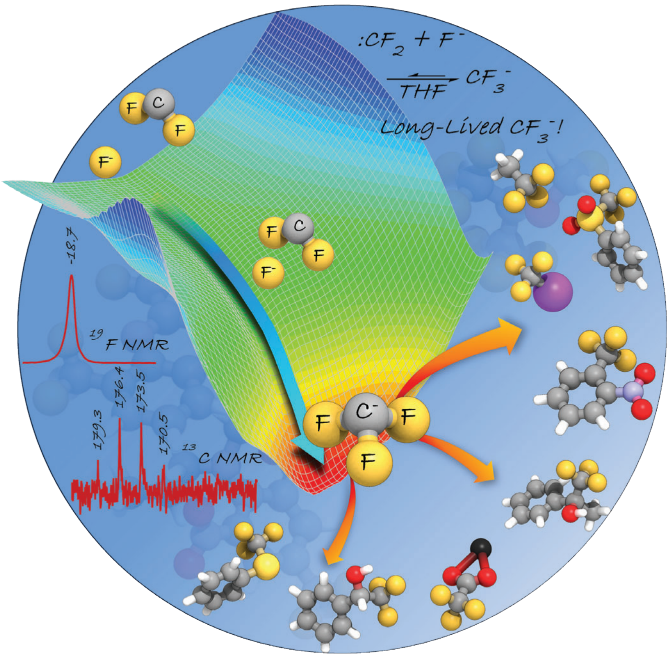
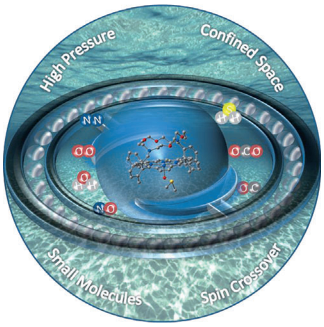
CF_3^- is a long-lived species! ...

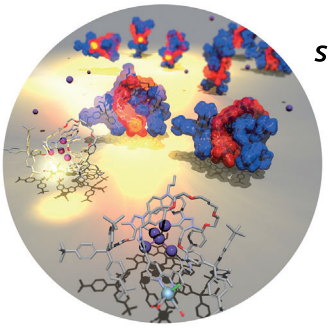


... For more than six decades, CF_3^- was believed to exist only as a short-lived and kinetically unstable species in the condensed phase. In their Communication on page 11575 ff., G. K. S. Prakash et al. have obtained the first direct evidence for the persistence of the trifluoromethanide anion in THF by NMR spectroscopy. The experiments explicitly show that CF_3^- with the $[K(18\text{-crown-}6)]^+$ counterion is quite stable at low temperatures.



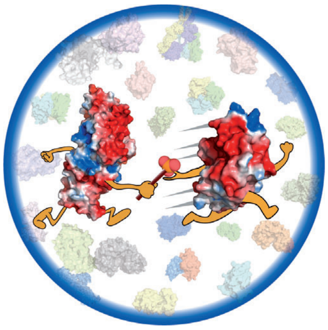
High-Pressure Chemistry

In their Communication on page 11452 ff., I. Ivanović-Burmazović et al. report the effect of confined space around a heme iron center.



Supramolecular Chemistry

In their Communication on page 11458 ff., P. D. Beer et al. describe the creation of a potent anion sensory system through the combination of halogen bonding and an optical probe in an interlocked host design.



NMR Spectroscopy

In their Communication on page 11501 ff., C. Tang, W.-P. Zhang, and co-workers show that phosphorylation can take place between two proteins with an ultra-weak binding affinity of only 25 mM and a complex lifetime in the μs–ms range.

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Service

Author Profile

"My favorite time of day is the morning—quiet moments before everyone else is awake.
In a spare hour, I go for a walk ..."
This and more about Martin Oestreich can be found on page 11408.

News

E. Nakamura

D. R. Spring

M. M. Stevens

M. Fuchter

S. L. Flitsch

G. Davies

T. B. Rauchfuss

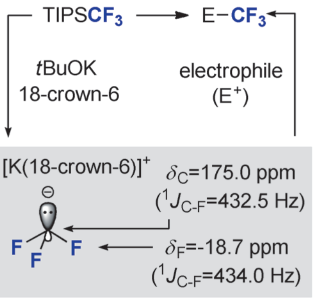
E. Bakker

A. I. Cooper

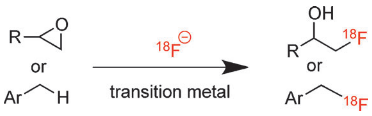
Books

Highlights

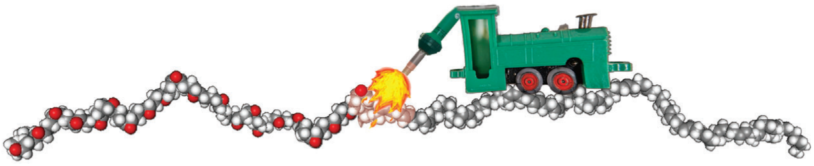
“Conditions, conditions, conditions!” Prakash et al. recently described “the long-lived trifluoromethanide anion”, thus completing a story that began decades ago. The anion can be generated in relatively large quantities and can be fully characterized by variable-temperature NMR spectroscopy. This discovery is one in a long list of reactive intermediates isolated and characterized by the Prakash/Olah group.



Without a trace? Recent advances in aliphatic radiofluorinations enabled by transition metals, specifically cobalt/salen and manganese/salen complexes, have been unveiled. These new approaches operate in a unique way which obviates the need for highly activated substrates for radiolabeling and offers a new synthetic strategy to prepare ^{18}F-labeled radiotracers.



Minireviews

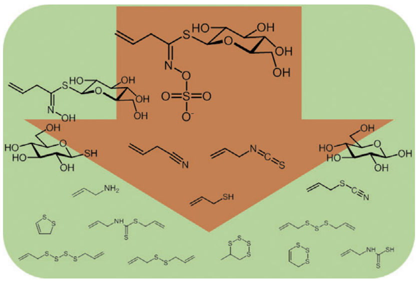


Hold the line: In processive catalysis, a catalyst binds to its substrate and performs multiple rounds of catalysis before dissociation. Nature leverages this phenomenon in its synthesis or processing of biopolymers. Processivity allows the achievement of rates of catalysis which cannot be matched by distributive systems. This Minireview describes processive catalysis and the advances that have been made in emulating it through supramolecular chemistry.

