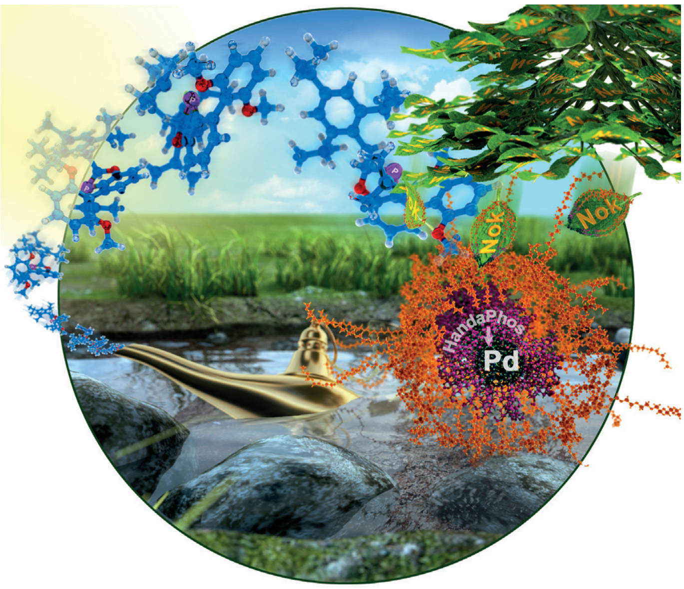
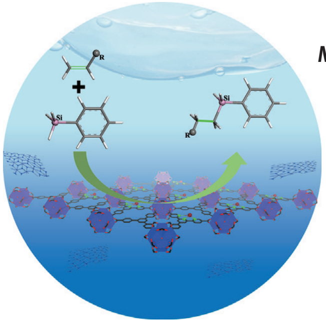
Catalysis with trace metals ...



… in water under mild conditions is how nature has done chemistry for billions of years. No DMF, no DCM, no ethers. So why, by contrast, do synthetic organic chemists typically use 1–5 mol % of a transition-metal catalyst, and in organic solvents oftentimes with heating or cooling? Enter HandaPhos, a new ligand described by B. H. Lipshutz et al. in their Communication on page 4914 ff., designed to enable Suzuki–Miyaura cross-couplings using ppm levels of Pd, 1:1 stoichiometry of reactants, all in water, and at RT. And everything (the water, the catalyst, etc.) is recyclable.

Programmable Release

In their Communication on page 4908 ff., V. V. Tsukruk and co-workers describe multicompartmental microcapsules that can be used to simultaneously encapsulate and sequentially release hydrophobic and hydrophilic molecules.

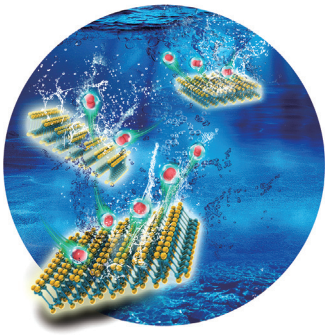


Metal–Organic Layers

In their Communication on page 4962 ff., W. Lin, J. Sun, and co-workers show that two-dimensional metal–organic layers can be used as recyclable and reusable single-site solid catalysts for the hydrosilylation of terminal olefins.

Black Phosphorus

In their Communication on page 5003 ff., X.-F. Yu, P. K. Chu, and co-workers designed a titanium sulfonate ligand to coordinate with black phosphorus, which yielded a material with robust stability in air and water.



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Author Profile

“If I had one year of paid leave I would go to Tibet. My favorite author (science) is Linus Pauling ...” This and more about Qun Liu can be found on page 4860.

News

A. P. Alivisatos

G. L. Richmond

J. M. DeSimone

H. Nakatsuji

J. Neugebauer

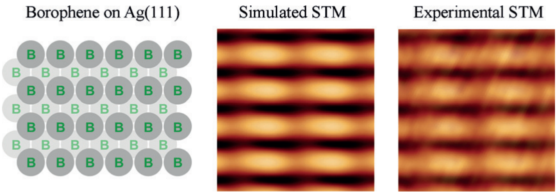
Books

Highlights

Boron Materials

R. D. Dewhurst, R. Claessen,*
H. Braunschweig* ________ **4866 – 4868**

Two-Dimensional, but not Flat: An All-Boron Graphene with a Corrugated Structure



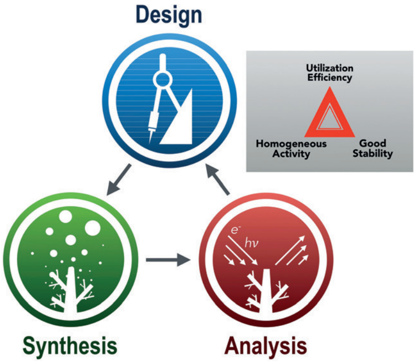
The construction of single-atom-thick sheets of boron on a silver substrate, which was published in late 2015, represents a significant advance towards the realization of useful two-dimensional materials based solely on boron. This Highlight provides background information on the topic of boron allotropes and an outlook for further work in this area.

