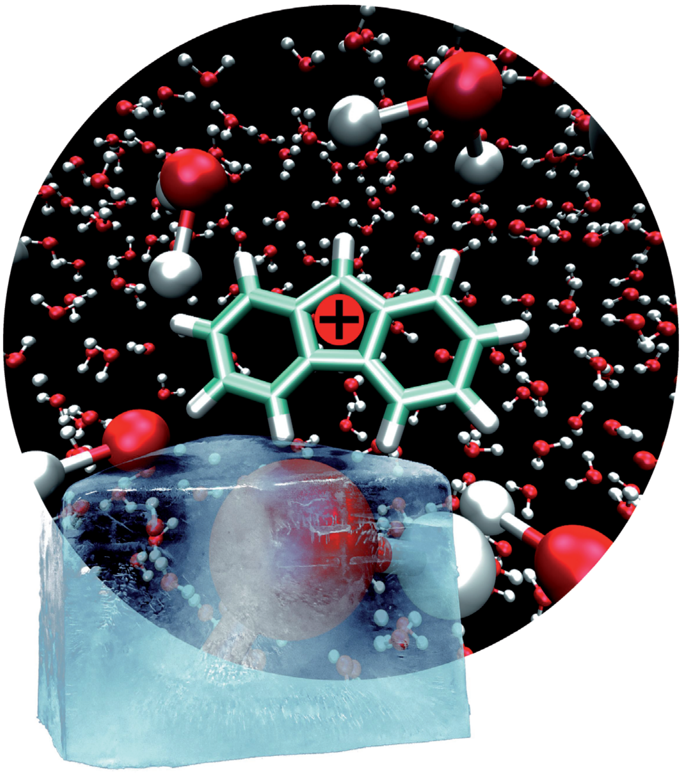
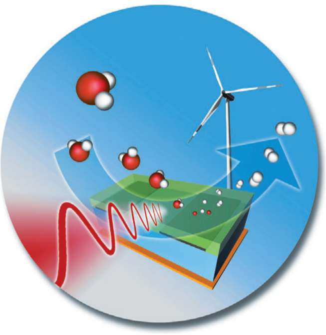
The fluorenyl cation …

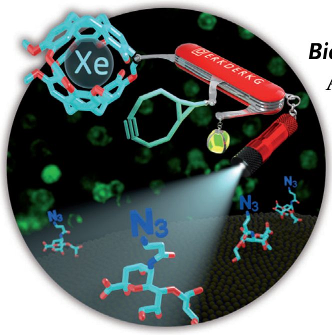


… is a highly reactive, antiaromatically destabilized carbenium ion. In their Communication on page 2656 ff., W. Sander, E. Sanchez-Garcia et al. report how this cation can be synthesized and spectroscopically characterized in amorphous water ice at cryogenic temperatures. In protic solvents at room temperature, the lifetime is only a few picoseconds, whereas in ice below 30 K, even after several hours, no reaction is observed.

Electrocatalysis

In their Communication on page 2628 ff., A. K. Opitz et al. show that a large increase in H_2 production rate is connected with the exsolution of metallic iron particles from a perovskite-type electrode.



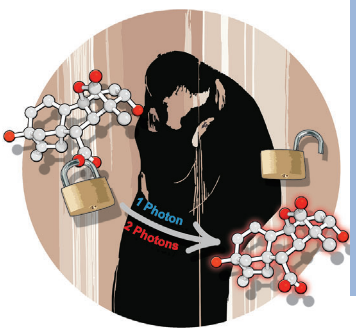


Biosensors

A bioorthogonal xenon MRI biosensor that can be used to image metabolically labeled cell-surface glycans with nanomolar sensitivity is reported by L. Schröder, C. P. R. Hackenberger et al. in their Communication on page 2806 ff.

Protein Dimerization

R. Wombacher et al. show in their Communication on page 2825 ff. that precise spatiotemporal control of intracellular protein dimerization by using light as an external stimulus is possible with the phytohormone gibberellic acid.



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GDCh
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Editorial

"... National Socialists were enthusiastic about technology and the natural sciences. Chemistry was of the highest importance in helping the Third Reich to become independent of imports from foreign countries and was crucial for the preparation of the war. The German chemical societies were of major importance in coordinating the contribution of their members to the war ..." Read more in the Editorial by Henning Hopf.

Service

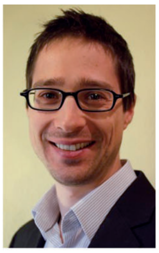
Author Profile

"The best advice I have ever been given is to be prepared for the unexpected.
The worst advice I have ever been given was not to try something because it had been tried before ..."
This and more about David Scheschkewitz can be found on page 2586.

News


T. Gaich


V. H. Däschlein-Geßner


M. Sommer


K. Ray


F. D. Toste


H. Dietz

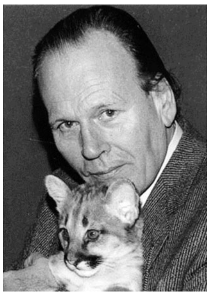

S. Grimme


C. Hertweck


C. Moberg


K. Ding

Obituaries

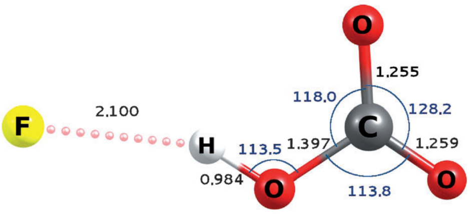


Rudolf Hoppe, emeritus professor at the University of Gießen, passed away on November 24, 2014. Hoppe was one of the biggest names in the field of inorganic solid-state chemistry, and was among the first to report the noble-gas compound XeF_2. His other achievements included the preparation of compounds with transition metals in uncommonly high or low oxidation states.

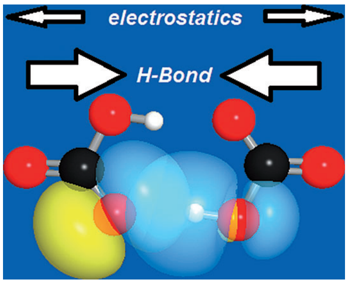
Books

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 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$ 11.738/10.206 (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.

Correspondence



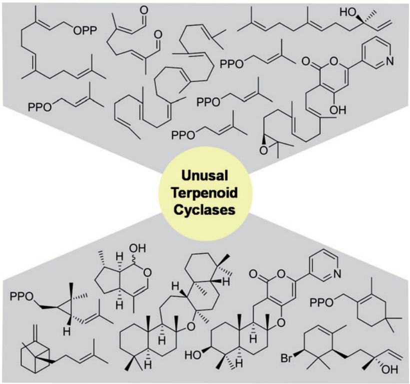
Hydrogen bonds: An approach based on energy decomposition analysis is discussed in the analysis of the bonding energy in hydrogen-bonded anion–anion and cation–cation complexes (see picture). The electrostatic Coulombic energy between the two fragments in the complexes is calculated based on the electron density distribution and not based on point charges.



Hydrogen bonds: Ab initio and hybrid density functional techniques were employed to characterize H-bonded complexes between ions of like charge (see picture). Using natural bond orbital (NBO) analysis obvious graphical similarities between NBO interactions in the complexes and conventional hydrogen-bonded species were shown.