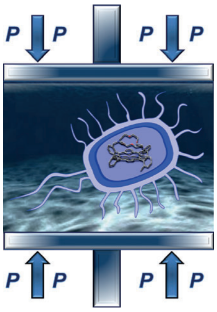
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Vegetables such as broccoli contain a variety of cancer-preventing agents, among them glucosinolates. These sulfur-containing compounds are precursors to a variety of enzymatically or chemically formed breakdown products that affect the quality of food with regard to nutritional value, flavor, and beneficial health effects. This Review provides an overview over the reactivity of glucosinolates and their breakdown products.

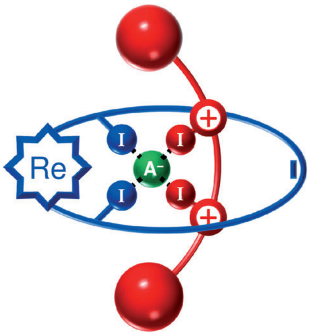


Communications

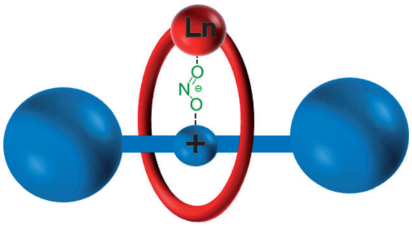


High-pressure chemistry: The effect of confined space around a heme iron center was studied. This effect is important for the adaptation of microorganisms to extreme high-pressure conditions and for the design of spin switches that can operate in reverse mode.

Sense and selectability: The first anion-templated rotaxane, assembled purely through halogen bonding, is described. A photoactive rhenium(I) bipyridyl bis(iodotriazole) macrocycle is combined with a bis(iodotriazolium)-functionalized carbazole axle to produce a rotaxane host system, which is capable of selectively sensing $\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{I^-}$ over a range of oxoanions in up to 50% H_2O/CH_3CN solvent mixtures.



“European” union: The first anion-templated synthesis of a lanthanide-containing interlocked molecule is demonstrated by the unprecedented use of a nitrite anion template. The europium [2]rotaxane is formed in high yield and is demonstrated to recognize and sense fluoride selectively.

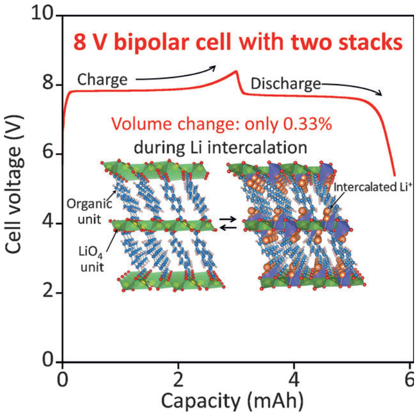


Lithium-Ion Batteries

N. Ogihara,* T. Yasuda, Y. Kishida,
T. Ohsuna, K. Miyamoto,
N. Ohba ______________ **11467 – 11472**

Organic Dicarboxylate Negative Electrode Materials with Remarkably Small Strain for High-Voltage Bipolar Batteries

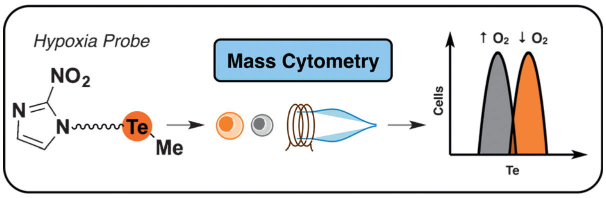
Corridors of power: 2,6-Naphthalene dicarboxylate dilithium (Naph(COOLi)$_2$), which has an organic–inorganic layered framework, shows reversible Li intercalation at a flat potential of 0.8 V. The layered framework is maintained during Li intercalation, and its volume change is only 0.33 %. An 8 V bipolar Naph(COOLi)$_2$/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cell with an Al current collector was constructed from only two cells connected in series.



Mass Cytometry

L. J. Edgar, R. N. Vellanki, A. Halupa,
D. Hedley, B. G. Wouters,
M. Nitz* ______________ **11473 – 11477**

Identification of Hypoxic Cells Using an Organotellurium Tag Compatible with Mass Cytometry



Tellurium tattletale: The identification of a compact telluroether scaffold has allowed the development of a new class of mass-cytometry-compatible reagents that do not rely on bulky metal-chelating polymers for detection. Using cellular hypoxia as a proof-of-concept target, this study demonstrates that the first-generation tellurium-bearing probe is synthetically accessible, stable under biological assay conditions, and exhibits low toxicity.

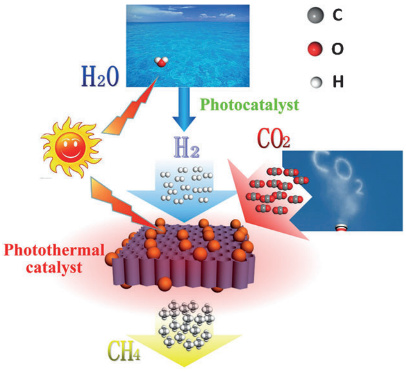
Solar Fuel Production

X. Meng, T. Wang, L. Liu, S. Ouyang,*
P. Li, H. Hu, T. Kako, H. Iwai, A. Tanaka,
J. Ye* ______________ **11478 – 11482**

Photothermal Conversion of CO$_2$ into CH$_4$ with H$_2$ over Group VIII Nanocatalysts: An Alternative Approach for Solar Fuel Production

Inside Cover

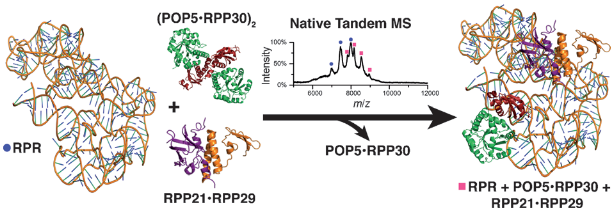
Heated by light: The photothermal conversion of CO$_2$ into CH$_4$ over Group VIII nanocatalysts provides a method for the production of solar fuels with high solar-light utilization efficiency. The overall water-based CO$_2$ conversion process is proposed to combine light-driven H$_2$ production by water splitting and photothermal CO$_2$ conversion with H$_2$.



RNA–Protein Complexes

X. Ma, L. B. Lai, S. M. Lai, A. Tanimoto, M. P. Foster, V. H. Wysocki,* V. Gopalan* ———— **11483 – 11487**

Uncovering the Stoichiometry of *Pyrococcus furiosus* RNase P, a Multi-Subunit Catalytic Ribonucleoprotein Complex, by Surface-Induced Dissociation and Ion Mobility Mass Spectrometry

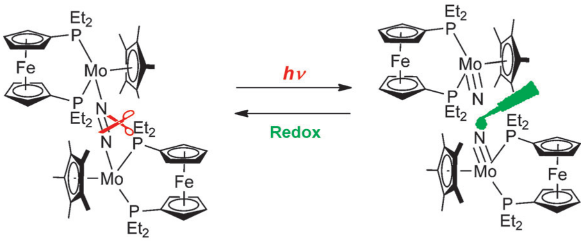


The subunit stoichiometry of archaeal RNase P, a multi-subunit ribonucleoprotein complex, was determined by surface-induced dissociation coupled with ion mobility mass spectrometry. Native MS studies with the proteins showed RPP21·RPP29 and (POP5·RPP30)$_2$ complexes, but indicated a 1:1 composition for all subunits when either one or both protein complexes bind the cognate RNA.

