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:

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

S. M. Lang, T. M. Bernhardt, R. N. Barnett, U. Landman**
Methane Activation and Catalytic Ethylene Formation on Free Au$_2^+$

G. Alcaraz, L. Vendier, E. Clot, S. Sabo-Etienne**
Ruthenium Bis(σ-B–H) Aminoborane Complexes from Dehydrogenation of Amine–Boranes: Trapping of H$_2$B–NH$_2$

K. Meindl, T. Schmiederer, K. Schneider, A. Reicke, D. Butz, S. Keller, H. Gühring, L. Vértesy, J. Wink, H. Hoffmann, M. Brönstrup, G. M. Sheldrick, R. D Süssmuth**
Labyrinthopeptins: A New Class of Carbacyclic Lantibiotics

*T. Mitsudome, K. Mizumoto, T. Mizugaki, K. Jitsukawa, K. Kaneda**
Wacker-Type Oxidation Using a PdCl$_2$–DMA Catalyst System under Copper-Free Conditions

*A. Pal, M. Bérubé, D. G. Hall**
Design, Synthesis, and Screening of a Library of Peptidyl Bisboroxoles as Low Molecular Weight Receptors for Complex Oligosaccharides in Water: Identification of a Receptor for the Tumor Marker TF-Antigen

*R. Kaminker, M. Lahav, L. Motiei, M. Vartanian, R. Popovitz-Biro, M. A. Iron, M. E. van der Boom**
Molecular Structure–Function Relations on the Optical Properties and Dimensions of Gold Nanoparticle Assemblies

Y.-Z. You, Z.-Q. Yu, M.-M. Cui, C.-Y. Hong**
Preparation of Photoluminescent Nanorings with Controllable Bioreducibility and Stimuli Responsiveness

D.-S. Ahn, S.-Y. Kim, G.-I. Lim, S. Lee, Y. S. Choi,* S. K. Kim**
Mode-Dependent Fano Resonances in the Predissociation of Diazirine in the S$_1$ State

Author Profile

"The most exciting thing about my research is observing unexpected but significantly important results. The biggest problem that scientists face is how to balance curiosity-driven research and applied research …"
This and more about Dawei Ma can be found on page 666.

News

M. J. Krische

M. Terada

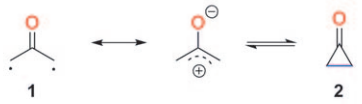
G. M. Whitesides

Books

Contents

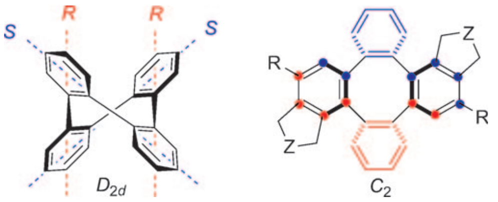
Highlights

Oxyallyl Diradical



A molecule on a slippery slope: Lineberger et al. finally managed to observe the oxyallyl diradical **1** using negative ion photoelectron spectroscopy. The singlet state of the oxyallyl diradical is lower in energy than the triplet and corresponds to the transition state for ring closure to cyclopropanone **2**.

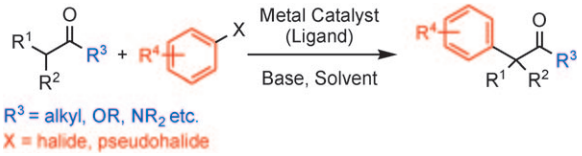
Chiral Tetraphenylenes



Intriguing scaffolds: Tetraphenylenes with symmetry-breaking substitution have chiral π systems and extraordinarily high barriers for racemization. Their applications as building blocks for chiral materials and as ligands in asymmetric synthesis are hindered by the difficulty in obtaining the chiral tetraphenylene core. Rhodium-catalyzed [2+2+2] cycloadditions of triynes provide an effective alternative synthesis.

Reviews

α-Arylation



A good alternative: The developments in the field of metal-catalyzed α-arylation of carbonyl compounds, such as ketones, esters, amides, dicarbonyl compounds, and nitriles are summarized and dicussed in this Review (see scheme). The focus is primarily on how the substrate range can be broadened through variation of the reaction conditions such as ligands, precatalysts, bases, and solvents.

