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:

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. Tolosa, C. Kub, U. H. F. Bunz**
Hyperbranched: A Universal Conjugated Polymer Platform?

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines**
Cationic Crown Ether Complexes of Germanium(II)

*R. Volinsky, R. Jelinek**
Laser-Modulated Ordering of Au Nanoparticles at the Air/Water Interface

*X. Zeng, H. Beckers, H. Willner**
Difluoro-λ^5-Phosphinonitrile $F_2P{\equiv}N$: Matrix Isolation and Photoisomerization into $FP{=}NF$

Author Profile

"My first experiment was the Wittig reaction to prepare chiral allenes. If I wasn't a scientist, I would be a historian. …"
This and more about Yoshiaki Nishibayashi can be found on page 4276.

News

S. J. Benkovic

G. M. Whitesides

M. F. Hawthorne

Books

Contents

Highlights

Photocrystallography

P. Coppens* ______________ **4280 – 4281**

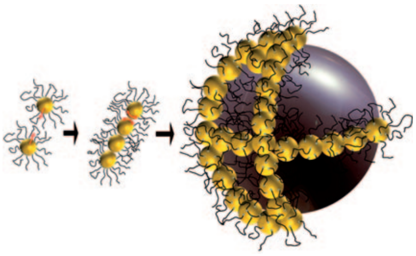
The New Photocrystallography

Shine your light: Recent work in photocrystallography demonstrates a large photoinduced increase in the magnetic susceptibility of a solid, which is accompanied by significant changes in the bond lengths of the Nd—NC—Fe moiety (see picture; black are ground-state bond lengths in Å, red are photoinduced bond lengths).

Supramolecular Chemistry

L. Carbone, L. Manna,
C. Sönnichsen* ______________ **4282 – 4283**

Self-Assembly of Amphiphilic Nanocrystals



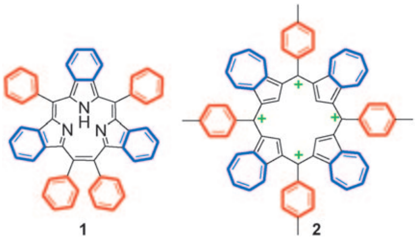
Amphiphilic hybrid materials are formed from polymer-coated semiconductor nanoparticles that simulate a surfactant-like response (see picture). The strength and density of the surface coating are the key assembling forces driving a transition from single particles to cylindrical or vesicular superstructures.

Porphyrinoids

N. Jux* ______________ **4284 – 4286**

Annulation and Arylation Stabilize New Porphyrinoids

More π, please! A free-base, benzannelated triphyrin with a [2.1.1] bridging pattern (**1**) and an azulene-derived tetracationic all-carbon porphyrinoid (**2**) are discussed. Compound **1** can be used to form metal triphyrin complexes, and **2** shows potential in molecular electronics and as a receptor for weakly binding anions.



1 2

Minireviews

Catalysis in Water

J. Paradowska, M. Stodulski,
J. Mlynarski* ______________ **4288 – 4297**

Catalysts Based on Amino Acids for Asymmetric Reactions in Water

Wet and wild: Water is a powerful force in nature, as evident in the painting "ES" by Zdzislaw Beksinski (1985, oil, 92 cm × 90 cm; reproduced with permission from Piotr Dmochowski), as well as a promising medium for asymmetric reactions. As catalysts, natural amino acids are ideal candidates. This Minireview summarizes recent advances in asymmetric catalysis in water, with amino acids and their derivatives as effective catalysts or essential components.

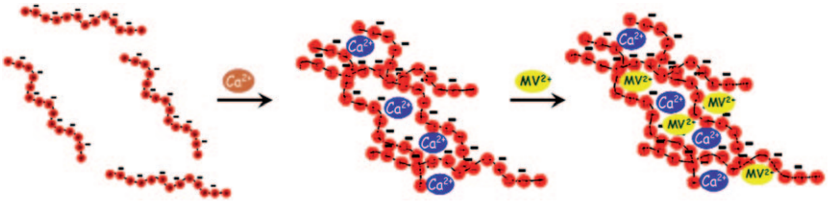
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/ sales tax.