Minireviews

Electrode Architecture

B. Jeong, J. D. Ocon, J. Lee* **4870 – 4880**

Electrode Architecture in Galvanic and Electrolytic Energy Cells



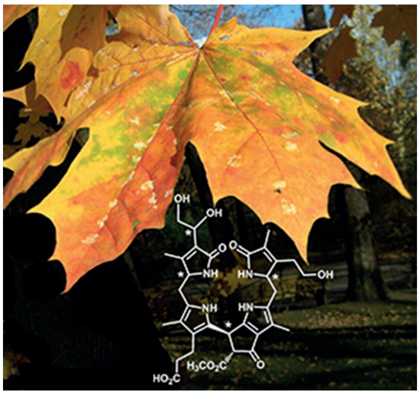
Full of potential: Electrode architecting is a conceptual electrode-fabrication strategy for drawing the full potential of electrode performance with given electrode materials. This procedure can now be realized through advanced bottom-up fabrication methods and in situ and operando analytical methods, such as 3D electron and X-ray imaging techniques and interface-probing technologies.

Reviews

Chlorophyll Breakdown

B. Kräutler* ________ **4882 – 4907**

Breakdown of Chlorophyll in Higher Plants—Phyllobilins as Abundant, Yet Hardly Visible Signs of Ripening, Senescence, and Cell Death



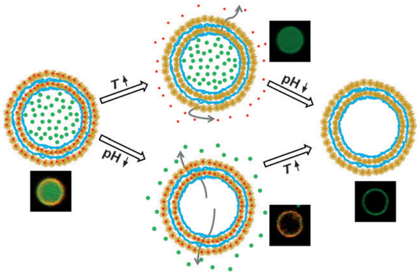
The time is ripe: The seasonal disappearance of chlorophyll has been a long-standing and striking biological enigma. In higher plants, chlorophyll is broken down by a largely common, regulated pathway to linear tetrapyrroles—phyllobilins—which are related to heme catabolites. They accumulate in degreened leaves and vegetables, as well as in ripening fruit, and are presumed to have relevant physiological functions.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 16.862/14.051 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Communications

Programmable Release

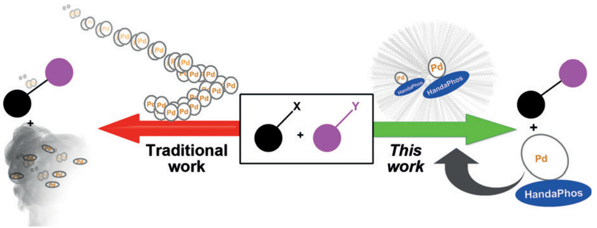
Frontispiece



Multicompartmental responsive microstructures with the capability for controlled, robust, pre-programmed, reversible release of multiple target molecules of different solubility (hydrophobic and hydrophilic) triggered by dual stimuli (pH and temperature) are demonstrated. A temperature increase leads to release from the shell first, whereas a pH decrease leads to initial core release.

Micellar Catalysis

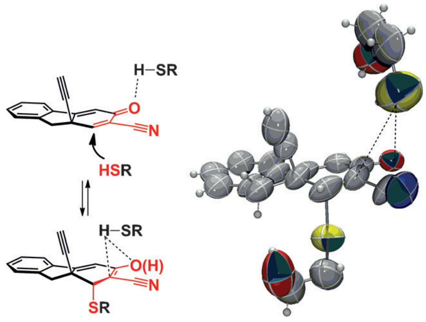
Front Cover



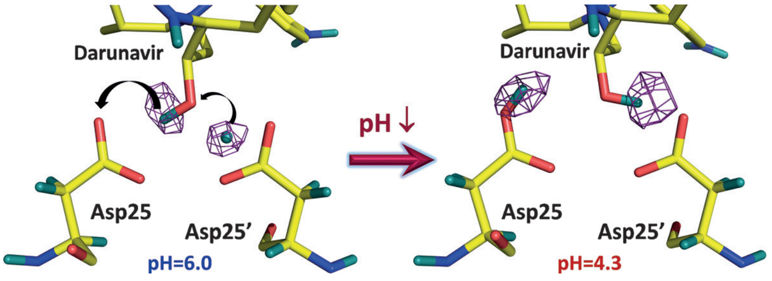
Breaking with tradition: A palladium catalyst with the new monophosphine ligand HandaPhos enables Pd-catalyzed Suzuki–Miyaura couplings involving highly functionalized reaction partners. The reactions proceed in the absence of organic solvents using environmentally benign nanoparticle reactors in water at ambient temperatures.

Crystalline Sponge Method

Seeing is believing: The formation of a cyanoenone Michael adduct, postulated to be involved in the mechanism-of-action of a new family of reversible covalent drugs, was crystallographically observed in situ in the pore of a crystalline sponge. The reaction was performed by treatment of the crystalline sponge first with the substrate followed by the thiol-based reagent of interest.



Neutron Crystallography

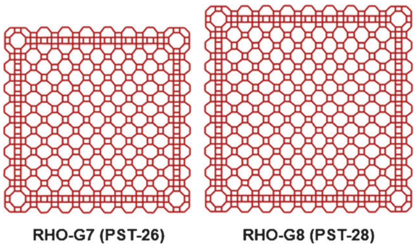


Neutron crystallography captures a two-proton transfer in the HIV-1 protease catalytic site triggered by changes in protonation states of distant amino acid side chains.

