Fireworks and Champagne ...

… feature on the cover and back cover of this anniversary issue, which inaugurates the 125th year of *Angewandte Chemie*. Fireworks and champagne are both products of chemistry with a large symbolic value. They are covered as chemical products in contributions from Justine Corbel et al. on page 290 ff. ("Strobes: Pyrotechnic Compositions that Shows a Curious Oscillatory Combustion") and Michèle Vignes-Adler on page 187 ff. ("The Fizzling Foam of Champagne"). Fireworks surely have symbolic status for the collection of more than 50 contributions in this issue, 16 alone from Nobel laureates in Chemistry, and the others from former and current members of the Editorial Board and the International Advisory Board. 125 years of *Angewandte Chemie* is also a reason to celebrate, and therefore the Gesellschaft Deutscher Chemiker (GDCh, German Chemical Society), to which *Angewandte Chemie* belongs, will be holding a symposium on March 12, 2013 in Berlin (see the advertisement in this issue and http://angewandte.org/symposium). After the scientific part, there shall also be a party with products of the brewing process, which was by the way, like the chemistry of fireworks, a topic that was covered in the very first issue of "*Zeitschrift für die Chemische Industrie*" (the predecessor to *Angewandte Chemie* published in 1887).

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In this issue, many articles are accompanied by a special symbol:

The articles marked with one of these symbols are from Nobel Laureates or have at least one author who is a member of the Editorial or International Advisory Boards.

Editorials

Miscellaneous

News

X. Bao

S. Q. Yao

V. W.-W. Yam

Interview

Meteorology

An interview with the Nobel Laureate Professor Paul Crutzen was carried out by Gregor Lax and Carsten Reinhardt (both University of Bielefeld) as part of the centenary of the Max Planck Institute for Chemistry in Mainz. Paul Crutzen gives a fascinating insight into his scientific career and the development of his research area, meteorology.

Essays

Surface Chemistry

Scratching the surface: For over 100 years the interactions of molecules at surfaces have been studied at the Fritz Haber Institute of the Max Planck Society, Berlin. Nobel Laureate Gerhard Ertl looks back at some of the key developments in this time, and the people who made them.

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Art Conservation

Science, music, art, life: Nobel Laureate Richard Ernst discusses the influence of music and art on his life and how advanced Raman spectroscopy comes to his aid as a "hobby chemist" and art restorer.

Protein Crystallography

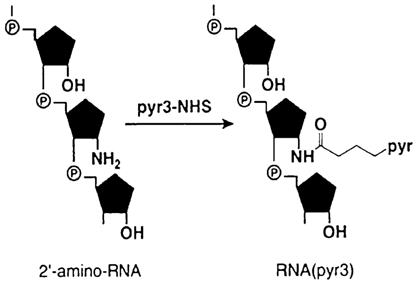
Crystal clear: "I was lucky to choose protein crystallography as the focus of my research activity at a time soon after its foundation by Perutz and Kendrew". Nobel Laureate Robert Huber reflects on how protein crystallography has developed and now has a fundamental role in our understanding of biological processes.

Nobel Prize

Collecting laureates: On receiving the Nobel Prize, Martin Chalfie found he was being added to lists. For example, he was the fourth Nobel Laureate his dentist knew. He discusses some of the other lists he has found himself on and explores the serious side of "collecting" Nobel Laureates.

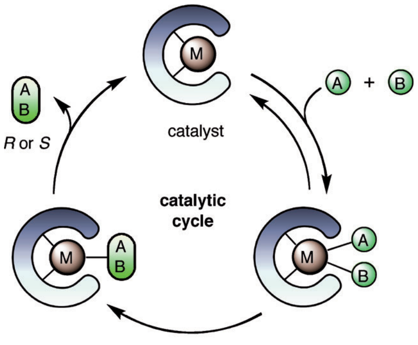
RNA Chemistry

RNA, just another starting material? Nobel Laureate Tom Cech shows that with an education steeped in kinetics, thermodynamics, and molecular structure, and armed with the ability to synthesize molecules, the chemist is ideally suited to investigate RNA.



Asymmetric Catalysis

The art of science: The field of asymmetric catalysis has evolved over nearly 50 years from a seemingly insignificant investigation into a copper-catalyzed cyclopropanation reaction to applications that bring global benefits. In this Essay, Nobel Laureate Ryoji Noyori outlines the history of asymmetric catalysis using a chiral organometallic complex, and explains how scientific discovery requires not only talent but also serendipity.

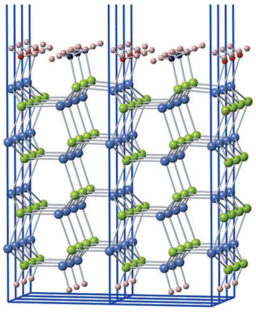


M = metal
A, B = reactant and substrate
X, Y = neutral or anionic ligand

Nanomaterials

R. Hoffmann* ———— **93–103**

Small but Strong Lessons from Chemistry for Nanoscience

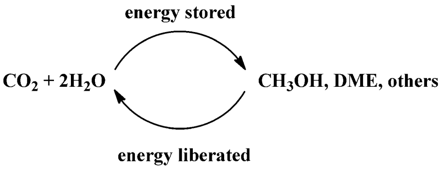


In a different light: In a provocative look at nanoscience, Nobel Laureate Roald Hoffmann considers the structural and electronic perplexities of dimensionality, the consequences of bond severance in nano-object formation, the implications of simple acid-base chemistry for stabilization of nanostructures, and what lessons might be learned from surface science on structural relaxation and reconstruction.

Methanol Economy

G. A. Olah* ———— **104–107**

Towards Oil Independence Through Renewable Methanol Chemistry



Recycling of CO_2 into methanol, dimethyl ether (DME), and derived fuels and materials is a feasible approach to address our carbon conundrum. It would free humankind from its dependence on fossil fuel while at the same time help mitigate the problems associated with excessive CO_2 emission. The energy needed for this carbon cycle can come from renewable sources (hydro, solar, wind) as well as atomic energy.

Future of Science and Society

A. Zewail,* M. Zewail ———— **108–111**

Science for the "Haves"

For centuries, the wisdom of the West of investing in basic science and technology led to its dominance in world politics and economics. Today, this wisdom is being put aside: fundamental research is losing its appeal to funding agencies and as a professional asset for job hunters. This state of affairs could exacerbate a dearth of innovations and lead to a transition of the "haves" into the "have-nots" of the world population. (Engraving: "Early Depiction of a Dutch Telescope" by Adriaen van de Venne, 1624).

University Education

R. N. Zare* ———— **112–113**

American Universities at Risk

Learning to count the costs: What does a university education cost? Why does it cost this much? Who should pay? And what are the consequences if costs outstrip what students can afford? Richard Zare examines the US higher education system and finds a great past is no guarantee of a rosy future.

Spotlight

E. Arunan, R. Brakaspathy,
G. R. Desiraju,* S. Sivaram ———— **114–117**

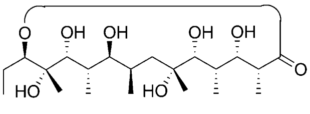
Chemistry in India—Unlocking the Potential

Hidden talents: Chemistry in India is currently ranked as fifth in terms of worldwide research output. G. R. Desiraju et al. discuss the current state of chemistry in India and the historic, social, cultural, and economic factors that influence its growth. They also address the issue of how to unlock the true potential of chemistry in India.

