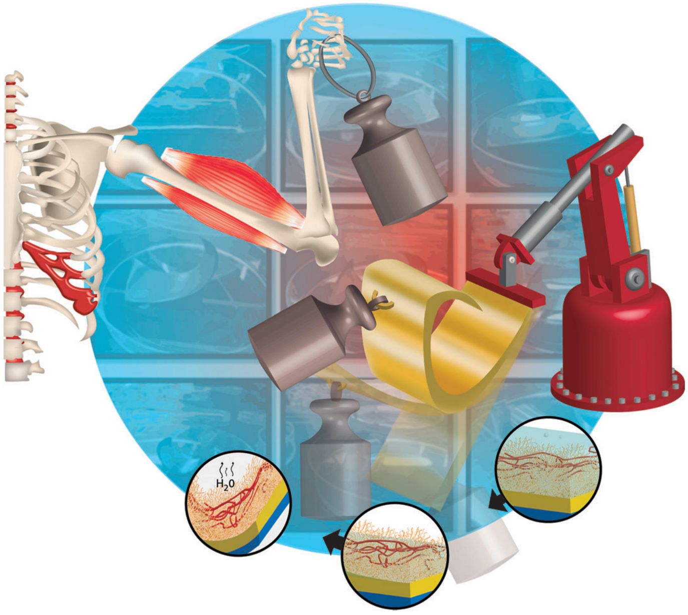
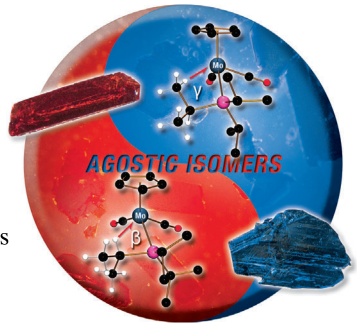
Humidity-responsive polymer-based muscles …

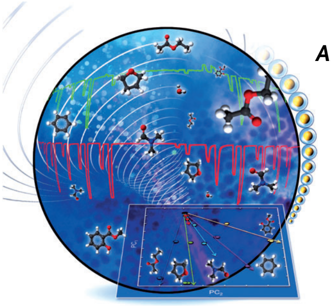


… were fabricated by exploiting charged microgel and polyelectrolyte interactions as is shown by M. J. Serpe and co-workers in their Communication on page 10330 ff. Favorable interactions between microgels and polyelectrolytes and microgels and a flexible substrate allow the substrate to bend in a manner that depends on environmental humidity. The resulting actuator, or muscle, is able to lift many times its mass in a reproducible manner.



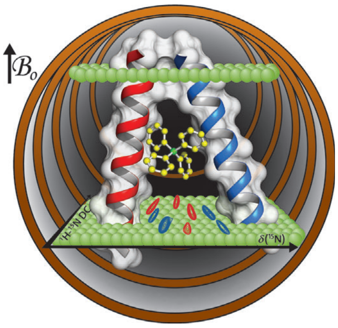
Agostic Interactions

In their Communication on page 10190 ff. E. F. van der Eide, P. Yang, and R. M. Bullock describe a molybdenum complex for which two agostic isomers can be isolated and characterized. The isomers are strikingly different colors.



Analytical Methods

In their Communication on page 10360 ff., R. A. Potyrailo et al. show that selective detection of individual vapors and their mixtures is achieved by using a single three-dimensional networked film of plasmonic nanoparticles.



Solid-State NMR Spectroscopy

In their Communication on page 10321 ff., N. J. Traaseth et al. used an oriented solid-state NMR method to detect changes upon ligand binding to the EmrE membrane transport protein. EmrE forms dimers in the membrane with different monomer tilt angles.

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Author Profile

"Chemistry is fun because it is an assault on the senses! My favorite quote is 'To strive, to seek, to find, and not to yield' from Tennyson's poem 'Ulysses' ..."
This and more about Gautam R. Desiraju can be found on page 10152.

News

I. P. Beletskaya

E. Hey-Hawkins

E. Reichmanis

C. Rovira

M. Vallet-Regí

Y. Xie

O. Ramström

J. M. Thomas

Books

Carbohydrates—Tools for Stereoselective Synthesis — Mike Martin Kwabena Boysen — *reviewed by G. A. O'Doherty* ____ **10156**

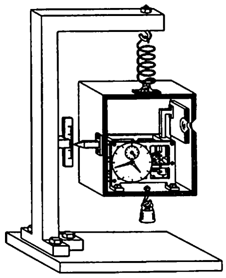
Reviews

Quantum Electrodynamics

S. Haroche* ____ **10158 – 10178**

Controlling Photons in a Box and Exploring the Quantum to Classical Boundary (Nobel Lecture)

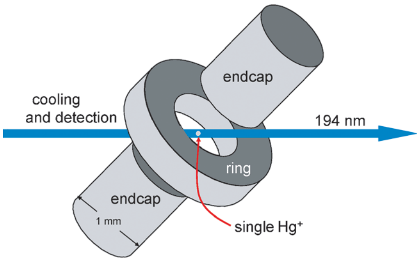
Photons trapped in a superconducting cavity constitute an ideal system to realize some of the thought experiments imagined by the founding fathers of quantum physics. Physics laureate S. Haroche gives a personal account of the experiments performed with this "photon box" at the Ecole Normale Supérieure.



Quantum Mechanics

D. J. Wineland* ____ **10179 – 10189**

Superposition, Entanglement, and Raising Schrödinger's Cat (Nobel Lecture)



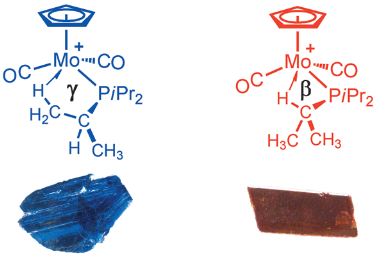
Experimental control of quantum systems has been pursued widely since the invention of quantum mechanics. Today, we can in fact experiment with individual quantum systems, deterministically preparing superpositions and entanglements. In his Nobel lecture, D. J. Wineland gives an overview of this research which has led to the Nobel prize in physics in 2012.

Communications

Agostic Isomers

E. F. van der Eide, P. Yang,*
R. M. Bullock* ____ **10190 – 10194**

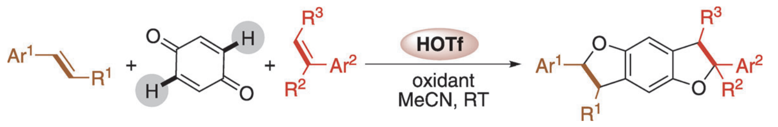
Isolation of Two Agostic Isomers of an Organometallic Cation: Different Structures and Colors



Two of a kind: Two agostic isomers of $[CpMo(CO)_2(PiPr_3)]^+ B(C_6F_5)_4^-$ have been isolated. Both were characterized in the solid state by X-ray crystallography and spectroscopic techniques, and also by DFT calculations. Significantly different LUMO energies cause the difference in color (blue versus orange, see picture) of these isomers.