Reviews

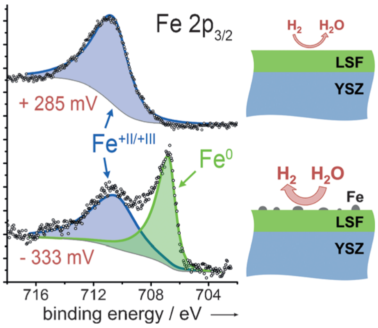
Terpene and terpenoid cyclizations are counted among the most complex chemical reactions occurring in nature and contribute crucially to the tremendous structural diversity of this largest family of natural products. This Review outlines novel terpenoid cyclases (TCs) beyond typical class I and II TCs, and showcases how their intriguing reaction mechanisms can inspire synthetic chemistry.



Communications

Electrocatalysis

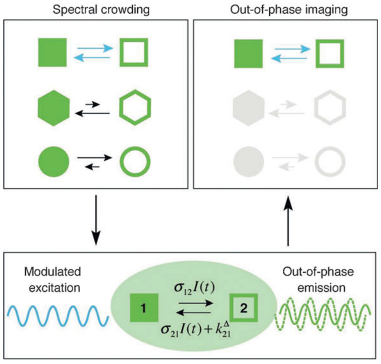
The water-splitting activity and surface chemistry of perovskite-type $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ thin film electrodes were simultaneously investigated by impedance spectroscopy and synchrotron-based near-ambient-pressure XPS. Upon cathodic polarization, the formation of metallic iron on the electrode surface could be observed, accompanied by a strong improvement of the electrochemical water-splitting activity.



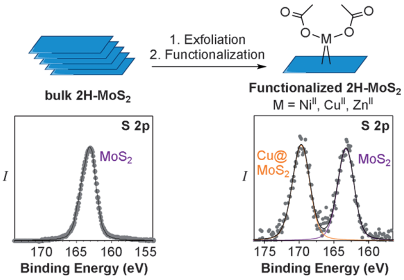
Frontispiece

Analytical Methods

OPIOM: Out-of-phase imaging after optical modulation enables selective and quantitative imaging of a photoswitching fluorescent probe in the presence of interfering species. The application of this method for selective imaging in mammalian cells and zebrafish was demonstrated.

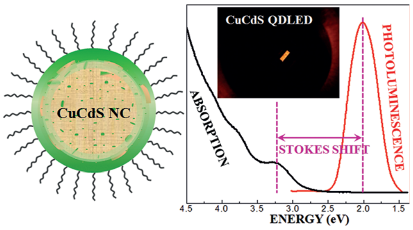


2D Materials

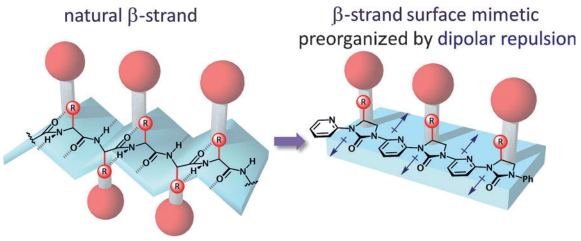


Surface modification: Functionalization of liquid-exfoliated, defect-free, layered 2H-MoS$_2$ was achieved through coordination of metal carboxylate salts by basal-plane sulfur atoms. The surface-coordinated metal center acts as an anchor for ligating organic functionalities. X-ray photoelectron spectroscopy (XPS) provides strong evidence for the coordination of MoS$_2$ surface sulfur atoms to the M(OAc)$_2$ salt (see picture).

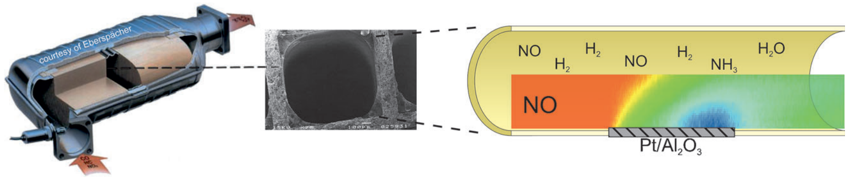
Light-Emitting Diodes



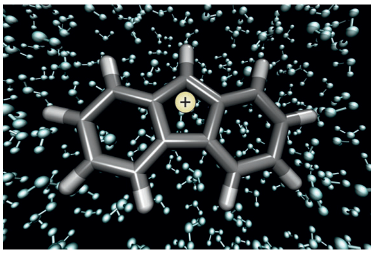
Color tunability over the entire visible spectrum and a remarkable Stokes shift of up to 1.25 eV were achieved for compositionally controlled ternary CuCdS nanocrystals synthesized in air. A two-level charge carrier recombination mechanism has been recognized, which was probed and correlated by EXAFS spectroscopy. Solid-state luminescence with a quantum yield of 55 % remains stable in air for a year enabling fabrication of LEDs with ease.



Stranded: Secondary structural elements are commonly found at the interfacial regions of protein–protein interactions. A strategy to mediate these therapeutically crucial targets using peptidomimetics has been validated for the α-helix but there are few analogous examples for the β-strand. Presented here is a foldamer for strand mimicry where dipolar repulsions are a central determinant of conformation.

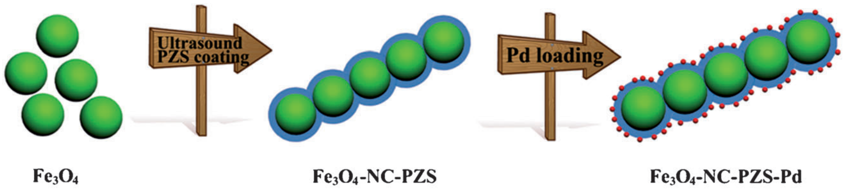


The measurement of two-dimensional species concentration profiles in the gas phase over catalytic walls is achieved by planar laser-induced fluorescence. The interaction of catalytic surface kinetics and mass transport is exemplarily studied for the reduction of NO by hydrogen to ammonia over a diesel oxidation catalyst with platinum as an active component.



Frozen: In spite of its antiaromatic destabilization, the elusive fluorenyl cation could be isolated in amorphous water ice at temperatures below 30 K by photolysis of diazofluorene. Its experimentally determined IR bands were found to nicely match predictions from QM/MM calculations.

Front Cover

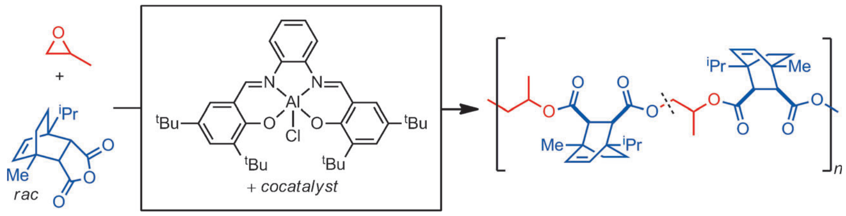


Nanostirrers: Nanometer-sized magnetic stirring bars containing Pd nanoparticles for heterogeneous catalysis in microscopic systems were prepared. They displayed far better catalytic activity than the commercial Pd/C for the hydrogenation of methylene blue in an array of microdroplets.

Sustainable Polymers

N. J. Van Zee,
G. W. Coates* ______ **2665 – 2668**

Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures

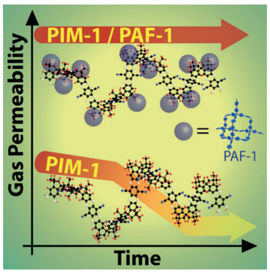


Terpene-based cyclic anhydrides are copolymerized with propylene oxide using metal salen catalysts to provide amorphous aliphatic polyesters with exceptionally high glass transition temperatures (T_g up to 109 °C). The polymerization conditions and choice of catalyst have a dramatic impact on the microstructure and ultimately the T_g value of the resulting polymer.