Reviews

Development of Materials

H. Jiang, P. Taranekar, J. R. Reynolds,*
K. S. Schanze* ______ **4300 – 4316**

Conjugated Polyelectrolytes: Synthesis, Photophysics, and Applications



Ionic polymers in action: Conjugated polyelectrolytes are an emerging class of multifunctional polymers that feature π-conjugated backbones festooned with ionic solubilizing groups. These materials have been exploited in a number of applications, including fluorescent biosensors, polymer light-emitting diodes, and polymer solar cells. MV^{2+} = methylviologen

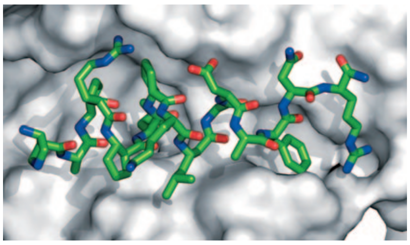
Communications

Peptide Mimics

E. F. Lee, J. D. Sadowsky, B. J. Smith,
P. E. Czabotar, K. J. Peterson-Kaufman,
P. M. Colman, S. H. Gellman,*
W. D. Fairlie* ______ **4318 – 4322**

High-Resolution Structural Characterization of a Helical α/β-Peptide Foldamer Bound to the Anti-Apoptotic Protein Bcl-x_L

Get into the groove: The first high-resolution structure of a foldamer bound to a protein target is described (see picture; foldamer in sticks). The foldamer consists of α- and β-amino acid residues and is bound to the anti-apoptotic protein Bcl-x_L. The overall binding mode and key interactions observed in the foldamer/Bcl-x_L complex mimic those seen in complexes of Bcl-x_L with natural α-peptide ligands. Additional contacts in the foldamer/Bcl-x_L complex involving β-amino acid residues appear to contribute to binding affinity.

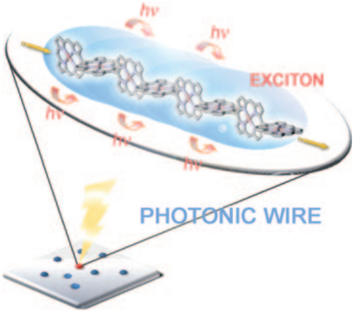


Single-Molecule Studies

J. Yang, H. Yoo, N. Aratani, A. Osuka,*
D. Kim* ______ **4323 – 4327**

Determination of the Superradiance Coherence Length of Directly Linked Linear Porphyrin Arrays at the Single-Molecule Level

Down to the wire: Photobleaching dynamics show the exciton delocalization length of directly linked porphyrin arrays (see picture) to be about four or five porphyrin units at the single-molecule level. This result provides a better understanding of how light-signal transmission occurs in the solid state and gives a perspective for the porphyrin arrays to be used as single-molecule photonic wires.




A Journal of the Gesellschaft Deutscher Chemiker
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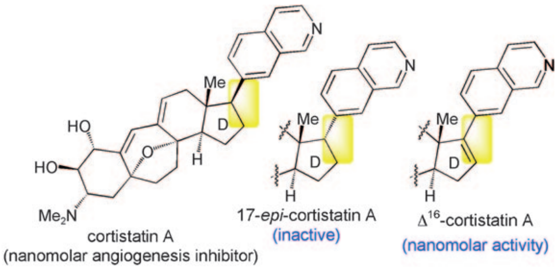
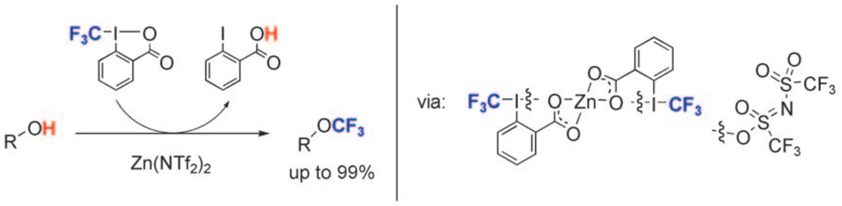
Natural Products



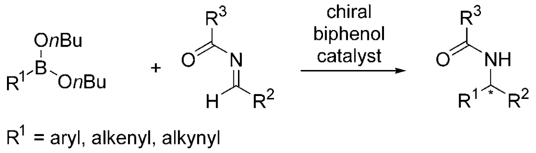
One stereocenter makes all the difference: The synthesis and biological evaluation of 17-*epi*-cortistatin A is reported from a common intermediate used to procure natural cortistatin A. The synthesis features a unique stereocontrolled Raney-Ni reduction process that can be employed to reliably produce both α- and β-configured D-ring aryl steroids. Biological evaluations of these "cortalogs" are reported for the first time.

Synthetic Methods



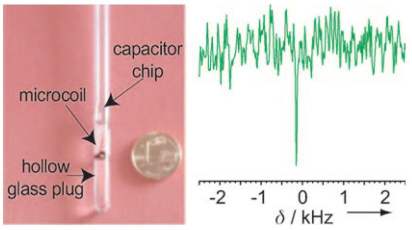
A (fluor)ry of activity: The transfer of an intact trifluoromethyl group from a hypervalent iodine reagent to an aliphatic alcohol occurs smoothly upon activation by zinc bis(triflimide). This constitutes a straightforward method for the preparation of trifluoromethoxy alkyl derivatives, compounds otherwise difficult to access.

