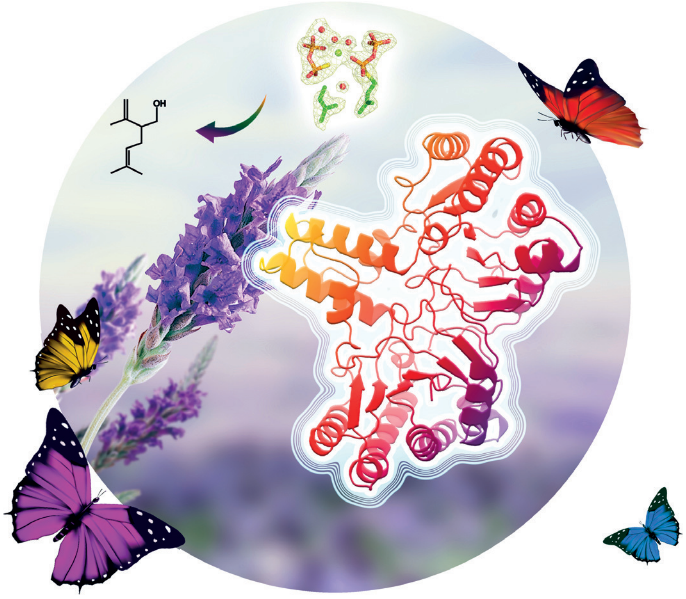
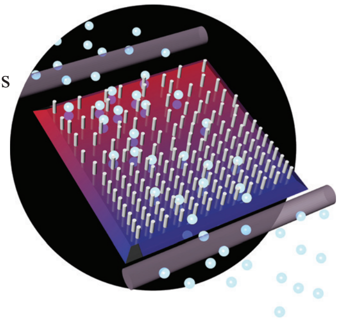
The irregular terpene synthase ...

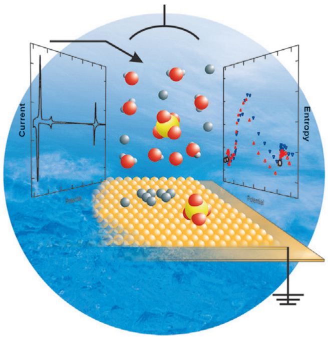


… lavandulyl diphosphate synthase (LPPS) produces the precursor of the commercially important lavender fragrance lavandulol by an unusual "head-to-middle" mechanism. In their Communication on page 4721 ff., E. Oldfield, R.-T. Guo, and Y. Ma et al. present the first structure of LPPS from lavender complexed with its substrate. The butterfly shape structure is remarkably similar to that of proteins involved in bacterial cell-wall biosynthesis, and led to the proposal of a unique condensation mechanism of action of general interest to terpene synthesis.

NMR Spectroscopy

In their Communication on page 4665 ff., A. Pines et al. describe how viscous ordered and disordered media can be probed by diffusion of hyperpolarized xenon through hollow fiber membranes into a contained sample.





Electrochemistry

R. Schuster et al. describe in their Communication on page 4688 ff. how they determined the reaction entropy of the electrodeposition of silver on a Au(111) surface by measuring the heat effects accompanying the electrochemical surface reactions.

Quantum Dots

In their Communication on page 4738 ff., Y. Guo, D. Zhou et al. report on polyvalent mannose-capped quantum dots that have been successfully employed to probe multivalent interactions of HIV/Ebola receptors.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT DEUTSCHER CHEMIKER

Service

Spotlight on Angewandte's Sister Journals **4632 – 4635**

Author Profile

"The worst advice I have ever given was 'it won't work'. If I were not a scientist, I would be a historian …"
This and more about Jianrong (Steve) Zhou can be found on page 4636.

Jianrong (Steve) Zhou **4636**

News

Wolf Prize in Chemistry:
K. C. Nicolaou and S. L. Schreiber **4637**

Israel Chemical Society Awards:
R. Klajn, R. Tenne, and M. Kol **4637**

Pittcon 2016 Award Winners:
S. A. Asher, D. R. Walt, J. Popp, S. Mukamel, and R. J. White **4637**


S. L. Schreiber


K. C. Nicolaou


R. Klajn


R. Tenne


M. Kol


S. A. Asher


D. R. Walt


J. Popp


S. Mukamel

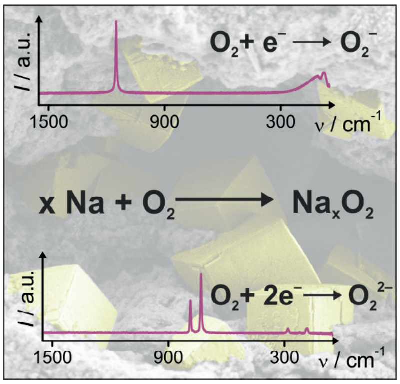

R. White

Minireviews

Sodium–Oxygen Batteries

C. L. Bender, D. Schröder, R. Pinedo,
P. Adelhelm, J. Janek* ______ 4640 – 4649

One- or Two-Electron Transfer? The Ambiguous Nature of the Discharge Products in Sodium–Oxygen Batteries



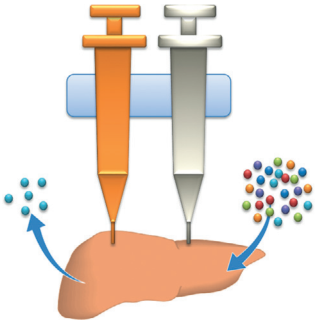
Two discharge products, NaO_2 and Na_2O_2, appear to compete in the non-aqueous sodium–oxygen battery, and cells forming either superoxide or peroxide have been reported. It is still unclear which factors determine the nature of the cell reaction. In this Minireview, available data are summarized, and important control parameters are discussed. Water and protons appear to play major roles.

Reviews

3D Tissue/Organ Models

F. Pati, J. Gantelius,
H. A. Svahn* ______ 4650 – 4665

3D Bioprinting of Tissue/Organ Models



Looking at the fine print: 3D bioprinting offers exciting prospects for printing 3D tissue/organ models. This technique can recreate the spatial and chemical complexity inherent to native tissues and organs. Hence, bioprinted tissues/organs have the potential to be useful in the prioritization of lead candidates, toxicity testing, and as disease/tumor models.

