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:

*T. J. Greshock, A. W. Grubbs, P. Jiao, J. B. Gloer, R. M. Williams**
Isolation, Structure Elucidation, and Biomimetic Total Synthesis of Versicolamide B and the Isolation of Antipodal (–)-Stephacidin A and (+)-Notoamide B from *Aspergillus versicolor* NRRL 35600

Y. V. Geletii, B. Botar, P. Kögerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill**
An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation

*Z. Liu, A. Kumbhar, D. Xu, J. Zhang, Z. Sun, J. Fang**
Co-Reduction Colloidal Synthesis of III-V Nanocrystals: The Case of InP

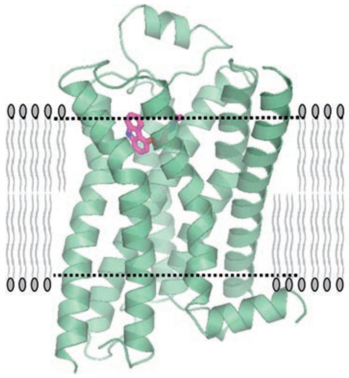
*Y. H. Sehlleier, A. Verhoeven, M. Jansen**
Observation of Direct Bonds Between Carbon and Nitrogen in Si–B–N–C Ceramic After Pyrolysis at 1400 °C

News

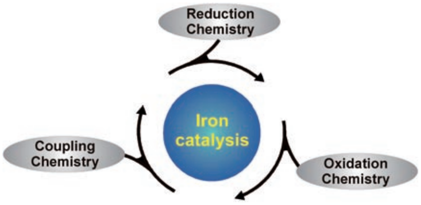
Books

Highlights

Rational drug design is still limited for many membrane proteins. For the β_2-adrenergic receptor, a prototype of the class A GPCR family, structures with up to 2.4-Å resolution have now been solved. The structure (see figure) shows detailed contacts of the receptor (green) with its ligand carazolol (pink), and makes possible the formulation of hypotheses for the mode of action of G-protein-coupled receptors.



G-Protein-Coupled Receptors



Among the shades! With respect to its availability, low toxicity, and price, iron should be one of the most used metals in homogeneous catalysis. Surprisingly, so far the application of iron is underdeveloped in comparison with other transition metals. Some promising attempts obtained in redox reactions and coupling chemistry which nicely illustrate the potential of iron and hopefully initialize a ferric future for catalysis are highlighted.

Homogeneous Catalysis

Contents

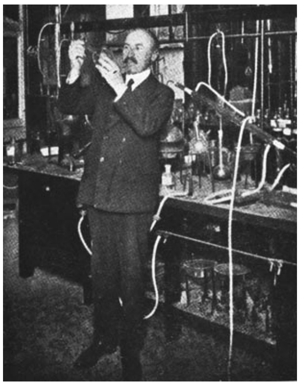
Essays

History of Science

D. Crespy,* M. Bozonnet,
M. Meier ______________ **3322 – 3328**

100 Years of Bakelite, the Material of a 1000 Uses

The beginning of the plastics age: Just over one hundred years ago, on July 13 1907, Leo H. Baekeland applied for a patent for the processing of a product that had an enormous influence on the development of our technology, and which changed our habits forever. The patent described Bakelite, the first synthetic plastic, which heralded our entrance into the plastics age.



Reviews

Pyrotechnics

G. Steinhauser,
T. M. Klapötke* __________ **3330 – 3347**

“Green” Pyrotechnics: A Chemists’ Challenge

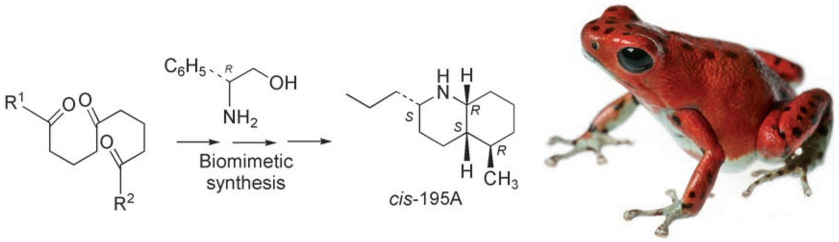
The other “dirty bombs”: Fireworks and pyrotechnic applications cause multifaceted environmental pollution. This Review gives an overview about the recent “greening” of pyrotechnics: the use of nitrogen-rich energetic materials and other strategies to avoid the production of toxic combustion products.

Communications

Biomimetic Synthesis

M. Amat,* R. Griera, R. Fabregat,
E. Molins, J. Bosch* _______ **3348 – 3351**

A Biomimetic Enantioselective Approach to the Decahydroquinoline Class of Dendrobatid Alkaloids



A princely synthesis: The hypothetical key step in the biosynthesis of the decahydroquinoline dendrobatid alkaloids, such as *cis*-195 A found in frogs, from 1,5-polycarbonyl derivatives is mimicked by using (*R*)-phenylglycinol as a chiral latent form of ammonia in a double cyclocondensation reaction.

