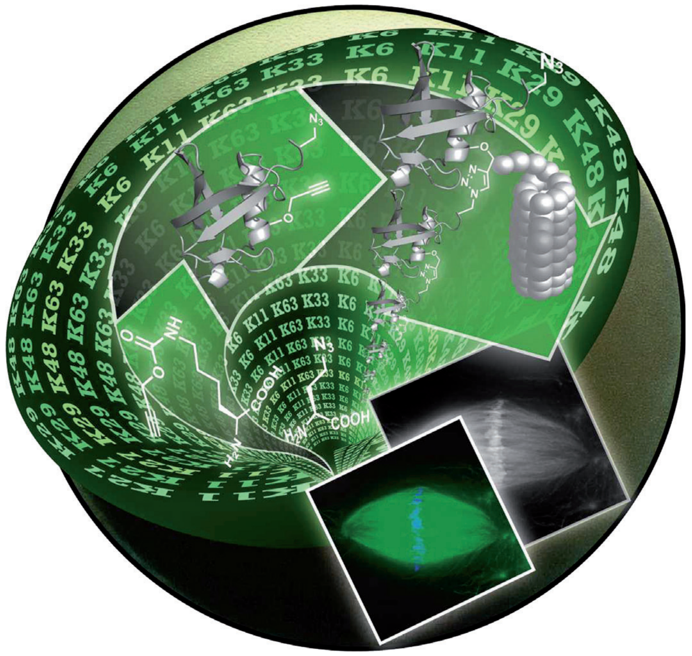
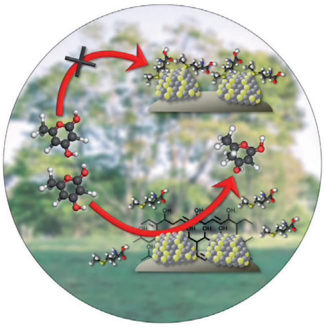
The fate of poly-ubiquitylated proteins ...

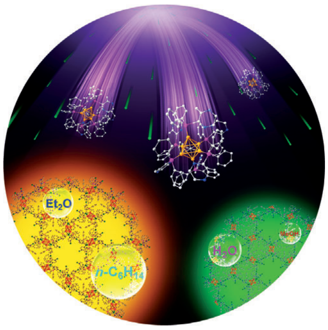


... is determined by the linkage type of the ubiquitin chains attached. In their Communication on page 12925 ff., T. U. Mayer, M. Scheffner, A. Marx et al. report a straightforward method that relies on codon expansion and bioorthogonal polymerization to generate linkage-defined and protease-resistant ubiquitin chains. These chains can be used to analyze ubiquitin signaling in cell extracts, as demonstrated by a study of linkage-dependent effects on cell-cycle progression.



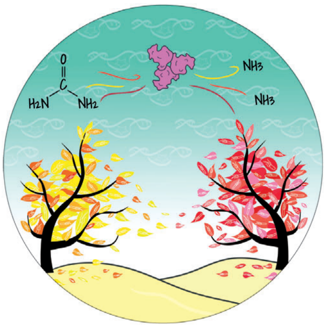
Catalyst Stability

In their Communication on page 12718 ff., J. A. Dumesic and co-workers show that microenvironments formed around the catalytic sites of supported metal hydrogenation catalysts can mitigate deactivation caused by biogenic impurities.



"Cluster Linker" Approach

The luminescence properties of clusters can be introduced into a bifunctional porous metal–organic framework as described by Q.-M. Wang et al. in their Communication on page 12771 ff.



Biosensors

S. Huan, Y. Li et al. describe in their Communication on page 12799 ff. how a DNAzyme, urease, and magnetic beads can be used to detect bacteria. The resulting increase in the pH value enables colorimetric detection using the litmus test.

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Service

Author Profile

*"In a spare hour—spare hour? What spare hour?
I admire the ability of my research group to take my ideas and make them work ..."*
This and more about Stephen T. Liddle can be found on page 12670.

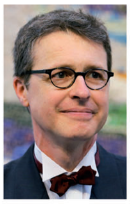
News


L. De Cola


M. Grätzel


D. Günther


M. Rief


S. P. A. Sauer


H. Schwalbe


H.-J. Quadbeck-Seeger


U. T. Bornscheuer


M. Walter


A. H. Hoveyda

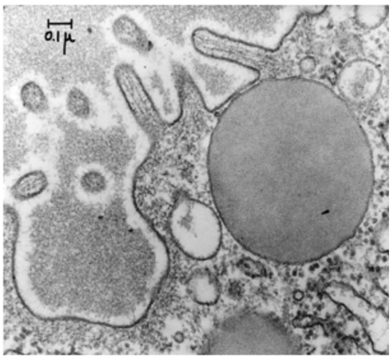

K. C. Nicolaou

Obituaries

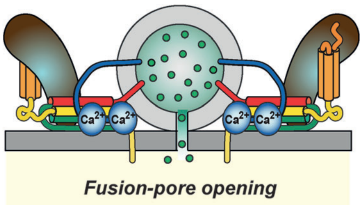
Books

Reviews

Membrane Fusion



Vesicle Transport



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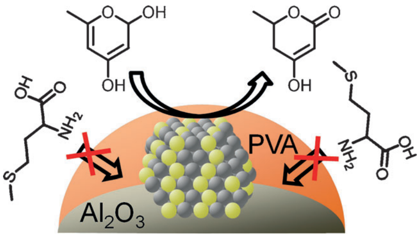
Catalyst Stability

T. J. Schwartz, R. L. Johnson, J. Cardenas, A. Okerlund, N. A. Da Silva, K. Schmidt-Rohr, J. A. Dumesic* ———— 12718–12722

Engineering Catalyst Microenvironments for Metal-Catalyzed Hydrogenation of Biologically Derived Platform Chemicals

Frontispiece

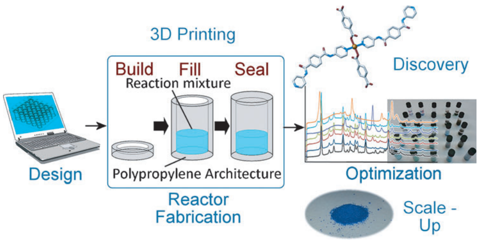


The surface properties of supported metal hydrogenation catalysts are modified by the formation of microenvironments inside the catalyst pores and surrounding the metal nanoparticles. These microenvironments are derived from poly(vinyl alcohol) (PVA), and they are used to mitigate catalyst deactivation that is due to biogenic impurities.

3D Printed Reactors

P. J. Kitson, R. J. Marshall, D. Long, R. S. Forgan,* L. Cronin* 12723–12728

3D Printed High-Throughput Hydrothermal Reactionware for Discovery, Optimization, and Scale-Up

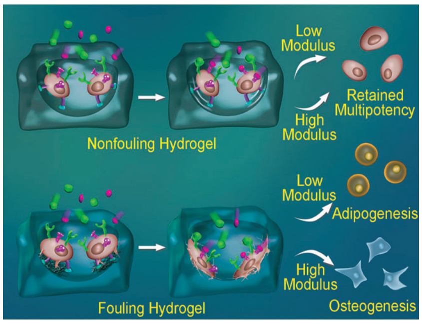


Form and function: Sealed, monolithic reactors suitable for use in hydrothermal synthesis are digitally designed and realized using 3D printing techniques. The utility of these reactors is shown by the fabrication of high-throughput-array reactors which were used to discover two new coordination polymers, and to optimize and scale up the synthesis of one of these.

