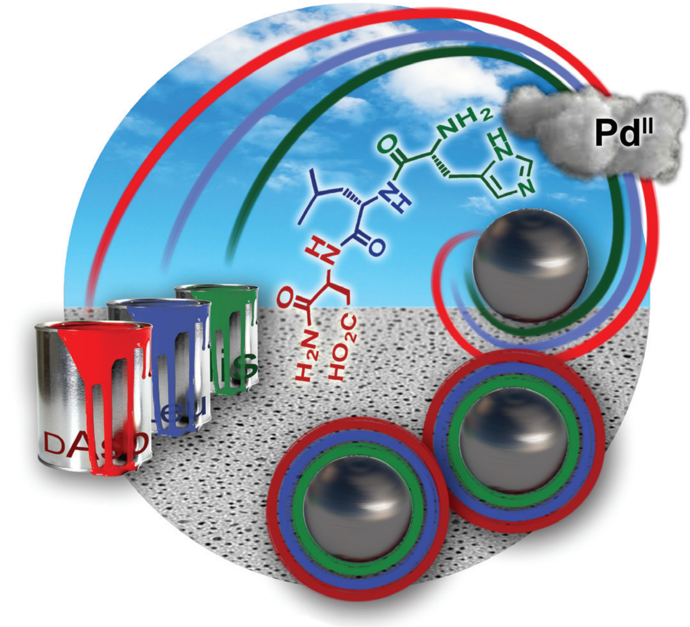
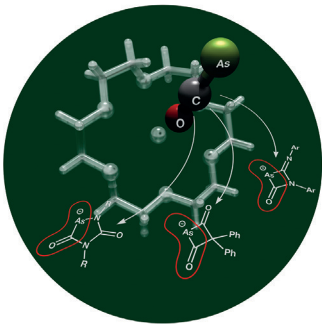
Monodisperse noble-metal nanoparticles ...

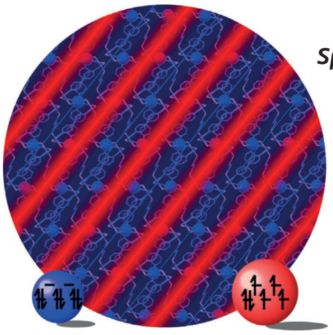


… (in the example, PdNPs) can be formed in aqueous solution in the presence of a thiol-free tripeptide, as shown by H. Wennemers and co-workers in their Communication on page 8542 ff. The picture illustrates how, upon complexation to Pd^{2+} ions and their reduction to Pd^0, the peptide controls nanoparticle generation by forming a compact peptidic coat around the metal core.

Anions

The synthesis of the 2-arsaethynolate anion $AsCO^-$ through carbonylation of $NaAsH_2$ is described in the Communication by J. M. Goicoechea and A. Hinz on page 8536 ff. $AsCO^-$ can undergo cyclization with unsaturated substrates to yield novel heterocyclic species.





Spin-Crossover Materials

In their Communication on page 8675 ff., J. A. Real, E. Collet et al. describe the formation of periodic and aperiodic spin-state concentration waves during "Devil's staircase"-type spin-crossover in the new bimetallic 2D coordination polymer $\{Fe[(Hg(SCN)_3)_2](4,4'\text{-bipy})_2\}_n$.

Nanocomposites

Gold nanorods (AuNRs) can be aligned on thiol-terminated poly(3-hexylthiophene) (P3HT) nanofibers to give nanoribbons. In their Communication on page 8686 ff., J. Peng, Z. Lin, and co-workers describe a facile strategy for crafting such hierarchical nanocomposites.

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Service

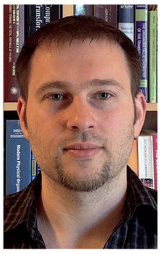
Author Profile

"What I appreciate most about my friends is their not taking themselves too seriously.
My motto is don't complain about things you can't change …"
This and more about Eric N. Jacobsen can be found on page 8482.

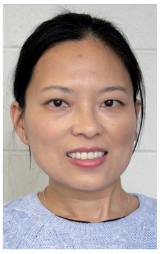
News

W. C. K. Pomerantz

M. J. Rose



T. J. Maimone



Y. Yu

H.-J. Freund

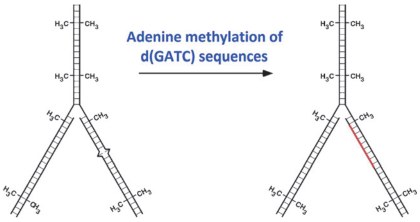
Meeting Reviews

Bürgenstock Conference

Tradition and innovation: The 51st Bürgenstock Conference on Stereochemistry took place from May 1–6, 2016 and offered its usual mixture of impressive science and superb discussions in a wonderful atmosphere. In the Meeting Review, Ivana Fleischer outlines the program.

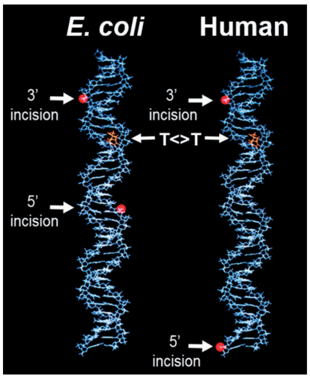
Nobel Lectures

Mismatch Repair



DNA molecules are not completely stable, they are subject to chemical or photochemical damage and errors that occur during DNA replication resulting in mismatched base pairs. Through mechanistic studies Paul Modrich showed how replication errors are corrected by strand-directed mismatch repair in *Escherichia coli* and human cells.

Nucleotide Excision Repair



Ultraviolet light damages DNA by converting two adjacent thymines into a thymine dimer which is potentially mutagenic, carcinogenic, or lethal to the organism. This damage is repaired by photolyase and the nucleotide excision repair system in *E. coli* by nucleotide excision repair in humans. The work leading to these results is presented by Aziz Sancar in his Nobel Lecture.

For the USA and Canada:
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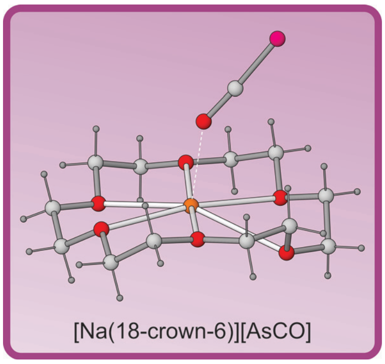
Our cells contain common molecules, such as water or oxygen, that can damage DNA. In his studies Tomas Lindahl has shown how specific repair enzymes remove and replace damaged parts of DNA in a process of vital importance.

