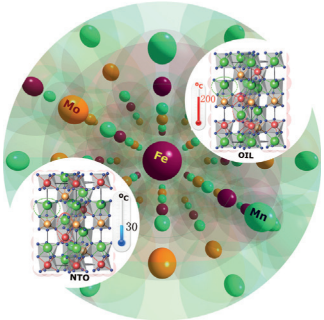
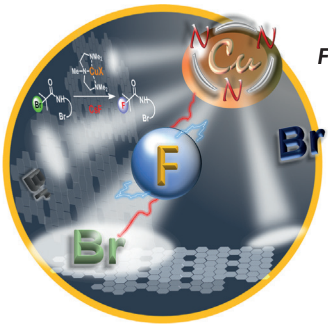
Geomimicking …

… is an innovative process inspired by the mineral world to produce new advanced materials. In nature, talc results from the hydrothermal alteration of bedrock over millions of years. In their Communication on page 9868 ff., F. Martin, C. Aymonier et al. show that by geomimicking, synthetic talc is obtained in only 20 s using a continuous supercritical fluids reactor (SCF). Synthetic nano-sized talc exhibits new crystal-chemistry signals and new properties, such as a hydrophilic character, opening the way to new applications.

Atomic-Scale Engineering

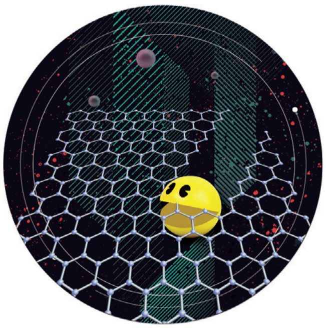
In their Communication on page 9862 ff., M. Greenblatt et al. describe how a cationic rearrangement in Mn_2FeMoO_6 at low temperature leads to an ordered ilmenite structzre with new magnetic and electrical properties.





Fluorination

The use of a copper catalyst system for the site-selective fluorination of α-bromoamides containing multiple brominated centers with CsF is described by T. Nishikata and co-workers in their Communication on page 10008 ff.



Graphene Nanostructures

By employing a multiscale simulation approach, a “Pac-Man” mechanism is revealed for the nickel-nanoparticle-catalyzed cutting of graphene, as reported by Z. Li et al in their Communication on page 9918 ff.

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Spotlight on Angewandte's Sister Journals **9820–9823**

Author Profile

Franziska Schoenebeck **9824**

*"My biggest motivation is my curiosity.
What I look for first in a publication is its innovative component. ..."*
This and more about Franziska Schoenebeck can be found on page 9824.

News

Arthur C. Cope Scholar Awards **9825–9826**

ACS Inorganic Nanoscience Award: R. E. Schaak **9826**

Priestley Medal: T. J. Marks **9826**


T. Akiyama

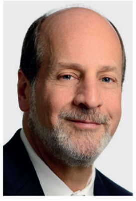

K. S. Anseth


G.-J. Boons


L. M. Campos


S. M. Cohen


M. J. Gaunt


M. M. Greenberg


T. J. Kodadek


L. T. Scott


D. A. Spiegel


R. E. Schaak


T. J. Marks

Books

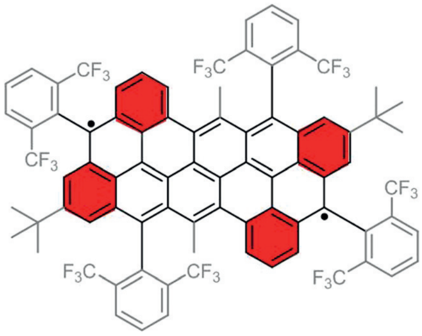
Catalytic Transformations via C–H Activation Jin-Quan Yu *reviewed by G. Dong** **9827**

Highlights

Polycycles

F. Hinkel, J. Freudenberg,
U. H. F. Bunz* ____ 9830 – 9832

A Stable π-Conjugated Singlet Biradical



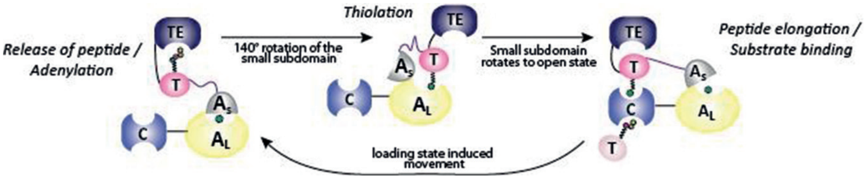
A large polycyclic hydrocarbon with a singlet biradical ground state has been obtained by the combined effects of topology and electron-accepting aromatic substituents, which stabilize its open-shell singlet state.

Minireviews

Nonribosomal Peptide Synthesis

T. Kittilä, A. Mollo, L. K. Charkoudian,*
M. J. Cryle* ____ 9834 – 9840

New Structural Data Reveal the Motion of Carrier Proteins in Nonribosomal Peptide Synthesis



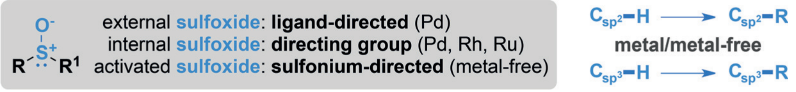
Have substrate, will travel: Nonribosomal peptide synthetases (NRPSs) show great potential for the generation of new bioactive molecules, however, a detailed model describing the NRPS mechanism is still lacking. Recent characterization of several multidomain NRPS structures has expanded our understanding of essential peptide carrier protein interactions and movements during NRPS catalysis.

Reviews

C–H Activation

A. P. Pulis,* D. J. Procter* ____ 9842 – 9860

C–H Coupling Reactions Directed by Sulfoxides: Teaching an Old Functional Group New Tricks



Classical sulfoxide directing groups have been given a new lease on life because of their unique ability to direct a variety of C–H couplings to form important C–C bonds. Sulfoxide direction operates through internal coordination to a metal (directing groups), through external coordination (ligands), or via sulfoxide capture of nucleophilic or electrophilic coupling partners (sulfonium-directed).

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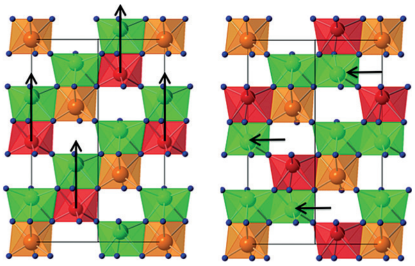
Communications



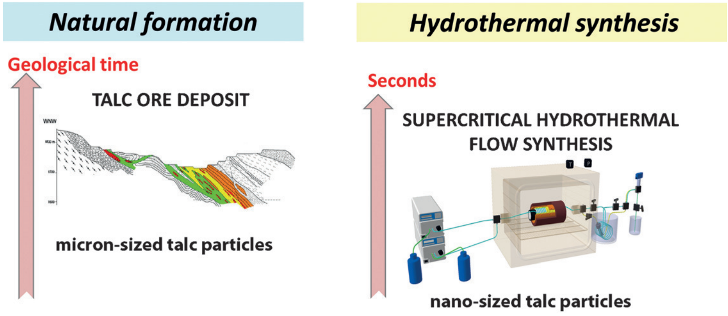
The unprecedented low-temperature (150–300 °C) cationic rearrangement in bulk Mn_2FeMoO_6 leads to a transition from a Ni_3TeO_6-type to an ordered-ilmenite structure, and dramatic changes of the electrical and magnetic properties, which demonstrates remarkable physical property tunneling through atomic-scale manipulation in bulk oxide under mild conditions.

Atomic-Scale Engineering

M. R. Li, M. Retuerto, P. W. Stephens, M. Croft, D. Sheptyakov, V. Pomjakushin, Z. Deng, H. Akamatsu, V. Gopalan, J. Sánchez-Benítez, F. O. Saouma, J. I. Jang, D. Walker, M. Greenblatt* ______ 9862 – 9867

Low-Temperature Cationic Rearrangement in a Bulk Metal Oxide

Frontispiece



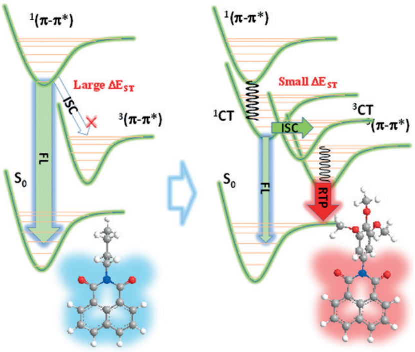
Small talc: The supercritical hydrothermal flow synthesis is a new method to produce model nanominerals, such as nano-talc, in just a few tens of seconds. As well as having different spectroscopic signals to natural talc, the nano-talc has new properties, such as its hydrophilic character, making it the first fluid talc filler for new applications.

Nanominerals

A. Dumas, M. Claverie, C. Slostowski, G. Aubert, C. Careme, C. Le Roux, P. Micoud, F. Martin,* C. Aymonier* ______ 9868 – 9871

Fast-Geomimicking using Chemistry in Supercritical Water

Front Cover



Purely organic: N-Substituted naphthalimides (NNIs) are purely organic materials that may show room-temperature phosphorescence (RTP). The relatively large energy gap between the NNI-localized $^1\pi$-π^* and $^3\pi$-π^* states can be bridged by intramolecular charge transfer (CT) states when the NNI is chemically modified with an electron donor.

