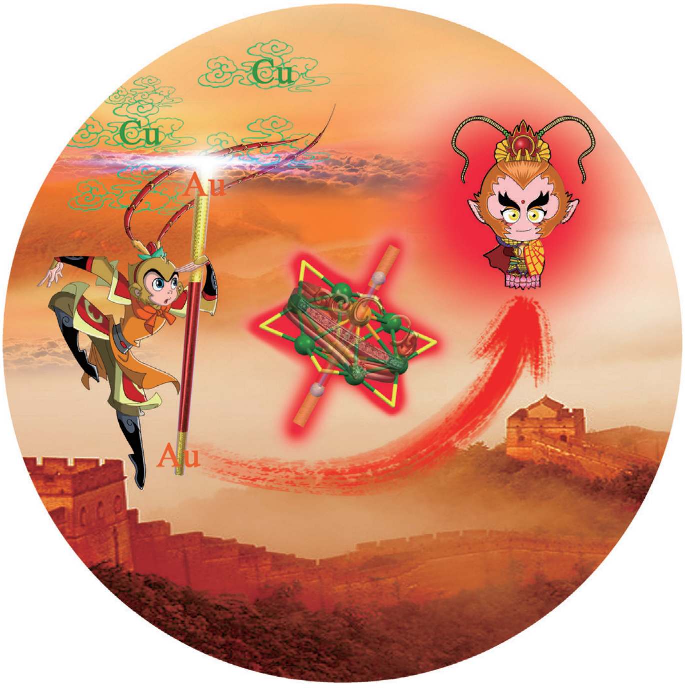
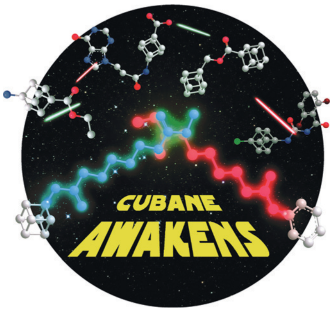
The Monkey King, ...

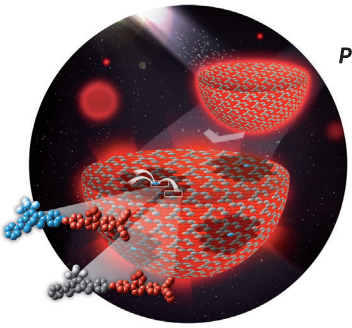


… a famous Chinese mythical creature with the magic golden cudgel tames and defeats the monsters in the journey to the West. In their Communication on page 3611 ff., M. Zhu, H. Yu, and co-workers describe how the aggregation of wild copper complexes with neutral gold species induces strong luminescence by the restriction of intramolecular rotations.

Bioisosteres

In their Communication on page 3580 ff., C. M. Williams, G. P. Savage, J. Tsanaktsidis et al. confirm that cubane can act as a benzene bioisostere by synthesizing and evaluating cubane derivatives of five biologically important molecules.



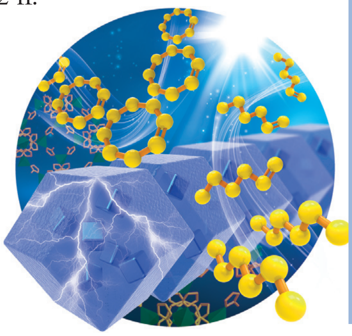


Photoswitchable Nanoparticles

Photoswitchable fluorescent nanoparticles, with enhanced properties arising from efficient intermolecular energy transfer are described by R. Métivier, T. Fukaminato et al. in their Communication on page 3662 ff.

MOF Composites

H.-L. Jiang and co-workers show in their Communication on page 3685 ff., that the composite material Pd nanocubes@ZIF-8 efficiently catalyzes the hydrogenation of olefins at room temperature under light irradiation.



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Service

Author Profile

“In a spare hour, I compose or translate poems. My favorite artist is Bodo Wartke, a fantastic piano cabaret artist …”
This and more about Stefanie Dehnen can be found on page 3542.

News


M. El-Sayed


A. Facchetti


S. H. Strauss

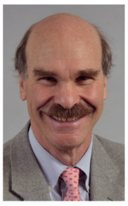

V. L. Pecoraro


T. P. Russell


K. I. Goldberg


E. I. Solomon


F. P. Gabbaï

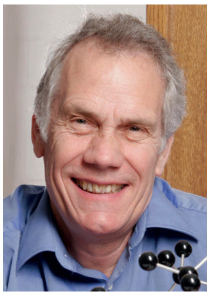

M. A. Ratner


A. J. R. Heck


E. J. Schelter


T. E. Albrecht-Schmitt

Obituaries



Malcolm H. Chisholm, Distinguished Professor of Mathematical and Physical Sciences at The Ohio State University, passed away on November 20, 2015. He is best known for his pioneering work on the chemistry of metal–metal multiple bonds, the molecular and electronic structure and bonding of transition-metal compounds, and the exploration of excited states of complexes with metal–metal quadruple bonds.

Malcolm H. Chisholm (1945–2015)

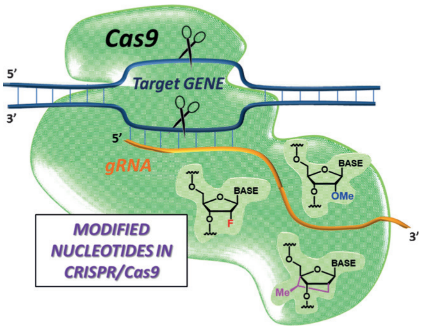
D. L. Clark,* B. E. Bursten* ______ **3545**

Highlights

Gene Editing

A. Latorre, A. Latorre,
Á. Somoza* ______ **3548 – 3550**

Modified RNAs in CRISPR/Cas9: An Old Trick Works Again



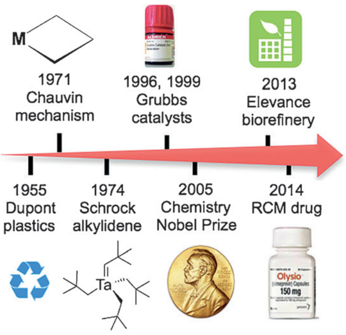
Old tricks, new dog: CRISPR/Cas9 is a powerful tool for gene editing that requires an endonuclease (Cas9) and RNA strands. It has been shown that chemical modification of the RNA structures, an approach that has been used to improve the efficiency of RNA interference, can also be applied to enhance the activity of CRISPR/Cas9 and reduce its off-target effects.

Minireviews

Industrial Olefin Metathesis

C. S. Higman, J. A. M. Lummiss,
D. E. Fogg* ______ **3552 – 3565**

Olefin Metathesis at the Dawn of Implementation in Pharmaceutical and Specialty-Chemicals Manufacturing



The metathesis industry: Olefin metathesis, the transformative potential of which was recognized with the Nobel Prize a decade ago, has changed the synthetic landscape in academia. This Minireview describes the beginning of a new era for metathesis in industry, illustrated by the first examples of its implementation in pharmaceutical and specialty-chemicals manufacturing.