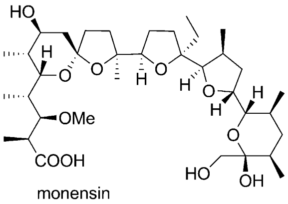
Scientific Best Practice

“Seven deadly sins” in modern academic research and publishing can be condensed into a list ranging from poorly described experimental or computational setups to falsification of data. This Essay describes these sins and their ramifications, and serves as a code of best practice for researchers in their quest for scientific truth. Picture: Detail from “The Seven Deadly Sins” by Hieronymus Bosch.

Natural Product Synthesis



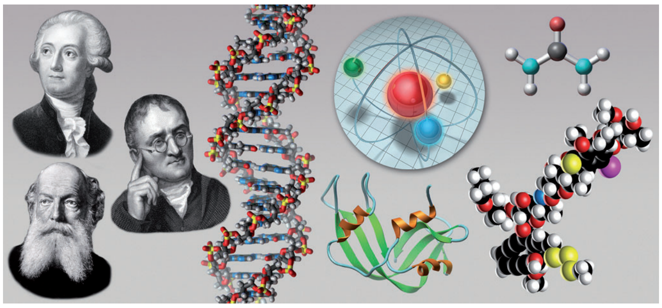
erythronolide A



monensin

For almost 200 years, the synthesis of natural products has been practiced. In this time span, not only the target structures have become increasingly more complex (see two examples from the 1970s), the objectives of natural product synthesis have also changed. Likewise, the standards and criteria for the conduction of natural product synthesis have changed. It is these changes that form the subject of this Essay.

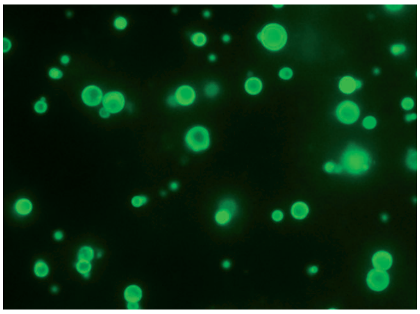
Total Synthesis



At the core of chemistry lie the structure of the molecule, the art of its synthesis, and the design of function within it. This Essay traces the understanding of the structure of the molecule, the emergence of organic synthesis, and the art of total synthesis from the 19th century to the present day.

From Chemicals to Chemistry

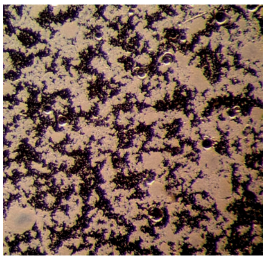
With its growing complexity and cross-linking of its disciplines, the profile of chemical sciences has changed radically over the last few decades: whereas individual molecules were originally the focus, emphasis has now shifted to intelligent chemistry in the form of holistic systems. How academia and industry find sustainable answers depends not least on the quality of the scientific dialogue, as documented and championed by *Angewandte Chemie* for 125 years.



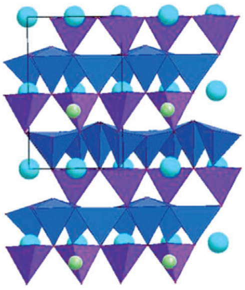
Synthetic life: The origin of life on the early Earth, and the ex novo transition of non-living matter to artificial living systems are deep scientific challenges that provide a context for the development of new chemistries with unknown technological consequences. This Essay attempts to re-frame some of the epistemological difficulties associated with these questions into an integrative framework of proto-life science. Chemistry is at the heart of this endeavour.

Origins of Life

Curds show the whey: The vexing problem of the glass transition has been frustrating experimentalists and theorists for more than a century. One difficulty is in quantifying the structure of an inhomogeneous system, even when "curds" and "whey" are made out of the same material. To explore the rich space of configurations of these complex systems, a new generation of experiments with a range of different local probes is needed.

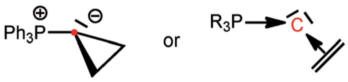


Glasses



Transition-metal oxides have been widely studied for understanding the physics of strongly electron-correlated systems. The crucial role of crystal chemistry for the discovery of three families: the high T_c superconducting cuprates, the colossal magnetoresistance manganates, the thermoelectric, and multiferroic cobaltates, is explored.

Metal Oxides

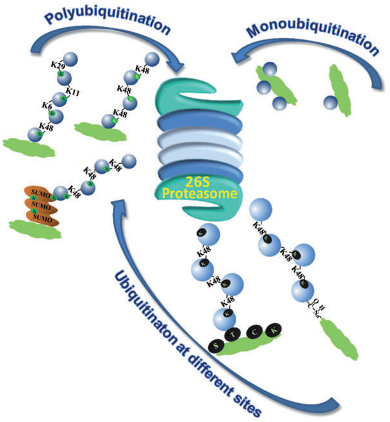


The revitalized concept of "coordination at carbon" allows relationships between seemingly unrelated families of carbon-centered compounds to be discovered generating fascinating patchwork families of compounds. It is shown how olefins and cyclopropanes can be regarded as donors for carbon acceptors C_1, C_2, and C_3. Through this approach, hydrocarbons such as spiropentane and dicyclopropylidene are found to be counterparts of the bis-ylidic carbodiphosphoranes and the corresponding mixed mono-ylidic systems.

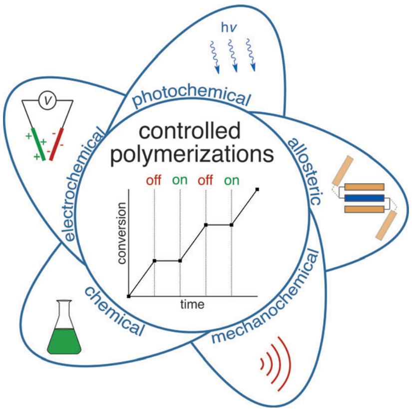
Carbon Complexes

Bubble, bubble: Why does champagne bubble? Why does it stop bubbling? Does the vintage affect its fizz? Chemistry can answer these and other questions about the wine that is so often associated with celebrations and anniversaries.

Minireviews



Since its discovery more than three decades ago, the proteasomal targeting signal was accepted to be a polyubiquitin chain, in which the ubiquitin moieties are linked to one another through lysine 48 (K48, see picture), and which is anchored to one of the internal lysines of the target substrate. However, recent evidence suggests that the signal for proteasomal targeting is far more diverse and complex.



So much control: Modern polymer chemists have the tools to create materials of almost infinite variety and architecture. The next frontier in controlled polymerization is external regulation, allowing the reactions to be turned “on” and turned “off” on demand. This temporal control may find significant utility in areas ranging from microelectronics to biomaterials.