Phosphorescence

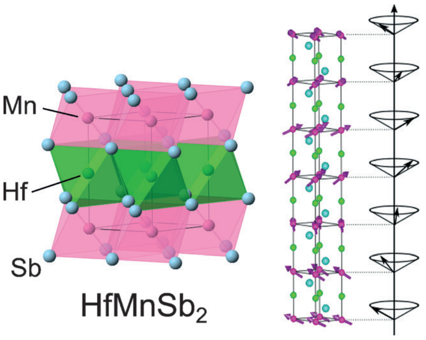
X. Chen, C. Xu, T. Wang, C. Zhou, J. Du, Z. Wang, H. Xu, T. Xie, G. Bi, J. Jiang, X. Zhang,* J. N. Demas, C. O. Trindle, Y. Luo, G. Zhang* ______ 9872 – 9876

Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation

Solid-State Structures

T. Murakami, T. Yamamoto, C. Tassel, H. Takatsu, C. Ritter, Y. Ajiro, H. Kageyama* ——— **9877 – 9880**

$HfMnSb_2$: A Metal-Ordered NiAs-type Pnictide with a Conical Spin Order

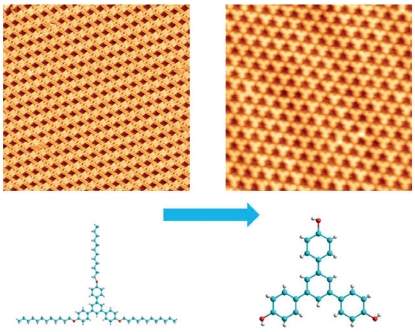


Metal order was obtained for the first time for a pnictide in $HfMnSb_2$ having a NiAs structure. The two-dimensional (2D) Mn network in $HfMnSb_2$ leads to a novel conical spin order via an RKKY interaction, in contrast to conventional ferromagnetism found in NiAs-type pnictides. This study suggests a new opportunity to study 2D-to-3D crossover in itinerant magnetic systems.

Surface Chemistry

B. Yang, H. P. Lin, K. J. Miao, P. Zhu, L. B. Liang, K. W. Sun, H. M. Zhang, J. Fan, V. Meunier, Y. Y. Li, Q. Li,* L. F. Chi* ——— **9881 – 9885**

Catalytic Dealkylation of Ethers to Alcohols on Metal Surfaces

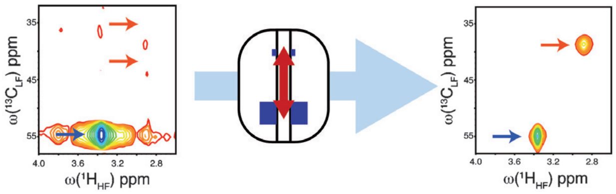


On-surface dealkylation: The dealkylation reaction from ethers to alcohols is controllably realized through on-surface synthesis techniques. This reaction was shown to be surface-assisted and universal for alkoxybenzene-containing ethers.

NMR Spectroscopy

S. F. Cousin, P. Kadeřávek, B. Haddou, C. Charlier, T. Marquardsen, J.-M. Tyburn, P.-A. Bovier, F. Engelke, W. Maas, G. Bodenhausen, P. Pelupessy, F. Ferrage* ——— **9886 – 9889**

Recovering Invisible Signals by Two-Field NMR Spectroscopy

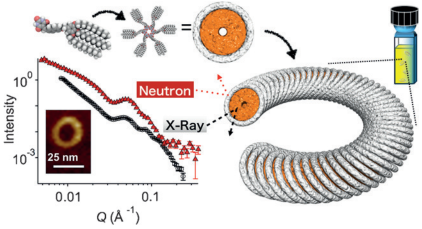


A two-field NMR spectrometer was designed to excite and observe nuclear spins in two distinct magnetic fields in a single experiment. This approach enables the detection of narrow resonances that are broadened beyond recognition at high fields because of internal dynamics.

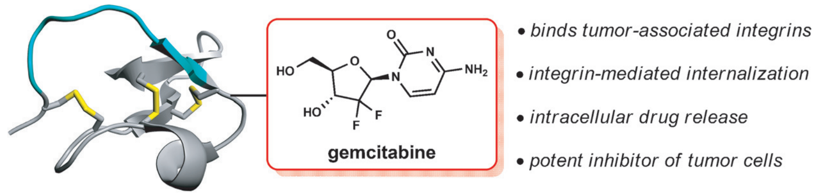
Supramolecular Chemistry

M. J. Hollamby,* K. Aratsu, B. R. Pauw, S. E. Rogers, A. J. Smith, M. Yamauchi, X. Lin, S. Yagai* ——— **9890 – 9893**

Simultaneous SAXS and SANS Analysis for the Detection of Toroidal Supramolecular Polymers Composed of Noncovalent Supermacrocycles in Solution



Deconstructing donuts: Molecules comprising a barbituric acid hydrogen-bonding unit, naphthalene body, and aliphatic tail self-assemble in solution into toroids. Using small-angle X-ray and neutron scattering, with complementary spectroscopic and microscopic data, a core–shell structure is revealed. This demonstrates the applicability of small-angle scattering analysis to complex solution-based self-assembled nanostructures.



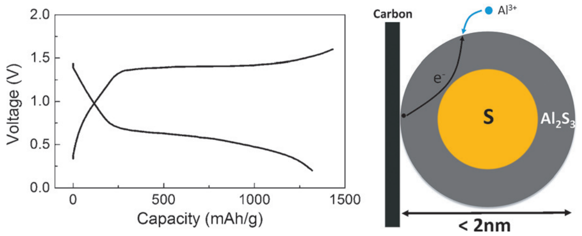
Tied up in knottins: Tumor-targeted knottin peptide-drug conjugates (KDC) are significantly smaller than antibody–drug conjugates, allowing for facile synthesis and conjugation. A KDC bearing the nucleoside gemcitabine is internalized by an integrin-mediated mechanism, releases its payload intracellularly, and is shown to be a highly potent inhibitor of several malignant cell lines.

Drug Delivery

N. Cox, J. R. Kintzing, M. Smith, G. A. Grant, J. R. Cochran* **9894 – 9897**

Integrin-Targeting Knottin Peptide–Drug Conjugates Are Potent Inhibitors of Tumor Cell Proliferation

Inside Cover

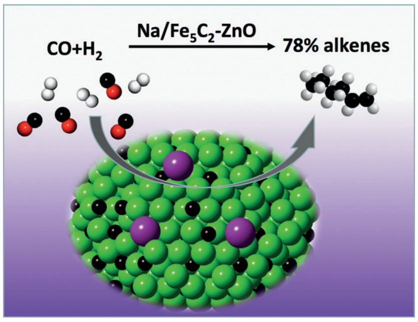


An ionic-liquid electrolyte is employed to give a rechargeable Al/S battery . The hurdle for oxidizing AlS_x is addressed by using a microporous carbon/sulfur cathode that can improve the electron access of sulfur species, enlarge interfacial reaction area, and reduce the Al^{3+} diffusion length (<2 nm). Experimental results indicate that sulfur undergoes solid state conversion reaction in the electrolyte.

Aluminum/Sulfur Batteries

T. Gao, X. Li, X. Wang, J. Hu, F. Han, X. Fan, L. Suo, A. J. Pearse, S. B. Lee, G. W. Rubloff, K. J. Gaskell, M. Noked,* C. Wang* **9898 – 9901**

A Rechargeable Al/S Battery with an Ionic-Liquid Electrolyte



Direct synthesis of olefins using Fe-based catalysts is a component of the traditional Fischer–Tropsch process. Na-doping of Fe catalysts alters the surface electronic structure, which promotes CO activation and desorption of products, while suppressing hydrogenation of double bonds. A Na-modulated catalyst is especially selective for alkenes (particularly C_{5+}).

Fischer–Tropsch Synthesis

P. Zhai, C. Xu, R. Gao, X. Liu, M. Li, W. Li, X. Fu, C. Jia, J. Xie, M. Zhao, X. Wang, Y.-W. Li, Q. Zhang,* X.-D. Wen,* D. Ma* **9902 – 9907**

Highly Tunable Selectivity for Syngas-Derived Alkenes over Zinc and Sodium-Modulated Fe_5C_2 Catalyst

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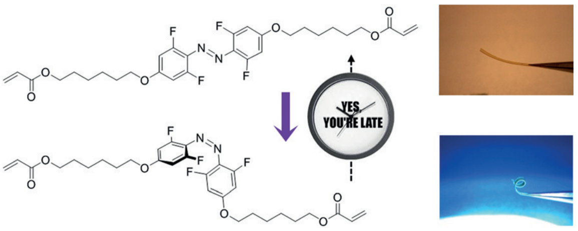


Liquid crystal polymers that contain fluorinated azobenzenes and retain a photochemically generated shape for more than eight days are reported. To preserve photoactivated molecular deformation on the macroscopic scale, the thermal stability of the photoswitch, the cross-linking density in the polymer network, and the molecular orientations in the material have been optimized.