Zeolites

J. Shin, H. Xu, S. Seo, P. Guo, J. G. Min, J. Cho, P. A. Wright, X. Zou,* S. B. Hong* **4928 – 4932**

Targeted Synthesis of Two Super-Complex Zeolites with Embedded Isoreticular Structures

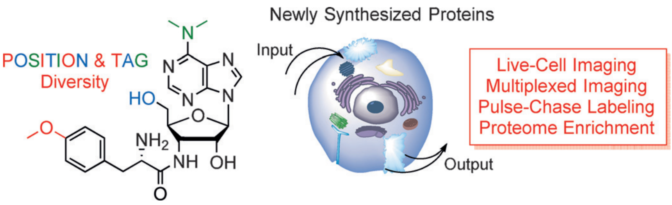


Welcome to the family: The targeted synthesis of two new members of the RHO family of zeolites with embedded isoreticular structures, denoted PST-26 and PST-28, is presented. The crystallization of these more complex, higher-generation zeolites was confirmed by a combination of powder X-ray and electron diffraction techniques.

Newly Synthesized Proteins

J. Ge, C.-W. Zhang, X. W. Ng, B. Peng, S. Pan, S. Du, D. Wang, L. Li, K.-L. Lim, T. Wohland, S. Q. Yao* **4933 – 4937**

Puromycin Analogues Capable of Multiplexed Imaging and Profiling of Protein Synthesis and Dynamics in Live Cells and Neurons



Tag and see: A suite of cell-permeable puromycin analogues that are capable of multiplexed imaging of newly synthesized proteins in live cells and neurons has been developed. For the first time, diffusion dynamics of newly synthesized proteins inside live neuron-like dendritic cells were quantitatively measured, revealing a heterogeneous behavior.

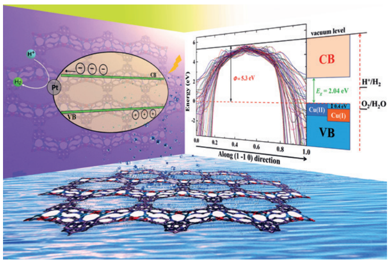
Photocatalysis

Z.-L. Wu, C.-H. Wang, B. Zhao,* J. Dong, F. Lu, W.-H. Wang, W.-C. Wang,* G.-J. Wu, J.-Z. Cui, P. Cheng **4938 – 4942**

A Semi-Conductive Copper–Organic Framework with Two Types of Photocatalytic Activity

Inside Cover

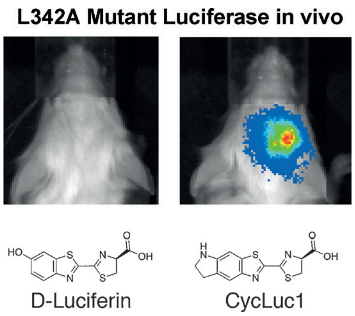
Narrow band gap: The metal–organic framework (MOF) $\{[Cu^{I}Cu^{II}_{2}(DCTP)_{2}]NO_{3}\cdot1.5\,DMF\}_{n}$ has a narrow band gap of 2.1 eV and is a semiconductor. Theoretical and experimental investigations confirmed its performance in photocatalytic hydrogen generation and in organic-dye degradation. It is the first report for MOFs exhibiting two different photocatalytic activities based on photogenerated electrons and holes.



Bioluminescence

S. T. Adams, Jr., D. M. Mofford, G. S. K. K. Reddy, S. C. Miller* **4943 – 4946**

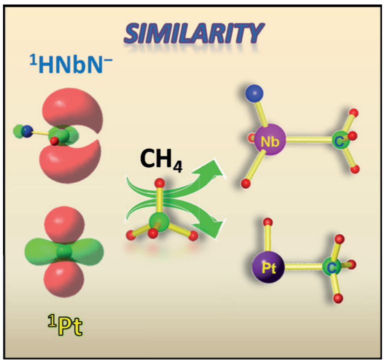
Firefly Luciferase Mutants Allow Substrate-Selective Bioluminescence Imaging in the Mouse Brain



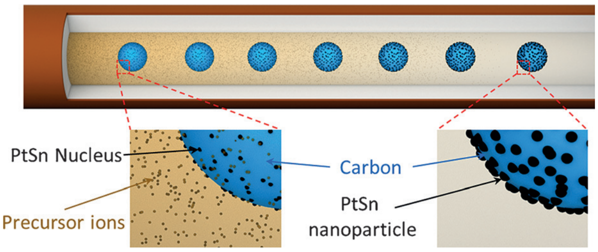
Glowing mutant brains: Bioluminescence requires the interaction of a luciferase enzyme with a small-molecule luciferin, and its scope has been limited by the mere handful of natural combinations. Firefly luciferase mutants were developed that can discriminate between natural and synthetic substrates in the brains of live mice.

C–H Activation

A less noble catalyst: The triatomic HNbN⁻ anion was shown to have a reactive electronic structure similar to a Pt atom, and displayed similar reactivities toward CH_4 and C_2H_6. Thus, transition metal nitride ions could potentially offer cheaper alternatives to traditional platinum-based catalysts for C–H activation.

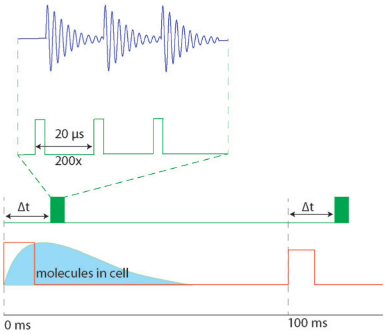


Microfluidic Synthesis



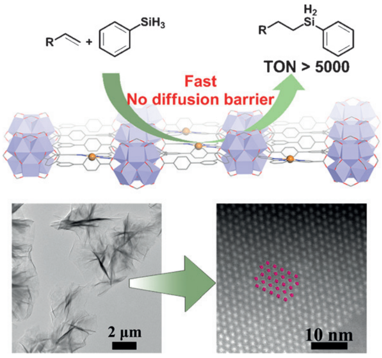
Fluid to the influence: Formation of ultrafine PtSn nanoparticles on a carbon sphere with uniform loading using a microfluidic reactor with a confined lateral dimension is described.

