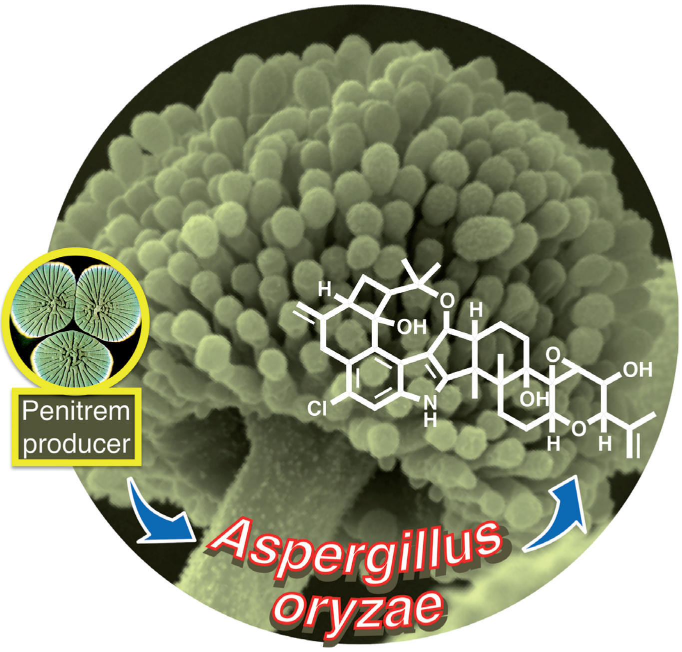
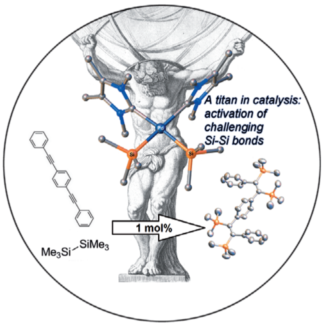
The biosynthetic gene cluster ...

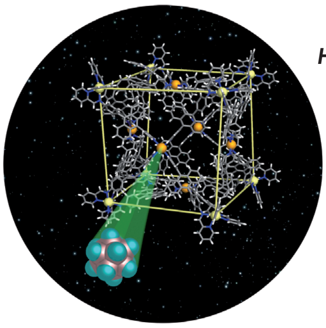


… of the highly complex indole diterpene penitrem is identified by H. Oikawa et al. in their Communication on page 5748 ff. Thirteen out of the seventeen involved transformations were elucidated by heterologous reconstitution of the relevant genes in Aspergillus oryzae and found to involve a prenylation-initiated cationic cyclization and two successive P450-catalyzed oxidative transformations for the installation of the characteristic bicyclo[4.2.0]octane skeleton.

***cis*-Disilylations**

In their Communication on page 5578 ff., O. Navarro, J. Spencer et al. present the oxidative cleavage of $Me_3SiSiMe_3$. This reaction generates a precatalyst for the *cis*-disilylation of internal alkynes with nonactivated disilanes.



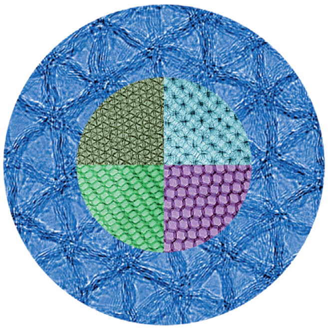


Host–Guest Chemistry

A rational strategy that allows the synthesis of a giant, heterometallic cube with an enclosed cavity capable of binding a variety of mono- and dianionic guests is reported by J. R. Nitschke et al. in their Communication on page 5636 ff.

Mesoporous Materials

A. Dong et al. describe in their Communication on page 5727 ff. the use of self-assembled superlattices of Fe_3O_4 nanocrystals to prepare highly ordered mesoporous graphene frameworks with ultrathin pore walls consisting of three to six stacked graphene layers.



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Service

Author Profile

"I admire creative people.
My favorite saying is 'Too much analysis leads to paralysis' …"
This and more about Hon Wai Lam can be found on page 5552.

News

A. G. Ewing

H. H. Girault

R. Schlögl

M. Cokoja

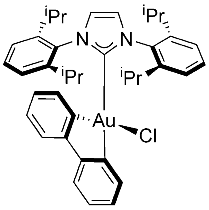
Books

Highlights

Homogeneous Gold Catalysis

J. H. Teles* ———— **5556 – 5558**

Oxidative Addition to Gold(I): A New Avenue in Homogeneous Catalysis with Au



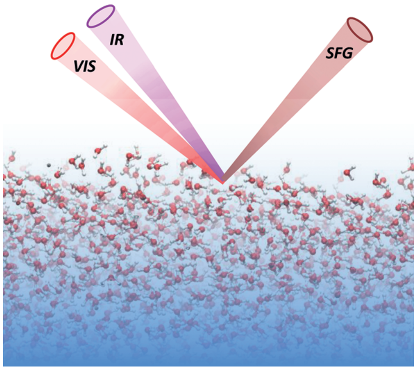
There's nothing like gold: New gold(III) catalysts, which can be easily obtained by the oxidative addition of biphenylene to NHC-gold(I) chlorides (see structure; NHC = N-heterocyclic carbene) prove not only to be very stable compounds but also competent catalysts for various reactions. Some of these reactions are new, and have never been observed before.

Reviews

Water–Air Interfaces

M. Bonn,* Y. Nagata,
E. H. G. Backus ———— **5560 – 5576**

Molecular Structure and Dynamics of Water at the Water–Air Interface Studied with Surface-Specific Vibrational Spectroscopy



Lightly scratching the surface: A central question regarding the water–air interface is to what extent the structure and dynamics of water molecules is influenced by the breaking of hydrogen bonds, and thus how they differ from those in the bulk water? One method to study the water–air interface is the laser-based surface-specific vibrational spectroscopy. The advances made by these investigations are presented and discussed.

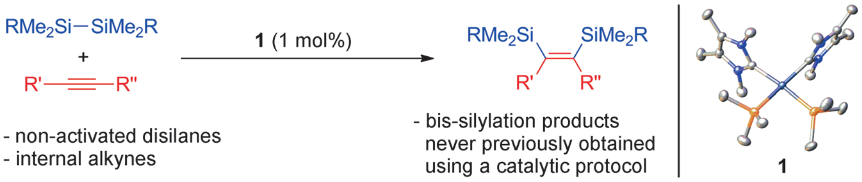
Communications

Homogeneous Catalysis

M. B. Ansell, D. E. Roberts, F. G. N. Cloke, O. Navarro,* J. Spencer* —— **5578 – 5582**

Synthesis of an [(NHC)$_2$Pd(SiMe$_3$)$_2$] Complex and Catalytic *cis*-Bis(silyl)ations of Alkynes with Unactivated Disilanes

Frontispiece



Double the Si: The novel complex *cis*-[(ITMe)$_2$Pd(SiMe$_3$)$_2$] (**1**, ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) has been synthesized by mild oxidative cleavage of Me$_3$SiSiMe$_3$ using [(ITMe)$_2$Pd^0]. The synthesized complex was used as a precatalyst for the *cis*-bis(silyl)ation of alkynes using unactivated disilanes.

