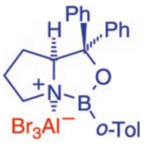
The following Communications have been judged by at least two referees to be "very important papers" and are published online at www.angewandte.org:

News

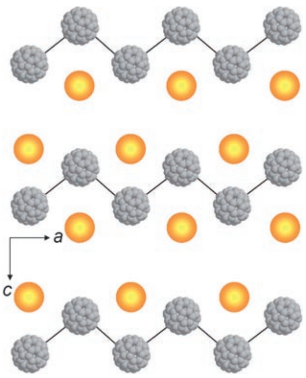
Books

Highlights



More and more applicable: The adduct of an oxazaborolidine and aluminum tribromide (see picture) turns out to be an efficient catalyst not only for enantioselective Diels–Alder reactions but now also for enantioselective [2+2] cycloadditions. The products are important enantiomerically pure building blocks for the synthesis of complex organic compounds.

Asymmetric Catalysis



Nuggets and buckyballs: Cationic small molecular gold clusters linked together by anions form ionic crystals. The cutting edge of such intercluster compounds involves combinations of Au_7 and Au_8 clusters and fullerides obtained by the reaction of KC_{60} with $[Au_8(PPh_3)_8](NO_3)_2$ in MeCN/THF. The picture shows a simplified view of the crystal structure of $[Au_7(PPh_3)_7]C_{60}\cdot THF$ in the direction of [010] (C gray, Au yellow).

Gold Clusters

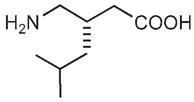
Contents

Essays

Drug Research

R. B. Silverman* — **3500 – 3504**

From Basic Science to Blockbuster Drug: The Discovery of Lyrica



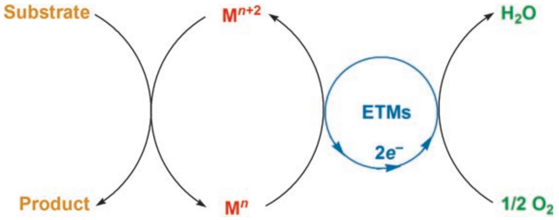
The anticonvulsant drug (*S*)-(+)-3-isobutyl-γ-aminobutyric acid ((*S*)-(+)-3-isobutyl-GABA, Lyrica; see structure) was developed from a study of fundamental science, which took an unexpected course. The activity of Lyrica was found to be unrelated to the originally anticipated activation of L-glutamic acid decarboxylase and the increase in the inhibitory neurotransmitter GABA; instead, it antagonizes a calcium ion channel, which inhibits the release of the excitatory neurotransmitter L-glutamate. The ultimate effect, however, is the same.

Reviews

Green Chemistry

J. Piera, J.-E. Bäckvall* — **3506 – 3523**

Catalytic Oxidation of Organic Substrates by Molecular Oxygen and Hydrogen Peroxide by Multistep Electron Transfer—A Biomimetic Approach

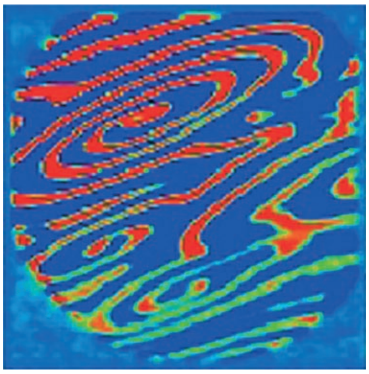


Going green: The use of environmentally friendly oxidation materials such as O_2 or H_2O_2 is a very important goal in organic chemistry, particularly for oxidations in industrial chemistry. The use of electron-transfer mediators (ETMs) to facilitate the use of these oxidants for the oxidation of organic substrates is described.

Heterogeneous Catalysis

G. Ertl* — **3524 – 3535**

Reactions at Surfaces: From Atoms to Complexity (Nobel Lecture)



The spatio–temporal formation of patterns on the surface during a chemical reaction is one phenomenon that can now be understood and modeled thanks to the Nobel Prize winning research on the course of heterogeneous catalysis. The picture shows a pattern formed by a feedback mechanism during the oxidation of CO. Reactions that have been illuminated by this work include the synthesis of ammonia and the purification of waste gases.