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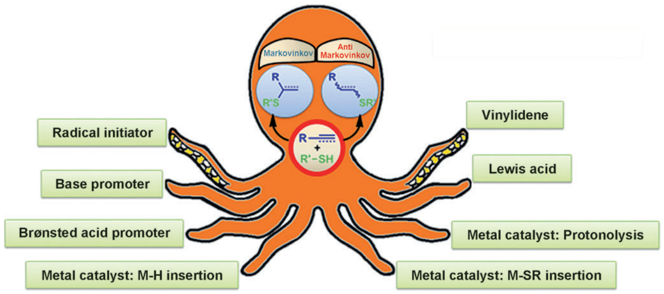
Hydrothiolation of Unsaturated Bonds

R. Castarlenas,* A. Di Giuseppe,
J. J. Pérez-Torrente, L. A. Oro* **211 – 222**

The Emergence of Transition-Metal-Mediated Hydrothiolation of Unsaturated Carbon–Carbon Bonds: A Mechanistic Outlook

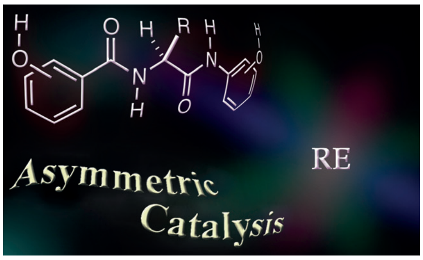


Juggling act: In recent years transition-metal-based catalysts for the control of the regio- and stereoselectivity in hydrothiolation of unsaturated carbon–carbon bonds have been developed. The complex mechanistic background of this transformation (see picture) is described to aid the design of better catalysts.

Synthetic Methods

N. Kumagai,* M. Shibasaki* **223 – 234**

Asymmetric Catalysis with Bis(hydroxyphenyl)diamides/Rare-Earth Metal Complexes



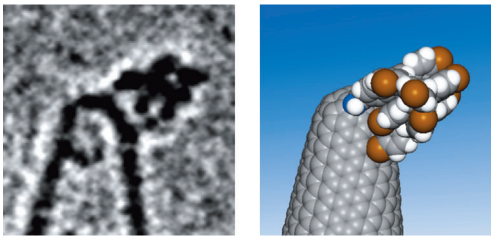
Cooperation: A series of asymmetric catalysts composed of conformationally flexible amide-based chiral ligands and rare-earth metals was developed for proton-transfer catalysis. The cooperative function of hydrogen bonding and metal coordination resulted in intriguing substrate specificity and stereocontrol, and the dynamic nature of the catalysts led to a switch of their function.

Reviews

Since the Time of Robert Hooke

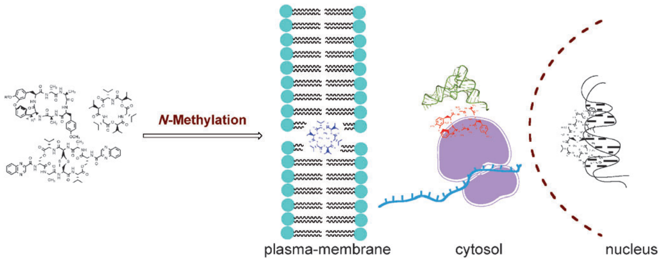
E. Nakamura* **236 – 252**

Movies of Molecular Motions and Reactions: The Single-Molecule, Real-Time Transmission Electron Microscope Imaging Technique



Robert Hooke was proud of watching a flea with his microscope, and now we can watch movies of the motions and reactions of single organic molecules through atomic-resolution transmission electron microscopy (see picture of a van der Waals molecular complex). Although the movie quality is still like that of the time of Edison, the new imaging method has great promise in research and the teaching of molecular science.

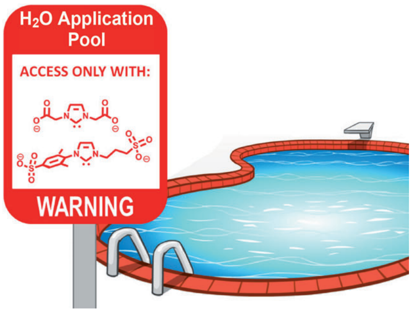
Medicinal Chemistry



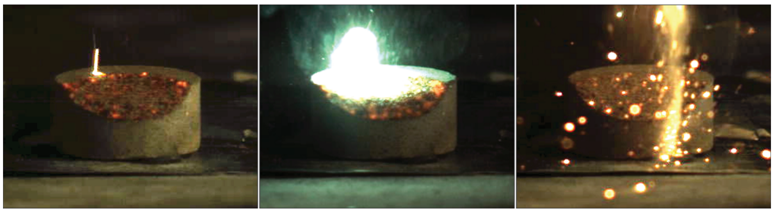
The peptide bond and Me: A large number of *N*-methylated peptides and proteins are found in nature; however, it is surprising that *N*-methylation of the peptide bonds is not used as a regulative element in proteins. On the other hand, many *N*-methylated peptides in natural bioactive peptides exhibit drug-like properties. Hence, *N*-methylation is a powerful tool in medicinal chemistry to modulate activity, selectivity, and bioavailability of peptidic drugs.

Organometallic Chemistry

Water lot of catalysts: Transition-metals bound to water-soluble N-heterocyclic carbene (NHC) ligands often have excellent catalytic properties and can be used in water. The synthetic paths towards such complexes are examined and their catalytic applications discussed. Areas with great potential for future research are also presented.



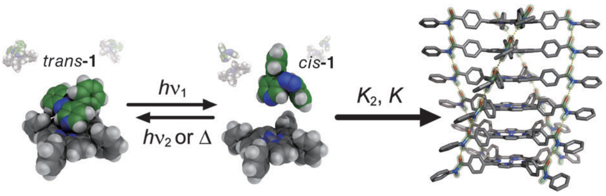
Pyrotechnics



Flash dance: Strobes are pyrotechnic compositions which burn in an oscillatory manner: a dark and a flash phase alternate periodically (see scheme). They have various applications in the fireworks industry and also as flares. However, their mechanism is not well understood. A few better understood oscillatory systems (Belousov–Zhabotinsky reactions, cool flames, self-propagating high-temperature synthesis) are compared to observations made on strobe mixtures.

Communications

Self-Assembly

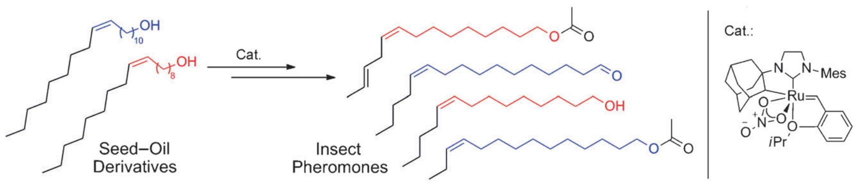


The cooperative self-assembly of chiral zinc porphyrins is regulated by a photoresponsive phenylazopyridine ligand (**1**; see picture). Porphyrin stacks depolymerize into dimers upon axial ligation and the strength of the coordination is regulated by its photoinduced isomerization, which shows more than 95 % conversion ratio for both photostationary states.

Olefin Metathesis

M. B. Herbert, V. M. Marx, R. L. Pederson,
R. H. Grubbs* **310–314**

Concise Syntheses of Insect Pheromones Using *Z*-Selective Cross Metathesis

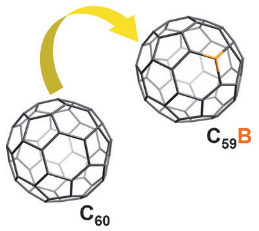


Very short synthetic routes to nine *cis*-olefin-containing pheromones containing a variety of functionality, including an unconjugated (*E*,*Z*) diene, are reported (see scheme). These lepidopteran pheromones are used extensively for pest control, and were easily prepared using ruthenium-based *Z*-selective cross metathesis, highlighting the advantages of this method over less efficient ways to form *Z* olefins.

