

VIP

The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

J.-J. Li, T.-S. Mei, J.-Q. Yu*

Synthesis of Indolines and Tetrahydroisoquinolines from Arylethylamines by Palladium(II)-Catalyzed C–H Activation Reactions

S. G. Srivatsan, N. J. Greco, Y. Tor*

Highly Emissive Fluorescent Nucleoside Signals the Activity of Toxic Ribosome-Inactivating Proteins

M. Mascal*, E. B. Nikitin

Direct, High-Yield Conversion of Cellulose into Biofuel

P. García-Álvarez, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey*, C. T. O'Hara, S. Weatherstone

Unmasking Representative Structures of TMP-Active Hauser and Turbo Hauser Bases

Self Assembly

John A. Pelesko

Books

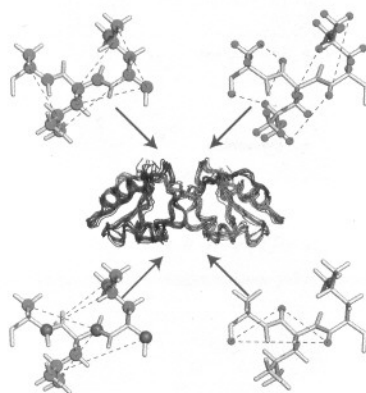
reviewed by J. R. Nitschke _____ 6108

Highlights

Protein Structures

A. Böckmann* _____ 6110–6113

3D Protein Structures by Solid-State NMR Spectroscopy: Ready for High Resolution



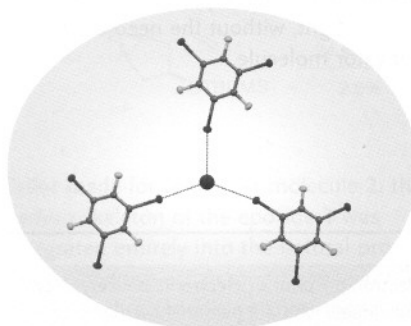
Protocols for determining high-resolution 3D structures of solid proteins are essential for structural studies of fibrils and membrane proteins. Advances in solid-state NMR spectroscopy have led to a multitude of approaches to access restraints and to calculate structures from highly ambiguous data sets. 3D structures at atomic resolution have been derived for several model proteins, as well as for the C-terminal portion of the Het-s prion protein.

Minireviews

Halogen Bonding

P. Metrangolo*, F. Meyer, T. Pilati, G. Resnati*, G. Terraneo _____ 6114–6127

Halogen Bonding in Supramolecular Chemistry



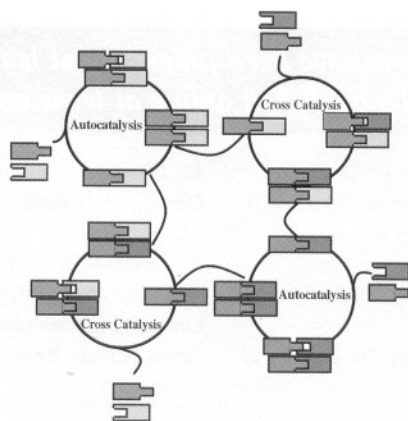
Building bridges: Halogen bonding is a noncovalent interaction where halogen atoms function as electrophilic species (see picture; gray C, green F, violet I). Halogen bonding has an impact on all fields where the control of recognition and self-organization plays a key role. The potential of the interaction is also shown by useful applications in the field of material science and in biological systems.

Synthetic Networks

Z. Dadon, N. Wagner,
G. Ashkenasy* 6128–6136



The Road to Non-Enzymatic Molecular Networks



A systematic viewpoint: Recent progress in transforming minimal self-replicating systems into small networks of dynamically interacting molecules is reviewed. The authors suggest that such synthetic self-organized networks can provide useful models for studying the behavior of complex systems.

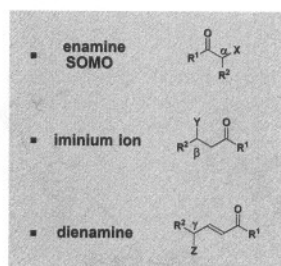
Reviews

Organocatalysis

P. Melchiorre,* M. Marigo,* A. Carlone,
G. Bartoli 6138–6171

Asymmetric Aminocatalysis—Gold Rush in Organic Chemistry

Gold! Gold! Gold from the American River! The seminal reports on asymmetric catalysis with secondary amines attracted waves of researchers to the “gold mine” of organocatalysis. Particular challenges, milestones, and future directions of asymmetric aminocatalysis are discussed in this Review.

