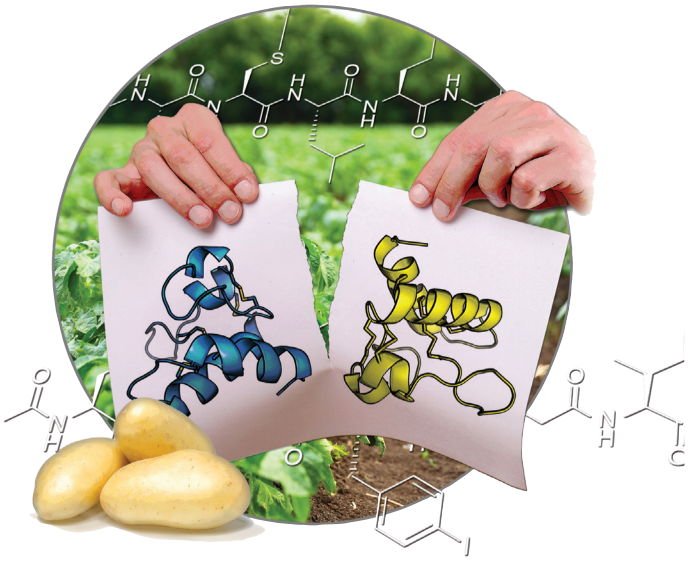
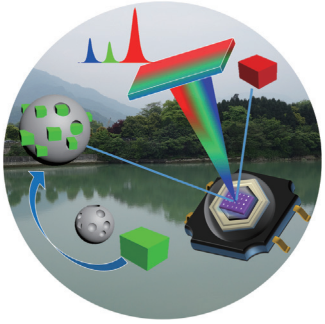
The antimicrobial protein snakin-1, …

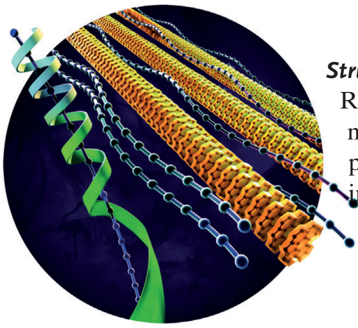


… isolated from potatoes, displays a uniquely folded three-dimensional structure held together by six disulfide bonds. In their Communication on page 7930 ff., M. A. Brimble, C. J. Squire, and co-workers describe how they used a radiation-damage-induced phasing (RIP) method to solve the racemic crystal structure of the protein, exploiting specific X-ray radiation induced breakage of an endogenous C–I bond.

Perovskite Quantum Dot LEDs

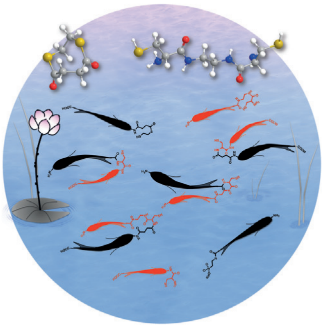
In their Communication on page 7924 ff., R. S. Liu et al. describe the generation of a white LED device through excitation of a silicone resin containing green mesoporous silica-$CsPbBr_3$ and red $CsPb(Br_{0.4}I_{0.6})_3$ perovskite quantum dots with a blue InGaN chip.





Structure Elucidation

R. Seshadri, F. Wudl et al. report in their Communication on page 8032 ff. the crystal structure of a pyrroloperylene–iodine complex, which shows infinite polyiodide chains.



Protein–Protein Interactions

In their Communication on page 8129 ff., Y.-W. Wu and co-workers use C-terminus to C-terminus and N-terminus to N-terminus ligation to trap protein–protein interactions.

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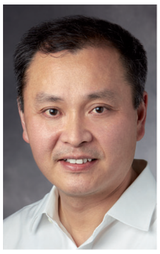
Service

Author Profile

"My favorite author (fiction) is Roberto Bolaño.
My favorite food is pies …"
This and more about Michael Greaney can be found on page 7888.

News



H. Dai

H. L. Ploegh

M. S. Sanford

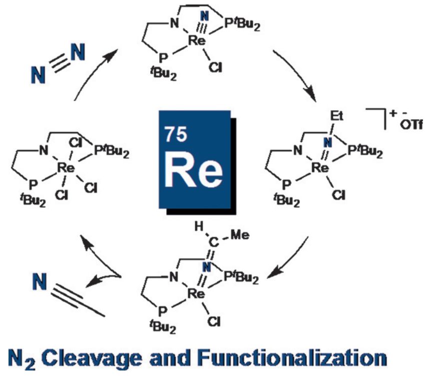
A. Pfaltz

K. Kohse-Höinghaus

Books

Highlights

Nitrogen Fixation

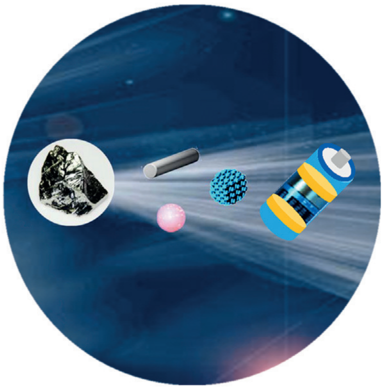


Early transition metals are well known to catalyze the cleavage and functionalization of N_2. In this Highlight, recent work showing that a rhenium catalyst is also capable of carrying out this difficult task is summarized, and a synthetic cycle for the stoichiometric incorporation of atmospheric N_2 into acetonitrile is presented.

Reviews

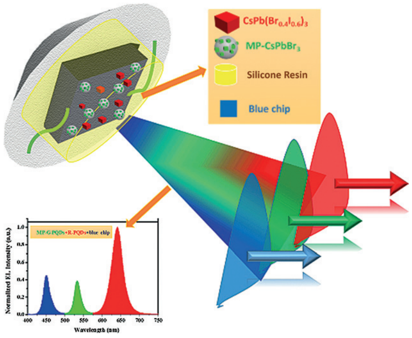
Germanium-Based Batteries

Germane germanium: Germanium has emerged as an important material for next-generation energy-storage devices. The elaborate structures and unique nature of Ge-based materials impart excellent electrochemical performance. This Review summarizes the progress in Ge-based materials for rechargeable energy-storage devices and suggests future research directions.



Communications

Perovskite Quantum Dot LEDs



Points of light: Green $CsPbBr_3$ perovskite quantum dots (PQDs), embedded in mesoporous silica (MP), were mixed with red $CsPb(Br_{0.4}I_{0.6})_3$ quantum dots in a silicone resin and placed on an InGaN blue chip. The green and red QDs were excited by blue light with $\lambda = 450$ nm. The resulting PQD white light emitting diode (LED) exhibits a wide color gamut because of its narrow emission wavelength.