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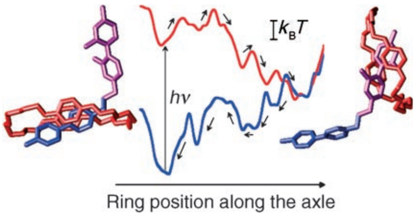
Molecular Machines

P. Raiteri,* G. Bussi, C. S. Cucinotta,
A. Credi,* J. F. Stoddart,
M. Parrinello ———— 3536 – 3539

Unravelling the Shuttling Mechanism in a Photoswitchable Multicomponent Bistable Rotaxane

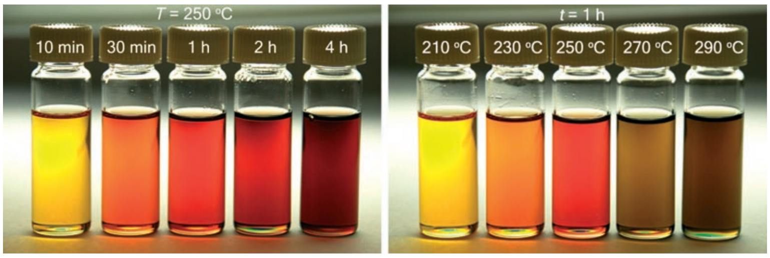


On the move: A computational investigation of the photo-triggered shuttling of a multicomponent bistable rotaxane in solution has shown that decomplexation of the counterions from the positively charged stations may be the efficiency-limiting step of the nanomachine. The picture shows the free-energy profile as a function of the ring position for the oxidized (ground) state (blue) and the reduced state (red) generated by photoexcitation.

Nanocrystal Synthesis

Z. Liu, A. Kumbhar, D. Xu, J. Zhang,
Z. Sun, J. Fang* ———— 3540 – 3542

Coreduction Colloidal Synthesis of III–V Nanocrystals: The Case of InP

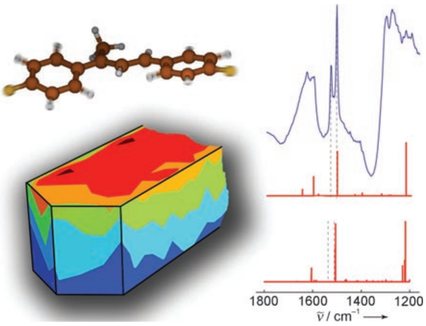


Finding the little InP particles: A coreduction method allows high-quality colloidal InP nanocrystals to be synthesized by using PCl_3 as the phosphorus source and superhydride as the reducing agent. Etching the as-grown nanocrystals with HF leads to high-efficiency photoluminescence. The synthetic strategy can be extended to the preparation of other III–V nanocrystals with the corresponding pnicogen halides.