Frontispiece

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. 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.

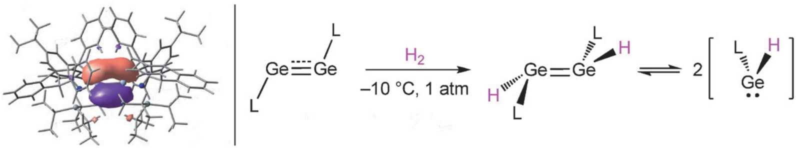


The proton did it! Tetrahydrobenzodifurans have been synthesized through the trifluoromethanesulfonic acid (HOTf) catalyzed direct oxidative C–H functionalization of benzoquinone with olefins. A variety of substituents were found to be tolerated, and a synergetic oxidative/[3+2] cyclization mechanism was proposed based on the experimental results.

Proton Catalysis

L. Meng, G. Zhang, C. Liu, K. Wu,
A. Lei* ________ **10195 – 10198**

Trifluoromethanesulfonic Acid Catalyzed Synergetic Oxidative/[3+2] Cyclization of Quinones with Olefins

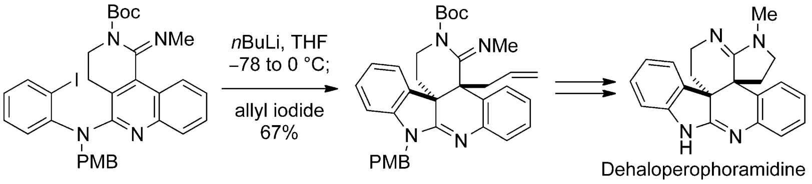


The long and the short of it. The first amido–digermyne to possess a short Ge–Ge multiple bond, [LGeGeL], has been prepared and shown to activate H_2 below 0 °C, thereby yielding the hydrido–digermene, [L(H)Ge=Ge(H)L]. This possesses a very long Ge=Ge bond. Spectroscopic and theoretical data indicate that the dimer dissociates in solution to give the two-coordinate hydrido–germylene, [:Ge(H)(L)]. L = N(Ar)(SiiPr$_3$), Ar = 2,6-[C(H)Ph$_2$]$_2$-4-iPrC$_6$H$_2$.

Germanium Complexes

T. J. Hadlington, M. Hermann, J. Li,
G. Frenking,* C. Jones* _ **10199 – 10203**

Activation of H_2 by a Multiply Bonded Amido–Digermyne: Evidence for the Formation of a Hydrido–Germylene



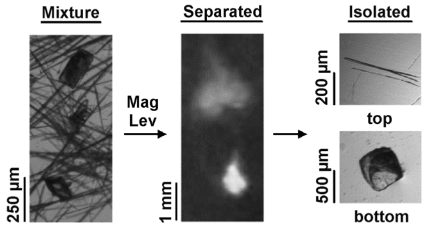
Dehaloperophoramidine, the dehalogenated analogue of the marine hexacyclic alkaloid perophoramidine was synthesized. The intramolecular nucleophilic dearomatizing arylation of aminoquinoline initiated by a lithium–iodine exchange and the subsequent direct allylation of the resultant azaenolate afforded a pentacyclic bisamidine compound bearing two contiguous all-carbon quaternary centers in good yield with excellent diastereoselectivity.

Natural Product Synthesis

T. Ishida, H. Ikota, K. Kurahashi,
C. Tsukano, Y. Takemoto* **10204 – 10207**

Dearomatizing Conjugate Addition to Quinolinyl Amidines for the Synthesis of Dehaloperophoramidine through Tandem Arylation and Allylation

Magnetic levitation (MagLev) provides a simple method for the separation of crystal polymorphs that differ in density ($\Delta\rho$) by greater than 0.001 g cm^{-3}. Density-based separations of multiple crystalline forms were shown for four organic compounds: 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, sulfathiazole, carbamazepine, and *trans*-cinnamic acid.



Crystal Polymorphs

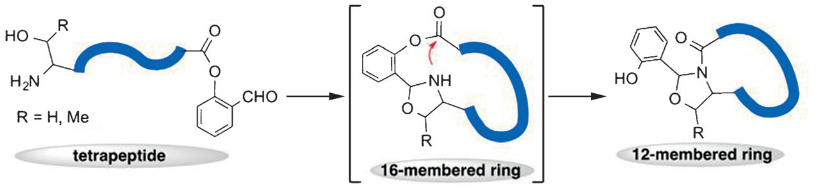
M. B. J. Atkinson, D. K. Bwambok, J. Chen,
P. D. Chopade, M. M. Thuo, C. R. Mace,
K. A. Mirica, A. A. Kumar, A. S. Myerson,*
G. M. Whitesides* _____ **10208 – 10211**

Using Magnetic Levitation to Separate Mixtures of Crystal Polymorphs

Peptide Cyclization

C. T. T. Wong, H. Y. Lam, T. Song, G. Chen,* X. Li* ______ **10212 – 10215**

Synthesis of Constrained Head-to-Tail Cyclic Tetrapeptides by an Imine-Induced Ring-Closing/Contraction Strategy

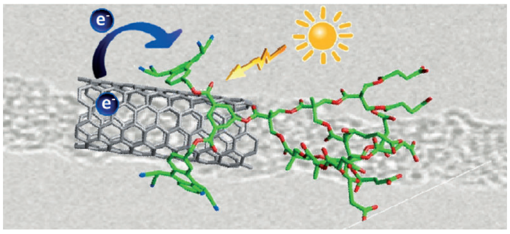


Making heads or tails of it: A strategy involving a head-to-tail imine-captured ring closure followed by ring contraction was used to synthesize otherwise difficult cyclic tetrapeptides. Compared with the direct lactamization process, the estimated activation energies for the cyclic imine formation and the ring contraction were lowered by 7.3 and 7.6 kcal mol^{-1}, respectively, which enables cyclization.

Carbon Nanotubes

C. Romero-Nieto, R. García, M. A. Herranz, L. Rodríguez-Pérez, M. Sánchez-Navarro, J. Rojo, N. Martín,* D. M. Guldi* ______ **10216 – 10220**

Stable Electron Donor–Acceptor Nanohybrids by Interfacing *n*-Type TCAQ with *p*-Type Single-Walled Carbon Nanotubes



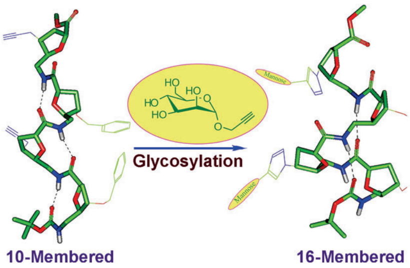
Tuning the electronics of nanotubes: Electron-accepting 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) nanotweezers endowed with a carboxylic acid-containing dendrimeric moiety form exceptionally stable *n*-/*p*-type dispersions with single-walled carbon nanotubes (SWCNTs) in water. Upon photoexcitation, the nanohybrids undergo a less common electron transfer from the SWCNTs to the TCAQ nanotweezers (see picture).