Cell Differentiation

T. Bai, F. Sun, L. Zhang, A. Sinclair, S. Liu, J. R. Ella-Menye, Y. Zheng, S. Jiang* ———— 12729–12734

Restraint of the Differentiation of Mesenchymal Stem Cells by a Nonfouling Zwitterionic Hydrogel

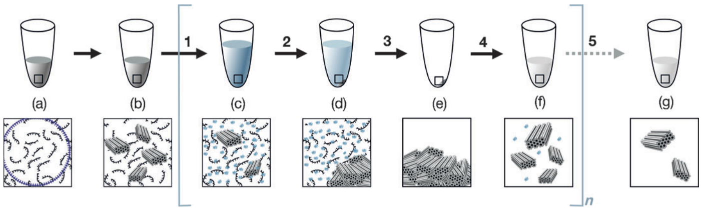


Not all dare to be different: The understanding that the fate of stem cells is determined by chemical and physical factors is challenged by the finding that human mesenchymal stem cells were not differentiated in the absence of nonspecific interactions, regardless of the chemical environment or the stiffness of the matrix. In the picture, cyclic-RGD moieties are represented as cyan hemispheres, and differentiation factors as colored particles.

Self-Assembly

E. Stahl, T. G. Martin, F. Praetorius, H. Dietz* ———— 12735–12740

Facile and Scalable Preparation of Pure and Dense DNA Origami Solutions



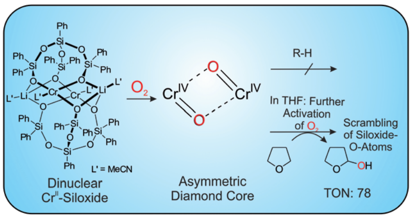
PEG packs them all: A depletion-based method is used for the preparation of self-assembled megadalton-scale DNA objects up to the limit of solubility, including the possibility for bringing such objects into a solid phase. Due to its fidelity and simplicity this method might benefit the development of new types of applications that use self-assembled DNA objects.

Dinuclear Complexes

F. Schax, E. Bill, C. Herwig,
C. Limberg* ———— 12741 – 12745

Dioxygen Activation by Siloxide Complexes of Chromium(II) and Chromium(IV)

A dinuclear Cr^{II} siloxide complex was synthesized that cleaves O_2 to yield a unique Cr^{IV} complex with an asymmetric core composed of two Cr^{IV}=O units. Although it is the stable product isolated after excess O_2 treatment, it further activates O_2 to yield an intermediate species that oxidizes THF or Me-THF. ^{18}O labeling studies show that $^{18}O_2$ and $PhI^{18}O$ thereby exchange with siloxide O atoms of the ligand.



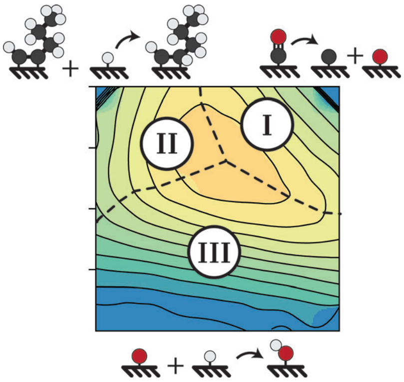
Fischer–Tropsch Kinetics

I. A. W. Filot, R. A. van Santen,
E. J. M. Hensen* ———— 12746 – 12750

The Optimally Performing Fischer–Tropsch Catalyst

Inside Cover

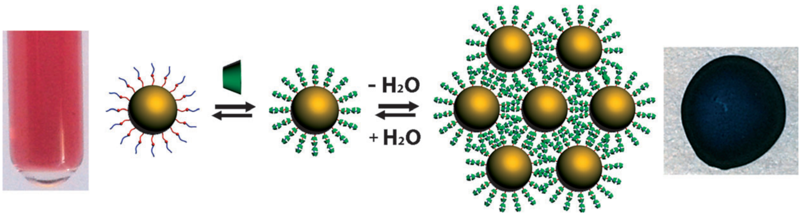
State-of-the-art quantum-chemical reaction data were used in a microkinetics simulations study to elucidate the different fundamental kinetic regimes underlying Fischer–Tropsch activity and selectivity. Based on the nature of the rate-controlling steps, three regimes were identified: I) monomer formation, II) chain-growth termination, and III) water formation.



Nanoparticle Self-Assembly

J. P. Coelho, G. González-Rubio,
A. Delices, J. O. Barcina, C. Salgado,
D. Ávila, O. Peña-Rodríguez, G. Tardajos,
A. Guerrero-Martínez* —— 12751 – 12755

Polyrotaxane-Mediated Self-Assembly of Gold Nanospheres into Fully Reversible Supercrystals



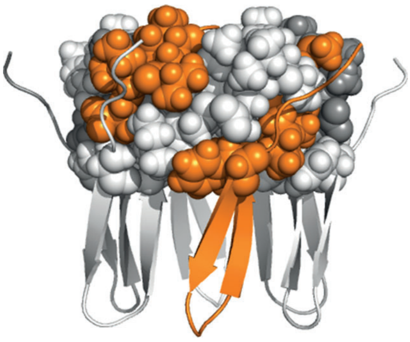
A golden get-together: A thiol-functionalized nonionic surfactant and α-cyclodextrin undergo complexation at the surface of gold nanoparticles to form polyrotaxane-stabilized nanocrystals. Under controlled drying conditions, the nanocrystals can reversibly self-assemble into homogenous hexagonal closed-packed supercrystals.

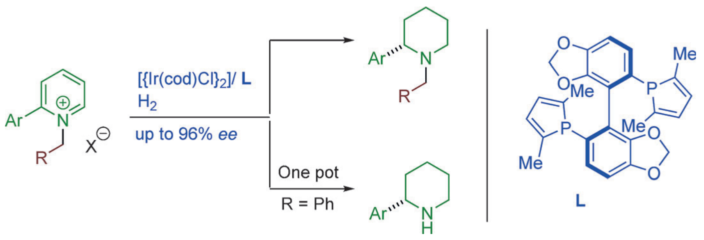
Protein Structures

C. Lendel, M. Bjerring, A. Dubnovitsky,
R. T. Kelly, A. Filippov, O. N. Antzutkin,
N. C. Nielsen, T. Härd* —— 12756 – 12760

A Hexameric Peptide Barrel as Building Block of Amyloid-β Protofibrils

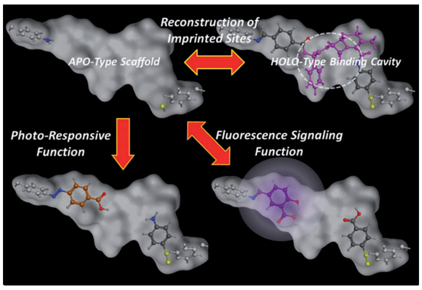
Amyloid-β protofibrils are precursors to amyloid fibrils found in plaques in the brains of patients with Alzheimer's disease. A stable form of Aβ protofibrils was engineered and studied by solid-state NMR spectroscopy. The structural model of hexameric building block oligomers clarifies biochemical issues related to the formation of protofibrils.





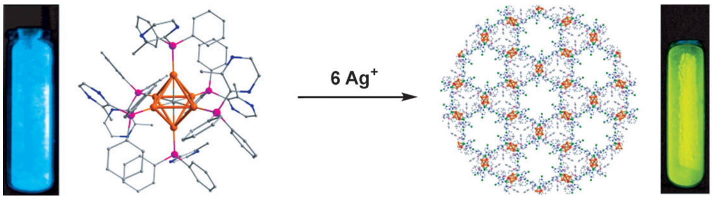
Ring to ring: Simple *N*-benzyl and *N*-alkyl groups successfully activated pyridine substrates toward hydrogenation. The use of the unusual chiral phosphole-based ligand **L** was the key to the success of this approach, which provides a versatile and practical procedure for the synthesis of chiral piperidines. cod = 1,5-cyclooctadiene.