Heterofullerenes

P. W. Dunk, A. Rodríguez-Fortea,
N. K. Kaiser, H. Shinohara, J. M. Poblet,*
H. W. Kroto* **315–319**

Formation of Heterofullerenes by Direct Exposure of C_{60} to Boron Vapor



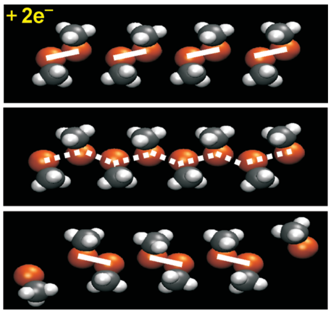
Introducing boron: Heterofullerenes that incorporate boron have been scarcely studied because a formation route from C_{60} is not known. It is now reported that $C_{59}B^{-}$, an electronically closed-shell species, is formed directly from pristine C_{60} in the gas-phase by facile atom exchange reactions.

Surface Science

Z. Ning, J. C. Polanyi* **320–324**

Charge Delocalization Induces Reaction in Molecular Chains at a Surface

The molecular dynamics of an electron-induced reaction in a self-assembled molecular chain of four dimethyldisulfide molecules on Au(111) are studied (see figure, S–S bonds highlighted). Charge delocalization weakens all the S–S bonds causing a concurrent reaction along the entire chain (middle). All the original S–S bonds are broken and new S–S bonds form giving three altered S–S bonds and two chemisorbed thiyl radicals (bottom).

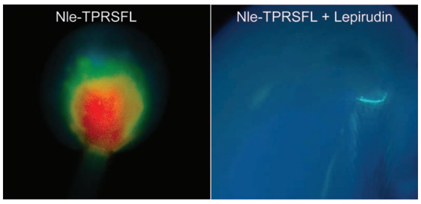


Live Imaging of Thrombin

M. Whitney, E. N. Savariar, B. Friedman,
R. A. Levin, J. L. Crisp, H. L. Glasgow,
R. Lefkowitz, S. R. Adams, P. Steinbach,
N. Nashi, Q. T. Nguyen,
R. Y. Tsien* **325–330**

Ratiometric Activatable Cell-Penetrating Peptides Provide Rapid In Vivo Readout of Thrombin Activation

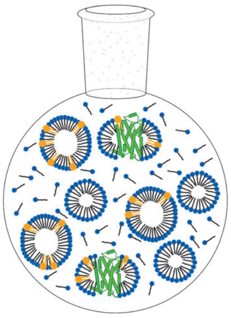
In real time: Thrombin activation in vivo can be imaged in real time with ratiometric activatable cell penetrating peptides (RACPPs). RACPPs are designed to combine 1) dual-emission ratioing, 2) far red to infrared wavelengths for in vivo mammalian imaging, and 3) cleavage-dependent spatial localization. The most advanced RACPP uses norleucine (Nle)-TPRSFL as a linker that increases sensitivity to thrombin by about 90-fold (see figure).



Structure Elucidation

R. Horst,* P. Stanczak, R. C. Stevens,
K. Wüthrich* ______ **331 – 335**

β_2-Adrenergic Receptor Solutions for Structural Biology Analyzed with Microscale NMR Diffusion Measurements

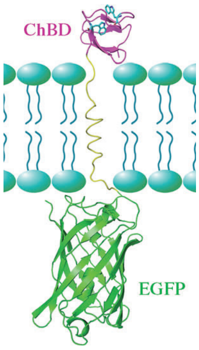


Microcoil NMR measurements were performed to determine the final composition of solutions of the β_2-adrenergic receptor (β_2AR) reconstituted with a detergent and to study the hydrodynamic properties of the detergent micelles containing β_2AR (see picture). Standards are established for the reproducible preparation of G-protein-coupled receptor solutions for crystallization trials and solution NMR studies.

Protein Engineering

Y. Peng, D. H. Kim, T. M. Jones, D. I. Ruiz,
R. A. Lerner* ______ **336 – 340**

Engineering Cell Surfaces for Orthogonal Selectability

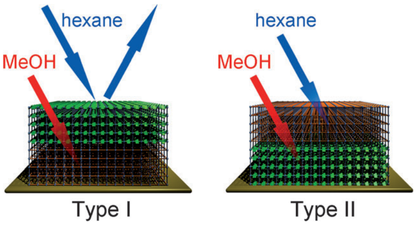


Vectors have been constructed that express the chitin-binding domain (ChBD) on eukaryotic cell surfaces. The ChBD is linked to enhanced green fluorescent protein (EGFP) through a protein that spans the plasma membrane (see picture). This binding functionality does not have a counterpart in eukaryotes, thereby endowing the modified cell surface with a property that is orthogonal to animal cells.

Metal–Organic Frameworks

M. Meilikhov, S. Furukawa,* K. Hirai,
R. A. Fischer, S. Kitagawa* ______ **341 – 345**

Binary Janus Porous Coordination Polymer Coatings for Sensor Devices with Tunable Analyte Affinity

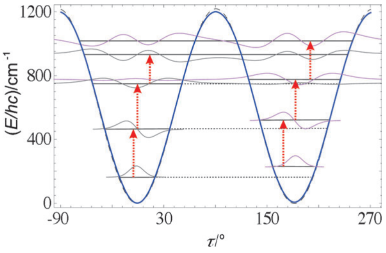


Janus MOF: Thin films consisting of noncentrosymmetric heterostructured metal–organic frameworks (MOFs) were fabricated directly on quartz-crystal microbalance (QCM) sensor devices. Depending on the spatial configuration of two frameworks, the thin MOF films could tune the affinity for analytes, thus giving high selectivity to the QCM sensors.

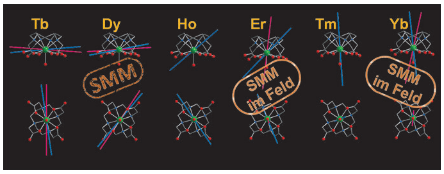
IR Spectroscopy

S. Albert,* P. Lerch, R. Prentner,
M. Quack* ______ **346 – 349**

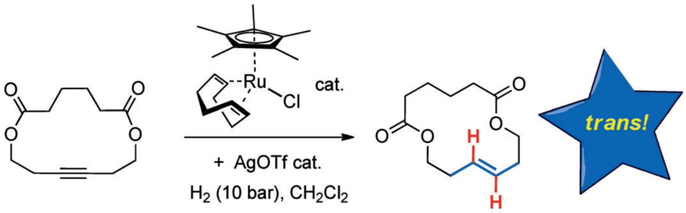
Tunneling and Tunneling Switching Dynamics in Phenol and Its Isotopomers from High-Resolution FTIR Spectroscopy with Synchrotron Radiation



Tunneling and chemical reactions by tunneling switching are reported for phenol and *ortho*-deuterophenol on the basis of high-resolution FTIR spectroscopy. Tunneling splittings are measured for the torsional motion in the ground and several vibrationally excited states of phenol. Tunneling times range from 10 ns to 1 ps, depending on excitation. For more-highly excited torsional levels in *ortho*-deuterophenol, delocalization and chemical reaction by tunneling switching is found.

