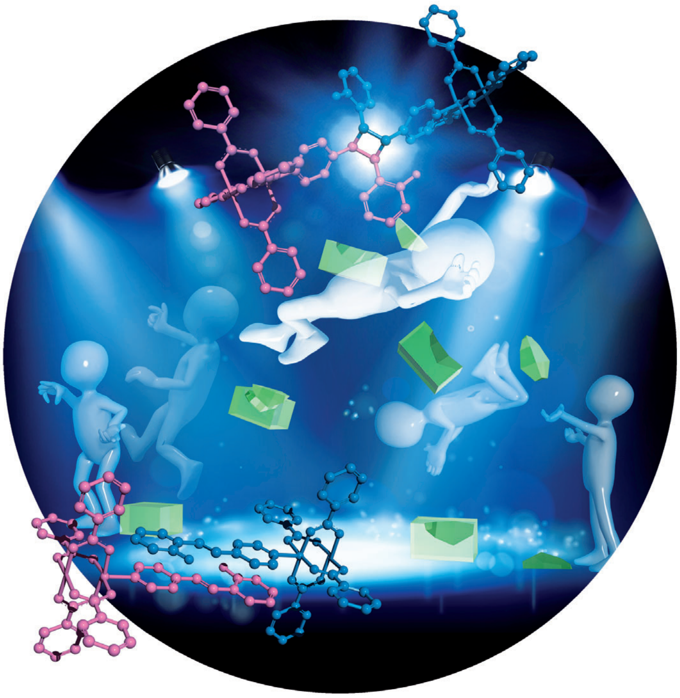
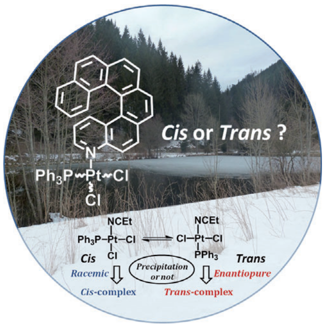
The self-propulsion of single crystals ...

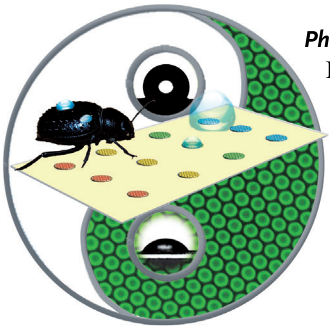


... of three Zn(II) complexes under UV light is described by P. Naumov, J. J. Vittal et al. in their Communication on page 5907 ff. This visually impressive dynamic behavior is a consequence of the accumulation and sudden release of strain created by crystal expansion following the formation of 1D coordination polymers by a [2+2] cycloaddition reaction. Understanding this effect, which is mechanistically analogous to the bursting of popcorn in a hot pan, may help in the design of new light-driven mechanical actuators.



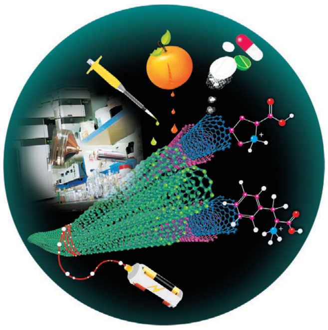
Chirality in Complexes

In their Communication on page 5786 ff., J. Crassous and co-workers show how *cis–trans* isomerism in [Pt^{II}Cl$_2$(4-aza[6]helicene)PPh$_3$] is controlled by the racemic and enantiopure forms of the 4-aza[6]helicene ligand.



Photonic Crystals

In their Communication on page 5791 ff., M. Li, Y. Song, et al. report a photonic-crystal microchip with a hydrophilic–hydrophobic micropattern, which was inspired by the fog-collecting structure on the back of the *Stenocara* beetle.



Mass Spectrometry

In their Communication on page 5936 ff., T. Pradeep et al. show that a piece of paper that is impregnated with multi-walled or single-walled carbon nanotubes generates ions from diverse analytes at voltages as low as 3 V.

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Editorial

"... Today, the research contexts in which the work on MOFs are, or will be placed, are enormously diverse and multilingual, and the technical backgrounds and motives of those involved develop equally as diversely, sometimes with a very distant reference to the original. Therefore, distinctions and care in the use of scientific language and expression are important. ..."
Read more in the Editorial by Roland A. Fischer.

Service

Books

Author Profile

"I admire those who do what they really want to do. I advise my students to read as many research articles as possible and get a big picture ..."
This and more about Insung S. Choi can be found on page 5740.

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News


F. Merkt


F. Laquai


O. Reich

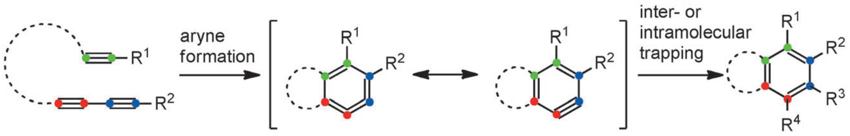

C. T. Campbell

Obituaries

Kenneth Wade passed away on March 16, 2014. He made significant advances in synthetic organometallic main-group chemistry and is best remembered for Wade's Rules, a set of empirical rules that relate the number of skeletal electron pairs to the polyhedral shape of borane and carborane clusters.

Highlights

Cycloaddition



Arynes are now accessible through the [4+2] Diels–Alder cycloaddition of triynes, a process that captures all atoms of the starting material in the aryne product. The atom economy and reagent-free conditions provide a new dimension to aryne chemistry and should enable exciting developments in the study and application of arynes in synthesis.

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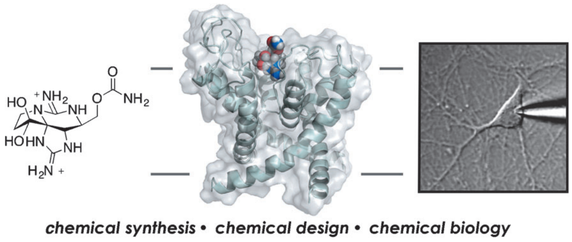
Minireviews

Drug Discovery

Go with the flow: Continuous flow reactors are increasingly used in synthetic organic chemistry. This enabling technology to access innovative chemotypes and efficiently explore chemical space in an automated manner is being adapted for chemical biology and drug discovery research. This Minireview describes the current status of this technique and provides an overview of key recent milestones.

Reviews

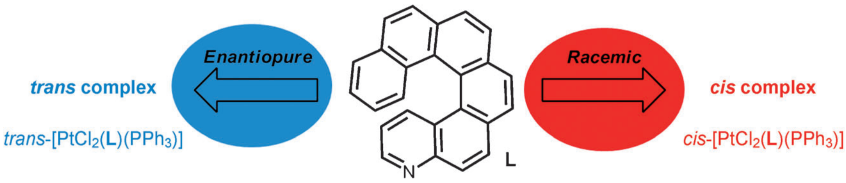
Natural Products



***... and the waters** that were in the river were turned to blood. And the fish that were in the river died* (Exodus 7:20-21). Its pharmacological effects having been documented since antiquity, saxitoxin holds a venerable place in the annals of natural product science. An account of both the chemistry and chemical biology of this most fascinating natural product is presented.