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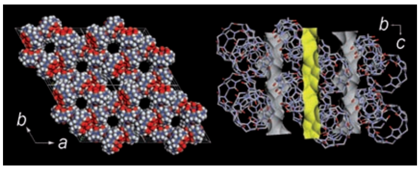
Organic Porous Materials

S. Lim, H. Kim, N. Selvapalam, K.-J. Kim, S. J. Cho, G. Seo,* K. Kim* **3352 – 3355**

Cucurbit[6]uril: Organic Molecular Porous Material with Permanent Porosity, Exceptional Stability, and Acetylene Sorption Properties

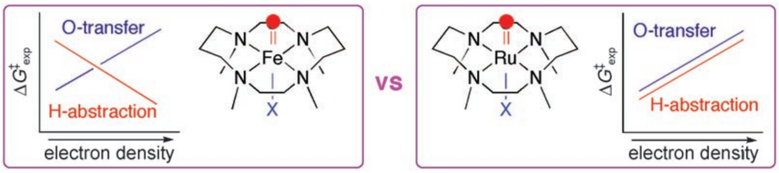


Holely organic solid: Effective packing of the rigid macrocycle cucurbituril through C–H···O hydrogen-bonding and van der Waals interactions leads to a honeycomb-like structure with unprecedented stability and porosity. It shows extraordinary sorption properties toward gases, particularly acetylene, which are comparable or superior to those of metal–organic frameworks in terms of storage capacity.

Enzyme Models

S. N. Dhuri, M. S. Seo, Y.-M. Lee, H. Hirao, Y. Wang, W. Nam,* S. Shaik* **3356 – 3359**

Experiment and Theory Reveal the Fundamental Difference between Two-State and Single-State Reactivity Patterns in Nonheme $Fe^{IV}=O$ versus $Ru^{IV}=O$ Oxidants

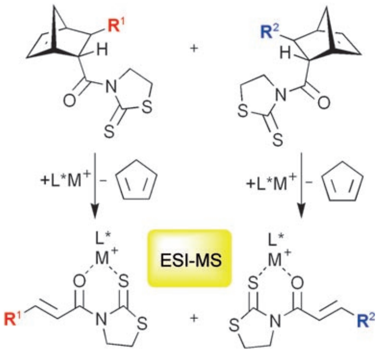


Two-state reactivity involving close triplet ground and quintet excited states is responsible for the opposite reactivity trends of Fe^{IV} oxo complexes in O-transfer and H-abstraction reactions in dependence on the electron richness of the axial ligand X (see picture), as shown by comparison with Ru^{IV} analogues, in which both reactivities are solely governed by the electrophilicity of the complex because the quintet state is inaccessible.

Catalyst Screening (1)

A. Teichert, A. Pfaltz* **3360 – 3362**

Mass Spectrometric Screening of Enantioselective Diels–Alder Reactions

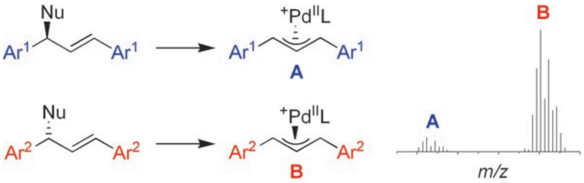


A rapid cat. scan: Mass spectrometric monitoring of reaction intermediates of the retro-Diels–Alder reaction has allowed the rapid screening of catalysts for enantioselective Diels–Alder reactions (see scheme). Copper catalysts as well as metal-free organocatalysts were tested. A protocol for the simultaneous screening of catalyst mixtures has also been developed, which offers new possibilities for high-throughput catalyst development.