Glycopeptide Foldamers

A. Siriwardena,* K. K. Pulukuri, P. S. Kandiyal, S. Roy, O. Bande, S. Ghosh, J. M. Garcia Fernández, F. Ariel Martin, J.-M. Ghigo, C. Beloin, K. Ito, R. J. Woods, R. S. Ampapathi,* T. K. Chakraborty* ______ **10221 – 10226**

Sugar-Modified Foldamers as Conformationally Defined and Biologically Distinct Glycopeptide Mimics

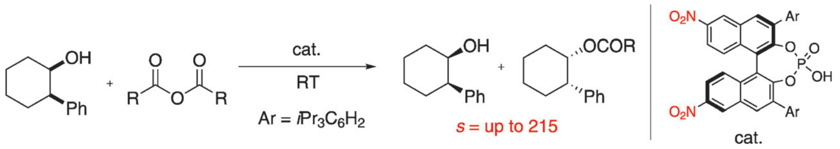
To fold or not to fold? It is shown that attached sugars play a defining role in the conformations adopted by a pair of novel SAA-derived foldamers in water and that these differences are reflected in the contrasting interactions of these glycofoldamers with various biological targets. C green, O red, N blue, H gray; yellow oval = mannose.



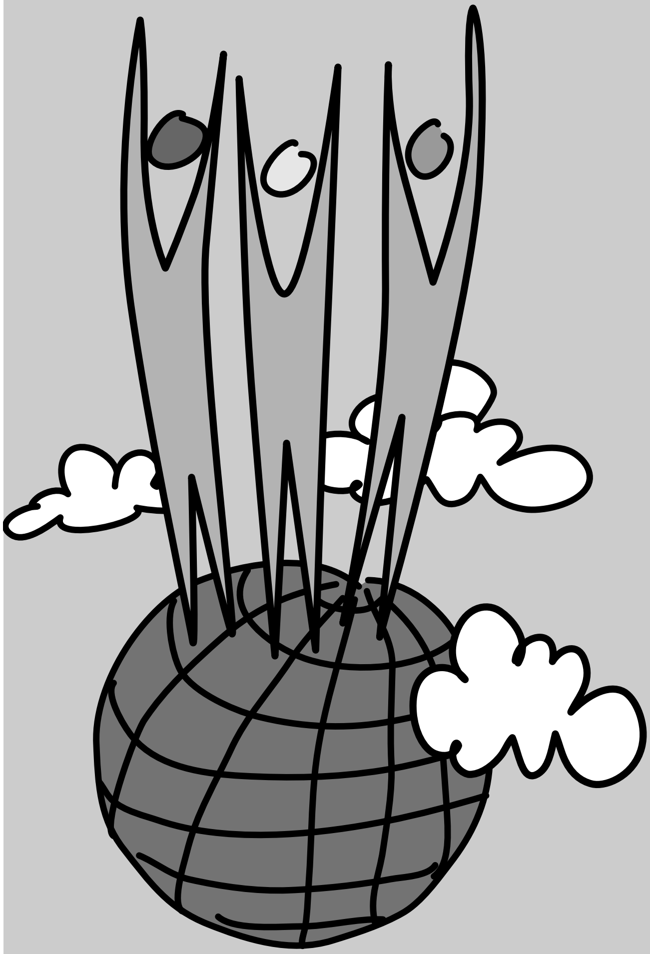
Kinetic Resolution

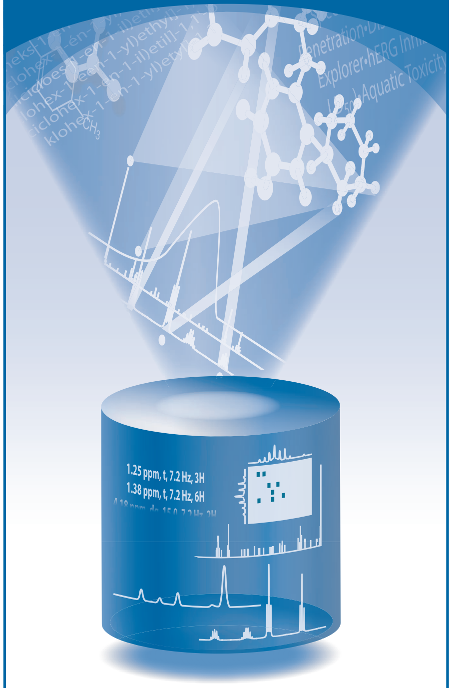
S. Harada, S. Kuwano, Y. Yamaoka, K. Yamada,* K. Takasu* __ **10227 – 10230**

Kinetic Resolution of Secondary Alcohols Catalyzed by Chiral Phosphoric Acids



Acid instead of base: Kinetic resolution of secondary alcohols is realized using chiral Brønsted acid catalyzed acylation instead of the conventional basic conditions. A broad range of functional groups are tolerated, such as aldehydes, carboxylic acids, and enoates. The selectivity factor (*s*) reaches up to 215 at ambient temperature.

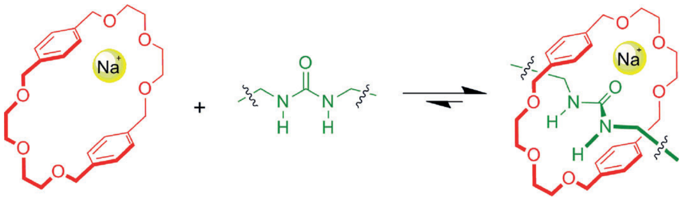



1.25 ppm, t, 7.2 Hz, 3H
1.38 ppm, t, 7.2 Hz, 6H

Template Synthesis

Y.-H. Lin, C.-C. Lai, Y.-H. Liu, S.-M. Peng,
S.-H. Chiu* ———— **10231 – 10236**

Sodium Ions Template the Formation of Rotaxanes from BPX26C6 and Nonconjugated Amide and Urea Functionalities

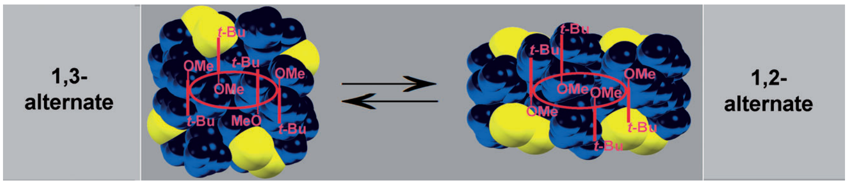


Picking up the thread: The macrocycle bis-*p*-xylyl[26]crown-6 is capable of forming pseudorotaxane-like structures with single, nonconjugated urea or amide moieties when assisted by templating Na^+ ions (see example). By using this approach, rotaxanes were synthesized with glycine residues or the repeating unit of nylon-6,6 as key components in the threadlike units.