Gas Separation

C. H. Lau,* K. Konstas, A. W. Thornton,
A. C. Y. Liu, S. Mudie, D. F. Kennedy,
S. C. Howard, A. J. Hill,
M. R. Hill* ______ **2669 – 2673**

Gas-Separation Membranes Loaded with Porous Aromatic Frameworks that Improve with Age

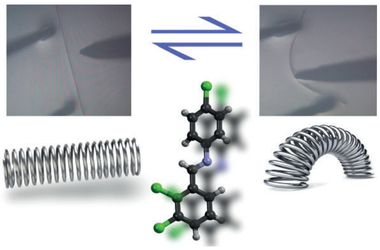


Like red wine, membranes can improve with age. Small cavities of a permeable membrane (PIM-1) are prevented from collapsing using PAF-1 nanoparticles. Larger cavities however collapse over time. The result is that as the membrane ages, the transport of small gas molecules over larger gas molecules is preferred. Thus the membrane's gas-separation properties improve with age.

Crystal Engineering

S. Ghosh, M. K. Mishra, S. B. Kadambi,
U. Ramamurty,*
G. R. Desiraju* ______ **2674 – 2678**

Designing Elastic Organic Crystals: Highly Flexible Polyhalogenated *N*-Benzylideneanilines

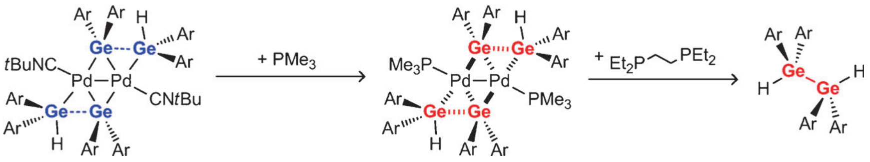


Slinky springs: Elastic organic crystals may be designed by selecting molecules that are likely to adopt isotropic packing with weak and only moderately polar interactions. The restorative ability of halogen bonds upon application of stress is particularly relevant in this context and is used in this family of Schiff bases.

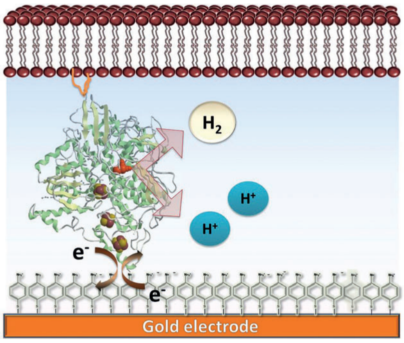
Reaction Mechanisms

M. Tanabe, S. Omine, N. Ishikawa,
K. Osakada,* Y. Hayashi,
S. Kawauchi ______ **2679 – 2683**

Bond Formation and Coupling between Germyl and Bridging Germylene Ligands in Dinuclear Palladium(I) Complexes



Cooperation of two metal centers: Electron-donating auxiliary ligands of the dipalladium(I) complexes promote coupling of the bridging germylene ($GeAr_2$) and terminal germyl ($GeAr_2H$) ligands. The Ge···Ge bonding interaction of the dipalladium intermediate is enhanced by an electron-donating PMe_3 ligand which activates Pd–Ge and Pd–Pd bonds.



Across the divide: The proton concentration at an electrode/phospholipid-bilayer interface was controlled and monitored electrochemically by immobilizing a membrane-bound hydrogenase (see picture). Thus, the energy from the electroenzymatic oxidation of H_2 could be used to generate a proton gradient across the supported biomimetic membrane.

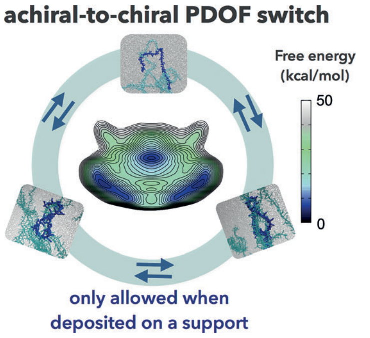
Enzymatic Electrodes

Ó. Gutiérrez-Sanz, C. Tapia,
M. C. Marques, S. Zacarias, M. Vélez,
I. A. C. Pereira,
A. L. De Lacey* ________ **2684 – 2687**

Induction of a Proton Gradient across a Gold-Supported Biomimetic Membrane by Electroenzymatic H_2 Oxidation

---

Taming of the screw: The chiral-switch properties of polyfluorene-based polymers are investigated by enhanced-sampling free-energy simulations. The chirality induction is feasible through a stepwise switching of the fluorene–fluorene dihedral angles. The chiral switch occurs only when the polymer is deposited on a support and not on an isolated chain or aggregated phases of the polymer.



Chiral Switches

A. Pietropaolo,* Y. Wang,
T. Nakano* ________ **2688 – 2692**

Predicting the Switchable Screw Sense in Fluorene-Based Polymers

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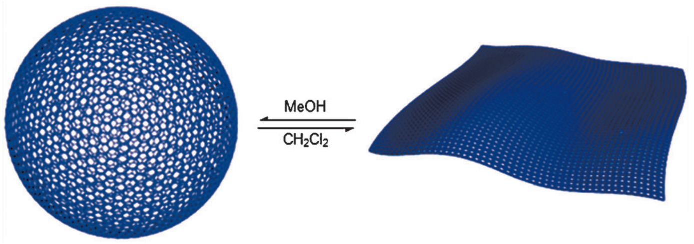


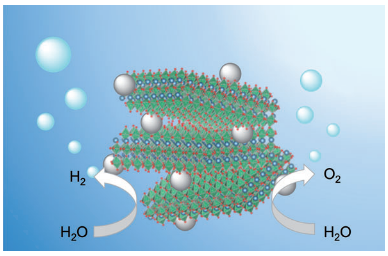
Nano-transformers: A facile synthesis of polymer nanocapsules and thin films by multiple in-plane cross-linking of mercaptopropylcucurbit[6]uril through disulfide bonds was achieved. The reversible nature of disulfide linkages allows reversible morphological transformations by simple solvent exchanges.

Morphology Transformation

J. Kim, K. Baek,* D. Shetty, N. Selvapalam,
G. Yun, N. H. Kim, Y. H. Ko, K. M. Park,
I. Hwang, K. Kim* ________ **2693 – 2697**

Reversible Morphological Transformation between Polymer Nanocapsules and Thin Films through Dynamic Covalent Self-Assembly

---



Efficient photocatalyst: Platinum nanoclusters with a diameter of about 1 nm were intercalated into the interlayer nanospace of $KCa_2Nb_3O_{10}$ nanosheets using the electrostatic attraction between a cationic Pt complex and a negatively charged $Ca_2Nb_3O_{10}^-$ sheet. This process provides an efficient photocatalyst for water splitting into hydrogen and oxygen (see picture).