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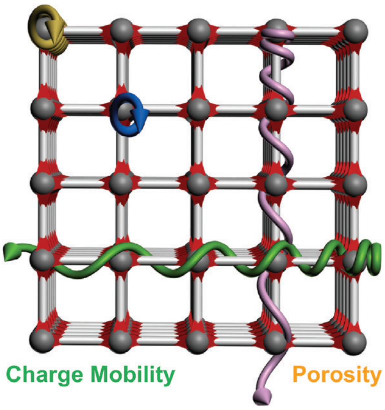
Reviews

Conductive MOFs

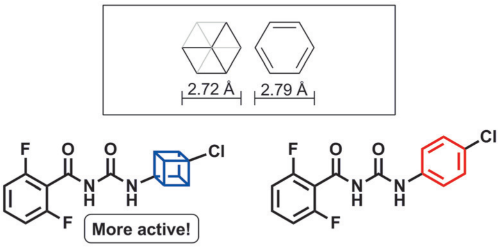
MOFs conduct: Metal–organic frameworks (MOFs) that simultaneously display permanent porosity and electrical conductivity are an emerging class of materials that display promise for a wide variety of next-generation technologies. This Review describes recent progress in this rapidly developing field, with a focus on the design principles that have enabled long-range charge transport in MOFs.



Communications

Bioisosteres

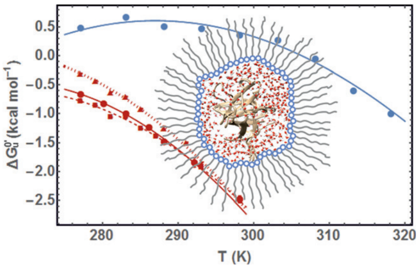
Frontispiece



Over 25 years ago, Eaton proposed that cubane could act as a benzene bioisostere. This hypothesis has now been confirmed with the synthesis and evaluation of cubane derivatives of five biologically important molecules: Two cubane analogues showed increased bioactivity compared to their benzene counterparts whereas two further analogues were of equal bioactivity.

Protein Stability

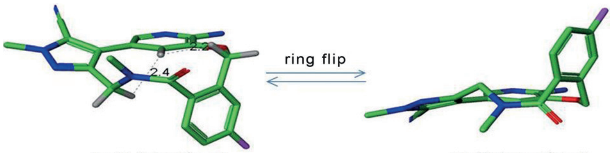
Under crowded conditions: Knowing how confinement in nanometer-sized spaces affects proteins is essential for understanding their roles in biology as well as for refining industrial applications and drug delivery. Using ^{19}F NMR spectroscopy and equilibrium thermodynamics it is shown how globular protein stability is affected by encapsulating in reverse micelles.



Anti-Cancer Drugs

J. Elleraas, J. Ewanicki, T. W. Johnson,
N. W. Sach, M. R. Collins,*
P. F. Richardson* **3590–3595**

Conformational Studies and Atropisomerism Kinetics of the ALK Clinical Candidate Lorlatinib (PF-06463922) and Desmethyl Congeners



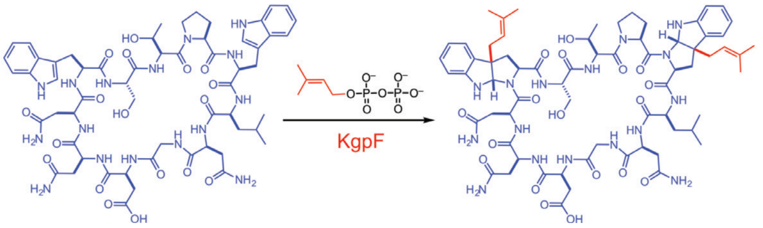
1a (0.0 kcal/mol) **1b** (0.0 kcal/mol)

Lorlatinib is an inhibitor of anaplastic lymphoma kinase for the treatment of non-small cell lung cancer. NMR spectroscopy of the desmethyl analogues reveals that the compound exists as a mixture of atropisomers (**1a**/**1b**). It is demonstrated how the benzylic methyl group in lorlatinib rigidifies the macrocycle to eliminate these complicating conformational effects.

Biosynthesis

A. Parajuli, D. H. Kwak, L. Dalponte,
N. Leikoski, T. Galica, U. Umeobika,
L. Trembleau, A. Bent, K. Sivonen,
M. Wahlsten, H. Wang, E. Rizzi,
G. De Bellis, J. Naismith, M. Jaspars,
X. Liu,* W. Houssen,*
D. P. Fewer* **3596–3599**

A Unique Tryptophan C-Prenyltransferase from the Kawaguchipeptin Biosynthetic Pathway

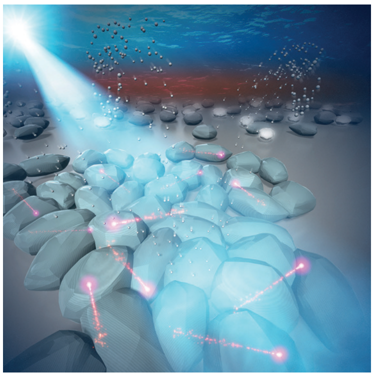


The macrocyclic undecapeptides Kawaguchipeptin A and B from *Microcystis aeruginosa* NIES-88 were shown to be products of the cyanobactin biosynthetic pathway. The 9 kb kawaguchipeptin (kgp) gene cluster was identified as being responsible for their production through heterologous expression in *Escherichia coli*, and the KgpF prenyltransferase was shown to prenylate C-3 of Trp residues in both linear and cyclic peptides in vitro.

Photocatalysis

Y. Ide,* N. Inami, H. Hattori, K. Saito,
M. Sohmiya, N. Tsunoji, K. Komaguchi,
T. Sano, Y. Bando, D. Golberg,
Y. Sugahara* **3600–3605**

Remarkable Charge Separation and Photocatalytic Efficiency Enhancement through Interconnection of TiO_2 Nanoparticles by Hydrothermal Treatment

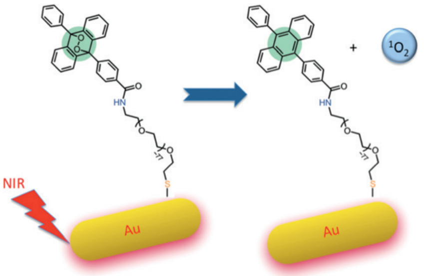


Connections matter: Hydrothermal treatment of P25 TiO_2 selectively converts the amorphous component into crystalline TiO_2, which is deposited between the original anatase and rutile component particles to increase the particle interfaces, and thus considerably enhances charge separation and photocatalytic efficiency.

Photodynamic Therapy

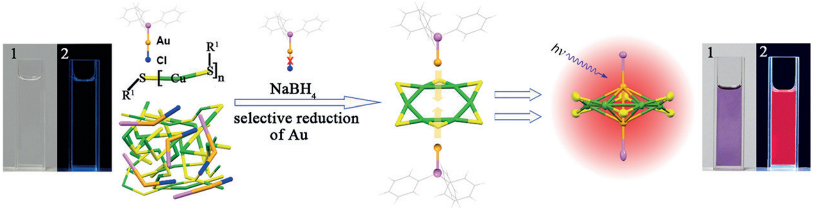
S. Kolemen, T. Ozdemir, D. Lee,
G. M. Kim, T. Karatas, J. Yoon,*
E. U. Akkaya* **3606–3610**

Remote-Controlled Release of Singlet Oxygen by the Plasmonic Heating of Endoperoxide-Modified Gold Nanorods: Towards a Paradigm Change in Photodynamic Therapy



EPT sees the light: When gold nanorods with tethered endoperoxides are irradiated with near-infrared light, the endoperoxides undergo thermal cycloreversion, resulting in the generation of singlet oxygen. The amount of singlet oxygen generated by these nanocomposites is sufficient for triggering apoptosis in cell cultures.