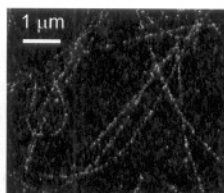
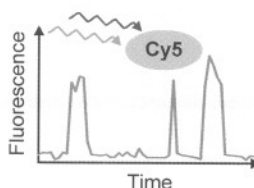


Communications

Microscopy

M. Heilemann,* S. van de Linde,
M. Schüttelpeiz, R. Kasper, B. Seefeldt,
A. Mukherjee, P. Tinnefeld,
M. Sauer* 6172–6176

Subdiffraction-Resolution Fluorescence Imaging with Conventional Fluorescent Probes



Eagle eyes: dSTORM uses conventional photoswitchable fluorescent dyes that can be reversibly cycled between a fluorescent and a dark state by irradiation with light of different wavelengths (see picture). This elegant approach can visualize cellular structures with a resolution of approximately 20 nm, far beyond the diffraction limit of light, without the need of an activator molecule.

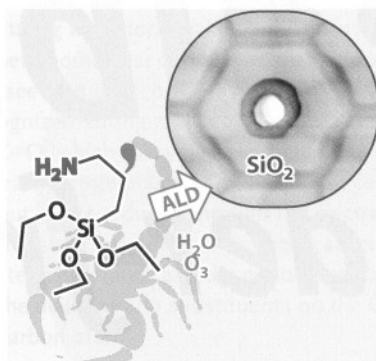
For the USA and Canada:

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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.

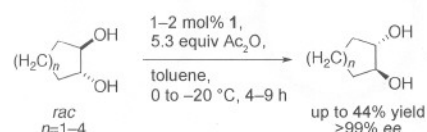
Molecular self-attack: According to mythology, a scorpion may sting itself to death; similarly, 3-aminopropyltriethoxysilane catalyzes its own hydrolysis in the atomic layer deposition (ALD) of SiO_2 thin films and nanostructures. Between 120 and 200 °C, the growth rate is constant at 0.06 nm per ALD cycle. The SiO_2 films are chemically and optically pure. SiO_2 nanotubes of aspect ratio 500 exhibit smooth walls of accurately controlled thickness.



Thin SiO_2 Films

J. Bachmann,* R. Zierold, Y. T. Chong, R. Hauert, C. Sturm, R. Schmidt-Grund, B. Rheinländer, M. Grundmann, U. Gösele, K. Nielsch* — 6177–6179

A Practical, Self-Catalytic, Atomic Layer Deposition of Silicon Dioxide



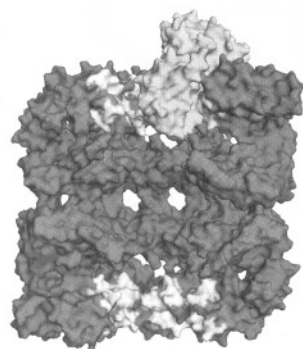
Finally! The title resolution is achieved with a nonnatural, partially rigid, lipophilic tetrapeptide at low catalyst loadings without additional base or cosolvents. The transition-state model (ball-and-stick

model in the scheme; C gray, N blue, O red) emphasizes the interplay between hydrogen-bonding and hydrophobic interactions.

Organocatalysis

C. E. Müller, L. Wanka, K. Jewell, P. R. Schreiner* — 6180–6183

Enantioselective Kinetic Resolution of *trans*-Cycloalkane-1,2-diols

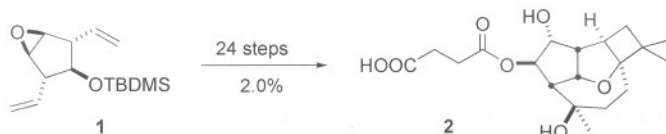


Molecular chaperones aid protein folding in the cell, but their effects on the conformation of the substrate protein have largely eluded experimental investigation. Single-molecule fluorescence spectroscopy was used to extract structural and dynamic information from a protein–chaperone complex (see figure; yellow: rhodanase, blue: GroEL). This approach will aid in a more physical understanding of the role of cellular factors in protein folding.