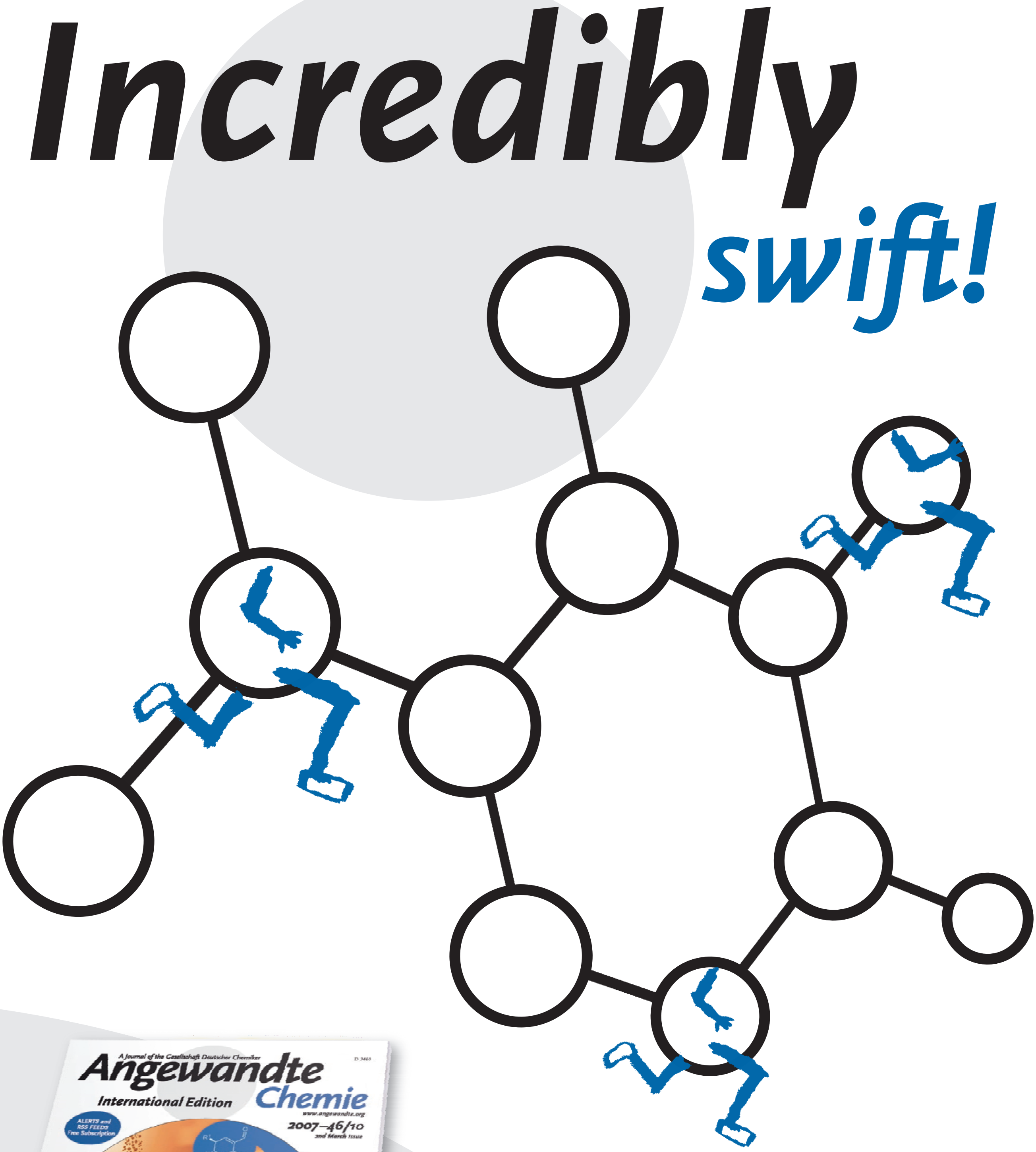
Heterogeneous Catalysis

E. Stavitski, M. H. F. Kox, I. Swart,
F. M. F. de Groot,
B. M. Weckhuysen* ———— 3543 – 3547

In Situ Synchrotron-Based IR Microspectroscopy To Study Catalytic Reactions in Zeolite Crystals



CSI: Carbocation species identification: The nonhomogeneous distribution of the reaction products of styrene oligomerization on large ZSM-5 crystals was mapped with in situ IR microspectroscopy. Diffraction-limited spatial resolution was achieved with synchrotron light. IR spectra for possible reaction products were calculated with DFT/B3LYP; by comparison with experimental results carbocationic reaction species formed in zeolite channels could be singled out.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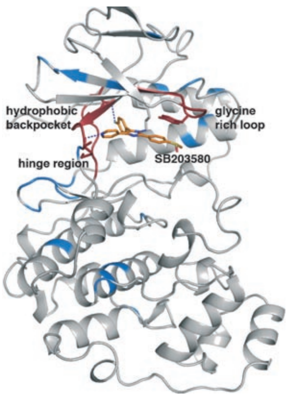
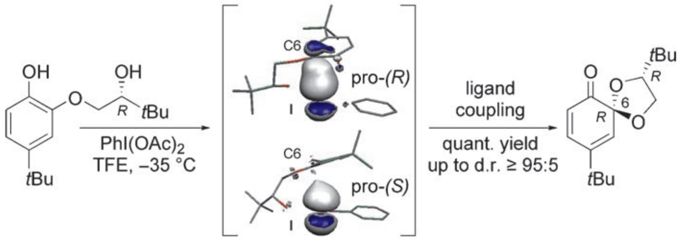
Enzyme–Inhibitor Complex



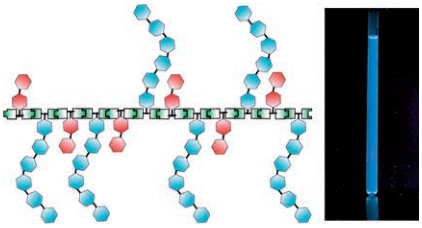
Added flexibility: NMR data for p38α MAP kinase in a complex with the SB203580 inhibitor show intermediate exchange of residues in the binding pocket (affected residues marked in blue and red on the structure), which indicates increased flexibility compared to that of the unbound protein. Based on residual dipolar couplings, the overall solution structure of p38α is very similar to the crystal structure. Thus, the increased mobility in solution is an effect of the inhibitor that is not reflected in the crystal structure.

