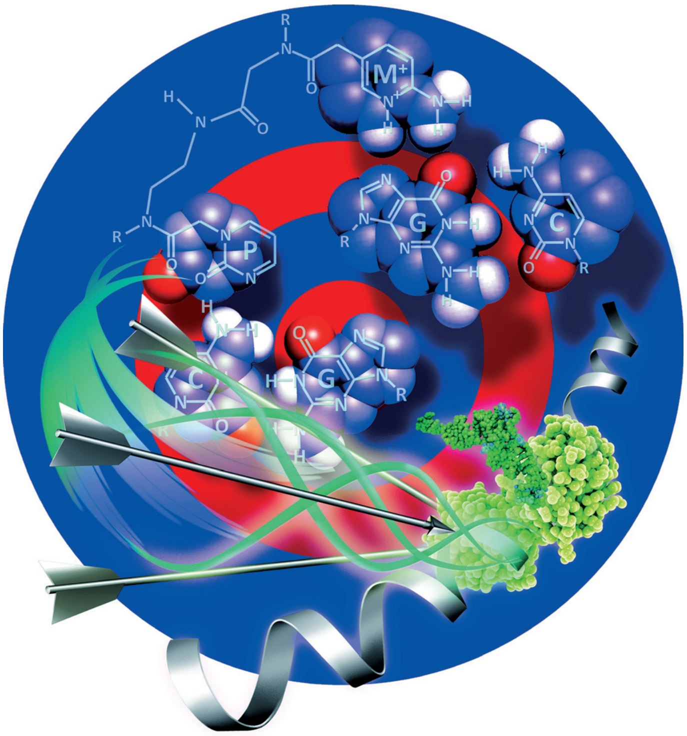
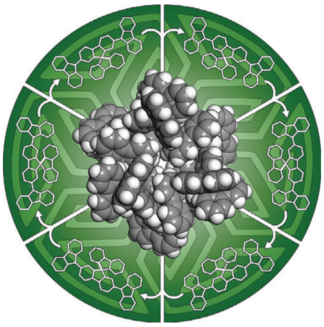
The biological activity ...

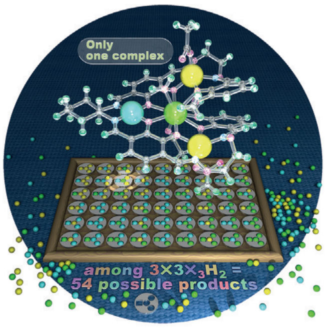


… of triplex-forming peptide nucleic acid (PNA) modified with unnatural nucleobases is described by N. Sugimoto and co-workers in their Communication on page 899 ff. The triplex formed between the PNA and the 5′ untranslated region of an mRNA enabled sequence-specific reduction of the protein expression levels both in vitro and in cells by blocking progression of the small ribosomal subunit. The triplex-forming PNA can thus be used as a modulator of RNA functions.

Dynamic Covalent Chemistry

The synthesis of giant macrocyclic hydrocarbons by a facile approach that is based on the reversible formation of carbon–carbon bonds is described by J. D. Wuest, D. Beaudoin et al. in their Communication on page 894 ff.



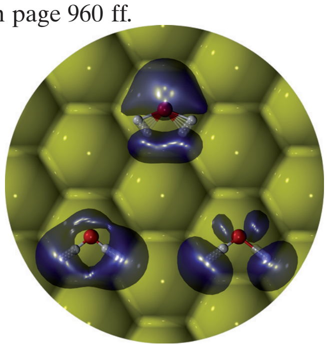


Heterometallic Complexes

The selective introduction of three different metal ions at specific positions of a cluster-like structure with a carefully designed ligand is reported by S. Akine, T. Nabeshima, and T. Matsumoto in their Communication on page 960 ff.

Raman Spectroscopy

Tip-enhanced non-resonant Raman spectroscopy is employed by Y. Luo and co-workers in their Communication on page 1041 ff. to visualize the vibrational motions of water molecules adsorbed on a Au(111) surface.



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Service

Author Profile

*"My favorite drink is a mojito.
Young people should study chemistry because rocket science is overrated ..."*
This and more about Andrei K. Yudin can be found on page 852.

News


J. Livage


D. Aurbach


S. Bordiga


R. G. Compton


K. de Jong


R. Guilard


D. A. Leigh


B. Meunier


V. W.-W. Yam


B. D. McCloskey


I. Siewert


D. W. Stephan

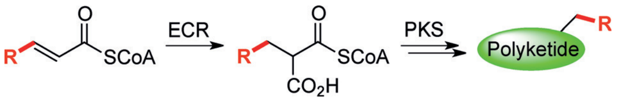
Books

Highlights

Polyketide Biosynthesis

J. Kundert, T. A. M. Gulder* **858 – 860**

Extending Polyketide Structural Diversity by Using Engineered Carboxylase/Reductase Enzymes



For a change: Enoyl-CoA carboxylase/reductases (ECRs) catalyze the selective α-carboxylation of α,β-unsaturated CoA-thioesters. Structure-based engineering of the active-site binding pocket of ECRs enabled significant alteration of their catalytic activity towards larger substrates. This facilitates the incorporation of unusual extender units into polyketide backbones, thus providing a novel method for the directed structural diversification of polyketides.

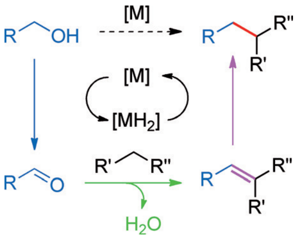
Minireviews

Alkylation

F. Huang, Z. Q. Liu, Z. K. Yu* **862 – 875**

C-Alkylation of Ketones and Related Compounds by Alcohols: Transition-Metal-Catalyzed Dehydrogenation

Something borrowed: The major advances during the past five years in transition-metal-catalyzed borrowing-hydrogen (BH) alkylation of ketones, secondary alcohols, and related compounds with alcohols are summarized. Water is formed as the only by-product, thus making the BH process atom-economical and environmentally benign.

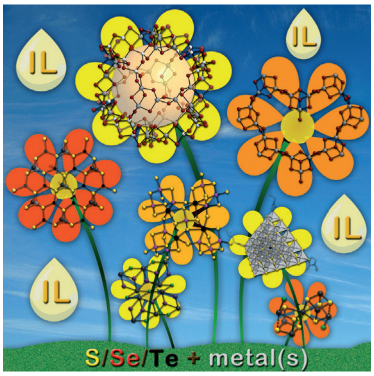


Reviews

Chalcogenide Synthesis

S. Santner, J. Heine,
S. Dehnen* **876 – 893**

Synthesis of Crystalline Chalcogenides in Ionic Liquids



Ionic liquids (ILs) are important reaction media for the synthesis of a large variety of crystalline chalcogen compounds. This Review presents the incorporation of polyanionic and polycationic substructures within the compounds along with parameters for selective product formation. The Review also sheds light on selected materials properties and emphasizes the meaningfulness of the use of ionic liquids for contemporary materials research.

For the USA and Canada:
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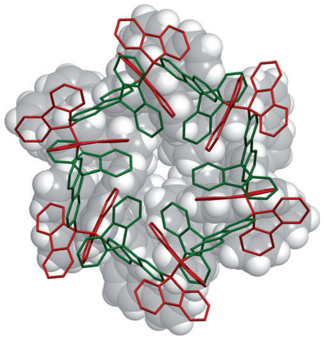
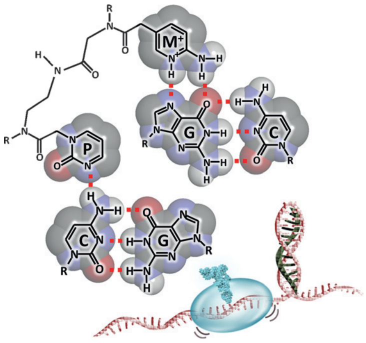
Communications



Giant macrocyclic hydrocarbons can be obtained by a facile approach that is based on the reversible formation of carbon–carbon bonds. Extended spirobifluorene-substituted derivatives of Wittig's hydrocarbon were synthesized and found to undergo oligomerization, leading to the largest hydrocarbon that has been crystallized and characterized by X-ray diffraction to date.

Dynamic Covalent Chemistry

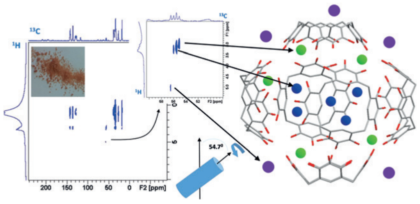
Frontispiece



Very specific: A 9-mer peptide nucleic acid (PNA) containing unnatural nucleobases forms a sequence-specific PNA–RNA triplex. The triplex formed within the 5′ untranslated region of an mRNA reduces the protein expression levels both in vitro and in cells. The biological effects of a PNA–RNA triple helix in live cells are thus evaluated for the first time.