Molecular Switches

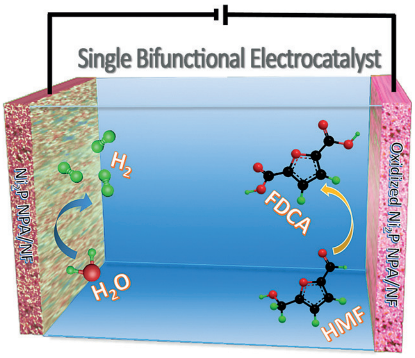
S. Iamsaard, E. Anger, S. J. Aßhoff, A. Depauw, S. P. Fletcher,* N. Katsonis* **9908 – 9912**

Fluorinated Azobenzenes for Shape-Persistent Liquid Crystal Polymer Networks

Biomass Conversion

B. You, N. Jiang, X. Liu,
Y. Sun* 9913 – 9917

Simultaneous H_2 Generation and Biomass Upgrading in Water by an Efficient Noble-Metal-Free Bifunctional Electrocatalyst



A strategy for simultaneous H_2 production and biomass valorization with high energy conversion efficiency is reported for coupling 5-hydroxymethylfurfural oxidation and H_2 generation in water catalyzed by a nonprecious bifunctional electrocatalyst, Ni_2P nanoparticle arrays coated on nickel foam. This strategy could provide a low-cost and energy-efficient alternative to standard electrocatalysts.

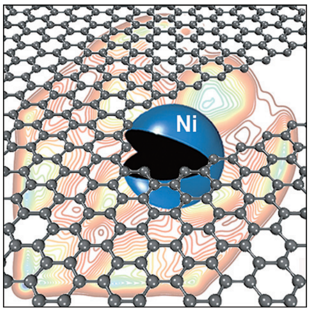
Graphene Nanostructures

Z. Qiu, L. Song, J. Zhao, Z. Li,*
J. Yang 9918 – 9921

The Nanoparticle Size Effect in Graphene Cutting: A "Pac-Man" Mechanism

Back Cover

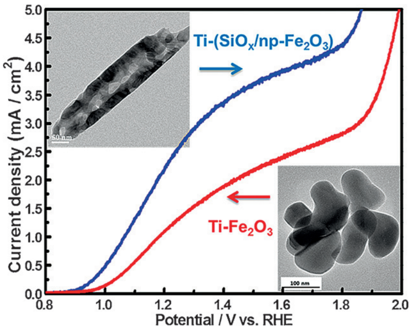
Surface or interface? By employing a multiscale simulation approach, a "Pac-Man" mechanism is revealed for the nickel-nanoparticle-catalyzed cutting of graphene. Although the overall cutting rate is proportional to the surface area of the nanoparticle, it is found that the rate-limiting step is actually at the graphene–metal interface instead of on the nanoparticle surface.



Nanoporous Structures

H. J. Ahn, K. Y. Yoon, M. J. Kwak,
J. H. Jang* 9922 – 9926

A Titanium-Doped SiO_x Passivation Layer for Greatly Enhanced Performance of a Hematite-Based Photoelectrochemical System

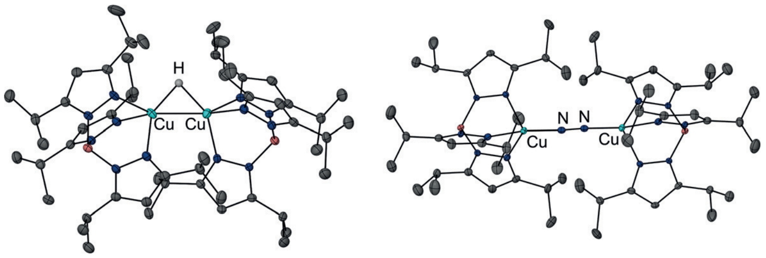


A nanoporous hematite with a Ti-doped SiO_x layer (Ti-(SiO_x/np-Fe_2O_3)) has a photocurrent density of 2.44 mA cm^{-2} at 1.23 V_{RHE} and 3.70 mA cm^{-2} at 1.50 V_{RHE}. This is due to a synergistic effect of decreased charge recombination, the increased number of active sites, and the reduced hole-diffusion pathway from the hematite to the electrolyte.

Dinitrogen Complexes

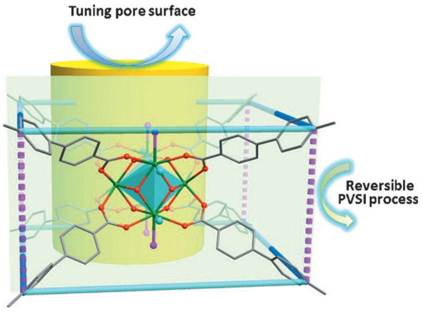
S. Zhang, H. Fallah, E. J. Gardner,
S. Kundu, J. A. Bertke, T. R. Cundari,*
T. H. Warren* 9927 – 9931

A Dinitrogen Dicopper(I) Complex via a Mixed-Valence Dicopper Hydride



Caught between two coppers: A tris(pyrazolyl)borate (Tp) dicopper N_2 complex $[Cu^I]_2(\mu\text{-}N_2)$ forms through the intermediacy of a mixed-valence dicopper hydride $[Cu^{1.5}]_2(\mu\text{-}H)$. Besides allowing a direct comparison between N_2 and O_2 binding at copper(I), this $[Cu^I]_2(\mu\text{-}N_2)$ complex represents a key member in a family of TpCu complexes $[Cu^I]_2(\mu\text{-}NH{=}NH)$ and $[Cu^I](NH_2NH_2)$ featuring reduced N_2 ligands.

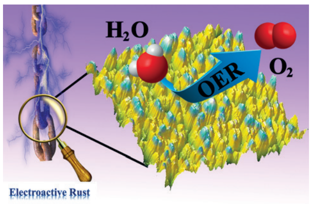
Bringing PSM into dynamic MOFs: Post-synthetic modification (PSM) is used to install/uninstall varied linkers into/from a flexible Zr-MOF. This post-synthetic variable-spacer installation (PVSI) strategy is used to tune elastic deformation, breathing behavior, and stabilization of the framework in controllable and predictable way. Tuning the pore surface leads to a larger surface area and improved gas separation and adsorption capacity.



Metal–Organic Frameworks

C.-X. Chen, Z. W. Wei, J.-J. Jiang, Y.-Z. Fan, S.-P. Zheng, C.-C. Cao, Y.-H. Li, D. Fenske, C.-Y. Su* ____ **9932 – 9936**

Precise Modulation of the Breathing Behavior and Pore Surface in Zr-MOFs by Reversible Post-Synthetic Variable-Spacer Installation to Fine-Tune the Expansion Magnitude and Sorption Properties

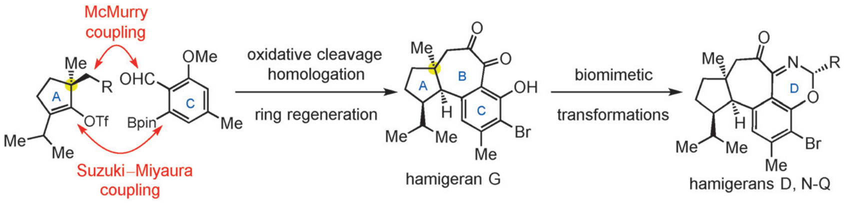


To turn waste into treasure, rusty stainless steel is recycled into low-cost, efficient, free-standing oxygen evolution reaction (OER) electrodes via an electrochemical oxidation–reduction cycle in an electrolyte.

Rust as Electrodes

H.–x. Zhong, J. Wang, F.-l. Meng, X.-b. Zhang* ____ **9937 – 9941**

In Situ Activating Ubiquitous Rust towards Low-Cost, Efficient, Free-Standing, and Recoverable Oxygen Evolution Electrodes

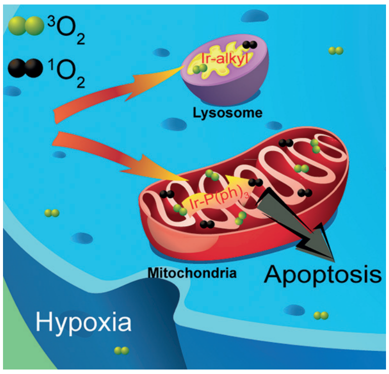


The *hammer*: The total synthesis of hamigerans D, G, L, and N–Q has been accomplished from a common intermediate bearing the basic 5-6-6 structure. A sequence of oxidative cleavage, homologation, and ring regeneration provided access to the 5-7-6 skeleton of hamigeran G which was transformed into hamigerans D, N–Q, and L efficiently based on a biomimetic hypothesis.