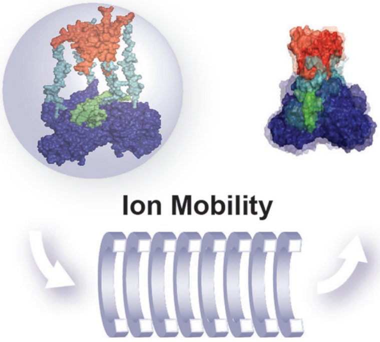


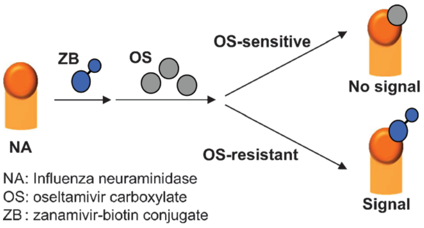
Spotting trends: Upon going from Tb^{III} to Yb^{III} centers in the complexes of the $DOTA^{4-}$ ligand, a reorientation of the easy axis of magnetization from perpendicular to parallel to the Ln–O bond of the apical water molecule is experimentally observed and theoretically predicted (see picture; SMM = single-molecule magnet). Only ions with an odd number of electrons show slow relaxation of the magnetization.



Against the rules: During the hundred years following Sabatier's groundbreaking work on catalytic hydrogenation, *syn* delivery of the H atoms to the π system of a substrate remained the governing stereochemical rule. An exception has now be found with the use of cationic [Cp*Ru] templates, which accounts for the first practical, functional-group-tolerant, broadly applicable and highly *E*-selective semihydrogenation method for alkynes (see scheme).

Spontaneous shrinking: The intrinsically disordered tumor suppressor protein p53 was analyzed by using a combination of ion mobility mass spectrometry and molecular dynamics simulations. Structured p53 subdomains retain their overall topology upon transfer into the gas phase. When intrinsically disordered segments are introduced into the protein sequence, however, the complex spontaneously collapses in the gas phase to a compact conformation.



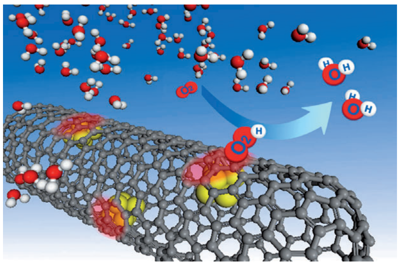


The wizard of OS (resistance): The binding difference of neuraminidase inhibitors (zanamivir versus oseltamivir (OS)) was used to establish an assay to identify the influenza subtypes that are resistant to OS but still sensitive to zanamivir (see scheme). This assay used a zanamivir-biotin conjugate to determine the OS susceptibility of a wide range of influenza viruses and over 200 clinical isolates.

Non-Precious-Metal Catalyst

D. H. Deng, L. Yu, X. Q. Chen, G. X. Wang, L. Jin, X. L. Pan,* J. Deng, G. Q. Sun, X. H. Bao* ______ **371 – 375**

Iron Encapsulated within Pod-like Carbon Nanotubes for Oxygen Reduction Reaction

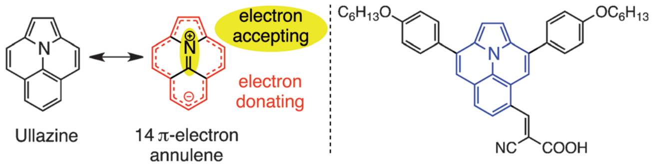


Chainmail for catalysts: A catalyst with iron nanoparticles confined inside pea-pod-like carbon nanotubes (see picture) exhibits a high activity and remarkable stability as a cathode catalyst in polymer electrolyte membrane fuel cells (PEMFC), even in presence of SO_2. The approach offers a new route to electro- and heterogeneous catalysts for harsh conditions.

Solar Cells

J. H. Delcamp, A. Yella, T. W. Holcombe, Md. K. Nazeeruddin, M. Grätzel* ______ **376 – 380**

The Molecular Engineering of Organic Sensitizers for Solar-Cell Applications



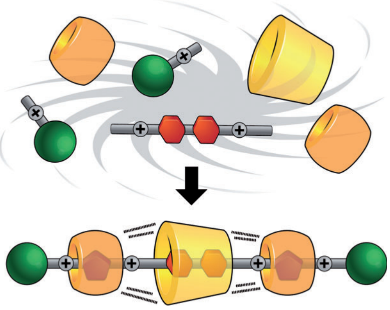
Positive to the core: Ullazine has both strong electron-donating and weak accepting properties. This heterocycle was incorporated into sensitizers for dye-sensitized solar cells (DSCs). One of these sensitizers demonstrated strong light absorption across the UV/Vis region. The corresponding DSC device has a maximum IPCE of 95 % at 520 nm, with a power conversion efficiency of 8.4 %.

Kinetic Covalent Chemistry

C. Ke, R. A. Smaldone, T. Kikuchi, H. Li, A. P. Davis, J. F. Stoddart* ______ **381 – 387**

Quantitative Emergence of Hetero[4]rotaxanes by Template-Directed Click Chemistry

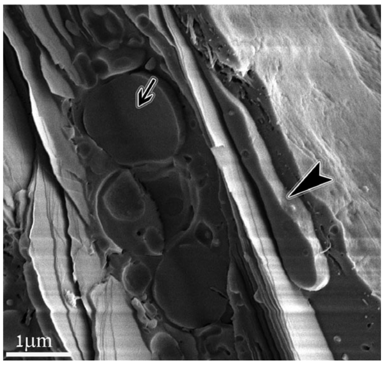
In one fell swoop, polyrotaxanes comprising up to 64 rings can be synthesized as a result of cucurbit[6]uril-templated 1,3-dipolar azide-alkyne cycloadditions accelerated in the presence of cyclodextrins as a consequence of self-sorting and positive cooperativity, brought about by hydrogen bonding. Mixing six components (see picture) in one pot affords a hetero[4]rotaxane in one minute in quantitative yield.



Biomineralization

D. Gur, Y. Politi, B. Sivan, P. Fratzl, S. Weiner, L. Addadi* ______ **388 – 391**

Guanine-Based Photonic Crystals in Fish Scales Form from an Amorphous Precursor



Starting from disorder: Anhydrous guanine crystals compose the photonic arrays responsible for the skin and scale iridescence found in Japanese Koi fish. These guanine crystals were found to form in intracellular vesicles (see picture) through an amorphous precursor phase. A combined cryo-SEM and synchrotron radiation X-ray diffraction study showed the evolution of the crystals in great detail.

Seven billion people already live on our planet, and the number is growing by 220,000 every day. How can we provide food for more and more people without damaging the environment?

How can we improve everyone's health and prevent diseases? How can we develop new materials to help us conserve resources?

To provide better answers to these questions, research is under way in Bayer's three subgroups: HealthCare, CropScience and MaterialScience. Fields in which Bayer is already a global leader – and whose importance to the future of humankind grows by the day.