For the USA and Canada:
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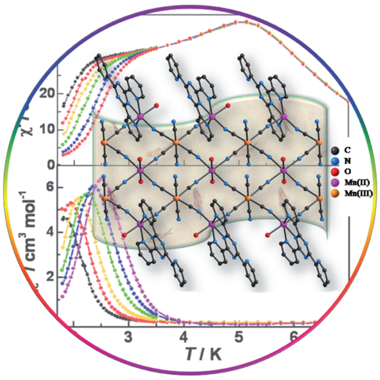


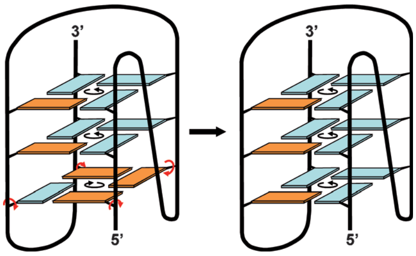
A tape-like compound consisting of quadruply cyanide-bridged $\mathrm{Mn^{III}}$-$\mathrm{Mn^{II}}$ zigzag chains based on hexacyanomanganate(III) was synthesized and characterized. Magnetic studies revealed that the compound exhibits long-range magnetic ordering below 5.1 K as well as single-chain magnetic behavior at lower temperatures with an effective energy barrier of 40.5(7) K.

Magnetic Cyanide Tape

Y.-Z. Zhang, H.-H. Zhao,* E. Funck,
K. R. Dunbar* ———— **5583 – 5587**

A Single-Chain Magnet Tape Based on Hexacyanomanganate(III)

Loop the loop: The substitution of 2′-deoxy-2′-fluoroguanosines for 2′-deoxyguanosines in an intramolecular G-quadruplex switches all glycosidic torsion angles within the 5′-terminal tetrad but leaves the overall topology unaffected. The quadruplex formed is a novel structural type exhibiting exclusively *syn–syn* and *anti–anti* steps along the stacked G-tetrads (guanosine conformation: *syn* = orange, *anti* = blue).



G-Quadruplexes

J. Dickerhoff, K. Weisz* ——— **5588 – 5591**

Flipping a G-Tetrad in a Unimolecular Quadruplex Without Affecting Its Global Fold

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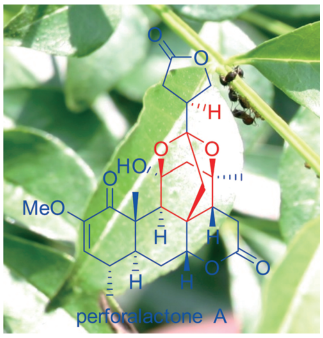
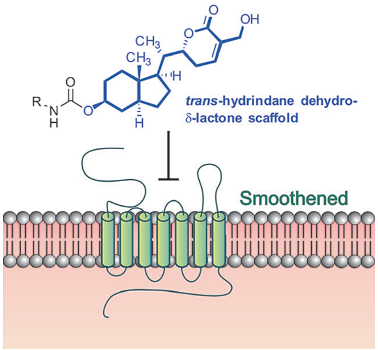


An active family: A quassinoid with a unique cagelike 2,4-dioxaadamantane ring system (see structure) was isolated along with biosynthetically related quassinoids from the twigs and stem of *Harrisonia perforata*. The compounds demonstrated insecticidal activity, antagonist activity at the nicotinic acetylcholine receptor of insects, and potent cytotoxicity. Their discovery provides an alternative origin of the quassinoid family of compounds.

Biosynthetic Pathways

X. Fang, Y. T. Di, Y. Zhang, Z. P. Xu, Y. Lu,
Q. Q. Chen, Q. T. Zheng,
X. J. Hao* ———— **5592 – 5595**

Unprecedented Quassinoids with Promising Biological Activity from *Harrisonia perforata*



BIOS delivers a collection of compounds with the *trans*-hydrindane dehydro-δ-lactone scaffold, which are based on the withanolide natural products, in a stereoselective fashion. A biological investigation of the compounds revealed novel and potent inhibitors of the Hedgehog signaling pathway, which bind to the protein Smoothened.

Inhibitors

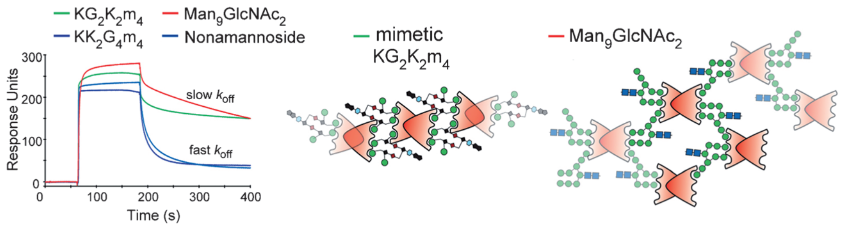
J. Švenda, M. Sheremet, L. Kremer,
L. Maier, J. O. Bauer, C. Strohmann,
S. Ziegler, K. Kumar,
H. Waldmann* ———— **5596 – 5602**

Biology-Oriented Synthesis of a Withanolide-Inspired Compound Collection Reveals Novel Modulators of Hedgehog Signaling

Carbohydrate Recognition

S. Lusvarghi, R. Ghirlando, C.-H. Wong, C. A. Bewley* ______ **5603 – 5608**

Glycopeptide Mimetics Recapitulate High-Mannose-Type Oligosaccharide Binding and Function



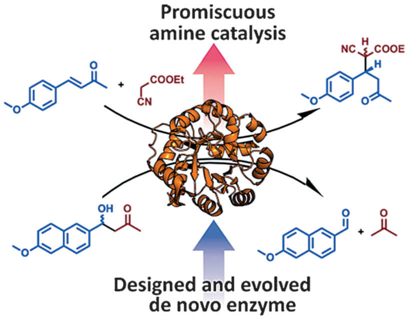
Spacing matters: NMR spectroscopic and biophysical measurements on rationally designed high-mannose-type glycan mimetics and natural glycans reveal that modes of binding are dictated by mannose spacing and valency (m_n = no. of mannosylated amino acids). For griffithsin, the most potent antiviral lectin known, intermolecular cross-linking and residence times, rather than affinity, are hallmarks for potent virus neutralization.

Enzyme Catalysis

X. Garrabou, T. Beck, D. Hilvert* ______ **5609 – 5612**

A Promiscuous De Novo Retro-Aldolase Catalyzes Asymmetric Michael Additions via Schiff Base Intermediates

Born promiscuous: Artificial enzymes obtained by computational design and directed evolution utilize relatively simple catalytic machineries to achieve remarkable levels of activity. These catalysts are potentially a rich source of novel chemical reactivity, as shown for the artificial retro-aldolase RA95.5-8, which also efficiently catalyzes asymmetric Michael additions via iminium ion intermediates.