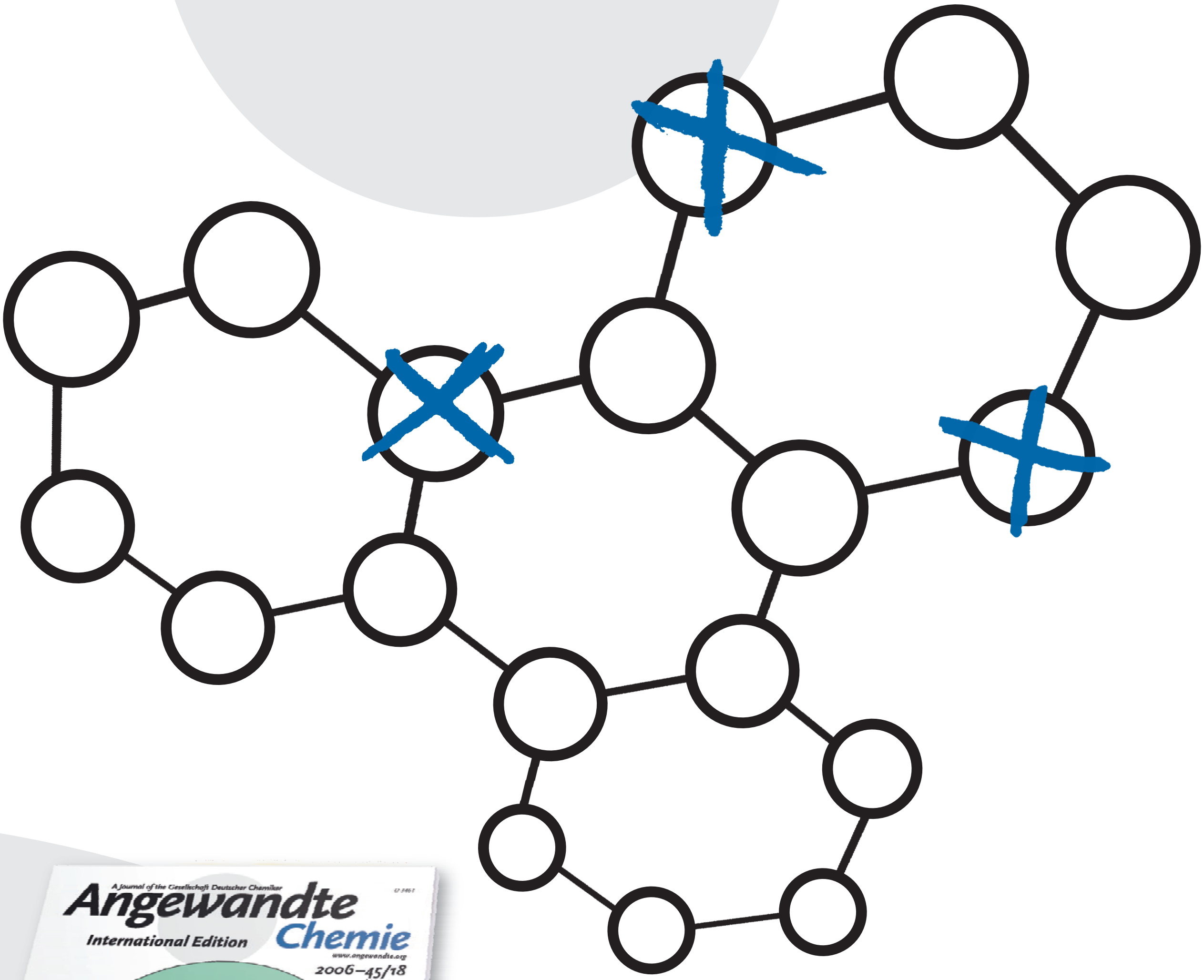
Catalyst Screening (2)

C. A. Müller, A. Pfaltz* **3363 – 3366**

Mass Spectrometric Screening of Chiral Catalysts by Monitoring the Back Reaction of Quasienantiomeric Products: Palladium-Catalyzed Allylic Substitution



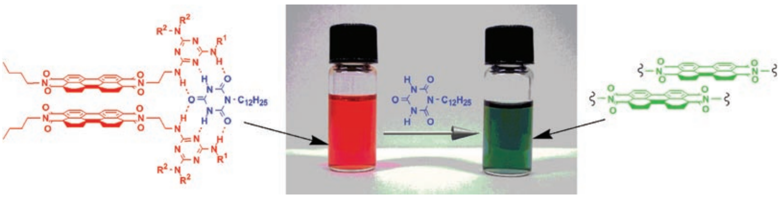
Back to basics: The principle of microscopic reversibility is the basis of a new screening method for chiral catalysts. Monitoring the back reaction of quasi-enantiomeric allylation products by ESI-MS reveals the intrinsic enantioselectivity of palladium catalysts in allylic substitution reactions (see scheme).



Dye Assemblies

S. Yagai,* T. Seki, T. Karatsu, A. Kitamura,
F. Würthner ________ **3367 – 3371**

Transformation from H- to J-Aggregated Perylene Bisimide Dyes by Complexation with Cyanurates

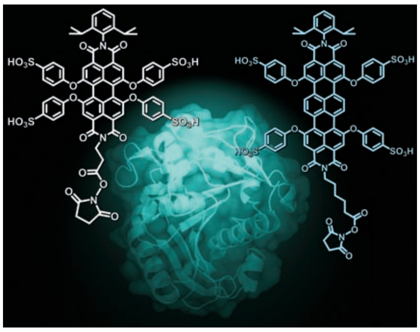


Me, myself, and dye: Core-unsubstituted perylene bisimide dyes bearing a melamine hydrogen-bonding unit link with cyanurates giving H- (red, see picture) and J-aggregates (green). In solution the aggregates can interconvert on thermal treatment or by changing the stoichiometry. In solid films the green to red color change occurs upon scratching the surface.