Protein Folding

F. Hillger, D. Hänni, D. Nettels, S. Geister, M. Grandin, M. Textor, B. Schuler* — 6184–6188

Probing Protein–Chaperone Interactions with Single-Molecule Fluorescence Spectroscopy



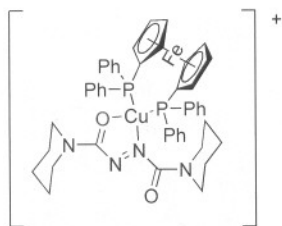
Tailor made for the target molecule **2**, the carbon skeleton of the epoxide **1** was integrated entirely into the natural product. A regioselective intramolecular [2+2] photocycloaddition and subsequent Wacker oxidation enabled the specific and

successive incorporation of the two terminal double bonds of **1** into the unusual oxatetracyclo[6.3.2.0^{1,4}.0^{5,13}]tridecane skeleton of **2**, which was synthesized in 24 steps and 2.0% overall yield. TBDMS = *tert*-butyldimethylsilyl.

Natural Products Synthesis

M. Fleck, T. Bach* — 6189–6191

Total Synthesis of the Tetracyclic Sesquiterpene (±)-Punctaporonin C

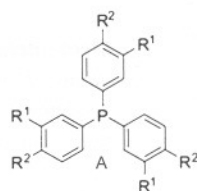
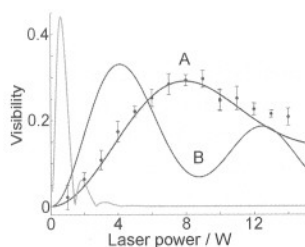


Strong acceptor, weak coordination: The heterodinuclear complex ion $[LCu(dppf)]^+$ (see formula) contains the as yet unrecognized strong π -acceptor system $N=N-C=O$, which is involved in a charge-transfer interaction with the copper center but is not reduced through full electron transfer. This situation is likely caused by steric hindrance and the donor function of the dialkylamino substituents on the $C=O$ carbon atom.

Chelate Ligands

S. Roy, M. Sieger, B. Sarkar,
B. Schwederski, F. Lissner, T. Schleid,
J. Fiedler, W. Kaim* 6192–6194

Establishing the Chelating α -Azocarbonyl
Function in π -Acceptor Ligands



Matter-Wave Interferometry

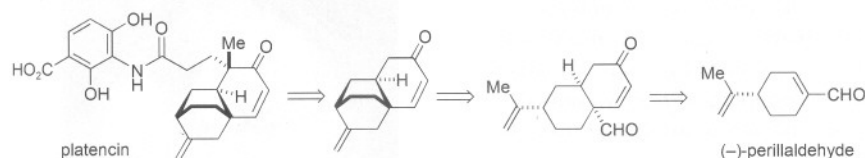
VIP

S. Gerlich, M. Gring, H. Ulbricht,
K. Hornberger,* J. Tüxen, M. Mayor,*
M. Arndt* 6195–6198

Matter-Wave Metrology as a
Complementary Tool for Mass
Spectrometry

Quantum interferometry can serve as a useful complement to mass spectrometry. The interference visibility (see picture) reveals important information on molecular properties, such as mass and polarizability. The method is applicable to a

wide range of molecules, and is particularly valuable for characterizing neutral molecular beams. In particular, fragmentation in the source can be distinguished from molecular dissociation in the detector.



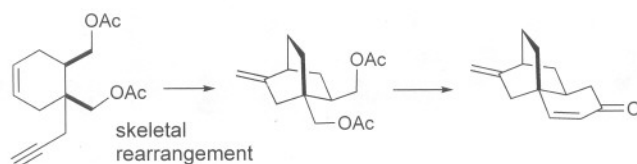
Natural Products

K. Tiefenbacher,* J. Mulzer* 6199–6200

Short Formal Synthesis of (-)-Platencin

Short and sweet: A five-step, protecting-group-free formal synthesis of (-)-platencin from commercially available (-)-perillaldehyde (see retrosynthetic

scheme) features a highly diastereoselective Diels–Alder reaction and a ring-closing metathesis as key steps.



A radical change: Implementation of a radical-mediated rearrangement of the bicyclo[3.2.1]octyl moiety to the bicyclo[2.2.2]octane structure has enabled a concise synthesis of the tricyclic core of

platencin, a newly discovered antibiotic. An intramolecular aldol and a ring-closing metathesis reaction were subsequently used to complete the synthesis of the tricycle (see scheme).