Water Splitting

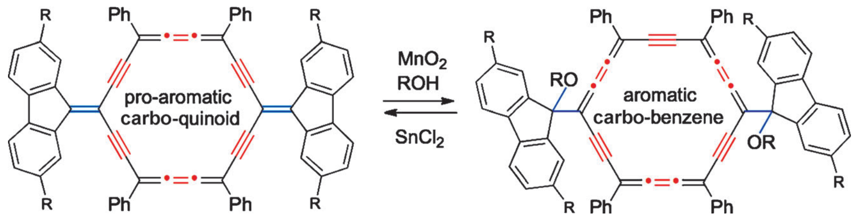
T. Oshima, D. Lu, O. Ishitani,
K. Maeda* ________ **2698 – 2702**

Intercalation of Highly Dispersed Metal Nanoclusters into a Layered Metal Oxide for Photocatalytic Overall Water Splitting

Aromaticity

K. Cocq, V. Maraval,* N. Saffon-Merceron, A. Saquet, C. Poidevin, C. Lepetit, R. Chauvin* **2703 – 2706**

Carbo-Quinoids: Stability and Reversible Redox-Proaromatic Character towards *Carbo*-Benzenes

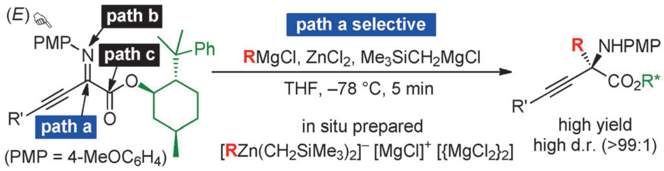


Back and forth: The carbo-mer of the *para*-quinodimethane core is stable within a bis(9-fluorenylidene) derivative. Oxidation of the *carbo*-quinoid with MnO_2 in the presence of $SnCl_2$ and ethanol affords *p*-bis(9-ethoxy-fluoren-9-yl)-*carbo*-benzene, which is converted back into the *carbo*-quinoid by reduction with $SnCl_2$, thus evidencing a chemical reversibility of the interconversion between a pro-aromatic *carbo*-quinoid and an aromatic *carbo*-benzene.

Synthetic Methods

M. Hatano, K. Yamashita, M. Mizuno, O. Ito, K. Ishihara* **2707 – 2711**

C-Selective and Diastereoselective Alkyl Addition to β,γ-Alkynyl-α-imino Esters with Zinc(II)ate Complexes

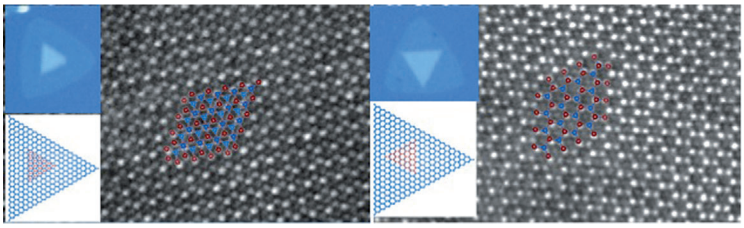


Reversing umpolung: Zinc(II)ate complexes, formed in situ from a Grignard reagent and $ZnCl_2$, promoted an unusual regio- and diastereoselective alkyl addition to β,γ-alkynyl-α-imino esters by virtue of cooperation between the high nucleophilicity of $[R_3Zn]^-$ and the high Lewis acidity of $[MgX]^+$. The corresponding α-quaternary C adducts were obtained in high to excellent yields.

Gallium Selenide

X. Li, L. Basile, M. Yoon, C. Ma, A. A. Puretzky, J. Lee, J. C. Idrobo, M. Chi, C. M. Rouleau, D. B. Geohegan, K. Xiao* **2712 – 2717**

Revealing the Preferred Interlayer Orientations and Stackings of Two-Dimensional Bilayer Gallium Selenide Crystals

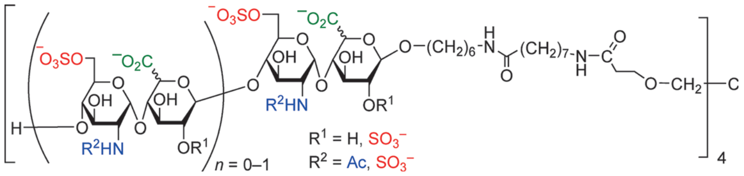


Bilayer GaSe 2D crystals with different twist angles were grown through a controllable vapor-phase deposition method. The commensurate stacking configurations (AA′ and AB stacking) and Ga-terminated edge structure in as-synthesized bilayer crystals are clearly observed at the atomic scale for the first time. Theoretical analysis reveals that the energies of the interlayer coupling are responsible for the preferred orientations.

Glycomimetics

P. C. Tyler, S. E. Guimond, J. E. Turnbull, O. V. Zubkova* **2718 – 2723**

Single-Entity Heparan Sulfate Glycomimetic Clusters for Therapeutic Applications

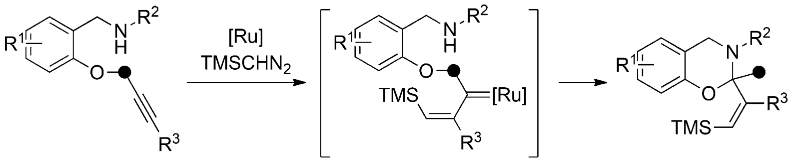


A four-legged copycat: Heparan sulfate (HS) has a variety of critical functions in cell signaling, but the exploitation of HS oligosaccharides as mimetic agents has been hindered by the complexity of their synthesis. Polyvalent displays of specific HS structures on dendritic cores are more accessible constructs (see example). Such HS glycomimetic clusters mimicked natural HS saccharides in their inhibition of the Alzheimer's disease protease BACE-1.

Synthetic Methods

C. González-Rodríguez,* J. R. Suárez, J. A. Varela, C. Saá* ——— 2724 – 2728

Nucleophilic Addition of Amines to Ruthenium Carbenes: *ortho*-(Alkynyloxy)benzylamine Cyclizations towards 1,3-Benzoxazines

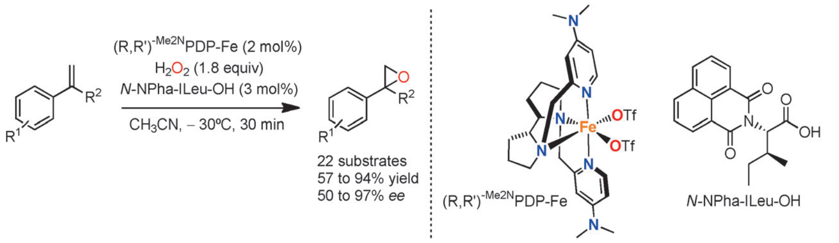


A new addition: A new ruthenium-catalyzed cyclization of *ortho*-(alkynyloxy)benzylamines to 1,3-benzoxazines is reported. Vinyl ruthenium carbenes are proposed as the key intermediates, and the mechanistic hypothesis supposes the first example of a nucleophilic addition of amines to vinyl ruthenium carbenes. Rearrangement of an internal C(sp) into a tetrasubstituted C(sp^3) is highly remarkable. TMS = trimethylsilyl.

Bioinspired Asymmetric Catalysis

O. Cussó, X. Ribas, J. Lloret-Fillol, M. Costas* ——— 2729 – 2733

Synergistic Interplay of a Non-Heme Iron Catalyst and Amino Acid Coligands in H_2O_2 Activation for Asymmetric Epoxidation of α-Alkyl-Substituted Styrenes

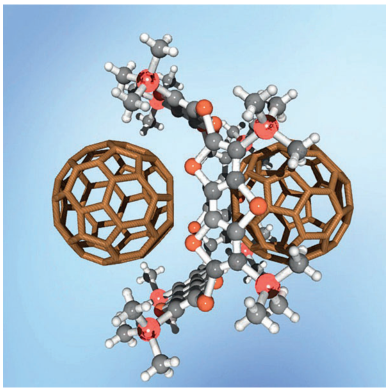


Come on styrene: Using amino acids as coligands for bioinspired non-heme iron catalysts, the substrate scope of epoxidation reactions with aqueous H_2O_2 is extended to the challenging α-styrenes. Thus, these systems can be adapted for new substrate classes simply by changing the amino acid coligand.