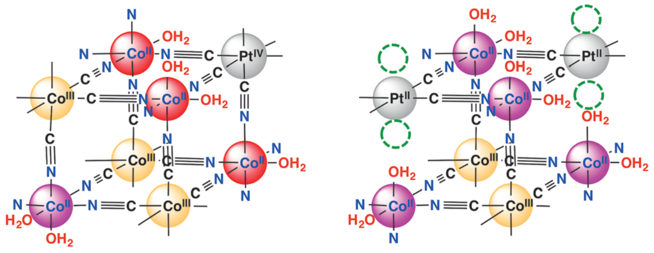


Heterogeneous Catalysis

Y. Yamada,* K. Oyama, R. Gates, S. Fukuzumi* ______ **5613 – 5617**

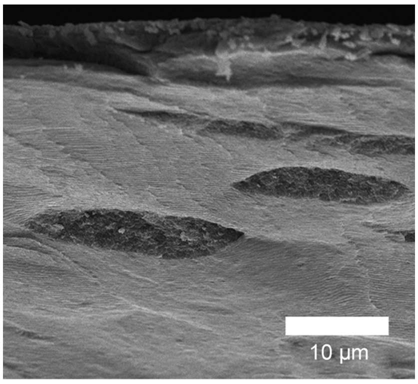
High Catalytic Activity of Heteropolynuclear Cyanide Complexes Containing Cobalt and Platinum Ions: Visible-Light Driven Water Oxidation

Inside Cover



A platinum assist: A near-stoichiometric amount of O_2 was evolved as observed in the visible-light irradiation of an aqueous buffer (pH 8) containing $[Ru^{II}(2,2'\text{-bipyridine})_3]$ as a photosensitizer, $Na_2S_2O_8$ as a sacrificial electron acceptor, and a heteropolynuclear cyanide complex as a water-oxidation catalyst. The synergistic effect between the Co and Pt ions was confirmed to facilitate the water-oxidation catalysis by the heteropolynuclear complex.

Entropically driven coassembly of rodlike cellulose nanocrystals and spherical latex nanoparticles yields suspensions that exhibit chiral nematic order. Upon drying, these suspensions form films (see SEM image) that preserve the long-range nematic order and exhibit a stratified morphology with close-to-uniform fluorescence, birefringence, and circular dichroism properties.



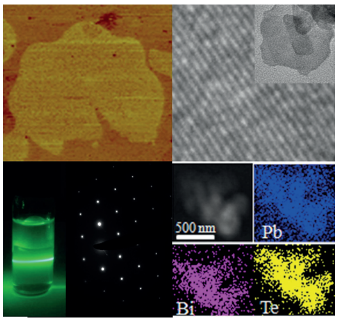
Chiral Films

H. Thérien-Aubin, A. Lukach, N. Pitch,
E. Kumacheva* **5618 – 5622**

Coassembly of Nanorods and Nanospheres in Suspensions and in Stratified Films

---

Saving on materials: Layered intergrowth compounds of the homologous $Pb_mBi_{2n}Te_{3n+m}$ family are examples of natural heterostructures. A simple solution-based method was used to synthesize two-dimensional $Pb_mBi_{2n}Te_{3n+m}$ nanosheets (see AFM image of $PbBi_2Te_4$, TEM images of $PbBi_2Te_5$, and elemental color mapping of $PbBi_2Te_5$) with narrow optical band gaps, semiconducting electronic-transport properties, and low thermal conductivity.



Heterostructures

A. Chatterjee, K. Biswas* **5623 – 5627**

Solution-Based Synthesis of Layered Intergrowth Compounds of the Homologous $Pb_mBi_{2n}Te_{3n+m}$ Series as Nanosheets

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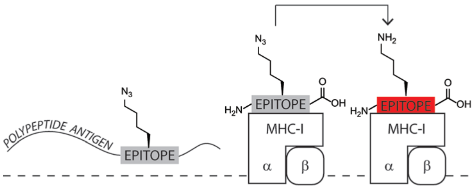

Antigen cross-presentation is the uptake of exogenous antigens followed by processing in the MHC-I complex, which is normally reserved for endogenous antigens. This process may now be studied by using masked epitopes: Azides are exploited as bioorthogonal protecting groups to generate antigens that are not recognized by their cognate T-cell unless they are deprotected using an on-cell Staudinger reduction.

Antigens

J. B. Pawlak, G. P. P. Gential,
T. J. Ruckwardt, J. S. Bremmers,
N. J. Meeuwenoord, F. A. Ossendorp,
H. S. Overkleeft, D. V. Filippov,
S. I. van Kasteren* **5628 – 5631**

Bioorthogonal Deprotection on the Dendritic Cell Surface for Chemical Control of Antigen Cross-Presentation

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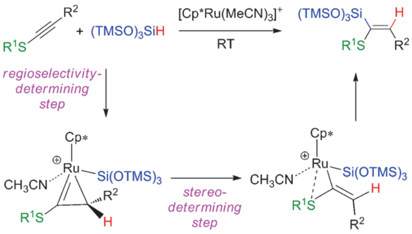


A rich source of vinyl silanes: A general, mild, and highly stereoselective hydrosilylation of electron-rich alkynes gave a range of stereodefined multisubstituted vinyl silanes with high efficiency (see scheme; R^1, R^2 = alkyl, aryl; TMS = trimethylsilyl). Unprecedented *syn* selectivity was observed with the cationic catalyst $[Cp^*Ru(MeCN)_3]^+$. DFT calculations provided important insight into the mechanism.

Synthetic Methods

S. Ding, L.-J. Song, Y. Wang, X. Zhang,*
L. W. Chung,* Y.-D. Wu,*
J. Sun* **5632 – 5635**

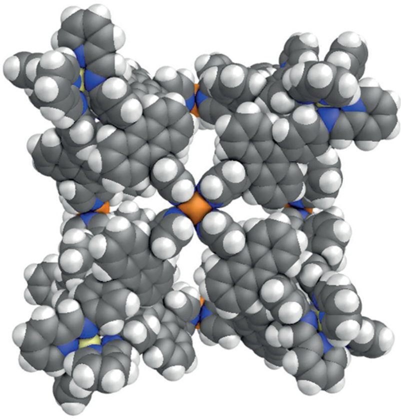
Highly Regio- and Stereoselective Hydrosilylation of Internal Thioalkynes under Mild Conditions

Host–Guest Chemistry

W. J. Ramsay, F. T. Szczypiński,
H. Weissman, T. K. Ronson,
M. M. J. Smulders, B. Rybtchinski,
J. R. Nitschke* ________ 5636 – 5640

Designed Enclosure Enables Guest Binding Within the 4200 Å^3 Cavity of a Self-Assembled Cube

Inside Back Cover

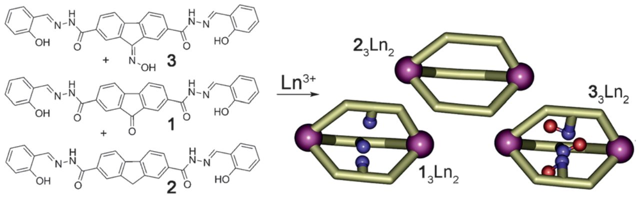


Brobdingnagian: A giant, heterometallic cube with host–guest properties was prepared by successful application of a rational strategy to increase the dimensions whilst maintaining an enclosed cavity (see X-ray crystal structure). A variety of mono- and dianionic guests was bound in the cavity in solution. Hierarchical aggregation of the cubes into a rigid monolayer was visualized by cryogenic transmission electron microscopy.