Natural Products

S. Y. Yun, J.-C. Zheng,
D. Lee* 6201–6203

Concise Synthesis of the Tricyclic Core of
Platencin

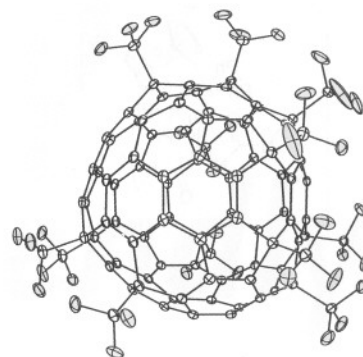
Higher Fullerenes

I. E. Kareev,* I. V. Kuvychko,
N. B. Shustova, S. F. Lebedkin,
V. P. Bubnov, O. P. Anderson, A. A. Popov,
O. V. Boltalina,*
S. H. Strauss* _____ **6204–6207**



$C_{1-(C_{84}-C_2(11))}(CF_3)_{12}$:
Trifluoromethylation Yields Structural
Proof of a Minor C_{84} Cage and Reveals a
Principle of Higher Fullerene Reactivity

Ribbon pattern: An isomer of $C_{84}(CF_3)_{12}$ fullerene with the $C_{84}-C_2(11)$ cage (see molecular structure determined by X-ray crystallography) demonstrates a new principle of hollow higher fullerene reactivity: For 1,4-additions of bulky groups that produce ribbons or loops of edge-sharing $p-C_6X_2$ hexagons, the “most reactive” double bonds remain intact.

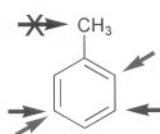
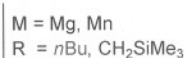


Polymetalation

V. L. Blair, L. M. Carrella, W. Clegg,
B. Conway, R. W. Harrington, L. M. Hogg,
J. Klett, R. E. Mulvey,* E. Rentschler,
L. Russo _____ **6208–6211**



Tuning the Basicity of Synergic Bimetallic
Reagents: Switching the Regioselectivity
of the Direct Dimetalation of Toluene from
2,5- to 3,5-Positions



Meta–meta metalation: Remarkably, toluene can be directly dimanganated or dimagnesiased at the 3,5-positions using bimetallic bases with active Me_3SiCH_2 ligands (see scheme, blue). In contrast, *n*-butyl ligands lead to 2,5-metalation (red). tmp = 2,2,6,6-tetramethylpiperidine.



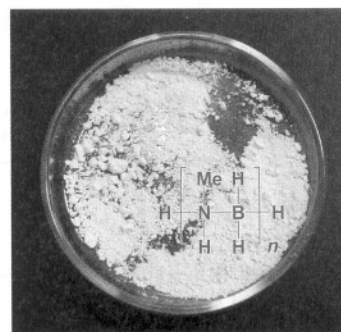
Boron–Nitrogen Compounds

A. Staubitz, A. Presa Soto,
I. Manners* _____ **6212–6215**



Iridium-Catalyzed Dehydrocoupling of
Primary Amine–Borane Adducts: A Route
to High Molecular Weight Polyamino-
boranes, Boron–Nitrogen Analogues of
Polyolefins

The B all and N all: Soluble, linear, high molecular weight polyaminoborane homopolymers and copolymers have been synthesized by iridium-catalyzed dehydrocoupling of readily available amine–borane adducts $\text{RNH}_2\text{-BH}_3$ ($\text{R} = \text{H, Me, } n\text{Bu}$).

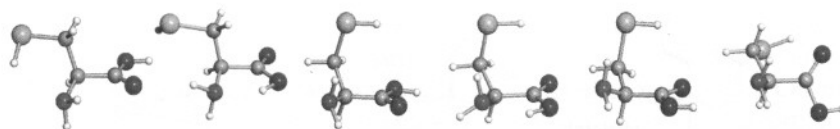


Conformational Analysis

M. E. Sanz, S. Blanco, J. C. López,
J. L. Alonso* _____ **6216–6220**



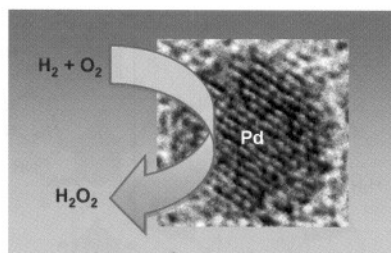
Rotational Probes of Six Conformers of
Neutral Cysteine



Six of one: Vaporization of solid cysteine by laser ablation followed by the generation of a supersonic jet in a vacuum chamber has enabled six low-energy conformers of this amino acid to be characterized by using Fourier transform

microwave spectroscopy (see picture). The information provided by this technique is directly comparable with that predicted from in vacuo ab initio computations.