3D Macrocycles

R. Inoue, M. Hasegawa,* T. Nishinaga, K. Yoza, Y. Mazaki ——— 2734 – 2738

Efficient Synthesis, Structure, and Complexation Studies of Electron-Donating Thiacalix[*n*]dithienothiophene

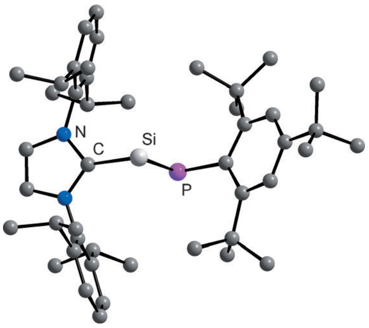


Binding two fullerenes: A series of thiacalix[*n*]dithiothiophenes ($n = 4$–10) was synthesized. The molecular geometry depends on the parity of "*n*" of the neutral state, and electronic delocalization was found in the cationic species. The 4-mer acted as a "Janus-head" cavitand for two C_{60} molecules, whereas the 5- and 6-mer formed stable 1:1 complexes with C_{60}.

Main-Group Multiple Bonds

D. Geiß, M. I. Arz, M. Straßmann, G. Schnakenburg, A. C. Filippou* ——— 2739 – 2744

Si=P Double Bonds: Experimental and Theoretical Study of an NHC-Stabilized Phosphasilenylidene

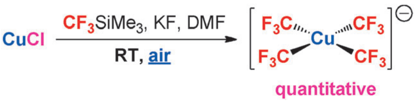


An NHC-stabilized phosphasilenylidene was obtained from $SiCl_2$(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and LiP(Mes*)(TMS) (Mes* = 2,4,6-$tBu_3C_6H_2$). The compound was characterized by various experimental and theoretical methods and compared with those of the isolobal congeners (IDipp)Si=Si(IDipp) and Mes*P=PMes*.

Copper Complexes

A. M. Romine, N. Nebra, A. I. Konovalov,
E. Martin, J. Benet-Buchholz,
V. V. Grushin* ______ **2745 – 2749**

Easy Access to the Copper(III) Anion $[Cu(CF_3)_4]^-$

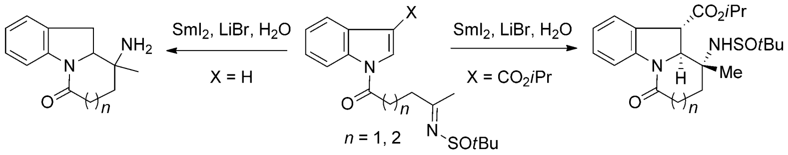


Easy as it gets: The Cu^{III} anion $[Cu(CF_3)_4]^-$ is finally easily accessible through the newly developed exceedingly simple and highly efficient one-step procedure directly from CuCl. The reaction occurs at room temperature in air to furnish quantitatively $[Cu(CF_3)_4]^-$, which can be used for the synthesis of other, previously unknown CF_3Cu^{III} compounds.

Polycyclic Amines

C. N. Rao, D. Lentz,
H.-U. Reissig* ______ **2750 – 2753**

Synthesis of Polycyclic Tertiary Carbinamines by Samarium Diiodide Mediated Cyclizations of Indolyl Sulfinyl Imines



Two ways to three rings: Indolyl sulfinyl imines undergo smooth SmI_2-mediated cyclizations and provide polycyclic tertiary carbinamines in good yield. *N*-Sulfinyl imines with unactivated indole units (X = H) undergo an *N*-desulfinylation—a previously unknown reaction—and then the cyclization. In contrast, activated indoles (X = CO_2R) undergo cyclization with intact *N*-sulfinyl imine moiety leading to the formation of enantiomerically pure tricyclic products.

DOI: 10.1002/anie.201580914

Flashback: 50 Years Ago . . .

The chemistry of heterosiloxanes was the subject of a Review by Hubert Schmidbaur, a former Chairman of the Editorial Board of *Angewandte Chemie*. 50 years later, at the age of 80, Schmidbaur is still actively publishing; his Review on argentophilic interactions appeared in a very recent issue (see *Angew. Chem. Int. Ed.* **2015**, *54*, 746).

Ernst Otto Fischer, who shared the 1973 Nobel Prize in Chemistry with Geoffrey Wilkinson, reported on isonitrilocyclopentadienyl complexes of lanthanoids. These complexes were formed by the reaction of lanthanoid tricyclopentadienyl complexes with cyclohexyl isonitrile, and were the first reported examples of compounds where a stable metal–carbon σ bond is formed for rare-earth metals.

Armin Weiss et al. reported on the crystal structure of strontium disilicide. The silicon atoms were found to form a three-dimensional network with Si–Si distances comparable to that of elemental silicon. This structure contrasts with those other disilicides that contain two-dimensional nets or isolated tetrahedra of silicon atoms.

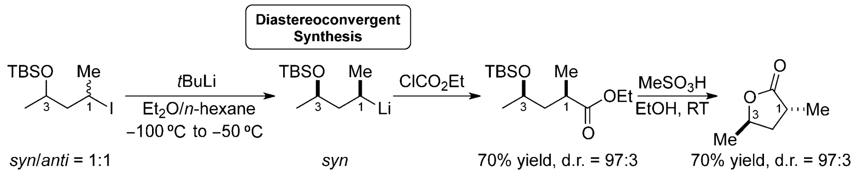
Horst Prinzbach et al. published two Communications on conjugated π-bond systems. The first report described the synthesis of a monobenzo derivative of cyclopropenylidenecyclopentadiene (calicene), which is a highly strained but also delocalized system. Interestingly, a report from Andrew S. Kende on a similar calicene derivative was published shortly afterwards (*J. Am. Chem. Soc.* **1965**, *87*, 1609). Prinzbach's second contribution was on stable methylenephenalene derivatives (phenalenes are three fused six-membered rings). Prinzbach was one of the most influential German organic chemists in the latter half of the last century, and was famous for the synthesis of a range of non-benzenoid organic compounds, including dodecahedrane (for more details see his Obituary: *Angew. Chem.* **2012**, *51*, 11936).

Read more in Issue 3/1965.

Alkyllithium Reagents

K. Moriya, D. Didier, M. Simon,
J. M. Hammann, G. Berionni,
K. Karaghiosoff, H. Zipse, H. Mayr,
P. Knochel* ______ **2754 – 2757**

Stereoselective Synthesis and Reactions of Secondary Alkyllithium Reagents Functionalized at the 3-Position

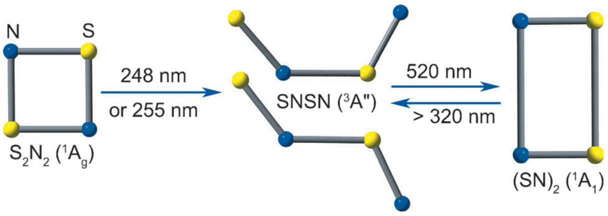


Stereoconvergent or not? Secondary alkyllithium reagents bearing an OTBS group (TBS = *tert*-butyldimethylsilyloxy) at the 3-position were prepared stereoconvergently through an I/Li exchange of a diastereomeric mixture of the corresponding secondary alkyl iodides. These lithium reagents react with a range of electrophiles, including carbon electrophiles, with retention of configuration to yield 3-functionalized derivatives with good diastereoselectivity.

Elusive Isomers

X. Q. Zeng,* A. Flores Antognini,
H. Beckers,* H. Willner ______ **2758 – 2761**

Isomers of Disulfur Dinitride, S_2N_2

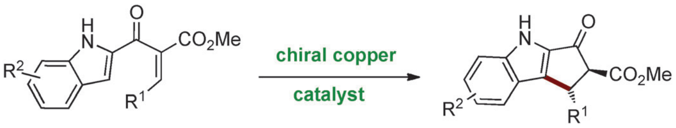


Two new open-shell S_2N_2 isomers, *trans* SNSN ($^3A''$) and *cis* SNSN ($^3A''$), as well as a closed-shell $(SN)_2$ dimer (C_{2v}, $^1A_1$) are formed by UV photolysis ($\lambda = 248$ or 255 nm) of cyclic S_2N_2 (^1A_g) in solid Ar at 16 K. These isomers were characterized by their IR spectra and their mutual photointerconversion reactions.