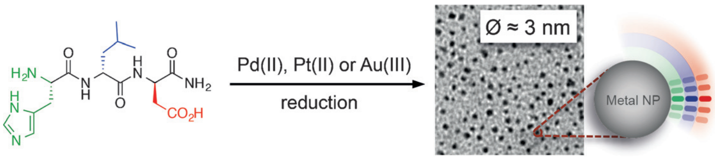
Mismatch Repair

Communications



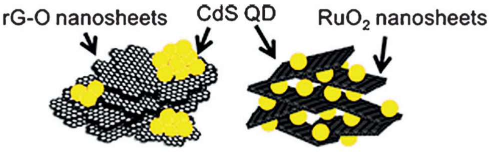
A look at As and Co.: Reported is the synthesis and isolation of the 2-arsaethynolate anion, $AsCO^{-}$, and its subsequent reactivity towards heteroallenes. Reactions with ketenes and carbodiimides afford four-membered anionic heterocycles in formal [2+2] cycloaddition reactions. By contrast, reaction with an isocyanate yielded a 1,4,2-diazaarsolidine-3,5-dionide anion and the unprecedented cluster anions As_{10}^{2-} and As_{12}^{4-}.

Anions



A coat of peptides: Monodisperse Pd-, Pt-, and AuNPs were formed in aqueous solution in the presence of a thiol-free tripeptide. The NPs were stable for months as a result of the formation of a compact peptidic monolayer around the metal core within which each amino acid fulfills a specific role.

Nanoparticles



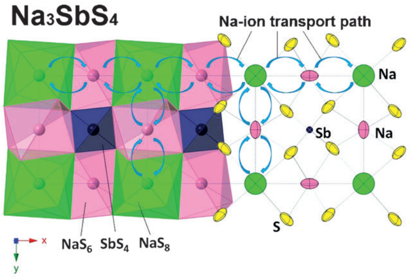
A universal method to efficiently improve the photocatalyst performance of semiconductors was developed by employing exfoliated RuO_2 nanosheets as conducting hybridization matrices. The resulting layered RuO_2-based nanohybrids show much better photocatalytic activity for visible-light-induced H_2 and O_2 generation than do the graphene-based (rG) homologues.

Photocatalysis

Superionic Conductors

H. Wang, Y. Chen, Z. D. Hood, G. Sahu,
A. S. Pandian, J. K. Keum, K. An,
C. D. Liang* ——— **8551 – 8555**

An Air-Stable Na_3SbS_4 Superionic Conductor Prepared by a Rapid and Economic Synthetic Procedure



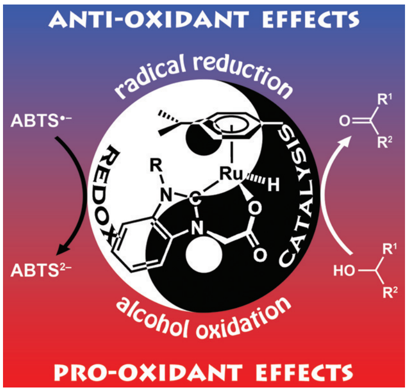
A Na_3SbS_4 superionic conductor was designed and synthesized on the basis of hard and soft acid and base theory. This new sulfide-based solid electrolyte shows excellent air stability and remarkable ionic conductivity, as well as great electrochemical compatibility with a metallic sodium anode.

Redox Catalysis

Y. Htet, A. G. Tennyson* ——— **8556 – 8560**

Catalytic Radical Reduction in Aqueous Solution by a Ruthenium Hydride Intermediate

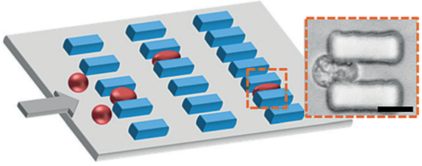
Catalytic radical reduction in buffered aqueous solutions was achieved by a Ru complex with non-tertiary alcohol terminal reductants. Primary kinetic isotope effects were observed with both C—H and O—H bonds. Radical reduction was faster at higher pH, and no reaction occurred in pure H_2O. Mechanistic studies suggest that the catalytically active species is a Ru-hydride intermediate formed by β-hydride elimination from a Ru-alkoxide.



Analytical Methods

X. Han, Z. Liu, L. Zhao, F. Wang, Y. Yu,
J. Yang, R. Chen, L. Qin* ——— **8561 – 8565**

Microfluidic Cell Deformability Assay for Rapid and Efficient Kinase Screening with the CRISPR-Cas9 System



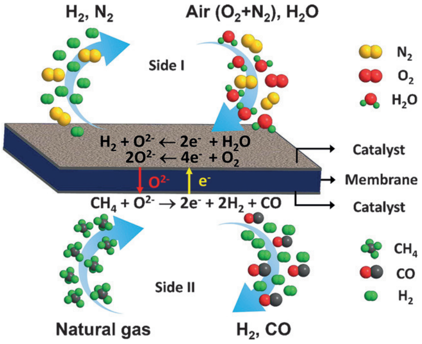
Gene genie: A microfluidic sorting system based on the mechanical properties of cells and CRISPR-Cas9 technologies has been developed that facilitates the rapid identification of genes that play roles in mechanical phenotypes, as well as in physiological and pathological processes. This approach allowed the identification of kinases whose loss results in cells becoming more deformable and invasive.

Membrane Reactors

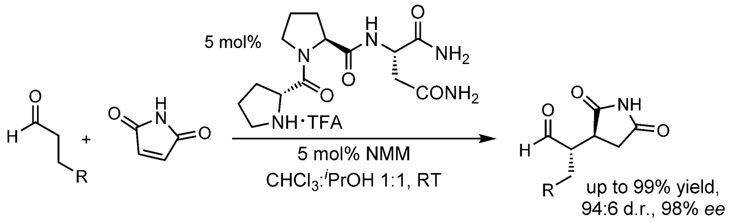
W. P. Li, X. F. Zhu,* S. G. Chen,
W. S. Yang* ——— **8566 – 8570**

Integration of Nine Steps into One Membrane Reactor To Produce Synthesis Gases for Ammonia and Liquid Fuel

Two sides to the story: A membrane reactor has been developed that can shorten the nine steps involved in the production of two types of synthesis gases (H_2/CO and H_2/N_2) to one step (see scheme). Water, air, and natural gas are used as feeds, and an energy saving of 63 % can be achieved for the production of the two synthesis gases compared to industrial processes.



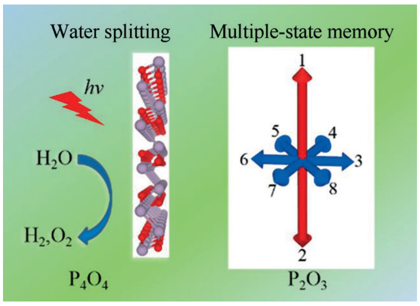
Organocatalysis



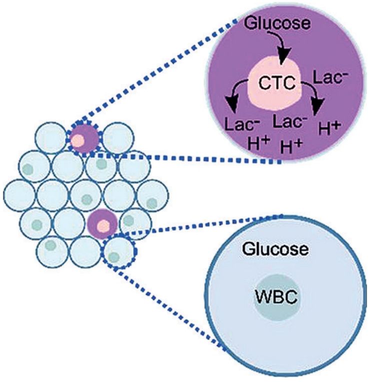
Imide dances to amide tunes: Unprotected maleimide reacts readily with aldehydes in the presence of a peptidic catalyst to form succinimides with high diastereo- and enantioselectivities. Hydrogen bonding between the peptide and maleimide is key for catalysis and the chemoselective formation of conjugate addition products. NMM = *N*-methylmorpholine.