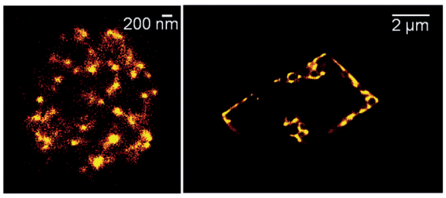
Peptide Nucleic Acids

Front Cover



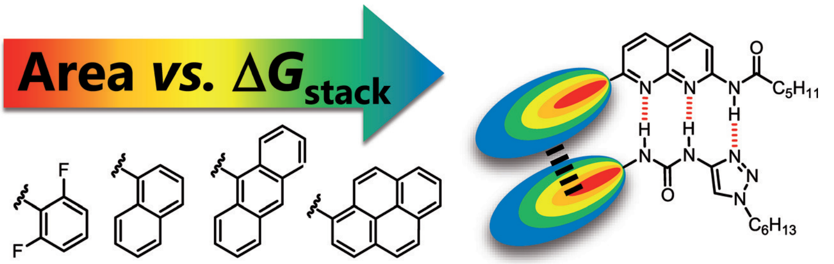
Peeking inside: Powders of pyrogallol[4]arene hexamers obtained by slow evaporation of the corresponding solutions were studied by various magic angle spinning solid-state NMR techniques. As a result, signals of the encapsulated and non-encapsulated solvent molecules were identified, the encapsulation process was shown to be reversible, and it was demonstrated that the encapsulated solvent molecules occupy different sites having different mobilities.

NMR Spectroscopy



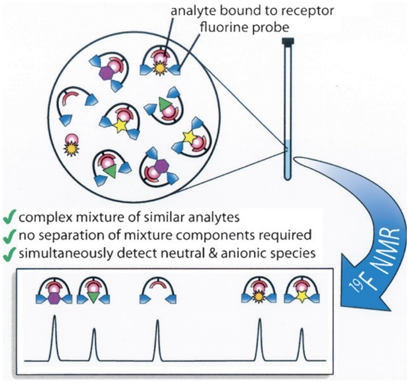
Seeing is believing: dSTORM imaging revealed the distributions of gelatin in vaterite microspheres (left image) and calcite rhombohedra (right image). The vaterite microspheres showed a gelatin distribution on the nanoscale, which provides insight into the formation of vaterite microspheres. By contrast, the gelatin tends to accumulate on the edges of calcite rhombohedra, which indicates a process in which the gelatin is excluded from the crystals.

Biomineralization



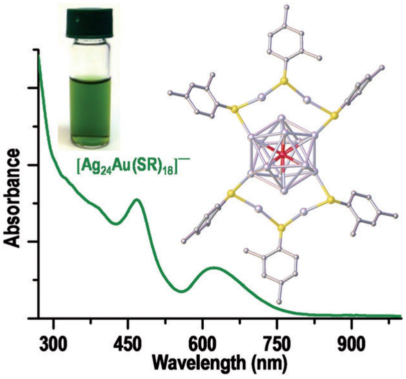
Size matters: Dispersion forces are found to govern the stacking interactions of aromatic rings even in the presence of a competitive polarizable organic solvent.

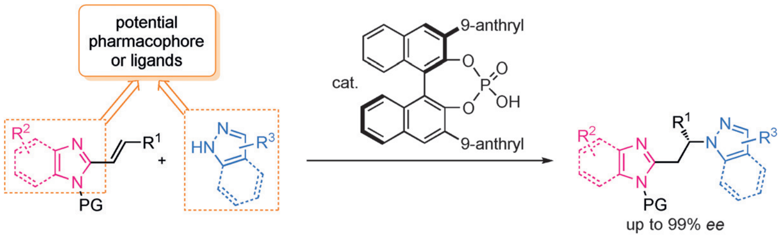
Regular or decaf? A chemosensory system based on a complex with palladium (see picture, red semicircles) and a pincer ligand with fluorinated groups (blue) is reported. The system operates without need of separation techniques and is capable of identifying multiple structurally similar analytes such as caffeine in complex mixtures by ^{19}F NMR spectroscopy. Neutral and anionic species are simultaneously detected by this method.



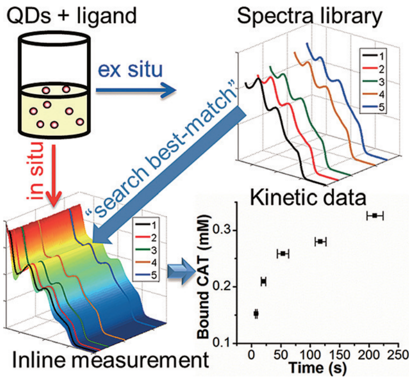
Inside Cover

A $[Ag_{24}Au(SR)_{18}]^-$ nanocluster was synthesized by a galvanic exchange strategy and characterized using mass spectrometry and single-crystal XRD. The replacement of the central Ag atom of $Ag_{25}(SR)_{18}$ by Au occurs without compromising Ag_{25} integrity. Subtle changes in the Ag_{25} structural framework after doping caused significant changes in the stability, electronic, optical, and luminescence properties relative to the properties of the parent Ag_{25}.





Heterocycle squared: Highly enantioselective Michael-type addition reactions to alkenyl benzimidazoles with pyrazoles and indazoles as nitrogen nucleophiles are accomplished using a chiral phosphoric acid catalyst. Theoretical studies elucidated the reaction pathway and the origin of the stereochemical outcome. The catalyst substituent and the N-protecting group (PG) of the benzimidazole contribute to the resulting high enantioselectivity.



Well-established libraries of target spectra that are derived by means of careful offline analysis and identification of equilibrium data within larger kinetic datasets can be used for any particle–ligand system. Kinetics of ligand binding to nanoparticles can be derived free of assumption, in situ, and with high time resolution.

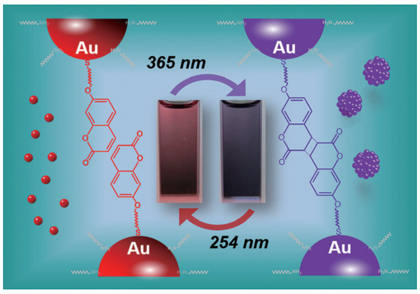
Ligand Exchange

W. Lin, M. Haderlein, J. Walter, W. Peukert,
D. Segets* **932 – 935**

Spectra Library: An Assumption-Free In Situ Method to Access the Kinetics of Catechols Binding to Colloidal ZnO Quantum Dots

---

Colloidal coumarin-functionalized Au nanoparticles were reversibly self-assembled based on coumarin photolysis in response to light irradiation. Facilitated by coumarin groups, 365 nm light irradiation triggers the stable assembly of monodisperse Au nanoparticles. The resulting self-assembly system can then be disassembled through a relatively short exposure to benign UV light; the reversible self-assembly cycles can be repeated 4 times.



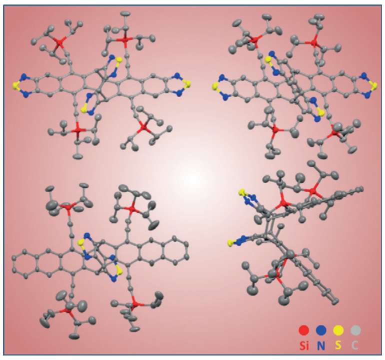
Reversible Self-Assembly

H. He, M. Feng,* Q. Chen, X. Zhang,
H. Zhan* **936 – 940**

Light-Induced Reversible Self-Assembly of Gold Nanoparticles Surface-Immobilized with Coumarin Ligands

---

Dimerization of heteroacenes: Layered electron acceptors equipped with terminal 1,2,5-thiadiazole groups were constructed using a one-pot protocol of acene dimerization. Crystal structures of the compounds and their photophysical and electrochemical properties were studied.



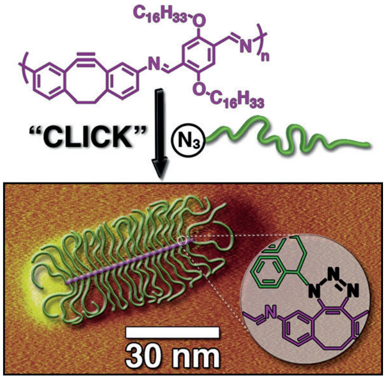
Organic Semiconductors

D. Xia, X. Guo, L. Chen, M. Baumgarten,*
A. Keerthi, K. Müllen* **941 – 944**

Layered Electron Acceptors by Dimerization of Acenes End- Capped with 1,2,5-Thiadiazoles

---

Click on a stick: Incorporation of a strained cyclooctyne monomer unit within the backbone of a conjugated polymer structure was achieved through Schiff-base polymerization, thereby resulting in a conjugated polymer backbone that could be subsequently modified with a variety of azide derivatives through strain-promoted azide–alkyne cycloaddition.