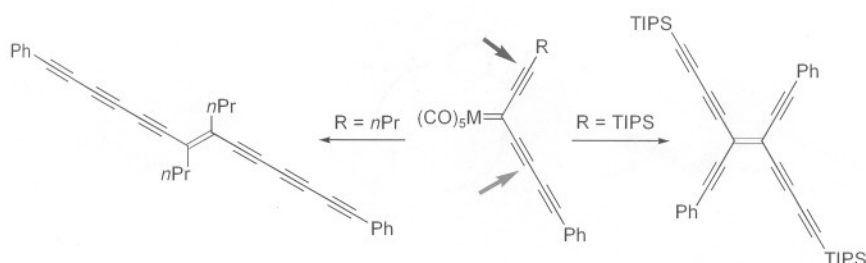
Ex situ synthesis is the key: Palladium nanoparticles having a narrow size distribution around 3.6 nm have been synthesized in a liquid phase and then loaded onto a carbon support with an overall efficiency of 85%. The resulting nanoparticles, which retained their size and morphology, were exceptionally active and selective as a catalyst for the direct formation of H_2O_2 from H_2 and O_2 in ethanol.



Nanoparticle catalysis

Q. Liu, J. C. Bauer, R. E. Schaak,
J. H. Lunsford* 6221–6224

Supported Palladium Nanoparticles: An Efficient Catalyst for the Direct Formation of H_2O_2 from H_2 and O_2



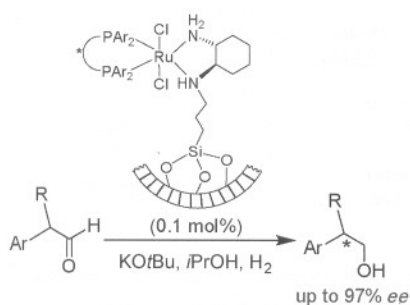
Heads or tails? Chemo-, regio-, and stereoselective access to cross- and linear conjugated poly-ynene scaffolds from alkynyl-derived group six metal carbenes is reported. The metal carbenes shown

($\text{M} = \text{Cr}, \text{W}$; TIPS = triisopropylsilyl) readily undergo low-temperature, tail-to-tail dimerization in the presence of potassium *tert*-butoxide by reaction at either of the C_β atoms to provide *E*-polyalkynylethenes.

Synthetic Methods

J. Barluenga,* D. de Sáa, A. Gómez,
A. Ballesteros, J. Santamaría,
A. de Prado, M. Tomás,
A. L. Suárez-Sobrinho 6225–6228

Metal Carbene Dimerization: Versatile Approach to Polyalkynylethenes



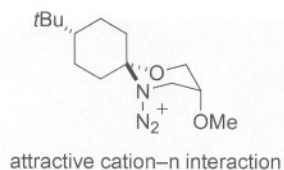
Chiral Ruthenium–diphosphine–diamine complexes with a siloxy pendant are grafted onto mesoporous silica nanospheres. The resulting supported ruthenium catalysts are highly active for the asymmetric hydrogenation of aromatic ketones to afford chiral secondary alcohols and racemic aryl aldehydes to give chiral primary alcohols (see scheme). This immobilization strategy should be amenable to the design of similar heterogeneous catalysts.

Supported Catalysts

D. J. Mihalczik, W. Lin* 6229–6232

Mesoporous Silica Nanosphere
Supported Ruthenium Catalysts for
Asymmetric Hydrogenation

Gaining control: An attractive electrostatic force stabilizes the conformation of an intermediate (see scheme; n = nonbonded electron), thus controlling the leaving group configuration to give superior diastereoselectivity in an asymmetric ring expansion.



attractive cation– n interaction

Asymmetric Ring Expansion

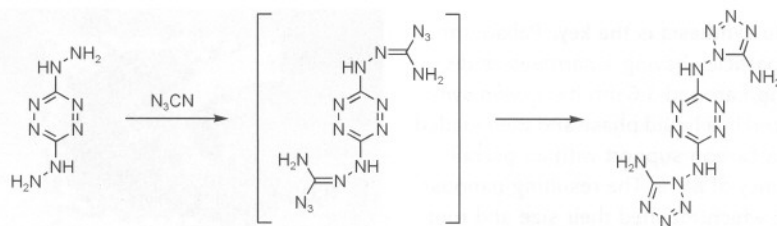
T. Ribelin, C. E. Katz, D. G. English,
S. Smith, A. K. Manukyan, V. W. Day,
B. Neuenswander, J. L. Poutsma,*
J. Aubé* 6233–6235

Highly Stereoselective Ring Expansion
Reactions Mediated by Attractive Cation– n Interactions