Functional Materials

Materials to remember: In a theoretical study of the structures and properties of 2D phosphorus oxides, P_4O_4 and P_2O_3 were identified as promising functional materials. P_4O_4 could be a good water-splitting material, since it has an appropriate direct band gap, good optical absorption, and high stability in water. Two 2D ferroelectric phases were found for P_2O_3, which could be used in nanoscale multiple-state memory devices (see picture).



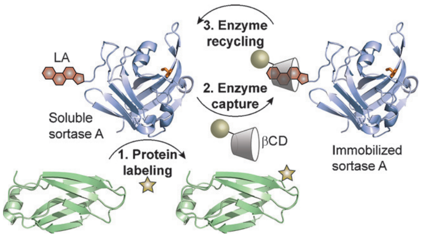
Microfluidics



An altered metabolism is one of the hallmarks of cancer cells. Differences between healthy and cancerous cell metabolism, hidden in bulk, are apparent in tiny (pL) droplets containing individual cells. Within minutes, cancerous cells generate a pH change in their microenvironment. By measuring the pH value in each droplet, circulating tumor cells (CTCs) can be detected in patient samples. WBC = white blood cell; lac = lactate.

Protein Modification

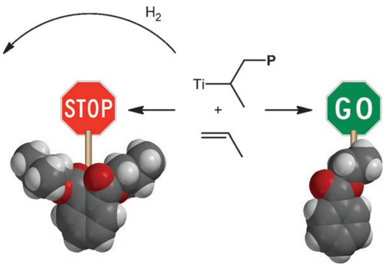
Reuse, recycle: A scalable and straightforward strategy is demonstrated for the efficient capture and recycling of enzymes using a small-molecule affinity tag. A proline variant of an evolved sortase A was labeled with lithocholic acid (LA). Capture and recycling of this bioconjugate from reaction mixtures was achieved using a βCD-modified sepharose resin (βCD = β-cyclodextrin).



Polymerization

Y. Yu, V. Busico, P. H. M. Budzelaar,
A. Vittoria, R. Cipullo* ______ 8590 – 8594

Of Poisons and Antidotes in Polypropylene Catalysis

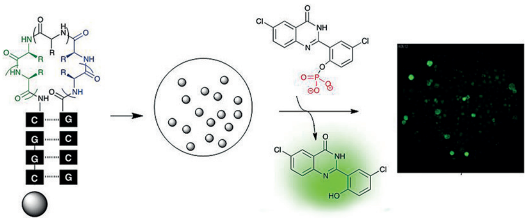


The occasional occurrence of regiodefects in Ziegler–Natta propene polymerizations has long been suspected to change active sites into dormant sites. Herein, combining quenched-flow kinetic studies with ^{13}C NMR fingerprinting of the nascent polymer, this behavior is shown to occur, but depends on system formulation. The data also confirm that H$_2$ is a powerful antidote to catalyst self-poisoning.

Peptide Catalysts

T. Machida, S. Dutt,
N. Winssinger* ______ 8595 – 8598

Allosterically Regulated Phosphatase Activity from Peptide–PNA Conjugates Folded Through Hybridization



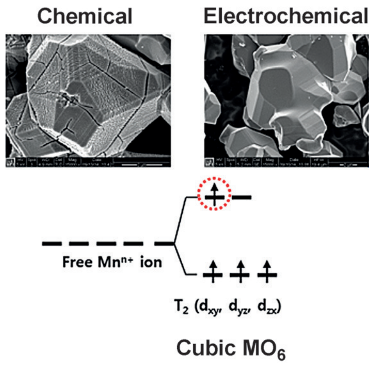
A library of peptides that are constrained in a hairpin loop by flanking peptide nucleic acids upon hybridization were synthesized. A screen for phosphatase activity led to the discovery of a catalyst with a more than 25-fold rate acceleration over the linear peptide. The hybridization-enforced folding of the peptide is decisive for the activity.

Electrocatalysis

S. Lee, G. Nam, J. Sun, J. Lee, H. Lee,
W. Chen, J. Cho,* Y. Cui* ______ 8599 – 8604

Enhanced Intrinsic Catalytic Activity of λ-MnO$_2$ by Electrochemical Tuning and Oxygen Vacancy Generation

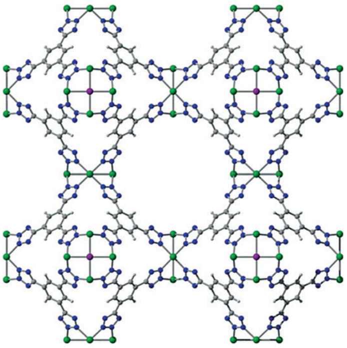
Highly crystalline λ-MnO$_2$ was prepared as an efficient electrocatalyst for the oxygen reduction reaction (ORR). The ORR activity of the material was further improved by introducing oxygen vacancies (OVs). This study demonstrates that differences in the electrochemical behavior of λ-MnO$_2$ depend on the preparation method and provides a mechanism for the catalytic behavior of cubic λ-MnO$_2$.



Metal–Organic Frameworks

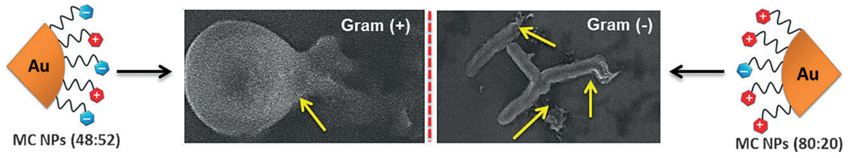
E. D. Bloch, W. L. Queen, M. R. Hudson,
J. A. Mason, D. J. Xiao, L. J. Murray,
R. Flacau, C. M. Brown,
J. R. Long* ______ 8605 – 8609

Hydrogen Storage and Selective, Reversible O$_2$ Adsorption in a Metal–Organic Framework with Open Chromium(II) Sites



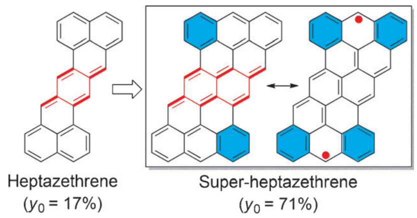
Reversible O$_2$ binding: A chromium(II)-based metal–organic framework Cr$_3$[(Cr$_4$Cl)$_3$(BTT)$_8$]$_2$ (Cr-BTT; BTT^{3-} = 1,3,5-benzenetristetrazolate) reversibly forms chromium(III) superoxide moieties, resulting in high separation capacity and reversibility for the separation of O$_2$ from air at room temperature. Atom colors: Cr green, Cl purple, C gray, N blue.

