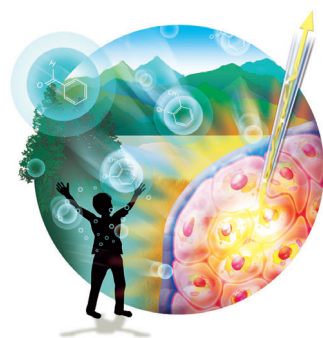
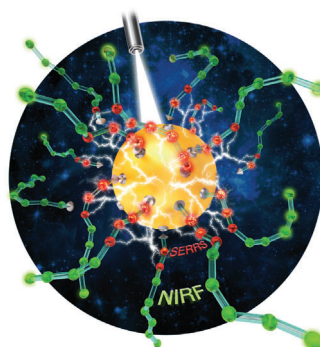


... (“Kohlensäure”) and its monomethyl ester can be readily prepared through the gas-phase pyrolysis of Boc_2O ($\text{Boc} = \text{tert-butylloxycarbonyl}$) and MeOC(O)OtBu , respectively, as described by P. R. Schreiner et al. in their Communication on page 11766 ff. This novel, independent preparation of the two structures and their unequivocal identification through IR spectroscopy show that the gas phase above the so-called α -polymorph of H_2CO_3 is actually the monomethyl ester, whereas only the β -polymorph is truly carbonic acid.

Imaging Agents

In their Communication on page 11756, M. F. Kircher and co-workers employed a biocompatible polymeric surface coating for gold nanoparticles. The resulting nanoprobe were shown to be capable of multiplexed lymph-node imaging.

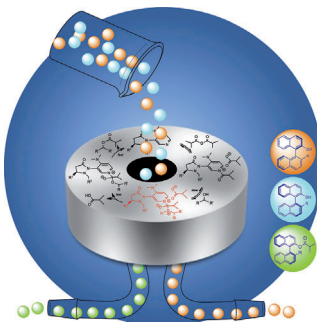


Biosensors

An electrophysiological technique to record the response to vapor odorants is reported by K. Sato and S. Takeuchi in their Communication on page 11798 ff.

Asymmetric Organocatalysis

In their Communication on page 11818 ff., M. P. Sibi and co-workers demonstrate that a novel 4-dimethylaminopyridine catalyst with fluxional chirality is efficient in promoting acylative kinetic resolution of axially chiral biaryl compounds.



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Spotlight on Angewandte's Sister Journals

11688 – 11691

Service



*"My favorite theorem is Koopman's theorem.
My favorite painter is Salvador Dalí ..."*

This and more about Hiroshi Sugiyama can be found on page 11692.

Author Profile

Hiroshi Sugiyama _____ 11692



C. V. Robinson



R. Zenobi



Y. O. Tsybin



G. Erker



B. L. Feringa

News

Thomson Medal: C. V. Robinson
and R. Zenobi _____ 11693

SGMS Award: Y. O. Tsybin _____ 11693

Cross of the Order of Merit of
the Federal Republic of Germany:
G. Erker _____ 11693

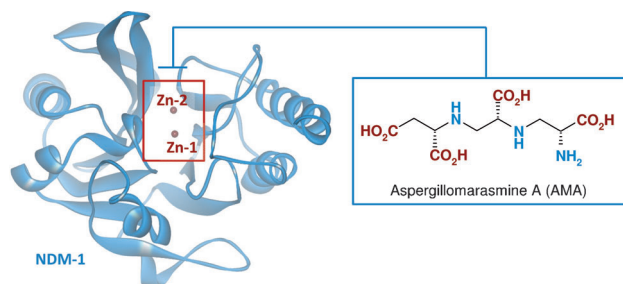
Theodor Förster Memorial Lecture:
B. L. Feringa _____ 11693

Highlights

Bacterial Resistance

F. von Nussbaum,*
G. Schiffer* ————— 11696–11698

Aspergillomarasmine A, an Inhibitor of
Bacterial Metallo- β -Lactamases
Conferring *bla*_{NDM} and *bla*_{VIM} Resistance



Silencing the deadly “bla-bla” of superbugs: The natural product aspergillomarasmine A (AMA) showed in vivo efficacy against Enterobacteriaceae, conferring broad β -lactam resistance *bla*_{NDM-1}

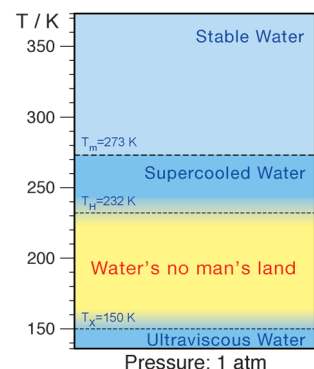
(NDM-1: New Delhi Metallo- β -lactamase 1). In rodents, the natural product restored efficacy of the gold standard meropenem by inhibition of the Zn-containing active site in NDM-1.

Water

D. Paschek,* R. Ludwig* . 11699–11701

Advancing into Water’s “No Man’s Land”:
Two Liquid States?

A tale of two liquids? Liquid water exhibits many anomalous properties which are strongly amplified in the supercooled state. A possible explanation for the unusual behavior is a phase transition between two distinct metastable forms of liquid water at deeply supercooled conditions. A recent theoretical study has confirmed the existence of this liquid–liquid phase transition.

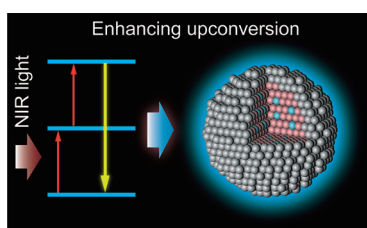


Minireviews

Upconversion

S. Han, R. Deng, X. Xie,
X. Liu* ————— 11702–11715

Enhancing Luminescence in Lanthanide-Doped Upconversion Nanoparticles



Lighten up: Light trapping by upconversion nanoparticles often suffers from low conversion efficiency because of the small absorption cross-section and surface quenching effects of the nanoparticles. To this end, effective strategies have been developed to enhance upconversion luminescence, thus paving the way for new biological approaches and inexpensive energy conversion methods.

For the USA and Canada:

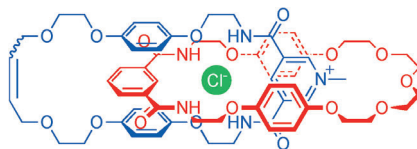
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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Since the start of this millennium, anion supramolecular chemistry has evolved substantially beyond the chemistry of anion receptors. Alongside the research that continues on the binding and sensing of anions, large strides have been made in areas that have previously been underdeveloped, such as the use of anions as templates and for membrane transportation, and importantly in chemical applications including catalysis, ion extraction, and responsive molecular systems.