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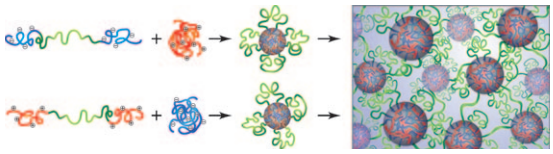
Communications

Gels

M. Lemmers,* J. Sprakel, I. K. Voets,
J. van der Gucht,
M. A. Cohen Stuart ______ 708–711

Multiresponsive Reversible Gels Based on Charge-Driven Assembly



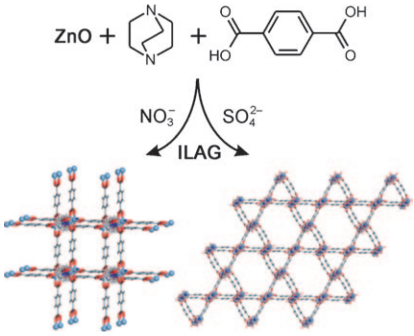
Linked in? Coassembly of an ABA triblock copolymer with charged end blocks and an oppositely charged polyelectrolyte yields gels that respond to changes in concentration, temperature, ionic strength, pH value, and charge composition. Above the critical gel concentration, the triblock copolymers bridge micelles, forming a sample-spanning transient network of interconnected micelles.

Mechanochemistry

T. Friščić,* D. G. Reid, I. Halasz,
R. S. Stein, R. E. Dinnebier,
M. J. Duer ______ 712–715

Ion- and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal–Organic Frameworks Reveals Salt Inclusion and Anion Templating

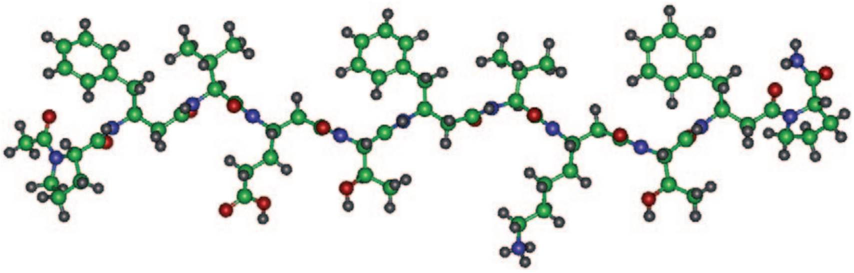
Just a pinch of salt: Small amounts of salts accelerate and direct the mechanochemical construction of metal–organic frameworks (MOFs) from a metal oxide (see scheme; ILAG = ion- and liquid-assisted grinding). The resulting rapid and room-temperature synthesis demonstrates the ability to control mechanosynthesis of metal–organic compounds by templating, as well as the ability to use mechanochemistry to include ionic guests within neutral MOFs.



Self-Assembly

S. Segman, M. R. Lee, V. Vaiser,
S. H. Gellman,* H. Rapaport* 716–719

Highly Stable Pleated-Sheet Secondary Structure in Assemblies of Amphiphilic α/β-Peptides at the Air–Water Interface

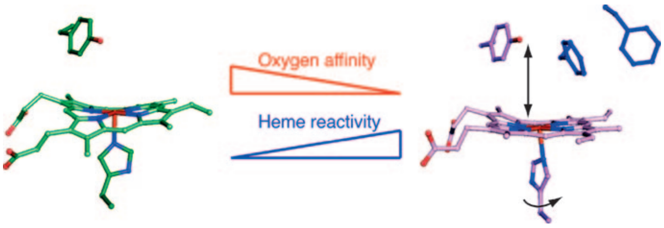


A nice gathering at the interface: The de novo design and characterization of amphiphilic α/β-peptides, which form ordered two-dimensional assemblies at the air–water interface composed of oligomers in pleated conformation similar to β-sheets of α-peptides, is reported. The positioning of ionic side chains along the backbone can exert a profound effect on the propensity to self-assemble.

