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:

*R. Rose, S. Erdmann, S. Bovens, A. Wolf, M. Rose, S. Hennig, H. Waldmann, C. Ottmann**
Identification and Structure of Small-Molecule Stabilizers of 14-3-3 Protein–Protein Interactions

*A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein**
A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica

*M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück, H. Marbach**
Electrons as "Invisible Ink"! Fabrication of Nanostructures by Local Electron Beam Induced Activation of SiO_x

*A. Takaoka, L. C. H. Gerber, J. C. Peters**
Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals

*J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao**
Single Fused Gene Approach to Photo-Switchable and Fluorescent Biliproteins

D. Sišak, L. B. McCusker, G. Zandomeneghi, B. Meier,* D. Bläser, R. Boese,* W. B. Schweizer, R. Gilmour, J. D. Dunitz**
The Crystal Structure of Ribose – At Last!

Y. Sohma, Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent**
Design and Folding of [GluA4(OβThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

*M. W. Powner, J. D. Sutherland**
Phosphate-mediated Interconversion of Ribo- and Arabino-configured Prebiotic Nucleotide Intermediates

Author Profile

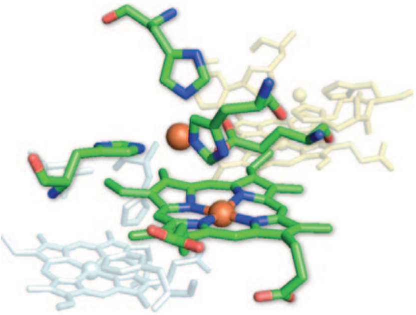
"The biggest problem that scientists face is funding and public recognition of the importance of basic research. If I could be anyone for a day, I would be the finance minister of our country. This would be a marvelous opportunity to be very generous towards the universities in our country ..."
This and more about David Milstein can be found on page 3866.

Books

Highlights

Bioinorganic Chemistry

How best to mimic a protein: Rational design based on the use of a metalloprotein as the molecular scaffold led to a structural (see picture) and functional model of a metalloenzyme that is difficult to obtain in high yield and for which no crystal structure has been determined. This approach will be useful for the preparation of models of sophisticated functional metal centers that are difficult to prepare by chemical synthesis.



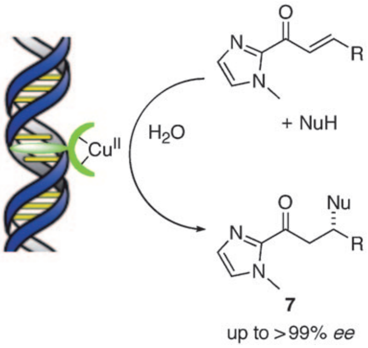
Contents

Minireviews

Asymmetric Catalysis

S. Park, H. Sugiyama* ____ **3870 – 3878**

DNA-Based Hybrid Catalysts for Asymmetric Organic Synthesis



The best of both worlds: The helical chirality of DNA has been exploited in asymmetric catalysis through the use of hybrid catalysts self-assembled from DNA and a metal complex. These catalysts promote a range of asymmetric carbon–carbon and carbon–heteroatom bond-forming reactions in aqueous media. The use of DNA in Lewis acid catalyzed reactions, such as Michael addition reactions (see scheme), led to high stereoselectivity and rate enhancement.

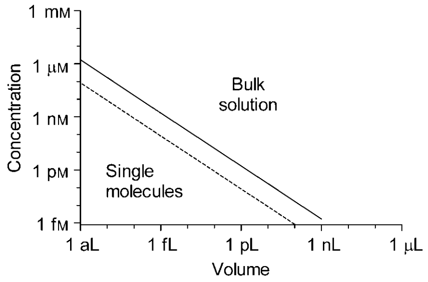
Reviews

Ultrasmall-Scale Analysis

H. H. Gorris,* D. R. Walt* _ **3880 – 3895**

Analytical Chemistry on the Femtoliter Scale

Smaller than small: Reducing the volume of containers leads to the rational limit at which on average one molecule is present per container (solid line in the plot). For femtoliter containers this concentration limit is in the picomolar range. Lower concentrations (dotted line) can be used to increase the probability of observing single-molecule events.