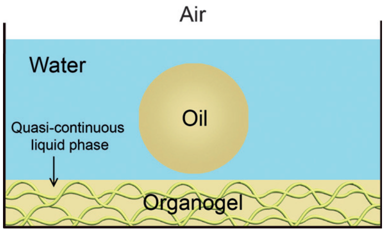
Luminescence



The aggregation of active metal complexes (Cu^{I}SR) with neutral gold species leads to strong luminescence with a quantum yield of 11.7% ("aggregation-induced emission"). The nanoclusters responsible for this emission were identified as $Au_2Cu_6(PPh_2Py)_2(SC_{10}H_{15})_6$ by X-ray crystallography.

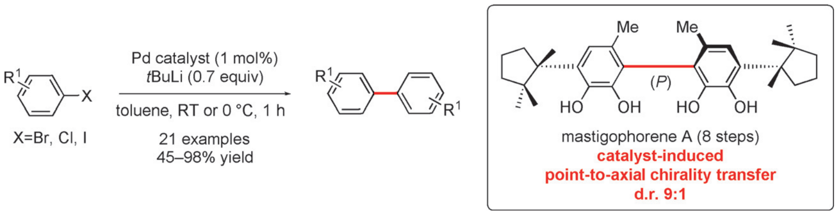
Front Cover

Thin Films



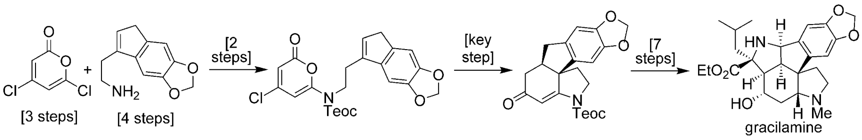
Superspreading on gel surfaces can be realized by utilizing hydraulic pressure and the liquid-like property of gel surfaces. The superspreading liquid layers can be converted into various functional thin polymer films with controlled thicknesses by a one-step polymerization reaction. Such films have promising applications in photovoltaic devices, flexible electronics, and separation films.

Biaryl Synthesis



It takes two: A palladium-catalyzed direct homocoupling of aryl halides in the presence of *t*BuLi enabled the synthesis of even tetra-*ortho*-substituted symmetric biaryl compounds in high yield (see scheme). The method was applied to the asymmetric synthesis of mastigophorene A in just eight steps through straightforward enantioselective installation of the benzylic quaternary stereocenter and highly diastereoselective homocoupling.

Natural Product Total Synthesis

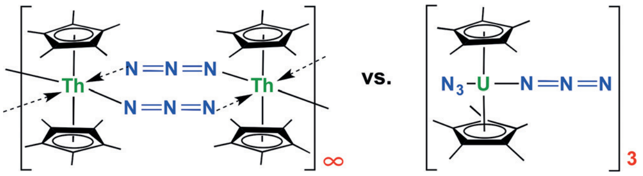


Pyrone-technics: A simple, robust, and readily modifiable strategy involving [4+2]/retro-[4+2]/hydrolysis cascade sequences generates a range of indolines and hydroindolines from 4,6-dichloropyrone and appropriate amines. A 10 step synthesis was achieved of a ketone previously accessed in 15 steps, thereby accomplishing the shortest formal total synthesis of the alkaloid gracilamine. Teoc = 2-(trimethylsilyl)ethoxycarbonyl.

Coordination Polymers

M. J. Monreal, L. A. Seaman, G. S. Goff,
R. Michalczyk, D. E. Morris, B. L. Scott,
J. L. Kiplinger* ________ 3631 – 3636

New Twists and Turns for Actinide Chemistry: Organometallic Infinite Coordination Polymers of Thorium Diazide



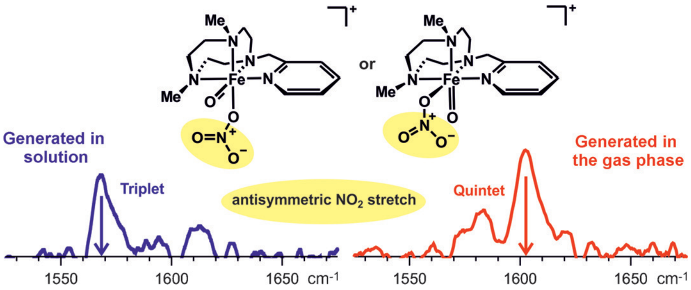
Azide from which: Metallocene thorium diazide complexes have been synthesized and structurally characterized, including by Raman spectroscopy. In contrast to organometallic uranium azides, the thorium azide complexes do not form rings, but open infinite polymeric chains, which are dense in thorium and nitrogen. Structural control of these systems to prevent formation of infinite chains could be achieved by the introduction of steric bulk.

Spin States

E. Andris, J. Jašík, L. Gómez, M. Costas,*
J. Roithová* ________ 3637 – 3641

Spectroscopic Characterization and Reactivity of Triplet and Quintet Iron(IV) Oxo Complexes in the Gas Phase

Inside Cover

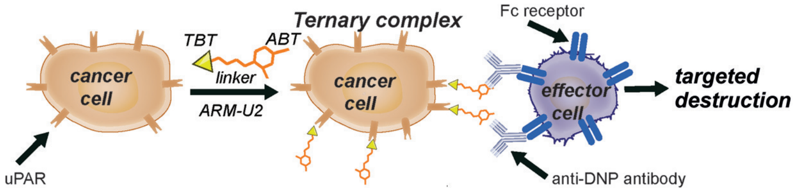


At full stretch: The stretching vibrations of the nitrate counterions of gaseous iron(IV) oxo complexes are used for spin-state assignment. It opens a route to compare hydrogen-atom- and oxygen-atom-transfer reactions of the isolated triplet- and quintet-state complexes under well-defined gas-phase conditions.

Antitumor Agents

A. F. Rullo, K. J. Fitzgerald, V. Muthusamy,
M. Liu, C. Yuan, M. Huang, M. Kim,
A. E. Cho, D. A. Spiegel* ___ 3642 – 3646

Re-engineering the Immune Response to Metastatic Cancer: Antibody-Recruiting Small Molecules Targeting the Urokinase Receptor

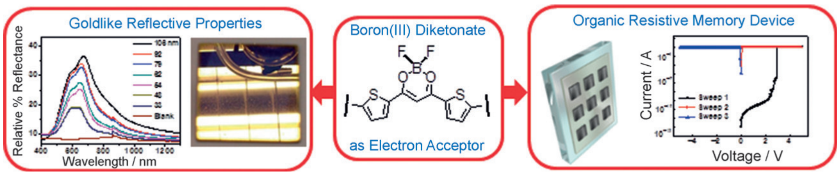


Marked for death: A small-molecule immunotherapeutic strategy involves the selective tagging of cancer cells for immune-cell recognition and targeted destruction. This approach holds tremendous promise in guiding the development of selective treatments against highly aggressive metastatic cancers with potentially few side effects.