Guest-Responsive Materials

J. Thomas, G. Reekmans, P. Adriaensens, L. Van Meervelt, M. Smet, W. Maes, W. Dehaen,*
L. Dobrzańska* ———— **10237 – 10240**

Actuated Conformational Switching in a Single Crystal of a Homodithiacalix[4]arene

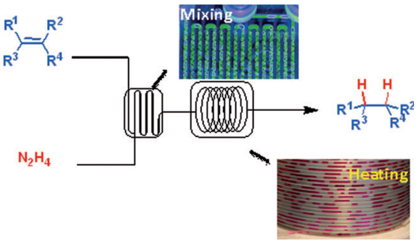


Frozen but flexible: The conformational flexibility of calixarene molecules is not only limited to solution. It can also manifest itself in single crystals as a response to the right external stimuli.

Flow Chemistry

B. Pieber, S. T. Martinez, D. Cantillo,
C. O. Kappe* ———— **10241 – 10244**

In Situ Generation of Diimide from Hydrazine and Oxygen: Continuous-Flow Transfer Hydrogenation of Olefins

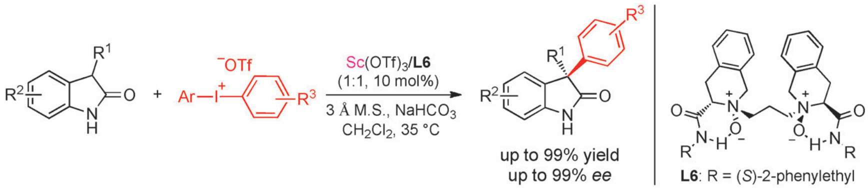


No catalyst required! A highly efficient, catalyst-free process to generate diimide in situ from hydrazine monohydrate and molecular oxygen for the selective reduction of alkenes has been developed. The use of a gas–liquid segmented flow system allowed safe operating conditions and dramatically enhanced this atom-economical reaction, resulting in short processing times.

Asymmetric Catalysis

J. Guo, S. X. Dong, Y. L. Zhang,
Y. L. Kuang, X. H. Liu, L. L. Lin,
X. M. Feng* ———— **10245 – 10249**

Chiral Scandium(III)-Catalyzed Enantioselective α-Arylation of N-Unprotected 3-Substituted Oxindoles with Diaryliodonium Salts

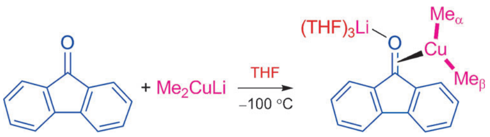


Catalytic asymmetric α-arylation of N-unprotected 3-substituted oxindoles with diaryliodonium salts has been realized by a chiral Lewis acid promoted electrophilic addition and aryl-rearrangement process. Single C3-arylated products containing a quaternary carbon center were generated in high enantioselectivity and reactivity.

Copper Complexes

S. H. Bertz,* R. A. Hardin, T. J. Heavey, C. A. Ogle* —— **10250 – 10252**

The X-ray Crystal Structure of a Cuprate–Carbonyl π-Complex

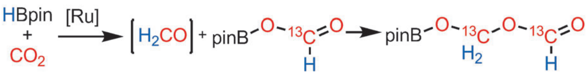


Why is it π? The first X-ray crystal structure of a cuprate–carbonyl π-complex has been obtained for the intermediate prepared from Me_2CuLi and fluorenone (see scheme). It is also the first structure of a π-complex between an organocuprate and a double bond of any kind.

Reaction Intermediates

S. Bontemps,*
S. Sabo-Etienne* —— **10253 – 10255**

Trapping Formaldehyde in the Homogeneous Catalytic Reduction of Carbon Dioxide

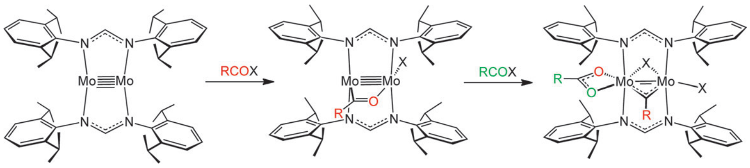


Formaldehyde detectives: Evidence for the production of formaldehyde during a ruthenium-catalyzed CO_2 reduction process, and for its involvement in the formation of the resulting C_2 compound, is disclosed. Ultimately, formaldehyde can be recovered by methanol trapping. HBPin = pinacolborane.

Quintuple Bond

H.-G. Chen, H.-W. Hsueh, T.-S. Kuo, Y.-C. Tsai* —— **10256 – 10260**

Haloacylation of the Quintuple-Bonded Group VI Metal Amidinate Dimers and Disproportionation of Acyl Groups to Form Carbynes

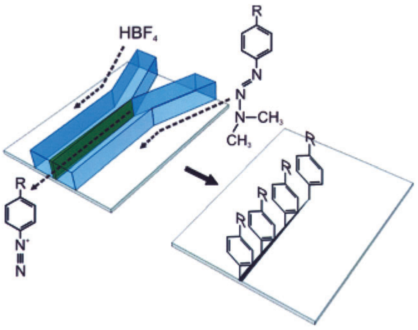


Give me five: Group VI metal quintuple bonds undergo Friedel–Crafts-type haloacylation reactions. Treatment of the quintuple-bonded molybdenum complexes with one equivalent of acyl halides RCOX (R = Me, C_6H_5, 2-MeC_6H_4; X = Cl, Br), yields metal–metal quadruple-bonded acyl complexes. Subsequent treatment with a second equivalent of acyl halides causes disproportionation of two acyl groups to give dimolybdenum carbyne carboxylate complexes.

Surface Modification

A. J. Gross, V. Nock, M. I. J. Polson, M. M. Alkaisi,
A. J. Downard* —— **10261 – 10264**

Surface Patterning Using Two-Phase Laminar Flow and In Situ Formation of Aryldiazonium Salts

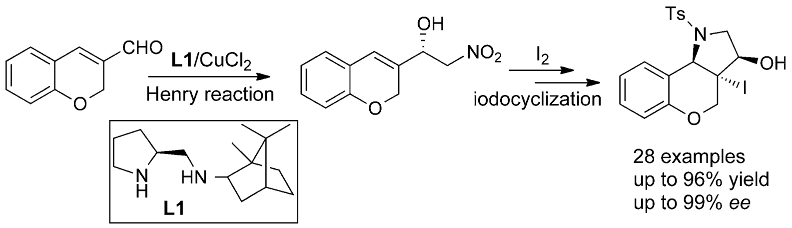


In the reaction zone: Reaction of an aryltriazene with acid generates the corresponding aryldiazonium ion. When this reaction takes place in the mixing zone, at the interface between two streams flowing laminarly and in parallel through a 100 μm microchannel, a submicrometer line of organic film is grafted at the substrate surface.