N_2 Cleavage and Formation

T. Miyazaki, H. Tanaka, Y. Tanabe, M. Yuki, K. Nakajima, K. Yoshizawa,* Y. Nishibayashi* ———— **11488 – 11492**

Cleavage and Formation of Molecular Dinitrogen in a Single System Assisted by Molybdenum Complexes Bearing Ferrocenyldiphosphine



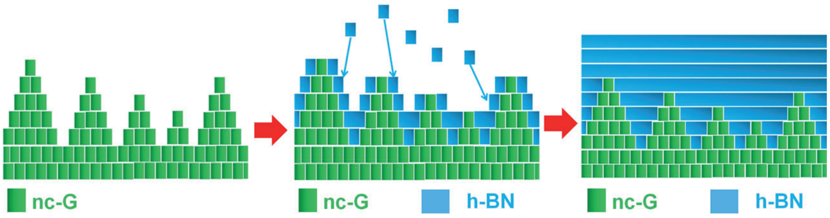
The N≡N bond bridging two molybdenum complexes (see scheme) is cleaved by visible light to afford two molybdenum nitride complexes. Conversely, the bridging N_2 is reformed by oxidation. Thus, cleavage and formation of N_2 is induced by two different external stimuli using a single system under ambient conditions.

2D Nanomaterials

VIP

K. H. Lee, H.-J. Shin, B. Kumar, H. S. Kim, J. Lee, R. Bhatia, S.-H. Kim, I.-Y. Lee, H. S. Lee, G.-H. Kim, J.-B. Yoo, J.-Y. Choi,* S.-W. Kim* ———— **11493 – 11497**

Nanocrystalline-Graphene-Tailored Hexagonal Boron Nitride Thin Films

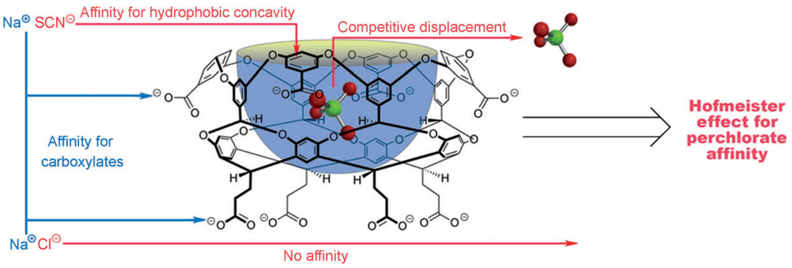


A hexagonal boron nitride (h-BN) thin film with an atomically flat surface was obtained using unintentionally formed nanocrystalline graphene (nc-G). A wafer-scale dielectric h-BN thin film was synthesized on a bare sapphire substrate with the assistance of nc-G, which prevented structural deformations during chemical vapor deposition. The sp^3-hybridized edges of nc-G play a key role during these processes.

Anion Complexation

R. S. Carnegie, C. L. D. Gibb,
B. C. Gibb* ______ **11498 – 11500**

Anion Complexation and The Hofmeister Effect

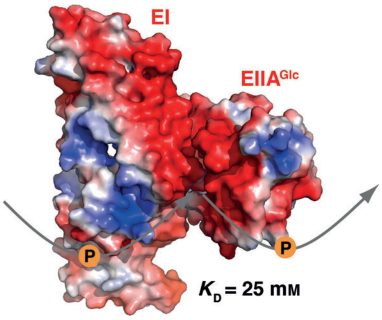


The strength of association between the hydrophobic, concave binding site of a deep-cavity cavitand and the ClO_4^- ion is controlled by co-salts in a manner that follows the Hofmeister series. A competitive binding of the co-salt anion to the hydrophobic pocket and its counterion to the external carboxylate groups accounts for the observed changes in ClO_4^- affinity.

NMR spectroscopy

Q. Xing, P. Huang, J. Yang, J.-Q. Sun,
Z. Gong, X. Dong, D.-C. Guo, S.-M. Chen,
Y.-H. Yang, Y. Wang, M.-H. Yang, M. Yi,
Y.-M. Ding, M.-L. Liu, W.-P. Zhang,*
C. Tang* ______ **11501 – 11505**

Visualizing an Ultra-Weak Protein–Protein Interaction in Phosphorylation Signaling



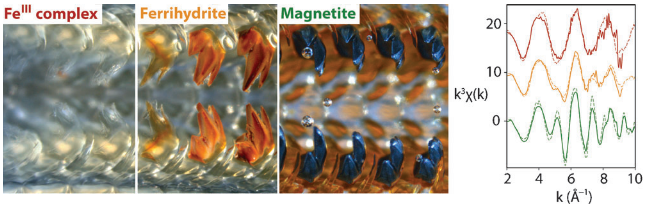
Phosphorylation signaling takes place between two bacterial enzymes EI and EIIA^{Glc}, which have a binding affinity of only 25 mM (see picture). The structure of the ultra-weak fleeting complex was determined to atomic resolution by a novel paramagnetic NMR technique, and it shows that electrostatic repulsion largely accounts for the low affinity between the two proteins.

Back Cover

Biomineralization

L. M. Gordon, J. K. Román, R. M. Everly,
M. J. Cohen, J. J. Wilker,
D. Joester* ______ **11506 – 11509**

Selective Formation of Metastable Ferrihydrite in the Chiton Tooth

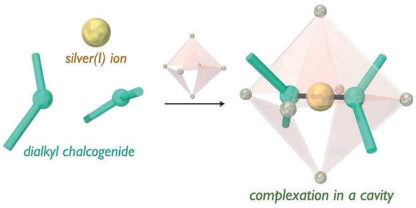


The ultrahard and self-sharpening cusp of the chiton tooth is formed by deposition of metastable ferrihydrite in an organic scaffold. Spectroscopic analysis revealed complexes of iron with acidic organic matrix molecules in "unmineralized" teeth. Furthermore, in vitro experiments demonstrated that such complexes facilitate the selective formation of ferrihydrite under physiological conditions.