Self-Assembly

A. M. Johnson, C. A. Wiley, M. C. Young,
X. Zhang, Y. Lyon, R. R. Julian,
R. J. Hooley* ________ 5641 – 5645

Narcissistic Self-Sorting in Self-Assembled Cages of Rare Earth Metals and Rigid Ligands



Equals among equals: The formation of self-assembled cages of rare earth metals and ligands proceeds through highly selective, narcissistic self-sorting. Pendant functionalities as similar as carbonyl and methylene groups are discriminated in this complex assembly process.

Photochemistry

C. R. S. Mooney, M. A. Parkes, A. Iskra,
H. H. Fielding* ________ 5646 – 5649

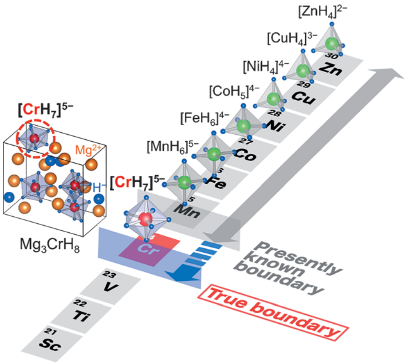
Controlling Radical Formation in the Photoactive Yellow Protein Chromophore

Isomerization or radical formation: The photochemical properties of *para*-coumaric acid were investigated by photoelectron spectroscopy and quantum chemical calculations. The role of chemical structure and low-frequency bond rotations on the control of the competition between isomerization and electron emission (radical formation; see picture) in the photoactive yellow protein chromophore is studied.

Transition-Metal Complexes

S. Takagi, Y. Iijima, T. Sato, H. Saitoh,
K. Ikeda, T. Otomo, K. Miwa, T. Ikeshoji,
K. Aoki, S. Orimo* ________ 5650 – 5653

True Boundary for the Formation of Homoleptic Transition-Metal Hydride Complexes

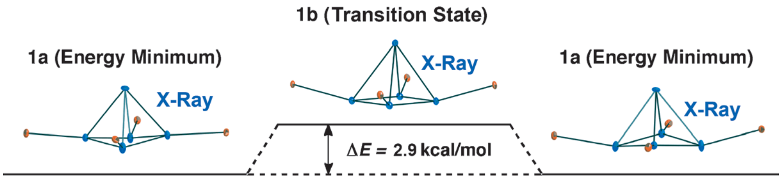


[CrH$_7$]$^{5-}$: The true boundary for the formation of homoleptic transition-metal hydride complexes was demonstrated through the synthesis of Mg$_3$CrH$_8$ containing [CrH$_7$]$^{5-}$. Given a general trend of increasing H coordination number with decreasing atomic number of transition metals, these findings will pave the way for further discovery of hydrogen-rich materials that are of both technological and fundamental interest.

Pyramidanes

V. Ya. Lee,* Y. Ito, O. A. Gapurenko,
A. Sekiguchi,* V. I. Minkin,*
R. M. Minyaev,
H. Gornitzka ———— **5654 – 5657**

Pentagermapyramidane: Crystallizing the "Transition-State" Structure

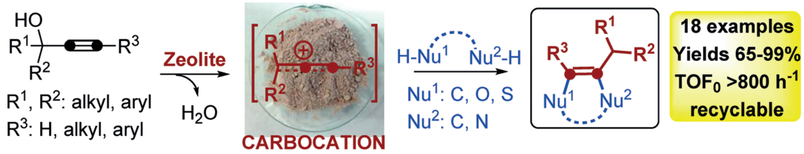


Germanium pyramids: The homonuclear pentagermapyramidane $Ge[Ge_4(SiMe\textit{t}Bu_2)_4]$ (**1**) was synthesized and characterized. Crystal structures of two structural variations of **1** are reported: the distorted pyramidal structure **1a**, corresponding to the energy minima on the Ge_5R_4 potential energy surface (PES), and the square-planar pyramidal **1b**, representing a transition state on the PES.

Heterogeneous Catalysis

J. R. Cabrero-Antonino, A. Leyva-Pérez,*
A. Corma* ———— **5658 – 5661**

Beyond Acid Strength in Zeolites: Soft Framework Counteranions for Stabilization of Carbocations on Zeolites and Its Implication in Organic Synthesis

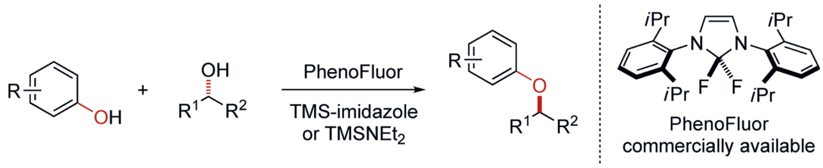


Stabilized carbocations: Zeolites are able to generate and stabilize medium-size (molecular weight ≈300 Da) delocalized carbocations on their surface under mild conditions to perform multifunctionalization reactions with catalytic activities comparable to that of strong homogenous Brønsted acids. Some of the products obtained here exhibit significant inhibition percentages against colon cancer cells.

Ether Synthesis

X. Shen, C. N. Neumann, C. Kleinlein,
N. W. Goldberg, T. Ritter* —— **5662 – 5665**

Alkyl Aryl Ether Bond Formation with PhenoFluor

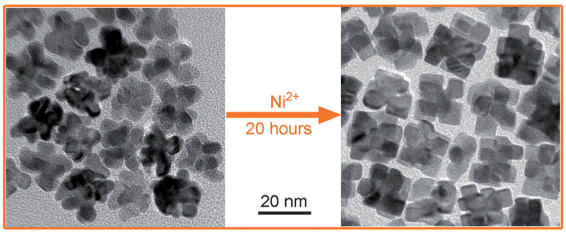


From fluorination to etherification: A method for the formation of alkyl aryl ethers directly from the corresponding alcohols and phenols with PhenoFluor has been developed. The reaction features a broad substrate scope, and substrates that are challenging for more conventional ether bond forming processes may be coupled. TMS = trimethylsilyl.

Nanostructures

L. Ma, C. Wang, B. Y. Xia, K. Mao, J. He,
X. Wu, Y. Xiong,* X. W. Lou* **5666 – 5671**

Platinum Multicubes Prepared by Ni^{2+}-Mediated Shape Evolution Exhibit High Electrocatalytic Activity for Oxygen Reduction



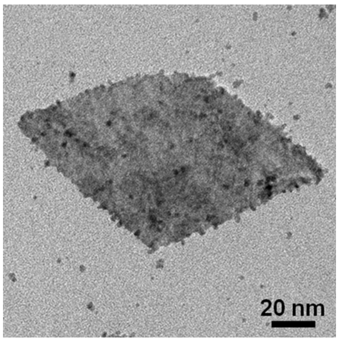
Facet to facet: A Ni^{2+}-mediated facet-evolution approach has been developed to synthesize novel Pt multicubes whose surface is mostly enclosed by {100} facets. The Pt multicubes exhibit very high electrocatalytic activity and remarkable durability in the oxygen reduction reaction because of the high-index facets at the junction between the cubic components.