Asymmetric Catalysis



Molecularly imprinted polymers that mimic conjugated proteins were obtained by molecular imprinting with a circumspectly designed template molecule and post-imprinting modifications. This strategy can be applied to develop synthetic materials with various functions.

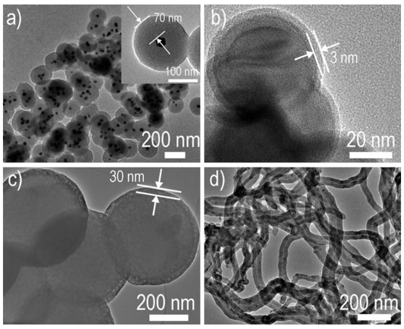
Molecular Recognition



Cluster linker: A luminescent gold(I) cluster prefunctionalized with pyrazinyl groups (left) was used as a cluster linker, similar to an organic linker, to connect silver ions in order to form a 3D framework. The intrinsic luminescence of the cluster was thus introduced into a bifunctional porous framework, which is characterized by an NbO topology and features 1D channels with a diameter of 1.1 nm.

Luminescent Frameworks

Inside Back Cover

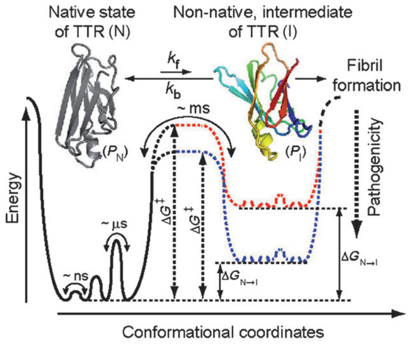


Uniform surface coatings of Al_2O_3 with a thickness controllable at the one nanometer level were achieved by a solution-based synthesis route. Application of this coating methodology to $LiCoO_2$ showed that its battery performance as a cathode material can be optimized by means of systematic surface control.

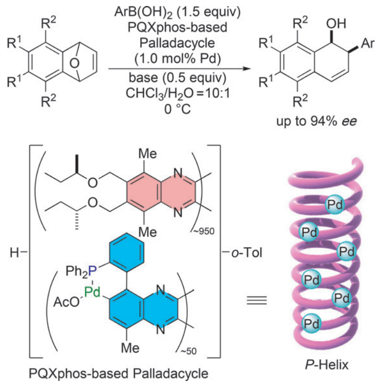
Core–Shell Structures

Amyloid Formation

States of being: Relaxation dispersion NMR on wild-type and mutant transthyretin (TTR) reveals that subtle differences in backbone dynamics tune the formation of an intermediate state. Pathogenic mutants (blue curve) systematically form a higher quantity of energetically stable intermediate than the wild type (red curve), thus hinting at the possibility of using protein dynamics as a predictor of pathogenicity for TTR and in other types of amyloidosis.

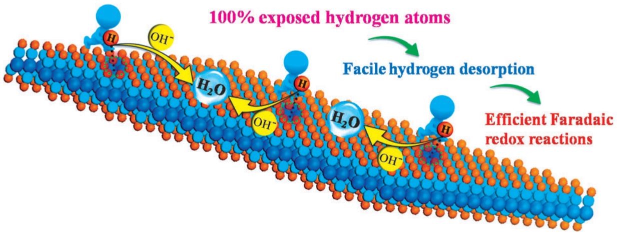


Helical Structures



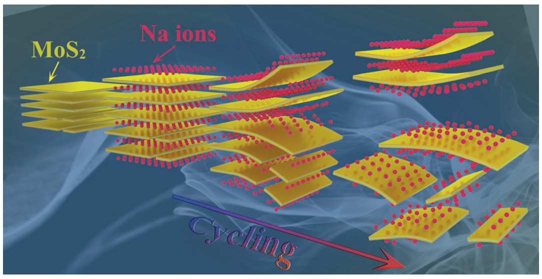
Polymers with a twist: Poly(quinoxaline-2,3-diyl)-based helically chiral phosphine ligands (PQXphos) have been used to generate chiral phosphapalladacycles. The palladacycles resulted in enantioselectivities of up to 94 % *ee* in the palladium-catalyzed asymmetric ring-opening arylation of 1,4-epoxy-1,4-dihydronaphthalenes with arylboronic acids.

Supercapacitors



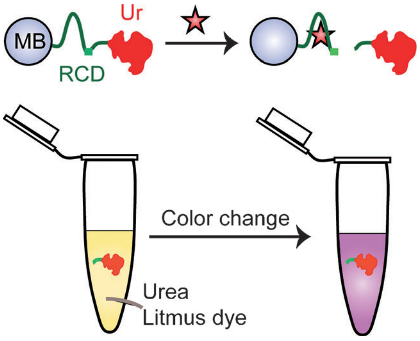
An atomically thin β-$Co(OH)_2$ sheet electrode was used to fabricate an all-solid-state asymmetric supercapacitor with high energy density. The β-$Co(OH)_2$ layers are characterized by 100 % exposed hydrogen atoms, thus facilitating efficient Faradaic redox reactions. The energy density of 98.9 Wh kg^{-1} can compete with the world's highest energy density for supercapacitors.

Sodium-Ion Batteries



More active sites through peeling: MoS_2 nanoflowers with expanded interlayers were investigated as a high-performance anode material for Na-ion batteries. Excellent discharge capacities and high cycling stability were observed and were directly correlated with the expanded layer space and the decreased layer numbers.

A new way to use the litmus test: Cheap and widely available litmus dyes and pH papers have been used to achieve the detection of a bacterial pathogen (star) through the use of an RNA-cleaving DNAzyme (RCD), urease (Ur), and magnetic beads (MB). The method allowed the sensitive detection of *E. coli* in complex sample matrices such as apple juice, milk, and lake water.



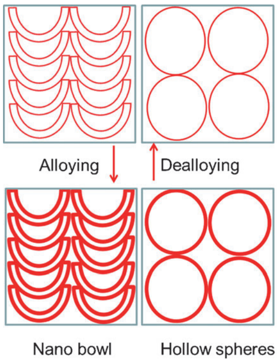
Biosensors

K. Tram, P. Kanda, B. J. Salena, S. Huan,*
Y. Li* **12799 – 12802**

Translating Bacterial Detection by DNAzymes into a Litmus Test

Back Cover

Super Bowl: A bowl-like hybrid hollow nanostructure of SnO_2@carbon is designed and fabricated as an anode material for lithium-ion batteries. With advantages of the unique architecture, the bowl-like SnO_2@carbon particles are able to deliver a high discharge capacity of 963 mAh g^{-1} even after 100 cycles at a current density of 0.4 A g^{-1}.



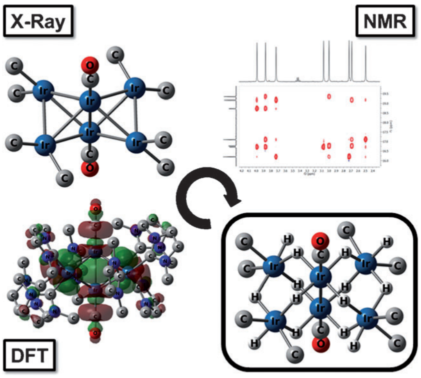
Lithium-Ion Batteries

J. Liang, X.-Y. Yu, H. Zhou, H. B. Wu,
S. Ding,* X. W. Lou* **12803 – 12807**

Bowl-like SnO_2@Carbon Hollow Particles as an Advanced Anode Material for Lithium-Ion Batteries

---

A heavy bow tie: A combination of techniques, including X-ray diffraction, NMR spectroscopy, and DFT calculations, revealed the unusual structure of the cluster $[Ir_6(IMe)_8(CO)_2H_{14}]^{2+}$. The bow-tie-shaped Ir_6 core is decorated with only two carbonyl, a record eight 1,3-dimethylimidazol-2-ylidene (IMe), and 14 hydride ligands (see structure: N blue, O red, C gray).