Conjugated Polymers

V. Kardelis, R. C. Chadwick,
A. Adronov* **945 – 949**

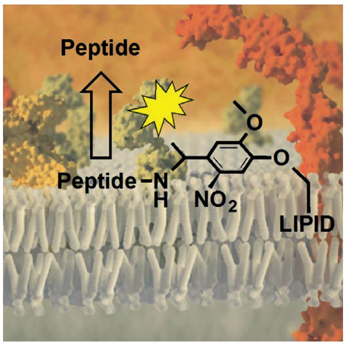
Click Functionalization of a Dibenzocyclooctyne-Containing Conjugated Polyimine

Peptide Therapeutics

C. P. O'Banion, L. T. Nguyen, Q. Wang, M. A. Priestman, S. P. Holly, L. V. Parise, D. S. Lawrence* ——— **950 – 954**

The Plasma Membrane as a Reservoir, Protective Shield, and Light-Triggered Launch Pad for Peptide Therapeutics

Gimme shelter: Attachment to the plasma membrane of erythrocytes can be used to protect therapeutic peptides from serum proteases. A photocleavable moiety is inserted between the lipid anchor and the peptide backbone, thereby enabling light-triggered release.

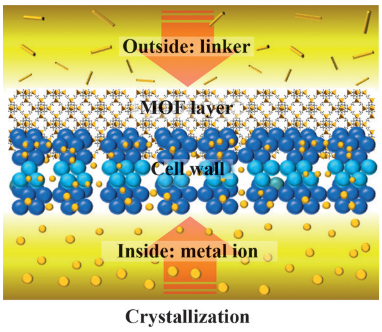


Biomaterials

W. Li, Y. F. Zhang, Z.H. Xu, Q. Meng, Z. Fan, S. J. Ye, G. Zhang* ——— **955 – 959**

Assembly of MOF Microcapsules with Size-Selective Permeability on Cell Walls

From two directions: MOF microcapsules were assembled on hollow cell walls (CWs) by inside/outside interfacial crystallization. Small molecules can be size-selectively and steadily released from the prepared MOF/CW microcapsules, and the size selectivity can be adjusted by changing the type of MOF.



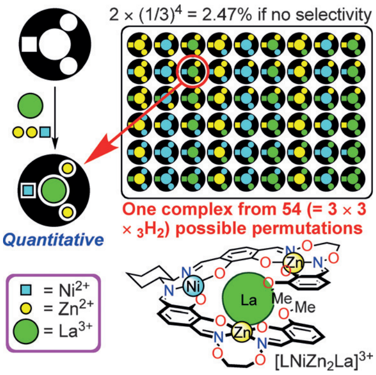
Heterometallic Complexes

S. Akine,* T. Matsumoto, T. Nabeshima* ——— **960 – 964**

Overcoming Statistical Complexity: Selective Coordination of Three Different Metal Ions to a Ligand with Three Different Coordination Sites

Inside Back Cover

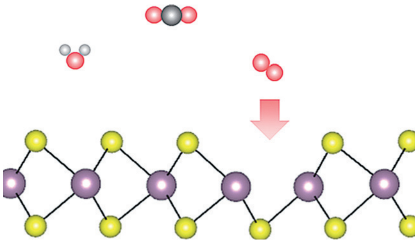
The selective introduction of three different metal ions at specific positions of a cluster-like structure was achieved with a carefully designed ligand H_6L. $[LNiZn_2La]^{3+}$ was quantitatively obtained by a stepwise process, but different products were obtained when the metal ions were added in a different order. However, upon heating to overcome the statistical probability, $[LNiZn_2La]^{3+}$ was almost solely formed among the 54 possible products.



Semiconductor Surfaces

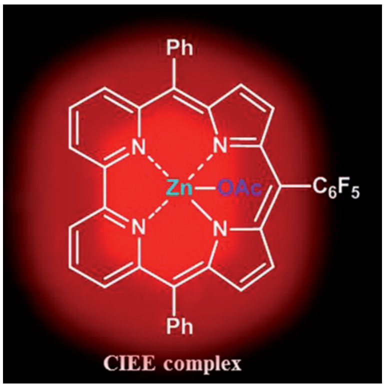
Y. Liu,* P. Stradins, S.-H. Wei* **965 – 968**

Air Passivation of Chalcogen Vacancies in Two-Dimensional Semiconductors



The interaction between air and chalcogen vacancies (V_X), the most typical defects in 2D semiconductors (SCs), is calculated. The chemisorbed O_2 changes the V_X from commonly believed harmful carrier-traps to electronically benign sites. This unusual behavior originates from the isovalence between O_2 and X when bonded with metal. A facile approach is proposed from this to improve the performance of 2D SCs by using air/O_2 to passivate the defects.

Ion-stabilizing corroles: The nonaromatic *meso*-triarylbipyricorrole with a monoanionic core was achieved by the combination of aromatic bipyridyl and π-conjugated dipyrromethene units. Upon coordination with a Zn^{II} ion, the bipyricorrole was found to exhibit chelation-induced emission enhancement (CIEE) characteristics and was further explored for selective detection of Zn^{II} ions.

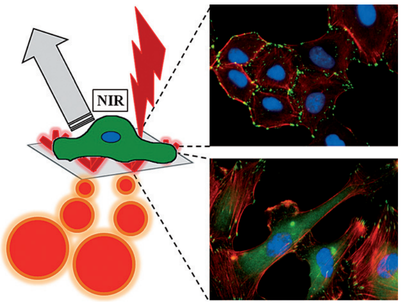


Corrole Chemistry

B. Adinarayana, A. P. Thomas, P. Yadav, A. Kumar, A. Srinivasan* ______ **969 – 973**

Bipyricorrole: A Corrole Homologue with a Monoanionic Core as a Fluorescence Zn^{II} Sensor

Cell harvesting: Tailored plasmonic substrates can be used to capture various types of cells, which can be further released by irradiation with near-infrared (NIR) light without being damaged. Facile functionalization with RGD peptide allows tuning of the morphology of integrin-rich cells.

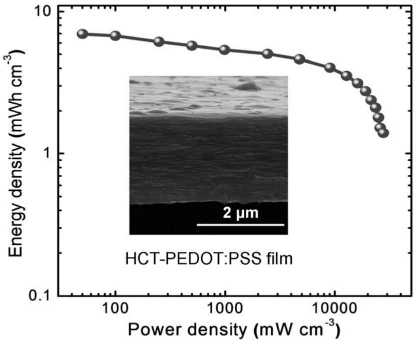


Nanoplasmonics

J. J. Giner-Casares,* M. Henriksen-Lacey, I. García, L. M. Liz-Marzán* __ **974 – 978**

Plasmonic Surfaces for Cell Growth and Retrieval Triggered by Near-Infrared Light

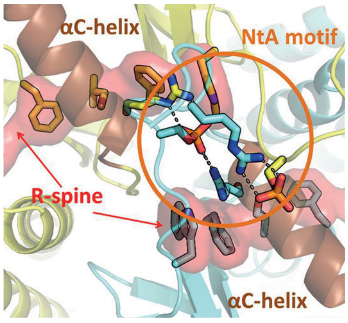
Energy conversion: Micrometer-thick, highly conductive poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (HCT-PEDOT:PSS) films were prepared. These films were obtained by dropping a PEDOT:PSS dispersion into a dilute sulfuric acid solution. Flexible solid-state supercapacitors based on the HCT-PEDOT:PSS electrodes displayed a high energy density of 3.15 mWh cm^{-3} at a very high power density of 16160 mW cm^{-3}.



Energy Conversion

Z. F. Li, G. Q. Ma, R. Ge, F. Qin, X. Y. Dong, W. Meng, T. F. Liu, J. H. Tong, F. Y. Jiang, Y. F. Zhou, K. Li, X. Min, K. F. Huo,* Y. H. Zhou* ______ **979 – 982**

Free-Standing Conducting Polymer Films for High-Performance Energy Devices



Back to back: Biochemical kinase assays and structural evidence from MD simulations reveal a key electrostatic role for the phosphorylated NtA motif in RAF kinase transactivation. Interprotomer salt bridges and a conserved tryptophan residue located at the N-terminal end of the kinase domain play crucial roles by connecting the R-spines of the two protomers, and phosphorylation leads to important structural changes in the highly conserved HRD motif.

Signaling Proteins

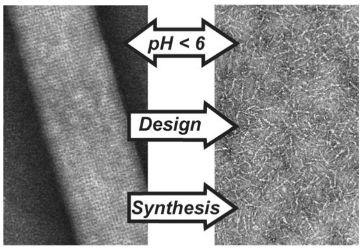
P. G. Jambrina, N. Rauch, R. Pilkington, K. Rybakova, L. K. Nguyen, B. N. Kholodenko, N.-V. Buchete, W. Kolch,* E. Rosta* ________ **983 – 986**

Phosphorylation of RAF Kinase Dimers Drives Conformational Changes that Facilitate Transactivation

Peptide Nanotubes

F. Thomas, N. C. Burgess, A. R. Thomson, D. N. Woolfson* ———— 987 – 991

Controlling the Assembly of Coiled–Coil Peptide Nanotubes

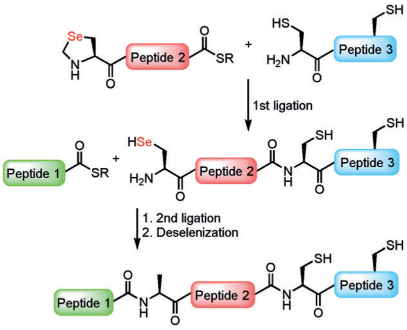


Thick to thin: The assembly in coiled–coil peptide nanotubes (PNTs) can be controlled. Arrays of hexameric coiled–coil PNTs can be reversibly disassembled by acidification. Accordingly, repulsive-charge interactions engineered into the coiled–coil units result in the formation of single PNTs at neutral pH. Non-covalent or covalent linkage by native chemical ligation can be used to vary the stability of, and small-molecule encapsulation by, the resulting PNTs.