Communications

Chirality in Complexes



Controlled by the ligand: The *cis* and *trans* isomerism in the complex [$\mathrm{Pt^{II}Cl_2}$(4-aza[6]helicene)$\mathrm{PPh_3}$] is unexpectedly controlled by the racemic and enantiopure forms of the starting 4-aza[6]helicene ligand.

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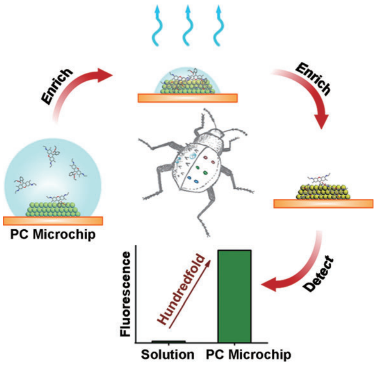
Photonic Crystals

J. Hou, H. Zhang, Q. Yang, M. Li,*
Y. Song,* L. Jiang ______ 5791 – 5795

Bio-Inspired Photonic-Crystal Microchip for Fluorescent Ultratrace Detection

Inside Back Cover

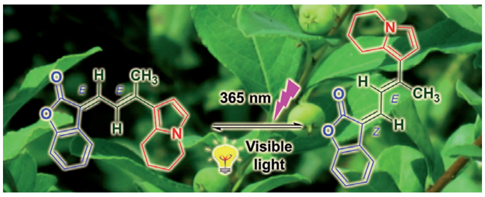


Ultratrace detection: Inspired by the fog-collecting structure on the back of the *Stenocara* beetle, a photonic-crystal (PC) microchip with a hydrophilic–hydrophobic micropattern was fabricated by inkjet printing. This PC microchip can enrich an analyte by wettability differences and enhance the fluorescence by the PC stop band effect (see picture).

Natural Products

Z.-L. Wu, B.-X. Zhao, X.-J. Huang,
G.-Y. Tang, L. Shi, R.-W. Jiang, X. Liu,
Y. Wang,* W.-C. Ye* ______ 5796 – 5799

Suffrutines A and B: A Pair of *Z*/*E* Isomeric Indolizidine Alkaloids from the Roots of *Flueggea suffruticosa*

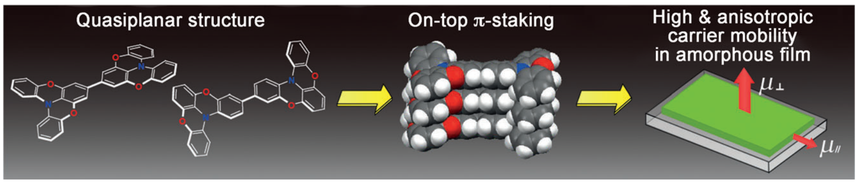


The discovery of a pair of novel indolizidine alkaloids, having a unique and highly conjugated C_{20} backbone, from the roots of *Flueggea suffruticosa* adds a new class to the indolizidine alkaloid family. Furthermore, they were shown to be *Z*/*E* isomers, interconvertible by light, and the *trans*,-*trans* form exhibits potent activity for regulating the morphology of Neuro-2a cells.

Heterocycles

A. Wakamiya,* H. Nishimura,
T. Fukushima, F. Suzuki, A. Saeki, S. Seki,
I. Osaka, T. Sasamori, M. Murata,
Y. Murata,* H. Kaji* ______ 5800 – 5804

On-Top π-Stacking of Quasiplanar Molecules in Hole-Transporting Materials: Inducing Anisotropic Carrier Mobility in Amorphous Films

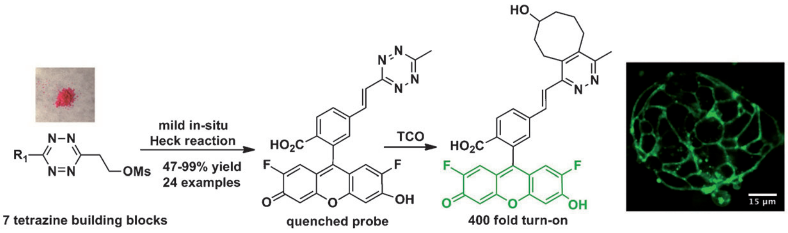


Taking charge: Dimers of partially oxygen-bridged triarylamines that form on-top π-stacking aggregates in the crystalline state were shown to induce high levels of anisotropic charge transport in the direction of the π-stacking. Surprisingly, these compounds retained some of the face-on π-stacking even in vacuum-deposited amorphous films, thus facilitating an out-of-plane carrier mobility.

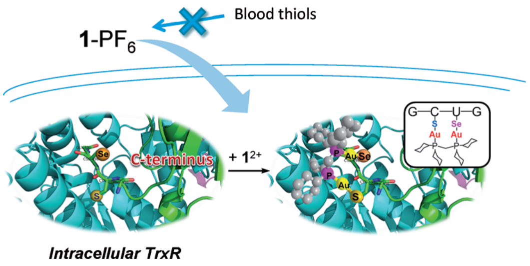
Synthetic Methods

H. X. Wu, J. Yang, J. Šečkutė,
N. K. Devaraj* ______ 5805 – 5809

In Situ Synthesis of Alkenyl Tetrazines for Highly Fluorogenic Bioorthogonal Live-Cell Imaging Probes



Stitching probes together: The in situ synthesis of (*E*)-3-substituted 6-alkenyl-1,2,4,5-tetrazine derivatives through an elimination–Heck cascade reaction is reported. 24 examples of π-conjugated tetrazine derivatives are provided, including conjugated fluorescent probes that show drastic fluorescent turn-on when reacted with dienophiles. Their suitability for live-cell imaging is demonstrated. TCO = *trans*-cyclooctene.

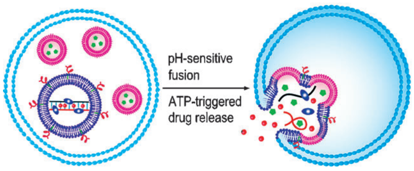


It's in the blood: A binuclear gold(I) complex **1**-PF_6 is stable towards blood thiols and is a tight-binding inhibitor of thioredoxin reductase (TrxR). In vivo antitumor studies show 81 % inhibition of tumor growth in mice with HeLa xenografts and 62 % inhibition of highly aggressive mouse B16-F10 melanoma.