Asymmetric Catalysis

S. Raja, M. Nakajima,
M. Rueping* ______ **2762 – 2765**

Experimental and Computational Study of the Catalytic Asymmetric 4π-Electrocyclization of N-Heterocycles



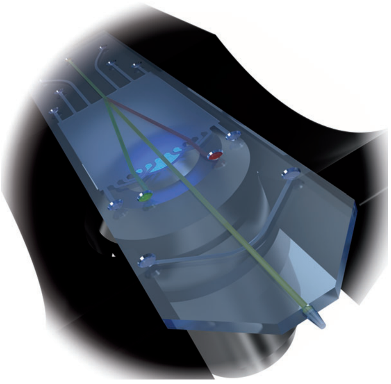
Facts and figures: The copper-catalyzed asymmetric Nazarov reaction of indole derivatives provides the corresponding cyclopenta[*b*]indoles under mild conditions in good yields and with excellent selectivity. Computer-aided studies provide a better understanding of the reaction mechanism and rationalize the absolute configuration of the products.

Lab-on-a-Chip

C. Benz, M. Boomhoff, J. Appun,
C. Schneider, D. Belder* ______ **2766 – 2770**

Chip-Based Free-Flow Electrophoresis with Integrated Nanospray Mass-Spectrometry

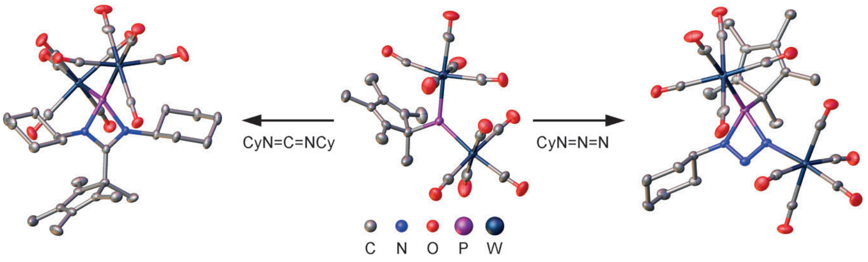
Going our separate weighs: Micro-free-flow electrophoresis is directly coupled with mass spectrometry and applied in a [3+2]-cycloannulation. This new method enables online purification and monitoring of chemical processes, thereby paving the way for more complex chemical synthesis on integrated lab-on-a-chip devices.



Group 15 Heterocycles

M. Seidl, C. Kuntz, M. Bodensteiner, A. Y. Timoshkin, M. Scheer* **2771 – 2775**

Reaction of Tungsten–Phosphinidene and –Arsinidene Complexes with Carbodiimides and Alkyl Azides: A Straightforward Way to Four-Membered Heterocycles

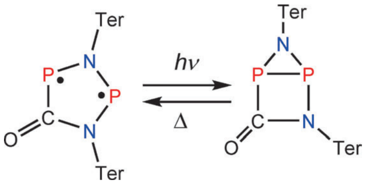


Making rings: The reaction of the complexes $[Cp^*E\{W(CO)_5\}_2]$ with carbodiimides by insertion into an E–R bond (E = P, As) yields four-membered heterocycles, which are observed for E = As for the first time. Cyclization also occurs between the phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ and alkyl azides RN_3 (R = cyclohexyl, hexyl) to give unprecedented triazaphosphete complexes, which can be regarded as an intermediate of the Staudinger reaction.

Biradicaloids

A. Hinz, A. Schulz,* A. Villinger **2776 – 2779**

Stable Heterocyclopentane-1,3-diyls

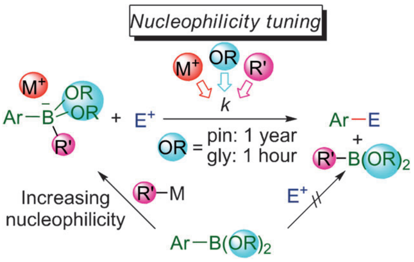


There is a house in UV light: By an unprecedented ring expansion reaction, diphosphadiazanediyls were utilized to activate carbon monoxide, leading to the first stable cyclopentane-1,3-diyl, which can be transformed into a housane by UV irradiation. Cyclopentane-1,3-diyl displays typical biradicaloid reactivity, such as activation of small molecules bearing single or multiple bonds. Ter = 2,6-dimesitylphenyl.

Boron Compounds

G. Berionni, A. I. Leonov, P. Mayer, A. R. Ofial, H. Mayr* **2780 – 2783**

Fine-Tuning the Nucleophilic Reactivities of Boron Ate Complexes Derived from Aryl and Heteroaryl Boronic Esters

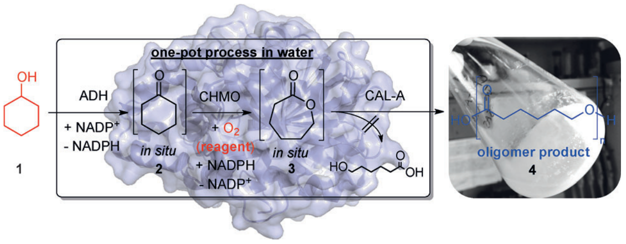


Tailor-made nucleophiles: Kinetic studies reveal that the nucleophilic reactivities of boron ate complexes depend mainly on the nature of the covalently bound ligands at boron. Thus ethylene glycol -B(gly) and neopentyl glycol -B(neo) derivatives are 10^4 times more reactive than analogous pinacol -B(pin) and catechol -B(cat) derivatives. These insights can be used to tailor the reactivities of boron ate complexes.

Biocatalysis

S. Schmidt, C. Scherkus, J. Muschiol, U. Menyes, T. Winkler, W. Hummel, H. Gröger, A. Liese, H.-G. Herz, U. T. Bornscheuer* **2784 – 2787**

An Enzyme Cascade Synthesis of ε-Caprolactone and its Oligomers

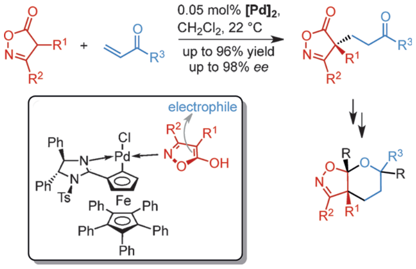


Let's polymerize! Oligo-ε-caprolactone was produced in a one-pot enzymatic cascade synthesis starting from cyclohexanol. In the first step, cyclohexanol is oxidized by an alcohol dehydrogenase (ADH) in combination with the cyclohexanone monooxygenase (CHMO) from *Acinetobacter calcoaceticus*, followed by direct ring-opening oligomerization of ε-caprolactone in an exclusively aqueous phase by lipase A from *Candida antarctica* (CAL-A).

Asymmetric Catalysis

T. Hellmuth, W. Frey,
R. Peters* ______ **2788 – 2791**

Regioselective Catalytic Asymmetric C-Alkylation of Isoxazolinones by a Base-Free Palladacycle-Catalyzed Direct 1,4-Addition



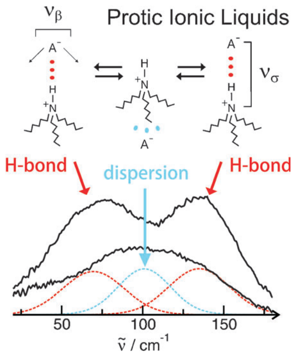
Control freak: Enantio- and regioselective C-alkylations of isoxazolinones to form products with all-carbon-substituted quaternary stereocenters are now possible. The controlled reaction was conducted with a sterically demanding planar-chiral palladacycle catalyst (TON up to 1900) in the absence of any other reagent.