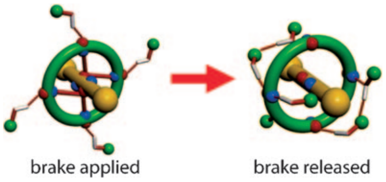
Communications

Molecular Devices

A. M. Rijs, N. Sändig, M. N. Blom,
J. Oomens, J. S. Hannam, D. A. Leigh,*
F. Zerbetto,* W. J. Buma* _ **3896 – 3900**

Controlled Hydrogen-Bond Breaking in a Rotaxane by Discrete Solvation

Controlling a molecular brake: Binding interactions between the thread and the macrocycle of a [2]rotaxane can be tuned in a quasi-continuous manner by adding hydrogen-bond-forming solvent molecules one at a time to an isolated [2]rotaxane molecule. Conformational changes that detach the thread from the macrocycle can be induced controllably, and the system resembles a molecular version of applying and releasing a brake.



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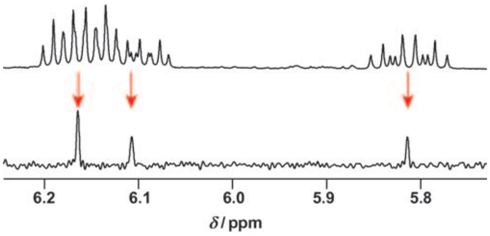
^{1}H NMR without Couplings

J. A. Aguilar, S. Faulkner, M. Nilsson,
G. A. Morris* **3901 – 3903**

Pure Shift ^{1}H NMR: A Resolution of the Resolution Problem?

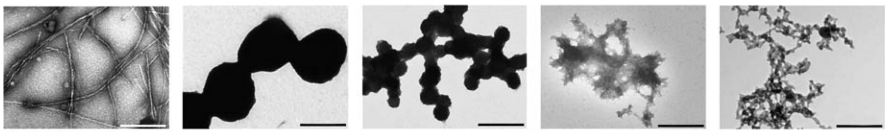


Suppressing multiplet structure in ^{1}H NMR spectra offers a large improvement in spectral resolution (see picture), equivalent to the use of a spectrometer in the GHz range. Such “pure shift” techniques are readily extended to multidimensional methods, for example DOSY.

Protein Aggregates

L. Wang, D. Schubert, M. R. Sawaya,
D. Eisenberg, R. Riek* **3904 – 3908**

Multidimensional Structure–Activity Relationship of a Protein in Its Aggregated States

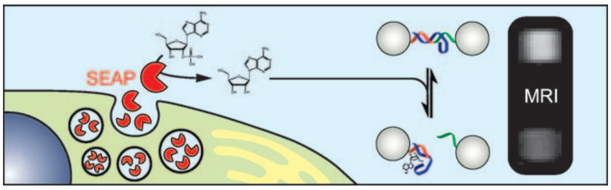


The same, but very different: Diverse chemical, physical, and biological conditions induced the aggregation of a single protein into five structurally distinct protein aggregates (see electron micrographs, scale bars: 500 nm), all of which contained the cross-β-sheet motif. The aggregates differed in their affinity for adenosine-5′-triphosphate, thioflavin T, DNA, and membrane mimics, and in their interference with cell viability.

Imaging Techniques

G. G. Westmeyer, Y. Durocher,
A. Jasanoff* **3909 – 3911**

A Secreted Enzyme Reporter System for MRI



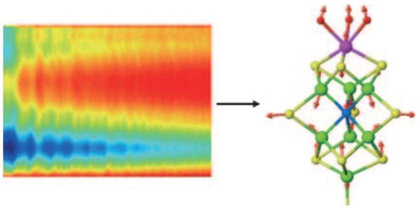
Let's see what comes out: An extracellular enzymatic gene-reporter system for magnetic resonance imaging (MRI) yields strong, reversible contrast changes in response to the expression of secreted alkaline phosphatase (SEAP; see picture). Products of SEAP activity were specifically detected using an iron-oxide-based sensor. The contrast agent is not used up by the enzyme, cell delivery is not required, and multimodal detection is possible.