Natural Product Synthesis

X. Li, D. Xue, C. Wang, S. Gao* ____ **9942 – 9946**

Total Synthesis of the Hamigerans



Two Ir^{III} complexes, Ir-P$(ph)_3$ and Ir-alkyl, were designed and synthesized to evaluate the mitochondria- and lysosome-targeted PDT effect under normoxic and hypoxic conditions. As Ir-P$(ph)_3$-treated cells could maintain a relatively high mitochondrial oxygen content under hypoxia, the mitochondria-targeted complex Ir-P$(ph)_3$ showed a superior PDT effect than lysosome-targeted complex Ir-alkyl.

Photodynamic Therapy

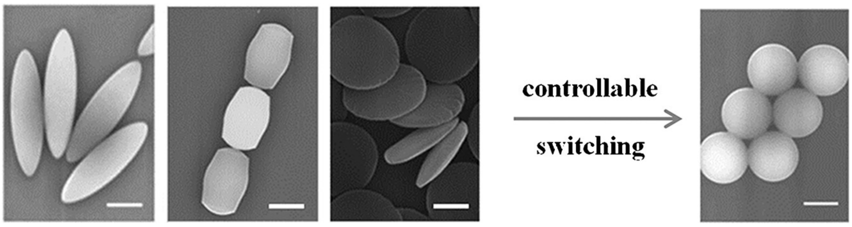
W. Lv, Z. Zhang, K. Y. Zhang, H. Yang, S. Liu, A. Xu, S. Guo, Q. Zhao,* W. Huang* ____ **9947 – 9951**

A Mitochondria-Targeted Photosensitizer Showing Improved Photodynamic Therapy Effects Under Hypoxia

Polymer Colloids

H. Wang, B. Li, A. G. Yodh,*
Z. Zhang* **9952 – 9955**

Stimuli-Responsive Shape Switching of Polymer Colloids by Temperature-Sensitive Absorption of Solvent

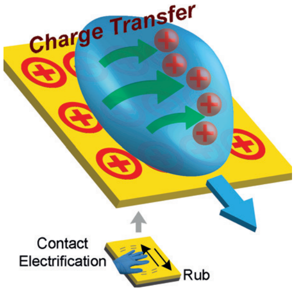


Turning up the heat on colloid particles: The shape of polymer colloidal particles can be switched in a temperature-dependent controllable manner from non-spherical to spherical in a water/2,6-lutidine binary mixture.

Charged Droplets

Y. Sun, X. Huang, S. Soh* **9956 – 9960**

Solid-to-Liquid Charge Transfer for Generating Droplets with Tunable Charge

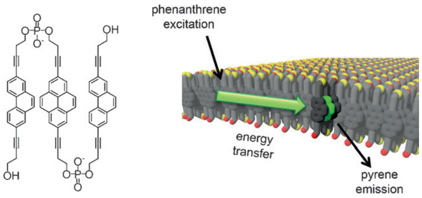


Charged water: When water droplets flow across surfaces that have been charged by contact electrification, the droplets also become charged. Depending on the charge of the surface, the polarity and magnitude of the charge of the droplets can be controlled. The charge allows the droplets to be manipulated, coalesced, and sorted. This method for generating charged droplet is general, simple and inexpensive.

Light-Harvesting Nanotubes

C. D. Bösch, S. M. Langenegger,
R. Häner* **9961 – 9964**

Light-Harvesting Nanotubes Formed by Supramolecular Assembly of Aromatic Oligophosphates

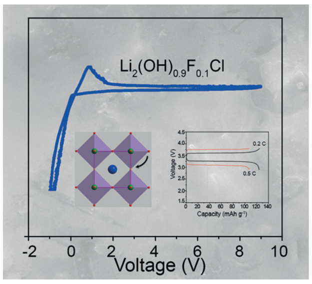


Exciting pyrenes: Phosphodiester-linked, 2,7-disubstituted phenanthrene trimers form supramolecular nanotubes in aqueous medium. Phenanthrenes are arranged in H-aggregates. Incorporation of small amounts of pyrene acceptor molecules leads to highly efficient light-harvesting nanotubes.

Lithium-Ion Batteries

Y. Li, W. Zhou, S. Xin, S. Li, J. Zhu, X. Lü,
Z. Cui, Q. Jia, J. Zhou, Y. Zhao,
J. B. Goodenough* **9965 – 9968**

Fluorine-Doped Antiperovskite Electrolyte for All-Solid-State Lithium-Ion Batteries



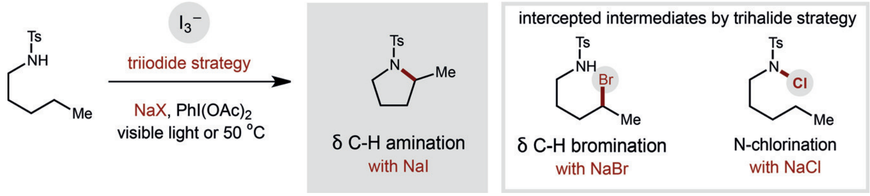
Higher conductivity: A fluorine-doped antiperovskite Li-ion conductor $Li_2(OH)_{0.9}F_{0.1}Cl$ shows electrochemical stability up to 9 V versus Li^+/Li and two orders of magnitude higher Li-ion conductivity than that of orthorhombic Li_2OHCl.

Radical Cations

Q. Zhu, E. C. Gentry,
R. R. Knowles* **9969 – 9973**

Catalytic Carbocation Generation Enabled by the Mesolytic Cleavage of Alkoxyamine Radical Cations

Carbocation intermediates can be accessed by mesolytic cleavage of alkoxyamine radical cations with a remarkably weak C–O bond. Spontaneous scission results in the formation of the stable nitroxyl radical TEMPO$^•$ and the reactive carbocation intermediate that can be intercepted by a wide range of nucleophiles.

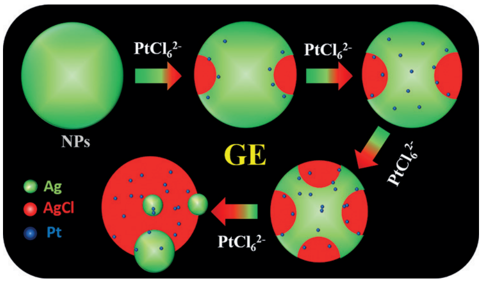


Just add salt: The C_δ–H amination of unactivated, secondary C(sp^3)–H bonds to form a broad range of functionalized pyrrolidines has been developed. By in situ oxidation of sodium iodide and sequestration of the transiently generated I_2 as I_3^-, this approach precludes undesired I_2-mediated decomposition. The mechanism is discussed and supported by NMR and UV/Vis data, as well as intercepted intermediates.

Radical Chemistry

E. A. Wappes, S. C. Fosu, T. C. Chopko, D. A. Nagib* ______ 9974 – 9978

Triiodide-Mediated δ-Amination of Secondary C–H Bonds



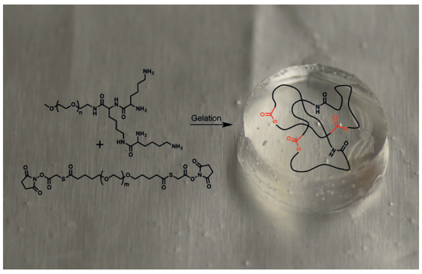
Nanoparticles show their metal: Galvanic exchange (GE) is an important method for the synthesis of bimetallic nanostructures. Single-nanoparticle (NP) spectroscopy reveals that the morphology of the nanostructure formed is a result of a dynamic sequence of structural transformations in the reaction.

Nanoparticles

J. G. Smith, I. Chakraborty, P. K. Jain* ______ 9979 – 9983

In Situ Single-Nanoparticle Spectroscopy Study of Bimetallic Nanostructure Formation

An easily removable dressing: A hydrogel-based dressing for second-degree burn wounds has been synthesized and tested in vivo. It is composed of a dendritic macromonomer and a poly(ethylene glycol) crosslinker that form a hydrogel upon mixing. An on-demand and atraumatic hydrogel dissolution proceeds through thiol–thioester exchange reaction in presence of a cysteine methyl ester solution.

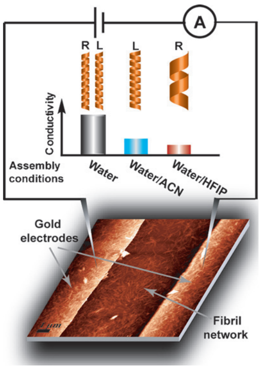


Hydrogel Wound Dressing

M. D. Konieczynska, J. C. Villa-Camacho, C. Ghobril, M. Perez-Viloria, K. M. Tevis, W. A. Blessing, A. Nazarian, E. K. Rodriguez, M. W. Grinstaff* ______ 9984 – 9987

On-Demand Dissolution of a Dendritic Hydrogel-based Dressing for Second-Degree Burn Wounds through Thiol–Thioester Exchange Reaction

Peptide circuit: Peptide fibrils functionalized with aromatic groups present efficient electron delocalization. The relationship between peptide assembly conditions, fibril microstructure and morphology, and conductivity was established. By augmenting self-assembly data with electrical characterization, conditions are established that lead to the fibril polymorph with the highest conductivity. ACN = acetonitrile, HFIP = hexafluoro-2-propanol.