Gold Medicine

T. Zou, C. T. Lum, C.-N. Lok, W.-P. To, K.-H. Low, C.-M. Che* ____ **5810 – 5814**

A Binuclear Gold(I) Complex with Mixed Bridging Diphosphine and Bis(N-Heterocyclic Carbene) Ligands Shows Favorable Thiol Reactivity and Inhibits Tumor Growth and Angiogenesis In Vivo



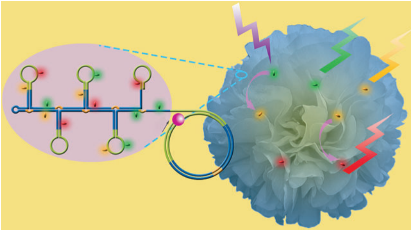
"Energy molecule" as a trigger: A co-delivery system consisting of both a fusogenic liposome encapsulating ATP-responsive elements and a small-molecule drug along with a liposome containing ATP was developed for ATP-triggered drug release mediated by the liposomal fusion. Directly delivering extrinsic ATP can promote the drug release from the fusogenic liposome in the acidic intracellular compartments upon pH-sensitive membrane fusion.

Drug Delivery

R. Mo,* T. Jiang, Z. Gu* ____ **5815 – 5820**

Enhanced Anticancer Efficacy by ATP-Mediated Liposomal Drug Delivery

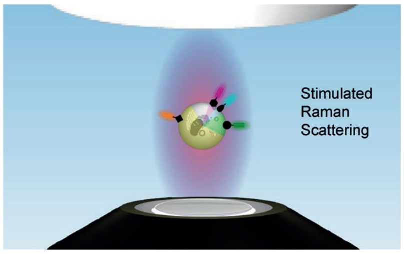
Colorful technique: A facile approach for making aptamer-conjugated FRET nanoflowers (NFs) by rolling circle replication for single-excitation multiplexed imaging and traceable targeted drug delivery was reported. NF assembly is independent of template sequences, avoiding the complicated design of DNA base-pairing in conventional nanostructure assembly.



Bioimaging

R. Hu, X. Zhang, Z. Zhao, G. Zhu, T. Chen, T. Fu, W. Tan* ____ **5821 – 5826**

DNA Nanoflowers for Multiplexed Cellular Imaging and Traceable Targeted Drug Delivery



Raman imaging: In addition to the clickable chemical reactivity, alkynes possess a unique Raman scattering within the Raman-silent region of a cell (see picture). Coupling this spectroscopic signature with Raman microscopy yields a new imaging modality beyond fluorescence and label-free microscopies.

Stimulated Raman Scattering

S. Hong, T. Chen, Y. Zhu, A. Li, Y. Huang,* X. Chen* ____ **5827 – 5831**

Live-Cell Stimulated Raman Scattering Imaging of Alkyne-Tagged Biomolecules

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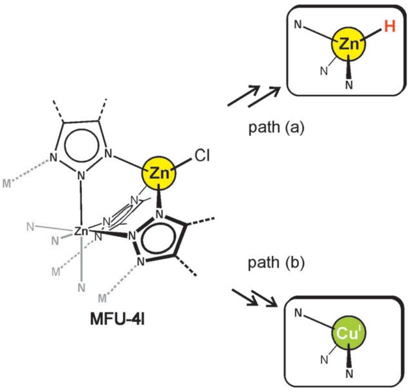
Small-Molecule Binding

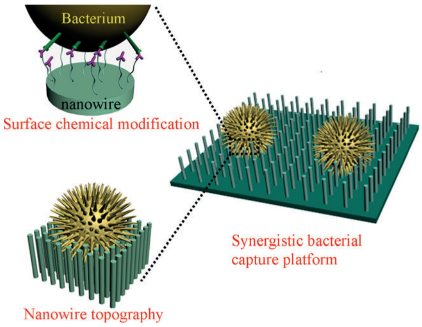


On again, off again: Coordinatively unsaturated metal centers, such as zinc(II) hydride and copper(I), were generated within the MFU-4*l* structure (see picture). Cu^I-MFU-4*l* showed reversible chemisorption of O_2, N_2, and H_2 with isosteric heats of adsorption of 32–53 kJ mol^{-1}. The demonstrated hydride transfer to electrophiles and strong binding of small gas molecules indicate the potential of these metal–organic frameworks as catalytic materials.

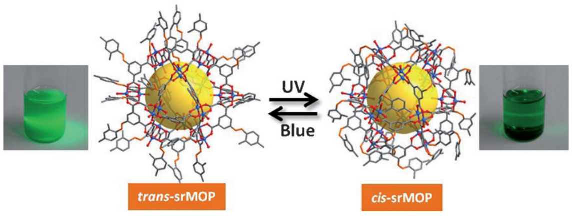
Nanotechnology

Inside Cover

Stuck fast: A strategy for efficient bacterial capture was developed based on the synergistic effect of surface nanotopography and surface chemistry on bacterial attachment. Packed silicon nanowires were functionalized with bacteria-binding molecules. The capture efficiency of the resultant substrate was greatly enhanced compared to surface-modified flat silicon, thus enabling highly sensitive detection and efficient elimination of bacterial pathogens.

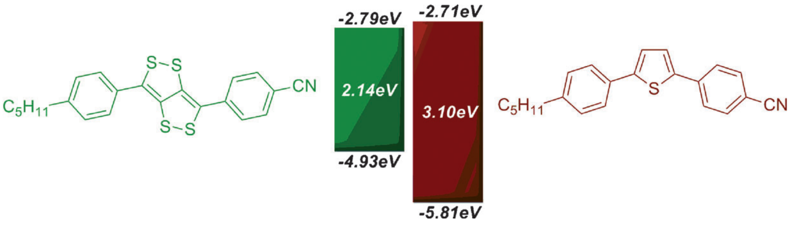


Metal–Organic Frameworks



Lock in the guests, later set them free: Stimuli-responsive metal–organic polyhedra (srMOPs) functionalized with azobenzene showed UV-light-induced isomerization from insoluble srMOPs substituted with *trans*-azobenzene to soluble srMOPs with *cis*-azobenzene units; irradiation with blue light reversed this process (see picture). Guest molecules were trapped upon *cis*-to-*trans* and released upon *trans*-to-*cis* isomerization of the azobenzene units.

Conjugated Materials



A series of compounds containing the dithiolodithiole (C_4S_4) heterocycle has been synthesized and characterized. The properties of C_4S_4-based compounds are readily tunable by variation of substituents. C_4S_4 derivatives exhibit complimentary optical and electronic properties to the similar and widely used thiophene analogues.