Asymmetric Synthesis



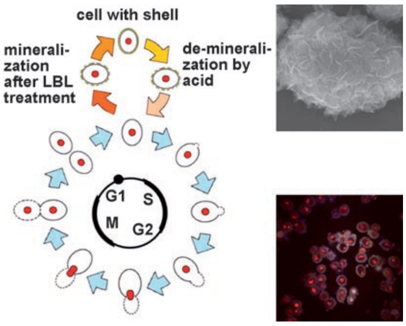
Versatile chiral substrates for asymmetric synthesis are formed through the spiroketalization of phenols with a chiral substituted ethanol unit O-tethered to the *ortho* position upon treatment with PhI(OAc)$_2$ (see example; TFE = 2,2,2-trifluoroethanol). Intermediates with a six-membered iodine(III)-containing ring (the natural localized molecular orbitals associated with the I–C6 bond are shown) undergo ligand coupling to give the spiroketals.

Dynamic Biopolymers



A change in the constitution: Dynamic glycopolymers based on a poly(acylhydrazone) main chain bearing lateral oligosaccharide groups have been obtained and their structure has been characterized as a bottlebrush type (see picture) by cryo-TEM and small-angle neutron scattering studies. They have remarkable fluorescence with emission wavelengths which are tunable by exchange/incorporation of components which modify the polymer constitution.

Cells with Mineral Shells



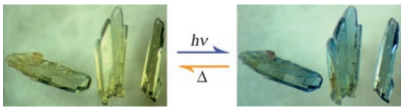
Inspired by eggshells in nature, living yeast cells were conferred with an artificial mineral coat by using a combination of the layer-by-layer (LBL) treatment with functional polymers and in situ biomimetic mineralization. The resulting hard inorganic shells have a tremendous effect on the storage, protection, delivery, and modification of the cells.

Photochromic Materials

M.-S. Wang, G.-C. Guo,* W.-Q. Zou,
W.-W. Zhou, Z.-J. Zhang, G. Xu,
J.-S. Huang ________ **3565 – 3567**

Photochromism of a 3D Cd^{II} Complex with Two Captured Ligand Isomers Generated In Situ from the Same Precursor

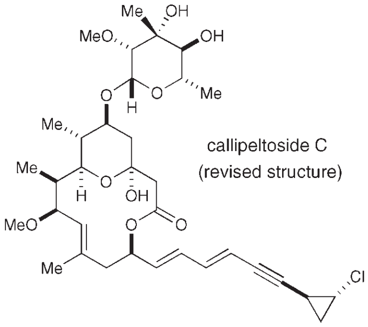
Color on command: A hydrothermally synthesized 3D Cd^{II} complex with an unusual $4^26^68^2$ topology consisting of cadmium centers as five-connected nodes and two in situ generated isomers from the same precursor as linkers was found to exhibit reversible redox photochromic behavior.



Natural Products

J. Carpenter, A. B. Northrup, dM. Chung,
J. J. M. Wiener, S.-G. Kim,
D. W. C. MacMillan* ________ **3568 – 3572**

Total Synthesis and Structural Revision of Callipeltoside C

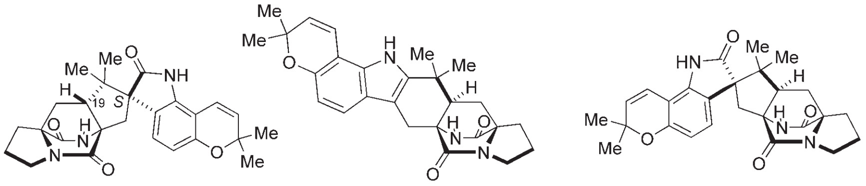


Look again: Highlights of the 20-step synthesis of callipeltoside C include the proline-catalyzed direct aldol reaction, enantioselective α-oxyamination reaction, and rapid access to the carbohydrate framework using a de novo synthesis protocol. Based on this work the previously assigned absolute configuration of the pendent 2-*O*-methylevalose unit has been revised.