Supramolecular Chemistry of Anions

N. H. Evans,* P. D. Beer* 11716–11754

Advances in Anion Supramolecular Chemistry: From Recognition to Chemical Applications

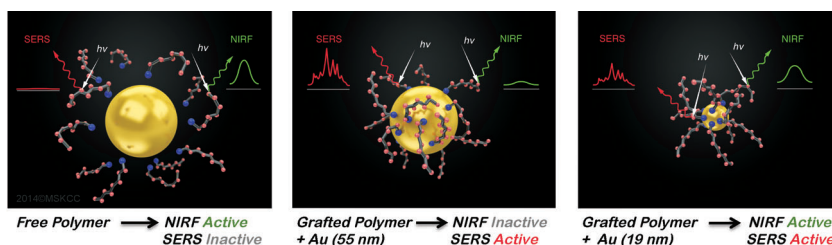
Communications

Nanoparticle Imaging Agents

P. Iacono, H. Karabeber,
M. F. Kircher* 11756–11761

A “Schizophotonic” All-In-One
Nanoparticle Coating for Multiplexed
SE(R)RS Biomedical Imaging

Frontispiece



Split personality: A biocompatible polymeric surface coating gives rise to dual emissive SERS/NIRF behavior when bound to gold nanoparticles of varying sizes. These polymers allow the first syn-

thesis of SERS nanoprobes with gold cores smaller than 20 nm. These nanoprobes are shown to be capable of multiplexed lymph-node imaging.



Crazy about ionic liquids: Throughout the southern United States, the invasive ant species *S. invicta* (fire ants) and *N. fulva* (tawny crazy ants) vie for resources. During confrontations, *N. fulva* is sprayed by *S. invicta* with a lipophilic, piperidine-based venom. The former defeats this chemical attack by grooming with its own venom, formic acid. The combination forms a protic ionic liquid, which is the first naturally occurring ionic liquid to be reported.

Ionic Liquids

L. Chen, G. E. Mullen, M. Le Roch,
C. G. Cassity, N. Gouault, H. Y. Fadamiro,
R. E. Barletta, R. A. O'Brien, R. E. Sykora,
A. C. Stenson, K. N. West, H. E. Horne,
J. M. Hendrich, K. R. Xiang,
J. H. Davis, Jr.* 11762–11765

On the Formation of a Protic Ionic Liquid
in Nature





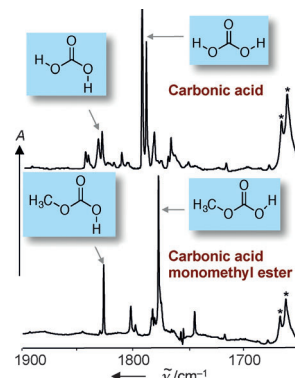
Carbonic Acid

H. P. Reisenauer, J. P. Wagner,
P. R. Schreiner* 11766–11771



Gas-Phase Preparation of Carbonic Acid
and Its Monomethyl Ester

The matrix-isolation IR spectrum of carbonic acid generated through gas-phase pyrolysis of Boc_2O ($\text{Boc} = \text{tert-butoxycarbonyl}$) or $(\text{tBuO})_2\text{CO}$ unequivocally shows that the long-claimed identity of the gas phase above its α -polymorph is not carbonic acid, but rather the monomethyl ester, which was analogously prepared from MeOC(O)OtBu and identified in the gas phase for the first time.



Front Cover

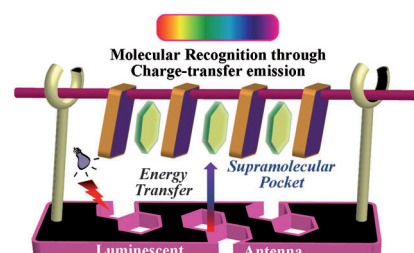
Molecular Recognition

R. Haldar, R. Matsuda, S. Kitagawa,
S. J. George,* T. K. Maji* 11772–11777



Amine-Responsive Adaptable
Nanospaces: Fluorescent Porous
Coordination Polymer for Molecular
Recognition

It all stacks up: A supramolecular host with a nano-coordination space built up by the assembly of a 1D coordination polymer has been synthesized for encapsulation and recognition of various aromatic amine guest molecules through an emission-readout process. In some cases, the charge-transfer emission is enhanced by energy transfer from the chromophoric naphthalene linker unit.



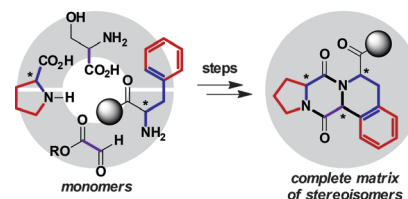
Molecular Diversity

R. Petersen, S. T. Le Quement,
T. E. Nielsen* 11778–11782



Synthesis of a Natural Product-Like
Compound Collection through Oxidative
Cleavage and Cyclization of Linear
Peptides

Complexity made simple: By harnessing the power of solid-phase peptide synthesis, readily available amino acid building blocks (monomers) were assembled into peptide sequences (oligomers) designed to undergo cascade reactions. Using simple reagents and reaction conditions, a collection of natural product-like compounds was synthesized, with excellent control of embedded scaffold stereocenters.

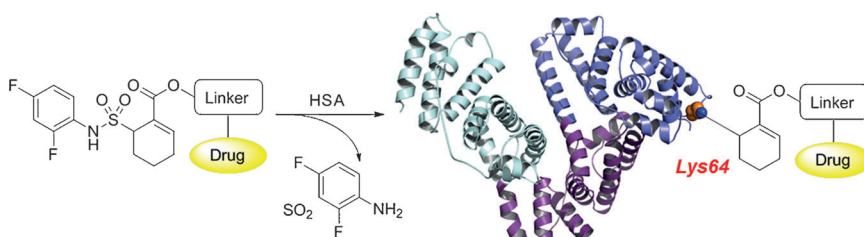


Bioconjugation

S. Asano, J. T. Patterson, T. Gaj,
C. F. Barbas III* 11783–11786

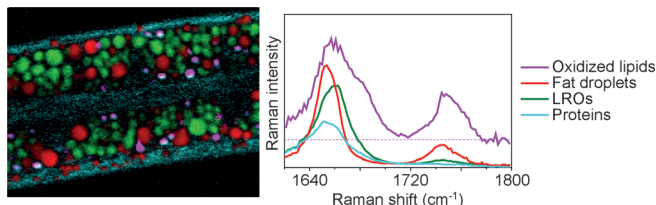


Site-Selective Labeling of a Lysine Residue
in Human Serum Albumin



Analogues of TAK-242, a small molecule inhibitor of Toll-like receptor 4, were synthesized and conjugated to human serum albumin (HSA). These TAK-242-based cyclohexene compounds demonstrated

high reactivity, and Lys64 was identified as the primary conjugation site. A bivalent HSA conjugate was also prepared in a site-specific manner.



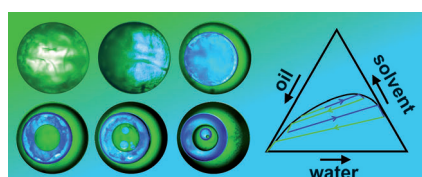
Fingerprinting cell metabolism: Hyper-spectral stimulated Raman scattering (SRS) imaging of live worms in the fingerprint vibration region and multi-variate analysis allowed the compositional analysis of subcellular compartments. The

method led to concentration maps of fat storage, degree of fat unsaturation, and lipid oxidation and showed that lysosome-related organelles are sites for the storage of cholesterol in *C. elegans*.