Core–Shell Nanostructures

Z. Fan, Y. Zhu, X. Huang, Y. Han, Q. Wang, Q. Liu, Y. Huang, C. L. Gan, H. Zhang* ________ **5672 – 5676**

Synthesis of Ultrathin Face-Centered-Cubic Au@Pt and Au@Pd Core–Shell Nanoplates from Hexagonal-Close-Packed Au Square Sheets

Phase change: Ultrathin Au@Pt and Au@Pd core–shell nanoplates were prepared from Au square sheets. A phase transformation from hexagonal close-packed (hcp) to face-centered cubic (fcc) is observed upon coating the hcp Au square sheets with Pt or Pd under ambient conditions. The prepared fcc Au@Pt and Au@Pd rhombic nanoplates demonstrate unique $(101)_f$ orientation (picture shows a typical fcc Au@Pt rhombic nanoplate).

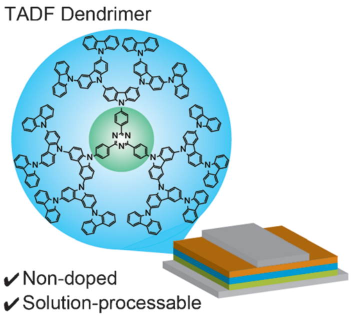


Organic Light-Emitting Diodes

K. Albrecht, K. Matsuoka, K. Fujita,* K. Yamamoto* ________ **5677 – 5682**

Carbazole Dendrimers as Solution-Processable Thermally Activated Delayed-Fluorescence Materials

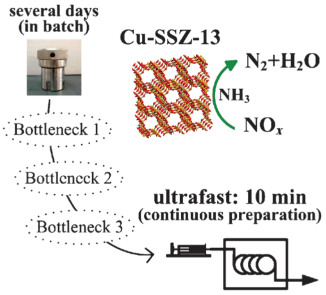
Fluorescent dendrimers: Carbazole dendrimers with a triphenyl-*s*-triazine core have been developed as the first solution-processable, non-doped, and high-molecular-weight thermally activated delayed fluorescence (TADF) materials. OLED devices with such dendrimers as the spin-coated emitting layer displayed external quantum efficiencies of up to 3.4 %, which suggests that this device is harvesting triplet excitons.



Zeolite Synthesis

Z. Liu, T. Wakihara, K. Oshima, D. Nishioka, Y. Hotta, S. P. Elangovan, Y. Yanaba, T. Yoshikawa, W. Chaikittisilp, T. Matsuo, T. Takewaki, T. Okubo* ________ **5683 – 5687**

Widening Synthesis Bottlenecks: Realization of Ultrafast and Continuous-Flow Synthesis of High-Silica Zeolite SSZ-13 for NO_x Removal

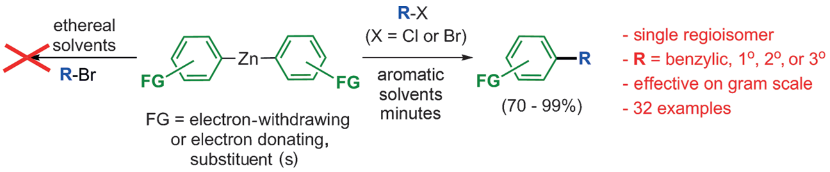


Bottle opener: SSZ-13 is a zeolite commercialized as a catalyst to remove nitrogen oxides (NO_x). However, its long synthesis time is one of the biggest barriers to large-scale production. An ultrafast synthesis route now allows SSZ-13 to be synthesized in 10 min and thus facilitates continuous preparation of SSZ-13. The fast-synthesized SSZ-13 exhibits outstanding performance for the NO_x removal.

C–C Coupling

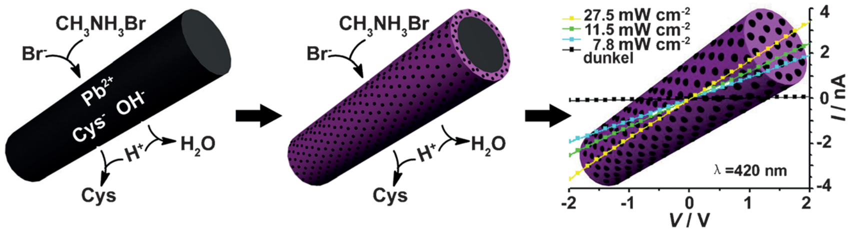
J. J. Dunsford, E. R. Clark, M. J. Ingleson* ________ **5688 – 5692**

Direct C(sp^2)–C(sp^3) Cross-Coupling of Diaryl Zinc Reagents with Benzylic, Primary, Secondary, and Tertiary Alkyl Halides



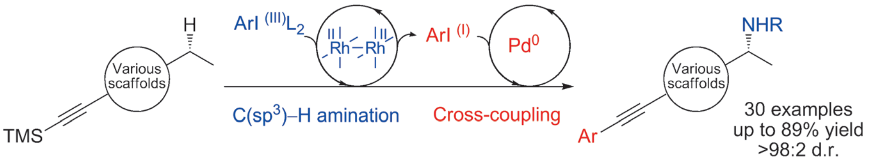
Zinc and you'll miss it! Direct C(sp^2)–C(sp^3) cross-coupling of diaryl zinc reagents with alkyl halides proceeded rapidly at ambient temperature without a coordinating ethereal solvent or an added catalyst (see scheme). This versatile, operationally simple approach to C(sp^2)–C(sp^3) bond formation enables the expedient construction of a diverse array of carbon-based structural motifs.

Perovskites



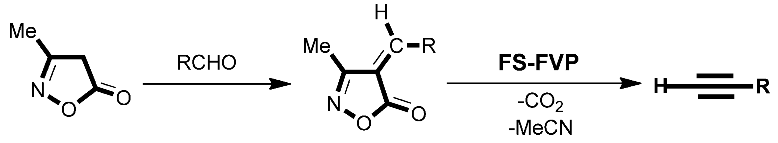
In solution: Porous $CH_3NH_3PbBr_3$ perovskite nanowires (PNW-$CH_3NH_3PbBr_3$) were fabricated by an efficient self-template-directed synthesis using the Pb-containing precursor nanowires as both the sacrificial template and the Pb^{2+} source in the presence of CH_3NH_3Br and HBr in solution. The perovskite nanowires are potential materials for visible-light photodetectors.