Antimicrobial Activity



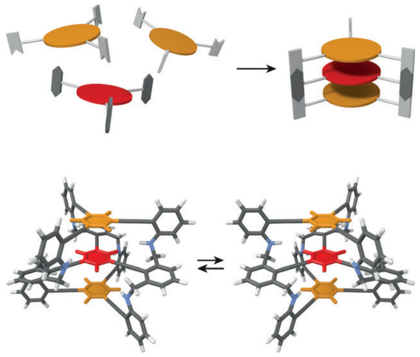
Gram-specific antimicrobial activity: Nanoparticles covered with mixtures of negatively and positively charged ligands in optimal proportions exhibit antibiotic properties that can be engineered specific to either Gram-positive or Gram-negative bacteria. Arrows in the experimental images point to the places at which the particles rupture the bacterial cell wall.

Polycyclic Hydrocarbons



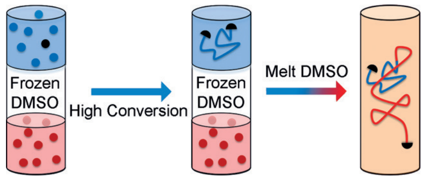
Expanding horizons: The complex polycyclic hydrocarbon super-heptazethrene was synthesized using a strategy involving a selective multiple intramolecular Friedel–Crafts alkylation followed by oxidative dehydrogenation. Super-heptazethrene displayed a much larger diradical character (y_0) than heptazethrene.

Stacked Assemblies



Discrete stacks: Two- and three-tiered covalent compounds are obtained through imine condensation. The final structures, formally fused cages, comprise a central stack of arenes embedded within a triple helix. The rate of racemization depends strongly on the number of tiers because of conformational coupling in these highly interconnected structures.

Block Copolymers

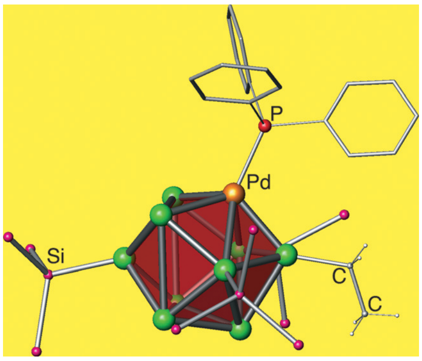


Keep it cool is the rule: AB diblock copolymers were prepared by conducting the solution polymerization of monomer A in a liquid layer above a frozen solution of monomer B. When the vessel is heated to above the melting point of the lower phase, monomer B is released, and the desired block copolymers are obtained.

Cluster Compounds

F. Li, A. Muñoz-Castro,
S. C. Sevov* ———— **8630–8633**

$[(Me_3Si)Si]_3EtGe_9Pd(PPh_3)$, a Pentafunctionalized Deltahedral Zintl Cluster: Synthesis, Structure, and Solution Dynamics



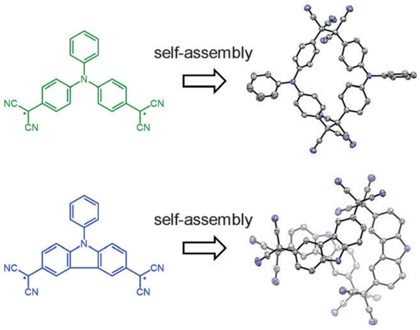
Cage closed: The title compound, an uncharged single-cage deltahedron with five functionalities, was synthesized through insertion of $Pd(PPh_3)$ into $[(Me_3Si)Si]_3EtGe_9$. The ten-atom core is a *closo*-cluster with the expected shape of a bicapped square antiprism, and the Ge_9Pd core is the first to incorporates a 5-connected transition metal other than from Group VI. In contrast to the Pd-free parent, the new compound is static in solution.

Self-Assembly

T. Kobashi, D. Sakamaki,*
S. Seki* ———— **8634–8638**

N-Substituted Dicyanomethylphenyl Radicals: Dynamic Covalent Properties and Formation of Stimuli-Responsive Cyclophanes by Self-Assembly

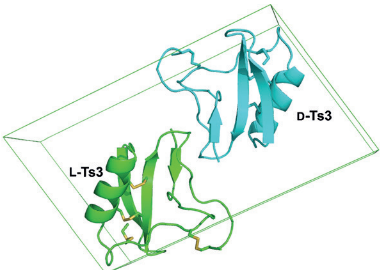
Back and forth: Triphenylamine (TPA) and carbazole (Cy) derivatives substituted with a dicyanomethyl radical were found to be useful building blocks in dynamic covalent chemistry because of the reversible association/dissociation reaction between radicals. The bond dissociation energy of the intermonomer bond can be tuned by appropriate substituents. The TPA- and Cz-based diradical analogues formed cyclic oligomers with defined sizes.



Protein Toxins

B. Dang, T. Kubota, K. Mandal,
A. M. Correa, F. Bezanilla,
S. B. H. Kent* ———— **8639–8642**

Elucidation of the Covalent and Tertiary Structures of Biologically Active Ts3 Toxin

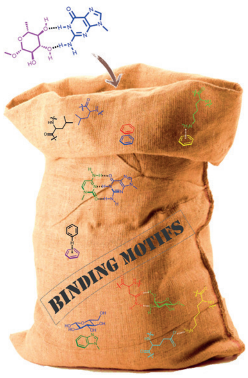


Sting in the tail: Total chemical synthesis and structure–activity studies were used to elucidate the covalent structure of biologically active Ts3, a protein toxin from the venom of the Brazilian scorpion *Tityus serrulatus*. Racemic protein crystallography was then used to determine the structure of the folded Ts3 protein by X-ray diffraction.

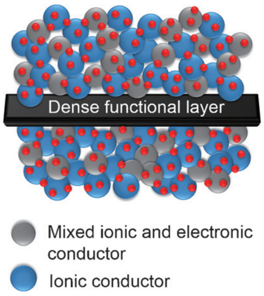
Noncovalent Interactions

E. Vengut-Climent, I. Gómez-Pinto,
R. Lucas, P. Peñalver, A. Aviñó,
C. Fonseca Guerra, F. M. Bickelhaupt,
R. Eritja, C. González,
J. C. Morales* ———— **8643–8647**

Glucose–Nucleobase Pseudo Base Pairs: Biomolecular Interactions within DNA

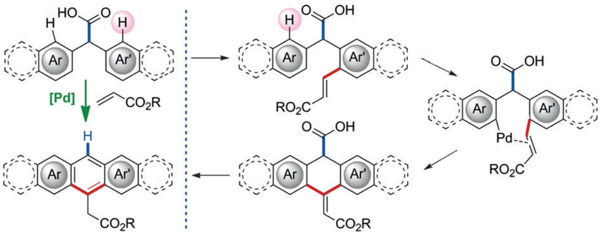


New lego pieces: The formation of a glucose–nucleobase pseudo base pair is proposed as a new type of biomolecular interaction. When formed within a DNA double helix, the high-resolution structure shows only a minor distortion. These DNA duplexes are less stable than natural ones, but glucose shows a preference for binding purine nucleobases. Moreover, quantum chemical calculations indicate that glucose–purine pairs are as stable as a natural T–A pair.