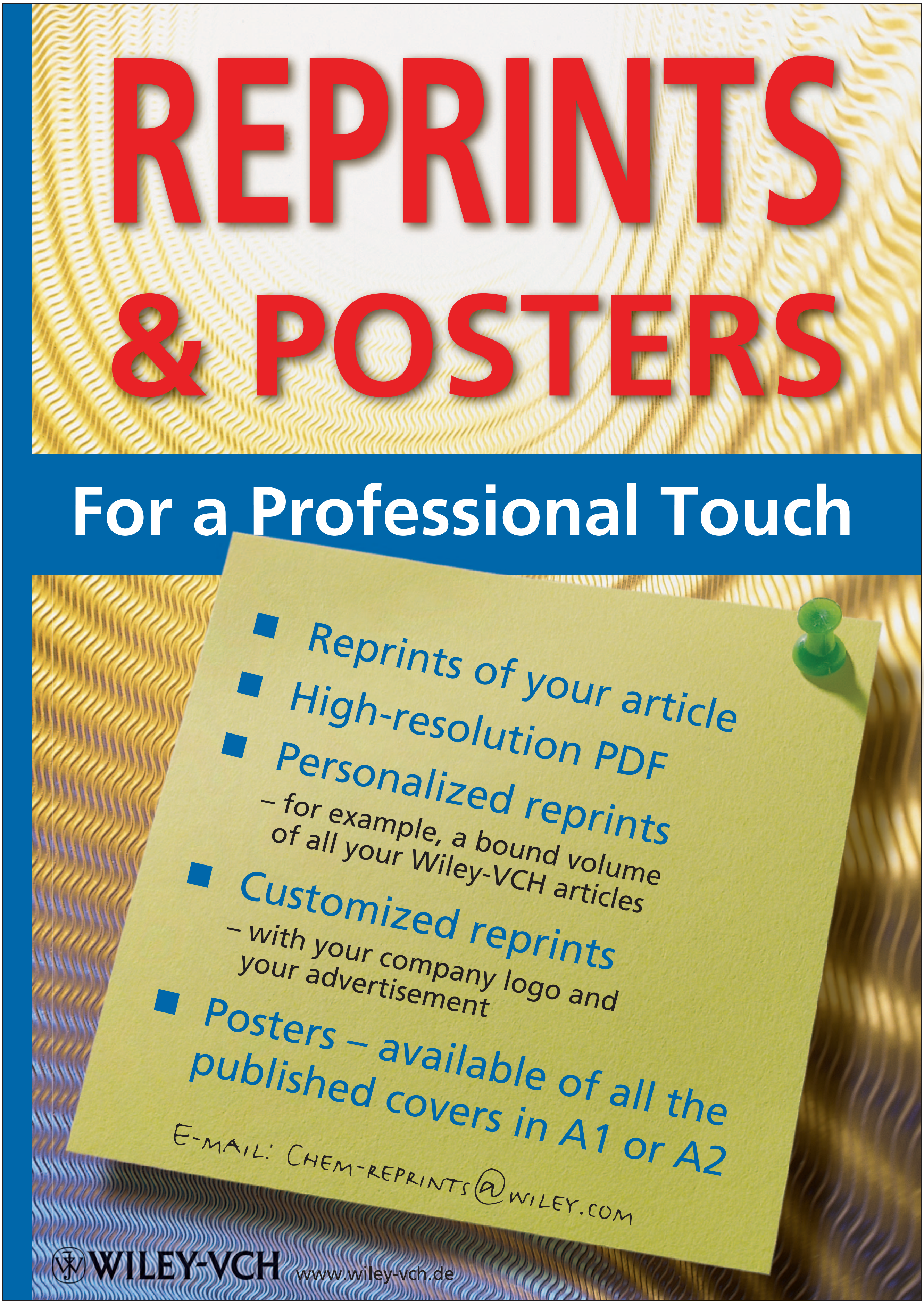
Heme Proteins

E. E. Weinert, L. Plate, C. A. Whited,
C. Olea, Jr., M. A. Marletta* ___ 720–723

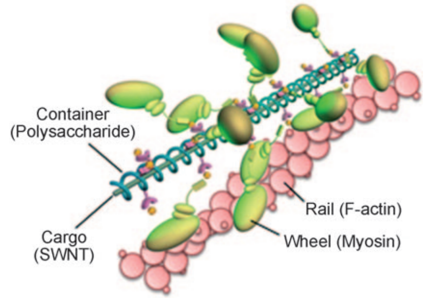
Determinants of Ligand Affinity and Heme Reactivity in H-NOX Domains



O_2 balks at extra bulk: The introduction of distal-pocket bulk into the *Thermoanaerobacter tengcongensis* H-NOX (heme nitric oxide/oxygen) domain caused key changes in the protein structure. Rearrangement of the heme pocket resulted in dramatic differences in O_2-binding kinetics and heme reactivity (see picture).



Molecular Transportation



A valuable cargo: Polysaccharides (β-1,3-glucans) act as a host compound to various nanomaterial cargoes such as single-walled carbon nanotubes. The cargo packed in the host container is transported on the rail (F-actin) by wheels and a molecular motor (myosin) attached to the container (see picture). This artificial system is inspired by a container transportation system based on the motion of vesicles in biological cells.