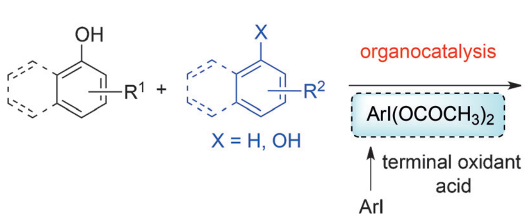
Materials Science

C.-T. Poon, D. Wu,
V. W.-W. Yam* ________ 3647 – 3651

Boron(III)-Containing Donor–Acceptor Compound with Goldlike Reflective Behavior for Organic Resistive Memory Devices



Goldlike reflecting memory: A push-pull chromophore with an electron-acceptor moiety was designed and synthesized. It exhibits goldlike reflective behavior in the neat thin-film sample from simple spin-coating preparation, and can serve as a potential organic thin-film optical reflector. Moreover, good organic resistive memory performance with low turn-on voltage, small operating bias, large ON/OFF ratio, and long retention time has been demonstrated.

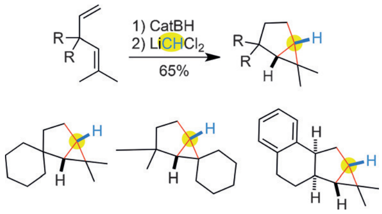


Criss-cross phenol: An organocatalytic intermolecular oxidative cross-coupling reaction of phenols uses a catalytic amount of an iodoarene with a stoichiometric amount of an inorganic oxidant. The reaction proceeds smoothly at room temperature, thereby enabling the efficient formation of biaryls from phenols without over-oxidation of the coupling products.

Biaryl Synthesis

K. Morimoto, K. Sakamoto, T. Ohshika, T. Dohi, Y. Kita* ________ **3652 – 3656**

Organo-Iodine(III)-Catalyzed Oxidative Phenol–Arene and Phenol–Phenol Cross-Coupling Reaction

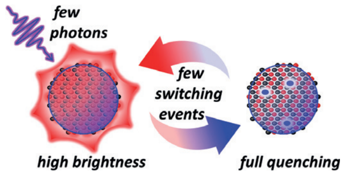


All at C: An intramolecular cyclopropanation involves cation intermediates rather than carbenes. Three new C–C bonds (red) are created at a single carbon center (yellow) derived from dichloromethane to give bicyclo[3.1.0]hexanes.

C–C Bond Formation

G. Xu, P. Renaud* ________ **3657 – 3661**

Intramolecular Cyclopropanation of 1,4-Dienes through Hydroboration–Homologation: Easy Access to Bicyclo[3.1.0]hexanes



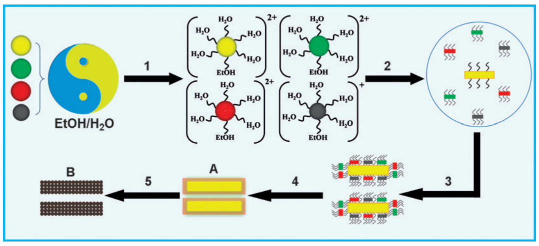
Amped up: Fluorescent photochromic organic nanoparticles, showing bright red emission, complete ON–OFF contrast with full reversibility, and excellent fatigue resistance, have been prepared. They exhibit a full fluorescence quenching and recovery under light illumination at very low photochromic conversion levels, leading to a "giant amplification of fluorescence photoswitching".

Photoswitching

J. Su, T. Fukaminato,* J.-P. Placial, T. Onodera, R. Suzuki, H. Oikawa, A. Brosseau, F. Brisset, R. Pansu, K. Nakatani, R. Métivier* ___ **3662 – 3666**

Giant Amplification of Photoswitching by a Few Photons in Fluorescent Photochromic Organic Nanoparticles

Inside Back Cover



Above the bar: A general and facile approach was developed for fabrication of 1D micro- and nanostructured manganese-based bars, with applicability to lithium-ion batteries. Key: 1) solvent effect; 2) nucleation ($H_2C_2O_4$ and H_2O/EtOH added); 3) oriented attachment; 4) Ostwald ripening; 5) calcination; A) precursor; B) product; Mn^{2+} 🟡; Ni^{2+} 🟢; Co^{2+} 🔴; Li^{+} ⚫; MnC_2O_4 🟨; NiC_2O_4 🟩; CoC_2O_4 🟥; $Li_2C_2O_4$ ■.

Lithium-Ion Batteries

G. Ma, S. Li, W. X. Zhang,* Z. H. Yang, S. L. Liu, X. M. Fan, F. Chen, Y. Tian, W. B. Zhang, S. H. Yang,* M. Li ________ **3667 – 3671**

A General and Mild Approach to Controllable Preparation of Manganese-Based Micro- and Nanostructured Bars for High Performance Lithium-Ion Batteries

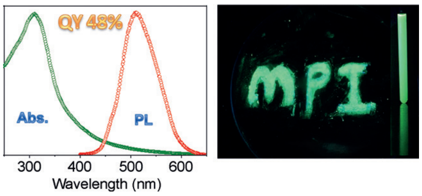
VIP

Carbon Nitrides

Q. Cui, J. Xu,* X. Wang, L. Li,*
M. Antonietti, M. Shalom — **3672 – 3676**

Phenyl-Modified Carbon Nitride Quantum Dots with Distinct Photoluminescence Behavior

A fluorescence quantum yield of approximately 48 % and a large Stokes shift of 200 nm were determined for phenyl-modified carbon nitride quantum dots, which were obtained through a supramolecular preorganization method. The remarkable emission properties are due to the structural surface organization of the phenyl groups, which alters the π-electron delocalization in the conjugated networks.

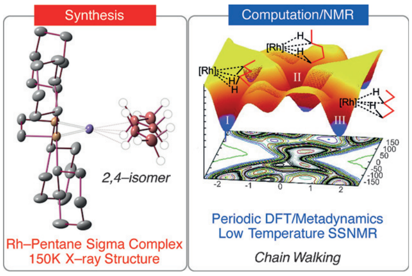


Alkane Complexes

F. M. Chadwick, N. H. Rees, A. S. Weller,*
T. Krämer, M. Iannuzzi,
S. A. Macgregor* — **3677 – 3681**

A Rhodium–Pentane Sigma-Alkane Complex: Characterization in the Solid State by Experimental and Computational Techniques

Pentane takes a walk: The pentane sigma complex $[\mathrm{Rh}\{\mathrm{Cy_2P(CH_2CH_2)PCy_2}\}(\eta^2{:}\eta^2\text{-}\mathrm{C_5H_{12}})][\mathrm{BAr^F}_4]$ can be synthesized by a solid/gas single-crystal to single-crystal transformation. Periodic DFT calculations, molecular dynamics, and NMR spectroscopy provided insights into the fluxional processes occurring in the solid state.



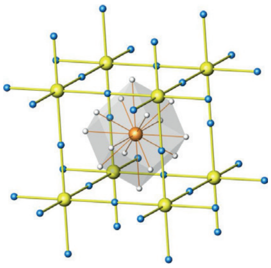
VIP

Superconductors

E. E. Gordon, K. Xu, H. Xiang,
A. Bussmann-Holder, R. K. Kremer,
A. Simon,* J. Köhler,*
M.-H. Whangbo* — **3682 – 3684**

Structure and Composition of the 200 K-Superconducting Phase of H_2S at Ultrahigh Pressure: The Perovskite $(SH^-)(H_3S^+)$

Under ultrahigh pressure (> 110 GPa), H_2S is converted into a metallic phase that becomes superconducting with a record T_c of approximately 200 K. It is proposed that in this phase a dissociation of $2\,H_2S$ into H_3S^+ and SH^- is present, leading to the perovskite structure $(SH^-)(H_3S^+)$. This phase consists of corner-sharing SH_6 octahedra with SH^- ions at the center of each S_8 cube.