Chemical Protein Synthesis

P. S. Reddy, S. Dery, N. Metanis* ———— 992 – 995

Chemical Synthesis of Proteins with Non-Strategically Placed Cysteines Using Selenazolidine and Selective Deselenization

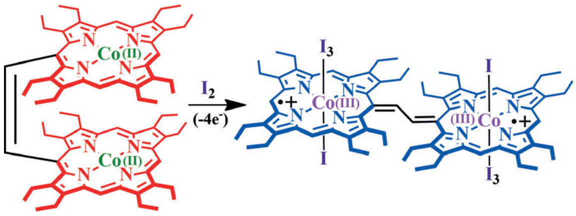


Stitching a protein together: A synthesis approach is reported using selenazolidine and deselenization to access a protein with non-strategically placed cysteine residues. The challenging human phosphohistidine phosphatase 1 (PHPT1) protein, a 125-residue enzyme with three cysteine residues near the C-terminus, was used as a model system.

Electronic Structure

S. Dey, D. Sil, S. P. Rath* ———— 996 – 1000

A Highly Oxidized Cobalt Porphyrin Dimer: Spin Coupling and Stabilization of the Four-Electron Oxidation Product

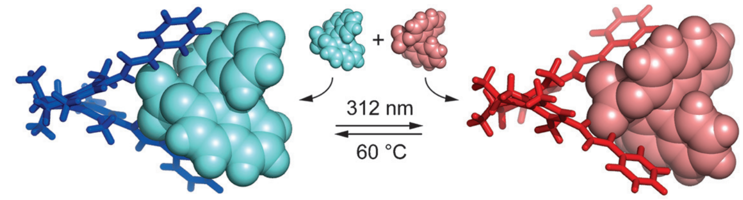


Four to be sure: The oxidation of a cobalt(II) porphyrin dimer with iodine readily produced a cobalt(III) porphyrin π-cation radical dimer (see scheme). Extensive π conjugation through the ethylene bridge led to several unusual spectral and geometrical features of this four-electron oxidized complex and stabilized the singlet state by enabling strong antiferromagnetic coupling between the π-cation radicals.

Chirality Inversion

M. Vlatković, B. L. Feringa,* S. J. Wezenberg* ———— 1001 – 1004

Dynamic Inversion of Stereoselective Phosphate Binding to a Bisurea Receptor Controlled by Light and Heat



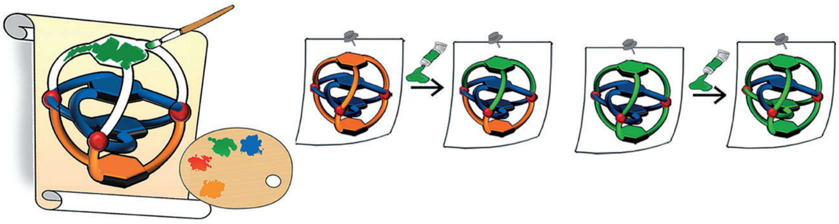
(*P,P*)-receptor prefers (*R*)-substrate (*M,M*)-receptor prefers (*S*)-substrate

At the flick of a switch: A chiral bisurea anion receptor, derived from a first-generation molecular motor, can be isomerized photochemically and thermally between two isomers with opposite helical chirality. The isomers display opposite enantioselectivities for binding binol phosphate and binding can be controlled dynamically using light and heat.

Supramolecular Chemistry

H. Lee, T. H. Noh,
O.-S. Jung* ______ **1005 – 1009**

Construction of Hetero-Four-Layered Tripalladium(II) Cyclophanes by Transannular π···π Interactions

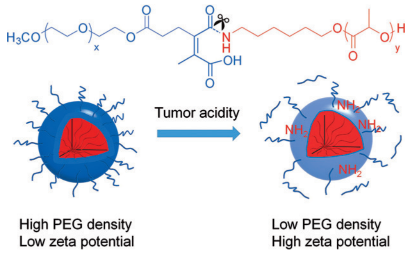


Hetero-four-layered tripalladium(II) cyclophanes have been prepared. The synthesis of this series of new compounds was accomplished by a combination of effective transannular π···π interactions, tailor-made short/long tridentate ligands, and Lewis basicity of donating groups.

Drug Delivery Vehicles

C. Sun, Y. Liu, J. Du, Z. Cao, C. Xu,
J. Wang* ______ **1010 – 1014**

Facile Generation of Tumor-pH-Labile Linkage-Bridged Block Copolymers for Chemotherapeutic Delivery

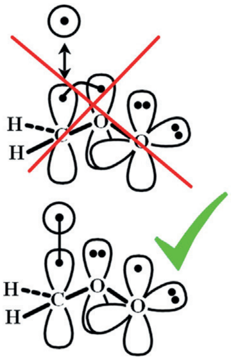


PEG-detachable delivery micelles: A chemotherapeutic vector with superior therapeutic efficacy and high biocompatibility is obtained by designing bridged PEGylated polylactide-containing tumor-acidity-responsive linkages. The decreased PEGylation and increased zeta potential in the tumor matrix enhanced cellular uptake of the vector, enabling safe and effective antitumor drug delivery.

Criegee Intermediates

E. Miliordos,
S. S. Xantheas* ______ **1015 – 1019**

The Origin of the Reactivity of the Criegee Intermediate: Implications for Atmospheric Particle Growth

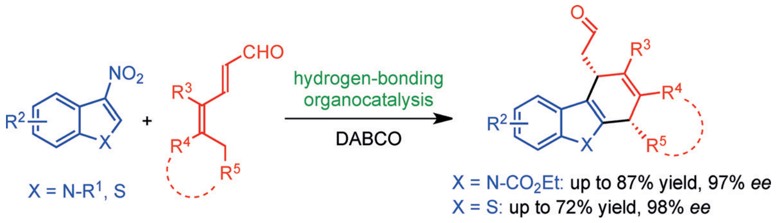


The electronic structure of the ground state of the simplest Criegee intermediate, H_2COO, is practically that of a closed shell. Its rich atmospheric chemistry is due to the mixing of its ground state with the first triplet excited state, which is a pure biradical ($H_2C^{\bullet}{-}O{-}O^{\bullet}$), leading to the formation of strongly bound products during reactions inducing atmospheric particle growth.

Cycloaddition

Y. Li, F. Tur, R. P. Nielsen, H. Jiang,
F. Jensen, K. A. Jørgensen* _ **1020 – 1024**

Enantioselective Formal [4+2] Cycloadditions to 3-Nitroindoles by Trienamine Catalysis: Synthesis of Chiral Dihydrocarbazoles

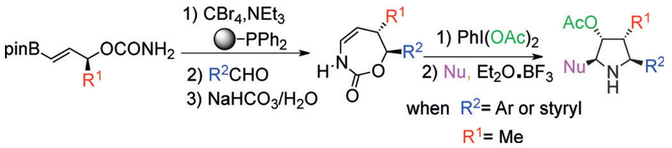


A formal event: Enantioselective formal [4+2] cycloadditions of 3-nitroindoles in the presence of an organocatalyst are presented. Chiral dihydrocarbazole scaffolds are formed in moderate to good yields. The reaction also proceeds with 3-nitrobenzothiophene. The mechanism of the reaction is discussed based on experimental and computational studies.

Heterocycles

A. Macé, S. Touchet, P. Andres, F. Cossío, V. Dorcet, F. Carreaux,* B. Carboni* ———— 1025 – 1029

[3,3]-Sigmatropic Rearrangement/Allylboration/Cyclization Sequence: Enantioenriched Seven-Membered-Ring Carbamates and Ring Contraction to Pyrrolidines

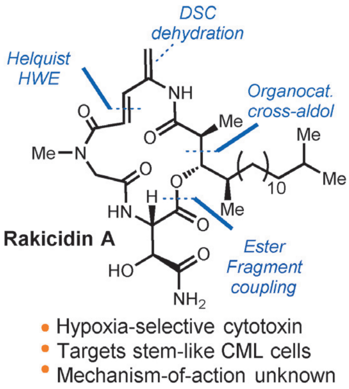


Honey I shrunk the rings: A new protocol for the diastereo- and enantiocontrolled synthesis of seven-membered-ring ene carbamates is described. These compounds were easily converted into diversely substituted 1,3-oxazepan-2-ones. Tetrasubstituted pyrrolidines were obtained by an unprecedented ring contraction rearrangement of a 5-acetoxy derivative in the presence of trifluoroboron etherate.