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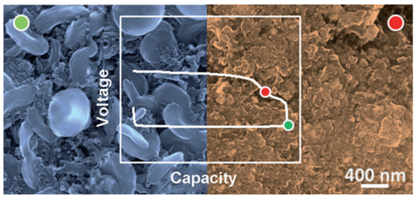
Electrocatalysis

R. Black, J.-H. Lee, B. Adams, C. A. Mims, L. F. Nazar* **392 – 396**

The Role of Catalysts and Peroxide Oxidation in Lithium–Oxygen Batteries

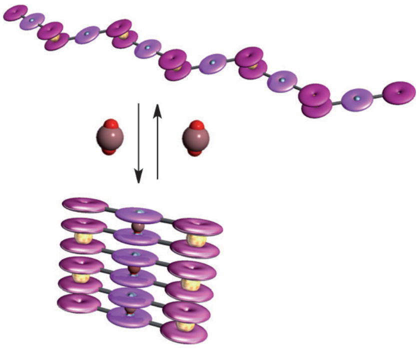


A promotor for lithium batteries: Nanocrystalline cobalt(II,III) oxide supported on graphene enhances the transport kinetics for both oxygen reduction and oxygen evolution in the lithium–oxygen cell. On cycling the lithium–oxygen cell, the effect of the promoter is, however, eventually overwhelmed by side reactions in the cell, such as, the deposition of carbonates (see picture).

Supramolecular Device

M. Shibata, S. Tanaka, T. Ikeda, S. Shinkai,* K. Kaneko, S. Ogi, M. Takeuchi* **397 – 400**

Stimuli-Responsive Folding and Unfolding of a Polymer Bearing Multiple Cerium(IV) Bis(porphyrinate) Joints: Mechano-imitation of the Action of a Folding Ruler



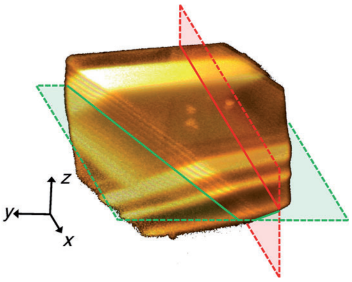
A pivotal guest role: A new porphyrin polymer, poly(PorZn·DD) (see picture, pink/purple), composed of a porphyrinatozinc and a porphyrin double-decker complex as a repeating unit was synthesized. In poly(PorZn·DD), porphyrinatozinc complexes recognize a divalent amine (tan/red) to induce an intramolecular pivoting motion through the rotation of porphyrin double-decker complexes and the polymer undergoes shortening and compaction.

Defects in Metal–Organic Frameworks

R. Ameloot, F. Vermoortele, J. Hofkens, F. C. De Schryver, D. E. De Vos, M. B. J. Roeffaers* **401 – 405**

Three-Dimensional Visualization of Defects Formed during the Synthesis of Metal–Organic Frameworks: A Fluorescence Microscopy Study

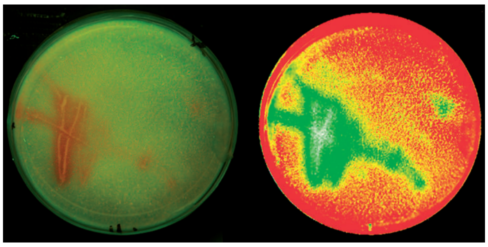
Imperfections in the spotlight: Fluorescence microscopy was used to detect defects in metal–organic frameworks formed during synthesis. In contrast to currently available techniques, confocal fluorescence microscopy offers the advantage of three-dimensional imaging at the single-crystal level combined with the sensitivity required to study the start of defect formation.



pH Nanosensor

X.-d. Wang,* R. J. Meier, O. S. Wolfbeis* **406 – 409**

Fluorescent pH-Sensitive Nanoparticles in an Agarose Matrix for Imaging of Bacterial Growth and Metabolism

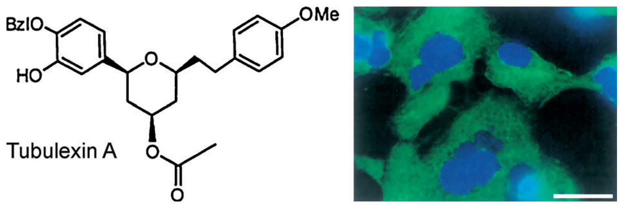


Living color: Fluorescent pH-sensitive nanoparticles 12 nm in diameter were prepared and incorporated into agarose gel in a Petri dish to image pH changes during bacterial growth and metabolism (see picture).

Biology-Oriented Synthesis

T. Voigt, C. Gerding-Reimers,
T. T. Ngoc Tran, S. Bergmann,
H. Lachance, B. Schölermann,
A. Brockmeyer, P. Janning, S. Ziegler,
H. Waldmann* ________ **410–414**

A Natural Product Inspired Tetrahydropyran Collection Yields Mitosis Modulators that Synergistically Target CSE1L and Tubulin

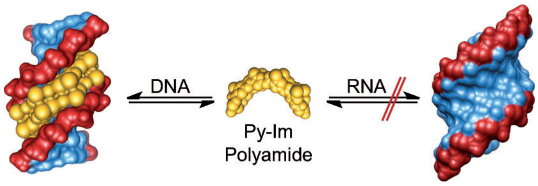


A Prins cyclization between a polymer-bound aldehyde and a homoallylic alcohol served as the key step in the synthesis of tetrahydropyran derivatives. A phenotypic screen led to the identification of compounds that inhibit mitosis (as seen by the accumulation of round cells with condensed DNA and membrane blebs; see picture). These compounds were termed tubulexins as they target the CSE1L protein and the vinca alkaloid binding site of tubulin.

Molecular Recognition

D. M. Chenoweth, J. L. Meier,
P. B. Dervan* ________ **415–418**

Pyrrole-Imidazole Polyamides Distinguish Between Double-Helical DNA and RNA



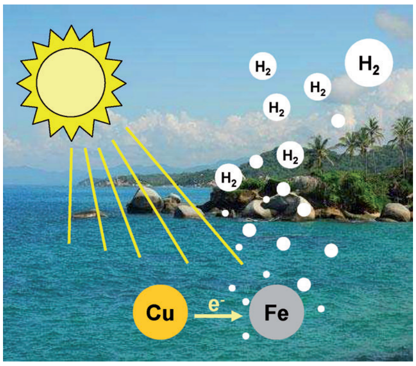
Groove specificity: Pyrrole-imidazole polyamides are well-known for their specific interactions with the minor groove of DNA (see scheme). However, polyamides do not show similar binding to duplex RNA, and a structural rationale for the molecular-level discrimination of nucleic acid duplexes by minor-groove-binding ligands is presented.

Hydrogen Generation

S. Luo, E. Mejía, A. Friedrich, A. Pazidis,
H. Junge, A.-E. Surkus, R. Jackstell,
S. Denurra, S. Gladiali, S. Lochbrunner,
M. Beller* ________ **419–423**

Photocatalytic Water Reduction with Copper-Based Photosensitizers: A Noble-Metal-Free System

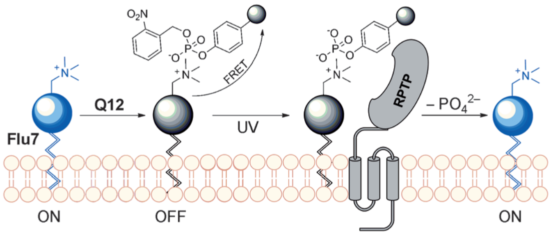
Of noble descent: A fully noble-metal-free system for the photocatalytic reduction of water at room temperature has been developed. This system consists of Cu^I complexes as photosensitizers and $[Fe_3(CO)_{12}]$ as the water-reduction catalyst. The novel Cu-based photosensitizers are relatively inexpensive, readily available from commercial sources, and stable to ambient conditions, thus making them an attractive alternative to the widely used noble-metal based systems.