Host–Guest Systems

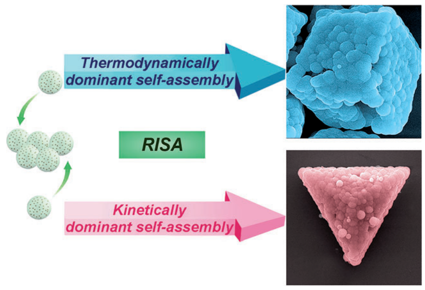
Y. Kohyama, T. Murase,
M. Fujita* ______ **11510 – 11513**

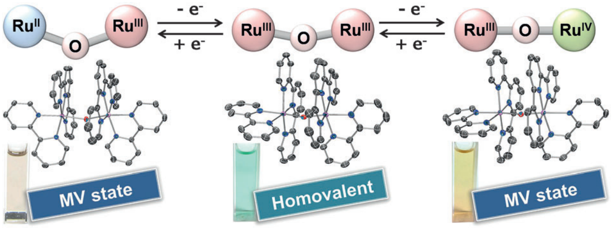
Control of Silver(I)–Dialkyl Chalcogenide Coordination by a Synthetic Cavity



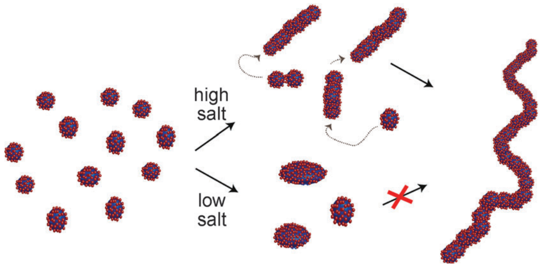
Complexed in a complex: Complexation of a silver(I) ion with dialkyl chalcogenides is performed in the cavity of a self-assembled cage. This method modulates the number and geometry of the chalcogenides coordinated to silver(I) and generates a metal–organic proximal state.

A recrystallization-induced self-assembly (RISA) strategy was proposed for the growth of 3D Cu_2O superstructures and employs Cu_2O mesoporous spheres (diameters ca. 300 nm) as the building blocks. Balancing the hydrolysis and recrystallization rates of the CuCl precursors is key to the successful assembly. Furthermore, the shape of the superstructures can be tuned to obtain either cubes or tetrahedra.

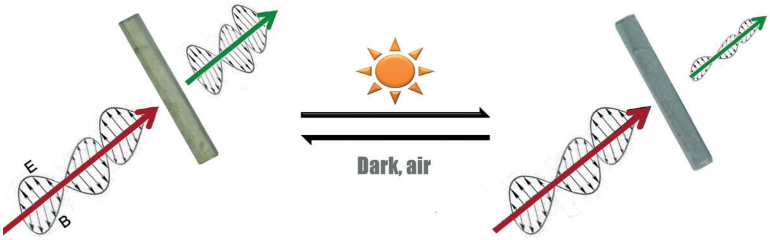




Ruthenium-O-Ruthenium: A series of dinuclear oxo-bridged Ru complexes was synthesized in three distinct redox states (Ru$^{II,III}_2$, Ru$^{III,III}_2$, and Ru$^{III,IV}_2$) with the same molecular framework. Crystallographic and spectroscopic studies of two mixed-valence complexes revealed that each unpaired electron is completely delocalized across the oxo-bridged dinuclear core.



Surfactants in action: The formation of “worm-like” micelles by fusion of globular micelles and short cylinders composed of sodium dodecyl sulfate, which occurs when the salt concentration is suddenly increased, is followed using a combination of time-resolved small-angle X-ray scattering and fast stopped-flow experiments.



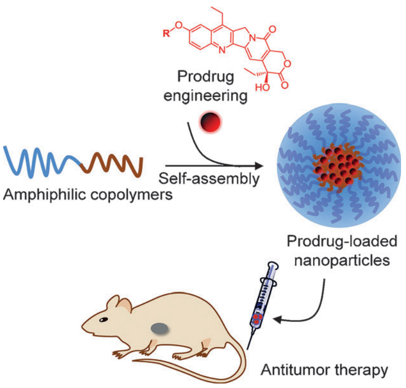
A light-driven switch: A photochromic zinc(II) compound, employing a photoactive asymmetric viologen ligand, exhibits electron-transfer-based photoswitching of bulk second-order nonlinear optical properties (NLO) with high contrast.

Prodrug Design

H. Wang, H. Xie, J. Wu, X. Wei, L. Zhou, X. Xu,* S. Zheng* ——— 11532–11537

Structure-Based Rational Design of Prodrugs To Enable Their Combination with Polymeric Nanoparticle Delivery Platforms for Enhanced Antitumor Efficacy

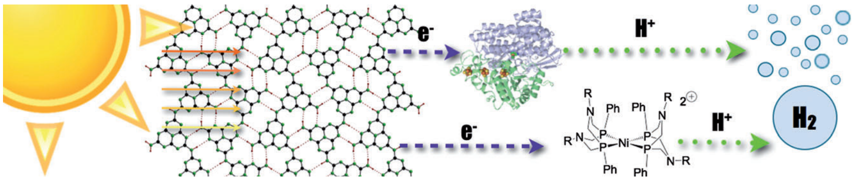
Lipophilicity enhancement of a chemotherapeutic agent was achieved by the introduction of a variety of hydrophobic moieties. This allows the self-assembly of the generated prodrugs with block copolymers into amphiphilic polymeric nanoparticles, which exhibited excellent antitumor activity compared to a clinically approved prodrug in a colorectal tumor xenograft model.



Photocatalysis

C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch, E. Reisner* ——— 11538–11542

Photocatalytic Hydrogen Production using Polymeric Carbon Nitride with a Hydrogenase and a Bioinspired Synthetic Ni Catalyst



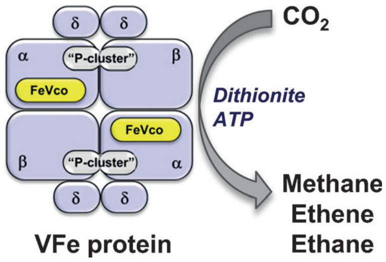
Light harvesting: The noble-metal-free photocatalytic hydrogen production system utilizes carbon nitride as a light-absorbing material in combination with a hydrogenase or a water-soluble synthetic bioinspired Ni catalyst. The stability of the carbon nitride leads to highly productive photocatalytic systems capable of sustained hydrogen production for more than 48 h for the semibiological system.