Pump–Probe Spectroscopy

I. Delfino, G. Cerullo, S. Cannistraro,
C. Manzoni, D. Polli, C. Dapper,
W. E. Newton, Y. Guo,
S. P. Cramer* **3912 – 3915**

Observation of Terahertz Vibrations in the Nitrogenase FeMo Cofactor by Femtosecond Pump–Probe Spectroscopy

Pump it up! The FeMo cofactor (see picture) has resisted characterization by resonance Raman spectroscopy. Impulsive coherent vibrational spectroscopy may be an alternative probe of its dynamics. A 15 fs visible laser pulse pumped the sample to an excited electronic state, and a second < 10 fs pulse probed the change in transmission as a function of the time delay.

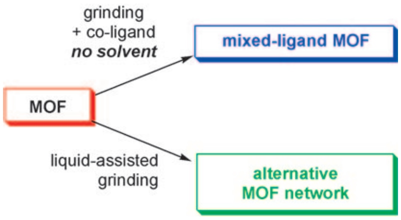


Mechanochemistry

W. Yuan,* T. Friščić,* D. Apperley,
S. L. James* ______________ 3916 – 3919

High Reactivity of Metal–Organic Frameworks under Grinding Conditions: Parallels with Organic Molecular Materials

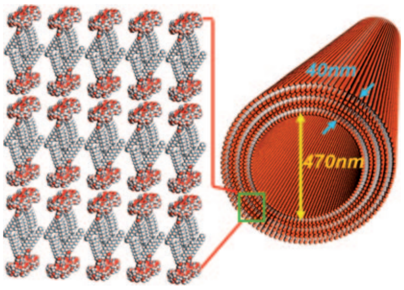
Interconversion made easy: Metal–organic frameworks (MOFs) are surprisingly reactive under grinding conditions and can perform various rearrangements (see picture). In this respect, the results reveal clear parallels between MOFs and organic molecular materials.



Functionalized Nanotubes

Y. Tang, L. P. Zhou, J. X. Li, Q. Luo,
X. Huang, P. Wu, Y. G. Wang, J. Y. Xu,
J. C. Shen, J. Q. Liu* _______ 3920 – 3924

Giant Nanotubes Loaded with Artificial Peroxidase Centers: Self-Assembly of Supramolecular Amphiphiles as a Tool To Functionalize Nanotubes

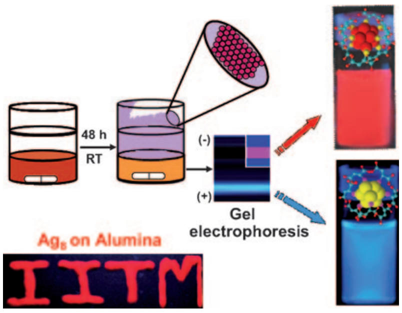


Test tubes: Large-diameter nanotubes have been obtained by direct self-assembly of cyclodextrin-based host–guest superamphiphiles (see picture). By manipulating the surface of the nanotubes with a combination of a molecular-imprinting strategy and self-assembly, the main catalytic components of glutathione peroxidase were fabricated on the nanotube scaffold.