Hypervalent Compounds



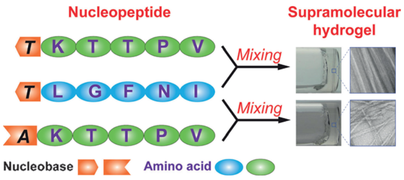
I(003) is a double agent: A tandem C—N and C—C bond-forming reaction has been achieved through Rh^{II}/Pd^0 catalysis. The sequence first involves an iodine(III) oxidant, then the in situ generated iodine(I) by-product is used as a coupling partner. The overall process affords complex building blocks with high yields, and demonstrates the synthetic value of iodoarenes produced in trivalent iodine reagent mediated oxidations.

Synthetic Methods



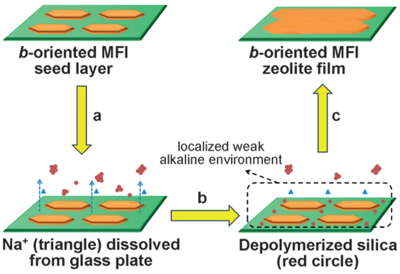
Taking the heat: Unlike in flash vacuum pyrolysis, involatile compounds can be used in falling-solid flash vacuum pyrolysis (FS-FVP). This method is employed for the rapid and efficient synthesis of a variety of arylacetylenes from 4-arylmethylidene-5(4*H*)-isoxazolones, which were in turn prepared from aldehyde precursors.

Supramolecular Chemistry



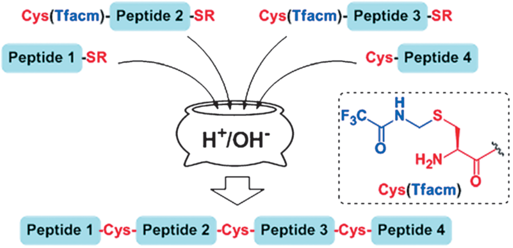
Just mix it! The simple mixing of heterodimers of nucleopeptides provides a facile approach to generate biostable and biocompatible supramolecular hydrogels as soft biomaterials.

Zeolites



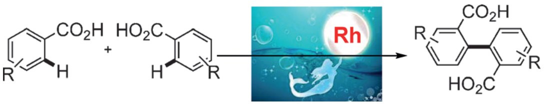
In one direction: Highly *b*-oriented MFI zeolite films have been successfully prepared for the first time under neutral conditions without the use of hydrogen fluoride. The Na_2O species dissolved from the glass plate support or a trace amount of NaOH facilitates the secondary growth of MFI seed crystals.

Protein Chemical Synthesis



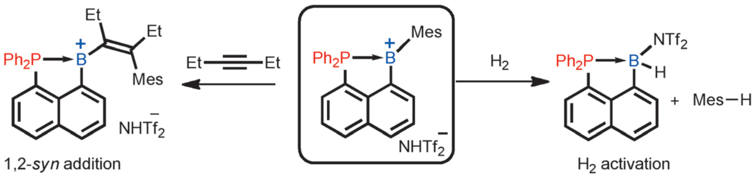
Pick up a peptide: Tfacm-protected cysteine is readily activated by pH adjustment, enabling the development of a highly efficient one-pot four-segment ligation method. Two proteins, crambin and the chemokine hCCL21, are prepared using this rapid and high-yielding synthetic route.

Cross-Coupling

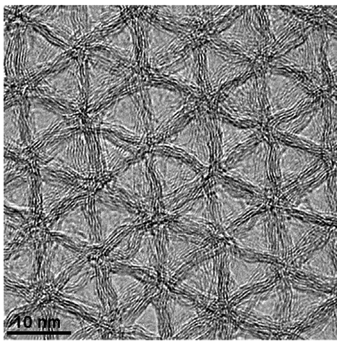


On the double: An efficient, regiospecific, and general oxidative dimerization of simple aryl acids to generate diaryl acids was developed. The reaction involves two direct aryl C—H activations catalyzed by rhodium, uses water as the solvent, and can be easily scaled up. The natural product ellagic acid was obtained in only two steps by using this method.

Borenium Cations



Versatile reactivity: A new type of borenium cation is reported in which a naphthyl bridge supports a strong P→B interaction. Borenium reacts with H_2 through side-on coordination of H_2 to boron, heterolytic splitting, and concomitant cleavage of the B—Mes bond. The molecule also reacts with 3-hexyne through a *syn* 1,2-carboboration reaction. NTf_2^- = triflimide.



Framed: The title frameworks were fabricated from self-assembled Fe_3O_4 nanocrystal superlattices. Because of their unique architectures and superior structure durability, the mesoporous graphene frameworks exhibit excellent electrochemical performance when used as anode materials for lithium-ion batteries.

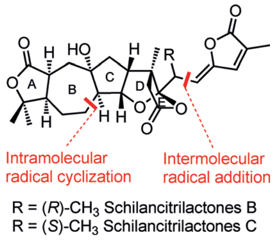
Mesoporous Materials

Y. Jiao, D. Han, L. Liu, L. Ji, G. Guo, J. Hu, D. Yang, A. Dong* ______ **5727 – 5731**

Highly Ordered Mesoporous Few-Layer Graphene Frameworks Enabled by Fe_3O_4 Nanocrystal Superlattices

Back Cover

In step: The first total syntheses of schilancitrilactones B and C have been accomplished by using an intramolecular radical cyclization to provide the seven-membered ring, late-stage iodination, and an intermolecular radical addition reaction as key steps. The approach provides a sequence for the syntheses of compounds related to the schilancitrilactones, as well as their derivatives and analogues.



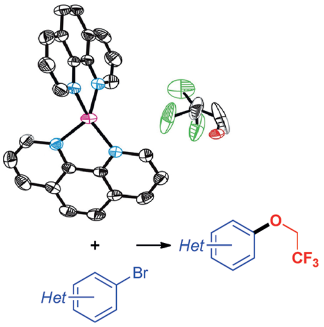
R = (R)-CH_3 Schilancitrilactones B
R = (S)-CH_3 Schilancitrilactones C

Natural Products

L. Wang, H. Wang, Y. Li, P. Tang* ______ **5732 – 5735**

Total Synthesis of Schilancitrilactones B and C

Efficiency drive: A series of copper(I) fluoroalkoxide complexes bearing N,N ligands have been prepared and structurally characterized. These well-defined complexes serve as efficient reagents for the fluoroalkoxylation of aryl and heteroaryl bromides to produce a wide range of trifluoroethyl, pentafluoropropyl, and tetrafluoropropyl (hetero)aryl ethers in good to excellent yields.



Synthetic Methods

R. Huang, Y. Huang, X. Lin, M. Rong, Z. Weng* ______ **5736 – 5739**

Well-Defined Copper(I) Fluoroalkoxide Complexes for Trifluoroethoxylation of Aryl and Heteroaryl Bromides

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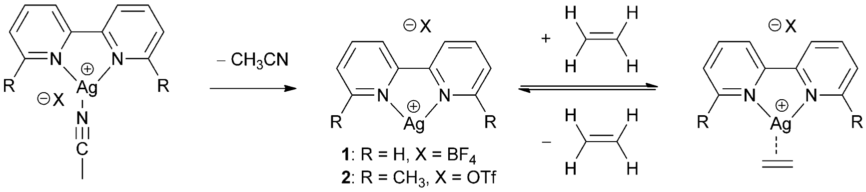


1: R = H, X = BF_4
2: R = CH_3, X = OTf

Site unseen: The coordination complexes **1** and **2**, having open silver(I) sites, were prepared and investigated for ethene/ethane binding. These complexes display ethene/ethane selectivity of up to 13 times higher than comparable solid sorbents, ethene loadings of up to 2.38 $mmol\,g^{-1}$, and saturation of silver(I) sites of up to 0.96 $mol_{ethene}/mol_{silver(I)}$. Tf = trifluoromethanesulfonyl.