Communications

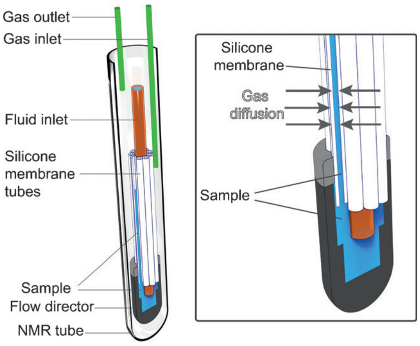
NMR Spectroscopy

A. E. Truxal, C. C. Slack, M. D. Gomes,
C. C. Vassiliou, D. E. Wemmer,
A. Pines* ______ 4666 – 4670

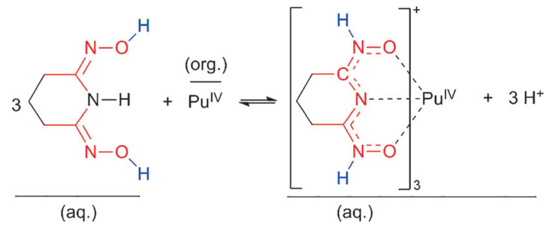
Nondisruptive Dissolution of Hyperpolarized ^{129}Xe into Viscous Aqueous and Organic Liquid Crystalline Environments

Frontispiece

Blending into the crowd: A new device that facilitates the direct dissolution of hyperpolarized ^{129}Xe into viscous liquid-crystalline media is presented. ^{129}Xe and ^{2}H NMR spectra show the nondisruptive dissolution of xenon, the presence of ordered phases, and, in the case of the thermotropic liquid crystal *N*-(4-methoxybenzylidene)-4-butylaniline, a nematic–isotropic phase transition.



For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 16.862/14.051 (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.



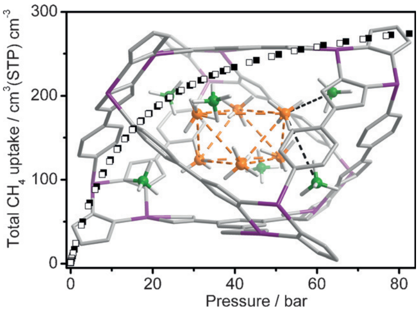
Waste not, want not: A salt-free reagent in 1 M HNO_3 can strip Pu^{IV} from a 30% TBP-kerosene mixture for plutonium and uranium recovery by extraction. The efficiency for removal of Pu^{IV} is high and it proceeds at a fast rate. Importantly it does not increase the volume of the waste.

Chelates

L. Xian, G. Tian,* C. M. Beavers, S. J. Teat,* D. K. Shuh* ____ 4671 – 4673

Glutarimidedioxime: A Complexing and Reducing Reagent for Plutonium Recovery from Spent Nuclear Fuel Reprocessing

---



Hold tightly: High-density methane storage is achieved in a metal–organic framework featuring a hierarchical pore system consisting of single-wall nanocages and strong organic binding sites. These enforce not only strong host–methane and methane–methane interactions, but also a dense packing of methane molecules.

Methane Storage

J.-M. Lin, C.-T. He,* Y. Liu, P.-Q. Liao, D.-D. Zhou, J.-P. Zhang,* X.-M. Chen ____ 4674 – 4678

A Metal–Organic Framework with a Pore Size/Shape Suitable for Strong Binding and Close Packing of Methane

Advertorial

Specialty Chemistry from the Lower Rhine

The ALTANA Group develops and manufactures high-quality, innovative specialty chemical products. Our four divisions BYK, ECKART, ELANTAS, and ACTEGA have set worldwide standards in their markets. With sales of 2 billion euros, we are one of the world's most innovative, fastest-growing, and most profitable chemical companies. We currently employ around 6,000 people who have good ideas for the world of the future. The headquarter – the heart of the successful group of companies – is based in Wesel in the beautiful Lower Rhine area.

While you will not directly find the ALTANA Group's products on the shelves of any supermarkets or shops, they are an integral part of our everyday lives. BYK, for example, ensures that paints can be applied without forming blisters and that varnishes are highly resistant to scratches. ACTEGA products give the right shine to items such as newspapers and make packaging materials particularly durable. Insulating materials from ELANTAS are found, for instance, in electric motors, household appliances, digital cameras, wind turbines and computers. ECKART pigments provide metallic effects on cars. And even in nail varnish and eye shadow you will find products from ALTANA.

Our success is no secret but the result of the effort put forward by qualified and innovative experts and executives like you. So this is your chance to accept our challenge and begin creating unique solutions with us. Discover your Career Plus in Specialty Chemistry: **www.altana.jobs**

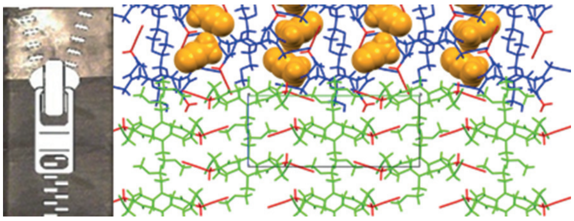
BYK Additives & Instruments
ECKART Effect Pigments
ELANTAS Electrical Insulation
ACTEGA Coatings & Sealants
ALTANA

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Crystal Engineering

A. Meli, E. Macedi, F. De Riccardis,
V. J. Smith, L. J. Barbour, I. Izzo,*
C. Tedesco* ____________ **4679 – 4682**

Solid-State Conformational Flexibility at Work: Zipping and Unzipping within a Cyclic Peptoid Single Crystal



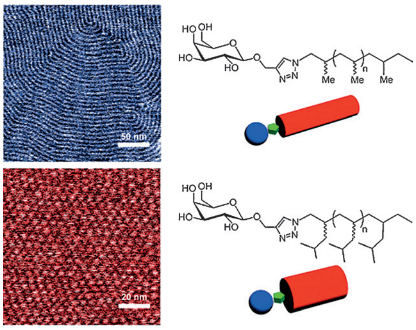
Zip it! A cyclic peptoid undergoes a reversible single-crystal-to-single-crystal transformation with drastic conformational changes within the structure upon guest release or uptake. As determined by single-crystal X-ray analysis, the structural changes are mediated by the formation of a CH–π zipper which can reversibly open and close upon adsorption or desorption of acetonitrile guest molecules (yellow).