Chemical Imaging

P. Wang, B. Liu, D. Zhang, M. Y. Belew, H. A. Tissenbaum,*
J.-X. Cheng* — 11787–11792

Imaging Lipid Metabolism in Live *Caenorhabditis elegans* Using Fingerprint Vibrations

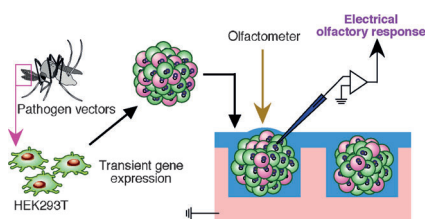


Multiple droplets within droplets: Mapping of the phase diagram revealed a linear relationship between the diameters of concentric layers of multiple emulsions with an “onion” topology. The slope of the line depended on the initial composition of the ternary mixture and the molecular weight of the surfactant. This general rule quantitatively predicted the number of droplet layers and enabled the self-assembly of polymer capsules and liposomes.

Microfluidics

M. F. Haase,* J. Brujic* — 11793–11797

Tailoring of High-Order Multiple Emulsions by the Liquid–Liquid Phase Separation of Ternary Mixtures



Gas sensing by ion channels: Insect olfactory receptors consist of ligand-gated ion channels. Using cell assembly and extracellular field potential recording techniques, olfactory receptor-expressing cell spheroids were formed (see picture). The spheroids electrically responded to chemical vapors at biologically relevant concentrations.

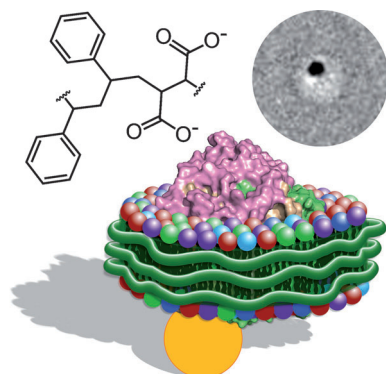
Biosensors

K. Sato, S. Takeuchi* — 11798–11802

Chemical Vapor Detection Using a Reconstituted Insect Olfactory Receptor Complex



Inside Back Cover



Best of both worlds: Reaction centers purified from bilayer membranes using an amphipathic copolymer offer the experimental advantages of a detergent-solubilized membrane protein, but retain functional properties of the protein in the native bilayer. Under stress, reaction centers in copolymer–lipid nanodiscs are more robust than when housed in a detergent micelle or even the native membrane.

Membrane Nanodiscs

D. J. K. Swainsbury, S. Scheidelaar, R. van Grondelle, J. A. Killian,*
M. R. Jones* — 11803–11807

Bacterial Reaction Centers Purified with Styrene Maleic Acid Copolymer Retain Native Membrane Functional Properties and Display Enhanced Stability



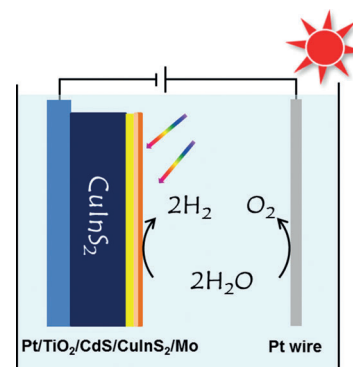
Photoelectrochemistry

J. Zhao, T. Minegishi, L. Zhang, M. Zhong, Gunawan, M. Nakabayashi, G. Ma, T. Hisatomi, M. Katayama, S. Ikeda,* N. Shibata, T. Yamada, K. Domen* **11808–11812**



Enhancement of Solar Hydrogen Evolution from Water by Surface Modification with CdS and TiO₂ on Porous CuInS₂ Photocathodes Prepared by an Electrodeposition–Sulfurization Method

Porous photocathodes: CuInS₂ porous films, prepared by sulfurization of electrodeposited metals and modified with thin layers of CdS and TiO₂, evolved H₂ from photoelectrochemical water reduction under simulated sunlight (see picture). The modified photocathodes showed a relatively high efficiency and stable H₂ production under the reaction conditions by surface modification.



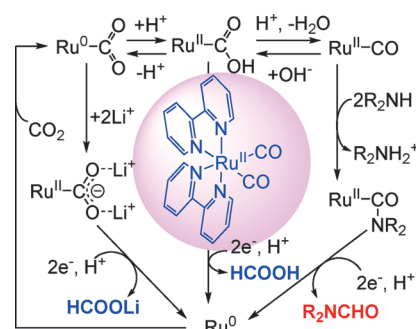
Photochemical CO₂ Reduction

K. Kobayashi, T. Kikuchi, S. Kitagawa, K. Tanaka* **11813–11817**



Selective Generation of Formamides through Photocatalytic CO₂ Reduction Catalyzed by Ruthenium Carbonyl Compounds

Formamide generation: Photochemical CO₂ reduction in the presence of a dialkyl amine and its ammonium salt affords a dialkyl formamide when a ruthenium carbonyl compound, [Ru(bpy)₂(CO)₂]²⁺, is used as a catalyst. Fast nucleophilic attack of the dialkyl amine on the Ru–CO scaffold with resulting formamide generation takes priority over the competing formation of formic acid.

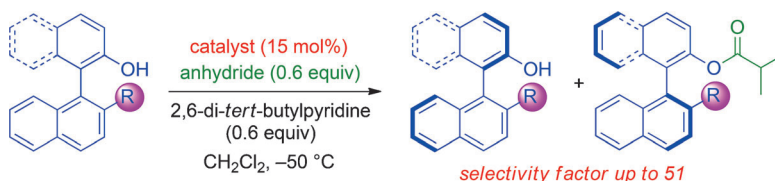


Asymmetric Organocatalysis

G. Ma, J. Deng, M. P. Sibi* **11818–11821**



Fluxionally Chiral DMAP Catalysts: Kinetic Resolution of Axially Chiral Biaryl Compounds



A catalyst for kinetic resolution: Chiral 4-dimethylaminopyridine catalysts with a fluxional group to relay stereochemical information from a fixed stereogenic center to the catalytic center promoted the acylative kinetic resolution of secondary

alcohols and axially chiral biaryl compounds with high enantioselectivity (see scheme). The highly modular design of the chiral DMAP catalysts enables significant variation of their structure.

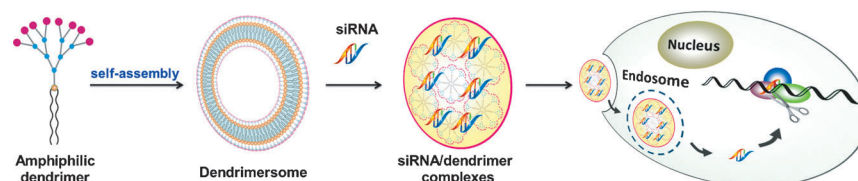
Back Cover

Adaptive Supramolecular Assemblies

X. Liu, J. Zhou, T. Yu, C. Chen, Q. Cheng, K. Sengupta, Y. Huang, H. Li, C. Liu, Y. Wang, P. Posocco, M. Wang, Q. Cui, S. Giorgio, M. Fermeglia, F. Qu, S. Pricl, Y. Shi, Z. Liang, P. Rocchi, J. J. Rossi, L. Peng* **11822–11827**

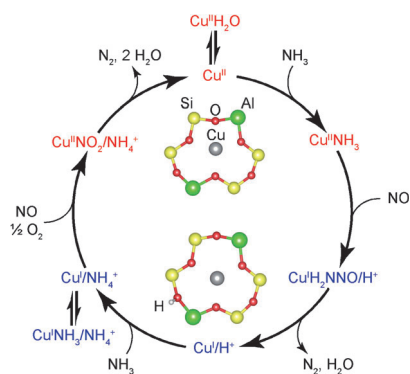


Adaptive Amphiphilic Dendrimer-Based Nanoassemblies as Robust and Versatile siRNA Delivery Systems



Vesicle-like dendrimerosomes formed through the self-assembly of an amphiphilic dendrimer are able to undergo structural rearrangement into spherical micelles to entrap and condense siRNA into stable nanoparticles, which protect siRNA and promote siRNA delivery in

various cells, including human primary and stem cells, as well as in vivo. This system combines the advantages of lipid and dendrimer vectors, hence constituting a novel and efficient siRNA delivery platform.