Frontispiece

For the USA and Canada:
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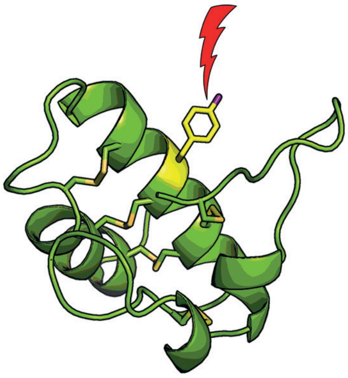
Protein Structures

H. Yeung, C. J. Squire,* Y. Yosaatmadja, S. Panjikar, G. López, A. Molina, E. N. Baker, P. W. R. Harris, M. A. Brimble* ______ **7930 – 7933**

Radiation Damage and Racemic Protein Crystallography Reveal the Unique Structure of the GASA/Snakin Protein Superfamily



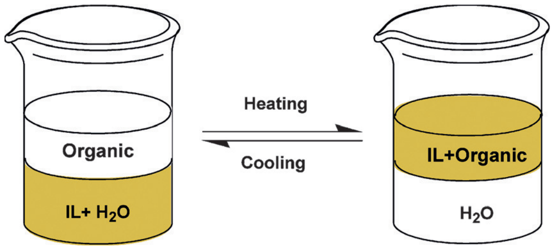
Ripping into quasiracemic crystals: The structure of the 63-residue antimicrobial protein snakin-1, the first structure of the GASA/snakin superfamily, has been determined using total chemical synthesis, racemic protein X-ray crystallography, and radiation-damage-induced phasing. The protein adopts a unique fold containing six disulfide crosslinks and presenting a distinct electrostatic surface.

Front Cover

Ionic Liquids

W. Yao, H. Wang, G. Cui, Z. Li, A. Zhu, S. Zhang, J. Wang* ______ **7934 – 7938**

Tuning the Hydrophilicity and Hydrophobicity of the Respective Cation and Anion: Reversible Phase Transfer of Ionic Liquids

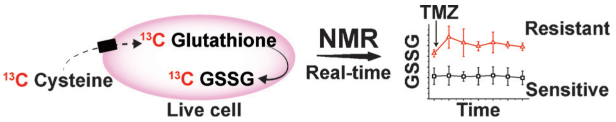


“Smart” liquids: Functionalized ionic liquids (ILs) were developed and show reversible phase transfer between water and organics upon heating and cooling owing to the conformation change of the PEG chain of the IL upon the change of temperature. A highly efficient, recyclable, and controllable CuI-catalyzed cycloaddition reaction was achieved by using ILs as the entrainer and catalyst activator, as well as the controller of the reaction.

Redox Homeostasis

X. Jin, S. Kang, S. Tanaka, S. Park* ______ **7939 – 7942**

Monitoring the Glutathione Redox Reaction in Living Human Cells by Combining Metabolic Labeling with Heteronuclear NMR

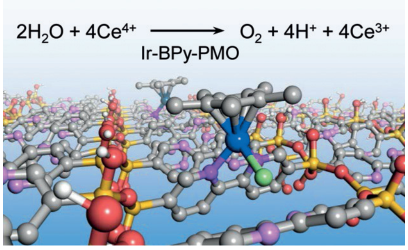


Oxidation counter measures: The glutathione (GSH) redox reaction is critical for defense against cellular reactive oxygen species. Endogenous synthesis of GSH from isotope-labeled cysteine was exploited to enable measurement of the intracellular GSH redox reaction in live cells by NMR spectroscopy. This enabled real-time monitoring of GSH redox reactions in cells resistant to the glioblastoma drug temozolomide (TMZ), and the results suggest a possible new mechanism of resistance.

Heterogeneous Catalysis

X. Liu, Y. Maegawa, Y. Goto, K. Hara, S. Inagaki* ______ **7943 – 7947**

Heterogeneous Catalysis for Water Oxidation by an Iridium Complex Immobilized on Bipyridine-Periodic Mesoporous Organosilica

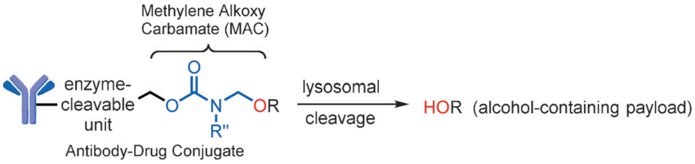


Uncharted waters: Using bipyridine-periodic mesoporous organosilica (BPy-PMO) as a solid chelating ligand, efficient heterogeneous iridium catalysts (Ir-Bpy-PMO) for water oxidation were obtained. This catalyst had an activity comparable to the analogous homogeneous iridium catalyst and showed one order of magnitude higher activity than that of the previously reported heterogeneous iridium catalysts.

Drug Delivery

R. V. Kolakowski,* K. T. Haelsig,
K. K. Emmerton, C. I. Leiske,
J. B. Miyamoto, J. H. Cochran, R. P. Lyon,
P. D. Senter, S. C. Jeffrey* **7948 – 7951**

The Methylene Alkoxy Carbamate Self-Immolative Unit: Utilization for the Targeted Delivery of Alcohol-Containing Payloads with Antibody–Drug Conjugates

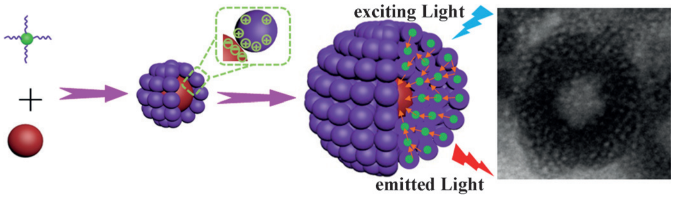


MAC out: A strategy for the conjugation of alcohol-containing payloads to antibodies has been developed using the methylene alkoxy carbamate (MAC) self-immolative unit. A series of MAC β-glucuronide model constructs were prepared and demonstrated high stability at physiological pH, and efficiently released alcohol drug surrogates under the action of β-glucuronidase.

Photochemistry

Y. N. Liu, J. Y. Jin, H. P. Deng, K. Li,
Y. L. Zheng, C. Y. Yu,
Y. F. Zhou* **7952 – 7957**

Protein-Framed Multi-Porphyrin Micelles for a Hybrid Natural–Artificial Light-Harvesting Nanosystem



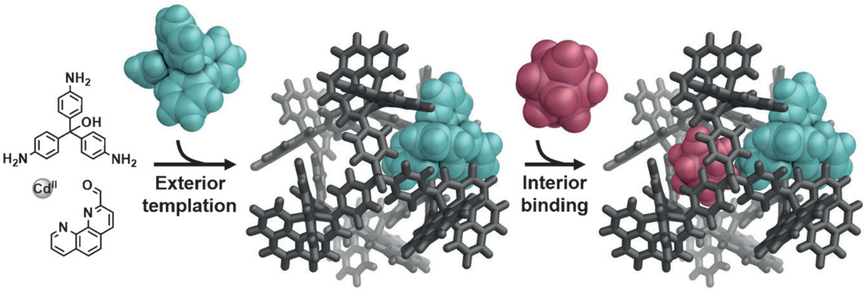
Nanopomegranate: A micellar light-harvesting nanosystem was prepared consisting of one phycocyanin protein acceptor in the core and many porphyrin donors packed in a pomegranate-like manner in the shell. The system inhibited donor self-quenching effectively and displayed efficient transfer of excitation energy in water.