Sandwich-like membrane reactor: H_2 production by means of water splitting coupled with partial oxidation of methane (POM) is conducted in a sandwich-like symmetrical dual-phase membrane reactor. The infiltrated Ni nanoparticles (red spheres) significantly enhance the number of reactive sites and also catalyze the POM reaction. Furthermore, the membrane reactor can regenerate the coked catalyst in situ using steam.

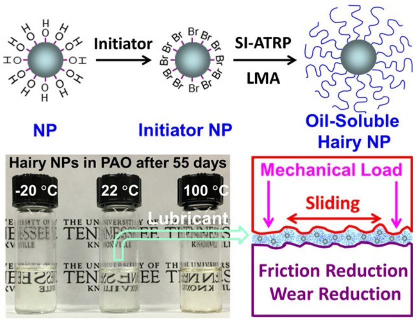
Hydrogen Production



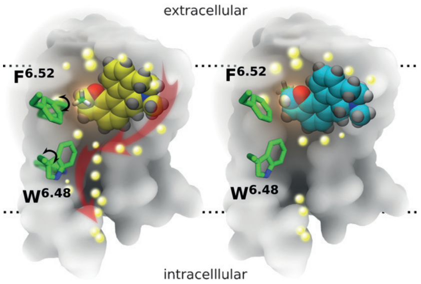
Driving tandem: A tandem strategy that generates useful anthracene derivatives involves carboxy-directed C-H alkenylation and secondary C-H activation, followed by rollover/intramolecular C—C bond formation/decarboxylative aromatization sequences. The synthetic route accommodates a broad range of substrates and their acene products.

Synthetic Methods

Oil-soluble polymer brush grafted nanoparticles (hairy NPs) were synthesized and evaluated as lubricant additives. These hairy NPs exhibited exceptional stability in a lubricating base oil at both low and high temperatures. High contact stress tribological tests at 100 °C revealed that the addition of 1 wt% of hairy NPs into the oil led to significant reductions in friction and wear volume.



Lubricants



Go with the flow: A pair of epimers of dihydrofuroaporphine act as an agonist and antagonist of the G-protein-coupled receptor (GPCR) 5-HT_{1A}. Molecular dynamics simulations show that binding of the agonist isomer (yellow) triggers molecular switching (black arrows), which leads to the formation of an internal continuous water channel (red arrows). By contrast, the antagonist isomer (cyan) is stabilized in the orthosteric site of 5-HT_{1A} and blocks this water movement.

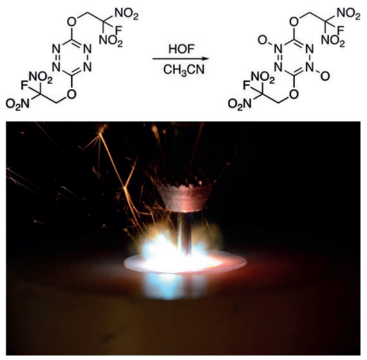
GPCRs

Heterocycles

D. E. Chavez,* D. A. Parrish,
L. Mitchell ———— **8666 – 8669**

Energetic Trinitro- and Fluorodinitroethyl Ethers of 1,2,4,5-Tetrazines

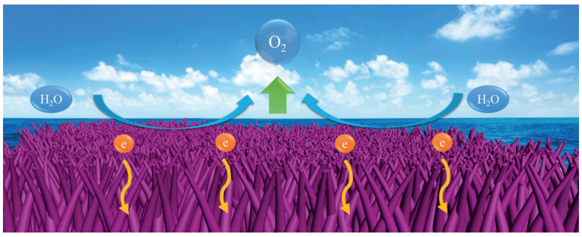
Bundles of energy: Several new 1,2,4,5-tetrazines have been synthesized and they display good thermal stability, good oxygen balance, and high densities. Included in these studies are a 2,2,2-trinitroethoxy 1,2,4,5-tetrazine and two fluorodinitroethoxy 1,2,4,5-tetrazines. One of these compounds was converted into the di-N-oxide derivative (see scheme). Overall the materials show promising energetic performance properties.



Electrocatalysis

Y. Zhang, B. Ouyang, J. Xu, G. Jia, S. Chen,
R. S. Rawat, H. J. Fan* ———— **8670 – 8674**

Rapid Synthesis of Cobalt Nitride Nanowires: Highly Efficient and Low-Cost Catalysts for Oxygen Evolution



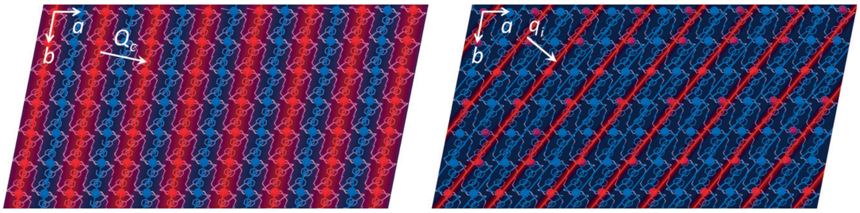
Down to the wire: CoN nanowire arrays were synthesized by means of a fast and efficient N_2 plasma method that is both safe and environmentally friendly. Owing to better conductivity and a large surface area, the obtained CoN nanowire arrays on nickel foam exhibit outstanding performance in the oxygen evolution reaction.

Spin-Crossover Materials

E. Trzop, D. Zhang, L. Piñeiro-Lopez,
F. J. Valverde-Muñoz, M. Carmen Muñoz,
L. Palatinus, L. Guerin, H. Cailleau,
J. A. Real,* E. Collet* ———— **8675 – 8679**

First Step Towards a Devil's Staircase in Spin-Crossover Materials

Inside Back Cover



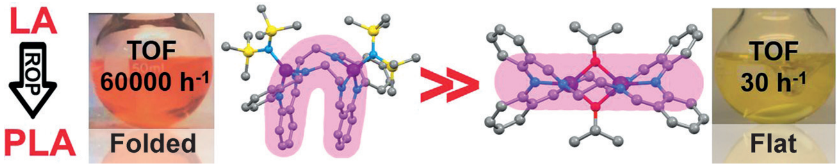
The devil is in the detail: Periodic and aperiodic spin-state concentration waves form during "Devil's staircase"-type spin-crossover in a new bimetallic 2D coordination polymer $\{Fe[(Hg(SCN)_3)_2](4,4'\text{-bipy})_2\}_n$.

