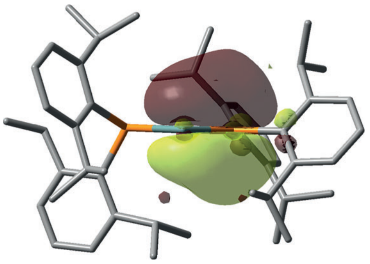


A new category of crystalline polymer electrolyte has been prepared by the supramolecular self-assembly of PEO (see picture, black), α-cyclodextrin (α-CD, blue), and $LiAsF_6$. In this polymer electrolyte, the nanochannels formed by α-CD provide the pathway for the directional motion of Li^+ ions (colored spheres, 5 different environments) and at the same time prevent access of the anions by size exclusion, thereby resulting in good separation of the Li^+ ions and the anions.

Solid Polymer Electrolytes

L.-Y. Yang, D.-X. Wei, M. Xu, Y.-F. Yao,*
Q. Chen* ________ **3631 – 3635**

Transferring Lithium Ions in Nanochannels: A PEO/Li^+ Solid Polymer Electrolyte Design

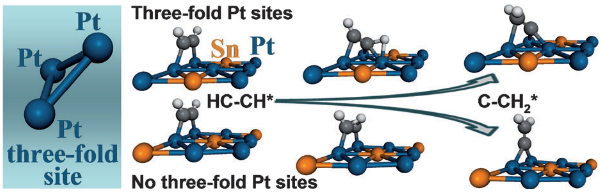


On a plane: An unusual sterically hindered diphosphagermylene $(R_2P)_2Ge$ has been synthesized (see picture; R = 2,6-$iPr_2C_6H_3$). This compound possesses a trigonal planar phosphorus atom; the planarity is due to extensive delocalization of the phosphorus lone pair into the vacant p-orbital at germanium. DFT calculations indicate that the Ge–P bond has significant multiple bond character.

Planar Phosphorus

K. Izod,* D. G. Rayner, S. M. El-Hamruni,
R. W. Harrington, U. Baisch **3636 – 3640**

Stabilization of a Diphosphagermylene through pπ–pπ Interactions with a Trigonal-Planar Phosphorus Center



A preferential catalytic mechanism has been identified for the transformation of acetylene to vinylidene on Pt-Sn surfaces. Unlike a direct H shift along the C–C bond in organometallic compounds, this mechanism requires three adjacent Pt atoms. The same requirement is identified for C–H bond cleavage. Without three-fold Pt sites, the reaction mechanism changes, and reactions of H transfer and C–H bond cleavage are suppressed.

Heterogeneous Catalysis

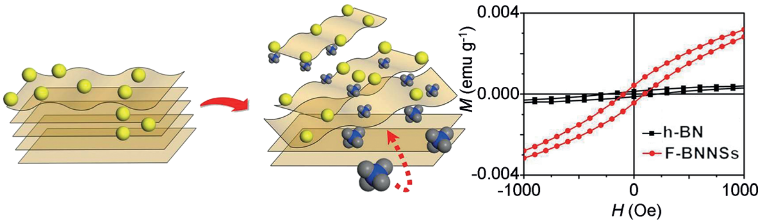
J. Gao, H. Zhao, X. Yang, B. E. Koel,*
S. G. Podkolzin* ________ **3641 – 3644**

Geometric Requirements for Hydrocarbon Catalytic Sites on Platinum Surfaces

Nanosheet Exfoliation

M. Du, X. L. Li, A. Z. Wang, Y. Z. Wu,
X. P. Hao,* M. W. Zhao* ___ **3645 – 3649**

One-Step Exfoliation and Fluorination of Boron Nitride Nanosheets and a Study of Their Magnetic Properties



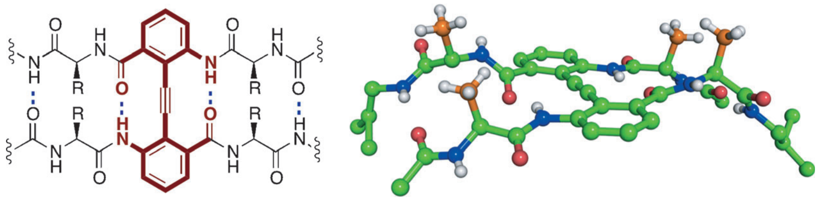
Wafer-thin and mint condition: Fluorinated hexagonal boron nitride nanosheets (F-BNNSs) can be prepared by using ammonium fluoride to exfoliate and fluorinate hexagonal boron nitride. The as-prepared products can exhibit ferromagnetic characteristics at room temperature, which would have good potential applications in spintronic devices.