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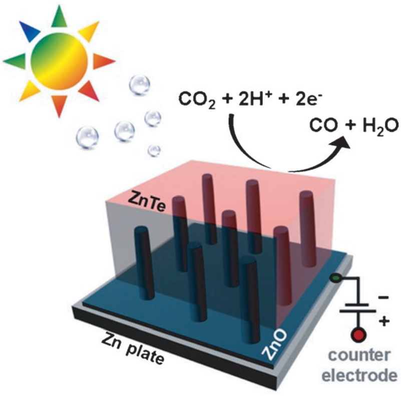
Photocathodes

J.-W. Jang, S. Cho, G. Magesh, Y. J. Jang, J. Y. Kim, W. Y. Kim, J. K. Seo, S. Kim, K.-H. Lee,* J. S. Lee* ______ 5852 – 5857

Aqueous-Solution Route to Zinc Telluride Films for Application to CO_2 Reduction

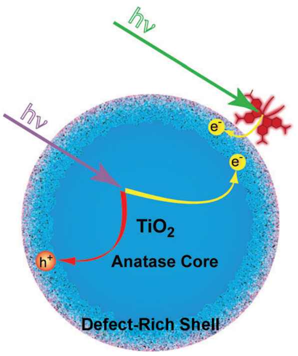
High performance without sacrifice: Zinc-blende zinc telluride (ZnTe) was directly formed on a Zn/ZnO-nanowire substrate by a simple dissolution–recrystallization mechanism without a surfactant. The ZnTe electrode was applied as a photocathode for CO_2 reduction (see picture) and showed efficient and stable CO formation at −0.2–−0.7 V versus the reversible hydrogen electrode (RHE) without a sacrificial reagent.



Titanium Traps

M. H. Rittmann-Frank, C. J. Milne, J. Rittmann, M. Reinhard, T. J. Penfold, M. Chergui* ______ 5858 – 5862

Mapping of the Photoinduced Electron Traps in TiO_2 by Picosecond X-ray Absorption Spectroscopy



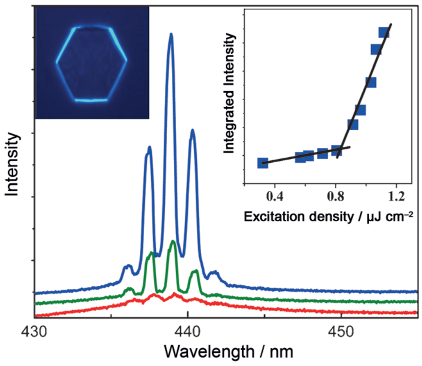
Electrons in the trap: Picosecond Ti K-edge and Ru L_3-edge X-ray absorption spectra of photoexcited bare and dye-sensitized TiO_2 nanoparticles (NPs) showed that electrons are trapped deep in the defect-rich surface shell of bare anatase TiO_2, whereas injection from the dye on both anatase and amorphous NPs leads to surface trapping (see picture). In bare amorphous TiO_2, trapping occurs at preexisting defects within the NP.

Organic Microlasers

X. D. Wang, Q. Liao,* Q. H. Kong, Y. Zhang, Z. Z. Xu, X. M. Lu, H. B. Fu* ______ 5863 – 5867

Whispering-Gallery-Mode Microlaser Based on Self-Assembled Organic Single-Crystalline Hexagonal Microdisks

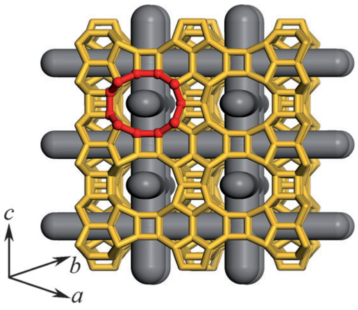
Organic microlasers: Organic hexagonal microdisks were fabricated by a facile solution self-assembly method. Whispering-gallery-mode (WGM) laser action was observed in these organic hexagonal microdisks (see picture). These microdisks contribute to the miniaturization of laser sources and integration of photonic devices.



Zeolite Structures

W. Hua, H. Chen, Z. B. Yu, X. Zou, J. Lin,* J. Sun* ______ 5868 – 5871

A Germanosilicate Structure with 11 × 11 × 12-Ring Channels Solved by Electron Crystallography



A stable germanosilicate with 3D 11 × 11 × 12 ring channels, PKU-16 (see picture), was synthesized with a simple organic structure-directing agent. Nanosized PKU-16 was structurally characterized by the new rotation electron diffraction methods. The structure of PKU-16 is related with zeolite β polymorph C by rotating half of the 4-rings in the double *mtw* units.

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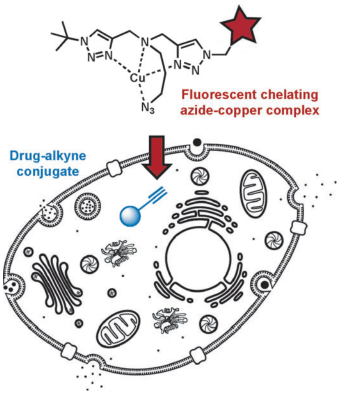
Bioorthogonal Click Chemistry

V. Bevilacqua, M. King, M. Chaumontet, M. Nothisen, S. Gabillet, D. Buisson, C. Puente, A. Wagner, F. Taran* ________ 5872 – 5876

Copper-Chelating Azides for Efficient Click Conjugation Reactions in Complex Media

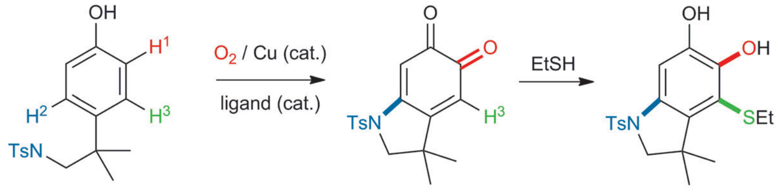
Chelating azides were designed to form clickable copper complexes for efficient ligation with alkynes in complex biological media. Among a series of azides that bear nitrogen heterocycles, a bis(triazole) azide allowed ultra-fast click reactions with alkynes within seconds under diluted conditions. The reactivity and stability of this copper complex enabled efficient click reactions inside living cells.