Organometallic Clusters

J. Campos,* L. S. Sharninghausen,
R. H. Crabtree,*
D. Balcells* **12808 – 12811**

A Carbene-Rich but Carbonyl-Poor $[Ir_6(IMe)_8(CO)_2H_{14}]^{2+}$ Polyhydride Cluster as a Deactivation Product from Catalytic Glycerol Dehydrogenation

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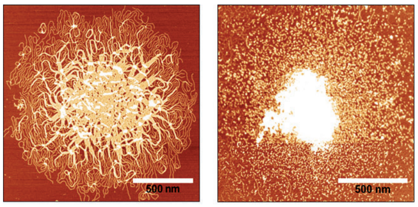


DNA condensation

tRNA aggregation

Pt bridges the gap: A general mechanism showing the biological effects of trinuclear platinum complexes, which bind to DNA through noncovalent interactions, may be associated with their unique ability to efficiently condense or aggregate nucleic acids with consequent inhibitory effects on crucial enzymatic activities. Scale bars in picture = 500 nm.

Nucleic Acids Condensation

J. Malina, N. P. Farrell,
V. Brabec* **12812 – 12816**

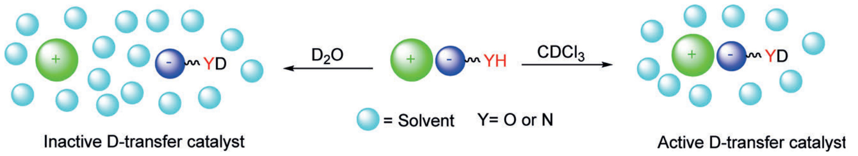
Substitution-Inert Trinuclear Platinum Complexes Efficiently Condense/Aggregate Nucleic Acids and Inhibit Enzymatic Activity

VIP

Ionic Liquids

M. Zanatta, A.-L. Girard, N. M. Simon,
G. Ebeling, H. K. Stassen, P. R. Livotto,
F. P. dos Santos,
J. Dupont* ______ **12817 – 12821**

The Formation of Imidazolium Salt Intimate (Contact) Ion Pairs in Solution

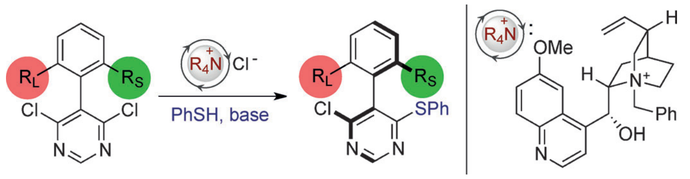


Remote pK_a control is the result of the formation of intimate contact ion pairs in $CDCl_3$ and CD_3CN of 1-*n*-butyl-2,3-dimethyl imidazolium ionic liquids associated with HCO_3 or prolinate anions. These salts are effective neutral catalysts for the H/D exchange reaction from $CDCl_3$ to substrates containing acidic H.

Asymmetric Catalysis

R. J. Armstrong,
M. D. Smith* ______ **12822 – 12826**

Catalytic Enantioselective Synthesis of Atropisomeric Biaryls:
A Cation-Directed Nucleophilic Aromatic Substitution Reaction

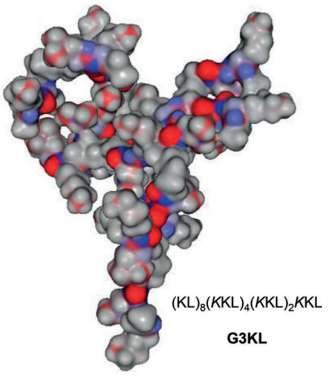


Asymm-Desymm: A catalytic asymmetric nucleophilic aromatic substitution reaction which yields axially chiral biaryls in excellent yields with e.r. values of up to 97:3 has been developed. This process uses a chiral counterion to direct the addition of thiophenolate to an achiral dichloropyrimidine by a tandem desymmetrization/kinetic resolution mechanism. The products can be derivatized, thus offering access to unexplored chiral biaryl architectures.

Antimicrobial Peptides

M. Stach, T. N. Siriwardena, T. Köhler,
C. van Delden, T. Darbre,*
J.-L. Reymond* ______ **12827 – 12831**

Combining Topology and Sequence Design for the Discovery of Potent Antimicrobial Peptide Dendrimers against Multidrug-Resistant *Pseudomonas aeruginosa*

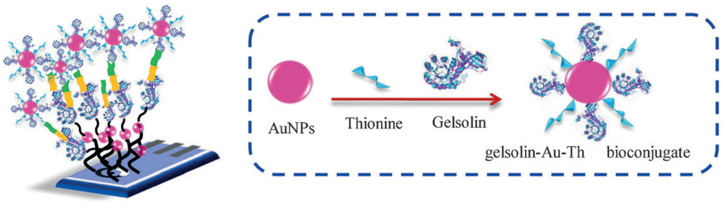


Multidrug-resistant bacteria, such as *Pseudomonas aeruginosa* and *Acinetobacter baumannii*, are a major public health threat. By combining topology and amino acid sequence design, new antimicrobial peptide dendrimers with high activity against these pathogens were found, which represents a new and general approach for the discovery of antimicrobial agents.

Biosensors

Y. Yu, L. Zhang, C. Li, X. Sun, D. Tang,
G. Shi* ______ **12832 – 12835**

A Method for Evaluating the Level of Soluble β-Amyloid$_{(1-40/1-42)}$ in Alzheimer's Disease Based on the Binding of Gelsolin to β-Amyloid Peptides



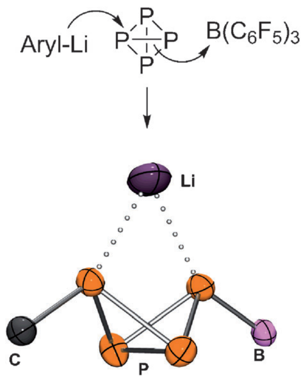
Amyloid assay: A selective gelsolin-based electrochemical probe was designed that can specifically bind the β-amyloid peptides Aβ$_{(1-40/1-42)}$ (yellow and green) to quantify variations in Aβ levels in Alzheimer's disease (AD). This sensitive method makes use of the amplifying features of AuNPs and was successfully used to evaluate variations in the Aβ content of the cerebrospinal fluid and brain tissues of normal and AD-affected rats.

P_4 Functionalization

J. E. Borger, A. W. Ehlers, M. Lutz,
J. C. Slootweg,
K. Lammertsma* ——— **12836–12839**

Functionalization of P_4 Using a Lewis Acid Stabilized Bicyclo[1.1.0]tetraphosphabutane Anion

Controlling P_4 transformations: Reacting P_4 with congested aryl lithium reagents and $B(C_6F_5)_3$ gives unique, Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane anions. Alkylating their nucleophilic site results in a non-symmetrical disubstituted bicyclic tetraphosphorus compound. This method enables the formation of P–C bonds in a controlled fashion using white phosphorus as the starting material.