Dispersion Forces

K. Fumino, V. Fossog, P. Stange,
D. Paschek, R. Hempelmann,
R. Ludwig* ______ **2792 – 2795**

Controlling the Subtle Energy Balance in Protic Ionic Liquids: Dispersion Forces Compete with Hydrogen Bonds

Inside Cover

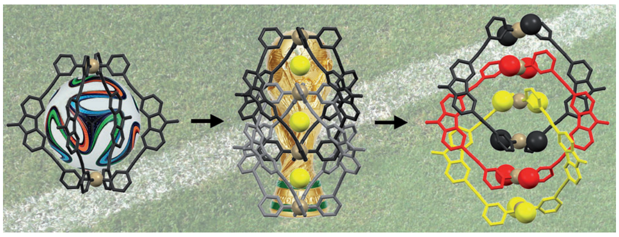


The winner is ... Dispersion forces compete with hydrogen bonds in a protic ionic liquid. The energy balance can be controlled by the hydrogen-bond interaction strength of the anion and the alkyl-chain lengths of the cation. The energy of conversion between the H-bonded and the dispersion-dominated ion pairs can be determined experimentally by far-infrared spectroscopy. Dispersion-corrected DFT methods are essential for reproducing the experimental results.

Coordination Cages

R. Zhu, J. Lübben, B. Dittrich,
G. H. Clever* ______ **2796 – 2800**

Stepwise Halide-Triggered Double and Triple Catenation of Self-Assembled Coordination Cages

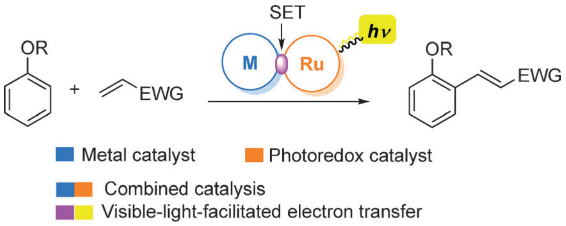


A ball-shaped self-assembled coordination cage $[\mathrm{Pd}_2\mathbf{L}_4]$ based on a carbazole backbone and $\mathrm{Pd}^{\mathrm{II}}$ cations is transformed into an interpenetrated double cage $[3\,\mathrm{X}@\mathrm{Pd}_4\mathbf{L}_8]$ upon addition of 1.5 equiv of halide anions ($\mathrm{X}=\mathrm{Cl}^-$, Br^-). Surprisingly, further addition of the same halide anion triggered a second structural transformation to yield the L6n1-linked $\{trans\text{-}[(\mathrm{PdBr}_2)_2\mathbf{L}_2]\}_3$.

Dual Catalysis

D. C. Fabry, M. A. Ronge, J. Zoller,
M. Rueping* ______ **2801 – 2805**

C–H Functionalization of Phenols Using Combined Ruthenium and Photoredox Catalysis: In Situ Generation of the Oxidant



Air and light: The direct *ortho* C–H functionalization of *o*-(2-pyridyl)phenols provides various olefinated phenol ethers in good yields (see Scheme). The ruthenium catalyst is regenerated through oxidation by a photoredox catalyst under visible-light irradiation.

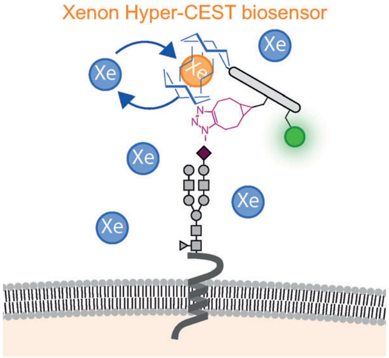
Biosensors

C. Witte, V. Martos, H. M. Rose, S. Reinke, S. Klippel, L. Schröder,* C. P. R. Hackenberger* ____ **2806 – 2810**

Live-cell MRI with Xenon Hyper-CEST Biosensors Targeted to Metabolically Labeled Cell-Surface Glycans

Inside Back Cover

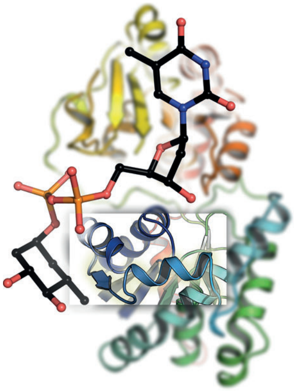
Xenon's sweet spot: A multimodal bioorthogonal xenon MRI biosensor was used to image the distribution of metabolically labeled cell-surface glycans with nanomolar sensitivity. This work expands the application of MRI to the imaging of glycome targets that have been difficult to investigate with conventional MRI contrast agents.



Antibiotics

H. K. Tam, J. Härle, S. Gerhardt, J. Rohr, G. Wang, J. S. Thorson, A. Bigot, M. Lutterbeck, W. Seiche, B. Breit,* A. Bechthold,* O. Einsle* __ **2811 – 2815**

Structural Characterization of O- and C-Glycosylating Variants of the Landomycin Glycosyltransferase LanGT2

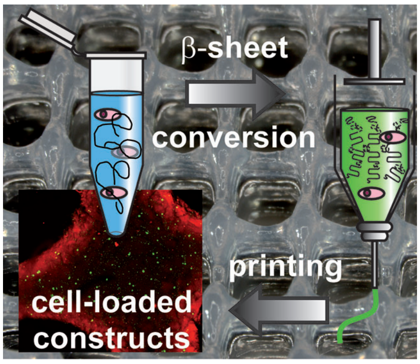


Oh to see glycosyl transfer: Crystal structures of the O-glycosyltransferase LanGT2 and the engineered C–C bond-forming variant LanGT2S8Ac show how the replacement of a single loop can change the functionality of the enzyme. Crystal structures of the enzymes in complex with a nonhydrolyzable nucleotide-sugar analogue revealed that there is a conformational transition to create the binding sites for the aglycon substrate.

Biofabrication

K. Schacht, T. Jüngst, M. Schweinlin, A. Ewald, J. Groll,* T. Scheibel* ____________ **2816 – 2820**

Biofabrication of Cell-Loaded 3D Spider Silk Constructs



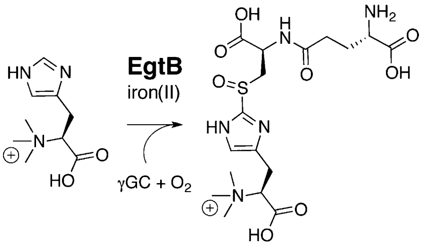
Printed silk: A novel bioink system based on recombinant spider silk proteins was developed. 3D cell-loaded spider silk hydrogel constructs prepared by using robotic dispensing supported viability of the embedded cells for at least a week. Cytocompatibility, physical cross-linking without the need for additives, and the possibility to tailor cell–material interactions through the introduction of cell-adhesion motifs render this a versatile system for biofabrication.