Synthetic Methods

K. V. N. Esguerra, Y. Fall, J.-P. Lumb* ________ 5877 – 5881

A Biomimetic Catalytic Aerobic Functionalization of Phenols

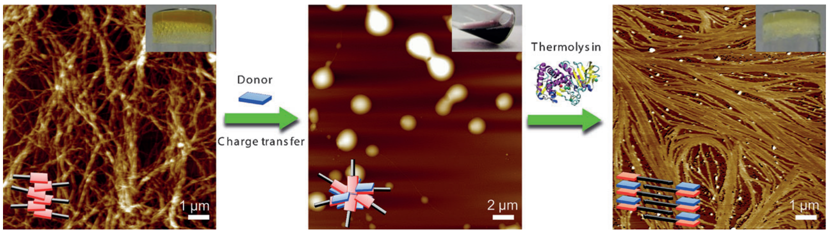


The direct approach: Polyfunctional aromatic rings have been generated by direct functionalization of C–H bonds to C–O, C–N, and C–S bonds at the sole expense of reducing O_2 to H_2O. The method hinges on a regio- and chemoselective, copper-catalyzed aerobic oxygenation of phenols to provide *ortho*-quinones (see scheme), thus mimicking the ubiquitous biosynthetic pathway of melanogenesis.

Charge-Transfer Nanostructures

S. K. M. Nalluri, C. Berdugo, N. Javid, P. W. J. M. Frederix, R. V. Ulijn* ________ 5882 – 5887

Biocatalytic Self-Assembly of Supramolecular Charge-Transfer Nanostructures Based on n-Type Semiconductor-Appended Peptides

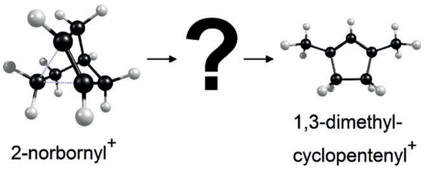


Built through biocatalysis: 1D chiral charge-transfer nanofibers were fabricated through the biocatalytic self-assembly of naphthalenediimide amino acid/dipeptide conjugate acceptors and dialkoxy/hydroxy naphthalene donors. In the obtained aqueous hydrogels, the charge-transfer-induced gel-sol-gel transformation led to major morphological changes.

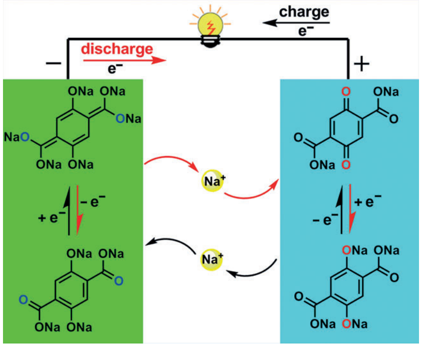
Carbocations

J. D. Mosley, J. W. Young, J. Agarwal, H. F. Schaefer, III, P. v. R. Schleyer, M. A. Duncan* ________ 5888 – 5891

Structural Isomerization of the Gas-Phase 2-Norbornyl Cation Revealed with Infrared Spectroscopy and Computational Chemistry

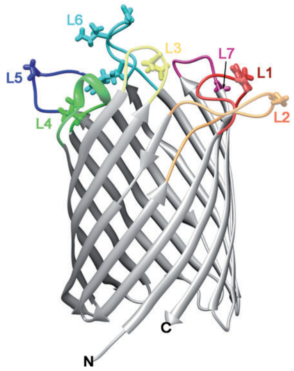


The most famous carbocation is the 2-norbornyl cation, $C_7H_{11}^+$. Although its structure in the condensed phase is known (see scheme, left) there is no direct evidence for its gas-phase structure. IR spectroscopy of $C_7H_{11}^+$ shows that 2-norbornyl can rearrange into the 1,3-dimethylcyclopentenyl cation. This ion is the global minimum on the $C_7H_{11}^+$ potential energy surface, a fact that has escaped previous theoretical analyses.



More salt, please: Organic tetrasodium salts of 2,5-dihydroxyterephthalic acid (Na_4DHTPA) can reversibly react with two Na^+ ions at 1.6–2.8 V and 0.1–1.8 V, respectively. This material can be used to build a symmetrical all-organic rocking-chair cell with an average voltage of 1.8 V and an energy density of about 65 Wh kg^{-1}.

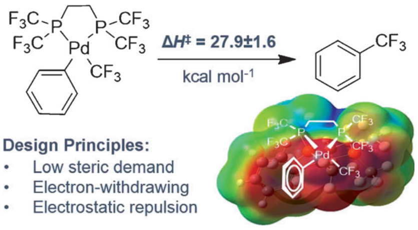
Sodium Batteries



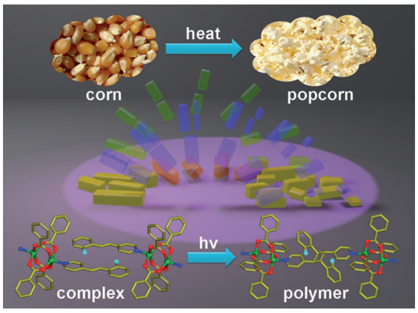
Loop-the-loop: The OmpG nanopore was engineered to keep each of its seven loops immobilized through dodecylation and anchoring in the membrane. Electrophysiological and NMR experiments were used to characterize each of the pinned loop mutations. Pinning loop 6 generates a constitutively open pore useful for further nanopore engineering and loops 1 and 5 form a scaffold that controls further loop motion on the nanosecond to millisecond timescales.

Protein Nanopores

Theory meets practice: Computational studies have been used to design a ligand that triggers reactions that are not self-evident and may upon first inspection contrast the generally accepted trends. This study led to the synthesis of a {$Pd^{II}(Ph)(CF_3)$} complex containing a bidentate trifluoromethylphosphine ligand with a small bite angle that demonstrates high reactivity towards the reductive elimination of $PhCF_3$.



Computational Design



Dancing crystals under UV light: The single crystals of three metal complexes burst under UV light like popcorn. The results demonstrate that solid-state [2+2] photocycloaddition reactions can be utilized for conversion of light into mechanical motion.

Solid State Reactivity

Front Cover

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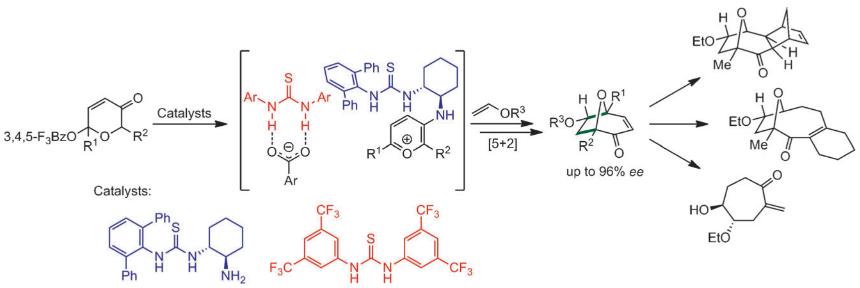
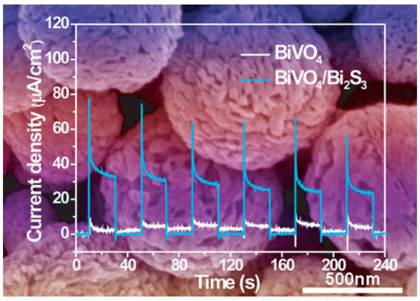
Synthetic Methods



A dual thiourea catalyst system enables the title reaction to be carried out to form useful chiral building blocks that can participate in a series of complexity-generating transformations to achieve varied molecular architectures.