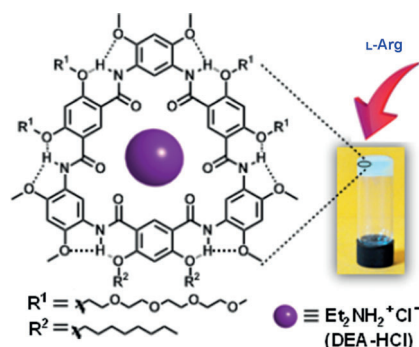


Copper redox catalysis: Operando spectroscopy and density functional calculations isolate copper oxidation and reduction half-cycles during the selective reduction of NO_x over a Cu-exchanged SSZ-13 zeolite catalyst containing only isolated Cu^{II} sites. NH_3 and NO together reduce Cu^{II} to Cu^{I} ions, and each reduction event generates a $\text{Cu}^{\text{I}}/\text{H}^+$ pair (see picture).

Zeolite Catalysis

C. Paolucci, A. A. Verma, S. A. Bates, V. F. Kispersky, J. T. Miller, R. Gounder, W. N. Delgass, F. H. Ribeiro,*
W. F. Schneider* — 11828–11833

Isolation of the Copper Redox Steps in the Standard Selective Catalytic Reduction on Cu-SSZ-13

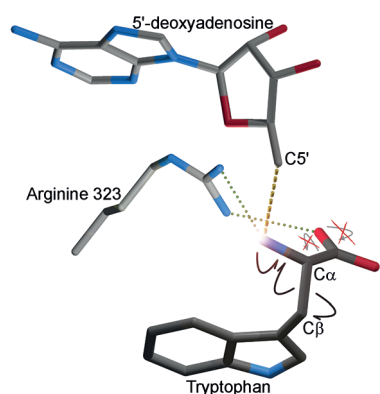


Picking and choosing: A supramolecular two-component gelation system based on the amphiphilic cyclo[6]aramide macrocycle and diethylammonium chloride is reported. This system provides a modularly tunable approach for creating functional two-component gel systems for highly specific recognition of L-arginine (L-Arg) from 19 other amino acids by competitive host-guest interactions.

Supramolecular Gels

Y. He, M. Xu, R. Gao, X. Li, F. Li, X. Wu, D. Xu,* H. Zeng, L. Yuan* — 11834–11839

Two-Component Supramolecular Gels Derived from Amphiphilic Shape-Persistent Cyclo[6]aramides for Specific Recognition of Native Arginine

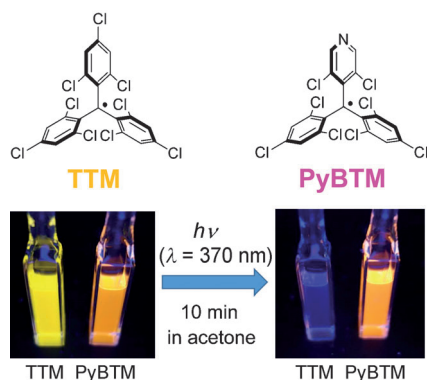


Radical control: The 3-methylindolic acid block of nosiheptide is synthesized from tryptophan by the radical S-adenosyl-L-methionine enzyme NosL. Its X-ray structure shows how the protein selects its substrate and how, starting from an amino nitrogen-centered radical species, it orients the radical-based reaction to selectively cleave the $\text{C}\alpha\text{--C}\beta$ bond of tryptophan, thus avoiding the spontaneous decarboxylation.

Reaction Mechanisms

Y. Nicolet,* L. Zeppieri, P. Amara, J. C. Fontecilla-Camps* — 11840–11844

Crystal Structure of Tryptophan Lyase (NosL): Evidence for Radical Formation at the Amino Group of Tryptophan



Enhanced photostability: A luminescent open-shell organic radical with high chemical stability was synthesized. The (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl (PyBTM) radical emits fluorescent light from the lowest doublet excited state and is up to 115 times more photostable than the previously reported luminescent tris(2,4,6-trichlorophenyl)methyl (TTM) radical.

Luminescent Organic Radicals

Y. Hattori, T. Kusamoto,*
H. Nishihara* — 11845–11848

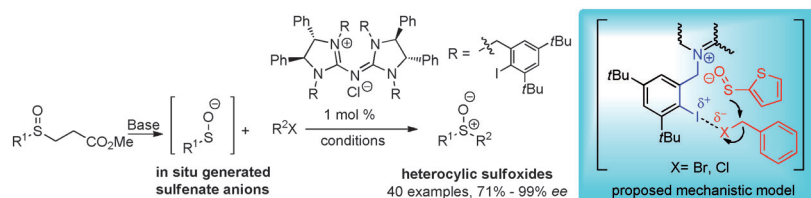
Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical

Organocatalysis

L. Zong, X. Ban, C. W. Kee,*
C.-H. Tan* 11849–11853



Catalytic Enantioselective Alkylation of Sulfonate Anions to Chiral Heterocyclic Sulfoxides Using Halogenated Pentanidium Salts



Phase transfer catalysis: Halogenated pentanidium salts are efficient phase-transfer catalysts for the enantioselective alkylation of sulfonate anions to sulfoxides with high enantioselectivity and high yield. Mechanistic studies indicate the ability of

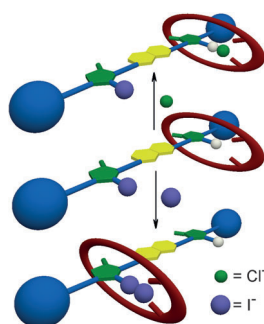
the catalysts to simultaneously activate/stabilize both nucleophile and electrophile through multiple noncovalent interactions (ion-pairing interaction, non-classical hydrogen bonds, and halogen bonds).

Halogen Bonding

A. Caballero, L. Swan, F. Zapata,
P. D. Beer* 11854–11858



Iodide-Induced Shuttling of a Halogen- and Hydrogen-Bonding Two-Station Rotaxane



Set the wheel in motion: Halogen-bonding (XB) anion recognition is used to control the molecular motion of an interlocked structure. A novel XB–HB two-station rotaxane (HB = hydrogen bonding) is demonstrated to undergo shuttling of the macrocyclic wheel component from the HB to the XB station driven by iodide recognition, whereas chloride binding results in the macrocycle residing at the HB station.