Ultrastable Dyes

K. Peneva, G. Mihov, F. Nolde, S. Rocha,
J. Hotta, K. Braeckmans, J. Hofkens,
H. Uji-i, A. Herrmann,
K. Müllen* ________ **3372 – 3375**

Water-Soluble Monofunctional Perylene and Terrylene Dyes: Powerful Labels for Single-Enzyme Tracking

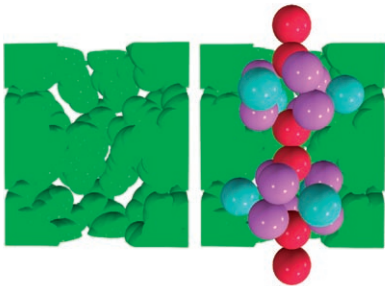


All in one: Exceptionally photostable, highly fluorescent, water-soluble, and monofunctional perylene and terrylene dyes bearing reactive groups for covalent attachment to biomolecules have been synthesized (see picture). Single-molecule enzyme tracking revealed that single enzymes could be visualized even on a substrate with fluorescent background.

Porous Coordination Polymers

H.-B. Cui, B. Zhou, L.-S. Long, Y. Okano,
H. Kobayashi,*
A. Kobayashi ________ **3376 – 3380**

A Porous Coordination-Polymer Crystal Containing One-Dimensional Water Chains Exhibits Guest-Induced Lattice Distortion and a Dielectric Anomaly

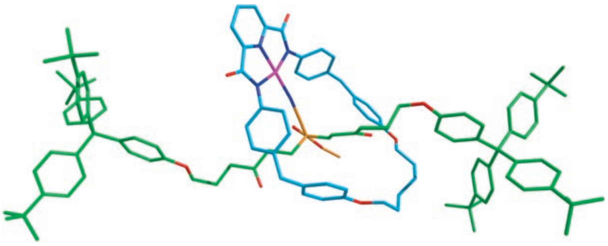


Ice one: A porous molecular crystal with guest water molecules in the channels—$[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ (see picture)—exhibits a distinct peak for the dielectric constant at 180 K ($\varepsilon_r \approx 150$) with the electric field parallel to the channel direction. This crystalline compound also shows a large enhancement of ε_r above 250 K and a characteristic antiferroelectric hysteresis coupled with a liquid–solid transition of the guest water molecules at around 350 K.

Molecular Shuttles

S. M. Goldup, D. A. Leigh,* P. J. Lusby,*
R. T. McBurney,
A. M. Z. Slawin ________ **3381 – 3384**

Active Template Synthesis of Rotaxanes and Molecular Shuttles with Switchable Dynamics by Four-Component Pd^{II}-Promoted Michael Additions



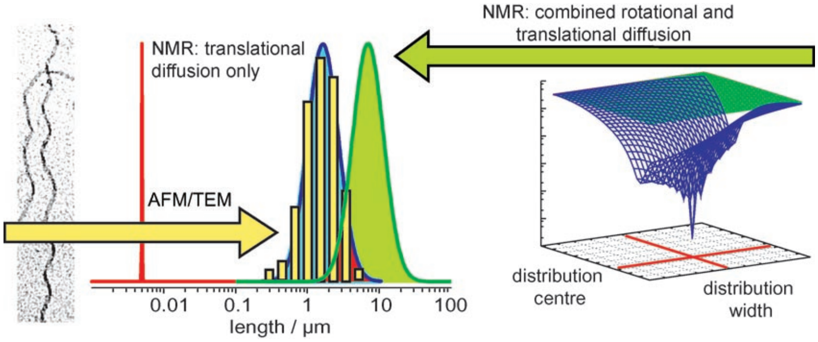
Taking the Michael: Rotaxanes (see structure) and molecular shuttles are prepared in up to 99% yield by successive Pd^{II}-promoted 1,4-conjugate additions in a one-pot four-component assembly process. This process represents the first active template reaction in which the template motif is retained in the interlocked product.