Asymmetric Catalysis



On the big screen: A chiral biphenol catalyst screening protocol was developed for the rapid identification of enantioselective nucleophilic boronate reactions with acyl imines (see scheme). The approach successfully identified a unique catalyst for the reaction of aryl, vinyl, and alkynyl boronates. Mechanistic studies demonstrate boronate ligand exchange with the catalyst is necessary for activation towards nucleophilic addition.

NMR Spectroscopy



Spin-noise appeal: Detection of NMR spin-noise is very appealing when dilute hyperpolarized species are considered. Continuous monitoring of the noise absorption at the Larmor frequency enables determination of T_1 and T_2*, independently of the static magnetic field. An inductively coupled microcoil located inside the NMR tube (see picture) allows acquisition of ^{129}Xe spin-noise spectra without radio-frequency excitation.

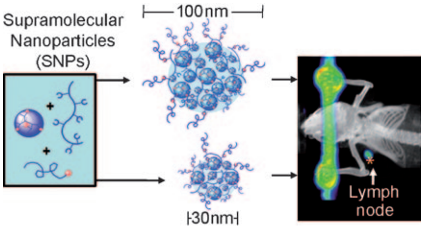
Contents

Supramolecular Chemistry

H. Wang, S. T. Wang, H. Su, K.-J. Chen, A. L. Armijo, W.-Y. Lin, Y. Wang, J. Sun, K. Kamei, J. Czernin,* C. G. Radu,* H.-R. Tseng* ______ **4344 – 4348**

A Supramolecular Approach for Preparation of Size-Controlled Nanoparticles

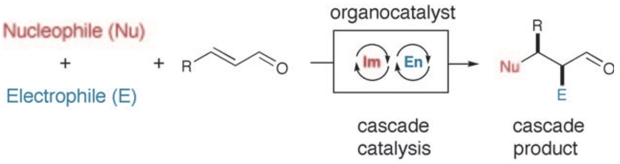
A supramolecular approach has been developed for the preparation of supramolecular nanoparticles (SNPs) with variable sizes (30–450 nm) from three different molecular building blocks using a cyclodextrin/adamantane recognition system. Positron emission tomography (PET) was employed to study the biodistribution and lymph node drainage of the SNPs in mice. The sizes of the SNPs affect their in vivo characteristics (see picture).



Organocatalysis

B. Simmons, A. M. Walji, D. W. C. MacMillan* ______ **4349 – 4353**

Cycle-Specific Organocascade Catalysis: Application to Olefin Hydroamination, Hydro-oxidation, and Amino-oxidation, and to Natural Product Synthesis



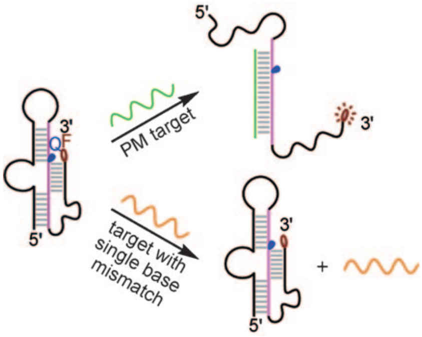
United in effort: The combined application of iminium (Im) and enamine (En) catalysts can effect a range of valuable asymmetric transformations including 1,2-hydroamination, -hydro-oxidation, and -amino-oxidation of olefins (see picture). An enantioselective organocascade catalysis was also applied in the synthesis of a complex natural product.

Fluorescent Probes

Y. Xiao, K. J. I. Plakos, X. H. Lou, R. J. White, J. R. Qian, K. W. Plaxco, H. T. Soh* ______ **4354 – 4358**

Fluorescence Detection of Single-Nucleotide Polymorphisms with a Single, Self-Complementary, Triple-Stem DNA Probe

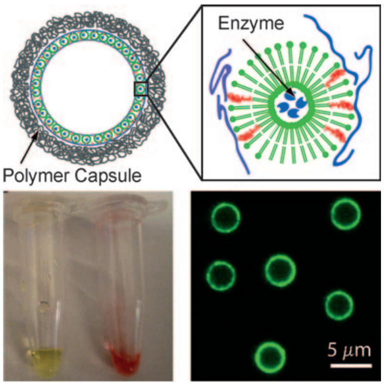
Singled out for its singularity: In a single-step, single-component, fluorescence-based method for the detection of single-nucleotide polymorphisms at room temperature, the sensor is comprised of a single, self-complementary DNA strand that forms a triple-stem structure. The large conformational change that occurs upon binding to perfectly matched (PM) targets results in a significant increase in fluorescence (see picture; F = fluorophore, Q = quencher).