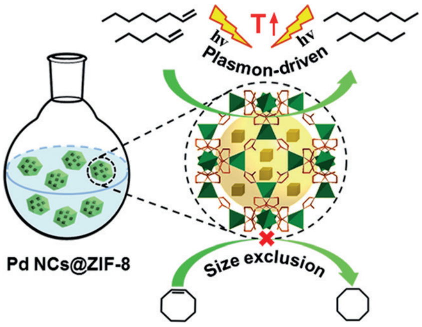


MOF Composites

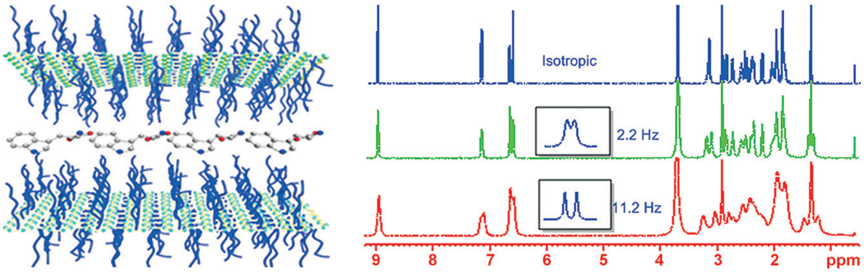
Q. Yang, Q. Xu, S.-H. Yu,
H.-L. Jiang* — **3685 – 3689**

Pd Nanocubes@ZIF-8: Integration of Plasmon-Driven Photothermal Conversion with a Metal–Organic Framework for Efficient and Selective Catalysis

The incorporation of palladium nanocubes (NCs) into the metal–organic framework ZIF-8 affords the composite Pd NCs@ZIF-8, which was utilized for the efficient catalytic hydrogenation of olefins at room temperature under light irradiation. The superior catalytic performance is due to the plasmonic photothermal effects of Pd NCs and the multiple roles (H_2 enrichment, size sieving, and Pd stabilization) of the ZIF-8 shell.



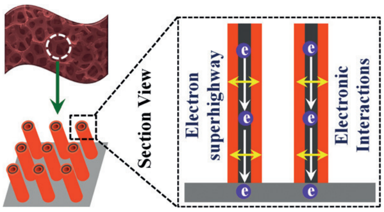
Back Cover



Alignment media: A novel, robust, adjustable anisotropic medium consisting of graphene oxide grafted with polymer brushes is presented for the measurement of residual dipolar couplings in pure DMSO. The developed medium is characterized by an absence of background signals, narrow NMR line-shape, instantaneous alignment, and blocking of π–π stacking with aromatic analytes.

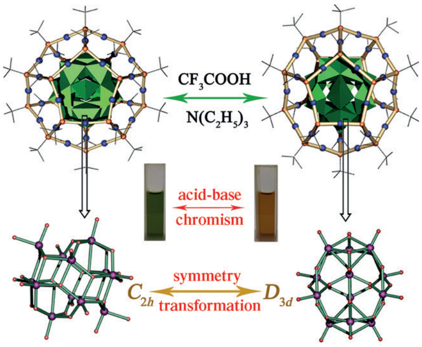
NMR Spectroscopy

FeOOH/Co/FeOOH hybrid nanotube arrays (HNTAs) supported on Ni foams were developed for the oxygen evolution reaction (OER). The FeOOH/Co/FeOOH HNTAs exhibit high electrocatalytic performance for OER, such as low onset potential, small Tafel slope, and excellent long-term durability, and are promising electrocatalysts for OER in alkaline solution.



Electrocatalysts

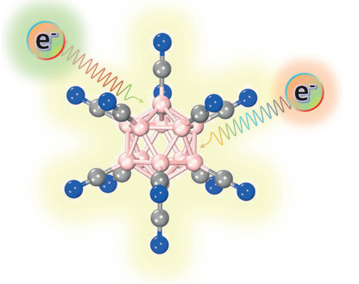
Silver cage: Self-assembly of metavanadate and organosilver(I) salts generates a dodecahedrane-like silver(I) thiolate $[Ag_{30}(^tBuS)_{20}]^{10+}$ nanocage that tightly wraps a polyoxovanadate core. Single-crystal X-ray crystallography was used to show that the core undergoes a reversible C_{2h} to D_{3d} configurational transformation in response to acid/base stimuli, which also result in a color change from green to dark yellow.



Cluster Compounds

VIP

Cluster together: By replacing H ligands in $B_{12}H_{12}^{2-}$ by cyano groups (see structure) a highly stable multiply charged cluster with second electron affinity as high as 5.3 eV was obtained. Such a cluster can serve as a good electrolyte in ion batteries.



Cluster Compounds

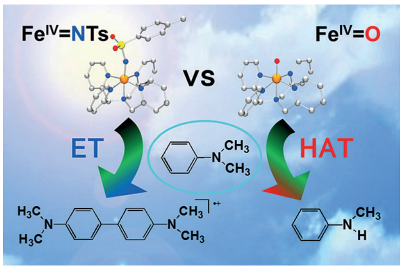
VIP

Electron Transfer Mechanisms

A. K. Vardhaman, Y.-M. Lee, J. Jung,
K. Ohkubo, W. Nam,*
S. Fukuzumi* ——— **3709 – 3713**

Enhanced Electron Transfer Reactivity of a Nonheme Iron(IV)–Imido Complex as Compared to the Iron(IV)-Oxo Analogue

A nonheme iron(IV)-tosylimido complex exhibits enhanced electron transfer reactivity compared to the iron(IV)-oxo analogue. This reactivity results in a drastic change of the reaction mechanism for the oxidation of *N*,*N*-dimethylaniline.

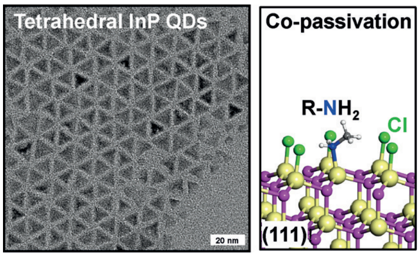


Quantum Dots

K. Kim, D. Yoo, H. Choi, S. Tamang,
J.-H. Ko, S. Kim, Y.-H. Kim,*
S. Jeong* ——— **3714 – 3718**

Halide–Amine Co-Passivated Indium Phosphide Colloidal Quantum Dots in Tetrahedral Shape

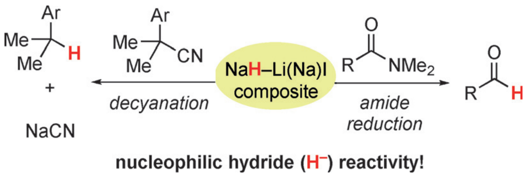
InP colloidal tetrahedral nanocrystals were synthesized through a simple acid-free approach using tris(dimethylamino) phosphine and indium trichloride dissolved in oleylamine. Their formation was attributed to the unique stabilization of the In-rich (111) facets by co-passivation with halide and primary amine.