Peptidomimetics

H. Lingard, J. T. Han, A. L. Thompson,
I. K. H. Leung, R. T. W. Scott,
S. Thompson,*
A. D. Hamilton* ___ **3650 – 3653**

Diphenylacetylene-Linked Peptide Strands Induce Bidirectional β-Sheet Formation

Front Cover



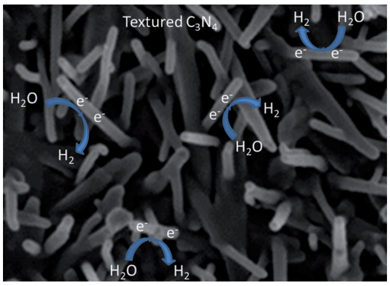
The importance of β-sheet structures at the interface of protein–protein interactions has prompted the development of a range of synthetic strategies to template and stabilize this secondary structural motif. A tetrasubstituted diphenylacetylene is examined as a central nucleating point for the projection of extended sheet structures in two directions.

Surface Chemistry

M. Shalom,* S. Gimenez, F. Schipper,
I. Herraiz-Cardona, J. Bisquert,
M. Antonietti ___ **3654 – 3658**

Controlled Carbon Nitride Growth on Surfaces for Hydrogen Evolution Electrodes

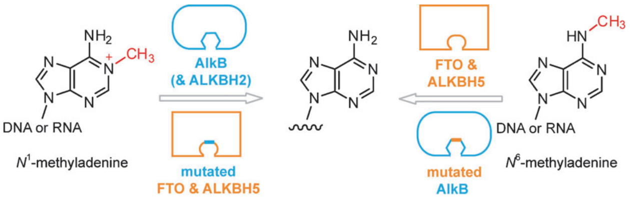
A scoff at non-nobles: The reduction of water to hydrogen using a metal-free carbon nitride (C_3N_4) electrocatalyst in neutral and alkaline environments is demonstrated. An efficient, easy, and general method for growing ordered carbon nitride on different electrodes was developed. The metal-free catalyst demonstrates low overpotential values, which are comparable to non-noble metals, with reasonable current densities.



Substrate Recognition

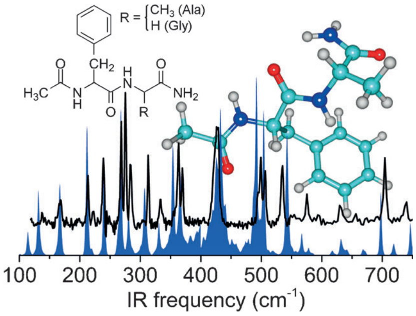
C. Zhu, C. Yi* ___ **3659 – 3662**

Switching Demethylation Activities between AlkB Family RNA/DNA Demethylases through Exchange of Active-Site Residues



Exchange program: Divergent active-site residues contribute to the substrate recognition and demethylation specificity of RNA/DNA demethylases AlkB, FTO, and ALKBH5. Swapping these residues results in partially switched demethylation activities (see picture). In the implicated inhibitor design principle, such divergent active-site sequences could aid the design of selective inhibitors that discriminate these demethylases.

The use of low-frequency modes (towards 100 cm^{-1}) for structural assignment of peptides is explored. This far-IR region possibly contains detailed information on the secondary structure. The use of Born–Oppenheimer molecular dynamics simulations is discussed to calculate the far-IR signature of peptides.