Structure Elucidation

T. J. Greshock, A. W. Grubbs, P. Jiao,
D. T. Wicklow, J. B. Gloer,
R. M. Williams* ________ **3573 – 3577**

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



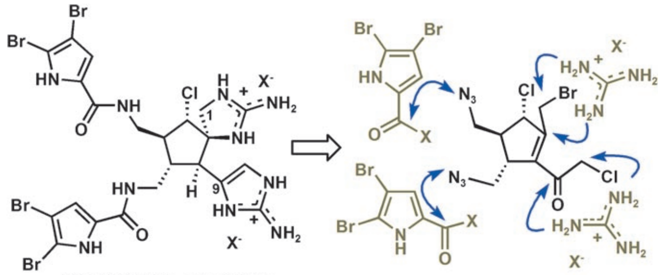
versicolamide B *ent*-stephacidin A *ent*-notoamide B

Stereochemically unique: A new prenylated indole alkaloid, (+)-versicolamide B, has been isolated from cultures of *Aspergillus versicolor* NRRL 35600. The structure has been assigned by 2D NMR experiments, and confirmed by a biomimetic total synthesis. Versicolamide B is the first member of the paraherquamide/stephacidin family of alkaloids found to possess the *anti* relative stereochemistry at C19. *ent*-Stephacidin A and *ent*-notoamide B were also isolated for the first time.

Natural Products

J. Yamaguchi, I. B. Seiple, I. S. Young,
D. P. O'Malley, M. Maue,
P. S. Baran* ________ **3578 – 3580**

Synthesis of 1,9-Dideoxy-pre-axinellamine



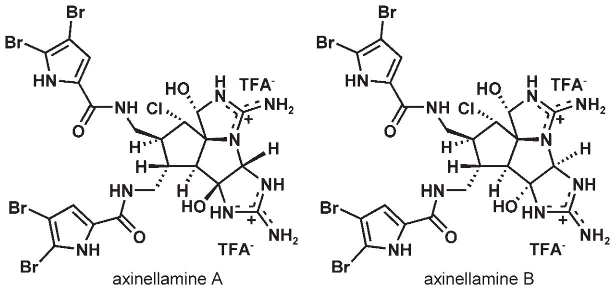
1,9-dideoxy-pre-axinellamine

Within reach: A 19-step route to 1,9-dideoxy-pre-axinellamine has been designed and executed. This key compound represents a hypothetical precursor to an entire family of alkaloid natural products.

Natural Products

D. P. O'Malley, J. Yamaguchi, I. S. Young,
I. B. Seiple, P. S. Baran* ___ **3581 – 3583**

Total Synthesis of (±)-Axinellamines A and B



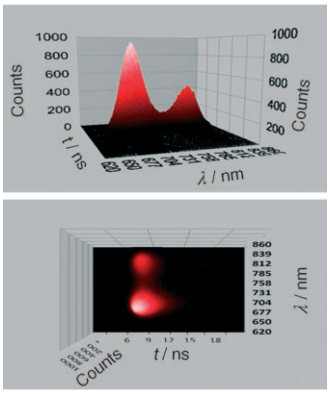
Chemoselective by design: The first total synthesis of members of the axinellamine/palau'amine/massadine class of pyrrole–imidazole alkaloids features unconventional transformations on completely unprotected polyamino and hydroxylated substrates and a new method for chemoselective oxidations in such settings.

Dichromic Molecules

Z. Zhang, M. Y. Berezin, J. L. F. Kao,
A. d'Avignon, M. Bai,
S. Achilefu* ___ **3584 – 3587**

Near-Infrared Dichromic Fluorescent Carbocyanine Molecules

Bilingual fluorescent molecules: An array of asymmetric carbocyanines capable of dual fluorescence emissions in the near-infrared region is described (see image). The fluorescent molecules are robust in different pH and solvents. Additionally, each fluorescence peak possesses a distinct fluorescence lifetime. These properties are retained after conjugation of the dyes with small bioactive peptides.