Host–Guest Chemistry

F. J. Rizzuto, W.-Y. Wu, T. K. Ronson,
J. R. Nitschke* **7958 – 7962**

Peripheral Templation Generates an $M^{II}_6L_4$ Guest-Binding Capsule

Inside Cover

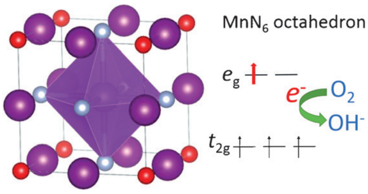


Are you in or out? A new series of $M^{II}_6L_4$ pseudo-octahedra can bind *endo* and *exo* guests concurrently; however, only in the presence of a peripherally bound tetraphenylborate anion do the shown subcomponents assemble to form their intended architecture. This templated structure can then encapsulate a carborate anion in its central cavity.

Oxygen Reduction

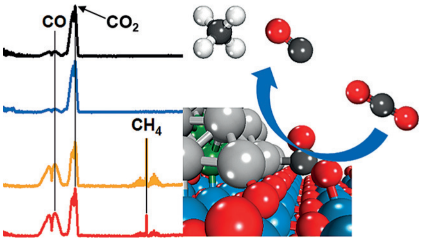
A. Miura,* C. Rosero-Navarro,
Y. Masubuchi, M. Higuchi, S. Kikkawa,
K. Tadanaga **7963 – 7967**

Nitrogen-Rich Manganese Oxynitrides with Enhanced Catalytic Activity in the Oxygen Reduction Reaction



The catalytic activities of manganese oxynitrides with different nitrogen contents in the oxygen reduction reaction (ORR) in alkaline solution were investigated. An increase in the nitrogen content of rock-salt-type manganese oxynitrides increases the valence of manganese and leads to enhanced catalytic activity.

By simply changing the oxide support, the selectivity of a metal–oxide catalyst can be tuned. For the hydrogenation of CO_2 over PtCo bimetallic catalysts supported on different reducible oxides, replacing a TiO_2 support by CeO_2 or ZrO_2 selectively strengthens the binding of C,O-bound and O-bound species at the PtCo–oxide interface, thereby leading to a different product selectivity.



Supported Catalysts

S. Kattel, W. Yu, X. Yang, B. Yan, Y. Huang, W. Wan, P. Liu,* J. G. Chen* **7968 – 7973**

CO_2 Hydrogenation over Oxide-Supported PtCo Catalysts: The Role of the Oxide Support in Determining the Product Selectivity

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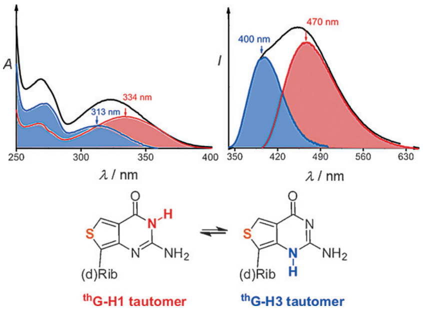

Channel surfing: A faithful isomorphic guanosine analogue, thG, exists in two emissive ground-state tautomers. Both forms are present in single-stranded oligonucleotides and show sensitivity to protein binding, while only the thG-H1 tautomer is favorable in duplexes. These tautomers and their distinct photophysics are shown to be highly valuable for analyzing G residues in oligonucleotides and their complexes. (d)Rib = 2′-deoxy-D-ribose.

Nucleic Acids

M. Sholokh, R. Improta, M. Mori, R. Sharma, C. Kenfack, D. Shin, K. Voltz, R. H. Stote, O. A. Zaporozhets, M. Botta, Y. Tor,* Y. Mély* **7974 – 7978**

Tautomers of a Fluorescent G Surrogate and Their Distinct Photophysics Provide Additional Information Channels

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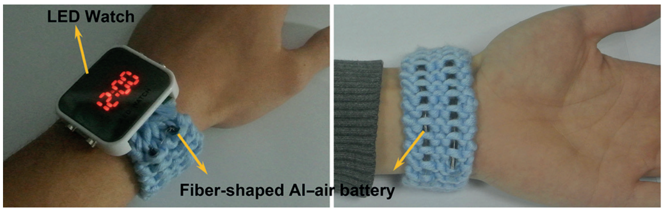

Wear it! A family of fiber-shaped aluminum–air batteries with high electrochemical performance was created by designing cross-stacked carbon-nanotube/Ag sheets as the air cathode to enhance gas diffusion, catalyze oxygen reduction, and promote charge transport. The batteries are flexible and stretchable, and can be woven into various textiles (see photographs of an LED watch powered by two fiber-shaped Al–air batteries connected in series).

Flexible Batteries

Y. Xu, Y. Zhao, J. Ren, Y. Zhang, H. Peng* **7979 – 7982**

An All-Solid-State Fiber-Shaped Aluminum–Air Battery with Flexibility, Stretchability, and High Electrochemical Performance

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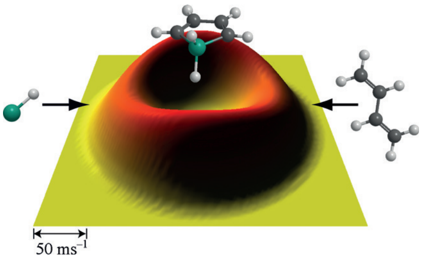


Silole (1-silacyclopenta-2,4-diene) was obtained by the bimolecular reaction of the simplest silicon-bearing radical, silylidyne (SiH), with 1,3-butadiene (C_4H_6) in the gas phase under single-collision conditions. The picture shows the flux contour map of this crossed-beam reaction, which leads to silole by loss of atomic hydrogen.

Gas-Phase Reactions

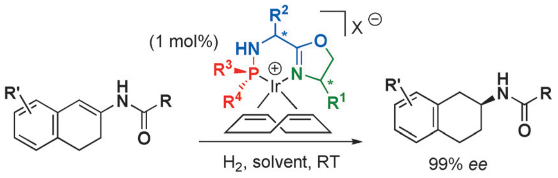
T. Yang, B. B. Dangi, A. M. Thomas, B. J. Sun, T. J. Chou, A. H. H. Chang,* R. I. Kaiser* **7983 – 7987**

Gas-Phase Synthesis of 1-Silacyclopenta-2,4-diene

Asymmetric Hydrogenation

E. Salomó, S. Orgué, A. Riera,*
X. Verdaguer* ———— 7988 – 7992

Highly Enantioselective Iridium-Catalyzed Hydrogenation of Cyclic Enamides

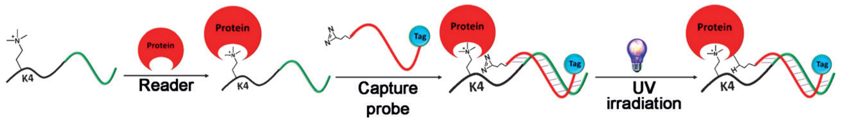


Diversity matters: Three chiral components (an amino acid, an amino alcohol, and a P-stereogenic phosphine) form the novel MaxPHOX ligand template and thus enable the synthesis of catalysts with broad structural diversity. From a small library of MaxPHOX–Ir complexes, two catalysts were identified for the highly enantioselective hydrogenation of enamides derived from α- and β-tetralones (see scheme).