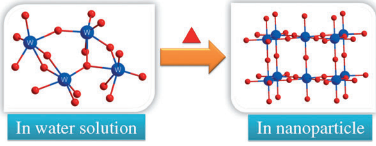


Far-IR Spectroscopy

S. Jaeqx, J. Oomens, A. Cimas, M.-P. Gaigeot,* A. M. Rijs* **3663–3666**

Gas-Phase Peptide Structures Unraveled by Far-IR Spectroscopy: Combining IR-UV Ion-Dip Experiments with Born–Oppenheimer Molecular Dynamics Simulations

Back Cover



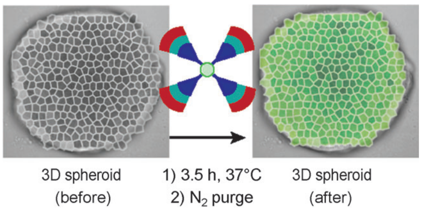
Hard facts about solution species: Nanoparticles of WO_3 crystallize from a complex precursor structure, as shown by in situ total scattering. The precursor structure exists in solution.

Nanoparticles

D. Saha, K. M. Ø. Jensen, C. Tyrsted, E. D. Bøjesen, A. H. Mamakhel, A.-C. Dippel, M. Christensen, B. B. Iversen* **3667–3670**

In Situ Total X-Ray Scattering Study of WO_3 Nanoparticle Formation under Hydrothermal Conditions

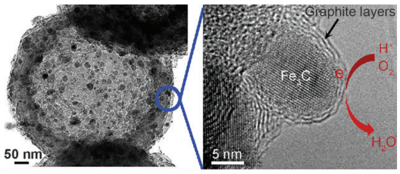
Embracing the CAOS: A click-assembled oxygen-sensing (CAOS) nanoconjugate was developed for studying oxygenation in complex tissue regions. Click-based ligation of preassembled subunits (shown as colored segments) was used to create tissue-penetrating near-infrared-emissive molecular probes, which enable oxygen-sensitive imaging within a 3D tumor spheroid model through the use of confocal phosphorescence microscopy.



In Situ Imaging

A. J. Nichols, E. Roussakis, O. J. Klein, C. L. Evans* **3671–3674**

Click-Assembled, Oxygen-Sensing Nanoconjugates for Depth-Resolved, Near-Infrared Imaging in a 3D Cancer Model



Oxygen reduction: Hollow spheres comprising uniform iron carbide (Fe_3C) nanoparticles encased by graphitic layers were synthesized (see picture). The spheres show excellent electrocatalytic activity and high stability in both acidic and alkaline media for the oxygen reduction reaction. A synergistic mechanism is proposed.

Electrocatalysis

VIP

Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing,* N. J. Bjerrum, Q. F. Li* **3675–3679**

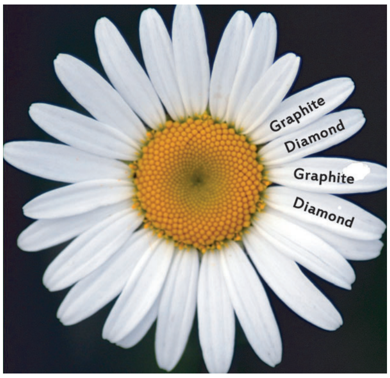
Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers as Oxygen Reduction Catalysts

Inside Back Cover

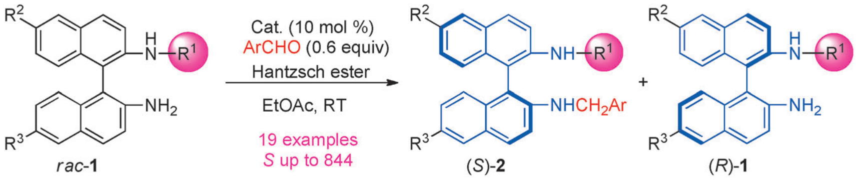
Carbon

Inside Cover

Graphite or diamond? The relative stabilities of graphite and diamond are revisited with hybrid density functional theory calculations. The electronic energy of diamond is computed to be more negative by 1.1 kJ mol^{-1} than that of graphite at a temperature of 0 K and in the absence of an external pressure.