Contents

Amyloid Fibrils

A. J. Baldwin, S. J. Anthony-Cahill, T. P. J. Knowles, G. Lippens, J. Christodoulou, P. D. Barker, C. M. Dobson* ______ **3385 – 3387**

Measurement of Amyloid Fibril Length Distributions by Inclusion of Rotational Motion in Solution NMR Diffusion Measurements

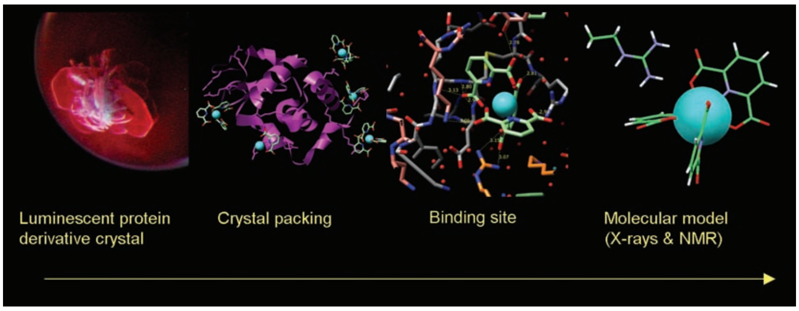


Telling fibrils: Diffusion data obtained by solution NMR spectroscopy from flexible regions of amyloid fibrils for both rotational and translation diffusion combined is of similar magnitude to that measured using AFM and TEM (see picture). Fibrils in solution are calculated to be somewhat longer on average than those deposited on surfaces for microscopy experiments, which can be partially attributed to the sensitivity of fibrils to fracture.

Protein Crystallography

G. Pompidor, A. D'Aléo, J. Vicat, L. Toupet, N. Giraud,* R. Kahn,* O. Maury* ______ **3388 – 3391**

Protein Crystallography through Supramolecular Interactions between a Lanthanide Complex and Arginine

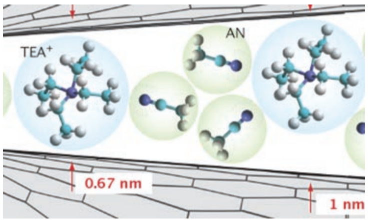


Crystal clear: Strong supramolecular interactions between tris(dipicolinate)-lanthanide complexes and arginine-like moieties have been evidenced by NMR chemical shift titration and X-ray diffraction analyses. Since the lanthanide atom is a strong anomalous scatterer, and the complex itself is luminescent, this interaction could be used as a powerful tool in the preparation of crystals of protein derivatives with high phasing power.

Ions in Subnanometer Pores

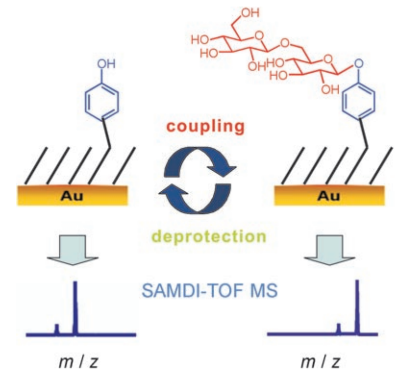
J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi* ______ **3392 – 3395**

Desolvation of Ions in Subnanometer Pores and Its Effect on Capacitance and Double-Layer Theory



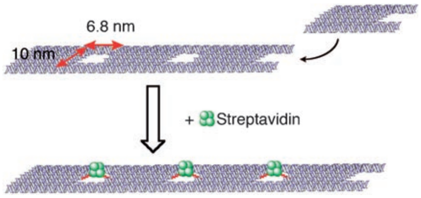
Recasting the double layer: The implicit assumption that electrochemical double layers are governed only by ion/electrode charge separation may be short-sighted and lead to a fundamental misunderstanding of the phenomenological response. This is shown in a study performed on ions confined in nanoporous carbon with pores smaller than the size of an ion surrounded by a solvation shell (see picture; TEA$^+$ = tetraethylammonium, AN = acetonitrile).

Microarrays



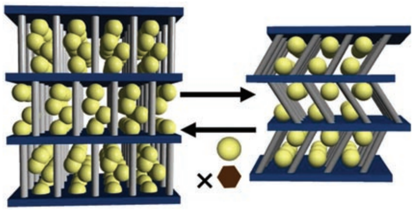
Sugar coated: A new strategy for solid-support oligosaccharide array synthesis and direct SAMDI-TOF (self-assembled monolayers for matrix-assisted laser desorption-ionization time-of-flight) mass spectrometry detection of the synthesis process is reported (see scheme). It incorporates an on-chip ligand array synthesis, a label-free detection method, and direct application to an enzymatic assay.

Protein Nanoarrays



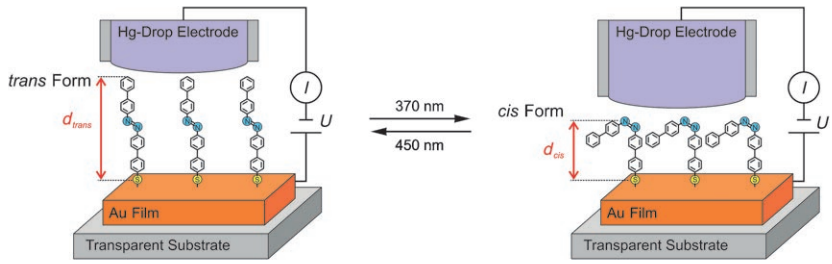
All’s well: A tapelike DNA scaffold with regularly arranged nanometer-scale wells is prepared by bundling nine DNA helices into U-shaped motifs (see picture). By attaching two biotin residues at two edges of each well, just one streptavidin tetramer is size-selectively captured to form a regularly oriented streptavidin nanoarray. The “anchored” tetramers nested in the wells are stable under repetitive AFM scanning.