Synthetic Methods

P. C. Too, G. H. Chan, Y. L. Tnay,
H. Hirao,* S. Chiba* ——— **3719 – 3723**

Hydride Reduction by a Sodium Hydride–Iodide Composite

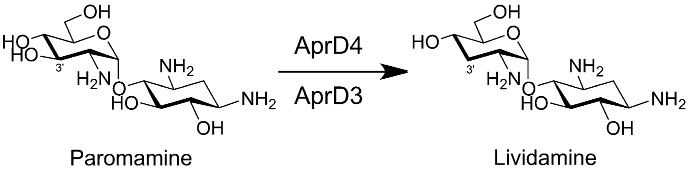


A new job for an old friend: Sodium hydride (NaH) is widely used as a Brønsted base in chemical synthesis and reacts with various Brønsted acids, but it rarely behaves as a reducing reagent through delivery of the hydride to polar π electrophiles. It has now been found that nitriles, amides, and imines undergo reduction by NaH as a hydride donor in the presence of LiI or NaI (see scheme).

Biosynthesis

H. J. Kim, J. LeVieux, Y.-C. Yeh,
H.-w. Liu* ——— **3724 – 3728**

C3′-Deoxygenation of Paromamine Catalyzed by a Radical *S*-Adenosylmethionine Enzyme: Characterization of the Enzyme AprD4 and Its Reductase Partner AprD3

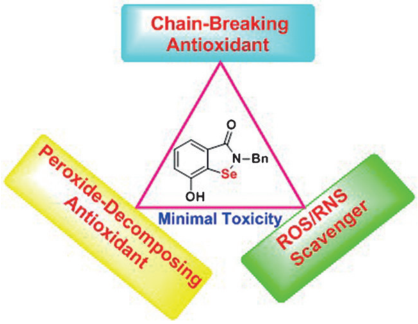


Enzymes in action: C3′-deoxygenation of paromamine is catalyzed by two enzymes, a radical *S*-adenosylmethionine (SAM) enzyme AprD4 and a NAD(P)H-dependent dehydrogenase AprD3. AprD4 catalyzes dehydration of the 3,4-dihydroxy moiety of paromamine and AprD3 reduces the nascent keto intermediate to complete the C3′-deoxygenation to form lividamine.

Antioxidants

S. Kumar, J. Yan, J. Poon, V. P. Singh, X. Lu, M. Karlsson Ott, L. Engman,* S. Kumar* ______ 3729 – 3733

Multifunctional Antioxidants: Regenerable Radical-Trapping and Hydroperoxide-Decomposing Ebselenols

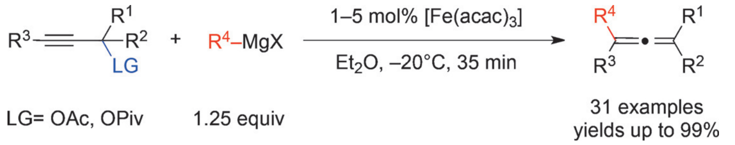


What a difference an OH makes: Ebselenols, bearing OH groups on the aryl rings, quenched lipid peroxyl radicals more efficiently than α-tocopherol and could be regenerated with aqueous-phase ascorbic acid. The compounds were nontoxic, showed higher glutathione peroxidase activity than the parent compound ebselen, and efficiently relieved the effect of an "oxidative burst" in human mononuclear cells.

Cross-Coupling

S. N. Kessler, J.-E. Bäckvall* 3734 – 3738

Iron-catalyzed Cross-Coupling of Propargyl Carboxylates and Grignard Reagents: Synthesis of Substituted Allenes

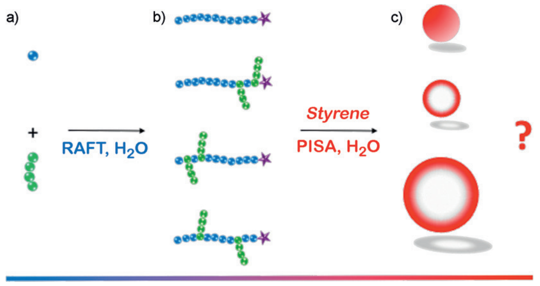


Iron clad: The title reaction is effective for the synthesis of substituted allenes using a low catalyst loading at −20 °C. The mild reaction conditions tolerated not only terminal acetylenes but also functional groups such as acetal, silyl ether, and ethyl carboxylate. A high degree of chirality-transfer was observed and the reaction conditions are compatible with radical probes.

RAFT-Mediated Polymerization

J. Lesage de la Haye, X. Zhang, I. Chaduc, F. Brunel, M. Lansalot,* F. D'Agosto* ______ 3739 – 3743

The Effect of Hydrophile Topology in RAFT-Mediated Polymerization-Induced Self-Assembly

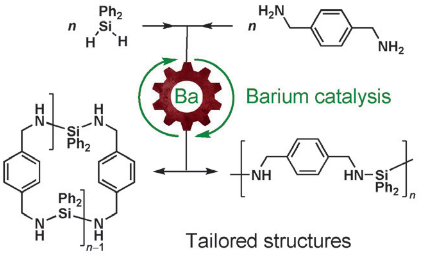


An average of three PEGA units were introduced either at the beginning, statistically, or at the end of a hydrophilic segment, resulting in formation of various block copolymer morphologies. Key: a) Same hydrophilic comonomers; b) various hydrophilic macroRAFTs; c) different particle morphologies (spheres, nanovesicles, large vesicles), N-acryloyl morpholine (●), PEG acrylate (●●●●).

Polymers

C. Bellini, C. Orione, J.-F. Carpentier,* Y. Sarazin* ______ 3744 – 3748

Tailored Cyclic and Linear Polycarbosilazanes by Barium-Catalyzed N−H/H−Si Dehydrocoupling Reactions

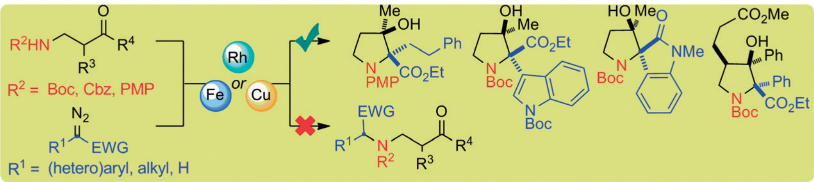


The rapid and controlled barium-catalyzed dehydrogenative polymerization of a diamine with diphenylsilane affords thoroughly characterized polycarbosilazanes. Their microstructures (cyclic versus linear), end-groups, and molecular weights can all be controlled by selection of the feed ratio of the comonomers.

Nitrogen Heterocycles

S. M. Nicolle, W. Lewis, C. J. Hayes, C. J. Moody* ———— **3749 – 3753**

Stereoselective Synthesis of Functionalized Pyrrolidines by the Diverted N—H Insertion Reaction of Metallocarbenes with β-Aminoketone Derivatives

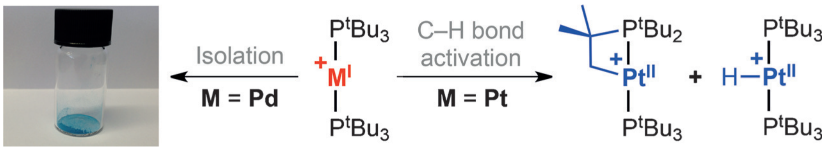


The metal-catalyzed reaction of diazocarbonyl compounds with β-aminoketone derivatives leads to highly substituted pyrrolidines with excellent diastereoselectivity under mild reaction conditions. The reaction starts as a metallocarbene N—H insertion but is diverted by an intermolecular aldol reaction.