Epigenetics

X. Bai, C. Lu, J. Jin, S. Tian, Z. Guo,
P. Chen, G. Zhai, S. Zheng, X. He, E. Fan,
Y. Zhang, K. Zhang* ———— 7993 – 7997

Development of a DNA-Templated Peptide Probe for Photoaffinity Labeling and Enrichment of the Histone Modification Reader Proteins

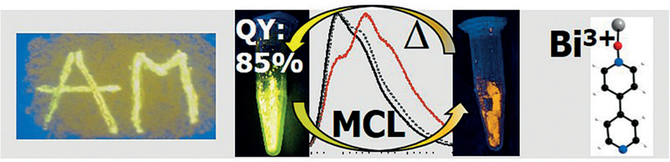


Do you read me? A DNA-templated peptide probe was developed to identify the reader proteins of histone post-translational modifications. The method, based on DNA-templated chemistry and photo-crosslinking technologies, can label and enrich the reader of H3K4me3 (histone H3 lysine 4 trimethylation) in a whole cell lysate.

Mechanochromic Materials

O. Toma, M. Allain, F. Meinardi, A. Forni,*
C. Botta,* N. Mercier* ———— 7998 – 8002

Bismuth-Based Coordination Polymers with Efficient Aggregation-Induced Phosphorescence and Reversible Mechanochromic Luminescence

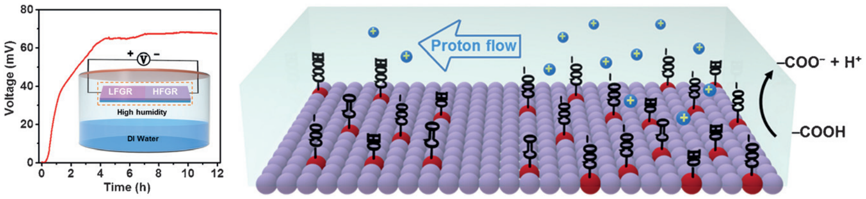


Coordination polymers based on bismuth(III) and *N*-oxide-4,4′-bipyridine strongly phosphoresce in the solid state with quantum yields of up to 85%, which is likely due to aggregation-induced emission. These materials also show reversible mechanochromic luminescence (MCL).

Electrochemistry

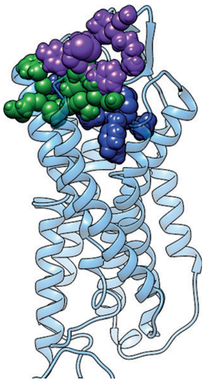
K. Liu, P. Yang, S. Li, J. Li, T. Ding, G. Xue,
Q. Chen, G. Feng, J. Zhou* 8003 – 8007

Induced Potential in Porous Carbon Films through Water Vapor Absorption



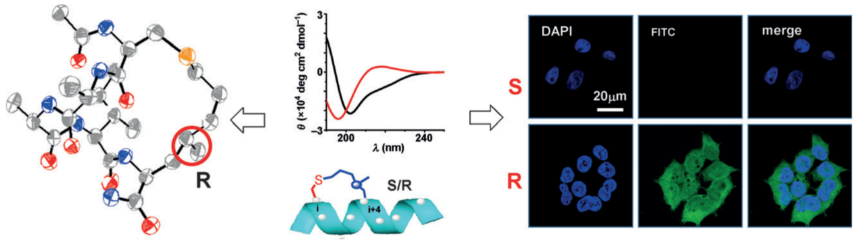
Sustainable electrical potential can be induced by water vapor adsorption on a piece of porous carbon film with two sides bearing different functional-group contents (LFGR and HFGR; see figure). Experimental results and theoretical calculations show that the induced potential arises from free proton transfer that is driven by the difference in proton concentration caused by an imbalance in the proportion of oxygen-containing functional groups.

Molecular Dynamics



Three distinct binding sites are revealed by molecular-dynamics simulations with metadynamics enhanced sampling for arginine vasopressin (AVP) within its V_2 receptor (V_2R). Two of these, the vestibule (magenta) and intermediate (green) sites, block (antagonize) the receptor, and the third is the orthosteric activation (agonist) site (blue). The resulting three-site mechanism separates agonists from antagonists and explains subtype selectivity.

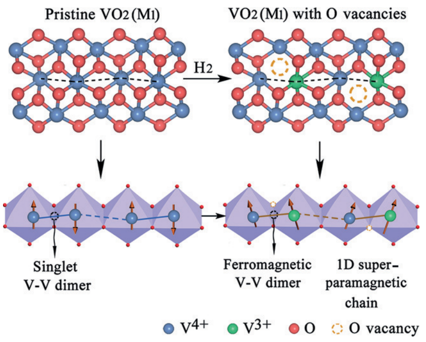
Peptide Modulators



Chirality induced helicity: A precisely positioned in-tether carbon chiral center was able to modulate the helicity, cell permeability, and target binding affinity of a peptide. This study provides an excellent method for studying the relationship between the conformation and biochemical/biophysical properties of peptides.

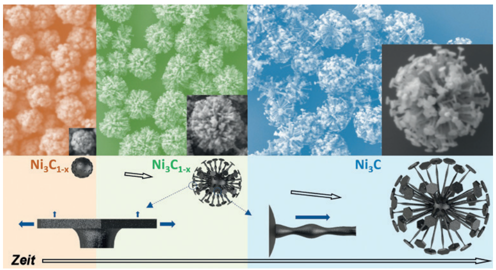
Superparamagnetism

VIP



Spin regulation: The spin structure of the one-dimensional V–V atomic chains in monoclinic VO_2 nanowires was modified by hydrogen treatment, which introduced V^{3+} ions into the 1D zigzag V–V chains, triggering the formation of ferromagnetically coupled V^{3+}–V^{4+} dimers. The new structure consists of 1D superparamagnetic chains and shows large negative magnetoresistance at room temperature.