Homogeneous Catalysis

A. Thevenon, C. Romain,
M. S. Bennington, A. J. P. White,
H. J. Davidson, S. Brooker,*
C. K. Williams* ———— **8680 – 8685**

Dizinc Lactide Polymerization Catalysts: Hyperactivity by Control of Ligand Conformation and Metallic Cooperativity

Inside Cover



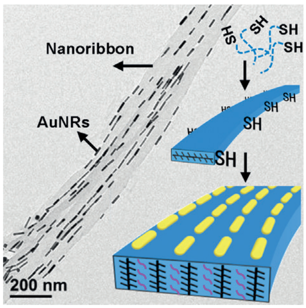
Ring-opening polymerization: Dinuclear and analogous mononuclear zinc complexes embedded in bis(imino)diphenylamido ligands were synthesized and used as catalysts for the ring-opening polymerization (ROP) of racemic lactide (LA). The catalysts with "folded" ligands show high turnover frequency (TOF) values, which are up to 5500 times higher than those for "flat" ligands (see picture).

Nanocomposites

S. Pan, L. He, J. Peng,* F. Qiu, Z. Lin* ———— **8686 – 8690**

Chemical-Bonding-Directed Hierarchical Assembly of Nanoribbon-Shaped Nanocomposites of Gold Nanorods and Poly(3-hexylthiophene)

Back Cover

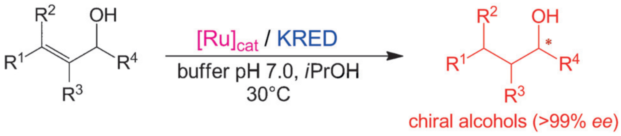


Turning fibers into ribbons: Nanoribbon-shaped nanocomposites composed of a conjugated polymer, poly(3-hexylthiophene) (P3HT), and plasmonic gold nanorods (AuNRs) are produced by a co-assembly of thiol-terminated P3HT nanofibers with dodecanethiol-coated AuNRs. Owing to plasmon coupling between adjacent aligned AuNRs, these nanocomposites show broadened and red-shifted absorption bands.

Enzyme Catalysis

N. Ríos-Lombardía, C. Vidal, E. Liardo, F. Morís, J. García-Álvarez,* J. González-Sabín* ———— **8691 – 8695**

From a Sequential to a Concurrent Reaction in Aqueous Medium: Ruthenium-Catalyzed Allylic Alcohol Isomerization and Asymmetric Bioreduction

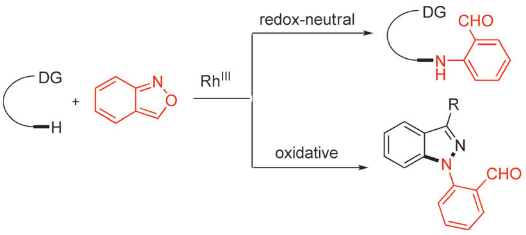


Metals and enzymes play together: A one-pot metal-catalyzed and biocatalyzed protocol for the enantioselective synthesis of alcohols in water is reported. The method establishes a new bridge between metal-catalyzed and enzyme-mediated enantioselective organic reactions. KRED = ketoreductases.

C–H Activation

S. Yu, G. Tang, Y. Li, X. Zhou, Y. Lan,* X. Li* ———— **8696 – 8700**

Anthranil: An Aminating Reagent Leading to Bifunctionality for Both C(sp^3)–H and C(sp^2)–H under Rhodium(III) Catalysis



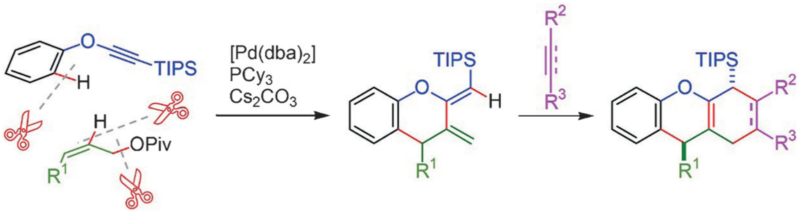
- ☐ New Aminating Reagent
- ☐ C(sp^3/sp^2) C-H Activation
- ☐ High Atom-Economy
- ☐ Redox-Neutral and Oxidative Couplings
- ☐ Diversely Bifuctional Product

Double agent: Anthranil was designed as a novel bifunctional aminating reagent for both C(sp^2)–H and C(sp^3)–H bonds under rhodium(III) catalysis, thus affording a nucleophilic aniline tethered to an electrophilic carbonyl. A tridendate rhodium(III) complex was isolated as the resting state of the catalyst, and DFT studies established the intermediacy of a nitrene species.

Heterocycle Synthesis

Y. Minami,* M. Sakai, T. Anami, T. Hiyama* ———— **8701 – 8705**

Annulation of Alkynyl Aryl Ethers with Allyl Pivalates To Give 2,3-Bismethylene-chromanes through Double C–H Bond Cleavage

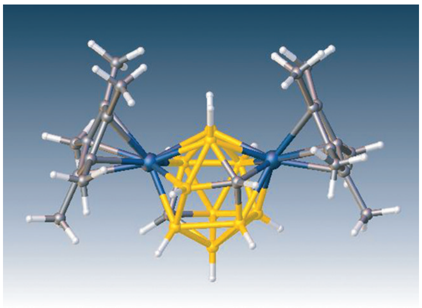


Double or nothing: Benzopyrans with bis(exomethylene) substitution were obtained by two C–H cleavage reactions: the intermolecular coupling of alkynyl aryl ethers with allylic pivalates at the *ortho* position and intramolecular hydrovinylation of the *ortho*-allylated alkynyl aryl ethers. The products enable the facile synthesis of linearly condensed multifunctional oxacycles (see scheme).

Metallacarboranes

A. P. M. Robertson, N. A. Beattie,
G. Scott, W. Y. Man, J. J. Jones,
S. A. Macgregor,* G. M. Rosair,
A. J. Welch* ______ **8706 – 8710**

14-Vertex Heteroboranes with 14 Skeletal Electron Pairs: An Experimental and Computational Study

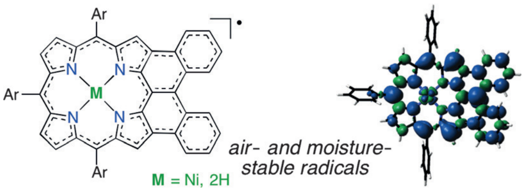


Living on the edge: The first three examples of 14-vertex heteroboranes with 14 skeletal electron pairs have been prepared and characterized by a combination of spectroscopic, crystallographic, and computational techniques. The compounds $[(Cp^*Ru)_2C_2B_{10}H_{12}]$ all share a unique cluster structure featuring a trapezoidal face. Atom colors: C gray, B yellow, Ru blue.