Y. Tsuchiya, T. Komori, M. Hirano, T. Shiraki, A. Kakugo, T. Ide, J.-P. Gong, S. Yamada, T. Yanagida, S. Shinkai* ______ **724 – 727**

A Polysaccharide-Based Container Transportation System Powered by Molecular Motors

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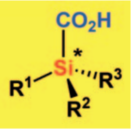
Chiral Organosilanes



Sila analogues: The first asymmetric synthesis of silacarboxylic acids with a stereogenic center at the silicon atom has been achieved from chiral nonracemic silanols, without loss of optical purity. Silacarboxylic acids can be converted into their corresponding esters using a Mitsunobu-type reaction.

K. Igawa, N. Kokan, K. Tomooka* ______ **728 – 731**

Asymmetric Synthesis of Chiral Silacarboxylic Acids and Their Ester Derivatives

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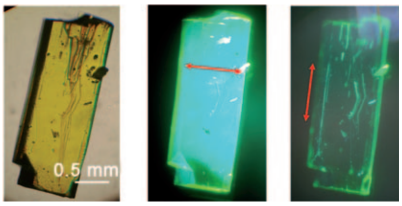
Solid-State Fluorescence

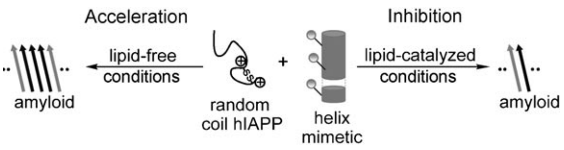


Low in, high out: Single crystals of a thiomethyl-terminated oligo(phenylene vinylene) exhibit unique photonic properties including strong anisotropic solid-state fluorescence (see depicted optical and fluorescence micrographs; arrows: polarization direction), high quantum yield, large two-photon absorption cross section, and stimulated emission, which make it a candidate for opto-electronic applications such as upconversion lasing.

F. Gao, Q. Liao, Z. Z. Xu, Y. H. Yue, Q. Wang, H. L. Zhang,* H. B. Fu* ______ **732 – 735**

Strong Two-Photon Excited Fluorescence and Stimulated Emission from an Organic Single Crystal of an Oligo(Phenylene Vinylene)

Proteomimetics



Split personality: A series of oligoamide-based helix mimetics bind to a complementary helical motif in Islet amyloid polypeptide (IAPP), a protein implicated in the pathology of type II diabetes. These compounds accelerated IAPP amyloid formation under lipid-free conditions, but inhibited it under lipid-catalyzed conditions. hIAPP = human IAPP.

I. Saraogi, J. A. Hebda, J. Becerril, L. A. Estroff, A. D. Miranker,* A. D. Hamilton* ______ **736 – 739**

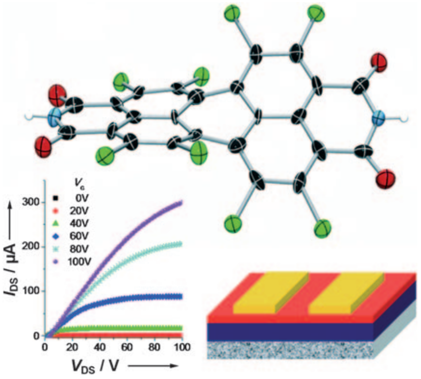
Synthetic α-Helix Mimetics as Agonists and Antagonists of Islet Amyloid Polypeptide Aggregation

Organic Semiconductors

M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A.-M. Krause, Z. Bao,* F. Würthner* ________ **740 – 743**

A Crystal-Engineered Hydrogen-Bonded Octachloroperylene Diimide with a Twisted Core: An n-Channel Organic Semiconductor

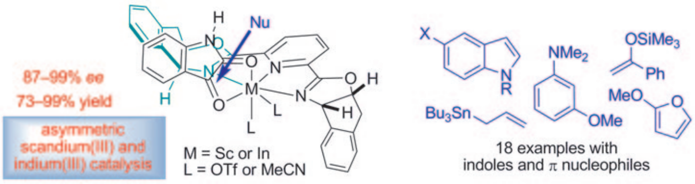
Twisted up: Perchlorination of perylene diimide afforded an exceptionally electron-poor organic semiconductor molecule (see picture; C black, Cl green, O red, N blue, H white) that crystallizes in an ideal brickstone arrangement with close π–π and chlorine–chlorine contacts. Vapor-deposited thin films of this molecule show excellent transistor performance, even in air ($\mu \approx 0.8\ \mathrm{cm^2V^{-1}s^{-1}}$, $I_{on}/I_{off} \approx 10^8$).