Adsorption

VIP

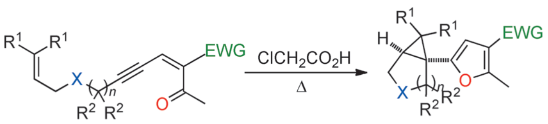
M. G. Cowan, W. M. McDanel, H. H. Funke, Y. Kohno, D. L. Gin,* R. D. Noble* ______ **5740 – 5743**

High Ethene/Ethane Selectivity in 2,2′-Bipyridine-Based Silver(I) Complexes by Removal of Coordinated Solvent

Cascade Reactions

J. S. Clark,* F. Romiti, K. F. Hogg,
M. H. S. A. Hamid, S. C. Richter, A. Boyer,
J. C. Redman, L. J. Farrugia **5744 – 5747**

Synthesis of Cyclopropyl-Substituted Furans by Brønsted Acid Promoted Cascade Reactions



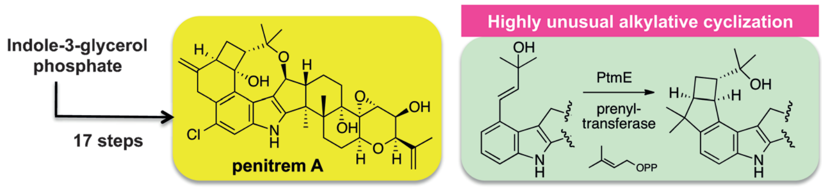
Chloroacetic acid promotes an efficient and diastereoselective intramolecular cascade reaction of electron-deficient ynenones to deliver products featuring a 2,3,5-trisubstituted furan bearing a fused cyclopropyl substituent at the 5-position. Synthetically relevant polycyclic building blocks featuring rings of various sizes and heteroatoms have been synthesized in high yield using this mild acid-catalyzed reaction. EWG = electron-withdrawing group.

Biosynthesis

C. Liu, K. Tagami, A. Minami,
T. Matsumoto, J. C. Frisvad, H. Suzuki,
J. Ishikawa, K. Gomi,
H. Oikawa* **5748 – 5752**

Reconstitution of Biosynthetic Machinery for the Synthesis of the Highly Elaborated Indole Diterpene Penitrem

Front Cover



The gene cluster that is responsible for the biosynthesis of the indole diterpene penitrem A has been identified. Thirteen out of the seventeen involved transformations were elucidated by heterologous reconstitution of the relevant genes and found to feature a prenylation-initiated cationic cyclization (PtmE) and two successive P450-catalyzed oxidative reactions to install the bicyclo[4.2.0]octane skeleton.

DOI: 10.1002/anie.201581914

Flashback: 50 Years Ago . . .

The use of mass spectrometry for the analysis of organic compounds was in its infancy but was already being explored by pioneers such as McLafferty and Djerassi. In a Review, Gerhard Spiteller and Margot Spiteller-Friedmann discuss structural elucidation of organic compounds by analysis of the fragmentation products.

Horst Prinzbach et al. reported on the photochemical isomerization of *exo*-tricyclo$[3.2.1.0^{2,4}]$octene derivatives to form tetracyclo$[3.3.0.0^{2,8}.0^{4,6}]$octane compounds. Various derivatives were investigated, and carboxylic acids were found to isomerize more efficiently than esters. Prinzbach's many achievements were summarized in his Obituary (see *Angew. Chem. Int. Ed.* **2012**, *51*, 11936).

In another Communication, Prinzbach and Arthur Lüttringhaus discussed the proton activity of 1,3-dithiolium cations. NMR spectroscopy was used to measure the half-lives of hydrogen–deuterium exchange at the 2-position. The cations were reacted further to produce tetrathiafulvalene derivatives, the mass spectra of which showed a peak corresponding to the resulting dithiacarbene fragment. Together with Gottfried Schill, Lüttringhaus reported the first templated synthesis of a catenane (for the full story see the Editorial by J. Fraser Stoddart in *Angew. Chem. Int. Ed.* **2014**, *53*, 11102).

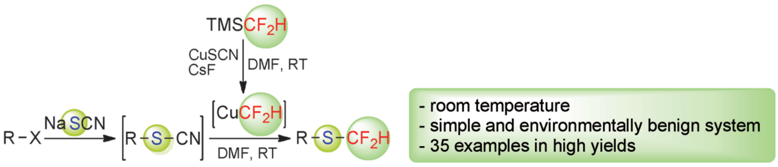
H. J. Berthold and H. Knecht published two Communications on the reactions of uranium trichloride and tetrachloride. The first report outlined the reactions of UCl_3 and UCl_4 with liquid ammonia at low temperature to produce ammoniates with the compositions $UCl_3\cdot(6.8–6.9)NH_3$ and $UCl_4\cdot(7.3–7.5)NH_3$. In the second Communication, the high-temperature reaction was discussed, and compounds such as UNH_2Cl_2, $U(NH_2)_2Cl$, and UNH_2Cl_3 were found to be formed.

Read more in Issue 5/1965.

Synthetic Methods

B. Bayarmagnai, C. Matheis, K. Jouvin, L. J. Goossen* ________ **5753 – 5756**

Synthesis of Difluoromethyl Thioethers from Difluoromethyl Trimethylsilane and Organothiocyanates Generated In Situ



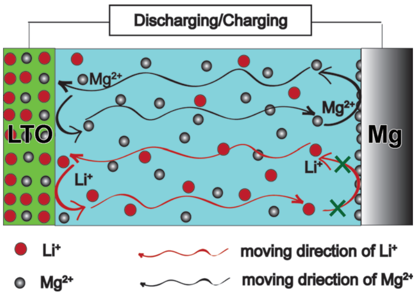
A copper–CF$_2$H complex generated in situ from copper thiocyanate and TMS–CF$_2$H smoothly converts organothiocyanates into valuable difluoromethyl thioethers. This reaction step can be combined with several thiocyanation methods to one-pot protocols, allowing late-stage difluoromethylthiolations of widely available alkyl halides and arenediazonium salts.