Carbon Dioxide

J. G. Rebelein, Y. Hu,* M. W. Ribbe* ——— 11543–11546

Differential Reduction of CO_2 by Molybdenum and Vanadium Nitrogenases

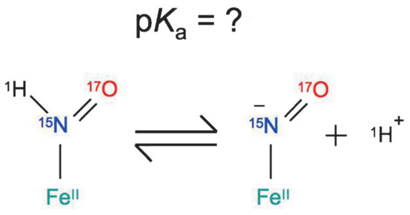
Vanadium nitrogenase can reduce CO_2 to CO, CD_4, C_2D_4, and C_2D_6. Its ability to reduce CO_2 to C_2 hydrocarbons adds another important reaction to the catalytic spectrum of the vanadium nitrogenase, that is, a reaction that involves C–C coupling from CO_2.



Isotopic Labeling

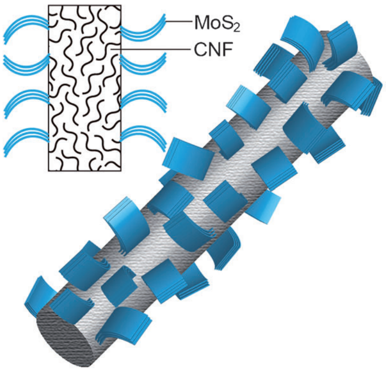
Y. Gao, A. Toubaei, X. Kong, G. Wu* ——— 11547–11551

Acidity and Hydrogen Exchange Dynamics of Iron(II)-Bound Nitroxyl in Aqueous Solution

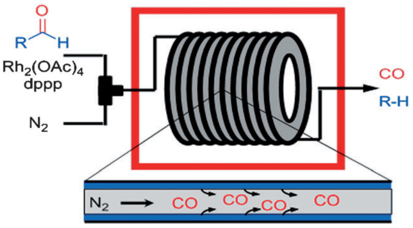


An acid test: The Fe^{II}-bound HNO is a very weak acid in aqueous solution with a pK_a value of greater than 11. However, HNO undergoes rapid hydrogen exchange with water and the process is catalyzed by both acid and base.

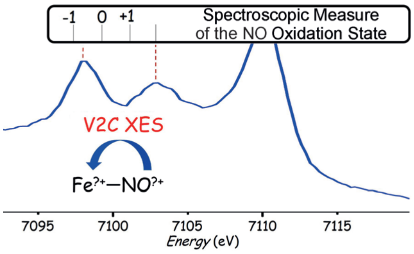
Carbon nanofibers (CNFs) decorated with molybdenum disulfide sheets are fabricated by a facile hydrothermal process with low-cost, biomass-derived carbonaceous nanofibers as the supports. On reacting with lithium, the nanofibers undergo novel electrochemical processes that are triggered by a synergistic lithium storage effect, leading to enhanced cycling and rate performance of the lithium-ion battery.

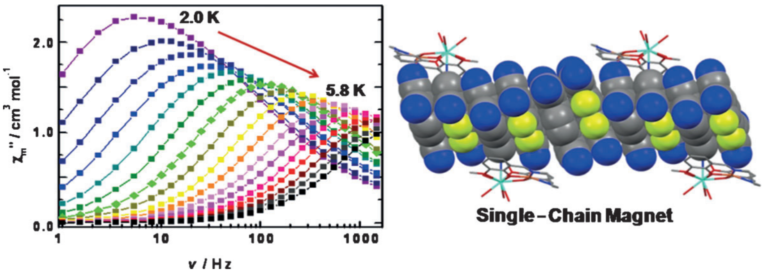


Swept away from the action: A biphasic gas/liquid continuous-flow protocol enabled the efficient decarbonylation of aldehydes with a rhodium catalyst. This transformation is made possible by the induction of an annular flow regime in a coil-based microreactor by using nitrogen as an inert carrier gas to remove CO from the equilibrium (see picture; dppp = 1,2-bis(diphenylphosphanyl)propane).



Valence-to-core X-ray emission spectroscopy (V2C XES) probes the $\Delta E_{\sigma 2s^*\text{-}\sigma 2p}$ of iron-bound NO. This method serves as a spectroscopic measure for the quantitative determination of the NO oxidation state in Fe–NO complexes.



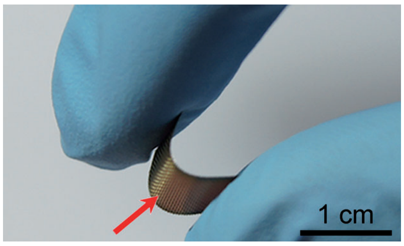


Stacking up single-chain magnets: A new route for the rational design of 1D magnetically bistable molecular materials has been exploited, in which the supramolecular π-stacking interactions between the 2p spins of TCNQF radicals (TCNQF = 2-fluoro-7,7,8,8-tetracyano-*p*-quinodimethane) help to correlate the 3d–4f dinuclear anisotropic units and enhance the effective energy barrier for spin reversal.

Wearable Solar Cells

Z. Zhang, X. Li, G. Guan, S. Pan, Z. Zhu, D. Ren, H. Peng* ——— 11571 – 11574

A Lightweight Polymer Solar Cell Textile that Functions when Illuminated from Either Side



A polymer solar cell textile has been developed by sandwiching a metal textile electrode between two ultrathin, transparent, and conducting carbon nanotube sheets. Because of its unique structure, the resulting solar cell textile shows the same energy conversion efficiency regardless of which side it is irradiated from. Furthermore, its energy conversion efficiencies were maintained even after 200 bending cycles.

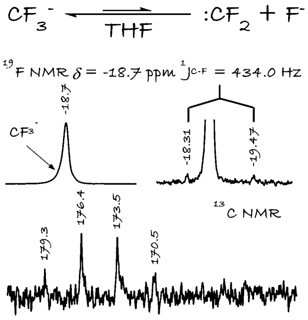
Reactive Intermediates

G. K. S. Prakash,* F. Wang, Z. Zhang, R. Haiges, M. Rahm, K. O. Christe, T. Mathew, G. A. Olah ——— 11575 – 11578

Long-Lived Trifluoromethanide Anion: A Key Intermediate in Nucleophilic Trifluoromethylations

Front Cover

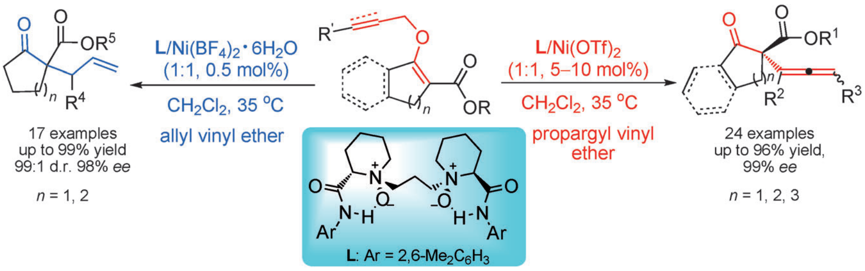
Rather persistent: For more than 60 years, the trifluoromethanide anion has been widely believed to exist only as an extremely transient species in the condensed phase, and to undergo swift decomposition to difluorocarbene and fluoride. The trifluoromethanide anion has now been successfully prepared, observed, and characterized for the first time in solution. Contrary to previous assumptions, the anion possesses considerable lifetime at subambient temperatures.