Synthetic Methods

N. V. Hanhan, A. H. Sahin, T. W. Chang, J. C. Fettinger, A. K. Franz* ____ **744 – 747**

Catalytic Asymmetric Synthesis of Substituted 3-Hydroxy-2-Oxindoles



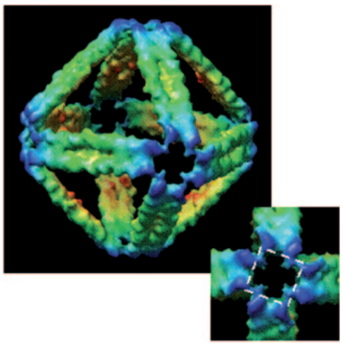
No more double trouble: The competing double-addition pathway was suppressed when chiral scandium(III) and indium(III) complexes were used to catalyze the addition of indoles and other π nucleophiles to N-alkylated and unprotected isatins (see picture). The resulting biologically relevant substituted 3-hydroxy-2-oxindoles were obtained in high yield with high enantioselectivity. Tf = trifluoromethanesulfonyl.

DNA Nanostructures

Y. He, M. Su, P.-A. Fang, C. Zhang, A. E. Ribbe, W. Jiang, C. Mao* **748 – 751**

On the Chirality of Self-Assembled DNA Octahedra

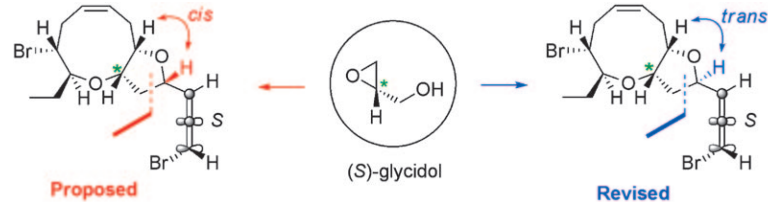
Why not let things go skew-whiff? A rational approach was used to program the self-assembly of a DNA octahedron (see structure; the color gradient indicates the distance from the center of the octahedron). Detailed structural characterization revealed that the assembly of the nanoobjects was stereoselective (a view of a vertex is shown with the skewed cavity that provided a handle for determination of the chirality of the octahedra).



Natural Products

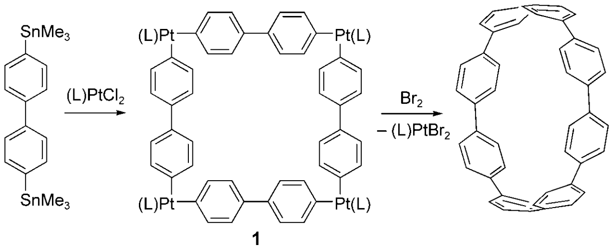
W. Jeong, M. J. Kim, H. Kim, S. Kim, D. Kim,* K. J. Shin ________ **752 – 756**

Substrate-Controlled Asymmetric Total Synthesis and Structure Revision of (+)-Itomanallene A



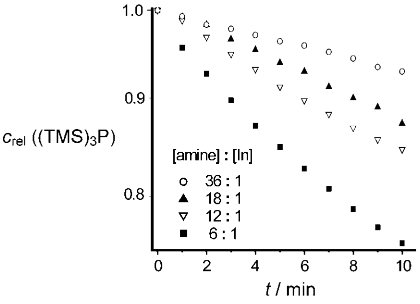
In control: The first asymmetric total synthesis of (+)-itomanallene A (revised structure) has been accomplished starting from commercially available (*S*)-glycidol in a substrate-controlled fashion. The approach yields α,α′-*cis*- or α,α′-*trans*-tetrahydrofuran isomers by intramolecular alkylation with either an amide enolate or a nitrile anion, respectively.

Cyclophanes



Square goes to loop: A selective synthesis of [8]cycloparaphenylene under mild and neutral reaction conditions was achieved in a small number of steps and in a high yield through the square-shaped platinum biphenyl intermediate **1**. Compound **1** is the smallest cycloparaphenylene derivative synthesized to date.