Asymmetric Catalysis

Y. Zhou, Y. Zhu, S. Yan,
Y. Gong* ______________ **10265 – 10269**

Copper-Catalyzed Enantioselective Henry Reaction of Enals and Subsequent Iodocyclization: Stereoselective Construction of Chiral Azatricyclic Frameworks

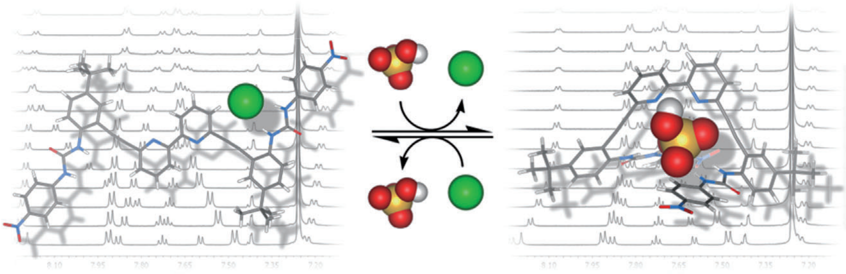


In the frame: A cascade sequence combining an asymmetric Henry reaction and a stereoselective intramolecular iodocyclization provides direct access to an enantioenriched tricyclic hexahydrochromeno[4,3-*b*]pyrrole framework (see scheme). The Henry reaction is catalyzed by copper in the presence of **L1**.

Molecular Devices

J. V. Gavette, N. S. Mills, L. N. Zakharov,
C. A. Johnson, II, D. W. Johnson,*
M. M. Haley* ________ **10270 – 10274**

An Anion-Modulated Three-Way Supramolecular Switch that Selectively Binds Dihydrogen Phosphate, $H_2PO_4^-$



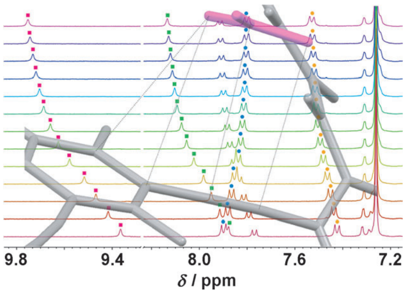
An anionic three-way switch: A bipyridyl bis(urea)-based anion receptor that is highly selective for dihydrogen phosphate demonstrates spectroscopically distinct anion-bound conformations toward halides and select oxoanions. ^{1}H NMR studies show the differing anion-induced conformations are reversible allowing this system to function as a three-way molecular switch.

Anion Binding

M. M. Watt, L. N. Zakharov, M. M. Haley,*
D. W. Johnson* ________ **10275 – 10280**

Selective Nitrate Binding in Competitive Hydrogen Bonding Solvents: Do Anion–π Interactions Facilitate Nitrate Selectivity?

New tripodal urea receptors demonstrate preferential binding of anions over competitive hydrogen bonding solvents. ^{1}H NMR titrations in 10% [D$_6$]DMSO/CDCl$_3$ show a higher affinity for nitrate over the halides for the fluorinated receptor, which is lost when the fluorine atoms are absent. An anion–π interaction between the nitrate and the π-system of the ethynyl-substituted arene is proposed as the source of this selectivity.

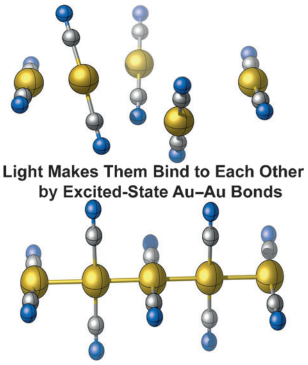


Gold Photochemistry

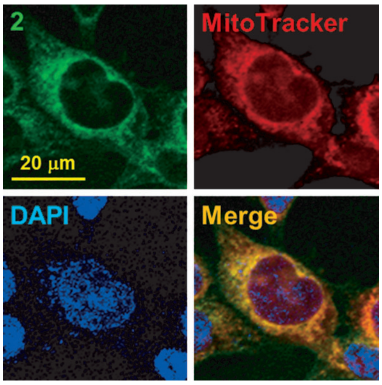
G. Cui, X.-Y. Cao, W.-H. Fang,* M. Dolg,*
W. Thiel* ______________ **10281 – 10285**

Photoinduced Gold(I)–Gold(I) Chemical Bonding in Dicyanoaurate Oligomers

Not only σ*σ but also σ*π: High-level electronic structure calculations reveal the σ*σ and σ*π bonding patterns for Au^I–Au^I bonding in excited states and suggest two conformation-dependent photophysical relaxation mechanisms for dicyanoaurate oligomers ($n=2$–5; see picture) in aqueous solution. These insights into the excited-state electronic structure should also be relevant for other gold complexes with a similar gold scaffold.



Tracking the target: To identify a protein that binds directly to the HIF-1α inhibitor LW6, a series of new chemical probes were synthesized with a clickable tag and/or a photoactivatable moiety. LW6 was found to be localized to the mitochondria (see picture) and MDH2 was identified as a target protein of LW6. These results indicate that the HIF-1α inhibitory activity of LW6 is a consequence of MDH2 suppression.



Target Identification

K. Lee, H. S. Ban, R. Naik, Y. S. Hong, S. Son, B.-K. Kim, Y. Xia, K. B. Song, H.-S. Lee, M. Won* ——— **10286 – 10289**

Identification of Malate Dehydrogenase 2 as a Target Protein of the HIF-1 Inhibitor LW6 using Chemical Probes

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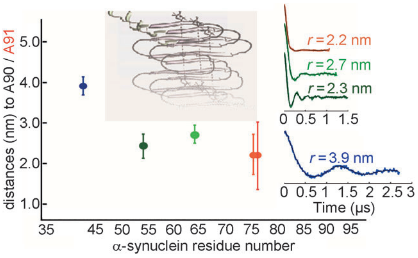
Distance measurements: Pulsed EPR distance measurements combined with strategic spin labeling provide structural constraints at the molecular level for the fold of α-synuclein in amyloid fibrils (see picture; r = distance). The detection of interstrand distances in fibrils will potentially make it possible to extend these measurements to oligomeric states of these protein families.



Biophysics

S. Pornsuwan, K. Giller, D. Riedel, S. Becker, C. Griesinger, M. Bennati* ——— **10290 – 10294**

Long-Range Distances in Amyloid Fibrils of α-Synuclein from PELDOR Spectroscopy

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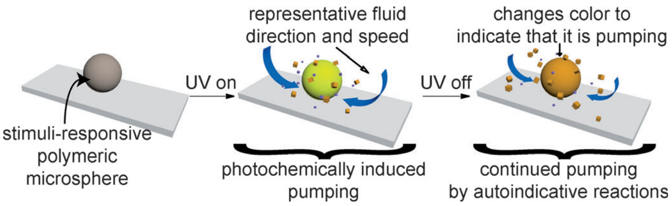

Pumped up: Building an autoinductive, self-propagating reaction directly into a polymer has resulted in stimuli-responsive materials that are capable of remembering the presence of a stimulus, even after the stimulus is no longer present. As a proof of concept, a non-mechanical, polymer-based pump has been made that is capable of pumping fluids surrounding the polymer when exposed to a fleeting signal (UV light, see picture).