Electrochemistry

N. Wu, Z.-Z. Yang, H.-R. Yao, Y.-X. Yin, L. Gu, Y.-G. Guo* ________ **5757 – 5761**

Improving the Electrochemical Performance of the $Li_4Ti_5O_{12}$ Electrode in a Rechargeable Magnesium Battery by Lithium–Magnesium Co-Intercalation

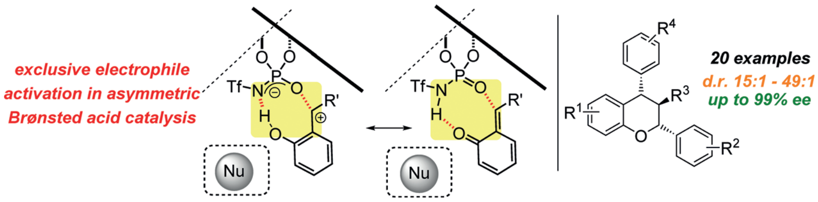
Synergy between Mg^{2+} and Li^+ ions: By controlling the collaborative electrochemistry of magnesium and lithium cations, $Li_4Ti_5O_{12}$ electrodes (LTO; see picture) close to sub-micron size gain extraordinary electrochemical energy storage capability. The electrodes show improved kinetics in rechargeable magnesium batteries.



Brønsted Acid Catalysis

C.-C. Hsiao, S. Raja, H.-H. Liao, I. Atodiresei, M. Rueping* _ **5762 – 5765**

Ortho-Quinone Methides as Reactive Intermediates in Asymmetric Brønsted Acid Catalyzed Cycloadditions with Unactivated Alkenes by Exclusive Activation of the Electrophile



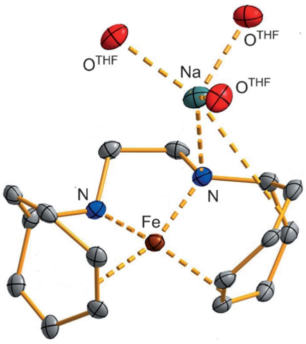
Exclusive chemistry: An efficient method for the highly enantioselective synthesis of chiral chromanes bearing multiple stereogenic centers was developed. A chiral BINOL-based *N*-triflylphosphoramide proved to be an effective catalyst for the in situ generation of *ortho*-quinone methides (o-QMs) and their subsequent cycloaddition reaction with unactivated alkenes provided chromanes with excellent diastereo- and enantioselectivity.

Low-Valent Iron Chemistry

C. Lichtenberg,* L. Viciu, M. Adelhardt, J. Sutter, K. Meyer, B. de Bruin,* H. Grützmacher* ________ **5766 – 5771**

Low-Valent Iron(I) Amido Olefin Complexes as Promotors for Dehydrogenation Reactions

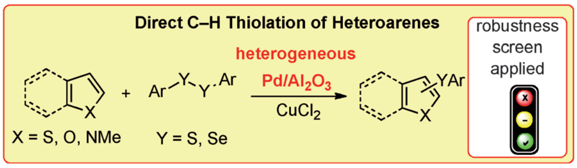
Square-planar Fe^I: A low-valent iron center has been stabilized in a distorted square-planar coordination geometry by using a diamido-diolefin ligand and an alkali metal counterion (see scheme). The heterobimetallic compounds of this type initiate the dehydrogenation of *N*,*N*-dimethylaminoborane and the dehydrogenative alcoholysis of silanes. The counterion $[Li(OEt_2)_2]^+$ or $[Na(thf)_3]^+$ affects the catalytic performance.



Catalytic Thiolation

S. Vásquez-Céspedes, A. Ferry, L. Candish, F. Glorius* ———— 5772 – 5776

Heterogeneously Catalyzed Direct C–H Thiolation of Heteroarenes

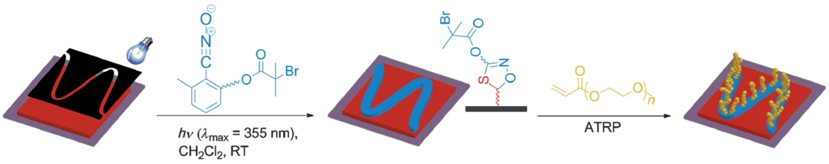


(Hetero)genius: A general method for the direct thiolation of electron-rich heteroarenes was developed by employing Pd/Al$_2$O$_3$, a recoverable and commercially available heterogeneous catalyst, and CuCl$_2$. Preliminary mechanistic studies indicate a heterogeneous active catalytic species, with the two metals playing complementary roles in the formation of the thiolated products.

Surface Chemistry

O. Altintas, M. Glassner, C. Rodriguez-Emmenegger, A. Welle, V. Trouillet, C. Barner-Kowollik* ———— 5777 – 5783

Macromolecular Surface Design: Photopatterning of Functional Stable Nitrile Oxides

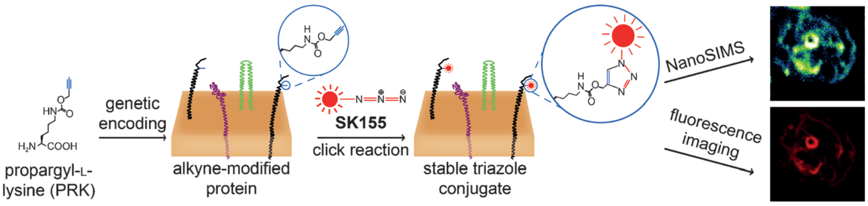


Perfect Patterning: The cycloaddition between a photogenerated thioaldehyde and stable nitrile oxides functions as a versatile and easy-to-use photoligation reaction in solution and on surfaces as confirmed by ESI-MS, XPS, and TOF-SIMS analysis. Polymer brushes were grown from the surface in a spatially confined regime by surface-initiated atom-transfer radical polymerization.

Protein Analysis

I. C. Vreja, S. Kabatas, S. K. Saka, K. Kröhnert, C. Höschen, F. Opazo, U. Diederichsen,* S. O. Rizzoli* ———— 5784 – 5788

Secondary-Ion Mass Spectrometry of Genetically Encoded Targets

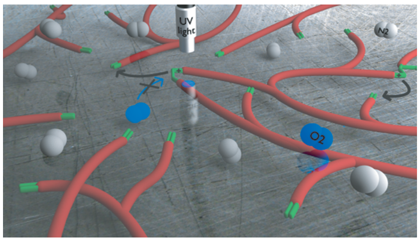


SPILLing the beans: a method of labeling specific proteins for secondary-ion mass spectrometry (SIMS), termed SPILL (specific protein isotopic and fluorescence labeling) is developed which involves unnatural amino acid incorporation and click reaction with a fluorescent probe enriched in ^{19}F (see scheme). The applicability of this method extends from cell culture systems to invertebrate model organisms.

Photopolymers

S. Kirschbaum, K. Landfester, A. Taden* ———— 5789 – 5792

Unique Curing Properties through Living Polymerization in Crosslinking Materials: Polyurethane Photopolymers from Vinyl Ether Building Blocks



Sleeping beauty: Living but dormant cationic polymerization sites can appear in vinyl ether functionalized polymer systems with high crosslinking capability as a result of network-induced vitrification. The concept characterizes a novel category of highly modular photopolymers, for which polymerization can proceed in the absence of light, is not hindered by oxygen inhibition, and can eventually be reactivated by heat and/or additional UV irradiation.

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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