Natural Products

M. Tsakos, L. L. Clement, E. S. Schaffert, F. N. Olsen, S. Rupiani, R. Djurhuus, W. Yu, K. M. Jacobsen, N. L. Villadsen, T. B. Poulsen* ———— 1030 – 1035

Total Synthesis and Biological Evaluation of Rakicidin A and Discovery of a Simplified Bioactive Analogue



Take my breath away: Rakicidin A, a depsipeptide natural product with hypoxia-selective antitumour activity, is comprised of a ring system containing sensitive and congested functionalities. A modular asymmetric synthesis and initial biological evaluation of the natural product, and the discovery of a simplified analogue displaying strongly enhanced hypoxia selectivity is reported.

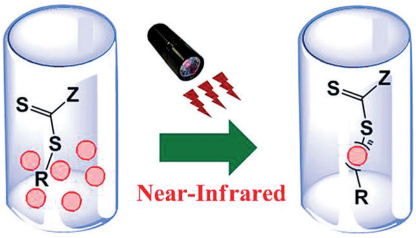
VIP

Photopolymerization

S. Shanmugam, J. Xu, C. Boyer* ———— 1036 – 1040

Light-Regulated Polymerization under Near-Infrared/Far-Red Irradiation Catalyzed by Bacteriochlorophyll *a*

An efficient photoinduced living radical polymerization reaction that involves the use of bacteriochlorophyll *a* as the photoredox catalyst is reported. This process can be conducted under irradiation with near-infrared or far-red light and proceeds with excellent control over molecular weight and polydispersity.

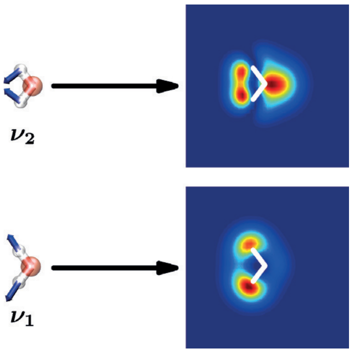


Raman Spectroscopy

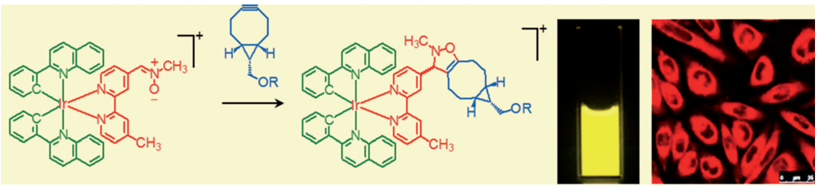
S. Duan, G. Tian, Y. Luo* ———— 1041 – 1045

Visualization of Vibrational Modes in Real Space by Tip-Enhanced Non-Resonant Raman Spectroscopy

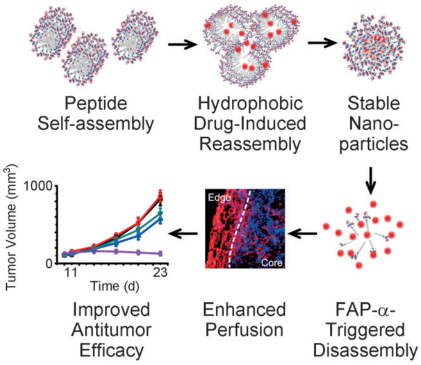
Back Cover



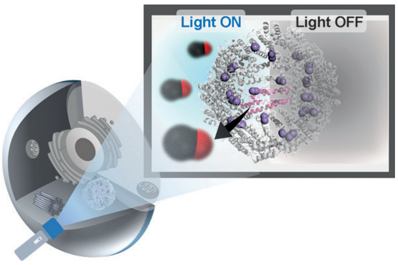
Simulations show that images obtained by tip-enhanced non-resonant Raman spectroscopy resemble the expected vibrational motions of water molecules adsorbed on Au(111) surfaces very well (see picture). A practical experimental method for the visualization of molecular vibrational modes in real space is thus suggested.



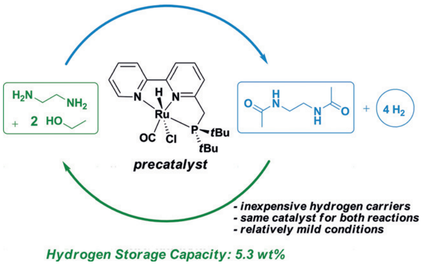
Serving quench: The nitrone unit is utilized as both the emission quencher and bioorthogonal functional group in Ir^{III} complexes. Owing to isomerization of the C=N group these complexes are non-emissive but show emission turn-on upon cycloaddition with cyclooctynes. They were used as phosphorogenic bioconjugation reagents and bioorthogonal probes for live cells.



A cleavable amphiphilic peptide (CAP) nanocarrier transforms from self-assembled nanofibers to spherical nanoparticles (NPs) by loading hydrophobic drugs, and cleavage by the tumor-specific protease, FAP-α, resulted in specific and efficient release of the encapsulated drugs at tumor sites. This Transformers-like drug nanocarrier could disrupt the stromal barrier, and enhance local drug accumulation.



Photoactivable protein cage: A ferritin protein cage retaining manganese–carbonyl complexes released carbon monoxide (CO; see picture) under visible-light irradiation. The amount of released CO is modulated by the irradiation period. The system showed an optimized CO dose for activating a cellular transcriptional factor.

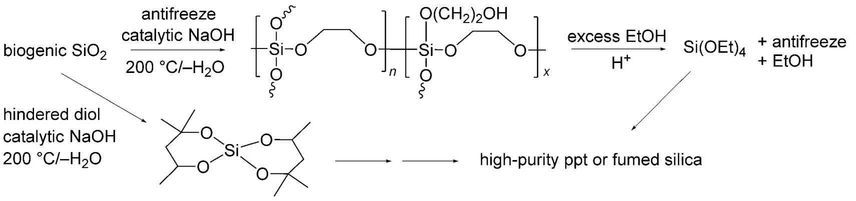


In support of the hydrogen economy: An efficient and simple homogeneous hydrogen carrier system was developed based on the dehydrogenative coupling of ethylenediamine with ethanol to form diacetylethylenediamine. The same ruthenium pincer catalyst is used for both hydrogen loading and unloading reactions.

Catalytic Depolymerization

R. M. Laine,* J. C. Furgal, P. Doan, D. Pan, V. Popova, X. Zhang ——— 1065 – 1069

Avoiding Carbothermal Reduction: Distillation of Alkoxysilanes from Biogenic, Green, and Sustainable Sources

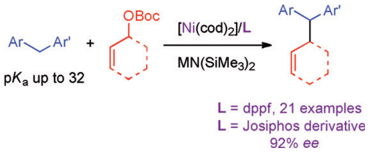


No detours: The base-catalyzed depolymerization of SiO_2 from different sources with diols led directly to distillable alkoxysilanes, including spirocyclic compounds, thus providing inexpensive routes to high-purity silica and compounds with single Si–C bonds (see scheme): The alkoxysilanes could be converted either into $Si(OEt)_4$ by treatment with EtOH and a catalytic amount of acid or into high-purity precipitated (ppt) or fumed silica.

Asymmetric Catalysis

S.-C. Sha, H. Jiang, J. Mao, A. Bellomo, S. A. Jeong, P. J. Walsh* ___ 1070 – 1074

Nickel-Catalyzed Allylic Alkylation with Diarylmethane Pronucleophiles: Reaction Development and Mechanistic Insights

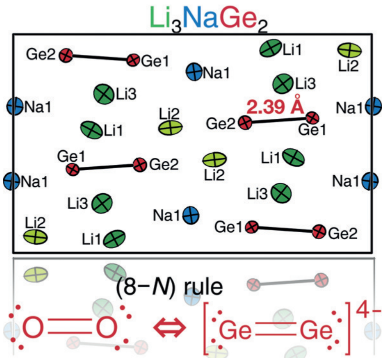


Just a softy: Contrary to what would be predicted, organosodium nucleophiles derived from diarylmethane pronucleophiles are shown to behave as soft nucleophiles in nickel-catalyzed allylic substitution reactions. This general reaction is demonstrated to proceed through a double inversion pathway. A promising asymmetric version is presented.

Zintl Phases

L. M. Scherf, A. J. Karttunen, O. Pecher, P. C. M. M. Magusin, C. P. Grey, T. F. Fässler* ——— 1075 – 1079

$[Ge_2]^{4-}$ Dumbbells with Very Short Ge–Ge Distances in the Zintl Phase Li_3NaGe_2: A Solid-State Equivalent to Molecular O_2



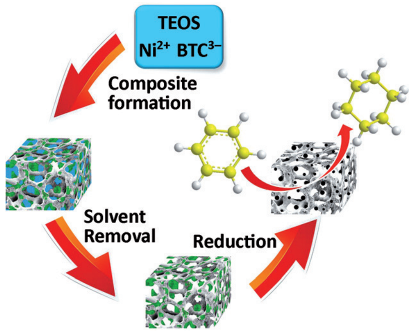
A true double bond between two germanium atoms was observed in Li_3NaGe_2. The π-bond character of the $[Ge_2]^{4-}$ dumbbells was experimentally confirmed by the upfield ^6Li NMR shift of the coordinating Li cations. As in molecular O_2, the π-bonding orbitals are degenerate and partially filled. In the neat solid they are expanded into bands, which results in metallic properties.