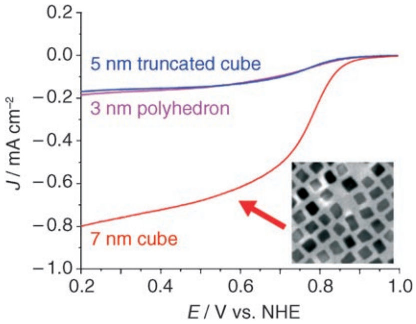
O_2 Reduction

VIP

C. Wang, H. Daimon, T. Onodera, T. Koda,
S. Sun* ___ **3588 – 3591**

A General Approach to the Size- and Shape-Controlled Synthesis of Platinum Nanoparticles and Their Catalytic Reduction of Oxygen

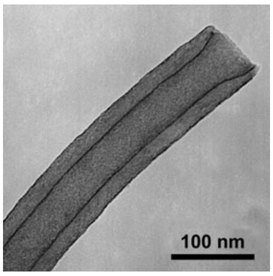
Catalytic cobblestones: Monodisperse platinum nanoparticles were prepared with controlled sizes (3–7 nm) and shapes (polyhedron, truncated cube, or cube). The cubic nanoparticles are a much more active cathode catalyst for the oxygen reduction reaction: the current density J from 7 nm cubes is four times that of the other shapes (see picture), indicating great potential for fuel cell applications.



Thin Films

E. Rauwel, G. Clavel, M.-G. Willinger,
P. Rauwel, N. Pinna* ___ **3592 – 3595**

Non-Aqueous Routes to Metal Oxide Thin Films by Atomic Layer Deposition



Controlled growth: A non-aqueous approach inspired from sol–gel chemistry and adapted to the formation of metal oxide thin films by means of atomic layer deposition is presented. The process is based on the reaction of a carboxylic acid with an alkoxide. Growth of metal oxides is achieved at temperatures as low as 50 °C on various supports including carbon nanotubes (see TEM picture). The as-grown films show excellent uniformity and possess good dielectric properties.

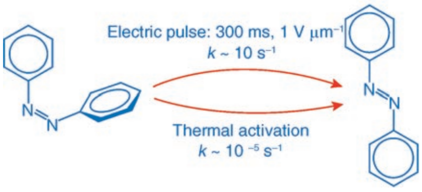
Contents

Electroisomerization

X. Tong, M. Pelletier, A. Lasia,
Y. Zhao* ________ **3596 – 3599**

Fast *Cis–Trans* Isomerization of an Azobenzene Derivative in Liquids and Liquid Crystals under a Low Electric Field

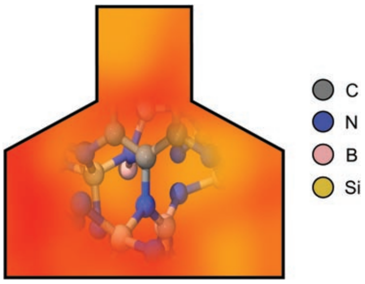
A dramatically increased rate of *cis–trans* isomerization of an azobenzene derivative dissolved in liquids (e.g. benzonitrile) and liquid crystals relative to the corresponding thermally activated process can be achieved by applying a low static electric field (see picture) without adding any supporting electrolyte. This electric-field-induced isomerization can affect the electrooptical behavior of azobenzene-doped liquid crystals.



Nitridic Ceramics

Y. H. Sehlleier, A. Verhoeven,
M. Jansen* ________ **3600 – 3602**

Observation of Direct Bonds between Carbon and Nitrogen in Si-B-N-C Ceramic after Pyrolysis at 1400 °C

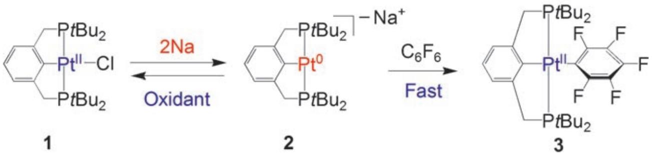


An unlikely couple: Carbon and nitrogen usually go separate ways above 600 °C, but in a precursor-derived high-performance SiBNC ceramic pyrolyzed at 1400 °C the presence of carbon–nitrogen bonds was demonstrated by using various double-resonance solid-state NMR techniques in combination with a novel isotope labeling scheme.

Coordination Chemistry

L. Schwartsburd, R. Cohen,
L. Konstantinovski,
D. Milstein* ________ **3603 – 3606**

A Pincer-Type Anionic Platinum(0) Complex



Holding a Pt^0 anion in a pincer: Reduction of the pincer-type Pt^{II} complex **1** results in the formation of the thermally stable anionic Pt^0 complex **2**. This complex adopts a T-shaped structure and exhibits diverse reactivity, including efficient electron-transfer processes in which **2** is re-oxidized quantitatively to Pt^{II}. Protonation of **2** with water gives a Pt^{II} hydride complex, and C–F activation under mild conditions leads to **3** (see scheme).