Multilayer Capsules

B. Städler, R. Chandrawati, A. D. Price, S.-F. Chong, K. Breheney, A. Postma, L. A. Connal, A. N. Zelikin, F. Caruso* ______ **4359 – 4362**

A Microreactor with Thousands of Subcompartments: Enzyme-Loaded Liposomes within Polymer Capsules

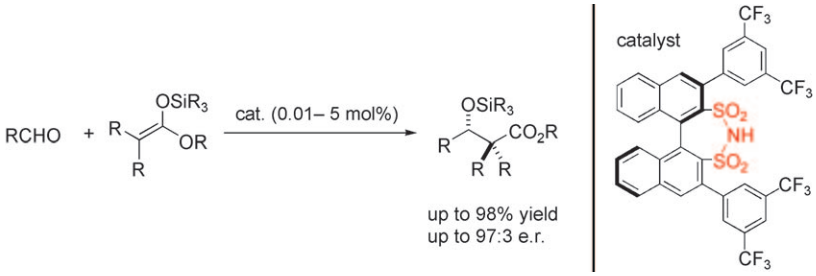


Fully loaded: Noncovalent anchoring of liposomes into polymer multilayered films with cholesterol-modified polymers allows the preparation of capsosomes—liposome-compartmentalized polymer capsules (see picture). A quantitative enzymatic reaction confirmed the presence of active cargo within the capsosomes and was used to determine the number of subcompartments within this novel biomedical carrier system.

Organocatalysis

P. García-García, F. Lay, P. García-García, C. Rabalakos, B. List* ______ **4363 – 4366**

A Powerful Chiral Counteranion Motif for Asymmetric Catalysis

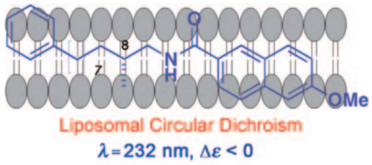


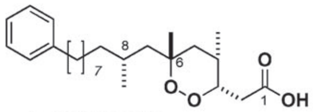
Room to swing a cat: A chiral disulfonimide has been designed as a powerful new motif for asymmetric catalysis. As a first illustration, a highly efficient and enantioselective Mukaiyama aldol reaction has been developed (see scheme). The actual catalyst is proposed to be an *N*-silyl imide which is generated in situ.

Natural Products

D. S. Dalisay, T. Quach, G. N. Nicholas, T. F. Molinski* ______ **4367 – 4371**

Amplification of the Cotton Effect of a Single Chromophore through Liposomal Ordering—Stereochemical Assignment of Plakinic Acids I and J





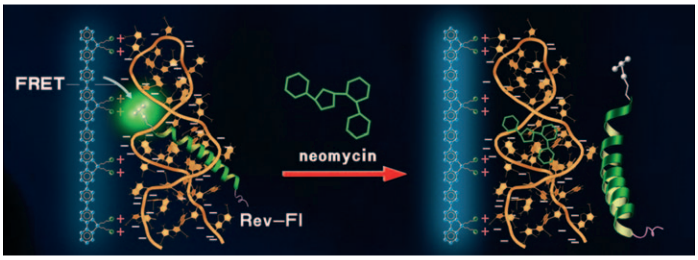
1: plakinic acid I

A dramatic effect is observed when acyclic *N*-(2-naphthamides) of medium-chain 1-amino-2-methylalkanes are partially ordered with the help of liposomes: the Cotton effect arising from π–π* transitions of the terminal naphthamide chromophore is enormously enhanced. This effect was exploited to assign the configuration of new polyketide peroxides such as **1** from the sponge *Plakortis halichondroides*.

Biosensors

L. An, L. Liu, S. Wang,* G. C. Bazan* ______ **4372 – 4375**

An Optical Approach for Drug Screening Based on Light-Harvesting Conjugated Polyelectrolytes

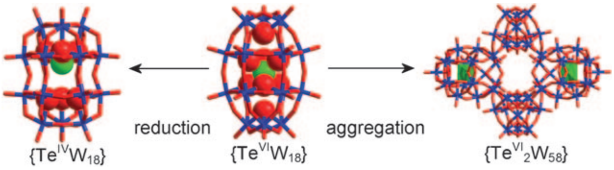


Drugs turn the light off: Conjugated polyelectrolytes (CPEs) have been used in fluorescent assays for real-time screening of small molecules that prevent the RNA–protein complexation that is important for virus replication and thereby can be considered potential initial candidates for drug discovery (see picture).