Functional Frameworks



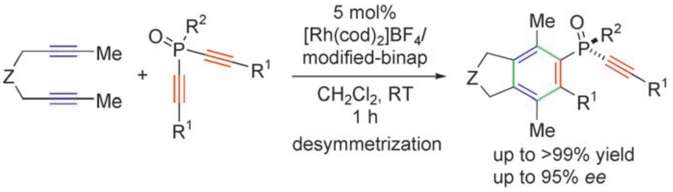
Like a sponge: Soft, three-dimensional, porous coordination frameworks $\{[Ln(tci)\cdot H_2O]\cdot 4H_2O\}_n$ (Ln = Ce, Gd; $tciH_3$ = tris(2-carboxyethyl)isocyanurate] were prepared from $Ln(NO_3)_3\cdot xH_2O$ and $tciH_3$. The flexible arms and secondary functional groups of the ligand allow the framework to show spongelike dynamic behavior such as selective and stepwise adsorption, associated with single crystal to single crystal structural transformation (see scheme).

Molecular Electronics



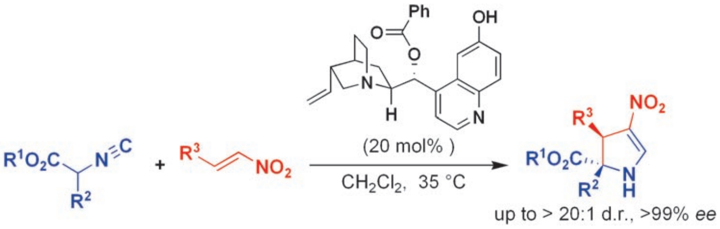
We have liftoff! Tightly packed self-assembled monolayers (SAMs) of ultrarigid conjugated azobenzenes incorporated into a Hg-based junction undergo reversible photoisomerization (see picture). The current–voltage curves indicate that the junction operates as a current photoswitch as result of the forces expressed by the SAMs, which act as a light-powered cargo lifter.

Asymmetric Catalysis



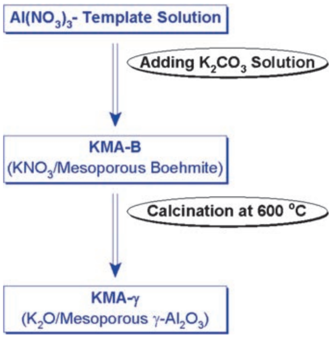
Two plus two plus two: An enantioselective synthesis of P-stereogenic alkynylphosphine oxides through a cationic rhodium(I)/modified-binap complex catalyzed [2+2+2] cycloaddition of symmetrical dialkynylphosphine oxides with 1,6-diynes was developed (see scheme; binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, Z = CH_2, O, or *N*-sulfonamide). Furthermore, this method permits the synthesis of a C_2-symmetric P-stereogenic bis(alkynylphosphine oxide).

Cycloaddition



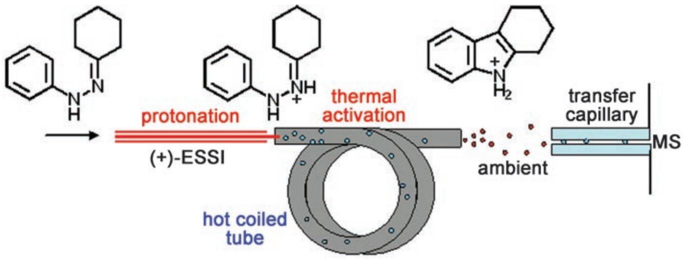
Closing the circle: The asymmetric [3+2] formal cycloaddition reaction of α-substituted isocyanoesters with nitroolefins is catalyzed by cinchona alkaloid derivatives to yield 2,3-dihydropyrroles with high diastereo- and enantioselectivities (see scheme).

Mesoporous Basic Catalysts



Basically super: Potassium-functionalized mesoporous γ-alumina solid superbases that have a high base strength (H_-) of 27.0, a well-expressed mesoporous structure, and which are efficient in the isomerization of 1-hexene are synthesized by a one-pot method. The success of this method can be ascribed to the flexible application of K_2CO_3 as a pH adjustor and close control of the calcination process (see picture).