Cell-Membrane Imaging

L. Li, X. Shen, Q.-H. Xu,
S. Q. Yao* ________ **424–428**

A Switchable Two-Photon Membrane Tracer Capable of Imaging Membrane-Associated Protein Tyrosine Phosphatase Activities

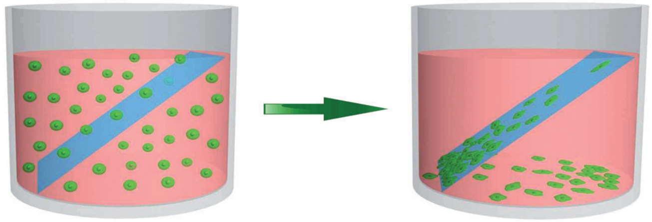


When I look into your cells: A two-photon dye (**Flu7**) was developed (see scheme), which strongly fluoresces only upon selective binding to the plasma membrane of mammalian cells. Upon addition of a UV- and phosphatase-controlled quencher (**Q12**), the system exhibits ON/OFF/ON fluorescence switching and can be used to image membrane-associated receptor-like protein tyrosine phosphatase (RPTP) activity.

Tissue Engineering

W. Liu, Y. Zhang, S. Thomopoulos,
Y. Xia* ______ 429–432

Generation of Controllable Gradients in Cell Density

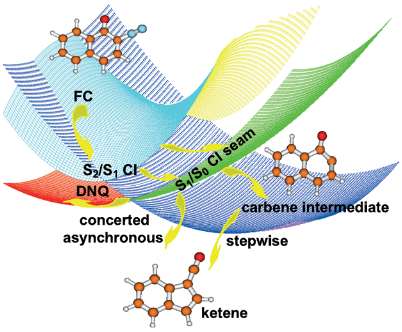


Making the grad(ient): A gradient in cell density was generated on a substrate that was inserted into a homogeneous suspension of cells at a specific tilt angle by taking advantage of the gradual change in the number of cells available for sedimentation (see scheme). Reverse gradients were also fabricated on the same substrate using multiple sedimentation procedures.

Computational Photochemistry

G. Cui, W. Thiel* ______ 433–436

Photoinduced Ultrafast Wolff Rearrangement: A Non-Adiabatic Dynamics Perspective

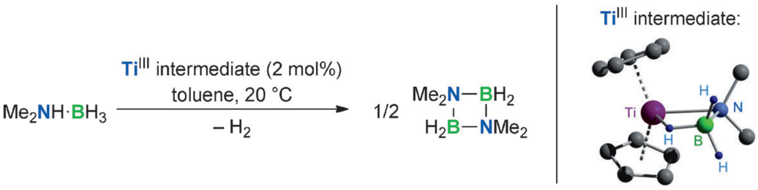


One reaction, two routes: Full-dimensional non-adiabatic dynamics simulations shed light on the ultrafast photoinduced Wolff rearrangement in an α-diazocarbonyl compound. The trajectories show both concerted asynchronous and stepwise processes leading to the corresponding ketene (see scheme).

Dehydrocoupling

H. Helten, B. Dutta, J. R. Vance,
M. E. Sloan, M. F. Haddow, S. Sproules,
D. Collison, G. R. Whittell,
G. C. Lloyd-Jones, I. Manners* 437–440

Paramagnetic Titanium(III) and Zirconium(III) Metallocene Complexes as Precatalysts for the Dehydrocoupling/Dehydrogenation of Amine–Boranes

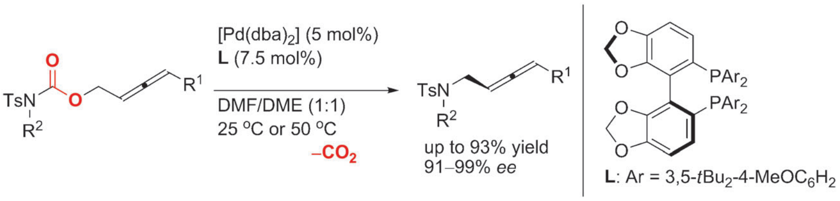


Complexes of Group 4 metallocenes in the +3 oxidation state and amidoborane or phosphidoborane function as efficient precatalysts for the dehydrocoupling/dehydrogenation of amine–boranes, such as $Me_2NH{\cdot}BH_3$ (see scheme). Such Ti^{III}–amidoborane complexes are generated in $[Cp_2Ti]$-catalyzed amine–borane dehydrocoupling reactions, for which diamagnetic M^{II} and M^{IV} species have been previously postulated as precatalysts and intermediates.

Synthetic Methods

B. Wan, S. Ma* ______ 441–445

Enantioselective Decarboxylative Amination: Synthesis of Axially Chiral Allenyl Amines



Getting axed: Synthesis of the title amines, bearing functionality (R^1 and R^2), involves the enantioselective palladium-catalyzed decarboxylation of allenyl *N*-tosylcarbamates. The reaction proceeds smoothly using both the chiral ligands (*S*)- and (*R*)-DTBM-Segphos (**1**) to afford the allenyl amines in good yields and with high enantioseletivities.

GDCh

Gesellschaft Deutscher Chemiker

GDCh Foundation Awards – Call for Nominations

The following Foundations administered by the German Chemical Society (GDCh) will award prizes in 2013.

Klaus Grohe Prize

The "Klaus Grohe Foundation" established with the German Chemical Society (GDCh), awards the Klaus Grohe Prize to outstanding young scientists (post graduate students and postdoctoral researchers up to three years after having completed their doctorate) working in the field of medicinal chemistry and drug research at research institutes in Germany or other European countries. In general, the prize winners should have some connection to medicinal chemistry/drug research in Germany.
The prize is endowed with 2,000 Euro.

Hellmut Bredereck Foundation Prize

The "Hellmut Bredereck Foundation" supports young scientists, who are active in the former fields of Professor H. Bredereck (1904 – 1981), namely organic and bioorganic chemistry with a focus on carbohydrates as well as heterocycles, proteins, and nucleotides. The prize winner will receive a certificate and 2,000 Euro.

Dr. Hermann Schnell Scholarships

The "Dr. Hermann Schnell Stiftung" supports young scientists in the field of macromolecular chemistry, its physico-chemical fundamentals, and its analysis. Support will be given to postgraduates from universities or other institutions under public law. Partial scholarships for participating in important scientific meetings are also on offer. Scholarships up to 6,000 Euro are available.

The Foundation prizes will be awarded during the Foundation Symposium at the GDCh Chemistry Forum, September 1 – 4, 2009, in Darmstadt.

Proposals should consist of a letter in support of the nomination (self-nominations are welcome), a curriculum vitae, and a list of publications. Please submit your nomination by **March 20, 2013** to Gesellschaft Deutscher Chemiker, Barbara Köhler, b.koehler@gdch.de, or by post to Varrentrappstraße 40 – 42, 60486 Frankfurt am Main, Germany.