Smart Materials

M. S. Baker, V. Yadav, A. Sen,* S. T. Phillips* ——— **10295 – 10299**

A Self-Powered Polymeric Material that Responds Autonomously and Continuously to Fleeting Stimuli

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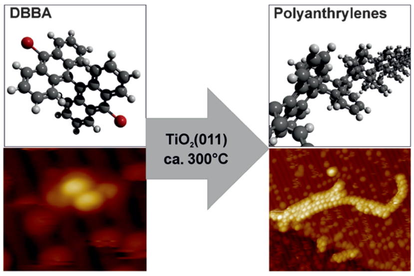
On-surface polymerization is feasible on semiconducting surfaces. Thermally triggered covalent coupling of 10,10′-dibromo-9,9′-bianthryl molecules on the $TiO_2(011)$-(2×1) surface is demonstrated. The result paves the way for application of the thermally driven on-surface polymerization on semiconducting surfaces and indicates that methods based on such a reaction are more universal than previously thought.



Surface Chemistry

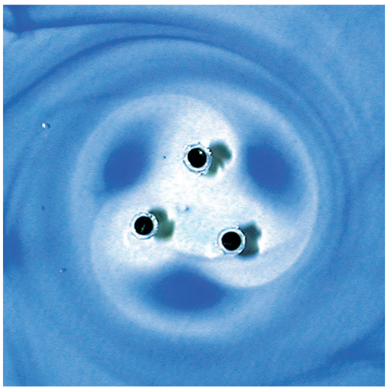
M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki,* W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski ——— **10300 – 10303**

Polymerization of Polyanthrylene on a Titanium Dioxide (011)-(2×1) Surface

Non-equilibrium Self-Assembly

K. V. Tretiakov, I. Szleifer,
B. A. Grzybowski* ______ **10304 – 10308**

The Rate of Energy Dissipation Determines Probabilities of Non-equilibrium Assemblies



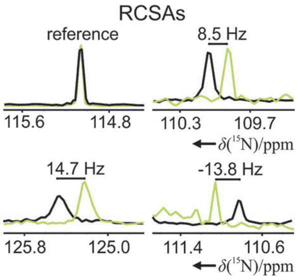
Outside thermodynamic equilibrium, outcomes of self-assembly can be dictated not by energy but by the energy dissipation rate. Remarkably, non-equilibrium self-assembly can lead to both low- and high-dissipation structures. The latter, thermodynamically more wasteful structures are exponentially less probable with increasing dissipation rate. This dependence is quantified in a Boltzmann-like relation for non-equilibrium systems.

NMR Spectroscopy

C. Merle, G. Kummerlöwe,
J. C. Freudenberger, F. Halbach,
W. Stöwer, C. L. v. Gostomski, J. Höpfner,
T. Beskers, M. Wilhelm,
B. Luy* ______ **10309 – 10312**

Crosslinked Poly(ethylene oxide) as a Versatile Alignment Medium for the Measurement of Residual Anisotropic NMR Parameters

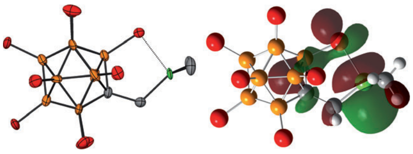
A universal alignment medium for the measurement of anisotropic NMR parameters that can be used for almost any type of sample would be highly useful for structure analysis in solution. Cross-linked poly(ethylene oxide) with incredible solvent and solute compatibility range provides this medium. The picture shows residual ^{15}N chemical shift anisotropies (RCSAs) of ^{15}N-labeled ubiquitin.



Silylium Cations

R. Ramírez-Contreras, N. Bhuvanesh,
J. Zhou, O. V. Ozerov* ___ **10313 – 10315**

Synthesis of a Silylium Zwitterion

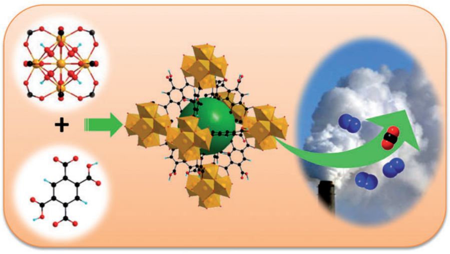


A zwitterionic construction has been synthesized that covalently links a trialkylsilylium cation and a weakly coordinating carborane anion in one neutral molecule (see X-ray structure; Si green, C gray, B orange, Cl red). The silylium character of this molecule is supported by DFT calculations (see LUMO), ^{29}Si CP/MAS NMR spectroscopy, and reactivity.

Metal–Organic Frameworks

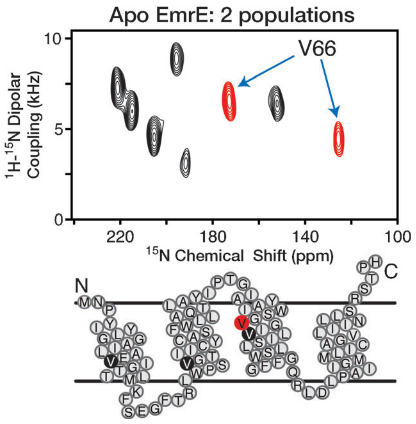
Q. Yang, S. Vaesen, F. Ragon,
A. D. Wiersum, D. Wu, A. Lago, T. Devic,
C. Martineau, F. Taulelle, P. L. Llewellyn,
H. Jobic, C. Zhong, C. Serre,*
G. De Weireld,*
G. Maurin* ______ **10316 – 10320**

A Water Stable Metal–Organic Framework with Optimal Features for CO_2 Capture



One flue over the cuckoo's nest: A novel porous Zr-based MOF combining a high chemical stability, easy "green" synthesis and scalability is prepared. This material incorporating carboxylic functions on its organic linkers has thermodynamically and kinetically very promising properties for CO_2 capture from post-combustion flue gas under real working conditions.

An EmrE-ging market: Oriented solid-state NMR spectroscopy and biochemical cross-linking experiments were used to show that the ligand-free membrane protein transporter EmrE forms anti-parallel dimers with different monomer tilt angles relative to the lipid bilayer. In addition, subtle conformational changes were detected upon drug binding that emphasize the need for an atomic-resolution structure.

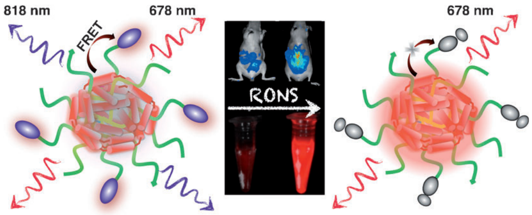


Membrane Proteins

A. Gayen, J. R. Banigan, N. J. Traaseth* ________ 10321 – 10324

Ligand-Induced Conformational Changes of the Multidrug Resistance Transporter EmrE Probed by Oriented Solid-State NMR Spectroscopy

Back Cover



Semiconducting polymer nanoparticles are used as a free-radical inert and light-harvesting nanoplatform for in vivo molecular imaging of reactive oxygen and nitrogen species (RONS). This nanoprobe permits detection of RONS in the microenvironment of spontaneous bacterial infection (see picture; FRET = fluorescence resonance energy transfer).