Gas-Phase Chemistry

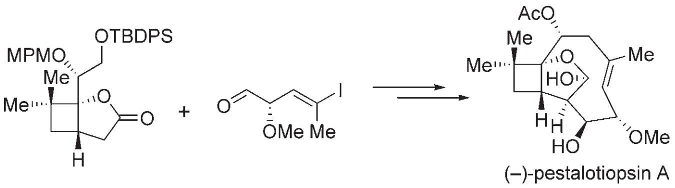


A mild-mannered process: Novel methodology, in which electrosonic spray ionization (ESSI, see schematic diagram) is used as the proton source, has been used to generate ionic reaction intermediates whose conversion into products can be promoted by atmospheric-pressure thermal activation. Reactions performed under these mild conditions include Borsche–Drechsel cyclization, Fischer indole synthesis, and pinacol rearrangement.

Natural Products

K. Takao, N. Hayakawa, R. Yamada, T. Yamaguchi, U. Morita, S. Kawasaki, K. Tadano* ______ 3426 – 3429

Total Synthesis of (−)-Pestalotiopsin A

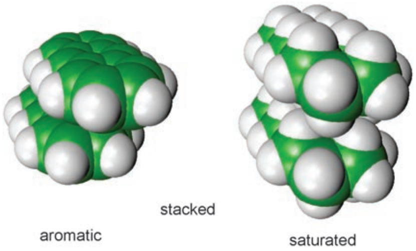


A big "+": The total synthesis of (−)-pestalotiopsin A has been achieved, thereby establishing the absolute stereochemistry of natural (+)-pestalotiopsin A (see scheme). The synthesis features a [2+2] cycloaddition, an aldol reaction, and an intramolecular Nozaki–Hiyama–Kishi reaction to construct the (*E*)-cyclononene ring.

Stacking Interactions

S. Grimme* ______ 3430 – 3434

Do Special Noncovalent π–π Stacking Interactions Really Exist?

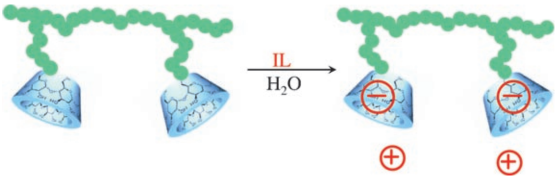


Van der Waals complexes are formed by almost all neutral molecules, which begs the question as to what is so special about the interaction between parallel stacks of arenes. The term π–π stacking interactions should primarily be used as a structural descriptor for unsaturated systems. Genuine π–π interactions are caused by specific electron correlations that are only at work for short intermolecular distances.

Cyclodextrin Complexes

S. Amajjahe, S. Choi, M. Munteanu, H. Ritter* ______ 3435 – 3437

Pseudopolyanions Based on Poly(NIPAAM-*co*-β-Cyclodextrin Methacrylate) and Ionic Liquids

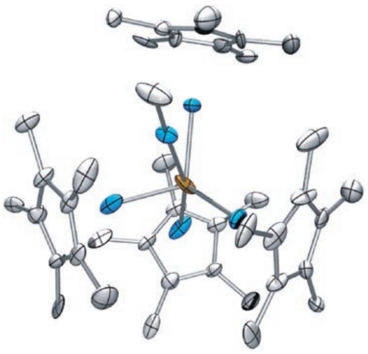


A fine host: Copolymers from methacrylated β-cyclodextrin and *N*-isopropylacrylamide form inclusion complexes with anions of ionic liquids (IL; see picture). Complex formation alters the solubility properties of the copolymer, leading to pseudopolyelectrolytes. Turbidity and dynamic light scattering measurements show that, depending on the anion, expansion or contraction of the polymer chain takes place owing to electrostatic effects.

Gallium Ligands

T. Cadenbach, C. Gemel, D. Zacher, R. A. Fischer* ______ 3438 – 3441

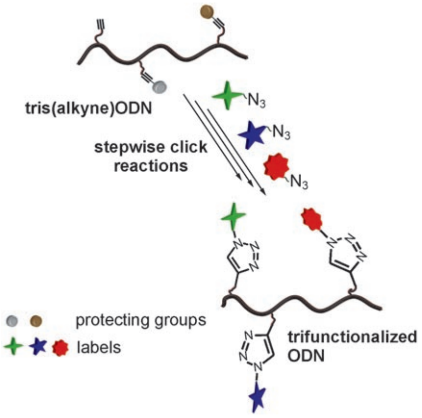
Methylgallium as a Terminal Ligand in $[(Cp^{*}Ga)_4Rh(GaCH_3)]^+$



The smallest possible gallium alkyl species, the otherwise elusive $GaCH_3$, has been generated by protolytic cleavage of Cp*H from a coordinated a {Ga(CH_3)Cp*} moiety and trapped in the title complex (see structure; C white, Ga blue, Rh brown). The counterintuitive shortening of the Rh–$GaCH_3$ bond upon adduct formation with pyridine illustrates that bond lengths alone are insufficient for the assignment of bond order.