Bio-electronics

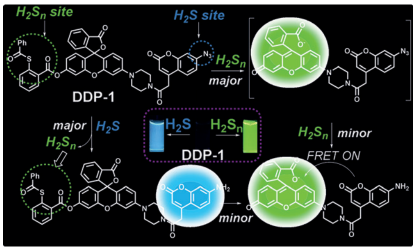
D. Ivnitski, M. Amit, O. Silberbush, Y. Atsmon-Raz, J. Nanda, R. Cohen-Luria, Y. Miller, G. Ashkenasy,* N. Ashkenasy* ______ 9988 – 9992

The Strong Influence of Structure Polymorphism on the Conductivity of Peptide Fibrils

Sensors

W. Chen, A. Pacheco, Y. Takano, J. J. Day, K. Hanaoka, M. Xian* ______ **9993 – 9996**

A Single Fluorescent Probe to Visualize Hydrogen Sulfide and Hydrogen Polysulfides with Different Fluorescence Signals

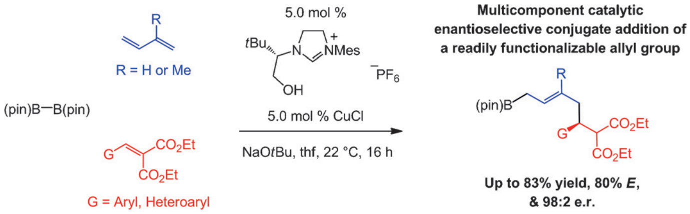


Dual-channel sensing: The first single fluorescent probe DDP-1 that can visualize hydrogen sulfide and hydrogen polysulfides with different emission channels was discovered (see picture). H_2S can be identified by the simultaneous appearance of two fluorescence signals in the blue and green channels, whereas H_2S_n can be characterized by the single emission in the green channel.

Multicomponent Catalysis

X. Li, F. Meng, S. Torker, Y. Shi, A. H. Hoveyda* ______ **9997 – 10002**

Catalytic Enantioselective Conjugate Additions of (pin)B-Substituted Allylcopper Compounds Generated in situ from Butadiene or Isoprene

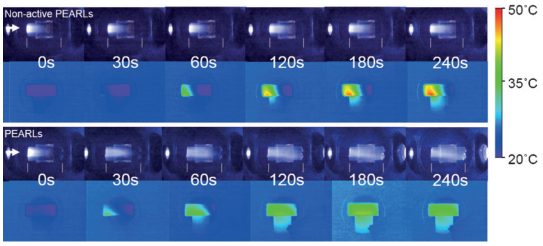


Catalysis with feedstock: Abundantly available butadiene and isoprene together with commercially available $B_2(pin)_2$ participate in enantioselective multicomponent conjugate addition to enoates. Transformations are catalyzed by a copper complex of an easily accessible NHC (N-heterocyclic carbene) ligand, affording products in up to 83 % yield, 80:20 *Z*:*E* and 98:2 e.r.

Photothermal Therapy

K. K. Ng, R. A. Weersink, L. Lim, B. C. Wilson, G. Zheng* **10003 – 10007**

Controlling Spatial Heat and Light Distribution by Using Photothermal Enhancing Auto-Regulated Liposomes (PEARLs)

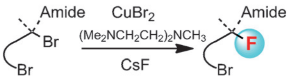


Evenly heated: Photothermal J-aggregate nanoparticles based on photothermal enhancing auto-regulating liposomes (PEARLs), have a closed-loop thermal feedback capability. This feedback mechanism enables an iterative increase in light transmission to achieve deeper and more homogeneous heating during photothermal therapy.

Fluorination

T. Nishikata,* S. Ishida, R. Fujimoto ______ **10008 – 10012**

Site-Selective Tertiary Alkyl–Fluorine Bond Formation from α-Bromoamides Using a Copper/CsF Catalyst System



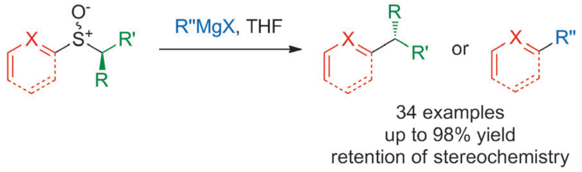
A picky copper: A copper catalyst system enables the site-selective fluorination of multi-brominated tertiary-alkyl compounds with the aid of an amide group. As the fluorination reagent, inexpensive CsF is used, and CuF_2 was found to be a reactive intermediate.

Inside Back Cover

Cross-Coupling

W. M. Dean, M. Šiaučiulis, T. E. Storr,
W. Lewis,
R. A. Stockman* ________ 10013 – 10016

Versatile C(sp^2)–C(sp^3) Ligand Couplings of Sulfoxides for the Enantioselective Synthesis of Diarylalkanes



34 examples
up to 98% yield
retention of stereochemistry

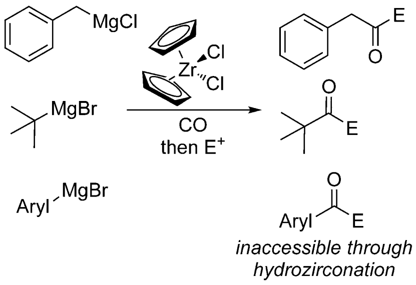
On three: The reaction of chiral (hetero)aryl benzyl sulfoxides with Grignard reagents affords diarylalkanes with greater than 99.5 % enantiomeric excess. The reaction is tolerant to multiple substitution patterns and proceeds in three operationally simple steps from commercially available reagents. This strategy provides orthogonal access to electron-deficient heteroaromatic compounds.

Synthetic Methods

M. Moss, X. Han,
J. M. Ready* ________ 10017 – 10021

Zirconocene-Mediated Carbonylative Coupling of Grignard Reagents

An inclusive approach: Acyl zirconocenes [Cp$_2$ZrCl(COR)] are valuable acyl anion equivalents in synthetic chemistry. Traditionally, they have been prepared by the hydrozirconation of alkenes or alkynes, thus precluding the generation of aryl, benzyl, tertiary alkyl, or branched acyl zirconocenes. Now a zirconium-mediated carbonylative coupling of Grignard reagents is described that involves previously inaccessible zirconocene intermediates (see scheme).

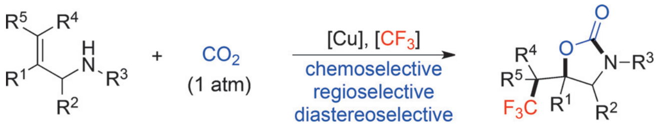


inaccessible through hydrozirconation

Heterocycle Synthesis

J.-H. Ye, L. Song, W.-J. Zhou, T. Ju,
Z.-B. Yin, S.-S. Yan, Z. Zhang, J. Li,
D.-G. Yu* ________ 10022 – 10026

Selective Oxytrifluoromethylation of Allylamines with CO$_2$



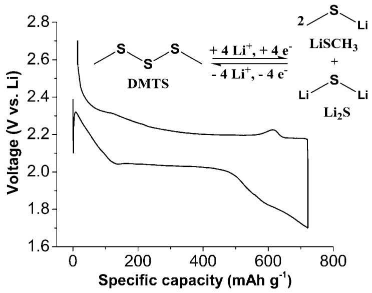
CO$_2$ changes things: The title reaction leads to important 2-oxazolidones. CO$_2$ plays a vital role in tuning the difunctionalization of alkenes from amino- to oxytrifluoromethylation. This reaction is highly chemo-, regio-, and diastereoselective under redox-neutral and mild reaction conditions. Moreover, these reactions feature good functional-group tolerance, broad substrate scope, and easy scalability.

Rechargeable Lithium Batteries

M. Wu, Y. Cui, A. Bhargav, Y. Losovyj,
A. Siegel, M. Agarwal, Y. Ma,
Y. Fu* ________ 10027 – 10031

Organotrisulfide: A High Capacity Cathode Material for Rechargeable Lithium Batteries

SSSsuitable for batteries: Dimethyl trisulfide (DMTS) was used as a model compound to demonstrate that organotrisulfide compounds can be high capacity cathode materials undergoing multi-electron redox reactions for rechargeable lithium batteries. The lithium/DMTS cell has a high specific energy density of 229 Wh kg^{-1} as a result of low electrolyte/DMTS ratios.

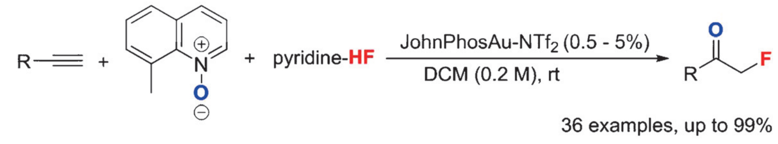


Carbenes

X. Zeng, S. Liu, Z. Shi, G. Liu,
B. Xu* ______ 10032 – 10036

Synthesis of α-Fluoroketones by Insertion of HF into a Gold Carbene

An HF insert: Insertion of hydrogen fluoride (HF) into a metal carbene is a new approach in transition metal catalyzed fluorination and provides an efficient synthesis of α-fluoroketones. This method gives excellent chemical yields for wide range of alkyne substrates.