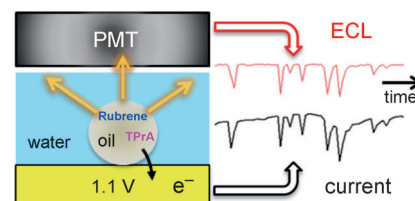
Electrochemistry

J. E. Dick, C. Renault, B. K. Kim,
A. J. Bard* 11859–11862



Simultaneous Detection of Single Attoliter Droplet Collisions by Electrochemical and Electrogenerated Chemiluminescent Responses

Shedding light on current events: A clear correlation between electrochemical and electrogenerated chemiluminescent (ECL) responses has been observed for collisions of nano- and micro-sized oil droplets on an ultra-microelectrode surface. The droplets serve as attoliter electrolysis reactors that, upon oxidation of the constituents within the droplet, display simultaneous current and ECL spikes. PMT = photomultiplier tube, TPrA = tri-*n*-propylamine.



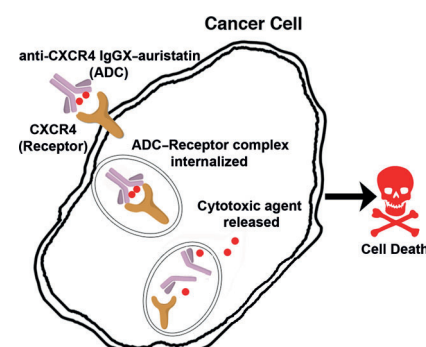
Antitumor Agents

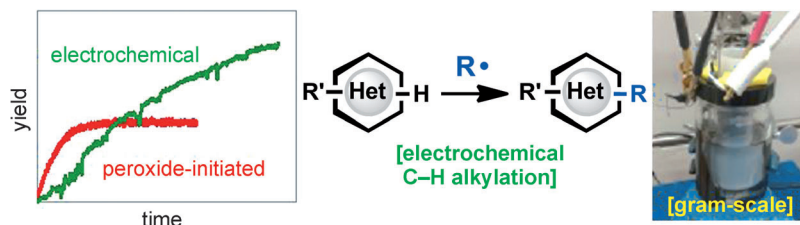
S. A. Kularatne, V. Deshmukh, J. Ma,
V. Tardif, R. K. V. Lim, H. M. Pugh, Y. Sun,
A. Manibusan, A. J. Sellers, R. S. Barnett,
S. Srinagesh, J. S. Forsyth,
W. Hassenpflug, F. Tian, T. Javahishvili,
B. Felding-Habermann, B. R. Lawson,
S. A. Kazane,*
P. G. Schultz* 11863–11867



A CXCR4-Targeted Site-Specific Antibody–Drug Conjugate

Hitting the mark(er): A chemically defined anti-CXCR4–auristatin antibody–drug conjugate (ADC) was produced that selectively targets and eliminates CXCR4⁺ metastatic cancer cells in vitro and in vivo with no significant overt toxicity. Because the CXCR4 receptor is highly expressed in the majority of metastatic cancers, a CXCR4–auristatin ADC may be useful for the treatment of a variety of metastatic malignancies.





Electrochemical reactions are shown to be effective for the C–H functionalization of a number of heterocyclic substrates that are recalcitrant to conventional peroxide radical initiation conditions and of inter-

est in medicinal chemistry. Monitoring reaction progress under electrochemical conditions provides mechanistic insight into the C–H functionalization process.

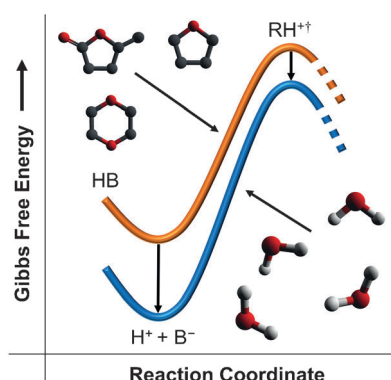
C–H Activation

A. G. O'Brien, A. Maruyama, Y. Inokuma, M. Fujita, P. S. Baran,*
D. G. Blackmond* 11868–11871

Radical C–H Functionalization of Heteroarenes under Electrochemical Control

In acid-catalyzed biomass conversion

(e.g., dehydration of xylose to furfural), the use of polar aprotic organic solvents, such as γ -valerolactone, affects the stabilization of the acidic proton relative to the protonated transition states. This leads to accelerated reaction rates and increased product selectivities compared to the transformations in aqueous media.



Biomass Conversion

M. A. Mellmer, C. Sener, J. M. R. Gallo, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic* 11872–11875

Solvent Effects in Acid-Catalyzed Biomass Conversion Reactions



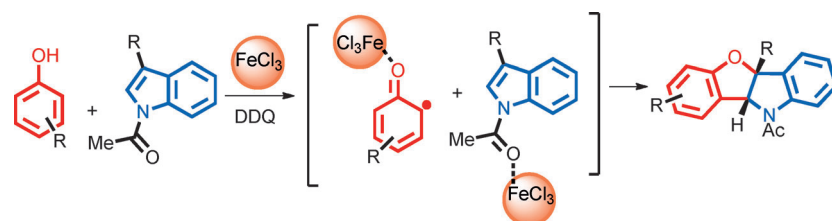
Like a postage stamp that neither alters a letter's weight nor changes its contents or destination, a new zwitterionic trifluoroborate radiosynthesis transforms complex molecules into ¹⁸F-tracers that are labeled in a single aqueous-phase step in high yield and at high specific radioactivity without HPLC purification.

¹⁸F-Labeling

Z. Liu, M. Pourghasian, M. A. Radtke, J. Lau, J. Pan, G. M. Dias, D. Yapp, K.-S. Lin, F. Bénard, D. M. Perrin* 11876–11880

An Organotrifluoroborate for Broadly Applicable One-Step ¹⁸F-Labeling

Inside Cover



Ironized! The unprecedented direct oxidative coupling between phenols and indole nuclei leading to the regioselective formation of the phalarine benzofuro-

indoline core is reported through the addition of phenoxy radicals to N-acetyl indoles mediated by FeCl₃. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Indole Chemistry

T. Tomakinian, R. Guillot, C. Kouklovsky, G. Vincent* 11881–11885

Direct Oxidative Coupling of N-Acetyl Indoles and Phenols for the Synthesis of Benzofuroindolines Related to Phalarine

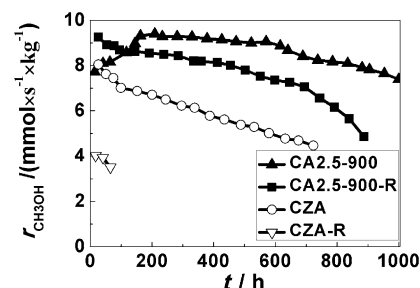
Heterogeneous Catalysis

H. Xi,* X. Hou, Y. Liu, S. Qing,
Z. Gao* 11886–11889



Cu–Al Spinel Oxide as an Efficient Catalyst
for Methanol Steam Reforming

Reforming reforming: Methanol steam reforming (MSR) was catalyzed by Cu–Al spinel oxide without prereduction. The catalysis is effectively initiated by the CuO phase present in CuAl₂O₄, which gradually releases active copper. Even the regenerated catalyst (CA2.5-900-R) was more active than the commercial Cu–Zn–Al (CZA) catalyst (see graph).