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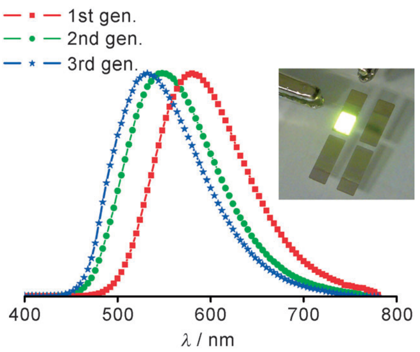
Dendrimers

M.-C. Tang, D. P.-K. Tsang,
M. M.-Y. Chan,* K. M.-C. Wong,
V. W.-W. Yam* **446–449**

Dendritic Luminescent Gold(III) Complexes for Highly Efficient Solution-Processable Organic Light-Emitting Devices

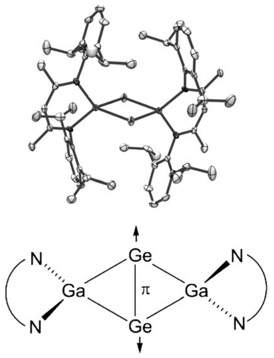
Emission control: Carbazole-based dendritic alkynylgold(III) complexes have been evaluated as phosphorescent emitters in organic light-emitting devices. The energy as well as the bathochromic shift of the emissions can be tuned effectively through a control of the dendrimer generation (see spectra). The optimized devices show high current and external quantum efficiencies of up to 24.0 cd A^{-1} and 7.8%, respectively.



Metalloid Clusters

A. Doddi, C. Gemel, M. Winter,
R. A. Fischer,* C. Goedecke, H. S. Rzepa,
G. Frenking* **450–454**

Low-Valent Ge_2 and Ge_4 Species Trapped by N-Heterocyclic Gallylene



Much π and no σ: Quantum chemical calculations showed that the Ge atoms of the Ga_2Ge_2 core in $Ge_2[Ga(DPP)]_2$ are not bonded by σ interactions, but rather by a transannular π interaction (see picture). The compound is formed by reduction of $(PCy_3)\cdot GeCl_2$ with Ga(DDP)/KC_8 which also yielded a further product $Ge_4[Ga(DPP)]_2$ with a Ge_4 tetrahedron (DDP = $HC(CMeNC_6H_3\text{-}2,6\text{-}i Pr_2)_2$).

DOI: 10.1002/anie.201209120

50 Years Ago . . .

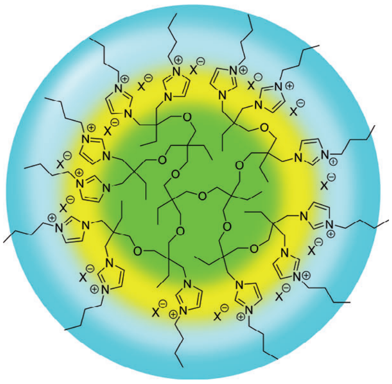
Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

The first issue of the year started with a Review by the late Emanuel Vogel on valence isomerization in compounds with strained rings. These rearrangement reactions are driven mostly by relief of strain in energy-rich small or medium-sized rings. Vogel's many achievements are recorded in a personal account of his research career spanning 50 years (*Angew. Chem. Int. Ed.* **2011**, *50*, 4278).

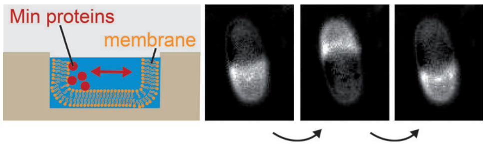
A Review by J. Heyna from the former company Hoechst AG on the topic of reactive dyes summarized recent progress on dyes that contain vinylsulfonylgroups and react with nitrogeneous and cellulose fibers. At that time, high-resolution color photography was not available and so the best way to show the results was to produce an insert bearing samples of dyed fabrics. The colors have still not faded!

The preparation of cyclopentadienylcycloheptatrienylchromium(0) was reported by E. O. Fischer and S. Breitschaft. The complex, which was air-sensitive and formed blue solutions in organic solvents, was prepared by reduction of the corresponding chromium(I) cation. Fischer was one of the pioneers of organometallic chemistry and won the Nobel Prize in Chemistry in 1973 for his work on sandwich compounds (see *Angew. Chem. Int. Ed.* **2011**, *51*, 6052 for a recent Essay by H. Werner on the subject).

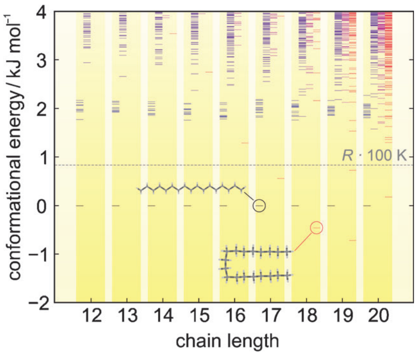
Read more in Issue 1/1963



A new family of hyperbranched polymeric ionic liquids (“hyperILs”) with onion-like topology and facile polarity design were tailored as transporters and compartmentalized systems. Applications include transport and dispersion of water-soluble dyes and functionalized graphene nanosheets from aqueous phase into nonpolar fluids, including polymer melts.



Cell division in bacteria is highly regulated in time and space. The use of micrometer-sized sample volumes and model membranes allows the pole-to-pole oscillations of spatial regulators for bacterial cell division to be reconstituted in a synthetic minimal system (see schematic picture left as well as the confocal images of Min proteins on lipid membranes in a polydimethylsiloxane microcompartment right).



Mother of all folding: Cold isolated linear alkanes C_nH_{2n+2} prefer an extended *all-trans* conformation before cohesive forces between the chain ends induce a folded hairpin structure for longer chains. It is shown by Raman spectroscopy at 100–150 K that the folded structure becomes more stable beyond $n_C = 17$ or 18 carbon atoms. High-level quantum-chemical calculations yield $n_C = 17 \pm 1$ as the critical chain length.

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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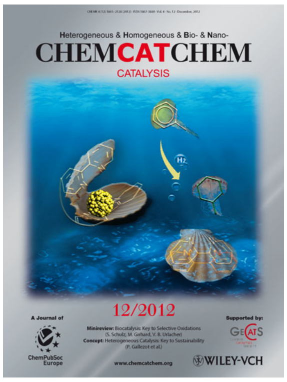

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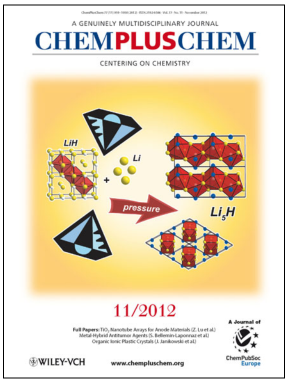

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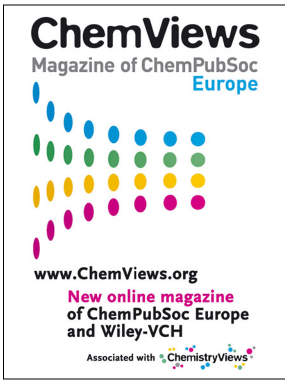

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