Photoelectrochemistry

Unique features: Uniform heterostructured $BiVO_4/Bi_2S_3$ hollow discoids with mesoporous shell are synthesized by a facile anion exchange reaction of $BiVO_4$ discoids in aqueous Na_2S solution. Because of their heterostructured nature they exhibit significantly enhanced photocurrent response and photocatalytic activity for reduction of Cr^{VI} under visible-light illumination.



DOI: 10.1002/anie.201404978

Flashback: 50 Years Ago . . .

Weight loss and hemorrhage, or even immunization against tuberculosis are just some of the biological actions of lipids produced by the tubercle bacillus, as discussed in a Review by E. Lederer. The biosynthesis and structure of these compounds were also outlined.

Burchard Franck published two Communications on secalonic acids, which are the pale yellow main pigment of ergot (*Calviceps purpurea*). In the first Communication, the chromatographic separation and physical properties of secalonic acids A and B were discussed, and in the second Communication, the authors outlined how mass spectrometry and NMR spectroscopy were used to confirm the structures of the acids.

Emanuel Vogel also contributed two “classics” on triene systems. His first Communication dealt with the synthesis of bicyclo[4,2,0]octa-2,4,7-triene by the dehalogenation of 7,8-dibromobicyclo-[4,2,0]-octa-2,4-diene. The target product can isomerize to form cyclooctatetraene. In his second Communication, Vogel reported the use of NMR spectroscopy to derive the energy barrier for the norcaradiene–cycloheptatriene equilibrium.

The use of anion-exchange thin-layer chromatography plates for the analysis of enzymatic reactions was reported by K. and E. Randerath.

Read more in Issue 6/1964.

Heterocycles

Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, L. D. Hao, X. Gao, Z. M. Liu* ——— **5922 – 5925**

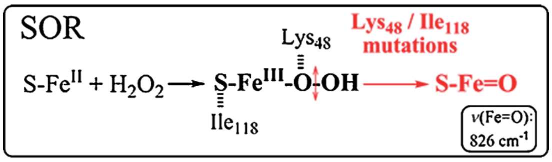
A Protic Ionic Liquid Catalyzes CO_2 Conversion at Atmospheric Pressure and Room Temperature: Synthesis of Quinazoline-2,4(1*H*,3*H*)-diones

No pressure: The reaction of CO_2 with various 2-aminobenzonitriles was achieved at atmospheric pressure and room temperature by using the bifunctional protic ionic liquid [HDBU$^+$][TFE$^-$], thus producing the title compounds in excellent yields. The ionic liquid serves as both the catalyst and solvent, and activates both CO_2 and the substrates simultaneously. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene, TFE = trifluoroethanol.

Iron–Oxo Species

F. Bonnot, E. Tremey, D. von Stetten, S. Rat, S. Duval, P. Carpentier, M. Clemancey, A. Desbois, V. Nivière* ——— **5926 – 5930**

Formation of High-Valent Iron–Oxo Species in Superoxide Reductase: Characterization by Resonance Raman Spectroscopy

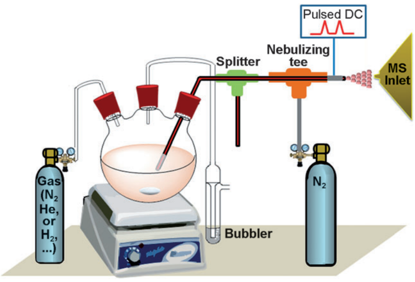


Superoxide reductase (SOR) was used as a model system to study the mechanism of the formation of high-valent iron–oxo species in metalloenzymes. The residues Lys48 and Ile118 in the second coordination sphere tightly control the evolution and the cleavage of the O—O bond of the ferric iron hydroperoxide intermediate that is formed in the SOR active site.

Mass Spectrometry

X. Yan, E. Sokol, X. Li, G. Li, S. Xu, R. G. Cooks* ——— **5931 – 5935**

On-Line Reaction Monitoring and Mechanistic Studies by Mass Spectrometry: Negishi Cross-Coupling, Hydrogenolysis, and Reductive Amination



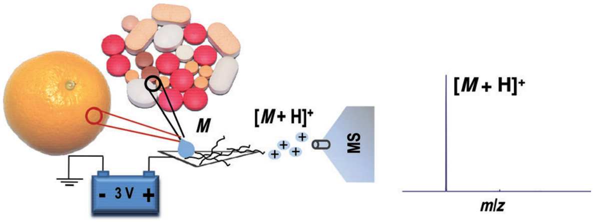
Fast and simple: A reaction monitoring system based on inductive ESI mass spectrometry provides a fast and simple way to monitor chemical reactions, including air-/moisture-sensitive reactions, continuously. It also provides information on solution-phase organic reaction mechanisms as shown by the observation of short-lived intermediates in Pd/C-catalyzed hydrogenolysis and several intermediates in Negishi cross-coupling reactions.

Mass Spectrometry

R. Narayanan, D. Sarkar, R. G. Cooks, T. Pradeep* ——— **5936 – 5940**

Molecular Ionization from Carbon Nanotube Paper

Back Cover



Low voltage: A carbon-nanotube-impregnated paper can be used to generate ions from organic molecules at potentials as low as 3 V. Common pesticides from the surface of an orange, ingredients of tablets, and a variety of analytes, such as amino acids, were characterized by this method.

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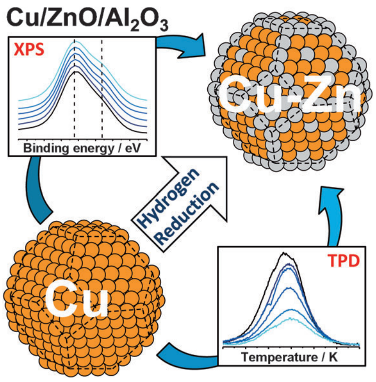
Catalyst Characterization

S. Kuld, C. Conradsen, P. G. Moses,
I. Chorkendorff,
J. Sehested* ______ **5941 – 5945**

Quantification of Zinc Atoms in a Surface Alloy on Copper in an Industrial-Type Methanol Synthesis Catalyst

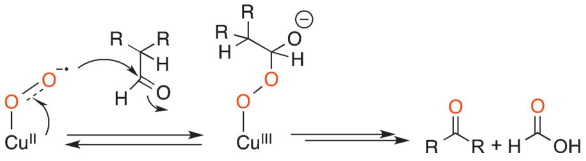


Metal–oxide interactions play an important role in surface chemistry. Investigations of the industrial methanol synthesis catalyst Cu/ZnO/Al$_2$O$_3$ under reducing conditions provide a quantification of the amount of metallic zinc in the copper surface. The developed method offers new insight into the Cu–ZnO synergy in this catalyst system and can be used for the study of similar systems.