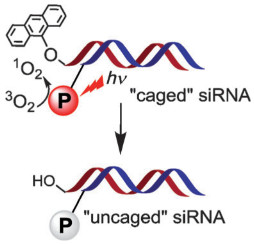


Caged RNA

A. Meyer, A. Mokhir* ——— **12840–12843**

RNA Interference Controlled by Light of Variable Wavelength

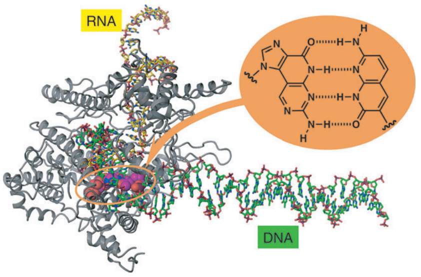
Photoactivation: Known "caged" small interfering RNAs are activated by UV light, which is toxic to cells. The activation of siRNAs by red light under mild conditions not affecting cells is reported. The uncaging is mediated by singlet oxygen (see picture) photogenerated on a photosensitizer, which is attached to the 3′-terminus of the lagging strand.



Expanding the Genetic Code

Y. Nomura, S. Kashiwagi, K. Sato,
A. Matsuda* ——— **12844–12848**

Selective Transcription of an Unnatural Naphthyridine:Imidazopyridopyrimidine Base Pair Containing Four Hydrogen Bonds with T7 RNA Polymerase

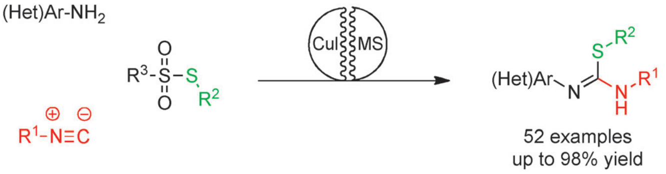


Four to be sure: The naphthyridine (Na):imidazopyridopyrimidine (Im) base pair containing four hydrogen bonds replicates selectively and efficiently under the action of DNA polymerases. Naphthyridine-*C*-ribonucleoside 5′-triphosphate (rNaTP) was transcribed successfully opposite a template DNA containing the Im base by T7 RNA polymerase. The transcription reaction was also applied to a longer transcript containing a part of the human c-Ha-Ras gene.

Synthetic Methods

P. Mampuys, Y. Zhu, T. Vlaar, E. Ruijter,*
R. V. A. Orru,*
B. U. W. Maes* ——— **12849–12854**

Sustainable Three-Component Synthesis of Isothioureas from Isocyanides, Thiosulfonates, and Amines

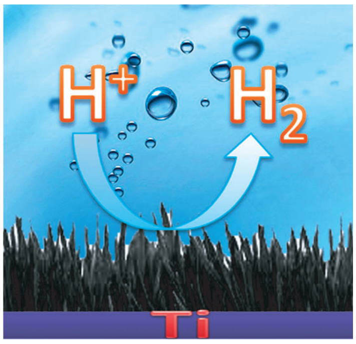


Safety first! A direct synthesis of isothioureas by a copper-catalyzed three-component reaction from readily available substrates (see scheme) avoids the toxic, flammable, and highly reactive reagents required in classical approaches. The reaction also enables the straightforward synthesis of *S*-aryl isothioureas, which are difficult to obtain by other methods.

Hydrogen Evolution

P. Jiang, Q. Liu, Y. Liang, J. Tian,
A. M. Asiri, X. Sun* ______ **12855 – 12859**

A Cost-Effective 3D Hydrogen Evolution Cathode with High Catalytic Activity: FeP Nanowire Array as the Active Phase

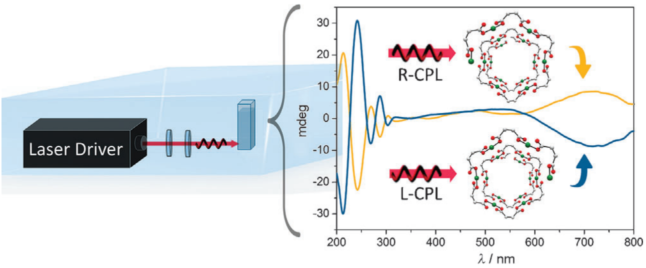


Low cost, high performance: A novel hydrogen evolution cathode composed of a FeP nanowire array supported on a Ti plate exhibits exceptionally high catalytic activity and good durability in strongly acidic solutions. It is among the best non-noble-metal HER catalysts showing promise for large-scale hydrogen fuel production.

Photochemistry

S.-T. Wu,* Z.-W. Cai, Q.-Y. Ye, C.-H. Weng,
X.-H. Huang, X.-L. Hu, C.-C. Huang,
N.-F. Zhuang ______ **12860 – 12864**

Enantioselective Synthesis of a Chiral Coordination Polymer with Circularly Polarized Visible Laser

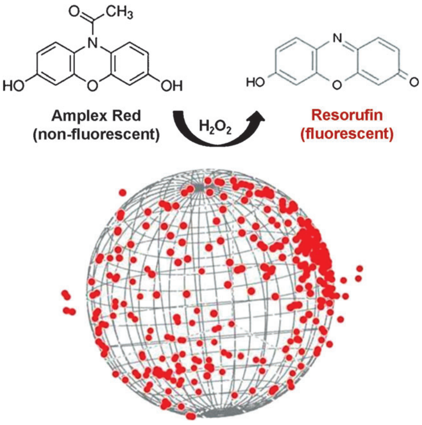


With a twist of light: The enantioselective synthesis of the [{P/M-Cu(succinate)(4,4′-bipyridine)}$_n$]·(4 H_2O)$_n$ coordination polymer was achieved by using a circularly polarized visible laser, and thus provides a strategy for the control of the chirality of chiral coordination polymers. CPL = circularly polarized light.

Heterogeneous Catalysis

R. Han, J. W. Ha, C. Xiao, Y. Pei, Z. Qi,
B. Dong, N. L. Bormann, W. Huang,*
N. Fang* ______ **12865 – 12869**

Geometry-Assisted Three-Dimensional Superlocalization Imaging of Single-Molecule Catalysis on Modular Multilayer Nanocatalysts

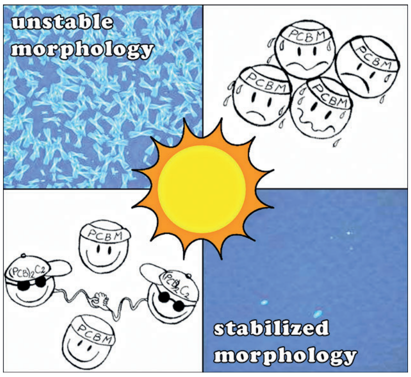


A multilayer catalyst that consists of a solid silica core, a mesoporous silica shell, and uniformly distributed Pt nanoparticles sandwiched between these layers was synthesized. 3D high-resolution super-localization was then used to image single fluorescent molecules produced at active sites on the core–shell model nanocatalysts.

Organic Photovoltaics

B. C. Schroeder,* Z. Li,* M. A. Brady,
G. C. Faria, R. S. Ashraf, C. J. Takacs,
J. S. Cowart, D. T. Duong, K. H. Chiu,
C.-H. Tan, J. T. Cabral, A. Salleo,
M. L. Chabinyc, J. R. Durrant,
I. McCulloch ______ **12870 – 12875**

Enhancing Fullerene-Based Solar Cell Lifetimes by Addition of a Fullerene Dumbbell

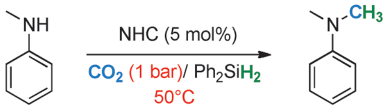


Fullerene dumbbells: Long-term operational stability of organic photovoltaics remains a challenge, especially at high temperatures. A novel fullerene dumbbell was synthesized and used as an additive in the active layer. The addition of the dumbbell not only leads to improved device efficiencies, but also to a dramatic increase in morphological stability (see picture) under simulated operating conditions.