Nitrogen-Rich Compounds

Y.-H. Joo, B. Twamley, S. Garg,
J. M. Shreeve* 6236–6239

 Energetic Nitrogen-Rich Derivatives of
1,5-Diaminotetrazole



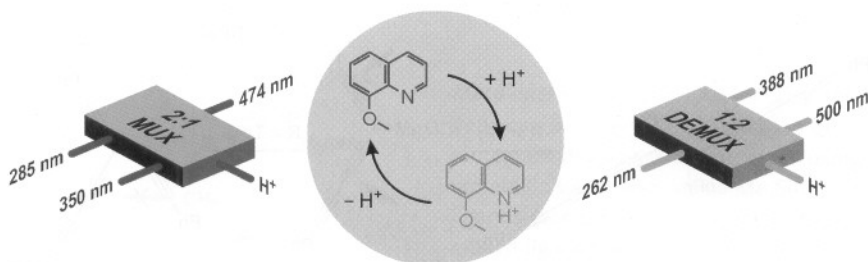
High-energy-density materials can be obtained by reaction of monosubstituted hydrazines with cyanogen azide to gener-

ate 1,5-diaminotetrazole derivatives. Azido-hydrazones are postulated as intermediates in this reaction (see scheme).

Molecular Logic

M. Amelia, M. Baroncini,
A. Credi* 6240–6243

 A Simple Unimolecular Multiplexer/
Demultiplexer



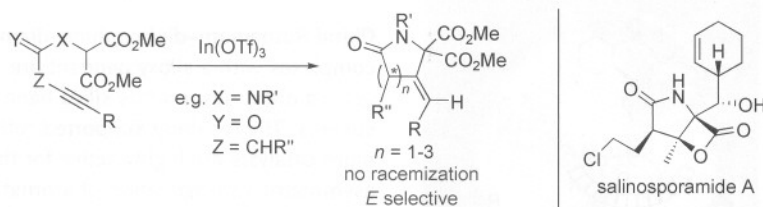
Simple but effective! 8-Methoxyquinoline, an unsophisticated fluorophore, displays both 2:1 multiplexer and 1:2 demultiplexer digital functions (see picture). Protonation of the fluorophore results in completely different optical spectral pro-

files and multiplexing/demultiplexing behavior is obtained by exploiting the proton-driven reversible modulation of two complementary absorption and fluorescence signals.

Heterocycle Synthesis

K. Takahashi, M. Midori, K. Kawano,
J. Ishihara, S. Hatakeyama* 6244–6246

 Entry to Heterocycles Based on Indium-Catalyzed Conia-Ene Reactions:
Asymmetric Synthesis of
(–)-Salinosporamide A



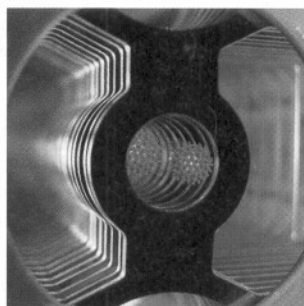
Conica can: The In(OTf)₃-catalyzed cyclization of nitrogen- and oxygen-tethered acetylenic malonic esters gives five- to seven-membered heterocycles in moderate to excellent yields (see scheme;

Tf=trifluoromethanesulfonyl). The asymmetric synthesis of (–)-salinosporamide A illustrates the synthetic utility of the method.

Protein Structures

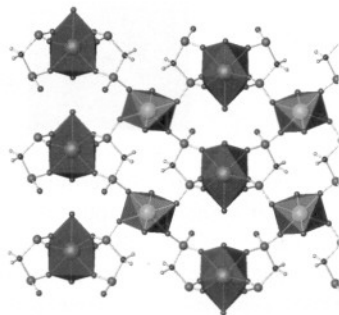
C. Uetrecht, C. Versluis, N. R. Watts,
P. T. Wingfield, A. C. Steven,
A. J. R. Heck* 6247–6251

 Stability and Shape of Hepatitis B Virus
Capsids In Vacuo



Viruses at a glance: Ion mobility mass spectrometry allows the identification and differentiation of states in a viral assembly not only by mass but also by conformation. This approach has been used to obtain a biophysical characterization of the hepatitis B virus capsids, and has shown that of its two distinct icosahedral geometries, the spherical capsid structure is preserved in vacuo (see picture).

Order out of chaos: The reduction of Np^{VI} to Np^{IV} readily occurs under mild hydrothermal conditions in the presence of phosphonates, sharply contrasting with U^{VI} , which maintains its oxidation state under identical conditions. By coupling the differing redox potentials of U^{VI} and Np^{VI} with the vastly different coordination chemistry of U^{VI} and Np^{IV} , the first example of an ordered $\text{U}^{\text{VI}}/\text{Np}^{\text{IV}}$ phosphonate is prepared (see structure: U green, Np purple (large), O red, P purple (small)).