Porphyrinoids

K. Kato, W. Cha, J. Oh, K. Furukawa,*
H. Yorimitsu,* D. Kim,*
A. Osuka* ______ **8711 – 8714**

Spontaneous Formation of an Air-Stable Radical upon the Direct Fusion of Diphenylmethane to a Triarylporphyrin

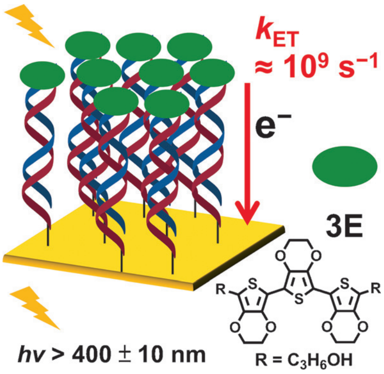


Stable as a table: The direct fusion of diphenylmethane to a Ni^{II} 5,10,15-triarylporphyrin through three linkages furnished an air- and moisture-stable neutral radical with extensive spin delocalization (see picture). The Ni^{II} and corresponding free-base porphyrin radicals were chemically oxidized and reduced to a cation and an anion, in which antiaromatic and aromatic electron circuits, respectively, were found to contribute to the electronic network.

DNA Technology

S.-H. Lin, M. Fujitsuka,*
T. Majima* ______ **8715 – 8717**

Sequence-Dependent Photocurrent Generation through Long-Distance Excess-Electron Transfer in DNA

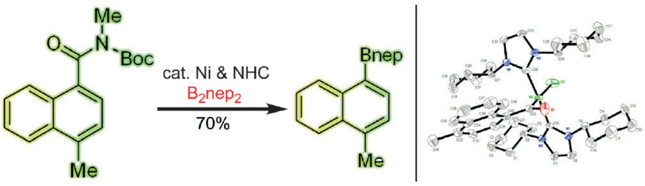


It's electrifying! Photocurrent generation by DNA oligomers on an Au electrode is described. Photocurrent generation in DNA oligomers assembled from ethylenedioxythiophene trimer (3E)-modified DNAs was measured by using a photoelectrochemical technique to clarify the sequence dependence of excess-electron transfer in DNA.

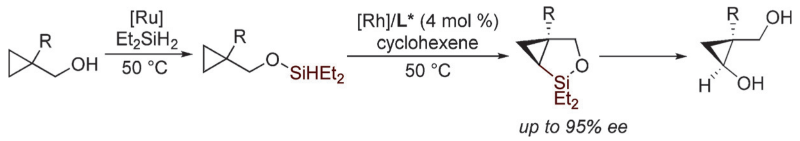
Decarbonylation

J. Hu, Y. Zhao, J. Liu, Y. Zhang,
Z. Shi* ______ **8718 – 8722**

Nickel-Catalyzed Decarbonylative Borylation of Amides: Evidence for Acyl C–N Bond Activation

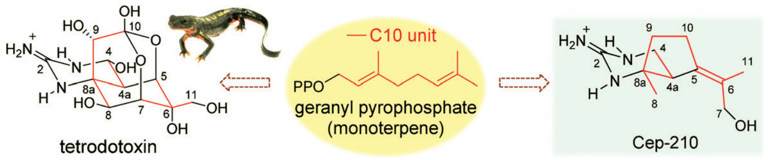


Keyed up: A Ni/N-heterocyclic carbene (NHC) catalytic system has been established for the title reaction, which proceeds by C–N bond activation. As a key intermediate, the structure of an acyl nickel complex was confirmed by X-ray analysis. The structure displays square-planar geometry, stabilized by two NHC ligands in *trans* position. These findings confirm the key mechanistic features of the acyl C–N bond activation process. Boc = *tert*-butoxycarbonyl, nep = neopentyl glycolato.



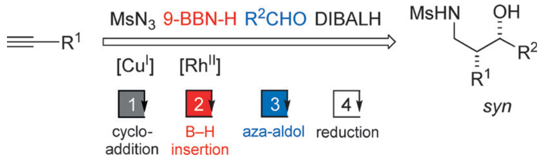
Enantioenriched cyclopropanes: Hydrosilyl ethers, generated in situ by the dehydrogenative silylation of cyclopropylmethanols, undergo asymmetric, intramolecular silylation of cyclopropyl C–H bonds in high yields and with high enantiomeric excesses in the presence of a rhodium catalyst. The silylation products are suitable substrates for Tamao–Fleming oxidation to form cyclopropanols with conservation of the *ee* value from the C–H silylation.

Asymmetric C–H Activation



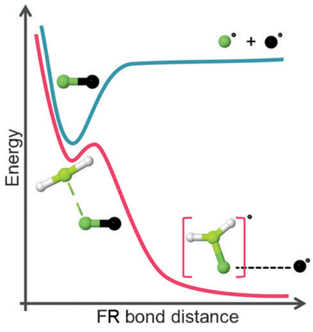
Eye of newt: On the basis of a proposed pathway for tetrodotoxin formation, a screening of biosynthetic intermediates was carried out. Five cyclic guanidine compounds, including Cep-210 (see picture), were found in toxic newts, and their elucidated structures support the hypothesis that tetrodotoxin is derived from a monoterpene.

Biosynthesis



All fours: *N*-Sulfonyl-1,2,3-triazoles react with 9-BBN-H in the presence of a rhodium(II) catalyst to produce *E* isomers of boron aza-enolates, which sequentially undergo aza-aldol reactions with aldehydes to form *syn* aza-aldol products. This method is successfully run as a four-step one-pot reaction for the stereoselective construction of 1,3-amino alcohols starting from terminal alkynes.

Aldol Reaction



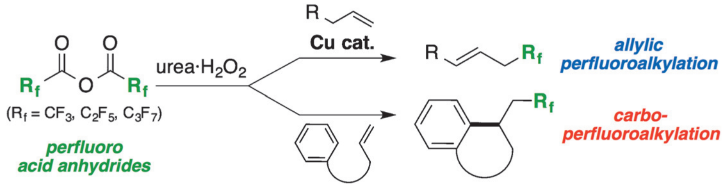
Be radical: The formation of a beryllium bond between a beryllium derivative and a Lewis base induces a reorganization of the electron density that results in the exergonic and spontaneous homolytic dissociation of the base. The effect of the BeX_2 attachment is twofold: it activates the covalent bond of the base and greatly stabilizes the radicals formed (see picture: Be light green, X white, F green, R black).