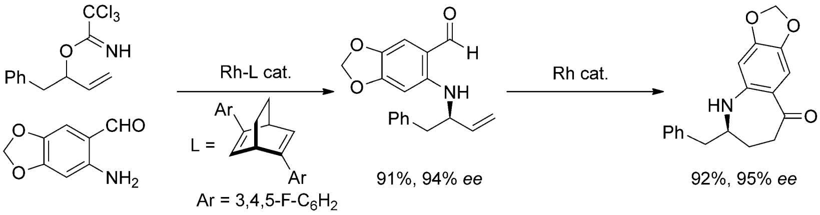


Kinetic Resolution



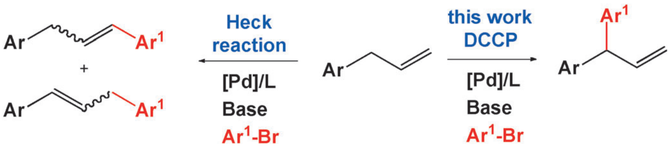
Chiral BINAMs on demand: A highly efficient strategy for the kinetic resolution of axially chiral BINAM derivatives involving a chiral Brønsted acid catalyzed imine formation and transfer hydrogenation cascade process was developed. The kinetic resolution provides a convenient route to chiral BINAM derivatives in high yields with excellent enantioselectivities.

Asymmetric Catalysis



A two-step process has been developed for the formation of enantioenriched seven-membered-ring aza ketones under mild conditions. The approach consists of a rhodium-catalyzed asymmetric amination of allylic trichloroacetimidates with 2-aminobenzaldehydes (C—N bond) followed by intramolecular hydroacylation (C—C bond) of the alkenal products and exhibits broad substrate scope and functional-group tolerance (see example).

Synthetic Methods

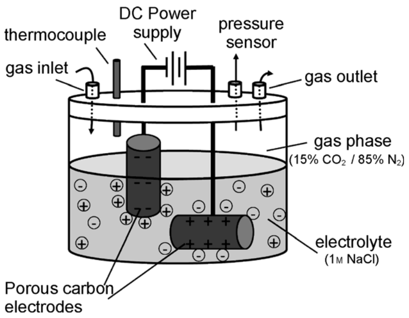


Basic chemoselectivity: Combination of aryl bromides, allylbenzene, base, and a palladium catalyst usually results in a Heck coupling reaction. With the same reagents, the Heck reaction can be circumvented when a strong base is used. While the base controls the chemoselectivity, the catalyst handles the regiochemistry, affording 1,1-diarylprop-2-enes that are inaccessible by the Heck pathway (see scheme; DCCP = deprotonative cross-coupling process).

Gas Adsorption

B. Kokoszka, N. K. Jarrah, C. Liu,
D. T. Moore,*
K. Landskron* ______ **3698 – 3701**

Supercapacitive Swing Adsorption of Carbon Dioxide

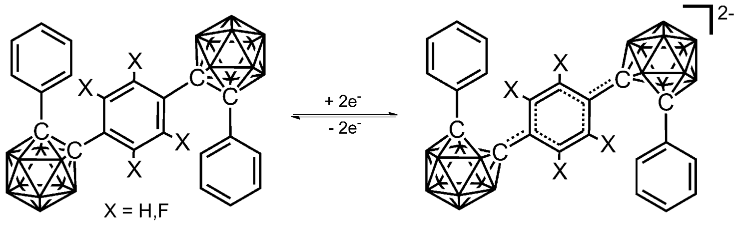


A new electrical effect, the so-called supercapacitive swing adsorption (SSA) effect, is reported for the first time. SSA enabled the reversible and selective adsorption and desorption of carbon dioxide by the capacitive charge and discharge of porous carbon materials.