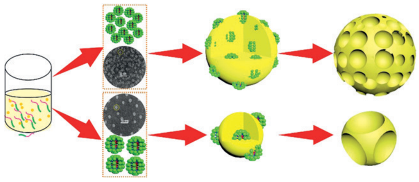


Mesoporous Metals

B. Jiang, C. Li,* J. Tang, T. Takei, J. H. Kim,
Y. Ide, J. Henzie, S. Tominaka,
Y. Yamauchi* ______ 10037 – 10041

Tunable-Sized Polymeric Micelles and Their Assembly for the Preparation of Large Mesoporous Platinum Nanoparticles

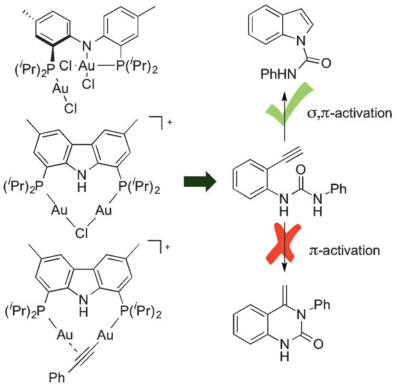
Dancing to a different tune: Platinum nanoparticles with continuously tunable mesoporous structures were prepared by a one-step approach based on polymeric micelles. Their particle and pore sizes were controlled by altering the solvent composition (see picture). By virtue of their high surface area, these mesoporous Pt structures were more efficient electrocatalysts for methanol oxidation than commercially available Pt catalysts.



Gold Catalysis

V. Vreeken, D. L. J. Broere, A. C. H. Jans,
M. Lankelma, J. N. H. Reek, M. A. Siegler,
J. I. van der Vlugt* ______ 10042 – 10046

Well-Defined Dinuclear Gold Complexes for Preorganization-Induced Selective Dual Gold Catalysis

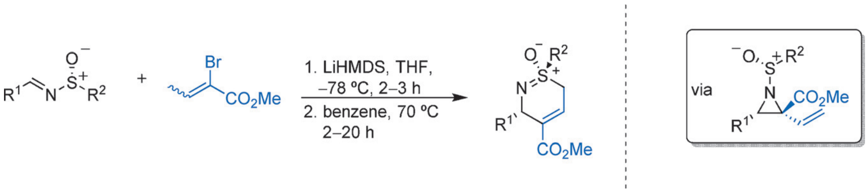


Worth its weight in gold: Coordination of gold(I) to a rigid bis(*o*-tolylamino)diphosphine ligand allows for versatile chemistry, including the isolation of a mixed-valent Au^{I}–Au^{III} species. Halide abstraction induces ligand-to-gold two-electron transfer, producing a carbazolyl-diphosphine analogue with a bridging chlorido ligand. This preorganized Au^{I}–Au^{I} species enables σ,π-activation of alkynes and is an isolable precatalyst for highly selective heterocyclizations.

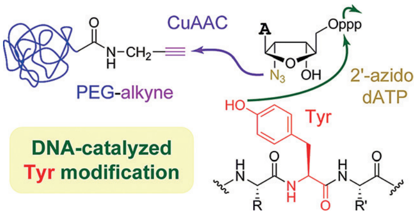
Rearrangements

T. Moragas, R. M. Liffey, D. Regentová,
J.-P. S. Ward, J. Dutton, W. Lewis,
I. Churcher, L. Walton, J. A. Souto,
R. A. Stockman* ______ 10047 – 10051

Sigmatropic Rearrangement of Vinyl Aziridines: Expedient Synthesis of Cyclic Sulfoximines from Chiral Sulfinimines



Making and breaking rings: A novel rearrangement of 2-vinyl aziridine 2-carboxylates to unusual chiral cyclic sulfoximines is described. The method allows the synthesis of substituted cyclic sulfoximines in high yields with complete stereocontrol, and tolerates a wide substrate scope. A one-pot process starting directly from sulfinimines provides access to complex chiral sulfoximines in only two steps from commercially available aldehydes.



Click onto tyrosine: Deoxyribozymes that attach azido groups at tyrosine residues of peptides are identified, including DNA enzymes with peptide sequence selectivity. The attached azido groups can be modified with useful moieties such as PEG and fluorophores.

Peptide Modification

P. Wang, S. K. Silverman* **10052–10056**

DNA-Catalyzed Introduction of Azide at Tyrosine for Peptide Modification

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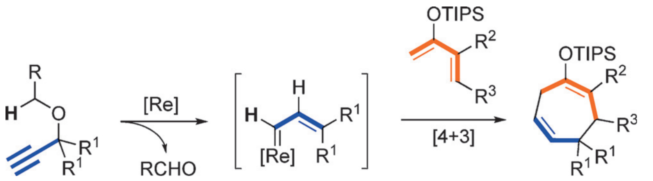

The rhenium(I)-catalyzed generation of α,β-unsaturated carbene complex intermediates from easily available propargyl ethers was achieved for the concise construction of cycloheptadiene derivatives through the formal [4+3] cycloaddition reaction with siloxydienes.

Cycloaddition Reactions

H. Sogo, N. Iwasawa* **10057–10060**

Rhenium(I)-Catalyzed Generation of α,β-Unsaturated Carbene Complex Intermediates from Propargyl Ethers for the Preparation of Cycloheptadiene Derivatives

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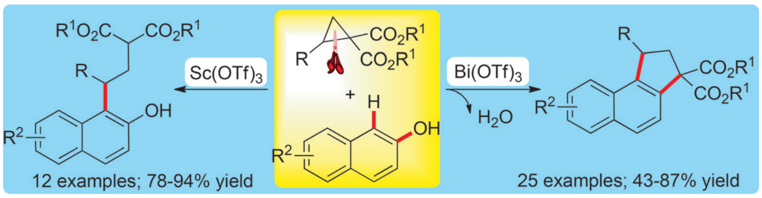

Ring donor: Lewis acid catalyzed selective reactions of donor–acceptor cyclopropanes with 2-naphthols are described. The use of $Bi(OTf)_3$ as the Lewis acid afforded naphthalene-fused cyclopentanes by a highly selective dehydrative [3+2] cyclopentannulation. Employing $Sc(OTf)_3$ as the Lewis acid, a Friedel–Crafts type addition of 2-naphthols to cyclopropanes was observed. Both reactions followed a dearomatization–rearomatization sequence of 2-naphthols.

Annulations

T. Kaicharla, T. Roy, M. Thangaraj, R. G. Gonnade, A. T. Biju* **10061–10064**

Lewis Acid Catalyzed Selective Reactions of Donor–Acceptor Cyclopropanes with 2-Naphthols

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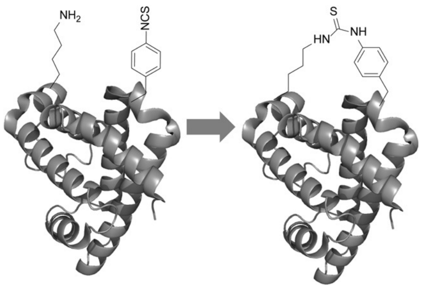
A handy handle: A novel noncanonical amino acid (ncAA) that contains an aryl isothiocyanate group was genetically incorporated into proteins in *E. coli*. This ncAA allows the selective conjugation of proteins to amine-containing molecules through formation of a thiourea bridge. It was also used to form intra- and intermolecular protein crosslinks through reaction with proximal Lys residues.



Noncanonical Amino Acids

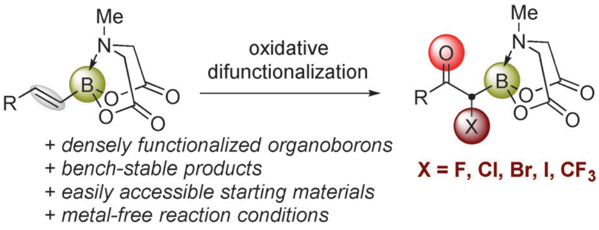
W. Xuan, J. Li, X. Luo, P. G. Schultz* **10065–10068**

Genetic Incorporation of a Reactive Isothiocyanate Group into Proteins

Synthetic Methods

W.-X. Lv, Y.-F. Zeng, Q. Li, Y. Chen, D.-H. Tan, L. Yang, H. Wang* ———— **10069 – 10073**

Oxidative Difunctionalization of Alkenyl MIDA Boronates: A Versatile Platform for Halogenated and Trifluoromethylated α-Boryl Ketones



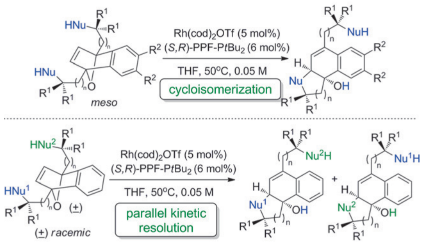
α-Boryl ketone synthesis: A one-pot oxidative difunctionalization of alkenyl MIDA boronates for the syntheses of densely functionalized α-boryl ketones was developed. The presence of multiple functional groups within the same molecule confers on these products great synthetic utility, as demonstrated by the successful synthesis of borylated furans.