Inorganic Radicals

Fluorine

S. Kawamura, M. Sodeoka* **8740 – 8743**

Perfluoroalkylation of Unactivated Alkenes with Acid Anhydrides as the Perfluoroalkyl Source

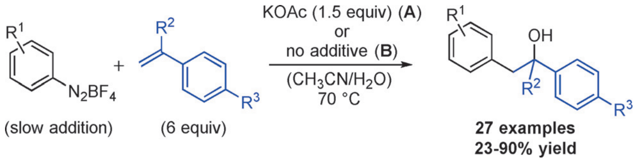


F for effective: Perfluoroalkylation of unactivated alkenes with perfluoro acid anhydrides as the perfluoroalkyl source was achieved. A copper catalyst enabled efficient allylic perfluoroalkylation with in situ generated diacyl peroxide. In addition, alkenes bearing an aromatic ring at an appropriate position on the carbon side chain afforded carboperfluoroalkylation products under metal-free conditions.

Carbohydroxylation

S. Kindt, K. Wicht, M. R. Heinrich* **8744 – 8747**

Thermally Induced Carbohydroxylation of Styrenes with Aryldiazonium Salts

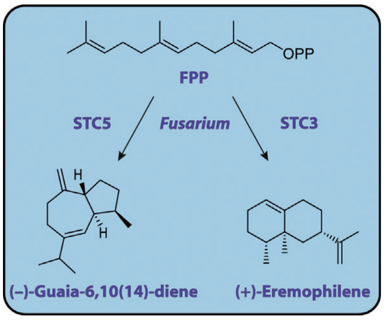


From radical to cation: The radical carbohydroxylation of styrenes with aryldiazonium salts has been achieved under mild thermal conditions. A broad range of aryldiazonium salts was tolerated and the reaction principle based on a radical–polar crossover mechanism could be extended to carboetherification as well as to a two-step, metal-free variant of the Meerwein arylation leading to stilbenes.

Natural Products

I. Burkhardt, T. Siemon, M. Henrot, L. Studt, S. Rösler, B. Tudzynski, M. Christmann,* J. S. Dickschat* **8748 – 8751**

Mechanistic Characterisation of Two Sesquiterpene Cyclases from the Plant Pathogenic Fungus *Fusarium fujikuroi*



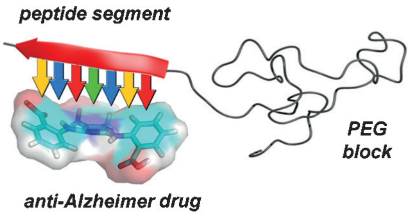
Round and round: The products of two sesquiterpene cyclases from *Fusarium fujikuroi* (STC5 and STC3) were identified by NMR spectroscopy. The absolute configuration of guaia-6,10(14)-diene was established through enantioselective synthesis and that of eremophilene from its optical rotation. STC5 was only functional after the correction of a critical point mutation. The enzymatic mechanisms were studied through isotopic labelling techniques.

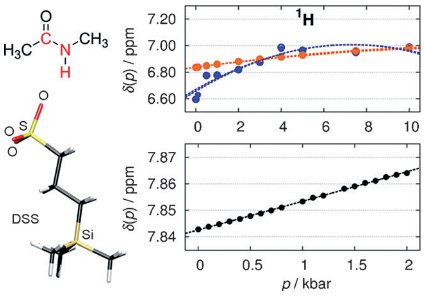
Medicinal Chemistry

C. Lawatscheck, M. Pickhardt, S. Wieczorek, A. Grafmüller, E. Mandelkow,* H. G. Börner* **8752 – 8756**

Generalizing the Concept of Specific Compound Formulation Additives towards Non-Fluorescent Drugs: A Solubilization Study on Potential Anti-Alzheimer-Active Small-Molecule Compounds

Specific solubilizers for non-fluorescent drugs that are based on peptide–PEG bioconjugates were identified by Raman microscopy. Peptide sequences that bind anti-Alzheimer drugs with high affinity were found, and the corresponding peptide–polymer conjugates solubilize the drugs very effectively. The drug/bioconjugate complexes induced the deaggregation of Tau protein aggregates in first in vitro assays.





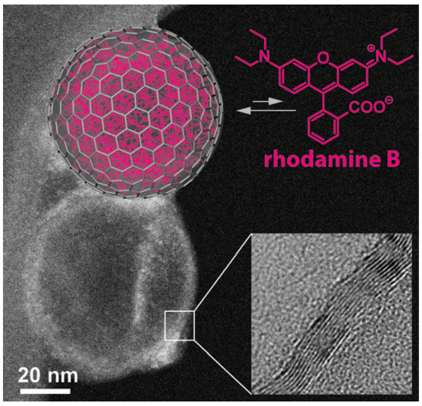
Solvent-induced electronic polarization in high-pressure NMR spectra of proteins: A pressurized polar solvent environment influences the electronic structure of both the reference standard and the target protein. Combined experimental and computational effort elucidates the pressure transparency of the common standard 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS, see picture) and the intrinsic, polarization-related chemical shift of *N*-methylacetamide, a prototype of the protein backbone.

High-Pressure NMR Spectroscopy

R. Frach, P. Kibies, S. Böttcher,
T. Pongratz, S. Strohfeldt, S. Kurrmann,
J. Koehler, M. Hofmann, W. Kremer,
H. R. Kalbitzer, O. Reiser, D. Horinek,
S. M. Kast* ——————— **8757 – 8760**

The Chemical Shift Baseline for High-Pressure NMR Spectra of Proteins 🖥

Hollow carbon nanobubbles: Water-dispersible, carbon-based nanobubbles, synthesized by metal templating, spontaneously take up cargo by hydrophobic interactions. The slow release of the cargo follows an unexpected out-of-equilibrium (hysteretic) behavior.



Nanocapsules

C. J. Hofer, R. N. Grass, M. Zeltner,
C. A. Mora, F. Krumeich,
W. J. Stark* ——————— **8761 – 8765**

Hollow Carbon Nanobubbles: Synthesis, Chemical Functionalization, and Container-Type Behavior in Water 🖥

🖥 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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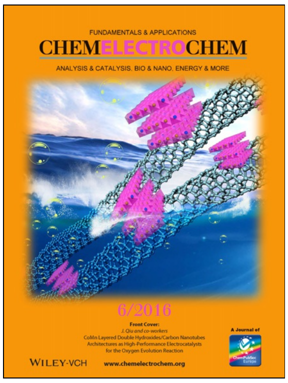

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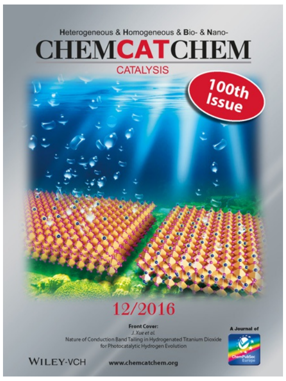

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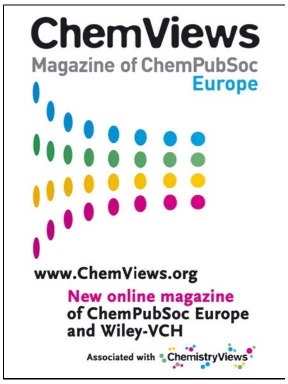

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