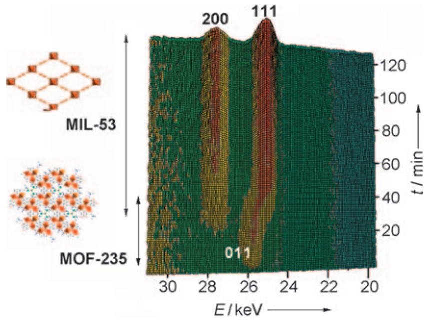
Quantum Dots



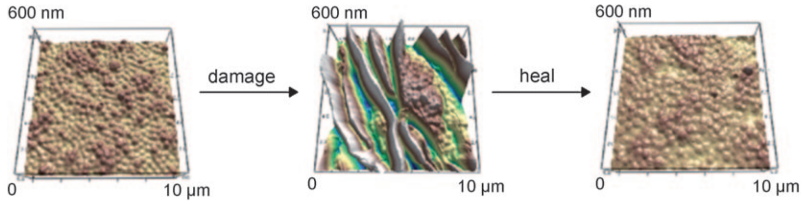
InP Kudos: The molecular mechanism of InP colloidal quantum dot (QD) syntheses was investigated by NMR spectroscopy. Unlike methods for monodisperse PbSe and CdSe, existing InP syntheses result in total depletion of molecular phosphorous species following nucleation, so QD growth is due exclusively to non-molecular ripening. Amines inhibit precursor depletion by solvation (see picture), contrary to previous reports.

MOF Crystal Growth

Inside story: In situ diffraction observations of the crystallization of metal–organic frameworks (MOFs) constructed from transition-metal ions and carboxylate ligands reveal that while some show classical nucleation-growth kinetics, others are formed via metastable transient phases (see picture).



Dynamic Materials

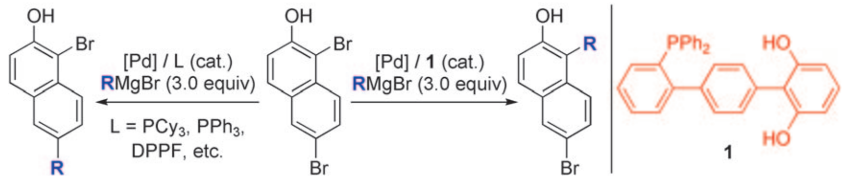


Soft yet strong: Colloidal hydrogel films, which are constructed using a layer-by-layer polyelectrolyte approach, are easily damaged by mechanical disruption, but can also autonomically heal (see picture). The healing event occurs within seconds once the film has been resolvated. The lability of the coulombic interactions between hydrogel particle and linear polymer plays a direct role in its ability to self-heal.

Palladium Catalysis

S. Ishikawa, K. Manabe* ______ **772 – 775**

DHTP Ligands for the Highly *Ortho*-Selective, Palladium-Catalyzed Cross-Coupling of Dihaloarenes with Grignard Reagents: A Conformational Approach for Catalyst Improvement

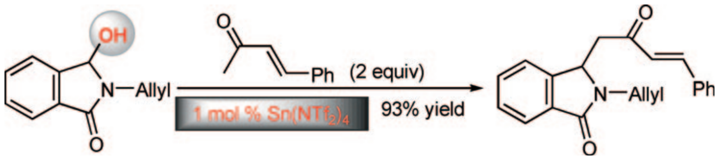


Palladium catalysts bearing dihydroxyterphenylphosphine ligands (such as **1**) are reported for the *ortho*-selective cross-coupling of Grignard reagents and dihaloarenes. The second hydroxy group onto the terphenylphosphine ligand dramatically improved the catalytic efficiency and expanded the scope of the reaction.

Lewis Superacid Catalysis

R. Ben Othman, R. Affani, M.-J. Tranchant, S. Antoniotti, V. Dalla,* E. Duñach* ______ **776 – 780**

N-Acyliminium Ion Chemistry: Highly Efficient and Versatile Carbon–Carbon Bond Formation by Nucleophilic Substitution of Hydroxy Groups Catalyzed by $Sn(NTf_2)_4$

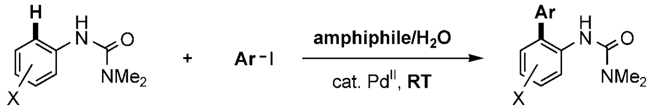


Atom-economical: Unmodified hemi-N,O-acetals are used in a catalytic, highly efficient α-amidoalkylation of a broad range of carbon-centered nucleophiles, including silicon-based components, active methylene derivatives, electron-rich arenes, and even simple ketones (see scheme). The reactions proceed in a highly efficient manner and typically require only 1 mol % of the Lewis superacidic reagent $Sn(NTf_2)_4$ as the catalyst.