Nanostructures

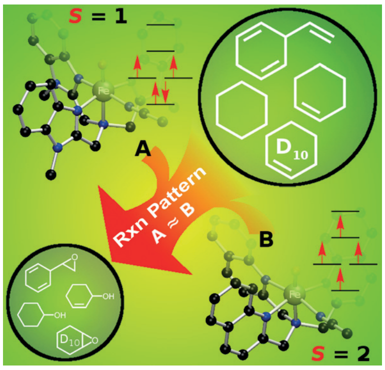


Dandelion clocks: Highly hierarchical but nonporous nanostructures of nickel carbide (Ni_3C) with a unique "dandelion" morphology are prepared. The time evolution of these nanostructures suggests a mechanism for their formation. This type of hierarchical nanocrystal, which provides large accessible specific surface area, can be valuable in numerous catalytic and electrocatalytic applications.

Bioinorganic Chemistry

S. H. Bae, M. S. Seo, Y.-M. Lee, K.-B. Cho, W.-S. Kim, W. Nam* ______ 8027 – 8031

Mononuclear Nonheme High-Spin ($S=2$) versus Intermediate-Spin ($S=1$) Iron(IV)–Oxo Complexes in Oxidation Reactions



Biomimetics: The reactivities of synthetic mononuclear nonheme high-spin ($S=2$) and intermediate-spin ($S=1$) iron(IV)–oxo complexes were studied. The complexes were found to exhibit similar reaction mechanisms and reactivity patterns in a C–H bond activation reaction of alkanes, the oxidation of cyclohexene, and the epoxidation of styrene.

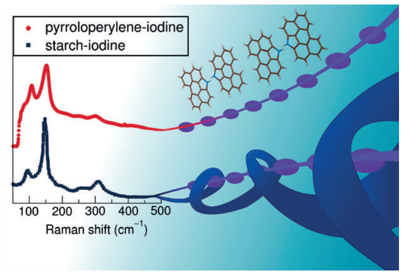
Structure Elucidation

S. Madhu, H. A. Evans, V. V. T. Doan-Nguyen, J. G. Labram, G. Wu, M. L. Chabinyc, R. Seshadri,* F. Wudl* ______ 8032 – 8035

Infinite Polyiodide Chains in the Pyrroloperylene–Iodine Complex: Insights into the Starch–Iodine and Perylene–Iodine Complexes

Inside Back Cover

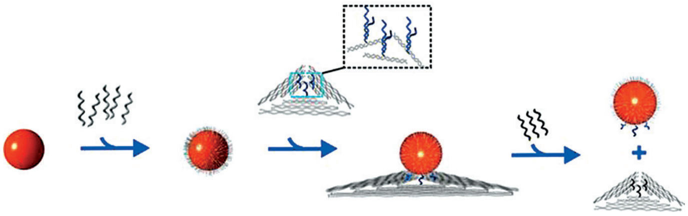
The crystal structure of the pyrroloperylene–iodine complex (with a formula close to pyrroloperylene–$I_{2.2}$) has been solved. The structure contains infinite polyiodide chains, the Raman spectrum of which resembles that of the famous starch–iodine complex, thus casting light on a historical puzzle (see picture). The complex displays nearly metallic conductivity and some signatures of a Peierls distortion of the chains at 150 K.



DNA Nanoimprinting

Y. Zhang, J. Chao, H. Liu,* F. Wang, S. Su, B. Liu, L. Zhang, J. Shi, L. Wang, W. Huang, L. Wang,* C. Fan* ______ 8036 – 8040

Transfer of Two-Dimensional Oligonucleotide Patterns onto Stereocontrolled Plasmonic Nanostructures through DNA-Origami-Based Nanoimprinting Lithography

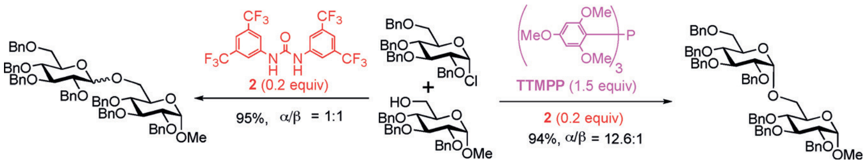


The transfer of knowledge: DNA origami acts as a copy-machine-like platform to precisely decorate the surface of gold nanoparticles (AuNPs) with DNA anchor strands. These strands are subsequently employed to construct discrete AuNP clusters with designed chirality.

Glycosylation

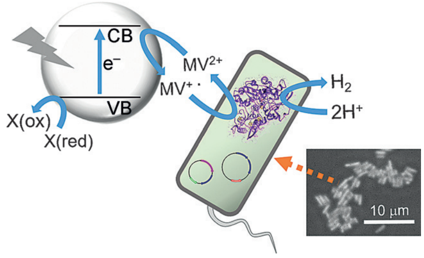
L. Sun, X. Wu, D.-C. Xiong, X.-S. Ye* ______ 8041 – 8044

Stereoselective Koenigs–Knorr Glycosylation Catalyzed by Urea

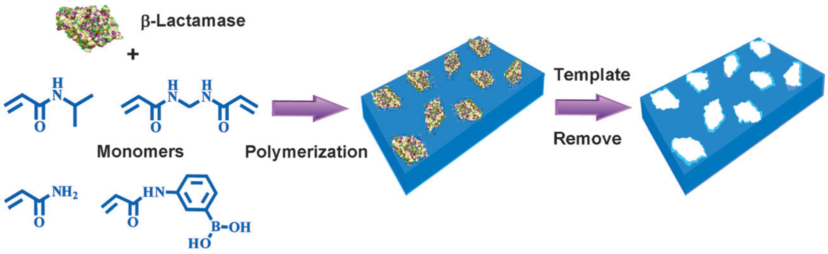


Sugar, sugar: Stereoselective Koenigs–Knorr glycosylation under urea catalysis is described. This method is characterized by urea-mediated hydrogen-bond activation and subsequent glycosylation with glycosyl chlorides or bromides. Excellent yields and high anomeric selectivity can be achieved in most cases, and the α-stereoselectivity when using perbenzylated glucosyl donors is greatly improved by the addition of TTMPP.

An inorganic–bio hybrid photocatalyst for photocatalytic H_2 production was developed. A biocatalyst involving whole-cell recombinant *E. coli* cells expressing genes encoding [FeFe]-hydrogenase and relevant maturases (rectangle) was combined with TiO_2 (circle) via the methylviologen $MV^{2+}/MV^{+\bullet}$ couple.