Hydrogenation Catalysis

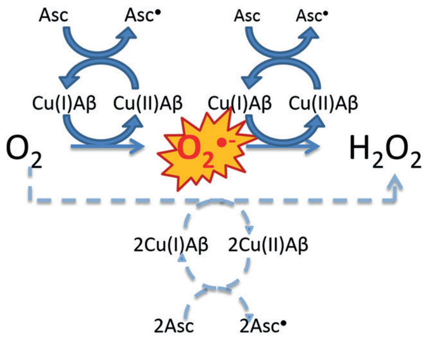
X. C. Kang, H. Z. Liu, M. Q. Hou, X. F. Sun, H. L. Han, T. Jiang, Z. F. Zhang, B. X. Han* ——— 1080 – 1084

Synthesis of Supported Ultrafine Non-noble Subnanometer-Scale Metal Particles Derived from Metal–Organic Frameworks as Highly Efficient Heterogeneous Catalysts

A fine catalyst: A strategy to immobilize ultrafine non-noble metal particles on supports is proposed. Ni/SiO_2 and Co/SiO_2 catalysts with average metal particle sizes of 0.9 nm were successfully synthesized from MOFs. The Ni and Co nanoparticles were supported uniformly on porous SiO_2 with a metal loading of about 20 wt%. The catalysts have very high activity for liquid-phase hydrogenation of benzene even at temperatures as low as 80 °C.



Cause of stress: Mechanistic studies reveal that copper-amyloid-β reduces dioxygen and produces predominantly superoxide as an intermediate for H_2O_2 formation. This finding implies that Cu-Aβ-catalyzed $O_2^{\bullet-}$ formation could contribute to oxidative stress in Alzheimer's disease.

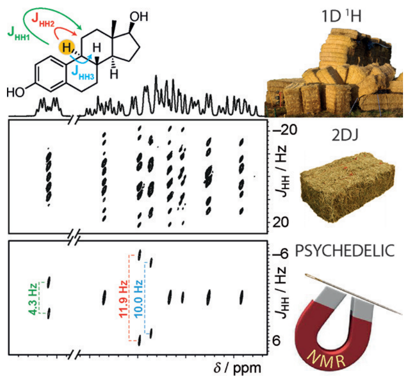


Amyloid Peptide

K. Reybier,* S. Ayala, B. Alies, J. V. Rodrigues, S. Bustos Rodriguez, G. La Penna, F. Collin, C. M. Gomes, C. Hureau, P. Faller* ______ **1085 – 1089**

Free Superoxide is an Intermediate in the Production of H_2O_2 by Copper(I)-Aβ Peptide and O_2

Finding a needle in a haystack: Measurement of ^{1}H-^{1}H couplings in very crowded ^{1}H NMR spectra is made straightforward by a general new method, PSYCHEDELIC. This resolves individual couplings at near-ideal resolution, without interference from other splittings, with good tolerance to strong coupling, and at high sensitivity.



NMR Spectroscopy

D. Sinnaeve,* M. Foroozandeh, M. Nilsson, G. A. Morris ___ **1090 – 1093**

A General Method for Extracting Individual Coupling Constants from Crowded ^{1}H NMR Spectra

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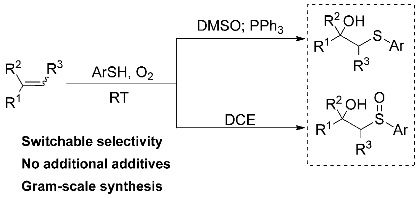
Solvent selection alters the reactivity of the generated reaction intermediate and drastically switches the reaction selectivity under simple and mild conditions. Various β-oxy sulfoxides and β-hydroxy sulfides could be facilely obtained from readily available starting materials. Importantly, neither a metal catalyst nor an additional additive was necessary in these transformations.



Radical Reactions

H. Wang, Q. Lu, C. Qian, C. Liu, W. Liu, K. Chen, A. Lei* __________ **1094 – 1097**

Solvent-Enabled Radical Selectivities: Controlled Syntheses of Sulfoxides and Sulfides

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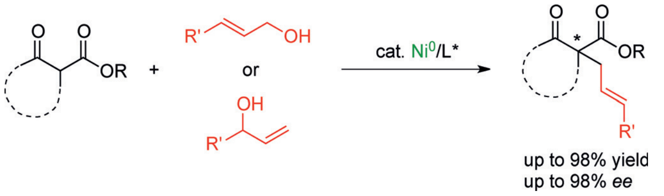


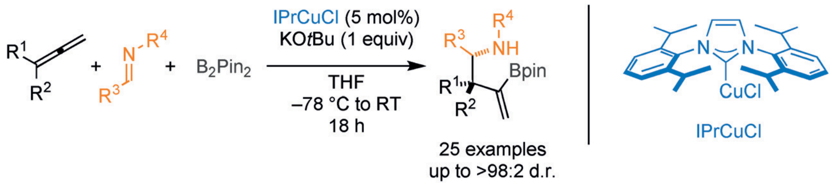
No activation necessary: A nickel/chiral diphosphine (L) system effectively catalyzed the asymmetric allylic alkylation of β-ketoesters to deliver quaternary chiral centers at the α position of the β-ketoesters. The present system is highly advantageous in that it requires no activator for either the nucleophiles or the allylic alcohols.

Asymmetric Catalysis

Y. Kita, R. D. Kavthe, H. Oda, K. Mashima* __________ **1098 – 1101**

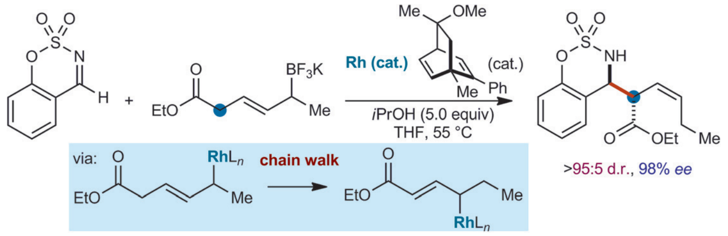
Asymmetric Allylic Alkylation of β-Ketoesters with Allylic Alcohols by a Nickel/Diphosphine Catalyst

Copper Catalysis



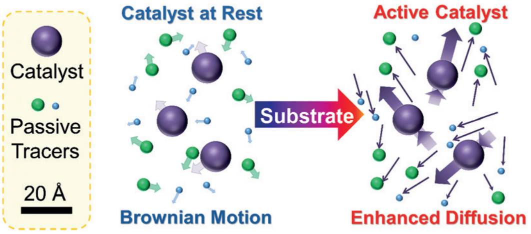
A triumvirate: Copper-catalyzed three-component couplings of allenes, B_2pin_2, and imines furnish functionalized homoallylic amines, or Mannich-type products, after oxidative workup. The process utilizes a commercially available copper catalyst, tolerates a range of allene and imine substrates, and affords complex products in high yield with high regio- and diastereocontrol. Computational studies were employed to understand the stereochemical course of the cross-coupling.

Chain Walking



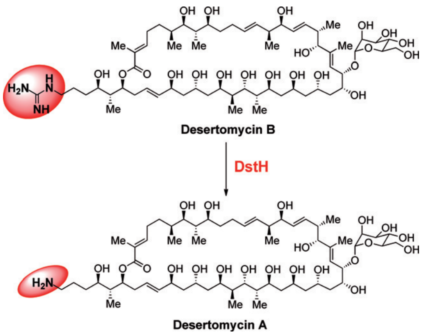
Migrate to create: Allylrhodium species from δ-trifluoroboryl β,γ-unsaturated esters undergo chain walking towards the ester moiety. The resulting allylrhodium species react with imines to give products with two new stereocenters and a Z-alkene. A chiral diene ligand leads to products with high enantioselectivities; a pronounced matched/mismatched effect with the chirality of the allyltrifluoroborate is evident.

Mechanochemistry



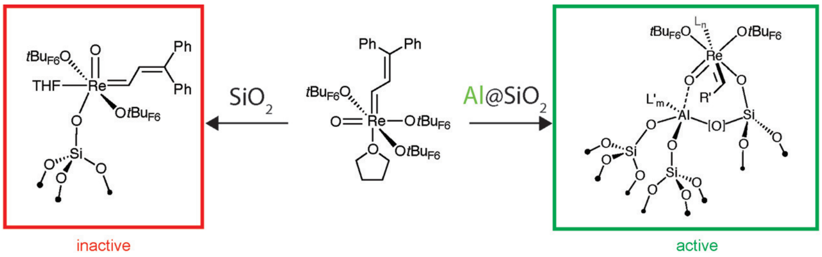
Diffusion: Ångström-scale molecular catalysts, when turning over substrate, can generate enough mechanical force to cause advective flows, resulting in enhanced diffusion of inert molecules in the ambient fluid (see picture). This study provides new insight into the role of active particles on advection and mixing at the Ångström scale.