Interfacial Synthesis

T. Udaya Bhaskara Rao,
T. Pradeep* ______________ 3925 – 3929

Luminescent Ag_7 and Ag_8 Clusters by Interfacial Synthesis

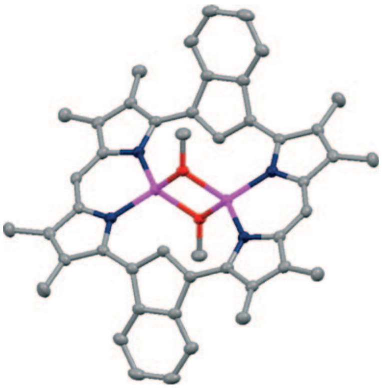


Interfacial etching of silver nanoparticles and separation of the products by polyacrylamide gel electrophoresis afforded Ag_8 and Ag_7 clusters with red and blue-green fluorescence emission, respectively (see picture). The strongly temperature-dependent emission of the clusters suggests potential applications, whilst their facile phase transfer to organic media facilitates further studies.

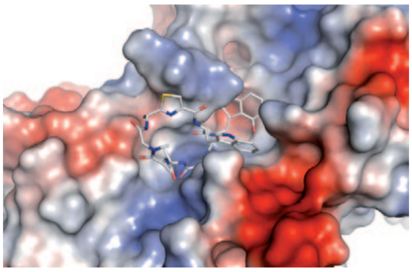
Porphyrinoids

G. R. Peterson, N. Bampos* 3930 – 3933

One-Pot Synthesis of Indene-Expanded Porphyrins



An in situ annulation has been added to the typical reactions which comprise aldehyde–dipyrromethane porphyrinoid syntheses. This reaction provides a novel route to fully conjugated aromatic-expanded porphyrins. The fast stepwise metalation with $Zn(OAc)_2$ provides monometalated and dimetalated species according to the stoichiometry see (picture; N blue, Zn magenta, O red).

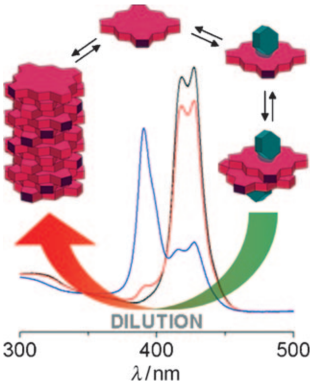


Complex considerations: The proteasome plays a key role in diseases and is thus an appealing drug target. A structural model (see picture) of the proteasome as a complex with argyrin, a cyclic heptapeptide with antitumoral activity, provides a rationale for the high biological activity of this natural product. The structure–activity-relationship data available for the drug are discussed on the basis of this model.

Proteasome Inhibition

B. Stauch, B. Simon, T. Basile,
G. Schneider, N. P. Malek, M. Kalesse,
T. Carlomagno* ———— **3934 – 3938**

Elucidation of the Structure and Intermolecular Interactions of a Reversible Cyclic-Peptide Inhibitor of the Proteasome by NMR Spectroscopy and Molecular Modeling



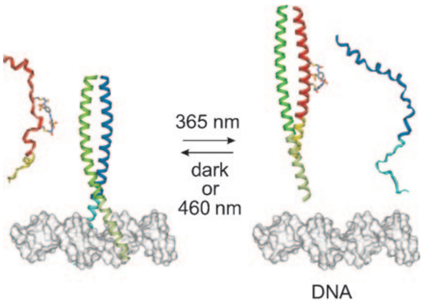
Piggy-back porphyrins: The presence of a Lewis base remarkably affects the cooperative self-assembly of zinc porphyrins. Driven by the susceptibility of the monomer towards the axial ligand, monomer scavenging caused depolymerization of porphyrin aggregates, and dilution caused aggregation by a re-entrant phase transition. Model predictions were validated by dilution experiments.

Porphyrin Aggregation

F. Helmich, C. C. Lee,
M. M. L. Nieuwenhuizen, J. C. Gielen,
P. C. M. Christianen, A. Larsen, G. Fytas,
P. E. L. G. Leclère, A. P. H. J. Schenning,*
E. W. Meijer* ———— **3939 – 3942**

Dilution-Induced Self-Assembly of Porphyrin Aggregates: A Consequence of Coupled Equilibria