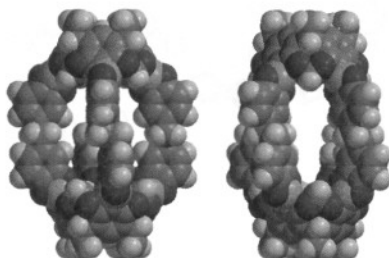


Actinoid Chemistry

A.-G. D. Nelson, T. H. Bray,
T. E. Albrecht-Schmitt* — 6252–6254

Capitalizing on Differing Coordination Environments and Redox Potentials to Prepare an Ordered Heterobimetallic $\text{U}^{\text{VI}}/\text{Np}^{\text{IV}}$ Diphosphonate

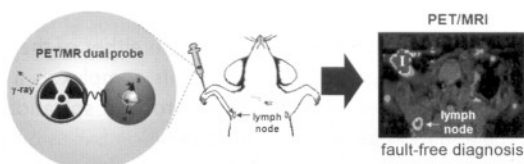
Be my guest: Two molecules of a cavitand tetraboronic acid and four molecules of a bis(catechol) linker quantitatively assemble into a capsule (see picture for two views), with highly selective guest-recognition, by dynamic boronic ester formation. The on/off control of capsule formation with guest encapsulation is achieved by removal/addition of methanol.



Supramolecular Chemistry

N. Nishimura,
K. Kobayashi* — 6255–6258

Self-Assembly of a Cavitand-Based Capsule by Dynamic Boronic Ester Formation



Creating a good image: A probe for combined positron emission tomography (PET) and magnetic resonance imaging (MRI) has high colloidal stability and demonstrates facile conjugation ability. Sentinel lymph nodes are clearly identified

in the fusion image (see picture; I: injection site) because of the complementary nature of the techniques, which makes accurate anatomical information and fault-free diagnosis possible.

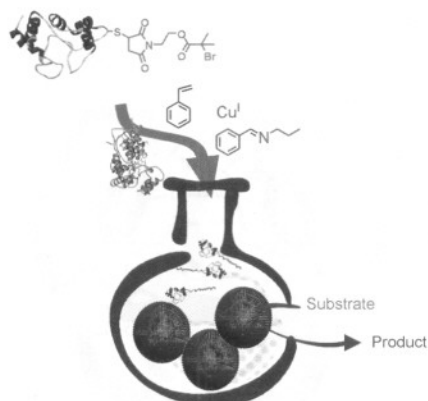
Imaging Probe

J.-s. Choi, J. C. Park, H. Nah, S. Woo, J. Oh,
K. M. Kim, G. J. Cheon, Y. Chang, J. Yoo,*
J. Cheon* — 6259–6262

A Hybrid Nanoparticle Probe for Dual-Modality Positron Emission Tomography and Magnetic Resonance Imaging



Functional giants: Amphiphilic bioconjugates can be synthesized in situ by grafting polystyrene from a protein (see scheme). The resulting giant amphiphiles display low polydispersities and the characteristic aggregation properties of amphiphilic biomacromolecules. A second, catalytically active guest protein can also be included within the superstructures.



Bionanoreactors

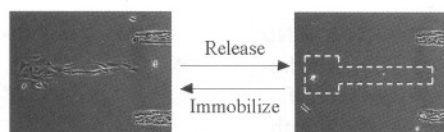
B. Le Droumaguet,
K. Velonia* — 6263–6266

In Situ ATRP-Mediated Hierarchical Formation of Giant Amphiphile Bionanoreactors



Electroactive Monolayers

E. W. L. Chan, S. Park,
M. N. Yousaf* — 6267–6271



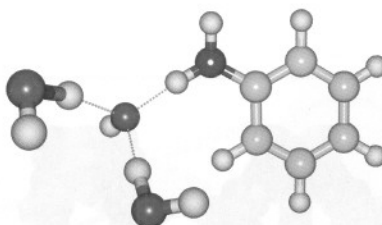
- An Electroactive Catalytic Dynamic Substrate that Immobilizes and Releases Patterned Ligands, Proteins, and Cells

Dynamic release: A quinone-terminated self-assembled monolayer captures and releases ligands and cells in situ through a pH-dependent electrochemical potential. The surface is catalytic for multiple rounds

of immobilization/release. When combined with a photochemical approach, peptide ligands that mediate cell attachment are captured and released on defined gradient patterns (see picture).