Rotational Spectroscopy



Conformational dynamics of 1,2-propanediol in cold (6 K) collisions with atomic helium were observed using microwave spectroscopy and buffer-gas cooling. Precise control of the collisional environment in the buffer gas allows for measurement of the absolute collision cross-section for conformational relaxation.

Metal–Organic Layers



A very thin catalyst: Two-dimensional metal–organic layers with the thinness of a single monolayer act as highly efficient single-site solid catalysts for alkene hydrosilylation. They outperform traditional metal–organic frameworks in terms of their activity as diffusional constraints on the substrates and products are removed.

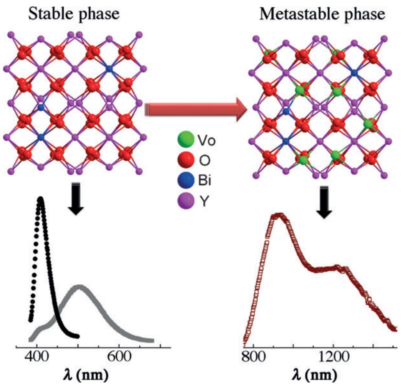
Inside Back Cover

Photoluminescence

B.-M. Liu, Z.-G. Zhang, K. Zhang,
Y. Kuroiwa, C. Moriyoshi, H.-M. Yu, C. Li,
L.-R. Zheng, L.-N. Li, G. Yang, Y. Zhou,
Y.-Z. Fang, J.-S. Hou, Y. Matsushita,
H.-T. Sun* **4967–4971**

Unconventional Luminescent Centers in Metastable Phases Created by Topochemical Reduction Reactions

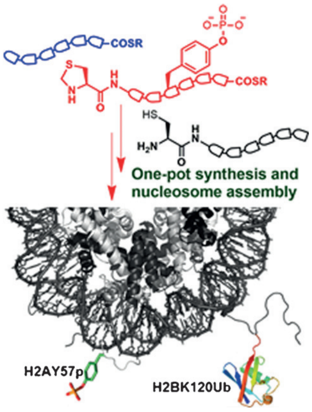
Out of the ordinary: A low-temperature topochemical reduction strategy is used to prepare unconventional bismuth-containing phosphors with luminescence covering the biological and/or telecommunications optical windows. CaH$_2$ treatment of Bi^{III}-doped Y$_2$O$_3$ (Y$_{2-x}$Bi$_x$O$_3$) creates randomly distributed oxygen vacancies in the matrix, leading to lowered oxidation states for the Bi centers and a change in the emission profile of the material.



Protein Synthesis

M. Jbara, S. K. Maity, M. Morgan,
C. Wolberger,* A. Brik* **4972–4976**

Chemical Synthesis of Phosphorylated Histone H2A at Tyr57 Reveals Insight into the Inhibition Mode of the SAGA Deubiquitinating Module



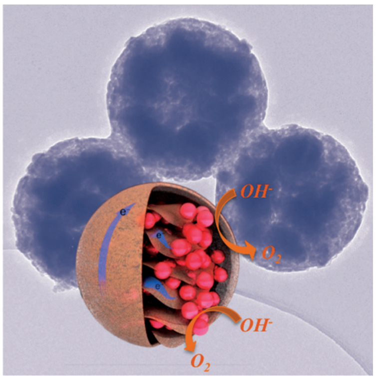
Two in one: Total chemical synthesis by the connection of three fragments via two consecutive ligation reactions carried out in a one-pot manner provided histone protein H2A homogeneously phosphorylated at Tyr 57 (see scheme). The assembly of phosphorylated H2A and ubiquitinated H2B with histone proteins H3 and H4 into a nucleosome provided direct evidence for the inhibition of the activity of the SAGA complex known to cleave ubiquitin from H2B.

VIP

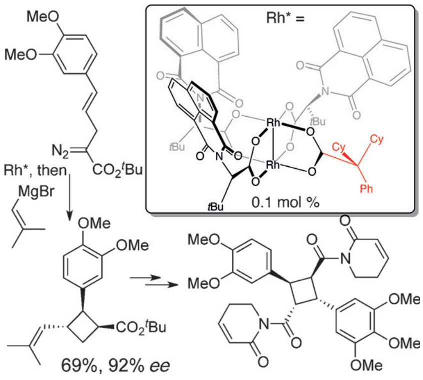
Electrocatalysis

G. Li, X. Wang, J. Fu, J. Li, M. G. Park,
Y. Zhang, G. Lui, Z. Chen* **4977–4982**

Pomegranate-Inspired Design of Highly Active and Durable Bifunctional Electrocatalysts for Rechargeable Metal–Air Batteries

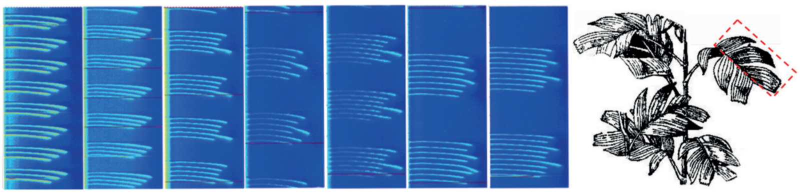


Persephone's battery: Bifunctional electrocatalysts with pomegranate-like architecture were designed and developed, exhibiting high catalytic activity for oxygen reduction and evolution reactions. These catalysts enabled the assembly of high-performance zinc–air batteries with long cycling durability.