Biosensors

K. Y. Pu, A. J. Shuhendler, J. Rao* ________ 10325 – 10329

Semiconducting Polymer Nanoprobe for In Vivo Imaging of Reactive Oxygen and Nitrogen Species

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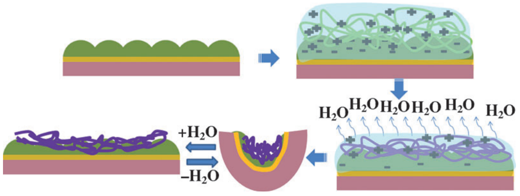


Weight lifting: A polymer-based device capable of lifting many times its own mass was fabricated by drying a solution of the polycation poly(diallyldimethyl ammonium chloride) (pDADMAC) on a surface coated with charged poly(*N*-isopropylacrylamide)-based microgels. Upon drying of the pDADMAC solution on the microgel-modified surface, it bends. Flexible surfaces then curl up into scroll-like structures, which can be opened up at high humidity.

Polymer Actuation

M. R. Islam, X. Li, K. Smyth, M. J. Serpe* ________ 10330 – 10333

Polymer-Based Muscle Expansion and Contraction

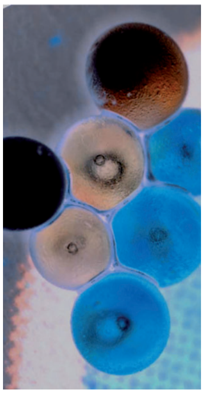
Front Cover

Controlled Release

P. Erni,* G. Dardelle, M. Sillick, K. Wong, P. Beaussoubre, W. Fieber ______ **10334 – 10338**

Turning Coacervates into Biohybrid Glass: Core/Shell Capsules Formed by Silica Precipitation in Protein/Polysaccharide Scaffolds

In case of emergency, break glass: Biohybrid core/shell capsules (see picture) suitable for encapsulation of volatile molecules can be formed through precipitation of amorphous silica in a protein/polyanion coacervate scaffold. The coacervate molds the final shape and structure of the capsule shell and provides an acidic microenvironment to locally induce hydrolysis and condensation of liquid silica precursors.

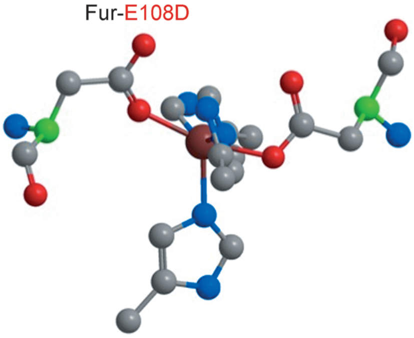


Bioinorganic Chemistry

A. Parent, C. Caux-Thang, L. Signor, M. Clémancey, R. Sethu, G. Blondin, P. Maldivi, V. Duarte,* J.-M. Latour* ______ **10339 – 10343**

Single Glutamate to Aspartate Mutation Makes Ferric Uptake Regulator (Fur) as Sensitive to H_2O_2 as Peroxide Resistance Regulator (PerR)

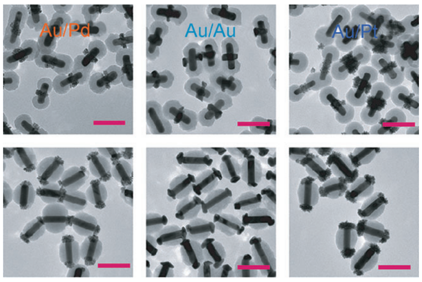
Let the Fur fly: Mutation of a single glutamate into an aspartate was shown to make the Fe sensor Fur as reactive to H_2O_2 as the peroxide sensor PerR. In vivo and in vitro peroxide sensitivities of a series of PerR and Fur Asp/Glu mutants were studied by mass spectrometry. A combination of Mössbauer spectroscopy analyses and DFT calculations gave a structural rationale for this behavior.



Metal Heterostructures

F. Wang, S. Cheng, Z. H. Bao, J. F. Wang* ______ **10344 – 10348**

Anisotropic Overgrowth of Metal Heterostructures Induced by a Site-Selective Silica Coating



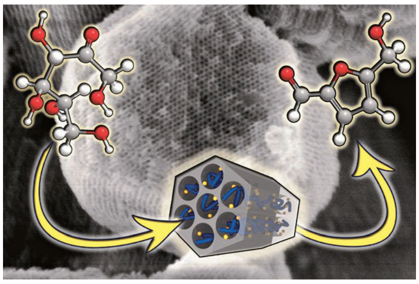
More than skin deep: A selective silica coating on the ends and side of gold nanorods enables the successful selective overgrowth of palladium, gold, platinum, and silver on these surfaces. As a result, eight types of unprecedented metal homo- and heterostructures are produced.

Hybrid Nanoreactors

R. Alamillo, A. J. Crisci, J. M. R. Gallo, S. L. Scott,* J. A. Dumesic* ______ **10349 – 10351**

A Tailored Microenvironment for Catalytic Biomass Conversion in Inorganic–Organic Nanoreactors

Building a better dehydrator: A nanocomposite catalyst was designed and synthesized expressly for the dehydration of fructose to the platform chemical, 5-hydroxymethylfurfural (HMF). When poly(vinylpyrrolidone) is intercalated and cross-linked inside the acid-functionalized mesopores of silica, the fructose tautomer equilibrium favors HMF production.

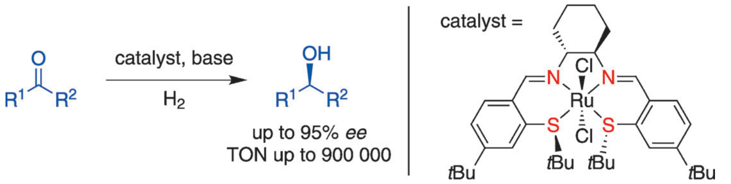


Inside Cover

Phosphine-Free Hydrogenation

R. Patchett, I. Magpantay, L. Saudan, C. Schotes, A. Mezzetti,* F. Santoro* ______ **10352 – 10355**

Asymmetric Hydrogenation of Ketones with H_2 and Ruthenium Catalysts Containing Chiral Tetradentate S_2N_2 Ligands

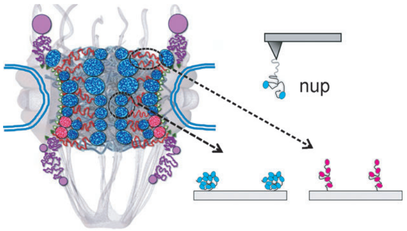


Getting more for less: In the presence of H_2 and a base, air- and moisture-tolerant Ru^{II} complexes catalyze the hydrogenation of ketones and aldehydes with excellent activity and chemoselectivity, and with enantioselectivity of up to 95 % under mild conditions. The ratio of substrate to catalyst can be lowered to 10^6:1. The reactions tolerate scale-up and can be carried out with almost no solvent. A base-free method is available for base-sensitive substrates.