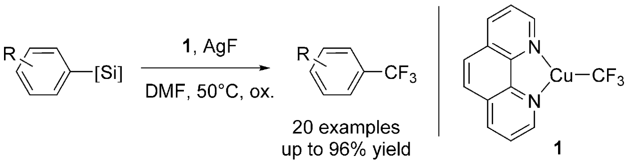


Biocatalysis



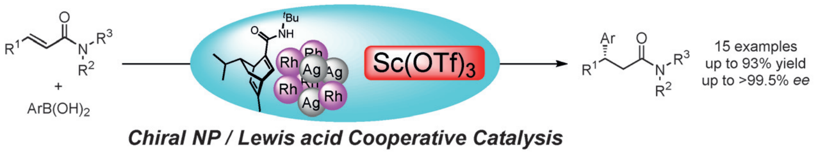
New hope for old drugs: β-Lactamase was used as a template molecule to fabricate a stimuli-responsive imprinted hydrogel (see picture). The hydrogel could trap β-lactamase excreted by drug-resistant bacteria, thus making the bacteria sensitive to conventional antibiotics. The thermoresponsive “binding sites” on the hydrogel could then be abolished to release β-lactamase for the degradation of antibiotic residues.

Molecular Imprinting



All about the source: The first trifluoromethylation of arylsilanes occurs with $[(phen)CuCF_3]$ as the CF_3 source and AgF as the activator under mild, oxidative conditions; the choice of both reagents was shown to be crucial for the reported transformation. The method shows high functional-group compatibility, and late-stage functionalization of active pharmaceutical ingredients is possible. DMF = *N*,*N*-dimethylformamide, phen = 9,10-phenanthroline.

Cross-Coupling



It can abide amides: Cooperative catalysts consisting of heterogeneous chiral Rh/Ag nanoparticles and a metal Lewis acid, $Sc(OTf)_3$, show high catalytic activities and outstanding enantioselectivities for asymmetric 1,4-addition reactions of arylboronic acids with α,β-unsaturated amides. The reaction is regarded as challenging owing to the low reactivity of the amide substrates.

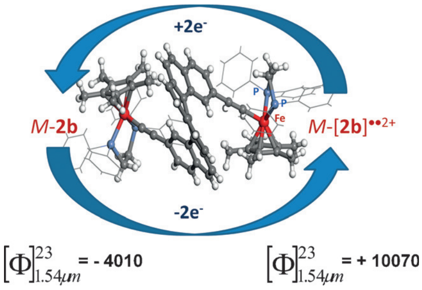
Asymmetric Catalysis

Organometallic Helicenes

C. Shen, G. Loas, M. Srebro-Hooper, N. Vanthuyne, L. Toupet, O. Cador, F. Paul, J. T. López Navarrete, F. J. Ramírez, B. Nieto-Ortega, J. Casado, J. Autschbach,* M. Vallet, J. Crassous* ______ **8062 – 8066**

Iron Alkynyl Helicenes: Redox-Triggered Chiroptical Tuning in the IR and Near-IR Spectral Regions and Suitable for Telecommunications Applications

Chiroptical switch: Iron alkynyl[6]helicene complexes have been synthesized. Vibrational circular dichroism and Raman optical activity spectra are used to investigate how the oxidation of the complexes to form radical cations influences their vibrational modes. The optical rotation of these chiral species ($[\Phi]^{23}_{1.54\,\mu m}$; measured in $^\circ\,cm^2\,dmol^{-1}$) changes sign at wavelengths typically used for telecommunications (1.54 µm).

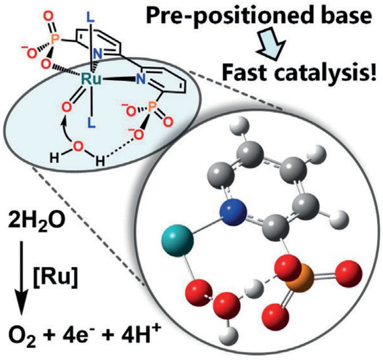


Water Oxidation

Y. Xie, D. W. Shaffer, A. Lewandowska-Andralojc, D. J. Szalda, J. J. Concepcion* ______ **8067 – 8071**

Water Oxidation by Ruthenium Complexes Incorporating Multifunctional Bipyridyl Diphosphonate Ligands

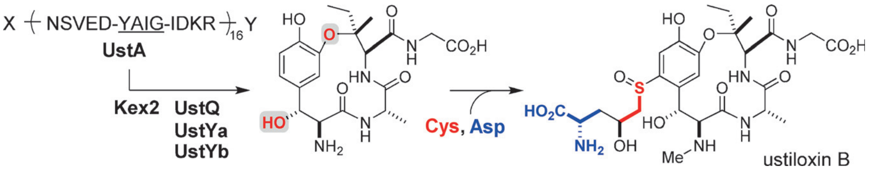
Breaking down barriers: Multifunctional bipyridyl diphosphonate ligands provide redox-potential leveling through charge compensation and σ donation to allow easy access to high oxidation states of ruthenium-based water oxidation catalysts (see structure; L = picoline or isoquinoline). They also shuttle protons in and out of the catalytic site, thus reducing activation barriers for proton-coupled processes.



Biosynthesis

Y. Ye, A. Minami, Y. Igarashi, M. Izumikawa, M. Umemura, N. Nagano, M. Machida, T. Kawahara, K. Shin-ya, K. Gomi, H. Oikawa* ______ **8072 – 8075**

Unveiling the Biosynthetic Pathway of the Ribosomally Synthesized and Post-translationally Modified Peptide Ustiloxin B in Filamentous Fungi

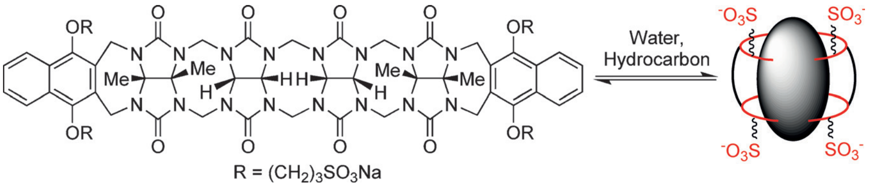


The biosynthetic machinery for the fungal ribosomally synthesized and post-translationally modified peptide (RiPP) ustiloxin was elucidated by gene inactivation, heterologous expression, and in vitro studies. The details include formation of a cyclic peptide by novel oxidases harboring a DUF3328 motif and unique modification reactions for construction of the side chain on the aromatic ring. These findings set the stage for elucidating the biosynthesis of fungal RiPPs.

Host–Guest Systems

X. Lu, L. Isaacs* ______ **8076 – 8080**

Uptake of Hydrocarbons in Aqueous Solution by Encapsulation in Acyclic Cucurbit[*n*]uril-Type Molecular Containers

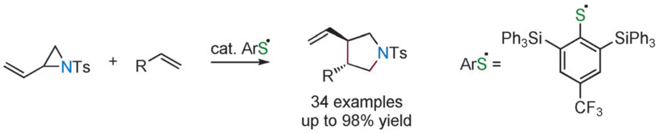


Be my guest: Acyclic cucurbit[*n*]uril (CB[*n*]) type containers are more efficient than macrocyclic CB[7] and CB[8] at promoting the efficient uptake of poorly water-soluble hydrocarbons into aqueous solution through formation of complexes. The hydrophobic driving force for complexation of aliphatic, alicyclic, and polycyclic hydrocarbons inside acyclic CB[*n*] rivals that of CB[7] and CB[8].