Self-Assembly

T. S. Thomas, W. Hwang,
L. R. Sita* ____________ **4683 – 4687**

End-Group-Functionalized Poly(α-olefinates) as Non-Polar Building Blocks: Self-Assembly of Sugar–Polyolefin Hybrid Conjugates

The tail that wags the dog: Living coordinative chain-transfer polymerization of α-olefins provides entry to end-group functionalized poly(α-olefinates) (x-PAOs) serving as non-polar building blocks with tailorable occupied volumes. Application of these x-PAOs for sugar–polyolefin hybrid conjugates demonstrates the ability to manipulate the morphology of the ultra-thin film nanostructure by variation in occupied volume of the x-PAO domain.

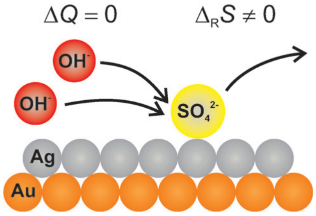


Electrochemistry

S. Frittmann, V. Halka,
R. Schuster* ____________ **4688 – 4691**

Identification of Non-Faradaic Processes by Measurement of the Electrochemical Peltier Heat during the Silver Underpotential Deposition on Au(111)

Heat seeker: Complementary information on electrochemical processes is obtained by measuring the heat effects accompanying electrochemical surface reactions. For the electrodeposition of silver on an Au(111) surface, the reaction entropy of the complete process, including non-Faradaic side reactions, becomes accessible.



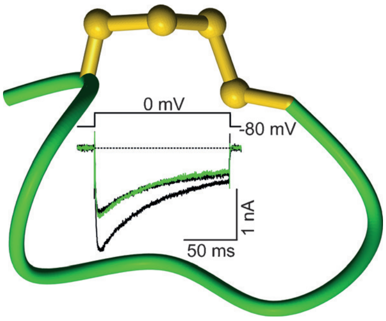
Inside Back Cover

Analgesics

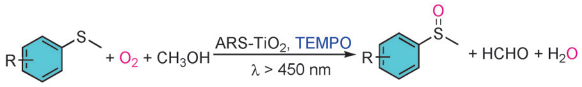
B. B. Carstens, G. Berecki, J. T. Daniel,
H. S. Lee, K. A. V. Jackson, H.-S. Tae,
M. Sadeghi, J. Castro, T. O'Donnell,
A. Deiteren, S. M. Brierley, D. J. Craik,
D. J. Adams, R. J. Clark* ____ **4692 – 4696**

Structure–Activity Studies of Cysteine-Rich α-Conotoxins that Inhibit High-Voltage-Activated Calcium Channels via $GABA_B$ Receptor Activation Reveal a Minimal Functional Motif

Downsizing venom peptides: Using NMR structural studies and functional assays a minimal functional epitope of an α-conotoxin was discovered that inhibits high-voltage-activated calcium currents via a GPCR-mediated mechanism. These downsized peptide toxins are promising lead molecules for the treatment of neuropathic pain.



Photoredox Catalysis



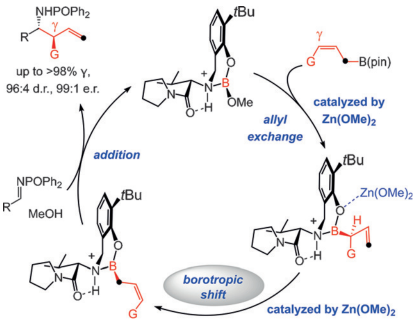
Dye-sensitized titanium dioxide and a catalytic amount of the redox mediator TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, served as a well-organized scheme of photoredox catalysis for the selective oxidation of sulfides into sulfoxides using oxygen under irradiation of visible light. The redox mediator enabled the organic transformations by visible-light-induced photoredox catalysis.

X. J. Lang, J. C. Zhao,
X. D. Chen* ______ 4697 – 4700

Visible-Light-Induced Photoredox Catalysis of Dye-Sensitized Titanium Dioxide: Selective Aerobic Oxidation of Organic Sulfides

Borotropic Shifts

VIP

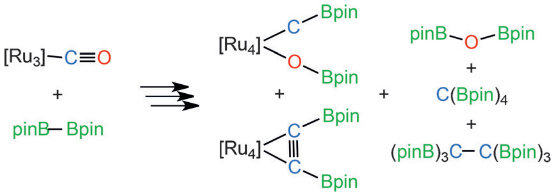


Managing shifts: Otherwise α-selective crotyl additions to aldimines are rendered highly γ-selective by adding small amounts of $Zn(OMe)_2$ into the reaction mixture. The Lewis acidic co-catalyst is believed to accelerate borotropic shifts that are responsible for the selectivity reversal, and cause faster exchange processes that generate the catalytically active chiral allylboron species.

F. W. van der Mei, H. Miyamoto,
D. L. Silverio,
A. H. Hoveyda* ______ 4701 – 4706

Lewis Acid Catalyzed Borotropic Shifts in the Design of Diastereo- and Enantioselective γ-Additions of Allylboron Moieties to Aldimines

Borylation

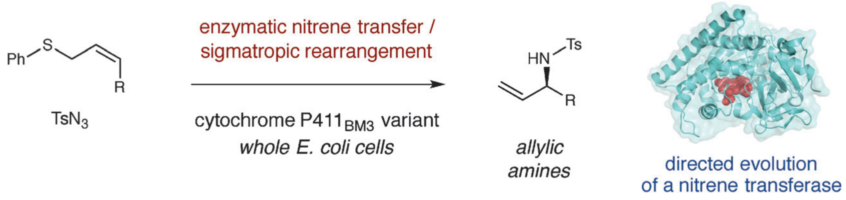


Piñacolato: The C–O bond of coordinated carbon monoxide can be cleaved by a diborane(4) compound. A combination of bis(pinacolato)diboron, B_2pin_2, with ruthenium carbonyl promotes the cleavage and reductive coupling of coordinated CO to give not only metallic complexes containing either CBpin or $C_2(Bpin)_2$ ligands but also metal-free highly borylated organic molecules, such as $C(Bpin)_4$ and $C_2(Bpin)_6$.