Methylation

S. Das, F. D. Bobbink, G. Laurenczy,
P. J. Dyson* ———— 12876 – 12879

Metal-Free Catalyst for the Chemoselective Methylation of Amines Using Carbon Dioxide as a Carbon Source

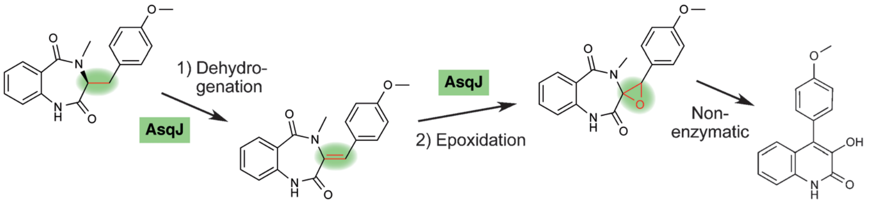


The methylation of amines with CO_2 as C_1 source and Ph_2SiH_2 as reducing agent was achieved with an N-heterocyclic carbene (NHC) as the catalyst. The catalyst is tolerant toward a variety of functional groups (including esters and ethers, nitro, nitrile, and carbonyl groups, and unsaturated C=C bonds); the reaction uses commercially available reagents and can be performed on a gram scale.

Natural Products

N. Ishikawa, H. Tanaka, F. Koyama,
H. Noguchi, C. C. C. Wang, K. Hotta,
K. Watanabe* ———— 12880 – 12884

Non-Heme Dioxygenase Catalyzes Atypical Oxidations of 6,7-Bicyclic Systems To Form the 6,6-Quinolone Core of Viridicatin-Type Fungal Alkaloids

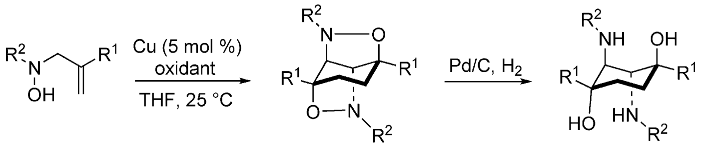


A double role: The isolation of an Aspergillal gene cluster responsible for the biosynthesis of 4′-methoxyviridicatin led to the discovery of the dioxygenase AsqJ, which performs two distinct oxidations: first dehydrogenation to form a double bond and then monooxygenation of the double bond to form an epoxide. Interestingly, the epoxidation promotes nonenzymatic rearrangement of a 6,7-bicyclic core into the 6,6-quinolone viridicatin scaffold.

Synthetic Methods

S. Ghorpade, R.-S. Liu* ———— 12885 – 12888

Copper-Catalyzed Oxidative Dimerizations of 3-*N*-Hydroxyaminoprop-1-enes to Form 1,4-Dihydroxy-2,3-diaminocyclohexanes with C_2 Symmetry

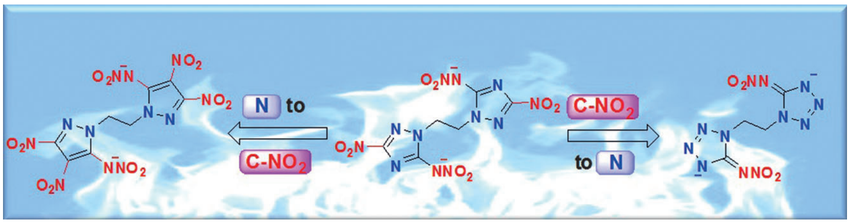


Skeletons! Copper-catalyzed aerobic oxidations of *N*-hydroxyaminopropenes to form C_2-symmetric N- and O-functionalized cyclohexanes are described. The catalytic oxidations proceed with remarkable stereocontrol and high efficiency. Reductive cleavage of the two N–O bonds of these products delivers 1,4-dihydroxy-2,3-diaminocyclohexanes, which are important skeletons of several bioactive molecules.

Energetic Materials

P. Yin, D. A. Parrish,
J. M. Shreeve* ———— 12889 – 12892

Bis(nitroamino-1,2,4-triazolates): *N*-Bridging Strategy Toward Insensitive Energetic Materials

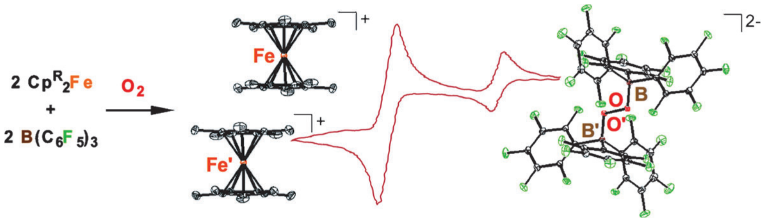


Explosive: Energetic bis(nitroamino-1,2,4-triazolates) were prepared by an *N*-bridging strategy and exhibited good thermal stabilities, excellent detonation properties, and low sensitivities. A detailed study involving different azole scaffolds showed that bis(triazolates) compete well with bis(tetrazolates) and bis(pyrazolates) with respect to energetic properties and molecular stabilities.

Boron Peroxide from O_2

J. T. Henthorn, T. Agapie* **12893 – 12896**

Dioxygen Reactivity with a Ferrocene–Lewis Acid Pairing: Reduction to a Boron Peroxide in the Presence of Tris(pentafluorophenyl)borane

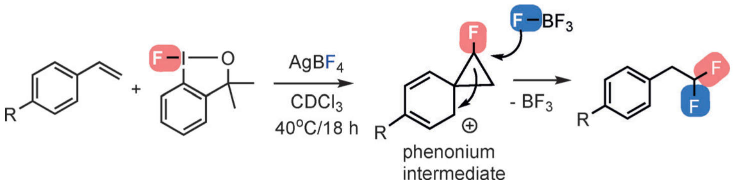


A bis(borane)-supported peroxide anion was synthesized and its structural and electrochemical characterization is described. Ferrocenes (see scheme; R = Me, H), which are typically air-stable outer-sphere single-electron transfer reagents, react with dioxygen in the presence of $B(C_6F_5)_3$, a Lewis acid unreactive to O_2, to generate bis(borane)peroxide.

Hypervalent Compounds

N. O. Ilchenko, B. O. A. Tasch, K. J. Szabó* ———— **12897 – 12901**

Mild Silver-Mediated Geminal Difluorination of Styrenes Using an Air- and Moisture-Stable Fluoroiodane Reagent

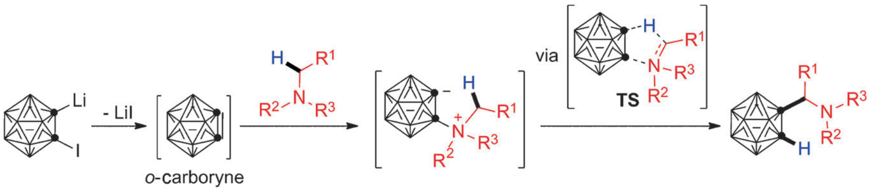


Phenomenal phenonium: A formal F_2 addition to styrenes was carried out by using stable and safe fluorinating reagents under mild reaction conditions. The reaction proceeds via a phenonium intermediate.