Radical Reactions

T. Hashimoto, K. Takino, K. Hato,
K. Maruoka* ________ **8081 – 8085**

A Bulky Thiyl-Radical Catalyst for the [3+2] Cyclization of *N*-Tosyl Vinylaziridines and Alkenes

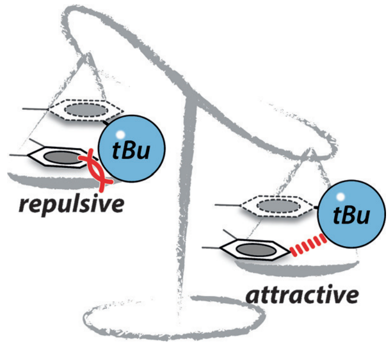


Bulk it up: A thiyl-radical-catalyzed cyclization reaction of *N*-tosyl vinylaziridines and alkenes was developed as a new synthetic method for the generation of substituted pyrrolidines (see scheme). The key to making this process accessible to a broad range of substrates is the use of a sterically demanding thiyl radical to prevent the undesired degradation of the catalyst.

Supramolecular Chemistry

J. Hwang, P. Li, M. D. Smith,
K. D. Shimizu* ________ **8086 – 8089**

Distance-Dependent Attractive and Repulsive Interactions of Bulky Alkyl Groups

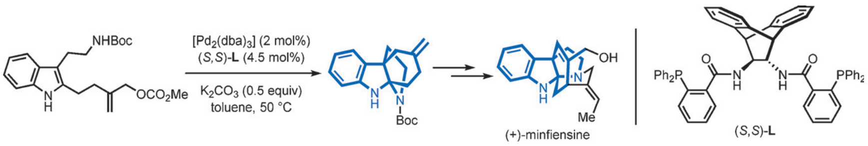


Bulk up: Bulky alkyl groups can form either stabilizing or destabilizing interactions depending on their relative distance from the molecular surface of interaction. The presented data point to the refinement of the classical paradigm for steric effects simply based on the molecular size.

Natural Products

Z.-X. Zhang, S.-C. Chen,
L. Jiao* ________ **8090 – 8094**

Total Synthesis of (+)-Minfiensine: Construction of the Tetracyclic Core Structure by an Asymmetric Cascade Cyclization

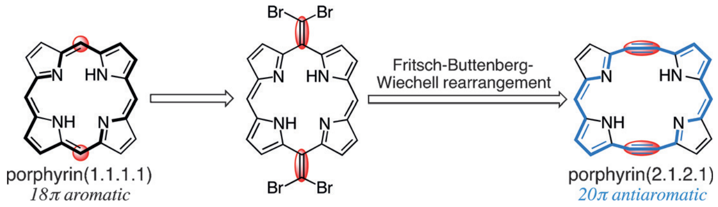


All at once: A palladium-catalyzed asymmetric cascade cyclization enabled one-step construction of the tetracyclic core framework of the indole alkaloid (+)-minfiensine. A palladium-catalyzed Heck-type cyclization completed its total synthesis efficiently.

Expanded Porphyrins

M. Umetani, T. Tanaka,* T. Kim, D. Kim,*
A. Osuka* ________ **8095 – 8099**

Double Ring Expansion from an Aromatic [18]Porphyrin(1.1.1.1) to an Antiaromatic [20]Porphyrin(2.1.2.1)

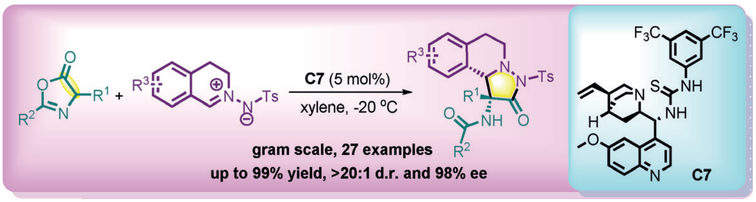


Building bridges: A reaction sequence involving oxidation with PbO_2, a Corey–Fuchs reaction, and Fritsch–Buttenberg–Wiechell rearrangement allowed double ring expansion from a porphyrin to a tetradehydro[20]porphyrin(2.1.2.1) (see scheme), which was reduced to a didehydro[20]porphyrin(2.1.2.1) and a [20]porphyrin(2.1.2.1). These planar porphyrins exhibited 20π antiaromatic character.

Organocatalysis

X. Liu, Y. Wang, D. Yang, J. Zhang, D. Liu,*
W. Su* ________________ 8100 – 8103

Catalytic Asymmetric Inverse-Electron-Demand 1,3-Dipolar Cycloaddition of C,N-Cyclic Azomethine Imines with Azlactones: Access to Chiral Tricyclic Tetrahydroisoquinolines

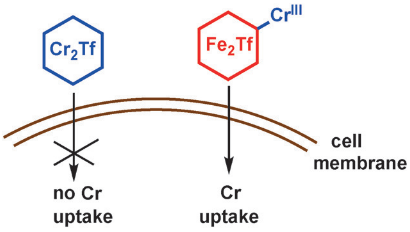


A bifunctional organocatalyst is employed to mediate the title reaction. The process affords a series of C1-substituted tetrahydroisoquinolines, featuring a pyrazolidinone scaffold, with excellent yields and stereoselectivities. Ts = 4-toluenesulfonyl.

Trace Elements

A. Levina, T. H. N. Pham,
P. A. Lay* ________________ 8104 – 8107

Binding of Chromium(III) to Transferrin Could Be Involved in Detoxification of Dietary Chromium(III) Rather than Transport of an Essential Trace Element



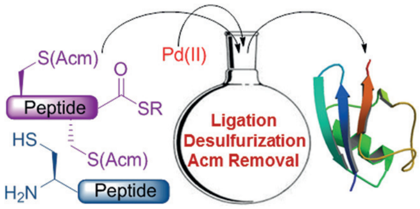
You shall not pass: Cr^{III} has been proposed to be an essential trace element and has been postulated to be taken up through binding to the Fe transport protein transferrin (Tf). However, binding of Cr^{III} to vacant Fe^{III} binding sites on transferrin was found to block rather than promote cellular accumulation of Cr^{III}. It thus appears that this process could in fact be a protective mechanism against Cr^{III} toxicity rather than a mechanism of Cr^{III} uptake.