A. S. Batsanov, J. A. Cabeza,*
M. G. Crestani, M. R. Fructos,
P. García-Álvarez, M. Gille, Z. Lin,
T. B. Marder* ______ 4707 – 4710

Fully Borylated Methane and Ethane by Ruthenium-Mediated Cleavage and Coupling of CO

Directed Evolution



A serine-ligated variant of cytochrome $P450_{BM3}$ has been engineered to initiate a sulfimidation/[2,3]-sigmatropic rearrangement sequence in whole *E. coli* cells, providing access to enantioenriched, protected allylic amines. The results highlight the ability of enzymes to adapt, through directed evolution, to facilitate valuable reaction pathways for which no natural enzymes have evolved.

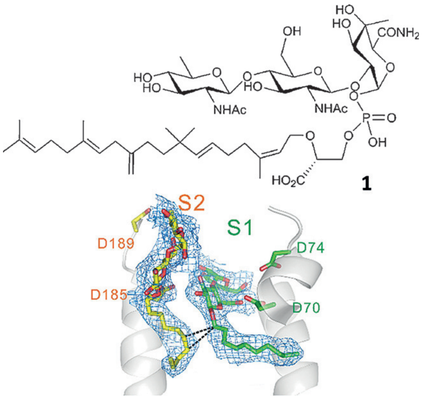
C. K. Prier, T. K. Hyster, C. C. Farwell,
A. Huang, F. H. Arnold* ______ 4711 – 4715

Asymmetric Enzymatic Synthesis of Allylic Amines: A Sigmatropic Rearrangement Strategy

Isoprenoid Biosynthesis

L. Zhang, C.-C. Chen, T.-P. Ko, J.-W. Huang, Y. Zheng, W. Liu, I. Wang, S. R. Malwal, X. Feng, K. Wang, C.-H. Huang, S.-T. D. Hsu, A. H.-J. Wang, E. Oldfield,* R.-T. Guo* **4716 – 4720**

Moenomycin Biosynthesis: Structure and Mechanism of Action of the Prenyltransferase MoeN5



The structure of MoeN5, a unique prenyltransferase essential for the biosynthesis of the antibiotic moenomycin, was determined by using a fusion-tag approach. MoeN5 catalyzes the production of a (C_{25}) moenocinyl trisaccharide (**1**), and the structures provide insight into the binding of substrates in the S1 and S2 sites. These results provide a structural basis for the mechanism of action of MoeN5, and could facilitate the design of new antibiotics.

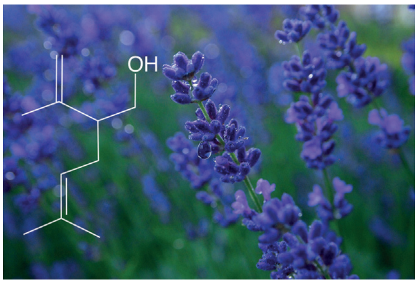
VIP

Monoterpenes

M. Liu, C.-C. Chen, L. Chen, X. Xiao, Y. Zheng, J.-W. Huang, W. Liu, T.-P. Ko, Y.-S. Cheng, X. Feng, E. Oldfield,* R.-T. Guo,* Y. Ma* **4721 – 4724**

Structure and Function of a "Head-to-Middle" Prenyltransferase: Lavandulyl Diphosphate Synthase

Front Cover



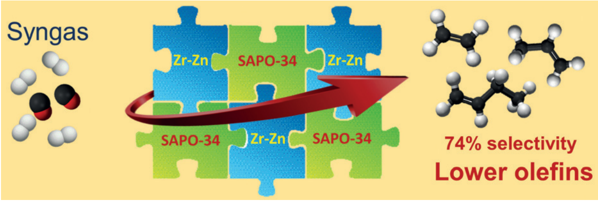
Fragrance of lavender: The structure of lavandulyl diphosphate synthase, an irregular monoterpene synthase, was determined and is remarkably similar to the *cis*-prenyl synthases involved in bacterial cell wall biosynthesis. Determination of two ligand-bound structures led to an unusual structure-based mechanism of action.

VIP

Heterogeneous Catalysis

K. Cheng, B. Gu, X. Liu, J. Kang, Q. Zhang,* Y. Wang* **4725 – 4728**

Direct and Highly Selective Conversion of Synthesis Gas into Lower Olefins: Design of a Bifunctional Catalyst Combining Methanol Synthesis and Carbon–Carbon Coupling



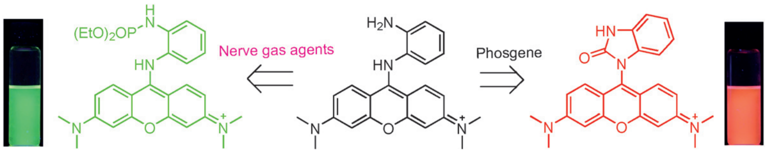
It's a gas: Syngas can be directly converted into C_2–C_4 olefins with a selectivity of 74 % at 673 K over a bifunctional catalyst composed of Zr–Zn oxide for methanol synthesis and SAPO-34 for selective C–C coupling. The control of the hydrogenation ability of the two components and their integration manner play crucial roles in obtaining high C_2–C_4 olefin selectivity.

VIP

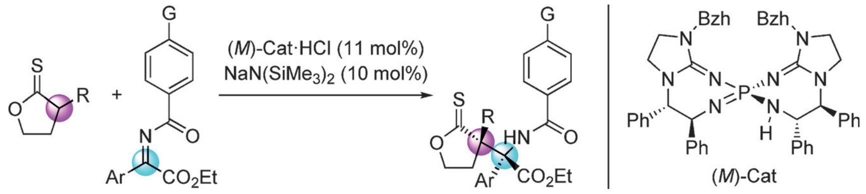
Sensors

X. Zhou, Y. Zeng, C. Liyan, X. Wu,* J. Yoon* **4729 – 4733**

A Fluorescent Sensor for Dual-Channel Discrimination between Phosgene and a Nerve-Gas Mimic



Getting the green light: An accurate and safe fluorescent sensor was developed for real-time monitoring of the nerve-agent mimic diethyl chlorophosphate (DCP) and phosgene gas in a discriminatory manner. The sensor is nonfluorescent; reaction with phosgene results in cyclization to form a red-light-emitting molecule, with DCP a green-light-emitting compound is formed.