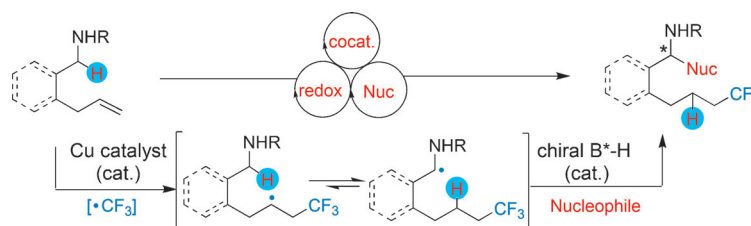


C–H Activation

P. Yu, J.-S. Lin, L. Li, S.-C. Zheng,
Y.-P. Xiong, L.-J. Zhao, B. Tan,*
X.-Y. Liu* 11890–11894



Enantioselective C–H Bond
Functionalization Triggered by Radical
Trifluoromethylation of Unactivated
Alkene



En route: The title redox-neutral reaction provides a convenient route to valuable enantioenriched trifluoromethylated N,O-aminals in good to excellent yields and

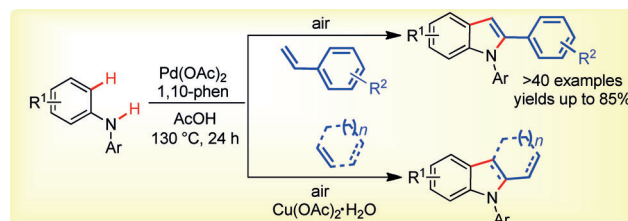
with excellent regio-, chemo-, and enantioselectivity. The reaction features a Cu^I/Brønsted acid system and broad substrate scope.

Heterocycle Synthesis

U. Sharma, R. Kancherla, T. Naveen,
S. Agasti, D. Maiti* 11895–11899



Palladium-Catalyzed Annulation of
Diarylamines with Olefins through C–H
Activation: Direct Access to N-Arylindoles



No group help needed: A palladium-catalyzed dehydrogenative coupling between diarylamines and olefins has been discovered for the synthesis of substituted indoles. This intermolecular annulation approach incorporates readily

available olefins and obviates the need for any additional directing group. An *ortho* palladation, olefin coordination, and β -migratory insertion sequence has been proposed for the generation of an olefinated intermediate.

Organopolymerization

M. Hong, E. Y.-X. Chen* 11900–11906

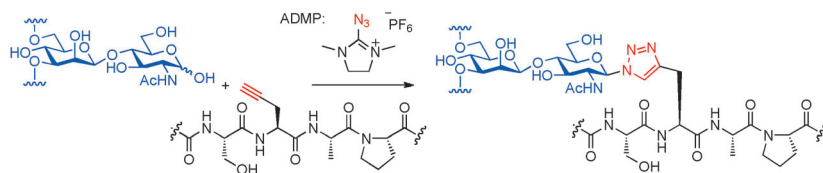


Proton-Transfer Polymerization (HTP):
Converting Methacrylates to Polyesters by
an N-Heterocyclic Carbene



Unsaturated polyesters are obtained specifically from dimethacrylates by a new

step-growth polymerization catalyzed by an N-heterocyclic carbene.



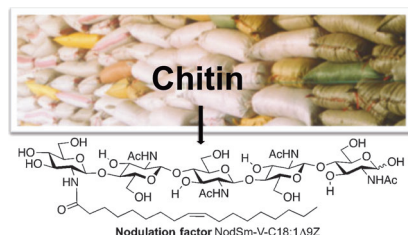
Sugars get sticky in water: The combined use of ADMP and the Cu-catalyzed Huisgen cycloaddition allows the synthesis of a range of glycoconjugates directly from the corresponding reducing sugar in one

step under aqueous conditions. The reaction is stereoselective and may be applied to the convergent synthesis of triazole-linked glycosides, oligosaccharides, and glycopeptides.

Carbohydrates

D. Lim, M. A. Brimble, R. Kowalczyk, A. J. A. Watson, A. J. Fairbanks* 11907–11911

Protecting-Group-Free One-Pot Synthesis of Glycoconjugates Directly from Reducing Sugars



Short cuts from chitin: Deconstruction of chitin and selective reconstruction to give well-defined oligosaccharides provide an effective approach to bioactive glycoconjugates. This method was applied to the preparation of the important symbiotic glycolipids.

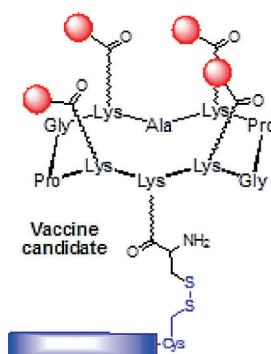
Carbohydrates

G. Despras, A. Alix, D. Urban,* B. Vauzeilles,* J.-M. Beau* 11912–11916

From Chitin to Bioactive Chitooligosaccharides and Conjugates: Access to Lipochitooligosaccharides and the TMG-chitotriomycin



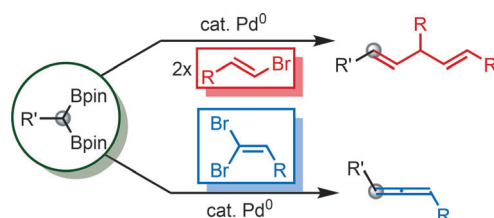
Fantastic four: Four clustered mimetics of the tumor-associated carbohydrate antigen Tn (red) and a T-helper-cell peptide epitope (blue) conjugated to a cyclopeptide carrier (RAFT) are the chemical components of a new improved vaccine prototype. This fully synthetic vaccine elicits a robust and long-lasting IgG/IgM antibody response and induces tumor protection in mice through a B-cell-mediated mechanism.



Cancer Vaccines

B. Richichi, B. Thomas, M. Fiore, R. Bosco, H. Qureshi, C. Nativi,* O. Renaudet,* L. BenMohamed* 11917–11920

A Cancer Therapeutic Vaccine based on Clustered Tn-Antigen Mimetics Induces Strong Antibody-Mediated Protective Immunity



It takes two B: The title reactions afford 1,4-dienes and allenes. These reactions utilize the high reactivities of both 1,1-

diboronates and allylboron intermediates generated in the initial coupling reaction.

Synthetic Methods

H. Li, Z. Zhang, X. Shangguan, S. Huang, J. Chen, Y. Zhang, J. Wang* 11921–11925

Palladium(0)-Catalyzed Cross-Coupling of 1,1-Diboronates with Vinyl Bromides and 1,1-Dibromoalkenes



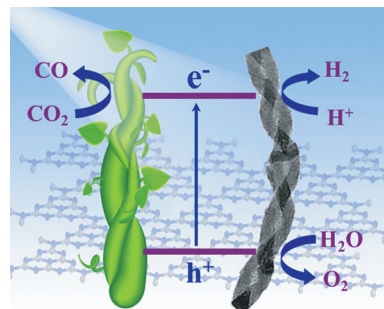
Photocatalysis

Y. Zheng, L. Lin, X. Ye, F. Guo,
X. Wang* — 11926–11930



Helical Graphitic Carbon Nitrides with Photocatalytic and Optical Activities

Helical nanorods: Graphitic carbon nitride with helical nanorod-like morphology similar to spiral vines is constructed for artificial photosynthesis. This helically conjugated polymer can also be fabricated with opposite chirality and shows photocatalytic activity for water splitting and CO₂ conversion.