Asymmetric Catalysis

Y. B. Liu, H. P. Hu, H. F. Zheng, Y. Xia, X. H. Liu, L. L. Lin, X. M. Feng* ——— 11579 – 11582

Nickel(II)-Catalyzed Asymmetric Propargyl and Allyl Claisen Rearrangements to Allenyl- and Allyl-Substituted β-Ketoesters

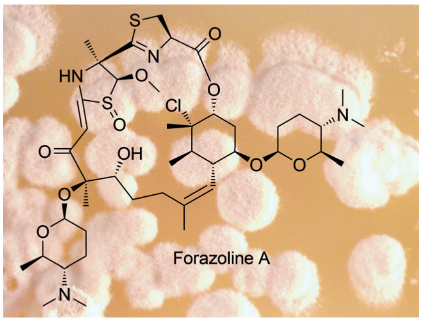


Oh, the O! Highly efficient catalytic asymmetric Claisen rearrangements of *O*-propargyl β-ketoesters and *O*-allyl β-ketoesters have been accomplished under mild reaction conditions. In the presence of the chiral *N,N'*-dioxide/Ni^{II} complex, a wide range of allenyl/allyl-substituted all-carbon quaternary β-ketoesters was obtained in generally good yield and high diastereoselectivity with excellent enantioselectivity. Tf = trifluoromethanesulfonyl.

Natural Products

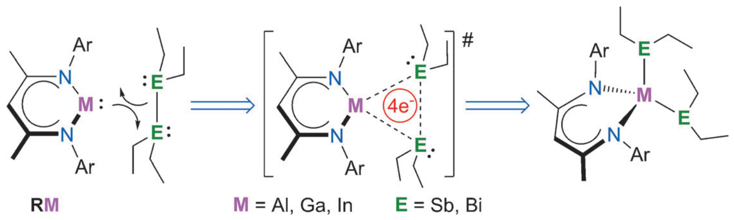
T. P. Wyche, J. S. Piotrowski, Y. Hou, D. Braun, R. Deshpande, S. McIlwain, I. M. Ong, C. L. Myers, I. A. Guzei, W. M. Westler, D. R. Andes, T. S. Bugni* ——— 11583 – 11586

Forazoline A: Marine-Derived Polyketide with Antifungal In Vivo Efficacy



A bit of structure: A novel antifungal natural product, forazoline A, was isolated from *Actinomadura* sp. The structure of forazoline A was elucidated by a combination of NMR spectroscopy, molecular modeling, and synthetic modifications. The compound demonstrated in vivo efficacy in a mouse model of *Candida albicans*. A chemical genomics approach suggested that forazoline A works through a new mechanism of action.

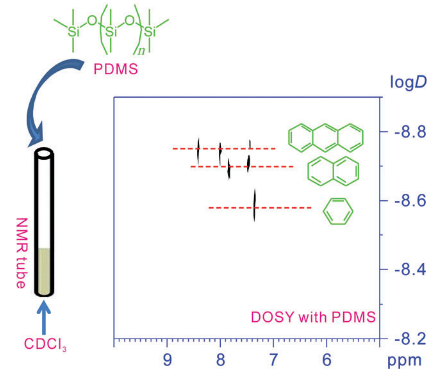
Intermetallic Compounds



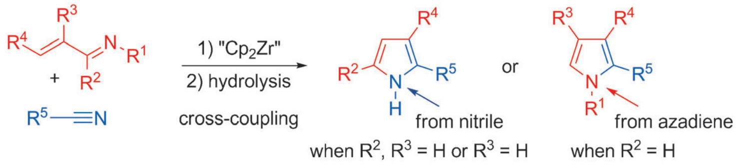
Doing the shuffle: Reactions of monovalent RAl with E_2Et_4 (E = Sb, Bi; Ar = 2,6-iPr$_2$C$_6$H$_3$) proceed with E–E bond cleavage and formation of RAl$(EEt_2)_2$, whereas RGa forms a reversible chemical equilibrium with E_2Et_4 and RGa$(EEt_2)_2$. RIn does not react with Sb_2Et_4, but also forms a reversible equilibrium with Bi_2Et_4 at low temperatures.

Analytical Methods

Virtually separate: In the presence of poly(dimethylsiloxane) (PDMS), mixtures of species with a similar molecular mass, size, or shape were baseline separated by liquid-state chromatographic NMR spectroscopy (see picture). Thus, PDMS holds the potential to be developed as a general virtual stationary phase.

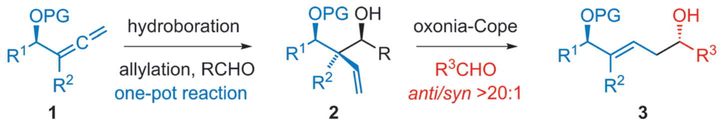


Pyrrole Synthesis



Exercise control: N–H and N-substituted pyrroles can be prepared through the direct insertion of nitriles into zirconocene-1-aza-1,3-diene complexes and their subsequent acidic aqueous work-up. The outcome of the reaction depends on the relative stability and reactivity of the corresponding enamine–imine tautomers formed through the hydrolysis of the diazazirconacycles.

Synthetic Methods

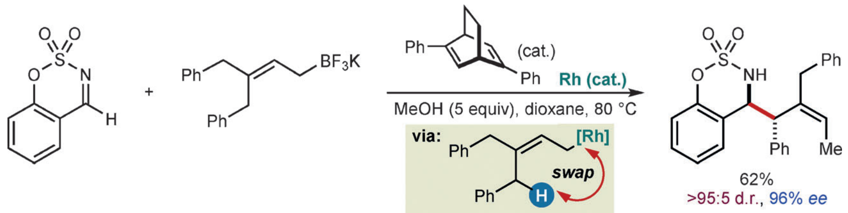


Coping: Skipped polyols represent a common motif in many biologically significant polyketide antibiotics. Starting *syn*,*syn*-2-vinyl-1,3-diols **2**, from the hydroboration of allenic alcohols **1** and subsequent allylboration of an aldehyde, undergo a stereoselective $SiCl_4$-promoted oxonia-Cope rearrangement to forge an array of anti-1,5-pentenediols **3** to provide polyhydroxylated motifs in a stereochemically defined manner.