It's a superbase: A chiral bis(guanidino)iminophosphorane catalyzes an asymmetric direct Mannich-type reaction of α-iminophenylacetate esters with thionolactones, bearing a substituent at the α-position, as a less acidic pronucleophile. The reaction affords densely functionalized amino-acid derivatives having vicinal quaternary stereogenic centers, one of which is an all-carbon quaternary stereogenic center, in good yield with high diastereo- and enantioselectivities. Bzh = benzhydryl.

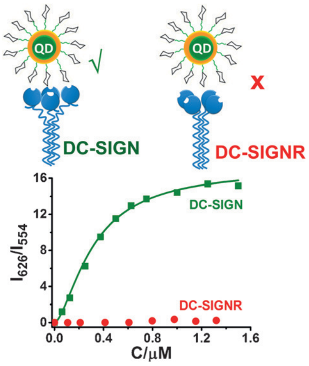
Asymmetric Catalysis

T. Takeda, A. Kondoh,
M. Terada* ______________ **4734 – 4737**

Construction of Vicinal Quaternary Stereogenic Centers by Enantioselective Direct Mannich-Type Reaction Using a Chiral Bis(guanidino)iminophosphorane Catalyst

---

Glycoconjugates: Compact, dense polyvalent mannose-capped quantum dots (QDs) have been prepared by a highly efficient ligand exchange approach. The quantum dots have been successfully employed to probe multivalent interactions of HIV/Ebola receptors (DC-SIGN and DC-SIGNR) using a rapid, sensitive, ratiometric readout strategy based on Förster resonance energy transfer.



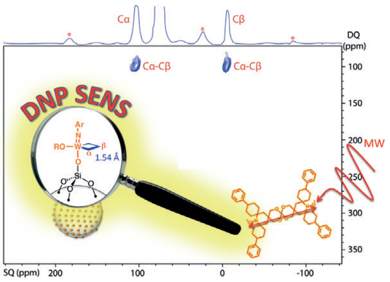
Quantum Dots

Y. Guo,* C. Sakonsinsiri, I. Nehlmeier,
M. A. Fascione, H. Zhang, W. Wang,
S. Pöhlmann, W. B. Turnbull,
D. Zhou* ______________ **4738 – 4742**

Compact, Polyvalent Mannose Quantum Dots as Sensitive, Ratiometric FRET Probes for Multivalent Protein–Ligand Interactions

Back Cover

Making SENS of a structure: Dynamic nuclear polarization surface-enhanced solid-state NMR spectroscopy (DNP SENS) was used to investigate the catalytic intermediates of a well-defined tungsten alkylidene metathesis catalyst, which is present in low concentration at the surface of a silica support. The increase in NMR signal sensitivity permits determination of C–C connectivity and distance measurements, by a combination of 1D and 2D NMR techniques, on only a minute amount of surface sites.



NMR Spectroscopy

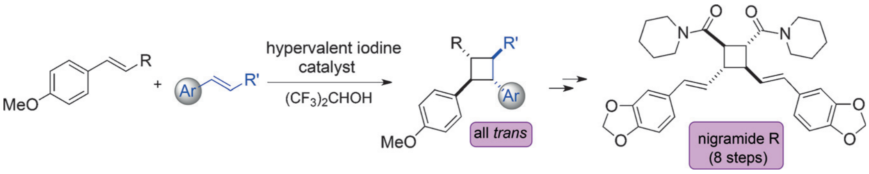
T. C. Ong, W.-C. Liao, V. Mougel, D. Gajan,
A. Lesage, L. Emsley,
C. Copéret* ______________ **4743 – 4747**

Atomistic Description of Reaction Intermediates for Supported Metathesis Catalysts Enabled by DNP SENS

Cyclization

I. Colomer, R. Coura Barcelos,
T. J. Donohoe* ______ **4748 – 4752**

Catalytic Hypervalent Iodine Promoters Lead to Styrene Dimerization and the Formation of Tri- and Tetrasubstituted Cyclobutanes

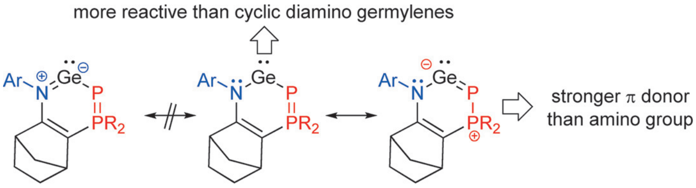


Squared away: The use of catalytic quantities of hypervalent iodine reagents (phenyliodine diacetate or Dess–Martin periodinane) allows the rapid and stereoselective formation of cyclobutanes under very mild reaction conditions. The presence of a fluorinated solvent is essential for the success of these reactions, which form unsymmetrical tri- and tetrasubstituted cyclobutanes through a highly diastereoselective heterodimerization process involving two different alkenes.

Main-Group Chemistry

N. Del Rio, A. Baceiredo,*
N. Saffon-Merceron, D. Hashizume,
D. Lutters, T. Müller,
T. Kato* ______ **4753 – 4758**

A Stable Heterocyclic Amino(phosphanylidene-σ^4-phosphorane) Germylene

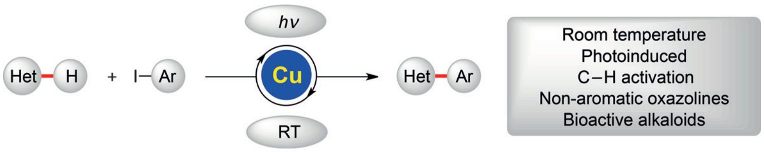


'Germs' of a different type: A stable heterocyclic germylene, in which the divalent germanium atom lies between a nitrogen atom and a phosphanylidene phosphorane group, was synthesized. Experimental and theoretical studies revealed the peculiar effect of the phosphanylidene phosphorane substituent, which presents π-donor abilities stronger than that of amino groups.