Carborane Conjugation

J. Kahlert, H.-G. Stammler, B. Neumann,
R. A. Harder, L. Weber,*
M. A. Fox* ______ **3702 – 3705**

Crystal Structures of the Carborane Dianions [1,4-$(PhCB_{10}H_{10}C)_2C_6H_4]^{2-}$ and [1,4-$(PhCB_{10}H_{10}C)_2C_6F_4]^{2-}$ and the Stabilizing Role of the *para*-Phenylene Unit on $2n+3$ Skeletal Electron Clusters

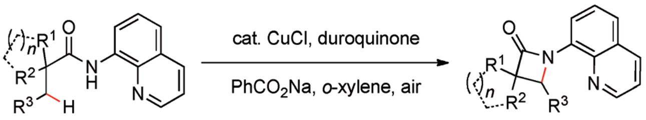


Reduction of two *ortho*-carboranyl-benzenes (see scheme) reversibly lead to the formation of stable, diamagnetic dianions which were isolated as tris(dimethoxyethane) sodium salts and characterized by X-ray crystallography and NMR spectroscopy. Both clusters in these dianions possess an unusual $2n+3$ skeletal electron count and are stabilized by π conjugation with the *para*-phenylene unit.

Homogeneous Catalysis

X.-S. Wu, Y. Zhao, G.-W. Zhang,
H.-B. Ge* ______ **3706 – 3710**

Copper-Catalyzed Site-Selective Intramolecular Amidation of Unactivated $C(sp^3)-H$ Bonds

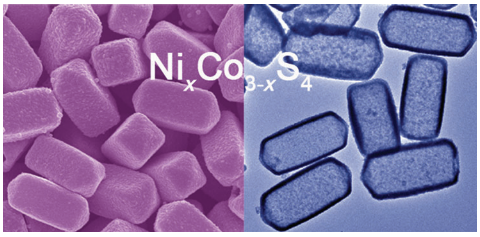


Getting ahead on tams: The intramolecular dehydrogenative amidation of aliphatic amides, directed by a bidentate ligand, was developed using a copper-catalyzed sp^3 C−H bond functionalization process to deliver β-lactams. The reaction favors the C−H bonds of β-methyl groups over the unactivated methylene C−H bonds, as well as aromatic $C(sp^2)-H$ bonds and unactivated secondary $C(sp^3)-H$ bonds of rings.

Hollow Nanostructures

L. Yu, L. Zhang, H. B. Wu,
X. W. Lou* ______ **3711 – 3714**

Formation of $Ni_xCo_{3-x}S_4$ Hollow Nanoprisms with Enhanced Pseudocapacitive Properties

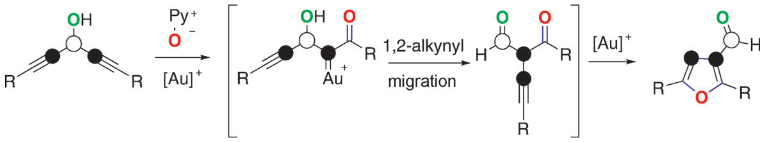


NiCo in prism: Uniform hollow $Ni_xCo_{3-x}S_4$ prisms with a tunable composition can be facilely synthesized through an efficient self-templating conversion method. Benefiting from the unique structural and compositional features, the as-obtained $Ni_xCo_{3-x}S_4$ hollow prisms show excellent electrochemical performance as electrode materials for supercapacitors.

Gold Catalysis

T. Wang, S. Shi, M. M. Hansmann,
E. Rettenmeier, M. Rudolph,
A. S. K. Hashmi* ________ **3715 – 3719**

Synthesis of Highly Substituted 3-Formylfurans by a Gold(I)-Catalyzed Oxidation/1,2-Alkynyl Migration/Cyclization Cascade



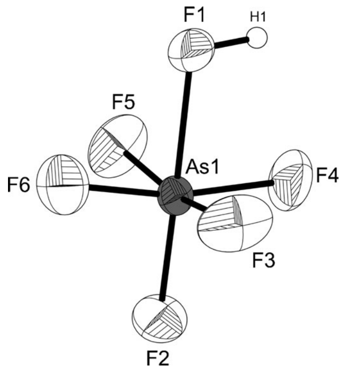
Blazing a new trail: 3-Formylfurans were prepared by a gold(I)-catalyzed cascade reaction that involves oxidation, 1,2-alkynyl migration, and cyclization from simple, easily available 1,4-diyn-3-ols. Isotope-labeling experiments and DFT calculations were carried out to elucidate the reaction mechanism.