Allylrhodium Isomerization

H. B. Hepburn,
H. W. Lam* ______________ **11605 – 11610**

The Isomerization of Allylrhodium Intermediates in the Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines

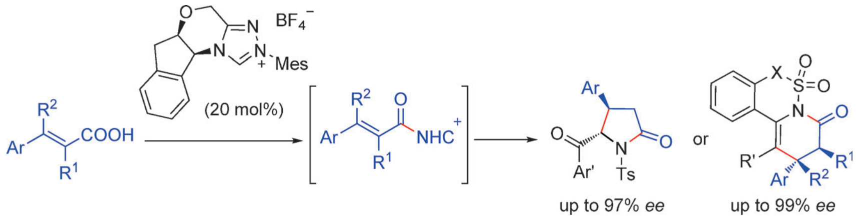


Rhodium dance: Allylrhodium species generated from potassium allyltrifluoroborates can undergo isomerization by a 1,4-rhodium(I) migration to give more complex isomers, which then react with cyclic imines to provide products with up to three new stereochemical elements. High enantioselectivities are obtained with chiral diene–rhodium complexes.

Organocatalysis

X.-Y. Chen, Z.-H. Gao, C.-Y. Song,
C.-L. Zhang, Z.-X. Wang,*
S. Ye* ______________ **11611 – 11615**

N-Heterocyclic Carbene Catalyzed Cyclocondensation of α,β-Unsaturated Carboxylic Acids: Enantioselective Synthesis of Pyrrolidinone and Dihydropyridinone Derivatives



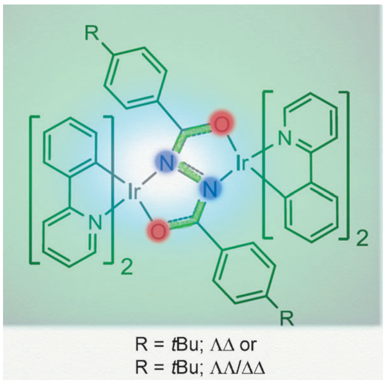
Into the mix: N-Heterocyclic carbenes (NHCs) catalyze the generation of α,β-unsaturated acyl azoliums from α,β-unsaturated carboxylic acids via in situ generated mixed anhydrides for the enantioselective [3+2] and [3+3] cyclocondensation with sulfonylated α-amino ketones and alkyl(aryl)imines, respectively. The corresponding pyrrolidinones and dihydropyridinones were isolated in good yields with high to excellent enantioselectivities.

Luminescence

Y. Zheng, A. S. Batsanov, M. A. Fox,
H. A. Al-Attar, K. Abdullah, V. Jankus,
M. R. Bryce,*
A. P. Monkman ______________ **11616 – 11619**

Bimetallic Cyclometalated Iridium(III) Diastereomers with Non-Innocent Bridging Ligands for High-Efficiency Phosphorescent OLEDs

Two phosphorescent dinuclear iridium(III) diastereomers are readily separated. The bridging diarylhydrazide ligand plays an important role in the electrochemistry and photophysics of the complexes. OLEDs using these complexes as green-emissive dopants have electroluminescence efficiencies (37 cd A^{-1}, 11 % EQE) that are remarkably high for dinuclear metal complexes in a simple device architecture.

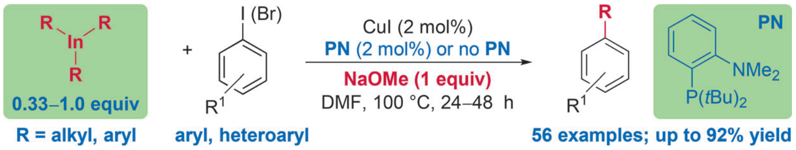


R = tBu; ΛΔ or
R = tBu; ΛΛ/ΔΔ

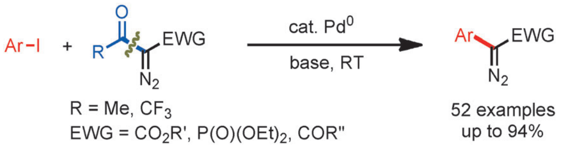
Cross-Coupling

S. Thapa, S. K. Gurung, D. A. Dickie,
R. Giri* ______________ **11620 – 11624**

Copper-Catalyzed Coupling of Triaryl- and Trialkylindium Reagents with Aryl Iodides and Bromides through Consecutive Transmetalations



All-out cross-coupling: All three nucleophilic moieties of triorganoindium reagents can be transmetalated onto copper(I) catalysts in the presence of NaOMe, which enables coupling with aryl iodides and bromides in a carbon–carbon bond-forming process. The transformation tolerates a wide range of functional groups and proceeds well with sterically hindered substrates and trialkylindium reagents.

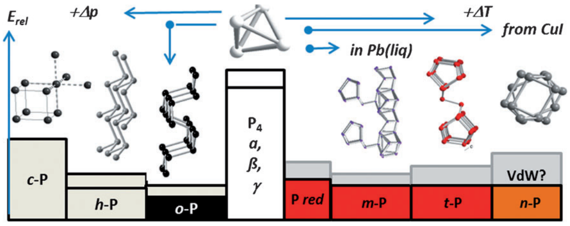


New access: An alternative method for the synthesis of aryldiazoacetates and related diazo compounds based on palladium(0)-catalyzed deacylative cross-coupling of aryl iodides and acyldiazocarbonyl compounds is presented. This highly efficient coupling reaction can be achieved at room temperature under mild reaction conditions and shows wide substrate scope.

Synthetic Methods

F. Ye, C. Wang, Y. Zhang,
J. Wang* ______ **11625–11628**

Synthesis of Aryldiazoacetates through Palladium(0)-Catalyzed Deacylative Cross-Coupling of Aryl Iodides with Acyldiazoacetates

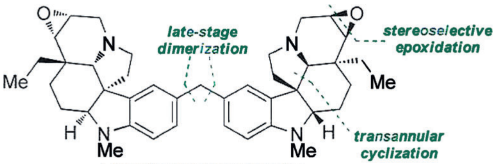


Phosphorus shows its shapes and colors: DFT methods with the Grimme correction can be used to predict the structures of P allotropes that have weak interactions. For the first time, the stabilities of energetically closely related allotropes could be comprehensively elucidated and correctly predicted on the basis of van der Waals interactions. Insight into previously unknown solid-state structures of P nanorods was also possible.