Photocatalysis

F. Yang, J. Koeller,
L. Ackermann* ______ **4759 – 4762**

Photoinduced Copper-Catalyzed C–H Arylation at Room Temperature



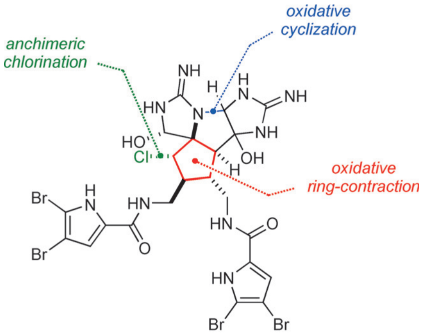
Copper light: Room-temperature C–H arylations of heteroarenes were accomplished with inexpensive copper compounds by photoinduced catalysis. The expedient copper catalysis leads to site-selective C–H arylations of non-aromatic oxazolines under mild reaction conditions, and provides step-economical access to the alkaloid natural products balsoxin and texamine.

Total Synthesis

Z. Ma, X. Wang, Y. Ma,
C. Chen* ______ **4763 – 4766**

Asymmetric Synthesis of Axinellamines A and B

From start to end: Axinellamines A and B are two dimeric pyrrole–imidazole alkaloids that have unusually high nitrogen and halogen atom contents. An asymmetric synthesis of these structurally complex natural antibiotics is described.

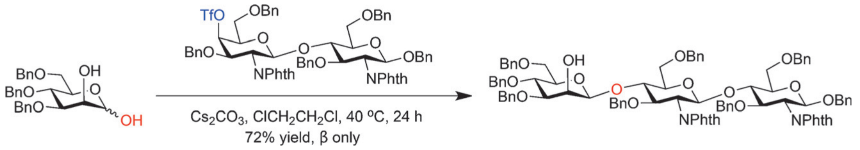


Axinellamine A/B

Glycosylation

H. Nguyen, D. Zhu, X. Li,* J. Zhu* ______ 4767 – 4771

Stereoselective Construction of β-Mannopyranosides by Anomeric *O*-Alkylation: Synthesis of the Trisaccharide Core of *N*-linked Glycans



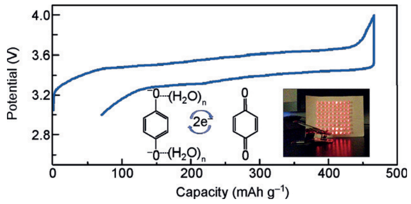
Lactol in control: The title reaction is believed to occur under synergistic control of a kinetic anomeric effect and metal chelation. The presence of a conformationally flexible C6 oxygen atom in the lactol is required for the reaction to be efficient, probably due to its chelation with cesium ion. This glycosylation method was successfully utilized for the synthesis of the trisaccharide core of complex *N*-linked glycans.

Sustainable Chemistry

Y. Ding, G. Yu* ______ 4772 – 4776

A Bio-Inspired, Heavy-Metal-Free, Dual-Electrolyte Liquid Battery towards Sustainable Energy Storage

Inside Cover

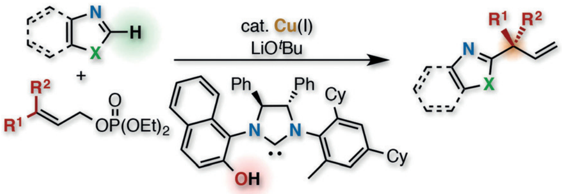


Versatile energy-storage devices: The use of metal-free redox-active organic materials is promising for the development of environmental-friendly, cost-effective, and sustainable energy-storage devices. As hydroquinone can be extracted from biomass directly, using such a bio-inspired organic compound in batteries enables access to green and sustainable energy-storage technology.

Asymmetric Catalysis

H. Ohmiya,* H. Zhang, S. Shibata, A. Harada, M. Sawamura* 4777 – 4780

Construction of Quaternary Stereogenic Carbon Centers through Copper-Catalyzed Enantioselective Allylic Alkylation of Azoles

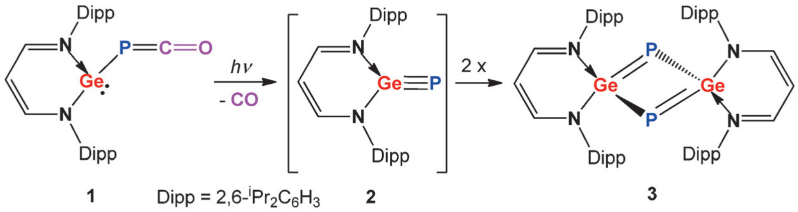


Branch out: The title reaction proceeds with γ,γ-disubstituted primary allylic phosphates and a new chiral N-heterocyclic carbene ligand bearing a naphtholic hydroxy group. The reaction occurs with excellent branch regioselectivity and high enantioselectivity, thus forming a controlled all-carbon quaternary stereogenic center at the position α to the heteroaromatic ring.

Main-Group Chemistry

S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess* ______ 4781 – 4785

From a Phosphaketenyl-Functionalized Germylene to 1,3-Digerma-2,4-diphosphacyclobutadiene

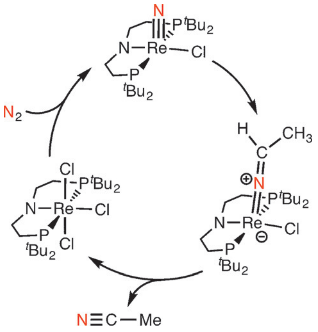


Elusive $Ge\equiv P$: A 4π-electron resonance-stabilized 1,3-digerma-2,4-diphosphacyclobutadiene derivative [$L^H{}_2Ge_2P_2$] (**3**; L^H = CH[CHN(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]), could be synthesized, isolated, and structurally characterized. This compound resulted from the phosphaketenyl-functionalized germylene [$L^HGe(P{=}C{=}O)$] (**1**) through photolytic release of CO and subsequent head-to-tail dimerization of the presumed phosphagermyne intermediate, [$L^HGe\equiv P$] (**2**).