Protein Synthesis

S. K. Maity, M. Jbara, S. Laps,
A. Brik* ________________ 8108 – 8112

Efficient Palladium-Assisted One-Pot Deprotection of (Acetamidomethyl)-Cysteine Following Native Chemical Ligation and/or Desulfurization To Expedite Chemical Protein Synthesis

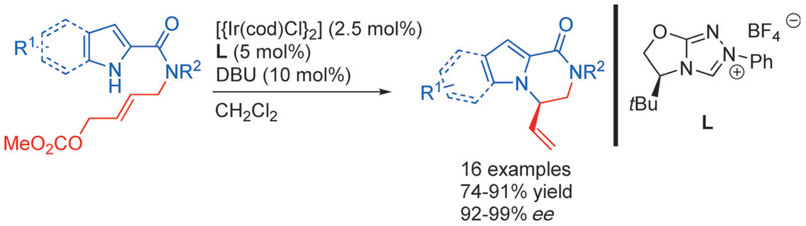
Three in one: An efficient method for the deprotection of (acetamidomethyl)cysteine using Pd complexes in aqueous medium was introduced and applied to the one-pot assembly of three peptides. UBL-5 was thus synthesized by one-pot native chemical ligation, desulfurization, and removal of the acetamidomethyl (Acm) group while keeping its two native Cys residues intact.



Asymmetric Catalysis

K.-Y. Ye, Q. Cheng, C.-X. Zhuo, L.-X. Dai,
S.-L. You* ________________ 8113 – 8116

An Iridium(I) N-Heterocyclic Carbene Complex Catalyzes Asymmetric Intramolecular Allylic Amination Reactions

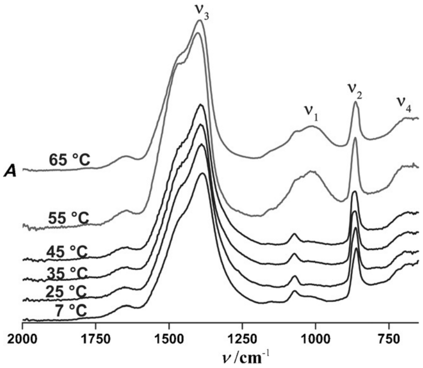


A chiral iridium(I) N-heterocyclic carbene complex catalyzes highly enantioselective intramolecular allylic amination reactions. This method provides facile access to biologically important enantioenriched indolopiperazinones and piperazinones in good yields. Mechanistic investigations reveal that the C–H activation occurs at the position *ortho* to the N-aryl group of the ligand.

Amorphous Calcium Carbonate

M. Farhadi-Khouzani, D. M. Chevrier, P. Zhang, N. Hedin, D. Gebauer* ———— 8117 – 8120

Water as the Key to Proto-Aragonite Amorphous $CaCO_3$



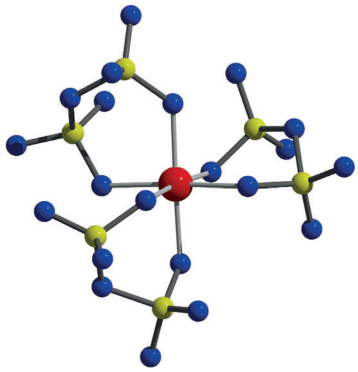
The binding of water molecules above 45 °C at pH 9.80 induces dipole moments across carbonate ions in proto-aragonite amorphous $CaCO_3$ as in the anhydrous crystalline polymorph aragonite, where the dipole moments are due to the crystal structure. This key role of water was inferred from IR (see picture) as well as NMR spectroscopy in combination with Ca K-edge EXAFS analysis.

Pd^{4+} Complexes

J. Bruns,* D. van Gerven, T. Klüner, M. S. Wickleder* ———— 8121 – 8124

Palladium(IV) in an Oxoanionic Environment: The XeF_2-Assisted Synthesis of $[Pd(S_2O_7)_3]^{2-}$

XeF_2 is the key: The first compound containing Pd^{4+} in an exclusively oxoanionic environment was obtained under harsh conditions from the reaction of $K_2[PdCl_6]$, SO_3, and XeF_2. In the structure of $K_2[Pd(S_2O_7)_3]$, stabilization of the Pd^{4+} ion is achieved by the coordination of three chelating disulfate anions. The structure of the complex is well reproduced by quantum chemical calculations.

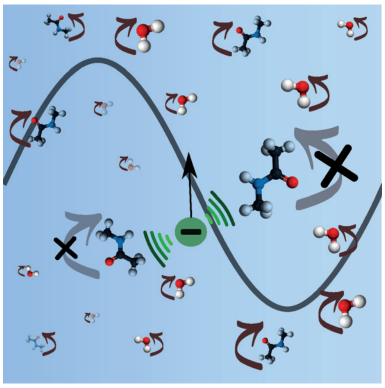


Ion–Amide Interactions

V. Balos, H. Kim, M. Bonn, J. Hunger* ———— 8125 – 8128

Dissecting Hofmeister Effects: Direct Anion–Amide Interactions Are Weaker than Cation–Amide Binding

Negative vibes: Anions interact directly with amide groups, and the interaction strength follows the direct Hofmeister series. However, the binding of anions to the amide group is weaker than that of comparable monovalent cations.

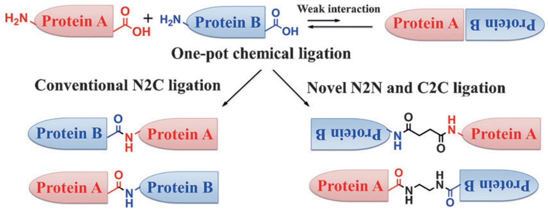


Protein–Protein Interactions

L. Zhao, C. Ehrt, O. Koch,
Y.-W. Wu* ________________ **8129 – 8133**

One-Pot N2C/C2C/N2N Ligation To Trap Weak Protein–Protein Interactions

Back Cover



Like-to-like: Weak transient protein–protein interactions play an important role in cellular dynamics. Novel C-terminus to C-terminus (C2C) and N-terminus to N-terminus (N2N) chemical protein ligation strategies give rise to a facile method for trapping weak protein–protein interactions in an unbiased manner using proximity-induced chemical ligations.

Supporting information is available on www.angewandte.org (see article for access details).

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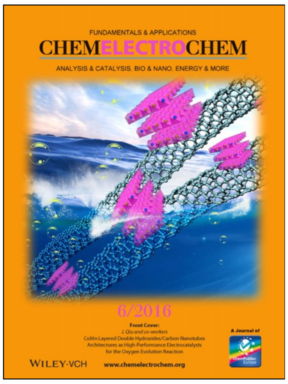

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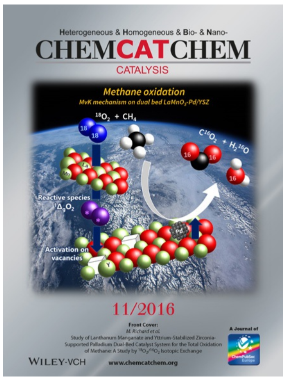

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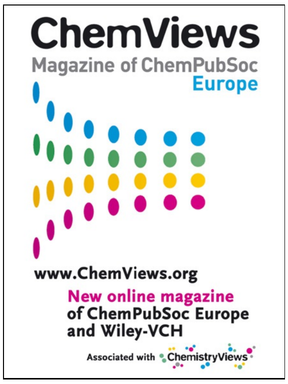

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