P Allotropes

F. Bachhuber, J. von Appen,
R. Dronskowski, P. Schmidt, T. Nilges,
A. Pfitzner, R. Weihrich* _ **11629–11633**

The Extended Stability Range of Phosphorus Allotropes



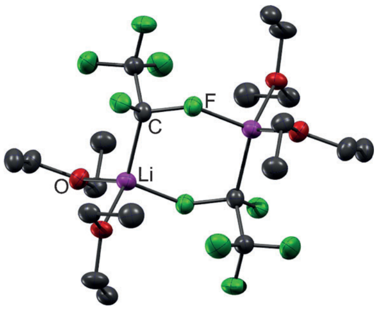
(–)-methylenebismehranine

Cyclize, oxidize, dimerize! A highly stereoselective transannular cyclization induced by the electrophilic activation of a chiral nine-membered lactam precursor allowed the rapid and efficient access to the *Aspidosperma* alkaloid skeleton. A late-stage stereoselective epoxidation afforded (−)-mehranine, which was dimerized using a formaldehyde equivalent to provide (−)-methylenebismehranine.

Alkaloid Synthesis

M. Mewald, J. W. Medley,
M. Movassaghi* ______ **11634–11639**

Concise and Enantioselective Total Synthesis of (−)-Mehranine, (−)-Methylenebismehranine, and Related *Aspidosperma* Alkaloids



Despite its explosive nature, crystals of the Li/F alkyl carbenoid pentafluoroethyllithium LiC_2F_5 could be isolated and the first experimental structure of its ether adduct determined. This structure clarifies earlier speculations on structure–reactivity relationships in carbenoid chemistry.

Lithium Carbenoids

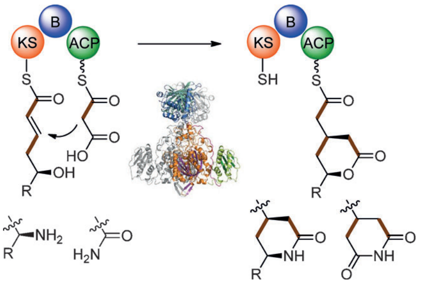
B. Waerder, S. Steinhauer, B. Neumann,
H.-G. Stammler, A. Mix, Y. V. Vishnevskiy,
B. Hoge, N. W. Mitzel* __ **11640–11644**

Solid-State Structure of a Li/F Carbenoid: Pentafluoroethyllithium

Polyketide Biosynthesis

D. Heine, T. Bretschneider, S. Sundaram, C. Hertweck* ______ 11645 – 11649

Enzymatic Polyketide Chain Branching To Give Substituted Lactone, Lactam, and Glutarimide Heterocycles



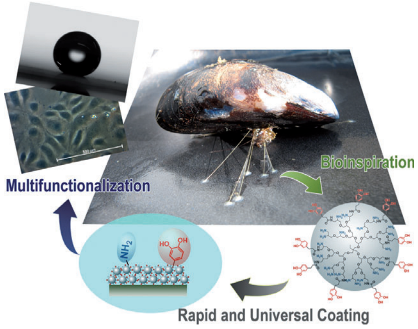
Branching out: Applying the reconstituted β-branching module of the rhizoxin polyketide synthase to the in vitro biotransformation of synthetic polyketide mimics led to the stereoselective formation of substituted lactone, lactam, and glutarimide moieties. These findings not only illuminate the biosynthesis of glutarimide-bearing polyketides but also demonstrate the utility of this module for pathway engineering.

Bioinspired Materials

Q. Wei, K. Achazi, H. Liebe, A. Schulz, P.-L. M. Noeske, I. Grunwald, R. Haag* ______ 11650 – 11655

Mussel-Inspired Dendritic Polymers as Universal Multifunctional Coatings

Rapid and universal coatings were developed from mussel-inspired dendritic polyglycerol that mimics mussel foot proteins with regard to functional groups, molecular weight, and molecular structure. Multiple further modifications can be achieved by either pre- or post-functionalization and control of surface roughness.

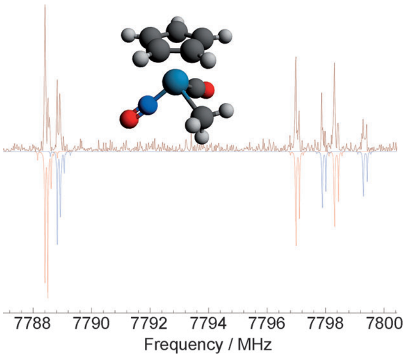


Parity Violation

C. Medcraft, R. Wolf, M. Schnell* ______ 11656 – 11659

High-Resolution Spectroscopy of the Chiral Metal Complex [CpRe(CH$_3$)(CO)(NO)]: A Potential Candidate for Probing Parity Violation

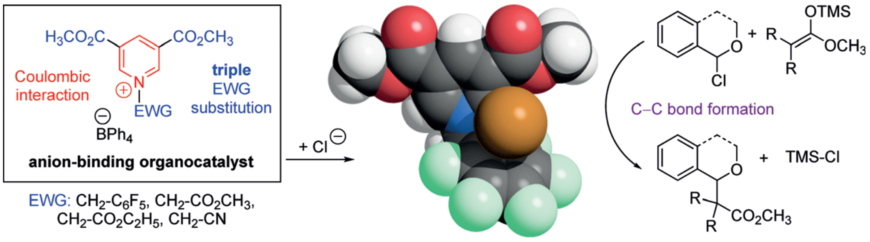
On the one hand: High-resolution rotational spectroscopy studies on the chiral heavy-metal containing complex [CpRe(CH$_3$)(CO)(NO)] show a rich hyperfine structure arising from rhenium and nitrogen nuclear quadrupole coupling. A detailed understanding of these processes is essential for upcoming precision studies on chiral molecules.



Organocatalysis

A. Berkessel,* S. Das, D. Pekel, J.-M. Neudörfl ______ 11660 – 11664

Anion-Binding Catalysis by Electron-Deficient Pyridinium Cations



A successful trio: Pyridinium cations carrying three electron-withdrawing substituents catalyze the alkylation of α-halo ethers with silyl ketene acetals through Coulombic anion binding. This C–C bond formation proceeds efficiently at low temperatures and at low catalyst loading.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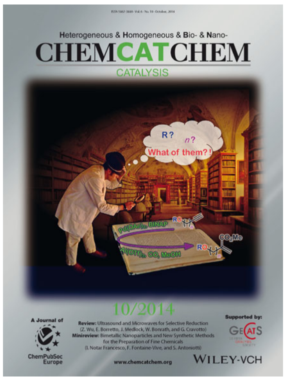
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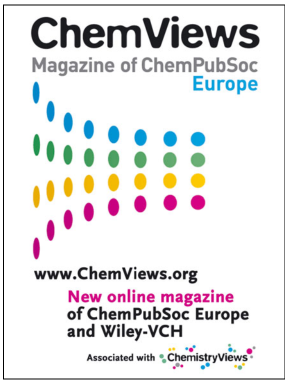
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