Reactive Intermediates

P. Pirovano, A. M. Magherusan,
C. McGlynn, A. Ure, A. Lynes,
A. R. McDonald* ______ **5946 – 5950**

Nucleophilic Reactivity of a Copper(II)–Superoxide Complex

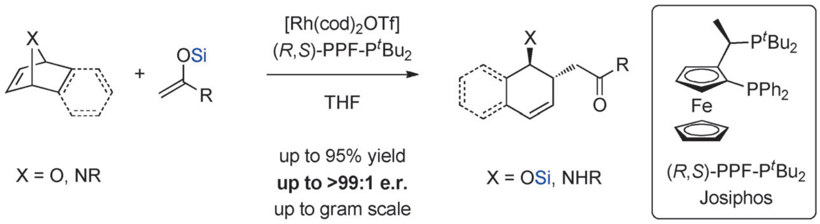


Nucleophilic superoxide: A copper(II)-superoxide complex has been found to be a highly reactive nucleophile. The complex reacts readily with certain electrophiles and is capable of the nucleophilic deformylation of electron-rich aldehydes (Baeyer–Villiger oxidation). These observations provide experimental support for the postulated nucleophilic reactivity of metal-superoxide intermediates in the catalytic cycles of certain nonheme iron enzymes.

Desymmetrization

L. Zhang, C. M. Le,
M. Lautens* ______ **5951 – 5954**

The Use of Silyl Ketene Acetals and Enol Ethers in the Catalytic Enantioselective Alkylative Ring Opening of Oxa/Aza Bicyclic Alkenes

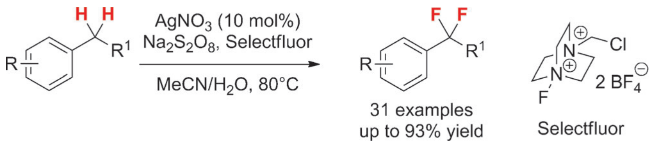


All purpose strain relief: Employing silyl ketene acetals and enol ethers as a diverse class of nucleophiles enabled the development of a general, mild, and functional group tolerant method for the alkylative asymmetric ring opening of strained and less-strained oxa/azabicyclic alkenes.

Fluorination

P. Xu, S. Guo, L. Wang,
P. Tang* ______ **5955 – 5958**

Silver-Catalyzed Oxidative Activation of Benzylic C–H Bonds for the Synthesis of Difluoromethylated Arenes



Selectfluor serves as the fluorine source and AgNO$_3$ as the catalyst in the oxidative activation of benzylic C–H bonds. This method was developed to transform methylated arenes with various functional groups into difluoromethylated arenes. The reaction is operationally simple and amenable to gram-scale synthesis.

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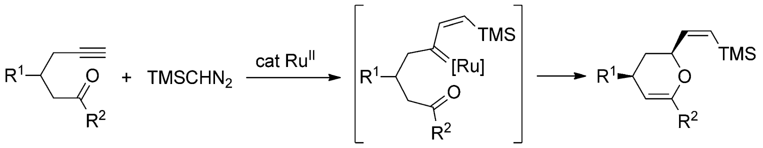
Homogeneous Catalysis

F. Cambeiro, S. López, J. A. Varela,
C. Saá* **5959 – 5963**

Vinyl Dihydropyrans and Dihydrooxazines: Cyclizations of Catalytic Ruthenium Carbenes Derived from Alkynals and Alkynones

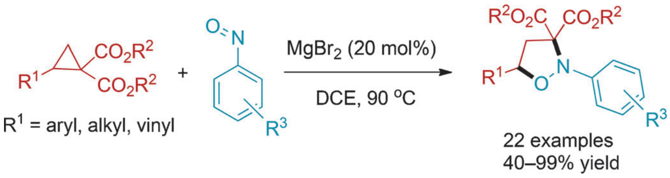


Setting a trap: A novel synthesis of 2-vinyldihydropyrans and dihydro-1,4-oxazines (morpholine derivatives) from alkynals and alkynones has been developed. The cyclizations require a mild generation of catalytic ruthenium carbenes from terminal alkynes and (trimethylsilyl)diazomethane followed by trapping with carbonyl nucleophiles.

Heterocycles

S. Chakrabarty, I. Chatterjee, B. Wibbeling,
C. G. Daniliuc, A. Studer* **5964 – 5968**

Stereospecific Formal [3+2] Dipolar Cycloaddition of Cyclopropanes with Nitrosoarenes: An Approach to Isoxazolidines

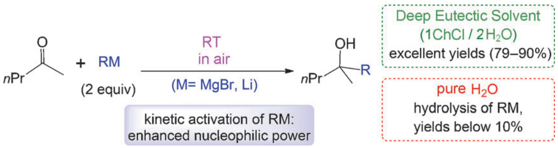


Stereospecific and regioselective: The $MgBr_2$-catalyzed formal [3+2] cycloaddition of donor–acceptor-activated cyclopropanes with nitrosoarenes offers a novel approach to structurally diverse isoxazolidines. The reactions, which are experimentally easy to conduct, occur with complete stereospecificity and perfect control of regioselectivity.

Green Chemistry

C. Vidal, J. García-Álvarez,*
A. Hernán-Gómez, A. R. Kennedy,
E. Hevia* **5969 – 5973**

Introducing Deep Eutectic Solvents to Polar Organometallic Chemistry: Chemoselective Addition of Organolithium and Grignard Reagents to Ketones in Air

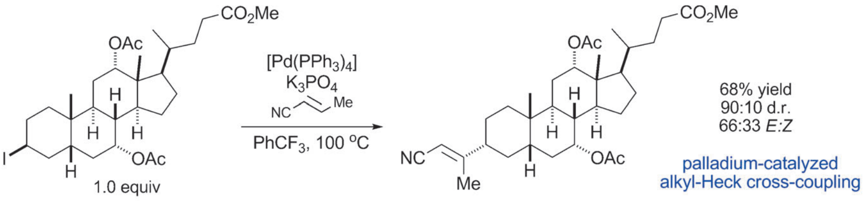


Turning lithium green: A new protocol for the selective addition of Grignard and organolithium reagents to ketones in green, biorenewable, and deep eutectic solvents (DESs) is reported. The protocol establishes a bridge between main-group organometallic compounds and green solvents (ChCl = choline chloride; see picture). The DESs are superior reaction media for highly polar organometallic compounds.