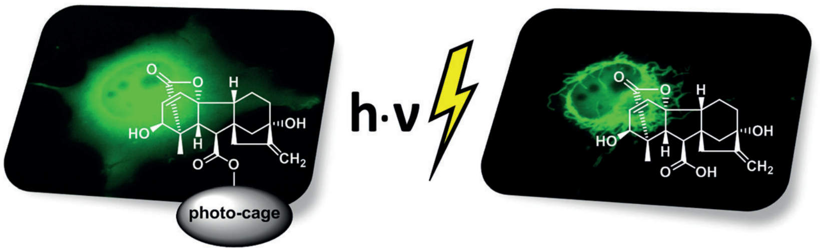
Enzymatic C–S Coupling

K. V. Goncharenko, A. Vit, W. Blankenfeldt,* F. P. Seebeck* ____________ **2821 – 2824**

Structure of the Sulfoxide Synthase EgtB from the Ergothioneine Biosynthetic Pathway

Ironing out the details: The crystal structure of the non-heme iron enzyme EgtB in complex with its substrates γ-glutamyl cysteine and *N*-α-trimethyl histidine reveals that the two substrates and three histidine residues define an octahedral iron binding site. This active-site geometry is consistent with a catalytic mechanism in which C–S bond formation is initiated by an iron(III)-complexed thiyl radical attacking the imidazole ring of *N*-α-trimethyl histidine.





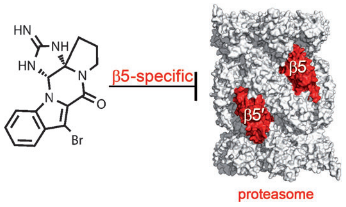
Come together, light now: Light-induced protein dimerization is possible using a derivative of the phytohormone gibberellic acid (see picture) that can be photo-activated. This reagent allows a precise spatiotemporal control of intracellular protein dimerization by using light as an external stimulus.

Protein Dimerization

K. M. Schelkle, T. Griesbaum, D. Ollech,
S. Becht, T. Buckup, M. Hamburger,
R. Wombacher* ________ **2825–2829**

Light-Induced Protein Dimerization by One- and Two-Photon Activation of Gibberellic Acid Derivatives in Living Cells

Back Cover



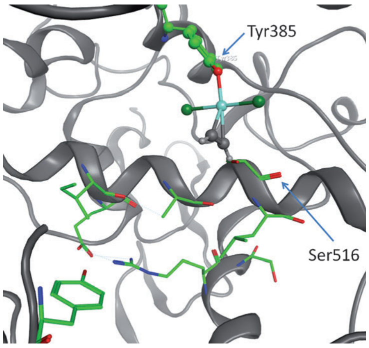
Nonpeptidic ligands: Inhibitors with new mechanisms of action are needed to tackle the ineffectiveness of currently marketed peptidic proteasome blockers for the treatment of solid tumors. The crystal structure of the yeast 20S proteasome in complex with a natural product inspired alkaloid reveals an unexpected binding action. The presented compound provides an ideal scaffold for the structure-based design of subunit-specific, nonpeptidic proteasome blockers.

Proteasome Inhibition

P. Beck, T. A. Lansdell, N. M. Hewlett,
J. J. Tepe,* M. Groll* ______ **2830–2833**

Indolo-Phakellins as β5-Specific Noncovalent Proteasome Inhibitors

Zeise screen: Organometallic compounds with aspirin substructure have interesting biological effects. Investigations into aspirin-derivatives of Zeise's salt demonstrate that Zeise's salt itself is pharmacologically active and represents a potent inhibitor of cyclooxygenase enzymes, which suggest its use as a pharmacophore in medicinal chemistry for the design of new metal-based drugs.

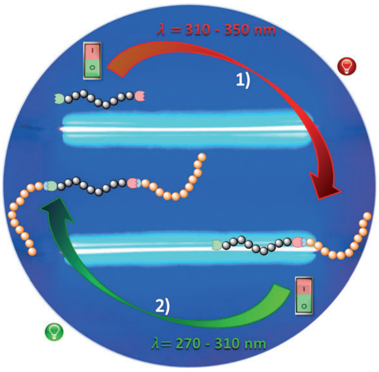


Bioinorganic Drugs

S. Meieranz, M. Stefanopoulou,
G. Rubner, K. Bensdorf, D. Kubutat,
W. S. Sheldrick, R. Gust* ___ **2834–2837**

The Biological Activity of Zeise's Salt and its Derivatives

It's up to the wavelength: The concept of λ-orthogonal photochemistry is presented using light-induced pericyclic photoreactions. A functionalized electron-poor alkene is reacted with various selectively photoactive groups on a polymer; the selectivity depends on the wavelength of the light used.



Polymer Photoreactions

K. Hiltebrandt, T. Pauloehrl, J. P. Blinco,
K. Linkert, H. G. Börner,
C. Barner-Kowollik* ________ **2838–2843**

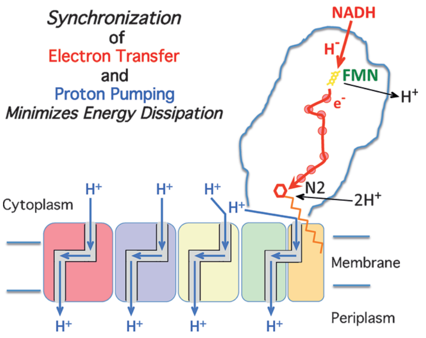
λ-Orthogonal Pericyclic Macromolecular Photoligation

VIP Enzyme Kinetics

S. de Vries,* K. Dörner,
M. J. F. Strampraad,
T. Friedrich* ______________ 2844 – 2848

Electron Tunneling Rates in Respiratory Complex I Are Tuned for Efficient Energy Conversion

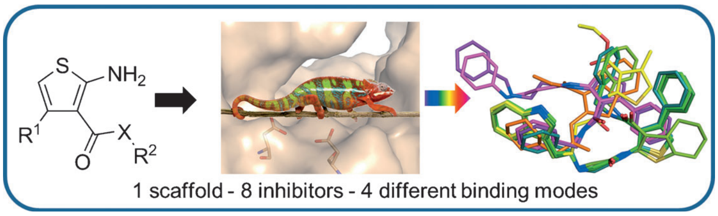
The reduction of ubiquinone by NADH is catalyzed by flavin mononucleotide and a chain of seven iron–sulfur centers. The electron transfer rates between the centers indicate that the Fe–S chain synchronizes the electron transfer rate to match the time scale of the conformational changes required for proton translocation.



Lead Structure Optimization

M. Kuhnert, H. Köster, R. Bartholomäus,
A. Y. Park, A. Shahim, A. Heine,
H. Steuber, G. Klebe,
W. E. Diederich* __________ 2849 – 2853

Tracing Binding Modes in Hit-to-Lead Optimization: Chameleon-Like Poses of Aspartic Protease Inhibitors



1 scaffold - 8 inhibitors - 4 different binding modes

Changing poses: The optimization of lead structures relies on the systematic variation of the substituents decorating a given hit scaffold which is based on one binding pose that is supposed to be invariable. For a given core scaffold, only minor chemical variations were found to result in four different binding modes. An indicative metric is suggested to assess candidates that qualify for structural revalidation.

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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This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Copper-Catalyzed Site-Selective Intramolecular Amidation of Unactivated C(sp3)–H Bonds

X.-S. Wu, Y. Zhao, G.-W. Zhang,
H.-B. Ge* ______________ 3706–3710

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201311263

In this Communication, the affiliations of two authors were accidentally wrongly assigned. Prof. Dr. Haibo Ge is only affiliated to the Department of Chemistry and Chemical Biology of Indiana University-Purdue University Indianapolis. Yan Zhao is affiliated to the Department of Chemistry and Chemical Biology of Indiana University-Purdue University Indianapolis as well as to the Institute of Chemistry and BioMedical Sciences and the School of Chemistry and Chemical Engineering of Nanjing University. The affiliations of the other authors were correct.