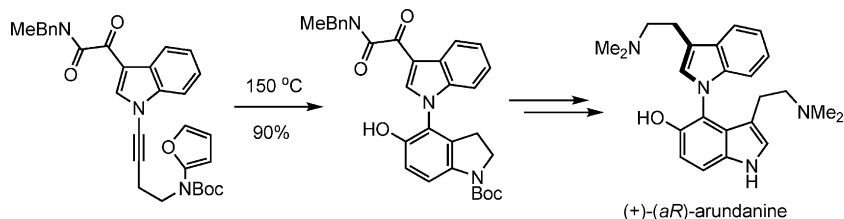


Natural Product Synthesis

J. Chen, A. J. Ferreira,
C. M. Beaudry* — 11931–11934



Synthesis of Bis(indole) Alkaloids from *Arundo donax*: The Ynindole Diels–Alder Reaction, Conformational Chirality, and Absolute Stereochemistry



Conformational chirality: Bis(indole) alkaloids from *Arundo donax* were synthesized using the first ynindole Diels–Alder reaction. The alkaloids are chiral, having stable enantiomeric conformations with

half-lives of racemization of $t_{1/2} = 4150\text{--}25100$ seconds at room temperature. Their absolute stereochemistry was determined using the exciton chirality method.

Electrochromic Supercapacitors

P. Yang, P. Sun, Z. Chai, L. Huang, X. Cai,
S. Tan, J. Song, W. Mai* — 11935–11939



Large-Scale Fabrication of Pseudocapacitive Glass Windows that Combine Electrochromism and Energy Storage



A pseudocapacitive glass window (15 × 15 cm²) is obtained by the deposition of WO₃ on fluorine-doped tin oxide glass. Such smart pseudocapacitive glass win-

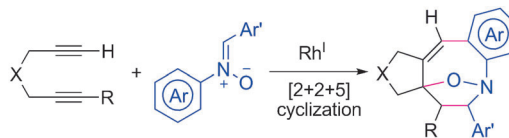
dows show great potential in functioning as electrochromic windows and concurrently powering electronic devices, such as mobile phones or laptops.

Cyclization

C. X. Wang, D. P. Wang, H. Yan,
H. L. Wang, B. Pan, X. Y. Xin, X. C. Li,
F. Wu, B. S. Wan* — 11940–11943

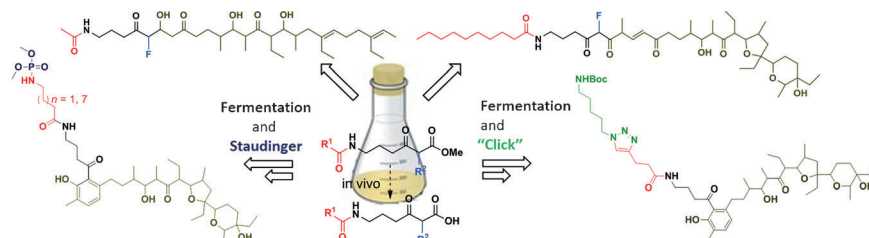


Rhodium-Catalyzed Cyclization of Diynes with Nitrones: A Formal [2+2+5] Approach to Bridged Eight-Membered Heterocycles



Five-atom building unit: N-aryl-substituted nitrones were employed as five-atom coupling partners in the rhodium-catalyzed cyclization with diynes. In this reaction, the nitron moiety served as

a directing group for the catalytic C–H activation of the N-aryl ring. This formal [2+2+5] approach allows rapid access to bridged eight-membered heterocycles with broad substrate scope.



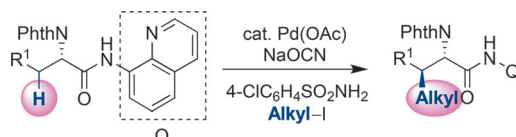
Towards novel “unnatural” products: Fermentation of ACP mutants of *S. lasaliensis* in the presence of functionalized chemical probes with subsequent

site-selective modifications generates a library of nonnatural lasalocid A precursors and derivatives.

Biosynthesis

E. Riva, I. Wilkening, S. Gazzola, W. M. A. Li, L. Smith, P. F. Leadlay, M. Tosin* 11944–11949

Chemical Probes for the Functionalization of Polyketide Intermediates



Branching off: The title reaction of unactivated β -methylene $C(sp^3)$ -H bonds of α -amino acid substrates with alkyl iodides is described. The $C(alkyl)$ - $C(alkyl)$ bond-

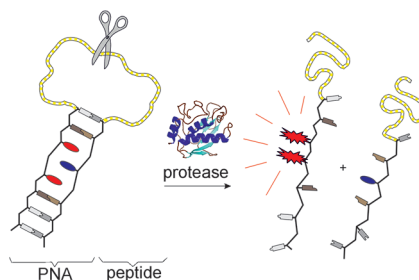
forming reaction proceeds in good yields, and β -branched amino acids can be obtained by using sequential reactions.

Amino Acids

K. Chen, B.-F. Shi* 11950–11954

Sulfonamide-Promoted Palladium(II)-Catalyzed Alkylation of Unactivated Methylene $C(sp^3)$ -H Bonds with Alkyl Iodides

Let there be excimer light: Large Stokes shifts and the long lifetime of excimer emission facilitate measurements in optically dense, autofluorescent media such as blood serum. However, proteolytic cleavage abolishes rather than installs proximity relationships required for excimer signaling. Herein, a new approach is introduced which enables on-switching of pyrene excimer emission upon proteolytic scission of hairpin-shaped PNA-peptide probe.



Fluorescence Probes

M. Fischbach, U. Resch-Genger, O. Seitz* 11955–11959

Protease Probes that Enable Excimer Signaling upon Scission

DOI: 10.1002/anie.201484414

Flashback: 50 Years Ago ...

Giulio Natta, who shared the 1963 Nobel Prize for Chemistry with Karl Ziegler, published a Review on the stereospecific homopolymerization of cyclopentene. Use of $MoCl_5/Al(C_2H_5)_3$ as catalyst was found to give the *cis*-polypentenamer, whereas use of $WCl_5/Al(C_2H_5)_3$ resulted in formation of the *trans*-polypentenamer.

Rolf Huisgen et al. reported on the stereospecific addition of ketenes onto

enol ethers to form 3-alkoxycyclobutanones. The *cis* or *trans* configuration of the enol ethers is retained in the product, and the reaction proceeds via a resonance-stabilized intermediate or a multi-step cycloaddition, depending on the geometry of the starting materials.