Synthetic Methods

C. M. McMahon,
E. J. Alexanian* **5974 – 5977**

Palladium-Catalyzed Heck-Type Cross-Couplings of Unactivated Alkyl Iodides



Success with palladium: A variety of unactivated alkyl iodides, including those with hydrogen atoms in the β position, were successfully coupled with different alkenes in Pd-catalyzed Heck-type reactions. The mild catalytic conditions enable the formation of intermolecular C–C bonds, with applications to substrates that contain base- or nucleophile-sensitive functionality.

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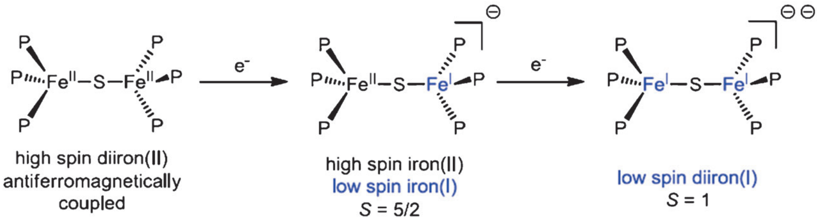
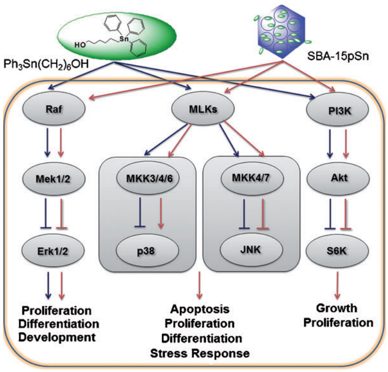
Iron–Sulfur Clusters



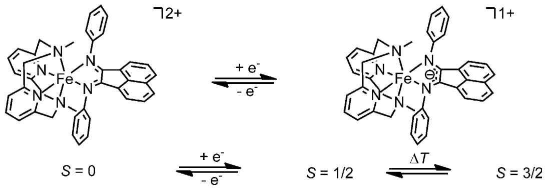
A new spin on Fe^{I}:Fe^{I} centers: A unique series of diiron $[(L_3Fe)_2(\mu\text{-}S)]$ complexes were isolated and characterized in the low-valent oxidation states Fe^{II}–S–Fe^{II}, Fe^{II}–S–Fe^{I}, and Fe^{I}–S–Fe^{I} as nearly isostructural but electronically distinct species. Structural, magnetic, and spectroscopic studies indicated a transition of the pseudotetrahedral iron centers to low-spin $S=1/2$ states upon reduction from Fe^{II} to Fe^{I} (see scheme).

Antitumor Agents

More than packaging: When a nanostructured material is loaded with an organotin(IV) compound, the efficacy of the anticancer drug is amplified dramatically. The loaded nanomaterial almost completely abolished tumor growth in syngeneic C57BL/6 mice. The reversion of the cancer cells to the normal phenotype is highly compatible with the surrounding tissue and presents a very safe mechanism for fighting cancer.



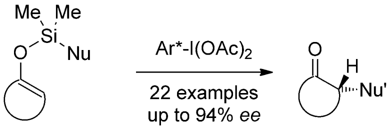
Spin Crossover



Redox-controlled changes in a coordinated ligand have been demonstrated to lead to a temperature-induced spin crossover in an octahedral iron(II) complex. The influence of the resulting coordinated π-radical on the spin crossover properties of the octahedral iron(II) ion is discussed. The structural and electronic differences between both oxidation states of the redox couple are presented.

Umpolung

A Nu approach: An efficient α-functionalization of ketones with a range of simple and useful nucleophiles is possible by using hypervalent iodine reagents (see scheme; Nu′ can be the Nu itself or a protected form of this nucleophile group).



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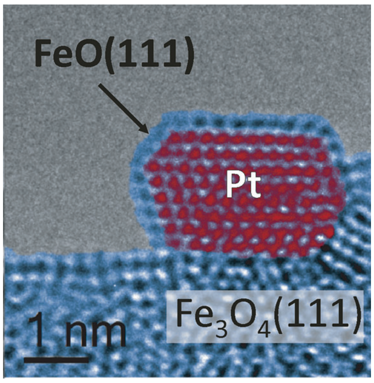
Interfaces in Catalysis

M. G. Willinger,* W. Zhang,
O. Bondarchuk, S. Shaikhutdinov*
H.-J. Freund, R. Schlögl ____ **5998 – 6001**

A Case of Strong Metal–Support Interactions: Combining Advanced Microscopy and Model Systems to Elucidate the Atomic Structure of Interfaces

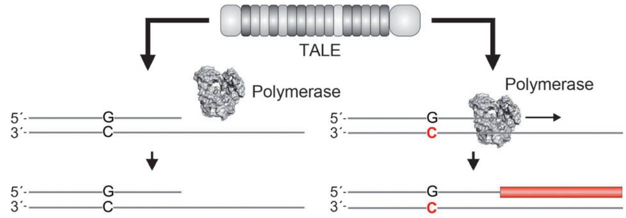


A symbiosis of advanced scanning probe and electron microscopy and a well-defined model system may provide a detailed picture of interfaces on nano-structured catalytic systems. This was demonstrated for Pt nanoparticles supported on iron oxide thin films, which undergo encapsulation by supporting oxide as a result of strong metal–support interactions (see picture).

Recognition of Nucleobases

G. Kubik, M. J. Schmidt, J. E. Penner,
D. Summerer* ____ **6002 – 6006**

Programmable and Highly Resolved In Vitro Detection of 5-Methylcytosine by TALEs



TALEored sensors for epigenetics: DNA-binding proteins that discriminate between cytosine and 5-methylcytosine (C) are important analytical tools in epigenetics. Programmable transcription-activator-like effectors (TALEs) were used to control DNA replication in response to single C positions in user-defined sequences. These studies reveal a significantly stronger C discrimination of TALEs in vitro than previously observed.

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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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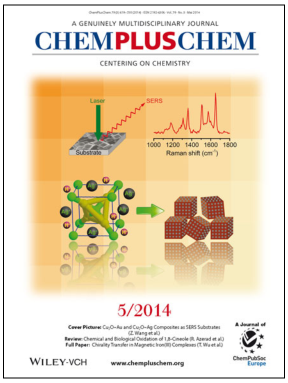

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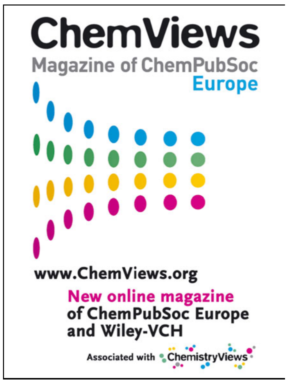

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