C–H Activation

D. Zhao, J. Zhang, Z. Xie* **12902 – 12906**

Regioselective Insertion of *o*-Carborynes into the α-C–H Bond of Tertiary Amines: Synthesis of α-Carboranylated Amines



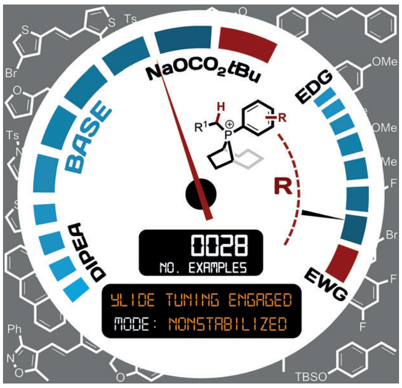
Electron-poor first: *o*-Carborynes can undergo α-C–H insertion reactions with tertiary amines, thus producing α-carboranylated amines in very good regioselectivity and yields. The more-electron-deficient C–H bonds are favored. Mechanistic studies as well as DFT calculations suggest that the pictured transition state (TS) is involved. This unique reactivity pattern provides an efficient method for the generation of a series of 1-aminoalkyl-*o*-carboranes for applications in medicine and catalysis.

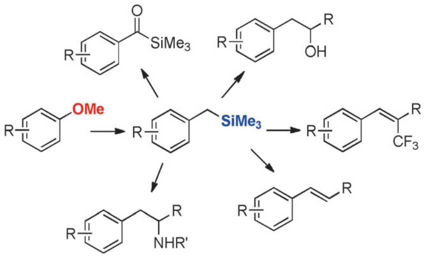
Olefination

E. E. Coyle, B. J. Doonan, A. J. Holohan, K. A. Walsh, F. Lavigne, E. H. Krenske,* C. J. O'Brien* ———— **12907 – 12911**

Catalytic Wittig Reactions of Semi- and Nonstabilized Ylides Enabled by Ylide Tuning

Time for a tune up: Catalytic Wittig reactions with semi- and nonstabilized ylides were enabled by use of a masked base ($NaOCO_2tBu$) and/or ylide tuning. The acidity of the ylide-forming proton was tuned by varying the electron density at the P center in the precatalyst, thus facilitating the use of relatively mild bases. Steric modification of the precatalyst structure resulted in significant enhancement of *E* selectivity.



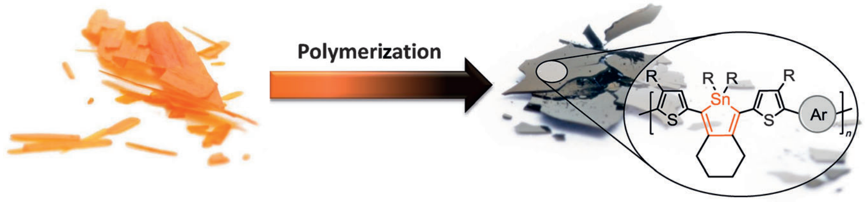


The direct replacement of aromatic methoxy groups with activated carbon nucleophiles would give rise to novel synthetic pathways for targeted and diversity-oriented syntheses. The use of a bifunctional nucleophile in a nickel-catalyzed cross-coupling reaction has resulted in diverse aryl methyl ethers being transformed into α-carbon-activated products.

Aryl Ether Cross-Coupling

M. Leiendecker, C.-C. Hsiao, L. Guo,
N. Alandini, M. Rueping* **12912 – 12915**

Metal-Catalyzed Dealkoxylative C_{aryl}–C_{sp^3} Cross-Coupling—Replacement of Aromatic Methoxy Groups of Aryl Ethers by Employing a Functionalized Nucleophile

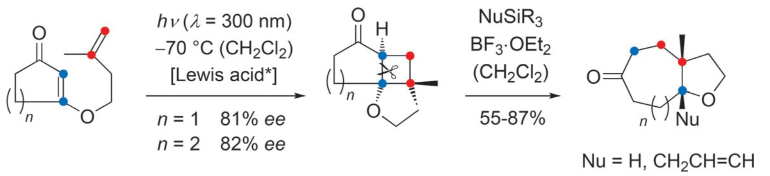


The budding potential of stannoles: A stannole monomer is prepared and employed in a highly tin-selective Stille coupling, giving a well-defined and non-annulated stannole-containing polymer, the first example from this class of π-conjugated polymers. Compared to polythiophenes, a strong bathochromic shift in the absorption spectrum was observed.

Nucleophile-Selective Cross-Coupling

J. Linshoeft, E. J. Baum, A. Hussain,
P. J. Gates, C. Näther,
A. Staubitz* **12916 – 12920**

Highly Tin-Selective Stille Coupling: Synthesis of a Polymer Containing a Stannole in the Main Chain

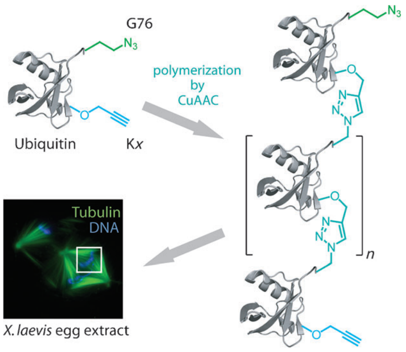


Ring-a-ring o'roses: An enantioselective, Lewis acid catalyzed [2+2] photocycloaddition (9 examples, 69–94 % yield, up to 94 % *ee*) leads to tricyclic products, in which the marked bond of the cyclobutane ring can be cleaved to form medium-sized rings as shown in the example above.

Photochemistry

R. Brimioulle, T. Bach* **12921 – 12924**

[2+2] Photocycloaddition of 3-Alkenyloxy-2-cycloalkenones: Enantioselective Lewis Acid Catalysis and Ring Expansion



It all clicks into place: The fate of ubiquitylated proteins is determined by the topology of the attached ubiquitin chains. A new concept is reported for generating linkage-defined ubiquitin chains that are resistant to de-ubiquitylating enzymes and adopt native-like functions. The potential of these artificial chains for analyzing ubiquitin signaling is demonstrated by topology-specific effects on cell-cycle progression.

Posttranslational Modifications

VIP

T. Schneider, D. Schneider, D. Rösner,
S. Malhotra, F. Mortensen, T. U. Mayer,*
M. Scheffner,* A. Marx* **12925 – 12929**

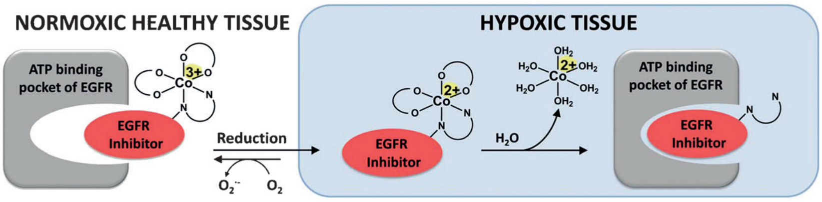
Dissecting Ubiquitin Signaling with Linkage-Defined and Protease Resistant Ubiquitin Chains

Front Cover

Drug Design

C. Karnthaler-Benbakka, D. Groza,
K. Kryeziu, V. Pichler, A. Roller, W. Berger,
P. Heffeter,* C. R. Kowol* **12930–12935**

Tumor-Targeting of EGFR Inhibitors by Hypoxia-Mediated Activation



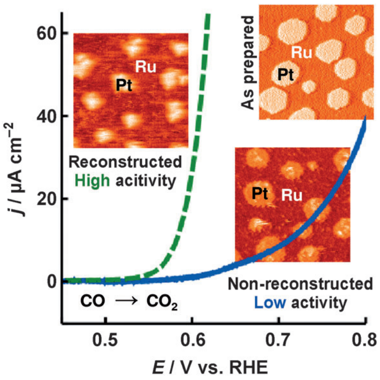
Targeted attack: Receptor tyrosine-kinase inhibitors are essential cancer therapeutics, but therapy is limited by strong adverse effects. A tumor-targeting strategy for epidermal growth factor receptor (EGFR) inhibitors through hypoxia-mediated activation has now been developed. The Co^{III}-based prodrug showed selective hypoxic activation with release of the active EGFR inhibitor and potent anticancer activity in human xenograft models.