Isomerization

C. C. J. Loh, M. Schmid, R. Webster, A. Yen, S. K. Yazdi, P. T. Franke, M. Lautens* ———— **10074 – 10078**

Rhodium-Catalyzed Asymmetric Cycloisomerization and Parallel Kinetic Resolution of Racemic Oxabicycles

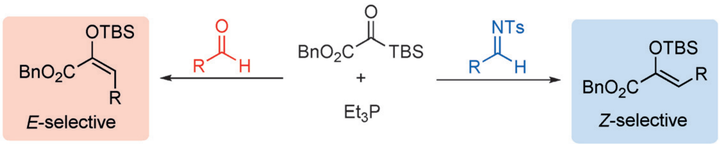
The oxabicycle dance! An unprecedented rhodium-catalyzed cycloisomerization of *meso*-oxabicyclic alkenes bearing bis-tethered nucleophiles is presented. A parallel kinetic resolution was also demonstrated, where racemic oxabicycles bearing two different tethered nucleophiles can be resolved enantioselectively to give two constitutional isomers by differential nucleophilic attack.



Rearrangements

Y. Matsuya,* K. Wada, D. Minato, K. Sugimoto ———— **10079 – 10082**

Highly Efficient Access to Both Geometric Isomers of Silyl Enol Ethers: Sequential 1,2-Brook/Wittig Reactions



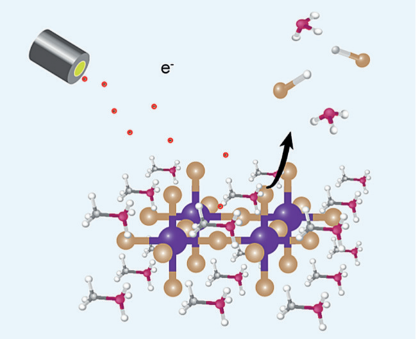
A witty brook: Novel sequential 1,2-Brook/Wittig reactions were developed for preparation of the title compounds. This method enables highly selective preparation of both geometric isomers of glyoxylate silyl enol ethers by using aldehyde (*E*-selective) and tosylimines (*Z*-selective) as a Wittig electrophile. Plausible explanations for the observed selectivity were also discussed.

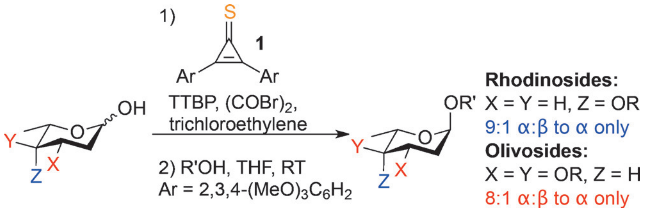
Perovskites

A. R. Milosavljević,* W. Huang, S. Sadhu, S. Ptasinska ———— **10083 – 10087**

Low-Energy Electron-Induced Transformations in Organolead Halide Perovskite

Explaining the break-up: Low-energy electrons (4.5 to 60 eV) can affect structural and chemical properties of methylammonium (MA) lead iodide perovskite (MAPbI$_3$) via interactions with the organic part. This results in MAPbI$_3$ decomposition and aggregation of the hydrocarbon layer.





No directors needed! A combination of cyclopropene-1-thione **1** and oxalyl bromide promotes reagent-controlled dehydrative glycosylation reactions with 2,6-dideoxy- and 2,3,6-trideoxy-sugar donors in good yield and high selectivity (see Scheme). The best selectivity is observed with secondary acceptors. Orthogonal protecting groups on the donor are tolerated, allowing the reaction to be used in oligosaccharide synthesis.

Oligosaccharide Synthesis

J. M. Nogueira, M. Bylsma, D. K. Bright, C. S. Bennett* ________ **10088 – 10092**

Reagent-Controlled α-Selective Dehydrative Glycosylation of 2,6-Dideoxy- and 2,3,6-Trideoxy Sugars

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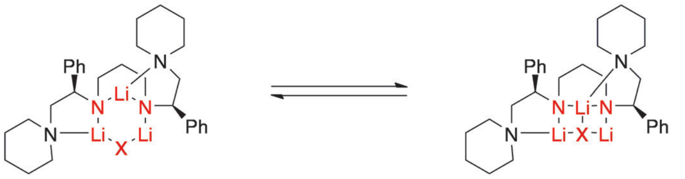

Koga's chiral dilithium amide used in asymmetric synthesis is shown to promiscuously form mixed aggregates with a wide variety of lithium salts including those containing halides, alkoxides, acetylides, and amides. Although largely isostructural, the presence or absence of Li–X transannular contacts distinguishes ladder from cyclic motifs.

Enantioselective Synthesis

Y. Ma, K. A. Mack, J. Liang, I. Keresztes, D. B. Collum,* A. Zakarian* ________ **10093 – 10097**

Mixed Aggregates of the Dilithiated Koga Tetraamine: NMR Spectroscopic and Computational Studies

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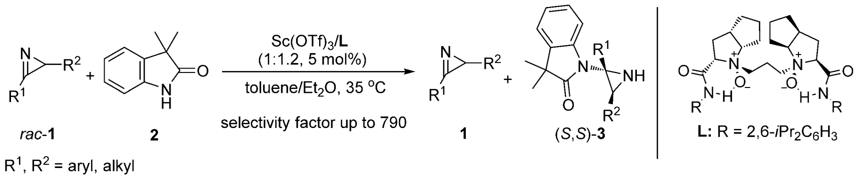

The *s* factor: The title reaction was achieved in the presence of the chiral *N*,*N*′-dioxide/Sc^{III} complex. The method provided a promising approach for obtaining the enantioenriched 2*H*-azirine derivatives and protecting-group free aziridines with excellent results (up to > 99% *ee* and 99% *ee*, > 19:1 d.r.).

Asymmetric Catalysis

H. P. Hu, Y. B. Liu, L. L. Lin, Y. H. Zhang, X. H. Liu,* X. M. Feng* __ **10098 – 10101**

Kinetic Resolution of 2*H*-Azirines by Asymmetric Imine Amidation

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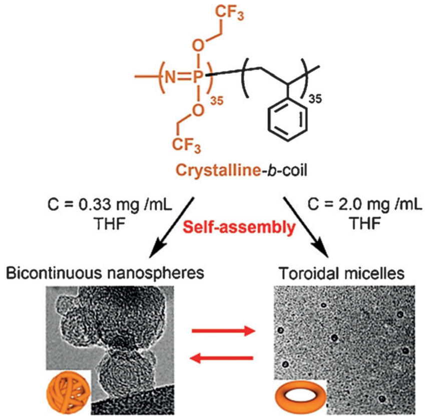
One polymer, two great looks: Two complex nanostructures were synthesized by the self-assembly of a structurally simple crystalline-*b*-coil diblock copolymer in THF without additives. The two morphologies are related by a reversible bicontinuous-to-toroidal morphological evolution triggered by changes in the polymer concentration (see picture). The final morphology of the aggregates is mostly determined by the ordering of the core-forming polymer blocks.



Nanostructures

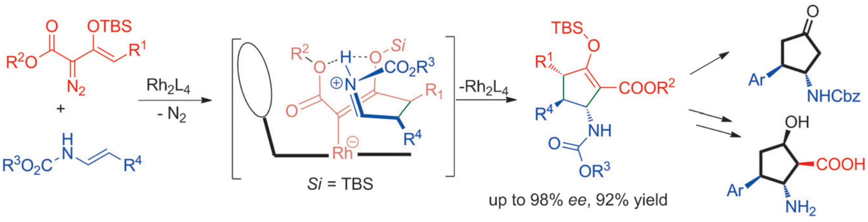
D. Presa-Soto, G. A. Carriedo, R. de la Campa, A. Presa Soto* ________ **10102 – 10107**

Formation and Reversible Morphological Transition of Bicontinuous Nanospheres and Toroidal Micelles by the Self-Assembly of a Crystalline-*b*-Coil Diblock Copolymer

Cycloaddition

Y. Deng, M. V. Yglesias, H. Arman, M. P. Doyle* ———— **10108 – 10112**

Catalytic Asymmetric Synthesis of Cyclopentyl β-Amino Esters by [3+2] Cycloaddition of Enecarbamates with Electrophilic Metalloenolcarbene Intermediates

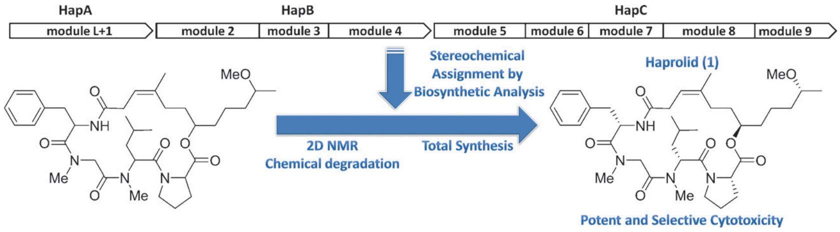


Valuable intermediates: The title compounds are formed catalytically by [3+2] cycloaddition reactions of enecarbamates with electrophilic metalloenolcarbenes with excellent diastereocontrol. β-silyl-substituted enoldiazoacetates, a chiral dirhodium catalyst, and *trans*-β-arylvinylcarbamates are optimal for this transformation, which occurs with hydrogen-bond association between the vinylcarbamate and metalloenolcarbene.