Wilhelm P. Neumann et al. published two Communications on stannanes. The first report discussed the synthesis of octabenzylcyclotetastannane, which

contains a four-membered ring of tin atoms. The target product was synthesized from dibenzyltin hydride, which itself was produced in situ from dibenzyltin dichloride and ignites spontaneously on filter paper in contact with air. The second Communication was on the synthesis of organic di- and polystannanes by the condensation of organotin hydrides with organotin oxides.

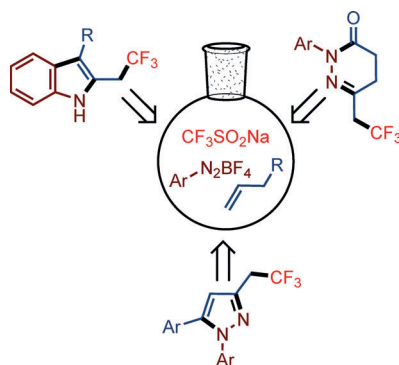
[Read more in Issue 11/1964.](#)

Heterocycles

K. Matcha,
A. P. Antonchick* — 11960–11964



Cascade Multicomponent Synthesis of Indoles, Pyrazoles, and Pyridazinones by Functionalization of Alkenes



Fischer-man's friend: A regioselective multicomponent route to indole synthesis by functionalization of simple alkenes has been developed and has a broad scope. The novel application of alkene trifluoromethylation provides entry into Fischer indole synthesis, and various trifluoromethylated nitrogen heterocycles can be conveniently obtained.

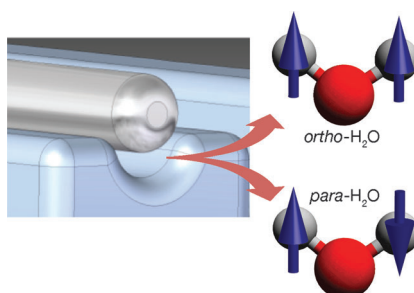


Spin Isomers of Water

D. A. Horke, Y.-P. Chang, K. Długolecki,
J. Küpper* — 11965–11968



Separating *Para* and *Ortho* Water



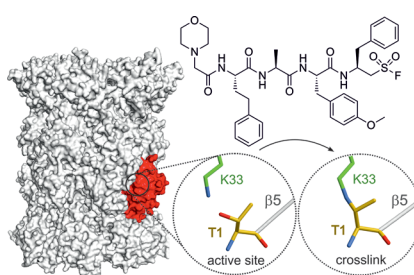
Keep them separated: The two nuclear-spin isomers *para* and *ortho* water can be isolated in their absolute ground state in pure molecular beams. No pure *para* sample had previously been produced. This method for the separation of quantum states is generally applicable to all polar neutral molecules and allows the spatial separation of single quantum states and nuclear-spin isomers.

Immunoproteasome Inhibition

C. Dubiella, H. Cui, M. Gersch,
A. J. Brouwer, S. A. Sieber, A. Krüger,
R. M. J. Liskamp,*
M. Groll* — 11969–11973



Selective Inhibition of the Immunoproteasome by Ligand-Induced Crosslinking of the Active Site



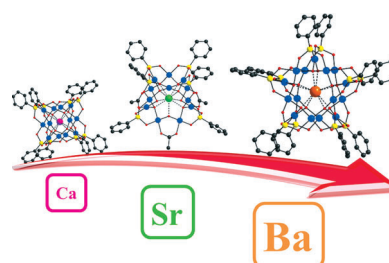
The current benchmark for proteasome inhibition, immunoproteasome inhibitors featuring α',β' -epoxyketones, were compared to peptido sulfonyl fluorides (PSF) in terms of their mechanism of action, selectivity, and cytotoxicity. PSFs were found to remove the catalytically active nucleophile and then crosslink the active site. Cell-based activity and viability assays designate this warhead for selective immunoproteasome blockage.

Noble Metalates

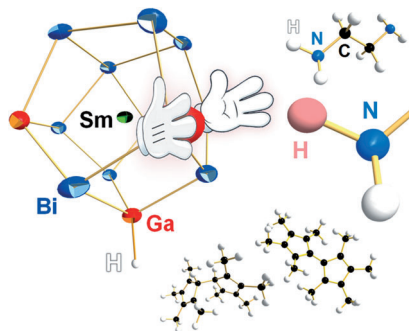
P. Yang, Y. Xiang, Z. Lin, B. S. Bassil,
J. Cao, L. Fan, Y. Fan, M.-X. Li,
P. Jiménez-Lozano, J. J. Carbó,
J. M. Poblet, U. Kortz* — 11974–11978



Alkaline Earth Guests in Polyoxopalladate Chemistry: From Nanocube to Nanostar via an Open-Shell Structure



The noble template effect: The size of the alkaline earth metal ion guest (Ca^{2+} , Sr^{2+} , Ba^{2+}) allows the shape and size of the resulting polyoxopalladate cluster to be tuned. The small Ca^{2+} ion leads to the 12-palladate nanocube, the large Ba^{2+} ion leads to the 15-palladate nanostar, and the intermediate-sized Sr^{2+} ion leads to an intermediary structure, an open-shell 12-palladate.



Desiring protons: The use of $[\text{GaBi}_3]^{2-}$ in reactions with $[\text{Sm}(\text{C}_5\text{Me}_4\text{H})_3]$ yielded the first protonated ternary intermetalloid clusters $[\text{Sm}@\text{Ga}_{3-x}\text{H}_{3-2x}\text{Bi}_{10+x}]^{3-}$ ($x=0,1$). By experimental and quantum chemical analyses, the presence of the Ga–H bonds was rationalized, and the transfer of electrons and protons during the formation process was elucidated.

Main-Group Chemistry

B. Weinert, F. Müller, K. Harms, R. Clérac, S. Dehnen* ————— 11979 – 11983

Origin and Location of Electrons and Protons during the Formation of Intermetalloid Clusters

$[\text{Sm}@\text{Ga}_{3-x}\text{H}_{3-2x}\text{Bi}_{10+x}]^{3-}$ ($x=0, 1$)



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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This article is accompanied by a cover picture (front or back cover, and inside or outside).



The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

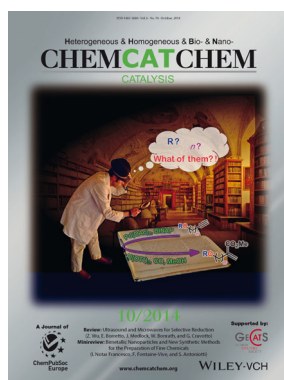


The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

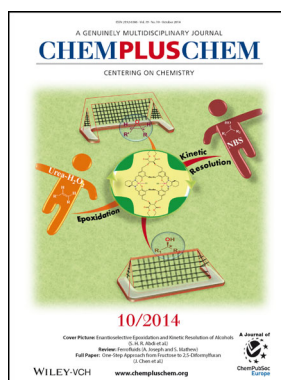
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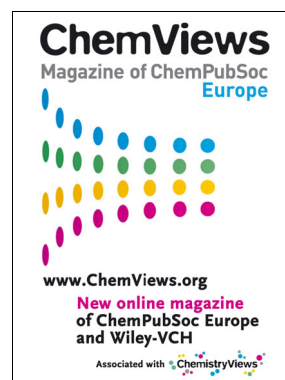
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