Electrocatalysis

A. K. Engstfeld, S. Brimaud,
R. J. Behm* ______________ **12936–12940**

Potential-Induced Surface Restructuring—The Need for Structural Characterization in Electrocatalysis Research

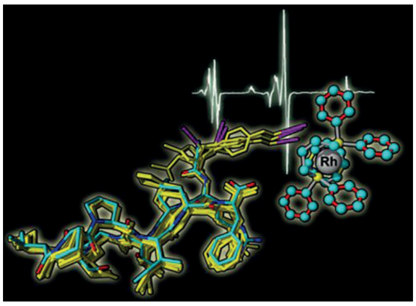
Take a closer look: Careful characterization of the surface of the electrodes is necessary to understand the molecular mechanism in electrocatalysis. This is shown for bulk CO oxidation on bimetallic PtRu electrodes. Scanning tunneling microscopy indicates a distinct restructuring of the electrodes during electrochemical measurements that leads to new highly active sites, which due to their low concentration are not evident in base voltammetry. Yet they, not PtRu sites as assumed previously, are responsible for the enhanced activity.



Hyperpolarization

G. Sauer, D. Nasu, D. Tietze,*
T. Gutmann, S. Englert, O. Avrutina,
H. Kolmar,*
G. Buntkowsky* ________ **12941–12945**

Effective PHIP Labeling of Bioactive Peptides Boosts the Intensity of the NMR Signal



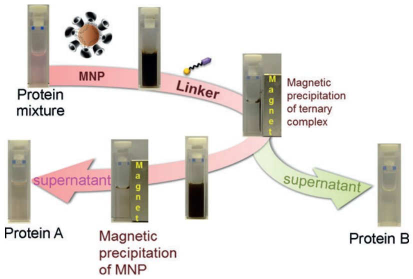
Hyperpolarization in bioactive peptides: Parahydrogen-induced polarization (PHIP) is achieved in a set of protease inhibitors. A substantial signal enhancement (SE) is realized through modular PHIP labels. The influence of the peptide's structural and functional elements on SE is elucidated.

Protein Separation

A. Samanta, B. J. Ravoo* **12946–12950**

Magnetic Separation of Proteins by a Self-Assembled Supramolecular Ternary Complex

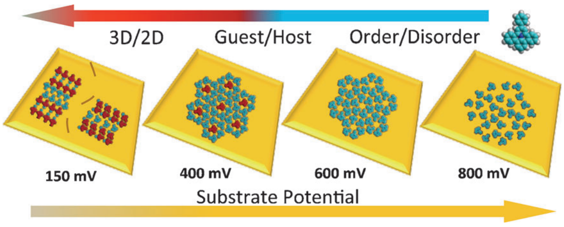
Separation by attraction: Proteins can be precipitated with a magnetic field by formation of a multivalent self-assembled complex from cyclodextrin-coated magnetic nanoparticles (MNPs), adamantane- and carbohydrate-functionalized noncovalent cross-linkers, and lectin. This supramolecular approach to purify proteins is highly selective and efficient.



3D Self-Assembly

K. Cui, K. S. Mali, O. Ivasenko, D. Wu,
X. Feng, M. Walter, K. Müllen,
S. De Feyter,*
S. F. L. Mertens* ________ 12951 – 12954

Squeezing, Then Stacking: From Breathing Pores to Three-Dimensional Ionic Self-Assembly under Electrochemical Control

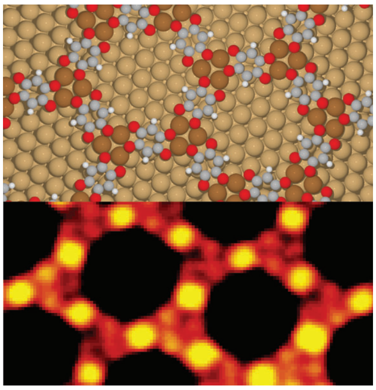


A reason to reorganize: When the substrate potential is tuned, a charged discoid polycyclic aromatic compound can be made to self-assemble to form a structure with open pores, an auto-host–guest structure, or a stratified bilayer (see picture).

Surface Coordination Networks

F. Bebensee, K. Svane, C. Bombis,
F. Masini, S. Klyatskaya, F. Besenbacher,
M. Ruben, B. Hammer,*
T. R. Linderoth* ________ 12955 – 12959

A Surface Coordination Network Based on Copper Adatom Trimers

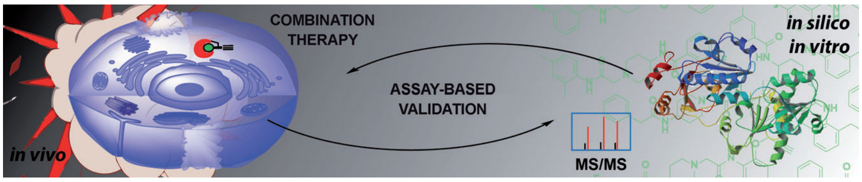


Cu-trimer nodes: Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, tetrahydroxybenzene (THB) is shown to dehydrogenate when adsorbed on a Cu(111) surface and form a highly reactive ligand. Density functional calculations confirm that the ligand stabilizes copper adatom trimers and creates a surface coordination network that is a two-dimensional analogue of metal–organic frameworks.

Cancer Sensitization

J. Eirich, S. Braig, L. Schyschka,
P. Servatius, J. Hoffmann, S. Hecht,
S. Fulda, S. Zahler, I. Antes, U. Kazmaier,
S. A. Sieber,*
A. M. Vollmar* ________ 12960 – 12965

A Small Molecule Inhibits Protein Disulfide Isomerase and Triggers the Chemosensitization of Cancer Cells



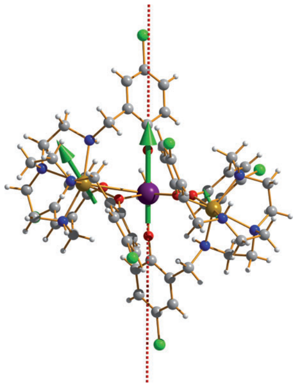
In the battle against the chemoresistance of cancer cells a screening approach has identified a novel compound class that sensitizes cancer cells in combination with etoposide. Proteomic target discovery revealed the reversible inhibition of protein disulfide isomerase as the molecular mechanism, which was further supported by cellular imaging studies and docking and biochemical assays in various cancer model systems.

Single-Molecule Magnets

J.-L. Liu, J.-Y. Wu, Y.-C. Chen, V. Mereacre, A. K. Powell,* L. Ungur,* L. F. Chibotaru, X.-M. Chen, M.-L. Tong* **12966 – 12970**

A Heterometallic Fe^{II}–Dy^{III} Single-Molecule Magnet with a Record Anisotropy Barrier

A record anisotropy barrier of 319 cm^{-1} was observed for a Fe^{II}-Dy^{III}-Fe^{II} single-molecule magnet, which possesses two asymmetric and distorted Fe^{II} ions and one quasi-D_{5h} Dy^{III} ion. The frozen magnetization of the Dy^{III} ions leads to the slowed relaxation of the Fe^{II} ions in the Mössbauer spectrum. Ab initio calculations suggest that tunneling is interrupted effectively thanks to the exchange doublets.



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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