Atomic Force Microscopy

M. Rangl, A. Ebner, J. Yamada, C. Rankl, R. Tampé, H. J. Gruber, M. Rexach,* P. Hinterdorfer* ______ **10356 – 10359**

Single-Molecule Analysis of the Recognition Forces Underlying Nucleo-Cytoplasmic Transport

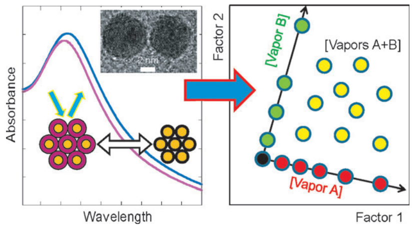


Transport forces: To move molecules across the nuclear envelope they have to overcome the selective barrier of the nuclear pore which is formed by nucleoporins (nups) with FG repeats. The molecules are chaperoned by shuttling receptors that interact with FG nups thereby passing the barrier using an unresolved mechanism. This process is explored by single-molecule force spectroscopy (see picture).

Multivariable Sensors

R. A. Potyrailo,* M. Larsen, O. Riccobono ______ **10360 – 10364**

Detection of Individual Vapors and Their Mixtures Using a Selectivity-Tunable Three-Dimensional Network of Plasmonic Nanoparticles



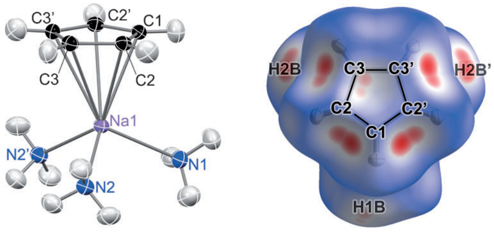
Sensor selectivity: Selective detection of individual vapors and their mixtures is achieved by using a single three-dimensional networked film of organothiol-functionalized plasmonic nanoparticles (see picture). This approach gives a new perspective for sensing, where tunable selectivity is achieved within a single sensing film, rather than from an array of separate conventional sensors.

Inside Back Cover

Sodium Cyclopentadienide

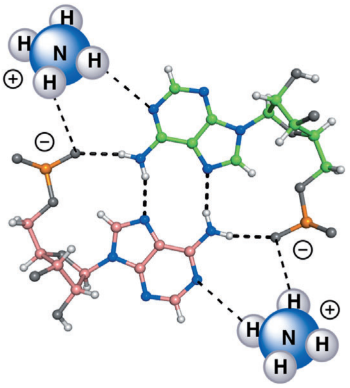
J. Hey, D. M. Andrada, R. Michel, R. A. Mata,* D. Stalke* ______ **10365 – 10369**

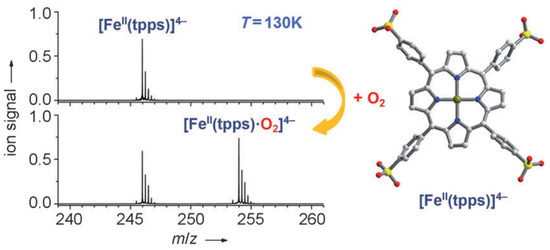
Strong Intermolecular Interactions Shaping a Small Piano-Stool Complex



The smallest piano stool [CpNa$(NH_3)_3$] is not a stand-alone unit in the solid state but is largely shaped by strong intermolecular N–H⋯π interactions. Small but important structural features, such as the bending of the C–H bonds inwards to the sodium atom that was confirmed by experimental charge density investigations, could only be reproduced by quantum mechanical calculations that included a lattice of more than 300 units.

The other double helix: The molecular structure of double-stranded poly(rA) was predicted in 1961, but it has only now been confirmed. The crystal structure of the parallel double helix of $(rA)_{11}$ obtained at physiological pH was solved using ab initio direct methods and refined to 1.0 Å resolution. The crystals have bound ammonium ions that are complexed by the RNA phosphates and adenine N1 atoms (see section of the structure).





The binding energies of O_2 and CO to iron(II) and manganese(II) porphyrin anions has been determined in the gas phase. Low-pressure ion–molecule equilibria have been measured in a cryogenically cooled trap of an FT-ICR mass spectrometer, and binding energies of (40.8 ± 1.3) $kJ\,mol^{-1}$ and (66.3 ± 2.6) $kJ\,mol^{-1}$ have been obtained for oxygen and carbon monoxide, respectively, with a heme-analogue Fe^{II} porphyrin complex.

DOI: 10.1002/anie.201306147

50 Years Ago . . .

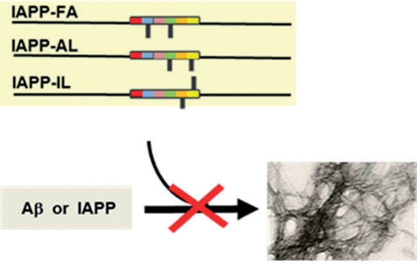
Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

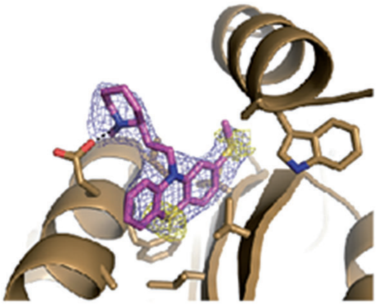
The Huisgen 1,3-dipolar cycloaddition reaction is one of the most explored organic reactions, and fifty years ago its wide range and versatility had already been realized. In a Review, Rolf Huisgen outlined recent developments in the area; more than 1000 cycloaddition products had already been prepared and analyzed in Huisgen's laboratory alone. This reaction has now become one of the most utilized transformations in the field of "click" chemistry (for more background information see: H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021).

Oskar Glemser published two contributions: The first was a short Review on the tungsten- or molybdenum-catalyzed preparation of carbon tetrachloride from phosgene at atmospheric pressure and between 300–450°C. In a Communication that featured the then PhD student Herbert Roesky as co-author, the synthesis of manganese tetrafluoride by direct fluorination of manganese powder is described. Roesky is now one of the top two authors who have published the most manuscripts in *Angewandte Chemie* since 1946 (for the full list see: F. Diederich, *Angew. Chem. Int. Ed.* **2013**, *52*, 2714), and he has recently been featured in an Author Profile (*Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201302592).

Ivar Ugi, who carried out his PhD with Huisgen, reported on a development of the four-component condensation that is now known as the Ugi reaction. Condensation of a chiral primary amine with an aldehyde, a carboxylic acid, and an isonitrile gave an L-amino acid when the reaction was subject to kinetically controlled asymmetric 1,3-induction, and a D-amino acid in the thermodynamically controlled case.

Read more in Issue 10/1963.





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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