Intracluster Proton Transfer

I. Wolf, A. Shapira, R. Giniger, Y. Miller,
R. B. Gerber,
O. Cheshnovsky* — 6272–6274

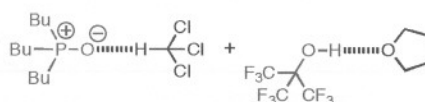


- Critical Size for Intracluster Proton Transfer from Water to an Anion

Bigger is better: Proton transfer in the electronic ground state for $(\text{C}_6\text{H}_5\text{NH}^-) \cdot (\text{H}_2\text{O})_n$ has been investigated by photoelectron spectroscopy. At a critical size of $n=3$, one proton of a water molecule is captured by the deprotonated aniline to form solvated OH^- (see picture). These experimental observations are supported by ab initio calculations that establish the greater stability of the solvated OH^- anion for $n \geq 3$.

Molecular Interactions

J. L. Cook, C. A. Hunter,* C. M. R. Low,
A. Perez-Velasco,
J. G. Vinter — 6275–6277



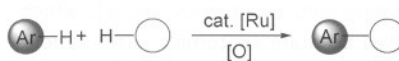
Preferential Solvation and Hydrogen Bonding in Mixed Solvents

Oak trees from acorns: A small amount ($< 1\%$) of a cosolvent can change the stability of the H-bonded complex on the right-hand side of the equation by an order of magnitude. Mixtures of chloroform and THF were found to be more

polar than either of the pure solvents by using this complex as a molecular-recognition probe of solvation. A quantitative interpretation based on preferential solvation accounts for the properties of solvent mixtures.

Synthetic Methods

G. Deng, L. Zhao, C.-J. Li* — 6278–6282

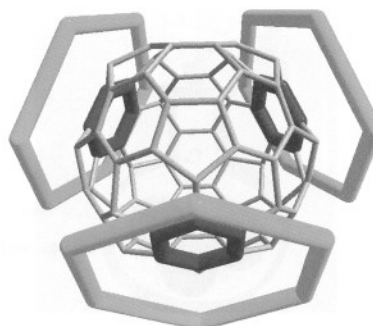


- Ruthenium-Catalyzed Oxidative Cross-Coupling of Chelating Arenes and Cycloalkanes

Alkane and arene join together: Various arenes were coupled directly with simple cycloalkanes. The reaction was catalyzed by ruthenium under oxidative conditions to give substituted cycloalkylarenes regioselectively (see scheme).

Fullerenes

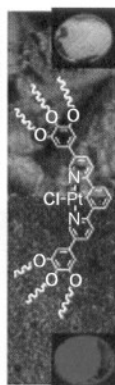
K. S. Simeonov, K. Y. Amsharov, E. Krokos,
M. Jansen* — 6283–6285



- An Epilogue on the C_{78} -Fullerene Family: The Discovery and Characterization of an Elusive Isomer

Missing relative found: The last representative of the first multi membered fullerene family, $\text{C}_{78}(4)$, has been synthesized and isolated. Its connectivity pattern was confirmed by a single-crystal X-ray analysis of its chlorinated derivative $\text{C}_{78}(4)\text{Cl}_{18}$ (see picture). The crystal structure also reveals the presence of unusual, short intermolecular chlorine contacts.

Liquid crystals shining bright. A highly efficient platinum(II) luminophore is rendered liquid crystalline using a simple and flexible synthetic approach. Ordering in the liquid-crystalline state allows monomer emission when the characteristic for the material is exciplex-like emission. More than that, emission characteristics are subject to tribological control, with the initial state re-obtained by thermal cycling.



Metallomesogens

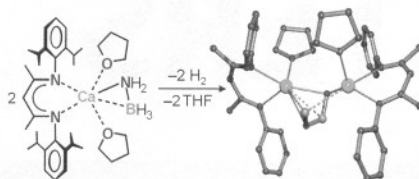
V. N. Kozhevnikov,* B. Donnio,
D. W. Bruce* 6286–6289

Phosphorescent, Terdentate, Liquid-Crystalline Complexes of Platinum(II): Stimulus-Dependent Emission



A model solution to hydrogen storage?

The recently introduced hydrogen storage material $[\{Ca(NH_2BH_3)_2\}_n]$ has been investigated on a molecular level. A hydrocarbon-soluble calcium amidoborane complex eliminates H_2 spontaneously at the very low temperature of 20–40°C (see scheme). The decomposition product shows a dimeric species with a bridging $[HN-BH-NH-BH_3]^{2-}$ ion that is isolobal to the allylic dianion $[HC-CH-CH-CH_3]^{2-}$.



Hydrogen Storage

J. Spielmann, G. Jansen, H. Bandmann,
S. Harder* 6290–6295

Calcium Amidoborane Hydrogen Storage Materials: Crystal Structures of Decomposition Products



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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