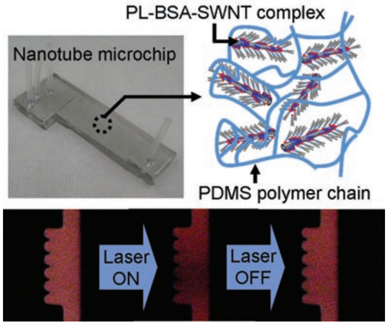
Nitrile Hydration

A. Goto, K. Endo, S. Saito* **3607 – 3609**

Rh^I-Catalyzed Hydration of Organonitriles under Ambient Conditions

$$\mathrm{RCN} + \mathrm{H_2O} \xrightarrow[\substack{i\mathrm{PrOH} \\ 4\text{–}25\ ^\circ\mathrm{C}}]{\text{Rh catalyst}} \mathrm{RCONH_2} \qquad \begin{array}{l}\text{93–99\% yield}\\ \text{21 examples}\end{array}$$

New scoop on scope and selectivity: The hydration of organonitriles catalyzed by a Rh^I(OMe) species under nearly pH-neutral and ambient conditions (25 °C, 1 atm) is chemoselective and high-yielding (93 to 99 %), has a broad substrate scope, and may thus be complementary to enzymatic hydration methods for the introduction of a terminal amido group (CONH$_2$) onto a carbon chain.



Rapid temperature control: A phospholipid–bovine serum albumin functionalized single-walled carbon nanotube complex (PL–BSA–SWNT) was found to be readily dispersible in poly(dimethylsiloxane) (PDMS). A photoinduced PDMS microchip encapsulating this complex is capable of achieving ultrarapid control of the temperature of a solution contained in one of its microchannels (see image).

Nanotube–Polymer Composites

E. Miyako,* H. Nagata, K. Hirano, T. Hirotsu ——— **3610–3613**

Carbon Nanotube–Polymer Composite for Light-Driven Microthermal Control

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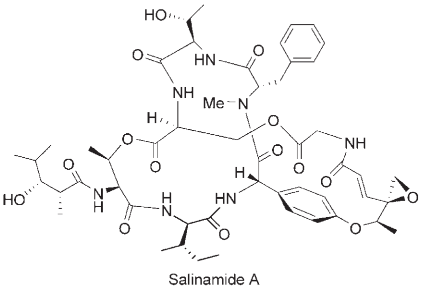
It's swell! The first total synthesis of potent anti-inflammatory agent salinamide A was achieved. This synthesis features a concise elaboration of the phenylglycine-derived epoxide fragment and the identification of two possible macrolactamization sites (see scheme).



Natural Products

L. Tan, D. Ma* ——— **3614–3617**

Total Synthesis of Salinamide A: A Potent Anti-Inflammatory Bicyclic Depsipeptide

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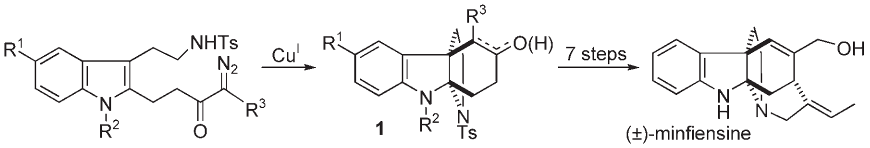

Cascading into (±)-minfiensine: An efficient method was developed for the assembly of tetracyclic skeleton **1** by a three-step, one-pot cascade reaction including cyclopropanation, ring opening, and ring closure (see scheme; Ts = *p*-toluenesulfonyl). The concise total synthesis of the (±)-minfiensine was completed in about a 4% overall yield.

Natural Products

L. Shen, M. Zhang, Y. Wu, Y. Qin* ——— **3618–3621**

Efficient Assembly of an Indole Alkaloid Skeleton by Cyclopropanation: Concise Total Synthesis of (±)-Minfiensine

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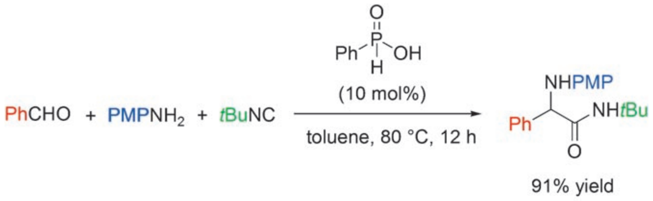


Perfect atom economy characterizes a novel catalytic three-component Ugi reaction (see example). Different α-amino amides are formed in good yields from aldehydes, primary amines, and isocyanides in the presence of phenyl phosphinic acid as the catalyst. The products will be useful for the synthesis of α-amino acid derivatives and in diversity-oriented synthesis.