Polyoxometalates

J. Yan, D.-L. Long,* E. F. Wilson, L. Cronin* ______ **4376 – 4380**

Discovery of Heteroatom-"Embedded" $Te\subset\{W_{18}O_{54}\}$ Nanofunctional Polyoxometalates by Use of Cryospray Mass Spectrometry

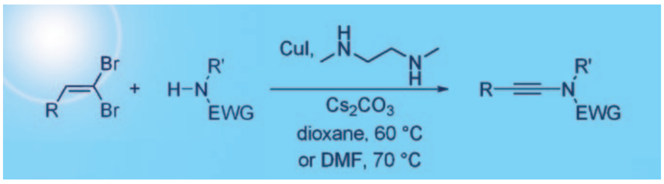


The cryo game: Heteroatom-embedded nanofunctional clusters are described that incorporate a $[Te^{VI}O_6]^{6-}$ species contained within a $\{W_{18}O_{54}\}$ cage. Not only does the tellurium-based species activate the $\{W_{18}O_{54}\}$ cluster surface for assembly of larger nanoscale structures, such as $[H_{10}Te^{VI}_2W_{58}O_{198}]^{26-}$, it also undergoes a redox transformation inside the cluster from $[Te^{VI}O_6]^{6-}$ to $[Te^{IV}O_3]^{2-}$.

Synthetic Methods

A. Coste, G. Karthikeyan, F. Couty, G. Evano* ——— **4381 – 4385**

Copper-Mediated Coupling of 1,1-Dibromo-1-alkenes with Nitrogen Nucleophiles: A General Method for the Synthesis of Ynamides



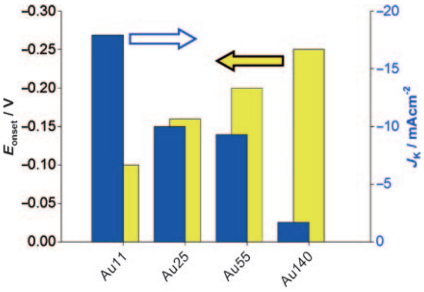
Mild reaction conditions are the advantage of the title reaction, which allows straightforward entry to a variety of ynamides starting from readily available 1,1-dibromo-1-alkenes, which act as attractive alkynylating agents (see scheme; EWG = electron-withdrawing group, DMF = *N*,*N*-dimethylformamide).

Electrocatalysis

W. Chen, S. Chen* ——— **4386 – 4389**

Oxygen Electroreduction Catalyzed by Gold Nanoclusters: Strong Core Size Effects

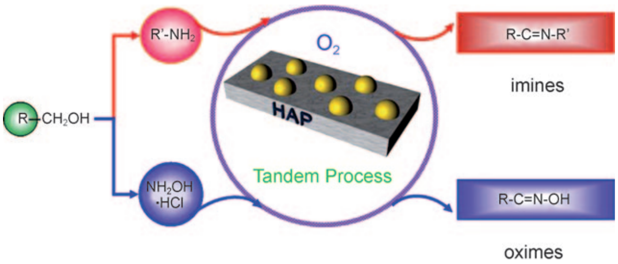
Bigger isn't better: Gold nanoclusters exhibit enhanced electrocatalytic activity in oxygen reduction when the core size decreased from Au$_{140}$ to Au$_{11}$, as reflected by the onset potential E_{onset} and peak current density J_K (see picture). The increasing fraction of surface atoms with low coordination numbers and the shift of the d-band center to the Fermi level facilitate oxygen adsorption.



Heterogeneous Tandem Catalysis

H. Sun, F. Z. Su, J. Ni, Y. Cao,* H. Y. He, K. N. Fan ——— **4390 – 4393**

Gold Supported on Hydroxyapatite as a Versatile Multifunctional Catalyst for the Direct Tandem Synthesis of Imines and Oximes



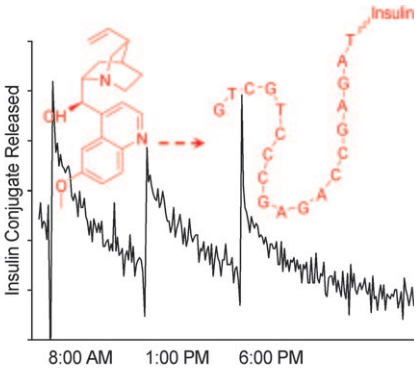
Two birds with one auric stone: The title system acts as a highly efficient heterogeneous catalyst for the one-pot tandem synthesis of imines or oximes from alcohols and the corresponding amines under mild conditions (see scheme; HAP = hydroxyapatite).