Nitrogen Fixation

I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider* ___ 4786 – 4789

Conversion of Dinitrogen into Acetonitrile under Ambient Conditions

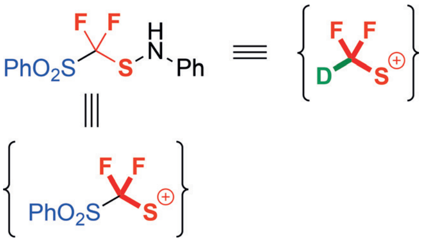


If it's broke, fix it: In contrast to synthetic NH_3 synthesis, the catalytic conversion of N_2 with concomitant C–N bond formation into organic products remains unknown and stoichiometric examples are scarce. Several routes for the rhenium mediated synthesis of acetonitrile at ambient conditions via N_2 splitting and alkylation are now possible, leading up to a full synthetic cycle in three steps with more than 50% overall yield.

Fluorinating Reagents

E. Ismalaj, D. Le Bars, T. Billard* ___ 4790 – 4793

Direct Electrophilic (Benzenesulfonyl)Difluoromethylthiolation with a Shelf-Stable Reagent

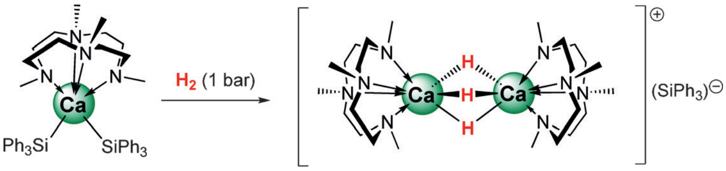


Chameleon-like reactivity: (Benzenesulfonyl)difluoromethanesulfenamide was developed as a new, shelf-stable reagent for the introduction of the $PhSO_2CF_2S$ group into organic molecules (see scheme). The versatility of the $PhSO_2$ moiety also provides an entry into reductive deuterations.

Main-Group Chemistry

V. Leich, T. P. Spaniol, L. Maron,* J. Okuda* ___ 4794 – 4797

Molecular Calcium Hydride: Dicalcium Trihydride Cation Stabilized by a Neutral NNNN-Type Macrocyclic Ligand

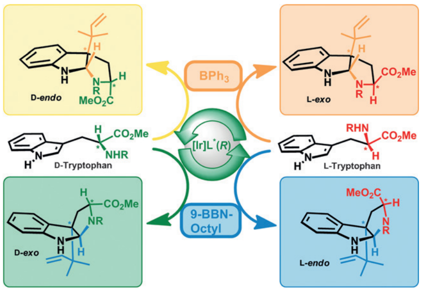


H,H,H-held together: Hydrogenolysis of the bis(triphenylsilyl)calcium complex $[Ca(Me_4TACD)(SiPh_3)_2]$ gave the cationic dinuclear calcium hydride $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ that undergoes fast deuteration.

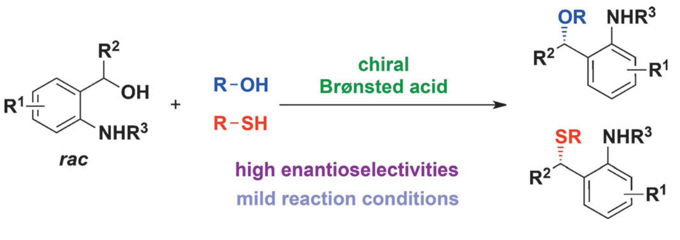
Indole Prenylation

J. M. Müller, C. B. W. Stark* 4798 – 4802

Diastereodivergent Reverse Prenylation of Indole and Tryptophan Derivatives: Total Synthesis of Amauromine, Novo-amauromine, and *epi*-Amauromine



Asymmetric prenylation: A regio- and stereoselective reverse prenylation of indole and tryptophan derivatives is presented. All four possible stereoisomers are accessible through this iridium-catalyzed reaction. The stereoselectivity is controlled by a chiral phosphoramidite ligand in combination with an achiral borane additive and can be switched by changing the nature of the borane.



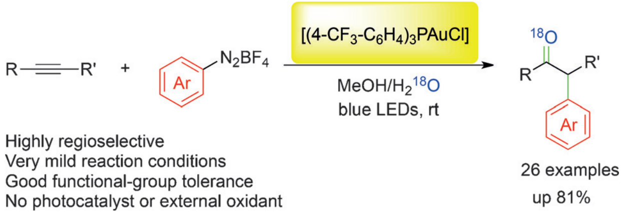
Take two: An enantioselective addition of thiols and alcohols to aza-*ortho*-quinone methides, starting from diaryl methanols, has been developed. The asymmetric oxa- and sulfa-Michael additions proceed under mild reaction conditions in the presence of chiral phosphoric acids to furnish the corresponding adducts with excellent yields and enantioselectivities.

Organocatalysis

A. Chatupheeraphat, H.-H. Liao, S. Mader, M. Sako, H. Sasai, I. Atodiresei, M. Rueping* ———— 4803 – 4807

Asymmetric Brønsted Acid Catalyzed Substitution of Diaryl Methanols with Thiols and Alcohols for the Synthesis of Chiral Thioethers and Ethers

---



Visible-light irradiation enables the gold-catalyzed intermolecular difunctionalization of alkynes with aryl diazonium salts for the formation of α-aryl ketones in good yields. This transformation represents a rare example of gold(I)/gold(III) redox catalysis without a photosensitizer or the need for an external oxidant.

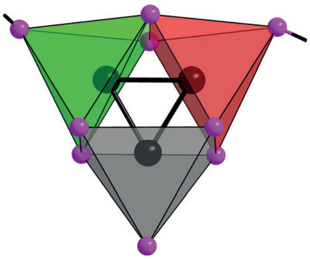
Photochemistry

VIP

L. Huang, M. Rudolph, F. Rominger, A. S. K. Hashmi* ———— 4808 – 4813

Photosensitizer-Free Visible-Light-Mediated Gold-Catalyzed 1,2-Difunctionalization of Alkynes

---

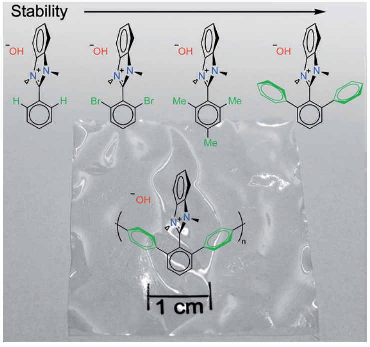


A halide exchange reaction between WCl_6 and SiI_4 yields a new stable tungsten iodide W_3I_{12} ($W_3I_8 \cdot 2I_2$) with the $[W_3I_8]$ cluster (see picture), which can be used in the synthesis of other tungsten iodides. The synthesis and the structure and bonding situation of compounds with this new trinuclear cluster are presented.