Multicomponent Reactions

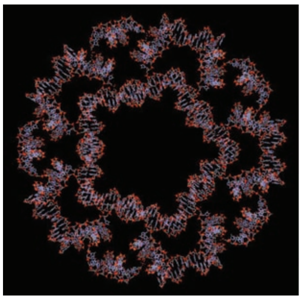
S. C. Pan, B. List* ——— **3622–3625**

Catalytic Three-Component Ugi Reaction

DNA Nanostructures

J. Zimmermann, M. P. J. Cebulla,
S. Mönninghoff,
G. von Kiedrowski* ________ **3626 – 3630**

Self-Assembly of a DNA Dodecahedron from 20 Trisoligonucleotides with C_{3h} Linkers

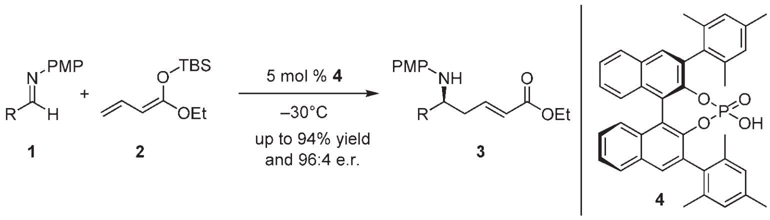


Can 20 trisoligonucleotides with 20×3 individual sequences be programmed to self-assemble into a DNA dodecahedron? The answer is yes if one starts from a new generation of trisoligonucleotides based on C_{3h}-symmetric linkers with proper flexibility. The resulting dodecahedron has C_1 symmetry and may facilitate the construction of multimodular scaffolds in the future.

Asymmetric Catalysis

M. Sickert, C. Schneider* __ **3631 – 3634**

The Enantioselective, Brønsted Acid Catalyzed, Vinylogous Mannich Reaction

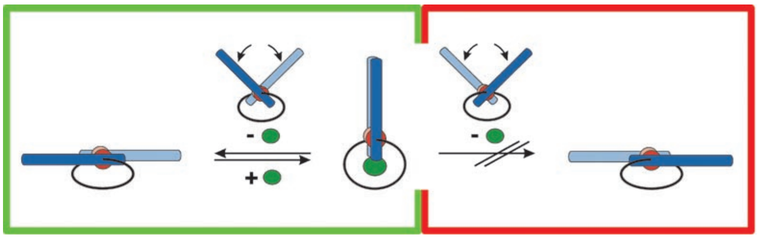


Chiral phosphoric acid 4 catalyzes enantioselectively the highly γ-regioselective addition of a silyl dienolate **2** to imines **1** in good yields and furnishes α,β-unsaturated δ-amino carboxylic esters **3** in one step. The reaction may also be carried out as a direct three-component coupling (PMP = *para*-methoxyphenyl; TBS = *tert*-butyldimethylsilyl).

Molecular Machines

G. Haberhauer* __________ **3635 – 3638**

Control of Planar Chirality: The Construction of a Copper-Ion-Controlled Chiral Molecular Hinge



An open-and-closed case: When a chiral clamp is attached to a molecular hinge the open–close motion induced by coordination to a metal ion becomes unidirectional (see scheme). The large change in amplitude caused by the unidirectional rotation and the relatively simple preparation of the hinge open up the possibility of using this concept for even more-complex molecular machines.

Ionic Liquids

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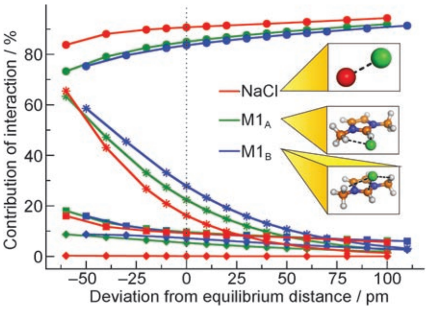
Intermolecular Forces in an Ionic Liquid ([Mmim][Cl]) versus Those in a Typical Salt (NaCl)



A subtle difference: In ionic liquids the "weak" dispersion forces have a significant impact on the shape of the potential energy surface, which results in a shallow profile when all of the contributions are considered. Such findings are commonly accepted to determine the liquid state.

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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