Drug Release

S. K. Taylor,* R. Pei, B. C. Moon, S. Damera, A. Shen, M. N. Stojanovic ——— **4394 – 4397**

Triggered Release of an Active Peptide Conjugate from a DNA Device by an Orally Administrable Small Molecule

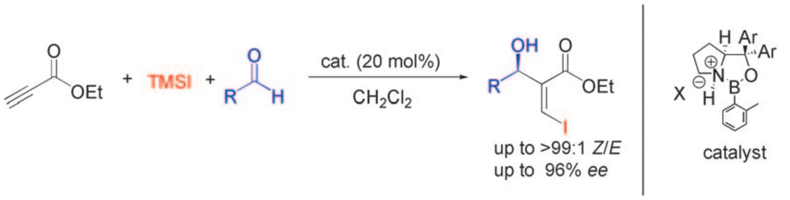
A real tonic: In a conceptually new approach to controlled release, the natural daily insulin profile in response to three meals is mimicked (see graph) with release of an insulin conjugate from a matrix, triggered by quinine, a component of tonic water.



Multicomponent Reactions

B. K. Senapati, G.-S. Hwang, S. Lee,
D. H. Ryu* ______________ **4398 – 4401**

Enantioselective Synthesis of β-Iodo Morita–Baylis–Hillman Esters by a Catalytic Asymmetric Three-Component Coupling Reaction



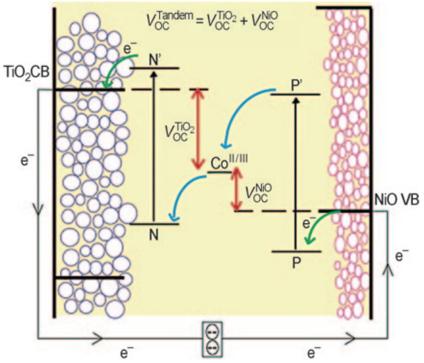
A catalytic route toward chiral Morita–Baylis–Hillman esters by asymmetric coupling between α,β-acetylenic esters, aldehydes, and trimethylsilyl iodide has been developed (see scheme). The reaction proceeds with high to excellent enantioselectivities, and the products can be transformed into β-branched derivatives in a single step and with excellent retention of configuration. TMS = trimethylsilyl

Solar Cells

E. A. Gibson, A. L. Smeigh, L. Le Pleux,
J. Fortage, G. Boschloo, E. Blart,
Y. Pellegrin, F. Odobel,* A. Hagfeldt,*
L. Hammarström* ________ **4402 – 4405**

A p-Type NiO-Based Dye-Sensitized Solar Cell with an Open-Circuit Voltage of 0.35 V

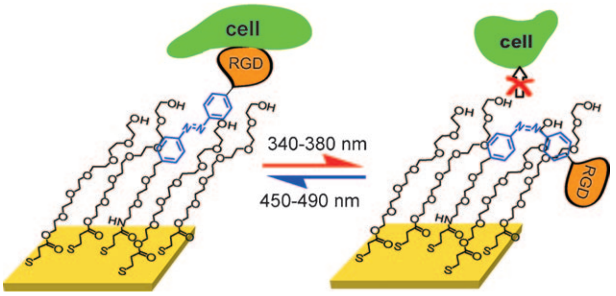
In tandem: Employing a molecular dyad and a cobalt-based electrolyte gives a threefold-increase in open-circuit voltage (V_{OC}) for a p-type NiO device ($V_{OC} = 0.35$ V), and a fourfold better energy conversion efficiency. Incorporating these improvements in a TiO_2/NiO tandem dye-sensitized solar cell (TDSC), results in a TDSC with a $V_{OC} = 0.91$ V (see figure; CB = conductance band, VB = valence band).



Cell Adhesion

D. B. Liu, Y. Y. Xie, H. W. Shao,*
X. Y. Jiang* ______________ **4406 – 4408**

Using Azobenzene-Embedded Self-Assembled Monolayers To Photochemically Control Cell Adhesion Reversibly



A celling point: A mixed self-assembled monolayer comprising two types of alkanethiols—one containing an azobenzene unit terminated with a peptide, the other containing a hexa(ethylene glycol) group that resists nonspecific cell adhesion—enables cell adhesion to be modulated photochemically. The reversible conversion of the azobenzene moiety between *E* and *Z* configurations allows the surface to either support or resist cell adhesion.