Polyketide Biosynthesis



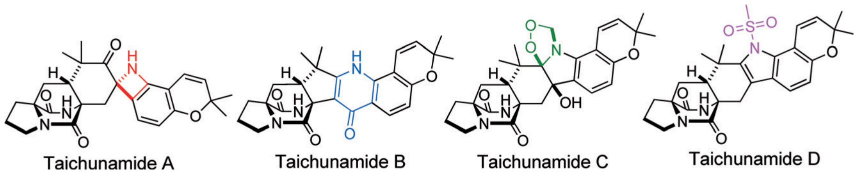
The desert trail: The macrocyclic aminopolyol polyketide desertomycin A bears a primary amino group, which unexpectedly arises through the use of 4-guanidinobutyrate as the starter unit for the desertomycin polyketide synthase. As the last step in the biosynthesis, the amino function is unmasked by the action of the amidinohydrolase DstH.

Metathesis Catalysts



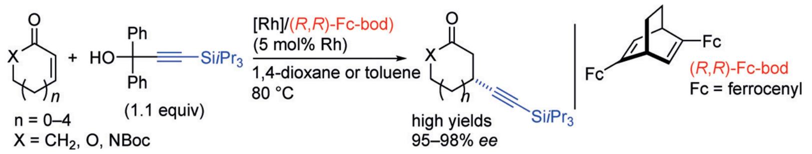
Al-ctivation: Supporting a well-defined Re oxo alkylidene on a silica–alumina support gives a highly active metathesis catalyst, while the corresponding species on silica is inactive. This work shows the importance of Lewis acid sites in activating these catalysts.

Natural Products



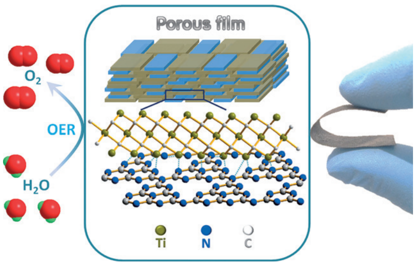
Magnificent seven: Seven new prenylated indole alkaloids were isolated from *A. taichungensis*. This fungus produces alkaloids containing an *anti*-bicyclo-[2.2.2]diazaoctane core, whereas *A. protuberus* and *A. amoenus* produce derivatives with a *syn*-bicyclo core. The structural diversity of tryptophan-derived secondary metabolites reveals unusually diverse stereochemical and structural secondary metabolite tailoring functions in these orthologous fungi.

Asymmetric Catalysis



Check the bod: Asymmetric alkynylation of cyclic α,β-unsaturated carbonyl compounds (ketones, esters, and amides) was realized by use of diphenyl[(triisopropylsilyl)ethynyl]methanol as an alkynylating reagent in the presence of a rhodium catalyst coordinated with a newly designed chiral diene ligand (Fc-bod). The reaction delivers high yields of the corresponding β-alkynyl-substituted carbonyl compounds with 95–98 % *ee*.

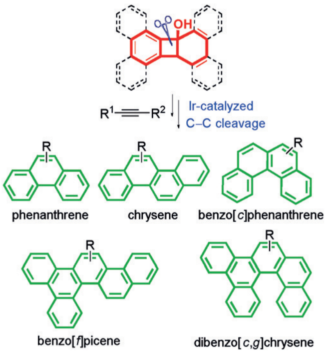
Electrocatalysis



A fascinating catalyst structure: Free-standing flexible films composed of strongly coupled carbon nitride and titanium carbide nanosheets through Ti–N_x interactions (see picture) exhibited outstanding electrocatalytic activity and stability towards the oxygen-evolution reaction (OER). The films could be directly used as efficient cathodes in rechargeable Zn–air batteries.

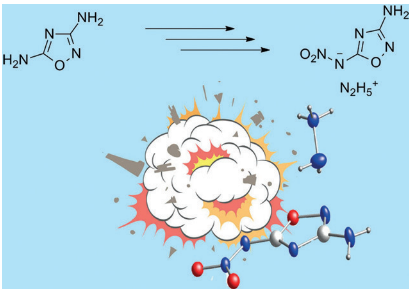
Polycyclic Aromatic Hydrocarbons

Expanding the family: The iridium-catalyzed intermolecular cyclization between ring-fused benzocyclobutenols and alkynes through C–C bond cleavage is described. A variety of elusive polycyclic aromatic hydrocarbons (PAHs) with multiple substituents are obtained in good yields under mild conditions. The transformation exhibits good functional-group tolerance and regioselectivity.

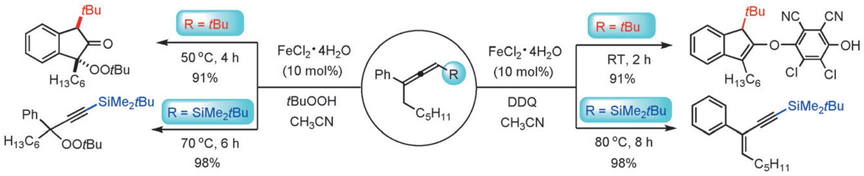


Energetic Materials

Going with a bang: Hydrazinium 1,2,4-oxadiazolate combines amino and nitramino groups in a single heterocyclic ring and can be synthesized in a straightforward manner from inexpensive starting materials. Owing to its high performance and insensitivity, this compound may find practical use as an RDX replacement.

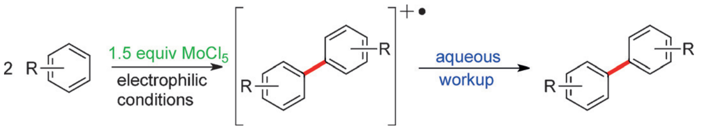


Oxidation



Profound impact: Iron(II)-catalyzed transformations of allenes induced by either DDQ or *t*BuOOH depend on the substituent on the allenes. Nonsilylated and silylated allenes show complementary reactivity upon exposure to DDQ and *t*BuOOH in the presence of an iron(II) catalyst. Nonsilylated allenes incorporate the oxidant at the sp-hybridized carbon, whereas the silylated allenes generate 1,4-dehydrogenated 1,3-enynes. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Oxidative Coupling

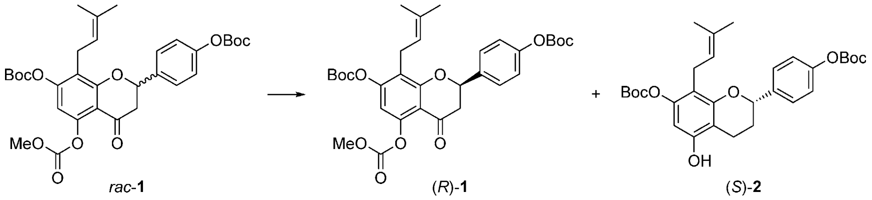


Over and out: Oxidation of arenes in the presence of $MoCl_5$ does not stop at the biaryl but rather forms the over-oxidized product which is protected from side reactions. In the presence of additional Lewis acids, $MoCl_5$ acts as a two-electron oxidant and the molybdenum containing "waste" serves as the reducing agent upon aqueous workup.

Flavonoids

A. Keßberg, P. Metz* ——— 1160–1163

Utilizing an *o*-Quinone Methide in Asymmetric Transfer Hydrogenation: Enantioselective Synthesis of Brosimine A, Brosimine B, and Brosimacutin L

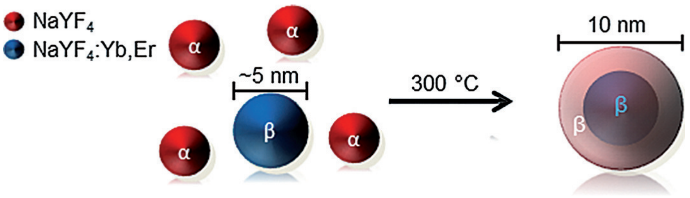


You got much flava: The single step transformation of a flavanone into a flavan in a highly enantioselective fashion by means of a non-enzymatic kinetic resolution enabled the concise synthesis of all three title compounds.