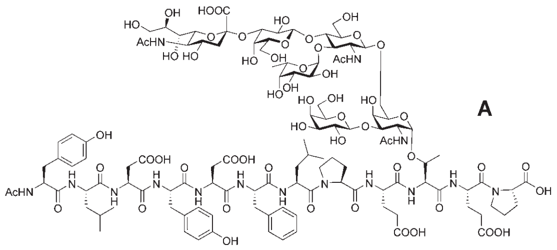
Contents

DNA Labeling



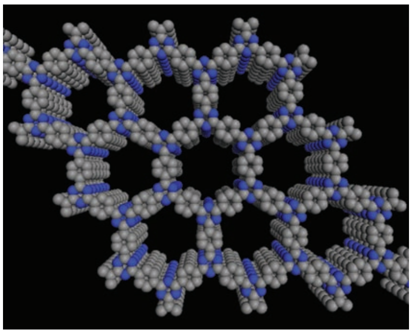
One, two, or three: An efficient, modular, and robust protocol has been developed for the multiple functionalization of DNA. It is based on the click reaction of azides with the alkyne substituents on an oligodeoxyribonucleotide (ODN), which was prepared by the standard phosphoramidite method (see scheme). ODNs can thus be labeled with two sensitive molecules, and even triple modification is possible.

Total Synthesis



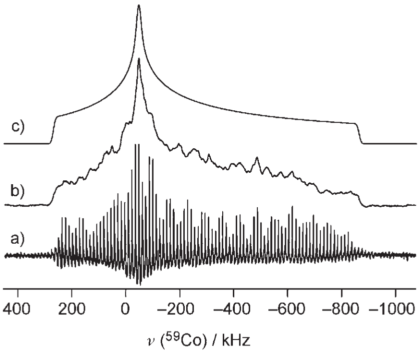
Block glycosylation of a T antigen–threonine conjugate with a sialyl Lewis^x trichloroacetimidate was used to synthesize a sialyl Lewis^x–T antigen–threonine building block. Selective protecting-group manipulations furnished a compound with exclusively acetyl-protected functions in the carbohydrate portion; this intermediate is sufficiently acid-stable that it is applicable to the solid-phase synthesis of binding site **A** of the P-selectin ligand PSGL-1.

Microporous Polymers



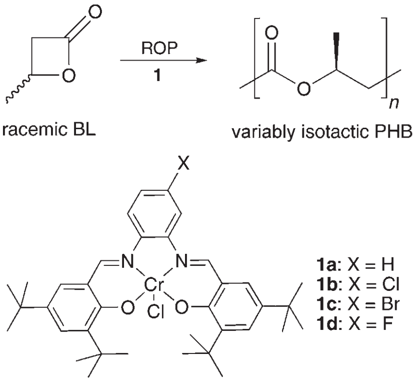
Ordered and amorphous microporous polytriazine networks have been obtained from the trimerization of nitriles in a $ZnCl_2$ melt at 400 °C (see structure of the polymer formed from 1,4-dicyanobenzene; C gray, N blue). The materials are high-performance polymers with very large surface areas and could find applications in gas storage, as sensors, or catalyst supports.

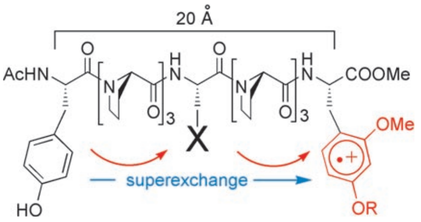
Ultrahigh-field NMR Spectroscopy



Highly suitable: The 1,2-polybutadiene catalyst $[Co(\eta^3:\eta^2\text{-}C_8H_{13})(\eta^4\text{-}C_4H_6)]$ (**1**) was isolated and structurally characterized by ultrahigh-field ^{59}Co solid-state NMR spectroscopy, demonstrating the utility of this technique. It can be applied to study the formation mechanism of syndiotactic 1,2-polybutadiene. The picture shows a QCPMG (a) and a quadrupole echo ^{59}Co NMR spectrum (b) as well as a simulated spectrum of **1** (c).

ROP artists: The ROP of racemic β-butyrolactone (BL) catalyzed by highly active chromium(III) salophen complexes **1** gives poly(hydroxybutyrate) (PHB) with high molecular weight and with isotacticities of 60–70%. The product is a biodegradable polymer material with mechanical properties that can be varied from crystalline to thermoplastic. DFT calculations indicate that the induction of stereochemical information occurs through the formation of dimeric cagelike structures.





It works both ways: The mechanism of electron transfer through peptides depends upon the side chain X located between the electron donor and the electron acceptor. Electron transfer occurs either by a slow single-step superexchange or by a two-step hopping process that is 20–30-times faster (see scheme). All intermediates in the hopping process could be observed simultaneously.

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

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