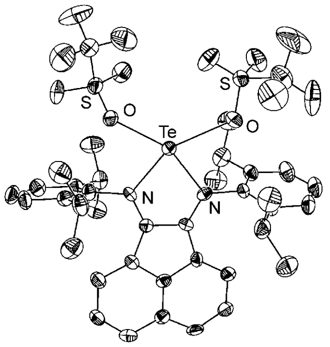
Contents

Tellurium Dications

J. L. Dutton, H. M. Tuononen,
P. J. Ragogna* ____________ **4409 – 4413**

Tellurium(II)-Centered Dications from the Pseudohalide "Te(OTf)$_2$"

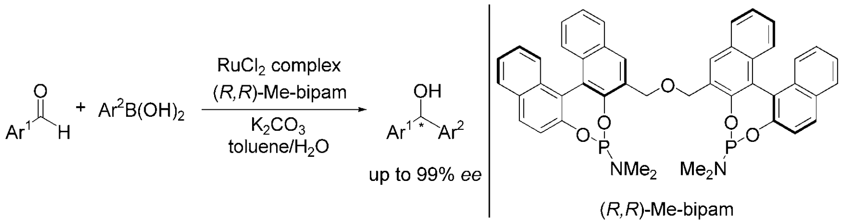
Te for two: Supported by pyridine- or carbene-based ligands, tellurium-centered dications are prepared in high yield and include a dicationic tellurium analogue of the recently synthesized "carbodicarbene". The key to accessing these compounds is the isolation of a base-stabilized form of TeOTf$_2$ (see structure), a new highly electrophilic reagent for tellurium chemistry.



Asymmetric Synthesis

Y. Yamamoto,* K. Kurihara,
N. Miyaura* ____________ **4414 – 4416**

Me-bipam for Enantioselective Ruthenium(II)-Catalyzed Arylation of Aldehydes with Arylboronic Acids

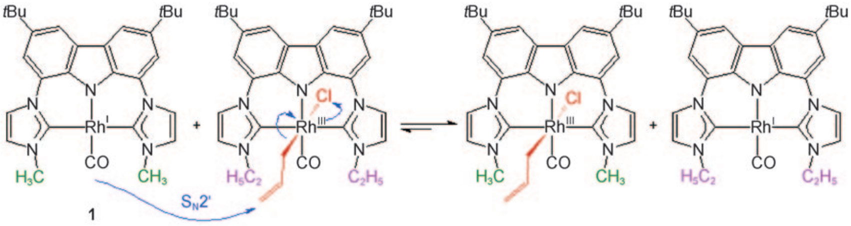


Ligand design by-pam: A ruthenium-catalyzed asymmetric arylation of aldehydes with arylboronic acids has been developed, giving chiral diarylmethanols in good yields. The use of a chiral bidentate phosphoramidite ligand ((*R*,*R*)-Me-bipam) led to excellent enantioselectivities.

η^1-Allyl Ligands

B. Wucher, M. Moser, S. A. Schumacher,
F. Rominger, D. Kunz* ______ **4417 – 4421**

First X-Ray Structure Analyses of Rhodium(III) η^1-Allyl Complexes and a Mechanism for Allylic Isomerization Reactions

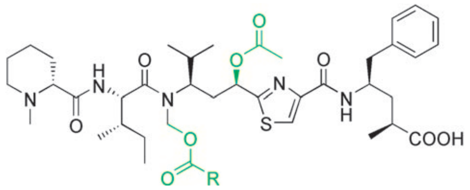


Metal-to-metal allyl transfer: Using the first structurally characterized rhodium η^1-allyl complexes it is shown that the σ-bound allyl substituent can be transferred from the Rh^{III} complex to a Rh^I complex in a fast equilibrium. This process may account for the decrease in regioselectivity observed in allylic alkylation reactions in which complex **1** is used as a catalyst.

Natural Products

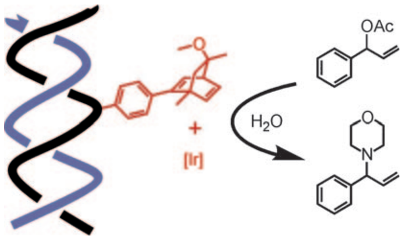
A. Ullrich, Y. Chai, D. Pistorius,
Y. A. Elnakady, J. E. Herrmann,
K. J. Weissman, U. Kazmaier,*
R. Müller* ____________ **4422 – 4425**

Pretubulysin, a Potent and Chemically Accessible Tubulysin Precursor from *Angiococcus disciformis*



Simplify, simplify, simplify! Pretubulysin (structure without the green substituents), a simplified tubulysin was prepared in the laboratory and also found in a natural myxobacterial source. This biosynthetic precursor of the tubulysins is not as active as tubulysins A and D but is still effective in picomolar concentrations against cancer cell lines.