Superacid Systems

J. Axhausen, K. Lux,
A. Kornath* ________ **3720 – 3721**

The Existence of Hexafluoroarsenic(V) Acid

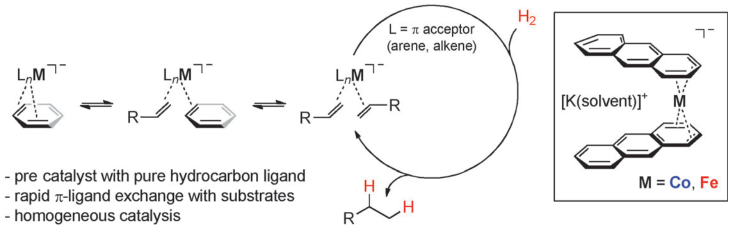
An unexpected encounter: The protonation of trimethylsilyl-*N*,*N*-dimethylcarbamate in the superacid media HF/AsF$_5$ leads under certain conditions, in addition to dimethyl ammoniumhexafluoridoarsenate [Me$_2$NH$_2$]$^+$[AsF$_6$]$^-$, to the hexafluoroarsenic(V) acid HAsF$_6$.



Hydrogenations

D. Gärtner, A. Welther, B. R. Rad, R. Wolf,*
A. Jacobi von Wangelin* ____ **3722 – 3726**

Heteroatom-Free Arene-Cobalt and Arene-Iron Catalysts for Hydrogenations

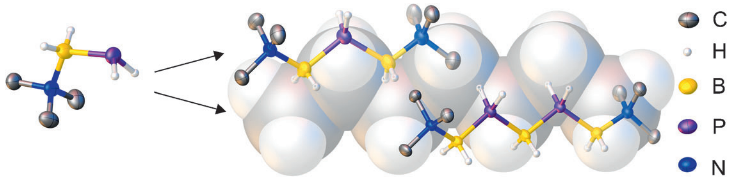


Especially high selectivities were observed in the hydrogenation of various alkenes, ketones, and imines with bis(anthracene)cobaltate(−I) [K(dme)$_2${**Co**(C$_{14}$H$_{10}$)$_2$}] under mild conditions (1–5 mol% cat., 1–10 bar H$_2$, 20–60 °C). Mechanistic studies indicate the operation in alkene hydrogenations of a homogeneous catalyst formed by initial ligand exchange and stabilized by the coordination of π-acidic alkenes or arenes.

Main-Group Chemistry

C. Marquardt, C. Thoms, A. Stauber,
G. Balázs, M. Bodensteiner,
M. Scheer* ________ **3727 – 3730**

Cationic Chains of Phosphanyl- and Arsanylboranes

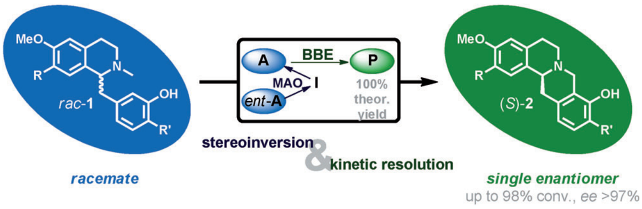


Inorganic alkanes: The monomeric Group 13/15 building blocks H$_2$EBH$_2$·NMe$_3$ (E = P, As) have been linked to form cationic chains in a straightforward synthesis in good yields. The backbone consists of alternating B and P or As atoms bearing only hydrogen substituents. DFT calculations give insight into the formation, the bonding situation, and also the structural parameters of the cationic inorganic alkanes.