Luminescent Materials

T. Rinkel, A. N. Raj, S. Dühnen, M. Haase* ——— 1164–1167

Synthesis of 10 nm β-$NaYF_4$:Yb,Er/$NaYF_4$ Core/Shell Upconversion Nanocrystals with 5 nm Particle Cores



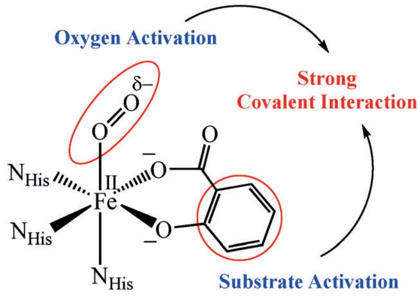
Very small β-$NaYF_4$:Yb,Er/$NaYF_4$ core/shell upconversion particles have been prepared by using small nanoparticles of the cubic α-phase as precursors. Careful control of the nucleation properties of the α-phase particles not only reduces the diameter of the β-$NaYF_4$:Yb,Er particle cores to only about 5 nm, but also suppresses the undesired nucleation of β-phase particles of the $NaYF_4$ shell material during shell growth.

O_2 Activation

S. Roy, J. Kästner* ——— 1168–1172

Synergistic Substrate and Oxygen Activation in Salicylate Dioxygenase Revealed by QM/MM Simulations

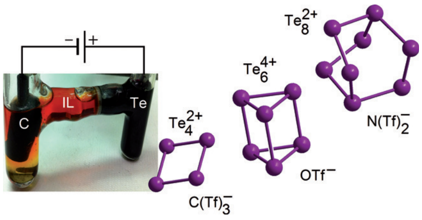
The non-heme Fe^{II} center in salicylate 1,2-dioxygenase (SDO) synergistically activates salicylate and O_2 to facilitate the reductive cleavage of O_2, as revealed by QM/MM simulations. The reactive oxygen species is a covalent salicylate–Fe^{II}–O_2 complex, and O_2 activation happens without a proton source.



Tellurium Clusters

C. Schulz, J. Daniels, T. Bredow, J. Beck* ——— 1173–1177

The Electrochemical Synthesis of Polycationic Clusters

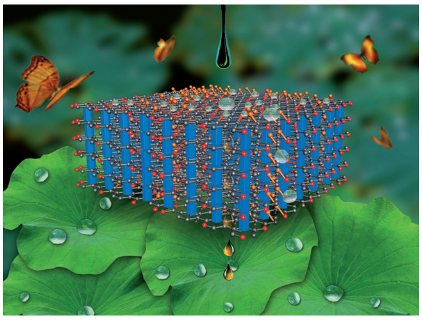


Anodic oxidation of elemental tellurium in ionic liquids provides access to the polycationic clusters $[Te_4]^{2+}$, $[Te_6]^{4+}$, and the new cluster $[Te_8]^{2+}$ with a barrelane structure (see picture). The characterization of the $[Te_8]^{2+}$ ion by ^{125}Te NMR spectroscopy in solution showed a dynamic molecule with fast valence isomerism.

Oil–Water Separation

K. Jayaramulu, K. K. R. Datta, C. Rösler, M. Petr, M. Otyepka, R. Zboril,* R. A. Fischer* ______ **1178 – 1182**

Biomimetic Superhydrophobic/Superoleophilic Highly Fluorinated Graphene Oxide and ZIF-8 Composites for Oil–Water Separation



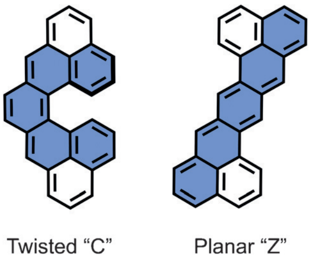
Pores for effect: The superhydrophobic and simultaneously superoleophilic **HFGO@ZIF-8** composites were utilized for oil–water separation. In this material zeolitic imidazolate (ZIF) nanocrystals serve as pillars between nanosheets of highly fluorinated graphene oxide.

Organic Biradicaloids

P. Ravat, T. Šolomek, M. Rickhaus, D. Häussinger, M. Neuburger, M. Baumgarten, M. Juríček* ______ **1183 – 1186**

Cethrene: A Helically Chiral Biradicaloid Isomer of Heptazethrene

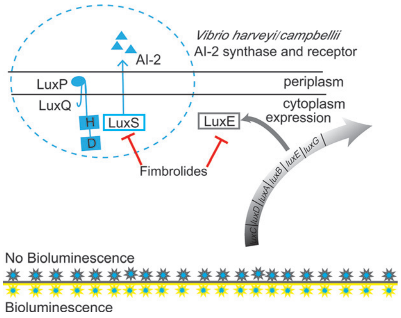
“C” versus “Z”: In chiral biradicaloid cethrene (“C”) the singlet–triplet energy gap is smaller than that in planar heptazethrene (“Z”) because of the helical twist. Cethrene gives well-resolved EPR and NMR spectra and its structure was confirmed by 2D NMR spectroscopy. The helical compound undergoes a transformation to a planar hydrocarbon and “lives” for several hours at room temperature.



Quorum Sensing

W. Zhao, N. Lorenz, K. Jung, S. A. Sieber* ______ **1187 – 1191**

Fimbrolide Natural Products Disrupt Bioluminescence of *Vibrio* By Targeting Autoinducer Biosynthesis and Luciferase Activity

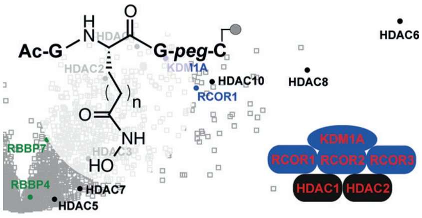


Studies in *Vibrio*: Fimbrolides represent natural products that interfere with quorum sensing in various organisms. Despite their importance in biological studies their cellular mechanisms have remained unknown. Chemical proteomics have been utilized to identify proteins involved in autoinducer biosynthesis (LuxS) and luciferase activity (LuxE) as molecular targets.

Biochemistry

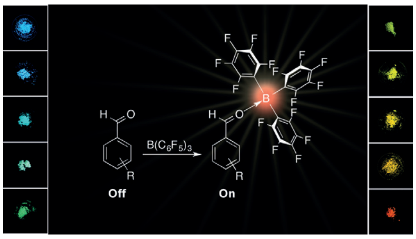
A. Dose, J. Sindlinger, J. Bierlmeier, A. Bakirbas, K. Schulze-Osthoff, S. Einsele-Scholz, M. Hartl, F. Essmann, I. Finkemeier, D. Schwarzer* ______ **1192 – 1195**

Interrogating Substrate Selectivity and Composition of Endogenous Histone Deacetylase Complexes with Chemical Probes

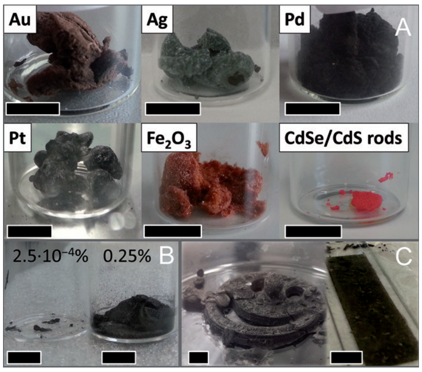


Ac removal: Histone deacetylases (HDACs) regulate the function of proteins by removing acetylation marks from regulatory lysine residues. Peptide-based HDAC probes have been developed that can be used to investigate the selectivity and redundancy of endogenous deacetylases in cell extracts. These probes, in combination with proteomics, can provide information about the composition of HDAC complexes.

Turn on the light: A straightforward methodology can be used to "switch on" the solid-state fluorescence of non-emitting carbonyl compounds. Subtle electronic changes in the aldehyde moieties lead to a variety of emission colors that cover the entire visible spectrum. The materials also display pressure-dependent luminescent properties (piezochromism).

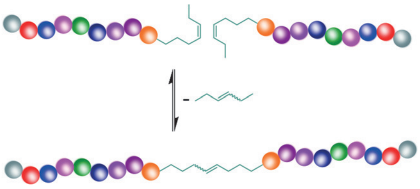


Solid-State Luminescence



A versatile method to fabricate self-supported porous monoliths of extremely low density consisting of nanoparticle (NP) building blocks is presented. Our approach is based on freezing and subsequent freeze drying of aqueous colloidal NPs. The assembly process is highly versatile: cryogelation is applicable for noble metal, metal oxide, and semiconductor NPs, and shaping of the aerogels is easily possible.

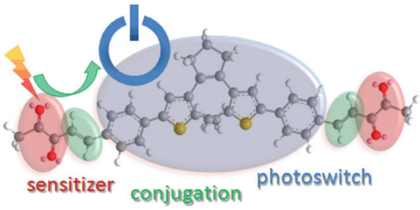
Nanoparticle Aerogels



Cleary defined: A sequence-defined decamer with ten different and selectable side chains can be synthesized efficiently (yield of each reaction step $>90\%$), also on a larger scale, and with simple workup procedures. Functional groups were installed at the side chains allowing for further modification. The self-metathesis reaction of the sequence-defined decamer led to a sequence-defined 20-mer with a molecular weight of more than 7 kDa.

Sequence-Defined Polymers

Flipping the spin: When biacetyl triplet sensitizers were linked to a dithienylethene core in a conjugated fashion, the photoswitching performance dramatically improved. This design makes it possible to switch diarylethenes with visible light in both directions in a highly efficient and robust fashion.



Photoswitches

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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