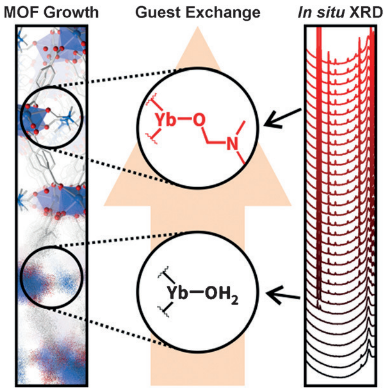
Mixing ligands: A new mixed-ligand chiral rhodium(II) catalyst, $Rh_2(S\text{-}NTTL)_3$-(dCPA), has enabled the first enantioselective total synthesis of the natural product piperarborenine B. Key to the synthesis is a rhodium-catalyzed bicyclobutanation/copper-catalyzed homoconjugate addition for complex cyclobutane synthesis. The natural product was prepared on 400 mg scale and in 8% overall yield.

Enantioselective Synthesis



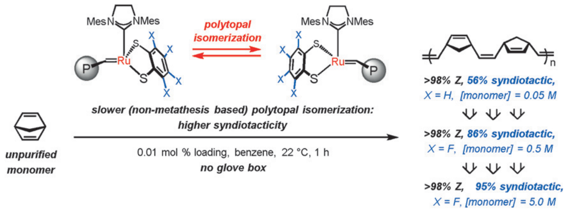
A copolymer gel consisting of NIPAAm and a photosensitive ruthenium catalyst was coupled with Belousov–Zhabotinsky reactants to obtain a diffusively fed reaction system. External periodic light perturbation induces wave groups analogous to certain developmental patterns such as pinnatisect-shaped leaves.

Oscillating Reactions



Things that are bound to change: High-energy X-ray diffraction measured during solvothermal crystallization provides structural information about the formation mechanism of a metal–organic framework (MOF). The results reveal how topochemical exchange of solvent occurs during crystal assembly from solution with continuous adjustment of electron density and lattice parameters.

Crystal Growth



Flexible but controllable: By adjustment of monomer concentration and alteration of steric and electronic attributes of Z-selective Ru catechothiolate complexes, the competing polytopal isomerization and product tacticity in ROMP reactions can be controlled. Reactions are easy to perform (unpurified monomer, no glove box), and the tactcity range can be fine-tuned.

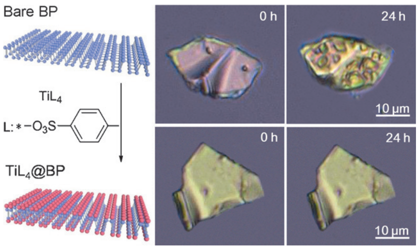
Polymer Synthesis

Surface Coordination

Y. Zhao, H. Wang,* H. Huang, Q. Xiao, Y. Xu, Z. Guo, H. Xie, J. Shao, Z. Sun, W. Han, X.-F. Yu,* P. Li, P. K. Chu* **5003 – 5007**

Surface Coordination of Black Phosphorus for Robust Air and Water Stability

Back Cover

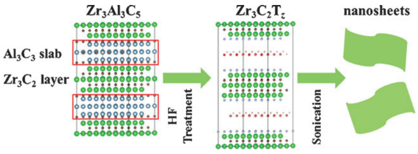


A titanium sulfonate ligand was synthesized and used to coordinate with black phosphorus (BP). In contrast to the serious degradation observed in bare BP, the BP after surface coordination exhibited excellent stability during dispersion in water and exposure to air for a long period of time, significantly extending the lifetime and spurring broader applications of BP.

Layered Structures

J. Zhou, X. H. Zha, F. Y. Chen, Q. Ye, P. Eklund, S. Y. Du,* Q. Huang* **5008 – 5013**

A Two-Dimensional Zirconium Carbide by Selective Etching of Al_3C_3 from Nanolaminated $Zr_3Al_3C_5$

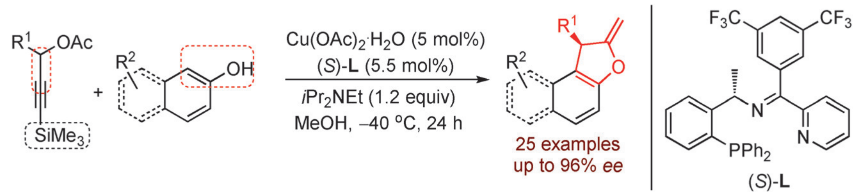


$Zr_3C_2T_z$ nanosheets: A 2D zirconium-containing carbide, $Zr_3C_2T_z$ MXene, is obtained by selective etching of Al_3C_3 units from layered ternary $Zr_3Al_3C_5$ beyond MAX phases (see picture) at room temperature. The structural, mechanical, and electronic properties of the 2D carbide were investigated combined with density functional calculations. The 2D $Zr_3C_2T_z$ exhibits excellent thermal stability, which exists even at 1200 °C in vacuum.