Natural Products

H. Steinmetz, J. Li, C. Fu, N. Zaburannyi, B. Kunze, K. Harmrolfs, V. Schmitt, J. Herrmann, H. Reichenbach, G. Höfle, M. Kalesse,* R. Müller* **10113 – 10117**

Isolation, Structure Elucidation, and (Bio)Synthesis of Haprolid, a Cell-Type-Specific Myxobacterial Cytotoxin



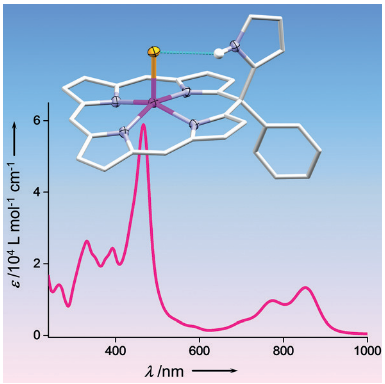
The macrolactone haprolid was isolated from *Byssovorax cruenta*. Bioinformatic analysis of the haprolid biosynthetic gene cluster aided stereochemical assignments based on the hybrid polyketide synthase/nonribosomal peptide synthetase origin of the compound. Total synthesis corroborated all predictions. Haprolid showed cytotoxicity against several cell lines in the nanomolar range whereas other cells were almost unaffected.

Isoporphyrins

P. Schweyen, M. Hoffmann, J. Krumsieck, B. Wolfram, X. Xie, M. Bröring* ———— **10118 – 10121**

Metal-Assisted One-Pot Synthesis of Isoporphyrin Complexes

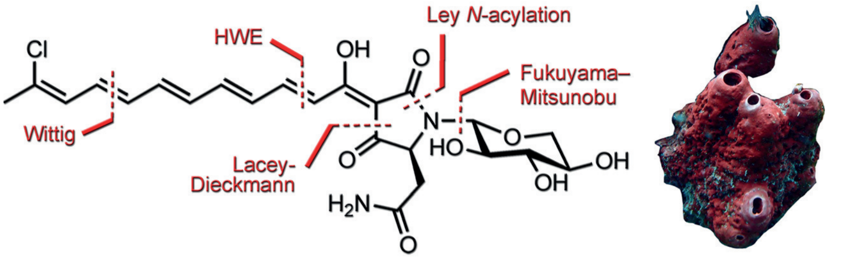
Old synthesis, new tricks: Isoporphyrins form in unprecedented amounts if the long-established Adler–Longo condensation for tetraarylporphyrin synthesis is performed in the presence of metal acetates as template agents. The isoporphyrins formed by this one-pot method are surprisingly stable and show the anticipated long-wavelength absorption typical for this class of porphyrinoids.



Natural Products

M. Petermichl, S. Loscher,
R. Schobert* ———— 10122 – 10125

Total Synthesis of Aurantoside G, an *N*-β-Glycosylated 3-Oligoenoyltetramic Acid from *Theonella swinhoei*

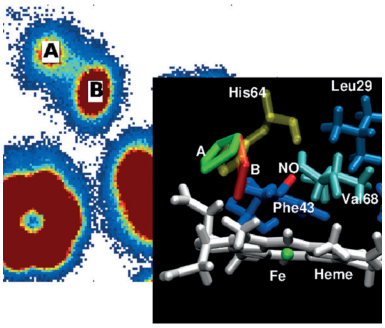


N-Glycotetramates: The first synthesis of a naturally occurring N-glycosylated 3-acyltetramic acid afforded aurantoside G, a metabolite of the marine sponge *Theonella swinhoei*, in 3.7 % yield over 12 steps. The β-configuration of the D-xylose, which is decisive for the biological activity, was established through the directing effect of bulky PMB protecting groups on the xylose during the Ley-type N-(β-keto)acylation step.

Computational Chemistry

M. Soloviov, A. K. Das,
M. Meuwly* ———— 10126 – 10130

Structural Interpretation of Metastable States in Myoglobin–NO



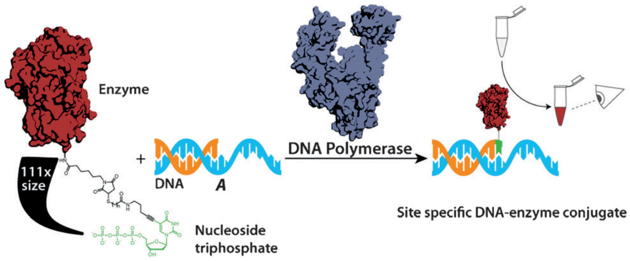
Reactive molecular dynamics simulations find two timescales for nitric oxide rebinding to myoglobin. These two timescales were assigned to the structures "A" and "B" of the His64 side chain, which controls ligand access to the heme iron center.

Modified Nucleotides

VIP

M. Welter, D. Verga,
A. Marx* ———— 10131 – 10135

Sequence-Specific Incorporation of Enzyme–Nucleotide Chimera by DNA Polymerases



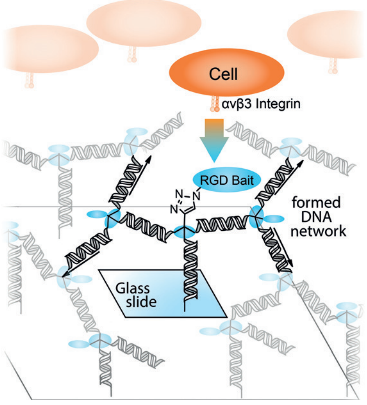
Think big: Despite their large size, enzyme-modified nucleotides are accepted as substrates by template-dependent DNA polymerases. This was exploited to develop a colorimetric system for the naked-eye detection of DNA and RNA targets at single-base resolution.

DNA Nanotechnology

A. Finke, H. Bußkamp, M. Manea,
A. Marx* ——— **10136 – 10140**

Designer Extracellular Matrix Based on DNA–Peptide Networks Generated by Polymerase Chain Reaction

Catch and release: A functional DNA-based network was generated by PCR and functionalized with a peptide that specifically interacts with certain cell types while others are repelled. By following this approach, specific cell types were attracted to functionalized surfaces. The cells remained viable and could also be easily detached for future studies.

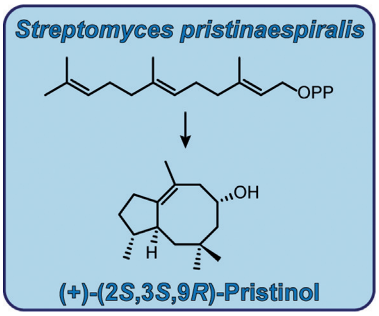


Natural Products

T. A. Klapschinski, P. Rabe,
J. S. Dickschat* ——— **10141 – 10144**

Pristinol, a Sesquiterpene Alcohol with an Unusual Skeleton from *Streptomyces pristinaespiralis*

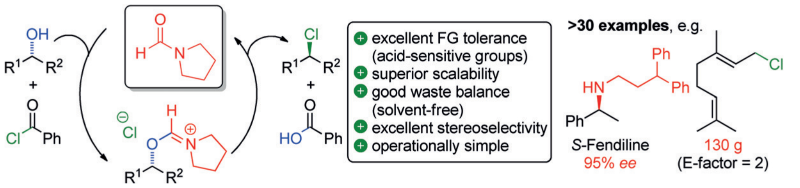
A terpene cyclase from *Streptomyces pristinaespiralis* was identified as the synthase for (+)-(2*S*,3*S*,9*R*)-pristinol. This compound represents a new sesquiterpene skeleton with a rare 8-membered ring topology. Isotopic labelling experiments revealed a surprising cyclization mechanism and allowed delineation of the EI-MS fragmentation mechanisms for pristinol.



Organocatalysis

P. H. Huy,* S. Motsch,
S. M. Kappler ——— **10145 – 10149**

Formamides as Lewis Base Catalysts in S_N Reactions—Efficient Transformation of Alcohols into Chlorides, Amines, and Ethers



A simple formamide catalyst enables highly efficient dehydroxychlorinations of alcohols with benzoyl chloride as the sole reagent. The novel method, which proceeds through iminium-activated alcohol intermediates, exhibits an excellent functional group tolerance, scalability and waste-balance. Enantioenriched alcohols (99% *ee*) are converted under inversion into the corresponding chlorides (≥95% *ee*).

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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Angewandte Corrigendum

The authors of this Communication have found that the NMR data reported for the compounds were incomplete. More comprehensive data are provided in the Supporting Information available for this Corrigendum.

A Toxic RNA Catalyzes the In Cellulo Synthesis of Its Own Inhibitor

S. G. Rzuczek, H. Park, M. D. Disney* ———— **10956–10959**

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