C—H Activation

T. Nishikata, A. R. Abela, B. H. Lipshutz* ______ **781 – 784**

Room Temperature C—H Activation and Cross-Coupling of Aryl Ureas in Water

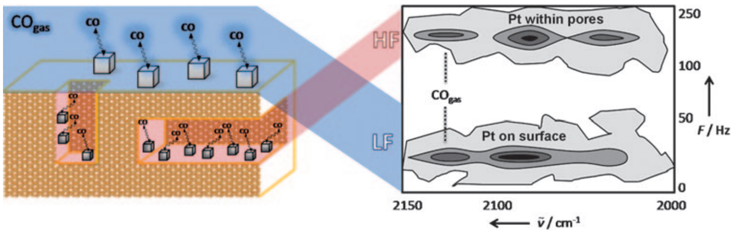


Just mix in water 'n stir: Pd-catalyzed C—H activation/cross-couplings can be carried out at room temperature in water/surfactant mixtures. The combination of $Pd(OAc)_2$ and HBF_4 allowed for reactions of aryl ureas with aryl iodides under very mild conditions, using micellar catalysis (see scheme). This reaction is made possible by use of an in situ generated cationic palladium catalyst.

Heterogeneous Catalysis

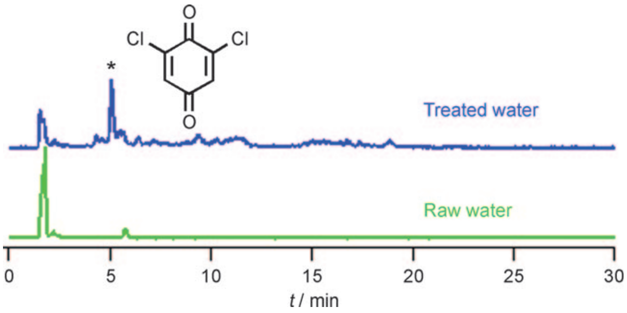
M. Rivallan, E. Seguin, S. Thomas, M. Lepage, N. Takagi, H. Hirata, F. Thibault-Starzyk* ______ **785 – 789**

Platinum Sintering on H-ZSM-5 Followed by Chemometrics of CO Adsorption and 2D Pressure-Jump IR Spectroscopy of Adsorbed Species



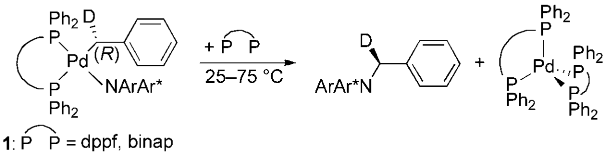
Jump to it! 2D IR pressure-jump spectroscopy of adsorbed CO can be used to assess the accessibility and location of platinum nanoparticles supported on a zeolite and investigate the behavior of Pt atoms after thermal treatment (activation, catalytic reaction, sintering). Different Pt nanoparticle sintering mechanisms were observed in the mesopores and on the external surface of the ZSM-5 support (see picture; HF = high and LF = low frequency).

Water Disinfection



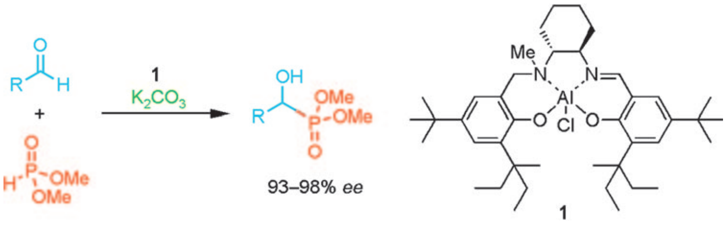
Coming clean? Liquid chromatography–ESI tandem mass spectrometry is used to detect 2,6-dichloro-1,4-benzoquinone (see picture) in drinking water treated with chlorine or chloramine.

Palladium Amido Complexes



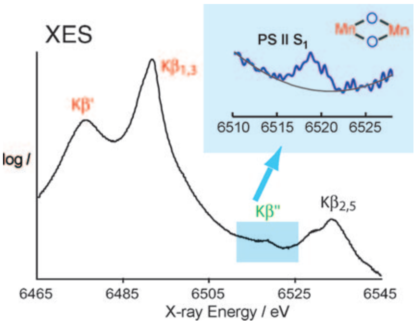
A rare event: The benzylpalladium amido complex **1** (Ar = napthyl) was used to study the mechanism of an unusual reductive elimination of amines (see scheme). The observed inversion of configuration is proposed to result from dissociation of the amido ligand, followed by nucleophilic attack on the benzylic carbon atom. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, dppf = 1,1′-bis(diphenylphosphanyl)ferrocene.