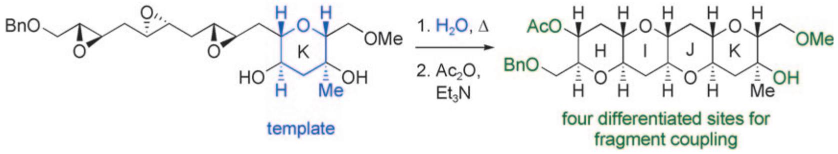
DNA hybrid catalysis goes organometallic: A DNA strand functionalized with diene ligands forms iridium(I) complexes that can efficiently catalyze an allylic amination in aqueous medium (see scheme). The DNA-based complexes show high stability and activity, and their secondary structure influences the stereoselectivity of the reaction.



Organometallic Hybrid Catalysis

P. Fournier, R. Fiammengo,
A. Jäschke* ______ **4426–4429**

Allylic Amination by a DNA–Diene–Iridium(I) Hybrid Catalyst



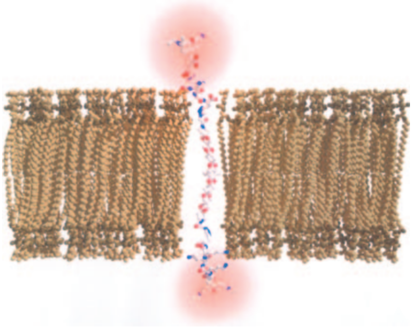
Extension ladder: The successful application of epoxide-opening strategies towards the synthesis of ladder-type polyethers is contingent upon further elaboration of the product. By employing two different functionalized templates, a fragment of gymnocin A that bears four sites for subsequent fragment coupling has been prepared (see scheme; Bn = benzyl).

Cascade Reactions

A. R. Van Dyke,
T. F. Jamison* ______ **4430–4432**

Functionalized Templates for the Convergent Assembly of Polyethers: Synthesis of the HIJK Rings of Gymnocin A

Getting stuck in: A hydrophobic molecular rod with terminal fluorescent moieties has been synthesized. The insertion of the rod into membranes was investigated and shown to incorporate efficiently into model and biological membranes (see picture; gray C, blue N, red O). Those rods can be used as stable membrane-associated anchors for functionalization of membrane surfaces.



Molecular Rods

P. Müller, J. Nikolaus, S. Schiller,
A. Herrmann,* K. Möllnitz, S. Czapla,
P. Wessig* ______ **4433–4435**

Molecular Rods with Oligospiroketal Backbones as Anchors in Biological Membranes

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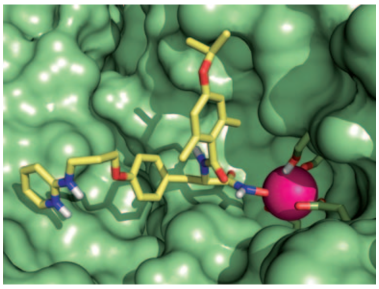


A suitable substitute: All integrin receptors bind their ligands, which contain an aspartate residue, in the metal-ion-dependent adhesion site (MIDAS). So far all attempts to replace the carboxyl group of aspartate with other, pharmacologically favorable isosteric groups have failed. Now it has been shown that a hydroxamic acid group can replace the carboxyl group; the resulting ligand retains its high binding activity. The picture shows one such ligand in the binding site of αvβ3.

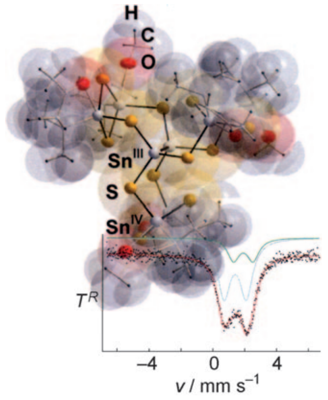
Integrin Ligands

D. Heckmann, B. Laufer, L. Marinelli,
V. Limongelli, E. Novellino, G. Zahn,
R. Stragies, H. Kessler* ______ **4436–4440**

Breaking the Dogma of the Metal-Coordinating Carboxylate Group in Integrin Ligands: Introducing Hydroxamic Acids to the MIDAS To Tune Potency and Selectivity

Mixed-Valent Stannates

In broad daylight: The double-decker thiostannate [(RSn^{IV})$_4S_6$] (**1**, R = CMe_2CH_2COMe) condenses to form [{(RSn^{IV})$_2$(μ-S)$_2$}$_3Sn^{III}{}_2S_6$] (**2**; see picture). This mixed-valent complex, which formally contains both Sn^{III} and Sn^{IV} atoms as confirmed by Mössbauer spectroscopy and DFT calculations, forms by a complicated, concerted mechanism. Additionally, **2** provides six carbonyl groups for further derivatization.



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).

Service

The issues for May 2009 appeared online on the following dates
Issue 20: April 28 · Issue 21: May 4 · Issue 22: May 12 · Issue 23: May 19