Asymmetric Catalysis

L. Shao, Y.-H. Wang, D.-Y. Zhang, J. Xu, X.-P. Hu* **5014 – 5018**

Desilylation-Activated Propargylic Transformation: Enantioselective Copper-Catalyzed [3+2] Cycloaddition of Propargylic Esters with β-Naphthol or Phenol Derivatives

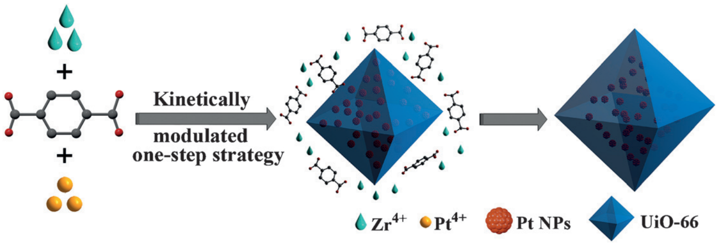


Cu on active duty: The highly enantioselective title reaction of 3-trimethylsilylpropargylic acetates has been realized on the basis of a desilylation-activated strategy. With the support of a finely modified ketimine P,N,N-ligand, the reaction gave rise to either chiral 1,2-dihydronaphtho- or benzofurans in good yields and with up to 96% *ee*.

Metal–Organic Frameworks

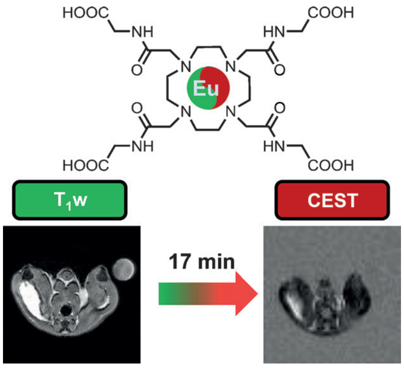
H. Liu, L. Chang, C. Bai, L. Chen, R. Luque,* Y. Li* **5019 – 5023**

Controllable Encapsulation of “Clean” Metal Clusters within MOFs through Kinetic Modulation: Towards Advanced Heterogeneous Nanocatalysts



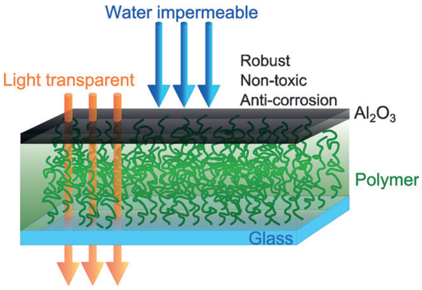
Small and alone: Surfactant-free Pt clusters were encapsulated within metal–organic frameworks (MOFs) by a kinetically modulated one-step strategy (see picture). The resulting Pt@MOF core–shell composites exhibited high activity and selectivity in the oxidation of alcohols as well as interesting molecular-sieving effects of the outer Pt-free MOF shell.

Relax and exchange: A Eu^{II} complex of DOTA tetra(glycinate) (see picture) has a far less negative redox potential than most Eu^{II} chelates reported to date. The reduced Eu^{II} form acts as an efficient water proton T_1 relaxation reagent, while the Eu^{III} form acts as a water-based chemical exchange saturation transfer (CEST) agent. The time course of oxidation was studied in vitro and in vivo by T_1-weighted and CEST imaging.

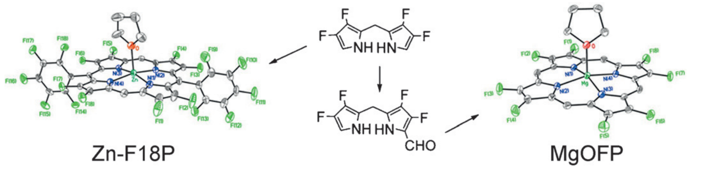


Lanthanide Contrast Agents

Waterproof and transparent: A method for the preparation of transparent Al_2O_3 coatings of polymer brushes is presented. Layer composition, morphology, and mechanical properties were characterized by a combination of XPS, SEM, and AFM. The presence of the alumina layer preserved the underneath brush from swelling in water.



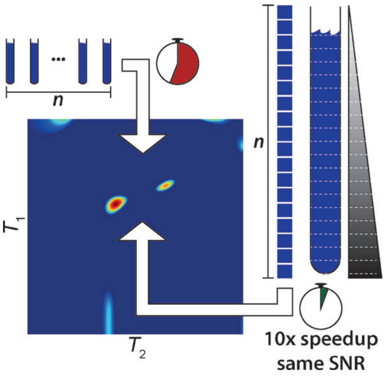
Coatings



At long last, the much anticipated octafluoroporphyrin (OFP) has been synthesized by condensation of tetrafluorodipyrrylmethane-2-carboxaldehyde in the presence of magnesium(II) salts. The fluorinated dipyrrylmethane also gives F18P with good yields. Both MgOFP and ZnF18P show an essentially flat structure in the solid state. The fluoro substituents impart a shift of oxidation and reduction potentials for the porphyrin ring.

Porphyrinoids

Ultrafast experiments—one to two orders of magnitude faster than traditional experiments—measure multidimensional NMR relaxation parameters. Here, the ultrafast measurements are demonstrated using single-sided magnets, offering new possibilities for monitoring fast processes with few restrictions on sample size. SNR = signal-to-noise ratio.