Tungsten Iodide

M. Ströbele, C. Castro, R. F. Fink, H.-J. Meyer* ———— 4814 – 4817

A Facile Method for the Synthesis of Binary Tungsten Iodides



It takes backbone: Through a novel synthetic pathway, pendant benzimidazolium groups attached to a poly(phenylene) backbone, which acts as the sterically protecting group, produces the most alkaline-stable polybenzimidazolium to date. Crystal structures and DFT calculations of model compounds are used to explain the observed alkaline stability.

Alkaline-Stable Benzimidazolium

VIP

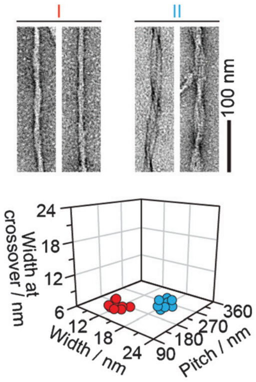
A. G. Wright, T. Weissbach, S. Holdcroft* ———— 4818 – 4821

Poly(phenylene) and *m*-Terphenyl as Powerful Protecting Groups for the Preparation of Stable Organic Hydroxides

Amyloid Fibrils

K. Annamalai, K.-H. Gührs, R. Koehler, M. Schmidt, H. Michel, C. Loos, P. M. Gaffney, C. J. Sigurdson, U. Hegenbart, S. Schönland, M. Fändrich* ____ **4822 – 4825**

Polymorphism of Amyloid Fibrils In Vivo



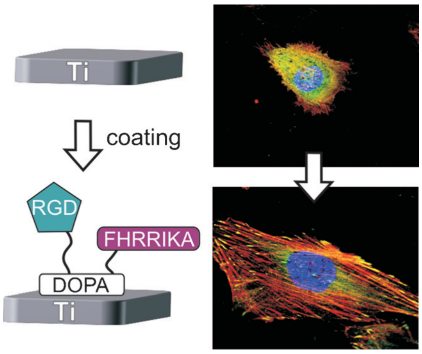
The structural polymorphism of amyloid fibrils is shown in organs of individual patients or diseased animals. The self-assembly process of polypeptide chains in vivo as well as in vitro thus probably follows similar chemical principles, resulting in structural polymorphism. Picture: TEM image of amyloid fibrils and a graph of structure parameters.

Cell Adhesion

M. Pagel, R. Hassert, T. John, K. Braun, M. Wießler, B. Abel, A. G. Beck-Sickinger* ____ **4826 – 4830**

Multifunctional Coating Improves Cell Adhesion on Titanium by using Cooperatively Acting Peptides

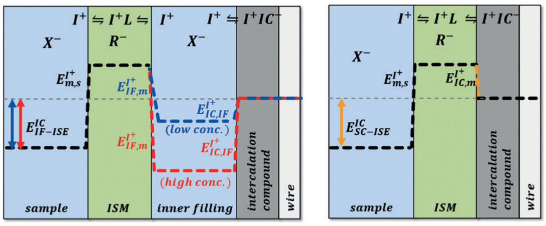
Let's stick together: An efficient on-resin combination of a Diels–Alder reaction with inverse electron demand and a Cu^I catalyzed azide–alkyne cycloaddition is used to link a stable and affine TiO_2-binding peptide to two cell adhesive motifs. The multifunctional construct improved the cell adhesion of osteoblast-like cells through the cooperative action of the peptides. DOPA = L-3,4-dihydroxylphenylalanine.



Ion-Selective Electrodes

Y. Ishige, S. Klink, W. Schuhmann* ____ **4831 – 4835**

Intercalation Compounds as Inner Reference Electrodes for Reproducible and Robust Solid-Contact Ion-Selective Electrodes



For reference: Solid-contact ion-selective electrodes require inner reference electrodes with defined interface potentials. Using intercalation compounds, such as $LiFePO_4$, highly reproducible and stable ion-selective electrodes can be fabricated for the clinical analysis of blood electrolytes.

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).

This article is available online free of charge (Open Access).

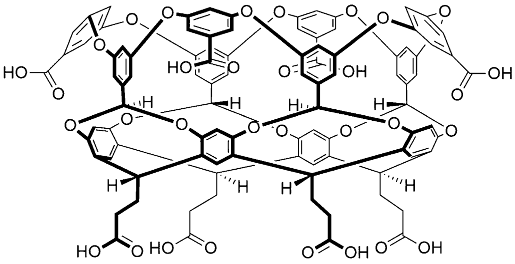
This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

There is an error in the structure of the cavitand receptor **19** in Figure 7 of this Review. The correct structure is shown below. The authors apologize for this error.



19

Anion Recognition in Water: Recent Advances from a Supramolecular and Macromolecular Perspective

M. J. Langton, C. J. Serpell,*
P. D. Beer* ______ **1974–1987**

Angew. Chem. Int. Ed. **2016**, *55*

DOI: 10.1002/anie.201506589

Angewandte Corrigendum

In the acknowledgements of this communication the Swiss National Science Foundation (SNSF) funding number was incorrectly written. Instead of the ETH internal project number (2-77204-14), the publically available SNSF project number 200021-156107 should be included as the funding source.

Furthermore, in Figure S8 in the Supporting Information, the legend denotes fresh catalysts by solid lines and used catalysts by dashed lines (p. 10). It should be vice versa, as it is correctly described in the text referring to Figure S8 in the main manuscript and shown in Figure 3 c.

The authors sincerely apologize for these mistakes which do not affect the validity of any data or conclusions reported in the manuscript or the Supporting Information.

Oxychlorination–Dehydrochlorination Chemistry on Bifunctional Ceria Catalysts for Intensified Vinyl Chloride Production

M. Scharfe, P. A. Lira-Parada,
V. Paunović, M. Moser, A. P. Amrute,
J. Pérez-Ramírez* ______ **3068–3072**

Angew. Chem. Int. Ed. **2016**, *55*

DOI: 10.1002/anie.201510903