Redox Deracemization

J. H. Schrittwieser, B. Groenendaal,
V. Resch, D. Ghislieri, S. Wallner,
E.-M. Fischereder, E. Fuchs, B. Grischek,
J. H. Sattler, P. Macheroux, N. J. Turner,*
W. Kroutil* ______ **3731 – 3734**

Deracemization By Simultaneous Bio-oxidative Kinetic Resolution and Stereoinversion

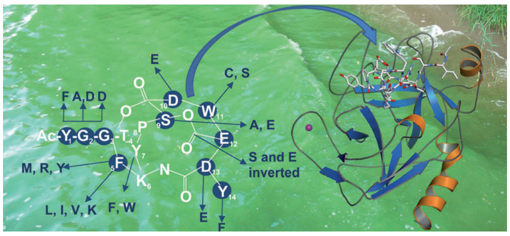


From two make one: Chemo-enzymatic stereoinversion and enzymatic kinetic resolution have been combined in a simultaneous cascade process to transform racemic substrates (**A**, *ent*-**A**) into optically pure product **P**. The concept was exemplified for benzylisoquinolines *rac*-**1** yielding optically pure berbines (*S*)-**2**. The reaction system comprised a monoamine oxidase (MAO-N), morpholine-borane, and the berberine bridge enzyme (BBE).

Tailor-Made Peptide Inhibitors

A. R. Weiz, K. Ishida, F. Quitterer,
S. Meyer, J. C. Kehr, K. M. Müller, M. Groll,
C. Hertweck, E. Dittmann* _ **3735 – 3738**

Harnessing the Evolvability of Tricyclic Microviridins To Dissect Protease–Inhibitor Interactions

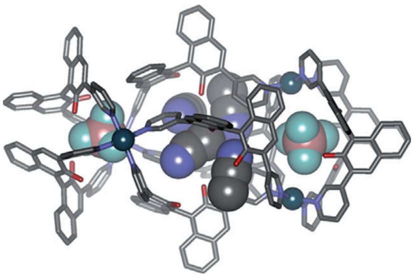


An expression platform for ribosomally produced tricyclic microviridins provides fundamental insights into protease–inhibitor interactions and sets the stage for the tailor-made design of peptides selectively targeting different serine-type proteases. The complex structure of trypsin and microviridin J uncovers the intimate protease–inhibitor interactions.

Self-Assembly

C. Klein, C. Gütz, M. Bogner, F. Topić,
K. Rissanen, A. Lützen* ___ **3739 – 3742**

A New Structural Motif for an Enantiomerically Pure Metallosupramolecular Pd_4L_8 Aggregate by Anion Templating

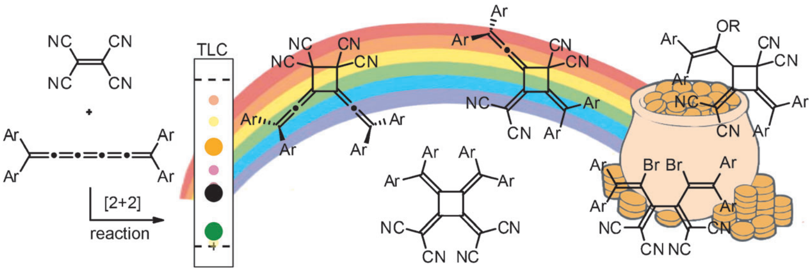


Close association: A BINOL-based bis(3-pyridyl) ligand assembles into a $[Pd_4L_8]$ complex upon coordination to Pd^{II} ions. The formation of the aggregate is templated by two BF_4^- ions that are encapsulated in peripheral cavities. The palladium ions are arranged in a distorted tetrahedral fashion, which forces the ligand to adopt two different conformations (see picture).

Reactions of [5]Cumulenes

J. A. Januszewski, F. Hampel, C. Neiss, A. Görling, R. R. Tykwinski* **3743 – 3747**

Unexpected Formation of a [4]Radialene and Dendralenes by Addition of Tetracyanoethylene to a Tetraaryl[5]cumulene



Unusual structures and interesting electronic properties characterize the cyclic products from the reaction of TCNE with tetraaryl[5]cumulene. Mechanistic investigations, aided by DFT calculations, outline a likely pathway to the observed products. The addition of MeOH, EtOH, and Br_2 to various intermediates leads to the interesting dendralene compounds.

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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