Asymmetric Catalysis



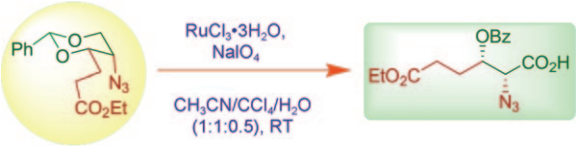
The dimethyl phosphonate hydrophosphonylation of conjugated- and non-conjugated aldehydes into their corresponding α-hydroxy phosphonates was achieved using chiral aluminum–salalen complex **1** (see scheme).

X-ray Spectroscopy



Seeing O: Mn $K\beta_{2,5}$ and $K\beta''$ X-ray emission spectra arise from transitions from the ligand 2s and 2p shells of the metal complexes to the metal 1s levels. In biological systems, it is difficult to specifically probe the O and N ligands. This spectroscopic technique is used to study the O ligands of the Mn_4Ca cluster that catalyzes photosynthetic water splitting and allows direct detection for the first time of the bridging oxo groups of Mn.

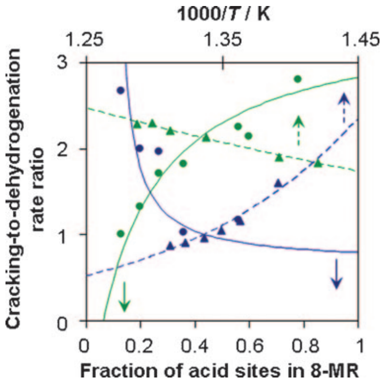
Synthetic Methods



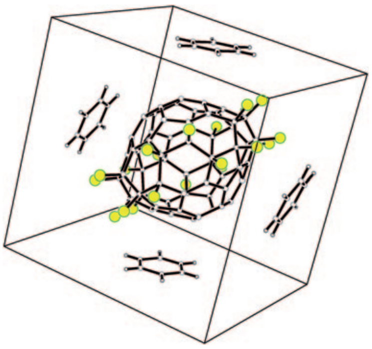
Ruthenium has twice the fun: The synthetic potential of the highly regio- and stereoselective title reaction, which relies on two oxidative cleavage steps promoted by $RuCl_3$ in combination with $NaIO_4$ (see example; Bz = benzoyl), was demonstrated with the synthesis of biologically active *cis*-(2*R*,3*S*)-3-hydroxypipecolic acid from D-glucose.

Heterogeneous Catalysis

Catalytic specificity of side pockets: Monomolecular reactions with higher activation energies—dehydrogenation of linear alkanes (*n*-butane: blue) and cracking of branched alkanes (isobutane: green)—show a stronger preference for acid sites located within eight-membered ring (8-MR) side pockets in mordenite, where reactants and transition states can only be partially confined. Partial confinement leads to higher entropies and lower free energies for ion pairs at late monomolecular transition states.



Fullerenes



Saturnene has four moons: Reactions of C_{60} with ternary metal fluorides yielded fluorofullerenes from $C_{60}F_2$ to $C_{60}F_{48}$, including elusive saturnene, $C_{60}F_{20}$, which has now been characterized by X-ray crystallography. Four benzene molecules “hover” over this D_{5d} molecule at the corners of a square inscribed in the idealized body-centered-cubic unit cell (see structure; F yellow). The tight unit-cell packing explains the very low solubility of saturnene.

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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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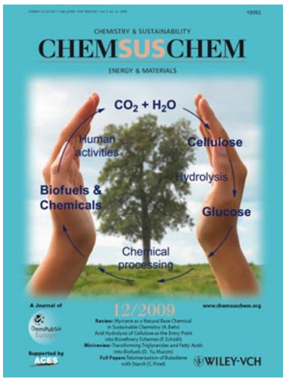

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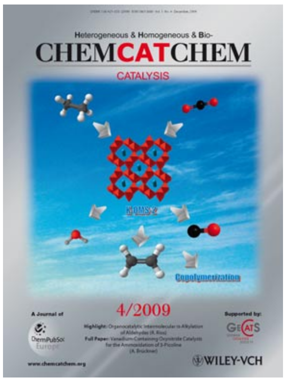

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