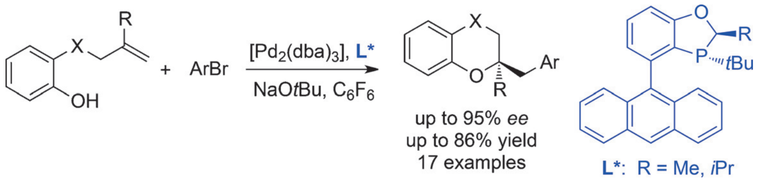


NMR Spectroscopy

Asymmetric Cyclization

N. Hu, K. Li, Z. Wang,
W. Tang* ———— 5044 – 5048

Synthesis of Chiral 1,4-Benzodioxanes and Chromans by Enantioselective Palladium-Catalyzed Alkene Aryloxyarylation Reactions

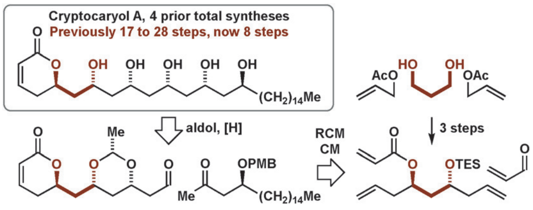


One P is plenty: A sterically bulky and conformationally well defined chiral monophosphorus ligand enabled the highly enantioselective synthesis of a series of O heterocycles containing a quaternary stereocenter by alkene aryloxyarylation (see scheme; X = O, C, N). The application of this transformation to the synthesis of the chiral chroman backbone of α-tocopherol is demonstrated.

Natural Product Synthesis

F. Perez, A. R. Waldeck,
M. J. Krische* ———— 5049 – 5052

Total Synthesis of Cryptocaryol A by Enantioselective Iridium-Catalyzed Alcohol C—H Allylation

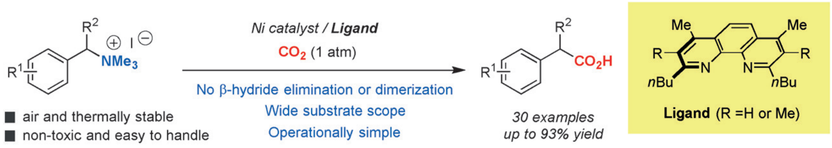


Less is more: The polyketide natural product cryptocaryol A is prepared in 8 steps via iridium-catalyzed enantioselective diol double C—H allylation, which directly generates an acetate-based triketide stereodiad. In 4 previously reported total syntheses, 17–28 steps were required.

Synthetic Methods

T. Moragas, M. Gaydou,
R. Martin* ———— 5053 – 5057

Nickel-Catalyzed Carboxylation of Benzylic C—N Bonds with CO$_2$

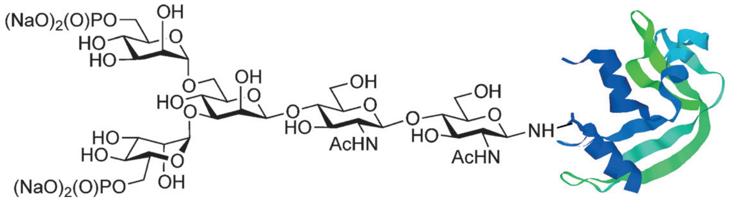


A user-friendly method for the Ni-catalyzed reductive carboxylation of benzylic C(sp^3)—N bonds with CO$_2$ is described. This new procedure outperforms state-of-the-art techniques for the carboxylation of benzyl electrophiles by avoiding commonly observed parasitic pathways, such as homodimerization or β-hydride elimination.

Glycoproteins

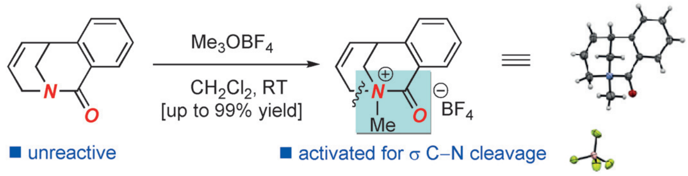
P. Priyanka, T. B. Parsons, A. Miller,
F. M. Platt, A. J. Fairbanks* 5058 – 5061

Chemoenzymatic Synthesis of a Phosphorylated Glycoprotein



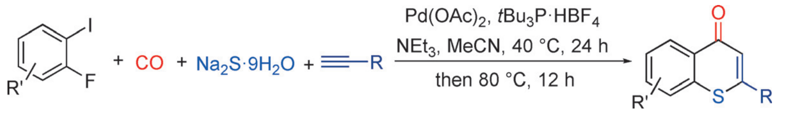
ENGase-ineering glycoproteins: The combination of chemical synthesis and ENGase-mediated biocatalysis enabled the production of a glycoprotein bearing mannose-6-phosphate-terminated N-glycans that are linked to the peptide backbone by natural linkages.

N–C Bond Activation



Tailored bond cleavage: N-alkylated twisted amides were prepared directly by N-alkylation of the corresponding non-planar lactams and structurally characterized for the first time. Most crucially, N-alkylation activates the otherwise unreactive amide bond towards the unconventional amide N–C bond cleavage through switchable N-/O-coordination.