Open-Shell Complexes

T. Troadec, S.-y. Tan, C. J. Wedge, J. P. Rourke, P. R. Unwin, A. B. Chaplin* ———— **3754 – 3757**

One-Electron Oxidation of $[M(P^tBu_3)_2]$ (M = Pd, Pt): Isolation of Monomeric $[Pd(P^tBu_3)_2]^+$ and Redox-Promoted C—H Bond Cyclometalation



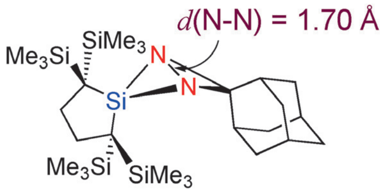
Uncharted territory: The reaction chemistry of palladium and platinum complexes bearing a +I formal oxidation state has been accessed through one-electron oxidation of $[M^0(P^tBu_3)_2]$ (M = Pd, Pt) using $[Fc][PF_6]$.

Main-Group Chemistry

X.-Q. Xiao, Z. Dong, Z. Li,* C. Yan, G. Lai, M. Kira* ———— **3758 – 3762**

1,3-Diazasilabicyclo[1.1.0]butane with a Long Bridging N—N Bond

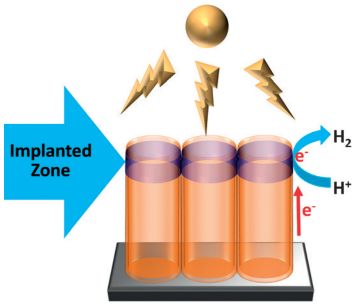
Come a long way: A 1,3-diazasilabicyclo-[1.1.0]butane was synthesized and features the longest N—N bond (1.70 Å) among known N—N singly-bonded compounds. The compound is intact in air but moisture sensitive, and no reaction occurs with hydrogen, even under pressure at 0.5 MPa. The origin of the N—N bond elongation is ascribed to significant interaction between a Si—C σ* orbital and N—N π and σ orbitals.



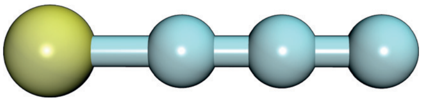
Photocatalysis

X. Zhou, V. Häublein, N. Liu, N. T. Nguyen, E. M. Zolnhofer, H. Tsuchiya, M. S. Killian, K. Meyer, L. Frey, P. Schmuki* ———— **3763 – 3767**

TiO_2 Nanotubes: Nitrogen-Ion Implantation at Low Dose Provides Noble-Metal-Free Photocatalytic H_2-Evolution Activity

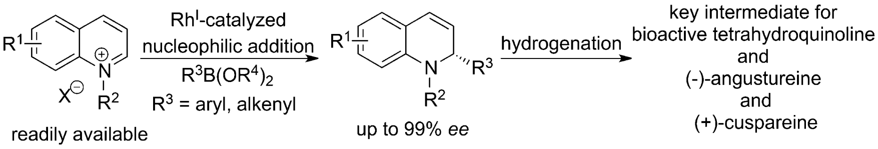


In the zone: Low-dose nitrogen implantation in TiO_2 nanotubes leads to "co-catalytic" activity for photocatalytic H_2 evolution. The ion implantation creates an active zone limited to the top part of the tubes. The coupling of this top layer and the underlying non-implanted part of the nanotubes additionally contributes to an efficient carrier separation and thus to a significantly enhanced H_2 generation.

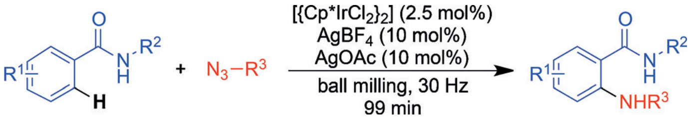


Walk the line: PtC_3 and PdC_3 carbenes have been generated in the gas phase through laser vaporization of a metal target in the presence of a low concentration of a hydrocarbon precursor undergoing supersonic expansion. Rotational spectroscopy and ab initio calculations confirm that both molecules are linear. Atom colors: Pt = yellow, C = blue.

Addiction therapy: Fentanyls are potent and addictive opioids implicated in many overdose deaths. A conjugate vaccine against fentanyl and fentanyl analogues was developed, which protected mice from lethal drug doses. A robust SPR-based biosensor was created to profile the low-nanomolar affinities of serum antibodies for various fentanyl analogues.



Rings made simple: The title reaction proceeds with readily available quinolines and has been developed to provide a practical way to furnish enantiopure dihydroquinolines. This method was successfully applied in the formal asymmetric synthesis of bioactive tetrahydroquinoline and the total syntheses of (−)-angustureine and (+)-cuspareine.

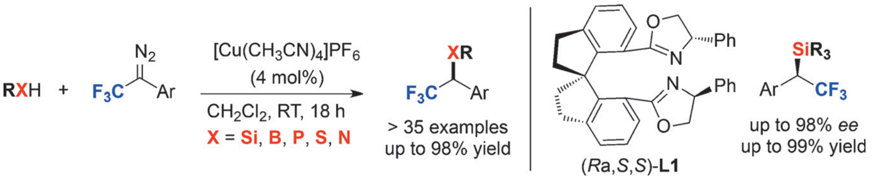


Mechanochemical activation enables the iridium(III)-catalyzed C–H bond amidation of benzamides in the *ortho* position under solvent-free conditions with sulfonyl azides as the nitrogen source. The corresponding products were formed in high yields within short reaction times and without external heating.

Carbenes

S. Hyde, J. Veliks, B. Liégault, D. Grassi, M. Taillefer, V. Gouverneur* **3785 – 3789**

Copper-Catalyzed Insertion into Heteroatom–Hydrogen Bonds with Trifluorodiazoalkanes

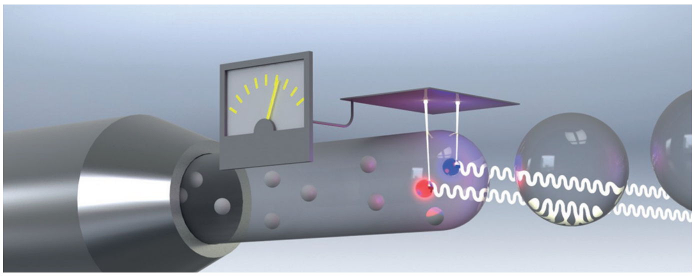


Suits all sorts: An efficient copper-catalyzed carbenoid insertion of 2,2,2-trifluorodiazoethane and 1-aryl 2,2,2-trifluorodiazoethanes into Si–H, B–H, P–H, S–H, and N–H bonds produced CF_3-containing products in high yields (see scheme). Catalytic asymmetric Si–H and B–H bond insertion reactions were also developed with chiral bisoxazoline ligands, such as (*Ra*,*S*,*S*)-**L1**.

Electrical Double Layer

M. A. Brown,* A. Goel, Z. Abbas **3790 – 3794**

Effect of Electrolyte Concentration on the Stern Layer Thickness at a Charged Interface

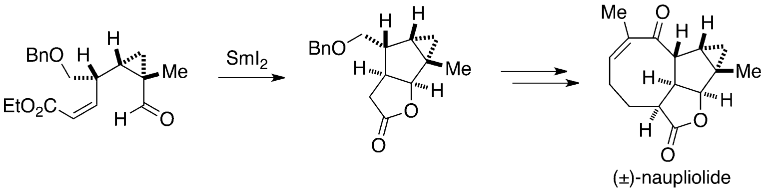


The electrical double layer (EDL) is presented in a simple and intuitive picture that explains the concurrent increase in surface charge density, but decrease in surface and zeta potentials, as electrolyte concentration is increased.