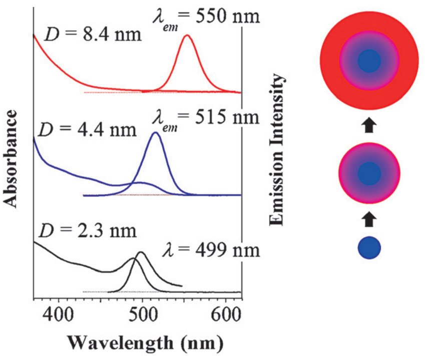
Multicomponent Reactions



Thiochromenones were prepared by a palladium-catalyzed carbonylative four-component reaction benefitting from the use of a reagent capsule, which prevents the poisoning of the transition-metal catalyst and improves the compatibility of the various reagents in this one-pot process. Thiochromenones were thus prepared from commercially available substrates in moderate to good yields.

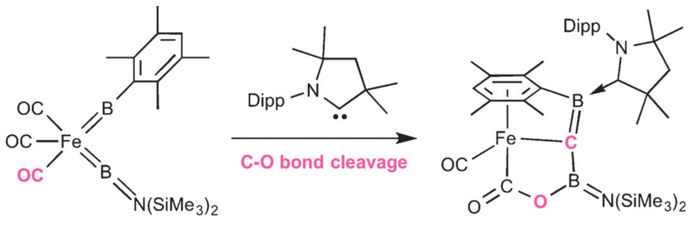
Stokes Shift-Engineered Quantum Dots

VIP



A nice warm coat: Graded $Cd_{1-x}Zn_xSe_{1-y}S_y$ and ZnS shells (see spectra: thick shells: red, thin: blue) were grown on the surface of CdSe cores (black) by a one-pot synthesis. The thicker ZnS shell over the graded $Cd_{1-x}Zn_xSe_{1-y}S_y$ shell resulted in the progressive red-shift of emission and the effective suppression of the first absorption peak from the innermost CdSe QD core.

Boron Ligands



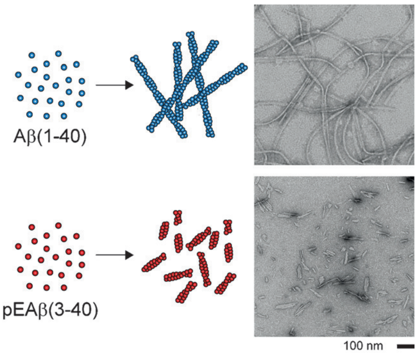
Inner turmoil: Reaction of a zerovalent iron bis(borylene) complex with a cyclic (alkyl)(amino)carbene revealed a selective intramolecular cleavage of the C–O bond of a carbonyl ligand at room temperature, leading to the formation of a highly unusual iron complex containing a base-stabilized (bora)alkylideneborane ligand.

Amyloids

M. Wulff, M. Baumann, A. Thümmler, J. K. Yadav, L. Heinrich, U. Knüpfer, D. Schlenzig, A. Schierhorn, J.-U. Rahfeld, U. Horn, J. Balbach, H.-U. Demuth, M. Fändrich* **5081 – 5084**

Enhanced Fibril Fragmentation of N-Terminally Truncated and Pyroglutamyl-Modified Aβ Peptides

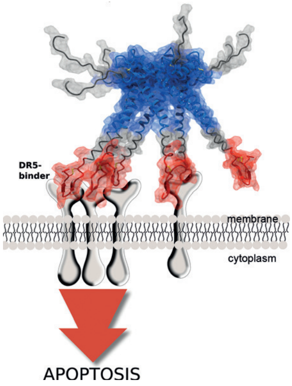
Now we're just falling apart: A naturally occurring chemical modification (pyroglutamyl, pE) affects the aggregation properties and toxicity of the Alzheimer's disease Aβ peptide. These effects were shown not to correspond to effects on the peptide fold or secondary structure but rather to be the result of an increased fragmentation propensity of the aggregates formed by the modified peptide.



Peptide Drugs

B. Valldorf, H. Fittler, L. Deweid, A. Ebenig, S. Dickgiesser, C. Sellmann, J. Becker, S. Zielonka, M. Empting, O. Avrutina, H. Kolmar* **5085 – 5089**

An Apoptosis-Inducing Peptidic Heptad That Efficiently Clusters Death Receptor 5

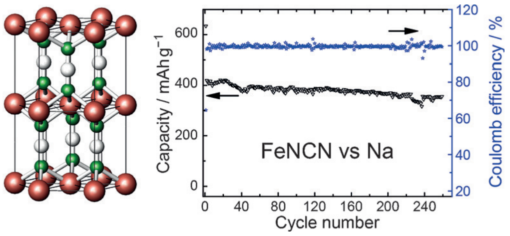


A modular approach to generate death receptor 5 (DR5) binding constructs comprising multiple copies of DR5 targeting peptide (DR5TP) covalently bound to biomolecular scaffolds of peptidic nature is presented. Multivalent ligands are obtained that specifically induce an apoptotic cascade in cancer cells. The number and spatial orientation of the copies are decisive for their receptor activation ability.

Batteries

M. T. Sougrati, A. Darwiche, X. Liu, A. Mahmoud, R. P. Hermann, S. Jouen, L. Monconduit, R. Dronskowski,* L. Stievano* **5090 – 5095**

Transition-Metal Carbodiimides as Molecular Negative Electrode Materials for Lithium- and Sodium-Ion Batteries with Excellent Cycling Properties



Durable and effective: Transition-metal carbodiimides, in particular FeNCN, are found to be effective negative electrode materials of Na and Li batteries. They show higher capacities than established electrodes, such as graphite or hard carbon, and show long lifetimes at current densities of up to 9 A g^{-1} for hundreds of charge–discharge cycles.

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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