Total Synthesis

H. Abe, T. Morishita, T. Yoshie, K. Long, T. Kobayashi, H. Ito* **3795 – 3798**

The Total Synthesis of (±)-Naupliolide: A Tetracyclic Sesquiterpene Lactone

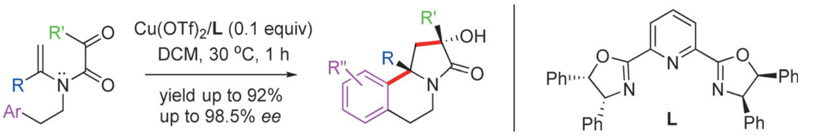


Start to finish: The first total synthesis of (±)-naupliolide has been achieved. The method includes a Simmons–Smith cyclopropanation of an allyl alcohol, diastereoselective cleavage of a benzylidene acetal group, radical cyclization of an aldehyde with a cyclopropane ring, and construction of an eight-membered ring by ring-closing metathesis.

Asymmetric Catalysis

X.-M. Xu, L. Zhao, J. Zhu, M.-X. Wang* **3799 – 3803**

Catalytic Asymmetric Tandem Reaction of Tertiary Enamides: Expeditious Synthesis of Pyrrolo[2,1-*a*]isoquinoline Alkaloid Derivatives



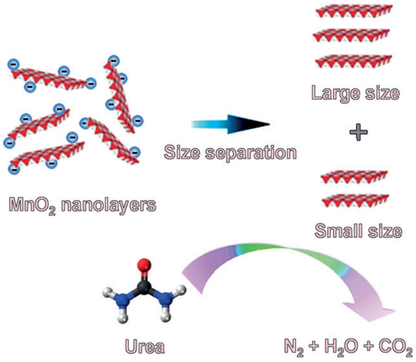
’Soul’ isomer: The title reaction proceeds under mild reaction conditions to produce tetrahydropyrrolo[2,1-*a*]isoquinolin-3-(2*H*)-one derivatives, which contain two tetrasubstituted stereogenic centers, as the sole diastereoisomers in high yields and excellent enantioselectivity. These products can be easily transformed into various hexahydropyrrolo[2,1-*a*]isoquinoline derivatives.

Nanocatalysis

S. Chen, J. J. Duan, A. Vasileff, S. Z. Qiao* ________ **3804 – 3808**

Size Fractionation of Two-Dimensional Sub-Nanometer Thin Manganese Dioxide Crystals towards Superior Urea Electrocatalytic Conversion

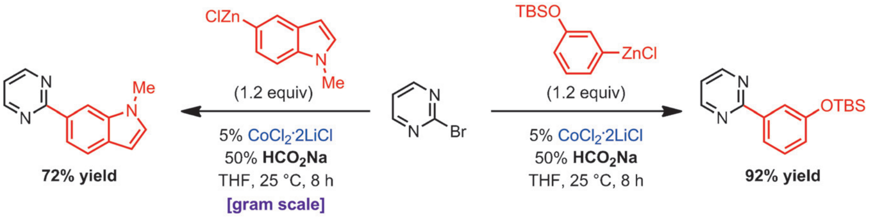
Two-dimensional manganese dioxide nanolayers with sub-nanometer thickness were produced by a size fractionation method based on tuning the zeta potential of their aqueous dispersions. The resultant materials showed excellent structural properties, such as highly exposed planar surfaces/edge sites and rich porosity, which led to a superior electrocatalytic performance towards the urea oxidation reaction.



Cross-Coupling

D. Haas, J. M. Hammann, F. H. Lutter, P. Knochel* ________ **3809 – 3812**

Mild Cobalt-Catalyzed Negishi Cross-Couplings of (Hetero)arylzinc Reagents with (Hetero)aryl Halides

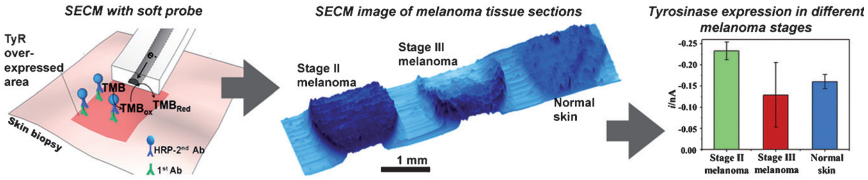


May the formate be with you! A simple, practical cobalt salt catalyzed procedure for cross-coupling reactions of halogenated ketones as well as N-heterocyclic chlorides and bromides with various electron-rich and -poor (hetero)arylzinc reagents was developed. The addition of sodium formate is essential for the efficiency of this cross-coupling. TBS = *tert*-butyldimethylsilyl.

Melanoma Diagnosis

T.-E. Lin, A. Bondarenko, A. Lesch, H. Pick, F. Cortés-Salazar, H. H. Girault* ________ **3813 – 3816**

Monitoring Tyrosinase Expression in Non-metastatic and Metastatic Melanoma Tissues by Scanning Electrochemical Microscopy



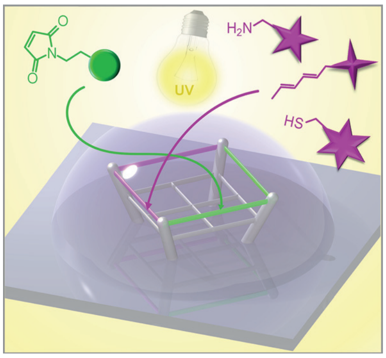
Black mark: Tyrosinase levels in melanoma skin biopsies of various patients were monitored by using scanning electrochemical microscopy. The employed probe, made from soft and flexible polymeric materials, scans the tissue sections in a gentle contact mode without inducing damage. The different expression levels and distributions of tyrosinase in metastatic and non-metastatic melanomas were mapped.

Surface Functionalization

T. K. Claus, B. Richter, V. Hahn, A. Welle,* S. Kayser, M. Wegener, M. Bastmeyer, G. Delaittre,* C. Barner-Kowollik* ________ **3817 – 3822**

Simultaneous Dual Encoding of Three-Dimensional Structures by Light-Induced Modular Ligation

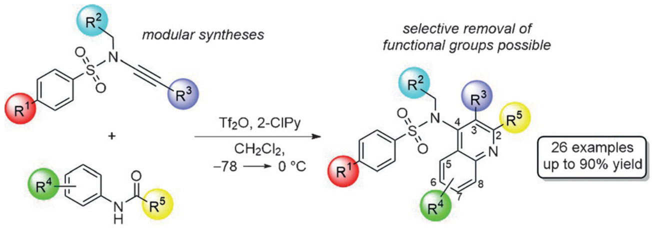
Never out of place: Under UV light, small molecules, peptides, and protein ligands in binary mixtures find their place on reactive microstructures obtained by direct laser writing with two novel reactive photoresists. Arbitrary patterns are achieved by rapid, concurrent, and orthogonal photochemical immobilization.



Heterocycle Synthesis

T. Wezeman, S. Zhong, M. Nieger,
S. Bräse* ________ **3823 – 3827**

Synthesis of Highly Functionalized 4-Aminoquinolines



Diverse products: Electrophilically activated amides easily react with sulfonyl ynamides to yield a diverse range of substituted 4-aminoquinolines. The ynamides can be easily modified by Sonogashira processes or generated from dichloroenamide precursors. Any substituent can thus be introduced at the C3 position of the quinoline. 2-ClPy = 2-chloropyridine, Tf_2O = triflic anhydride.

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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