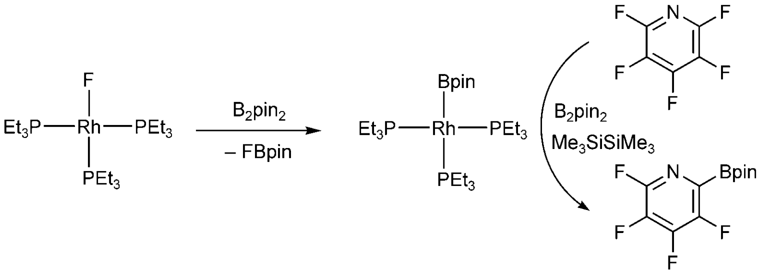
Light switching of the activity of a coiled-coil protein, the AP-1 transcription factor, in living cells was made possible by the introduction of a designed azobenzene-cross-linked dominant negative peptide, XAFosW (red and yellow in the picture). In the dark, XAFosW showed decreased helical content and decreased affinity for target Jun proteins (green); irradiation at 365 nm enhanced helicity and target affinity.



Light-Switchable Proteins

F. Zhang, K. A. Timm, K. M. Arndt,*
G. A. Woolley* ———— **3943 – 3946**

Photocontrol of Coiled-Coil Proteins in Living Cells



C–F bond borylation: A 16-electron rhodium(I)–boryl complex was synthesized by borylation of a rhodium(I)–fluorine complex. The former reacts with benzene or 2,3,5,6-tetrafluoropyridine by C–H activation. A catalytic C–F borylation reaction of pentafluoropyridine was also developed, which uses $[Rh(Bpin)(PEt_3)_3]$ as a catalyst and $Me_3SiSiMe_3$ as a solvent. pin = pinacol.

Boryl Complexes

M. Teltewskoi, J. A. Panetier,
S. A. Macgregor,* T. Braun* **3947 – 3951**

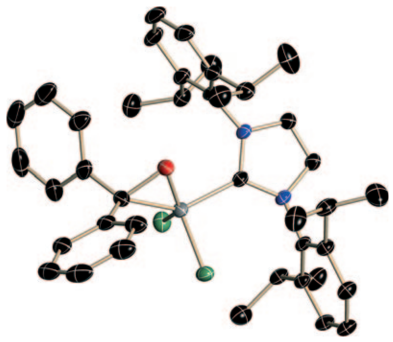
A Highly Reactive Rhodium(I)–Boryl Complex as a Useful Tool for C–H Bond Activation and Catalytic C–F Bond Borylation

Silicon Chemistry

R. S. Ghadwal, S. S. Sen, H. W. Roesky,*
M. Granitzka, D. Kratzert, S. Merkel,
D. Stalke* ______________ **3952–3955**

Convenient Access to Monosilicon Epoxides with Pentacoordinate Silicon

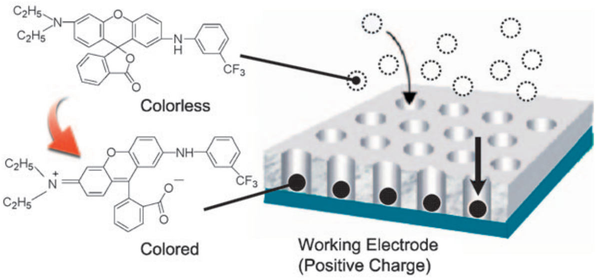
From intermediate to stable molecule: Stable monosilicon epoxides with pentacoordinate silicon were prepared for the first time by [2+1] cycloaddition reactions of Lewis base stabilized chlorosilylenes with ketones. Molecular structures of these compounds with SiOC three-membered rings were established by X-ray diffraction studies (e.g., see picture; N blue, O red, Cl green).



Mesoporous Materials

W. Weng,* T. Higuchi, M. Suzuki,
T. Fukuoka, T. Shimomura, M. Ono,
L. Radhakrishnan, H. Wang, N. Suzuki,
H. Oveisi, Y. Yamauchi* ___ **3956–3959**

A High-Speed Passive-Matrix Electrochromic Display Using a Mesoporous TiO_2 Electrode with Vertical Porosity

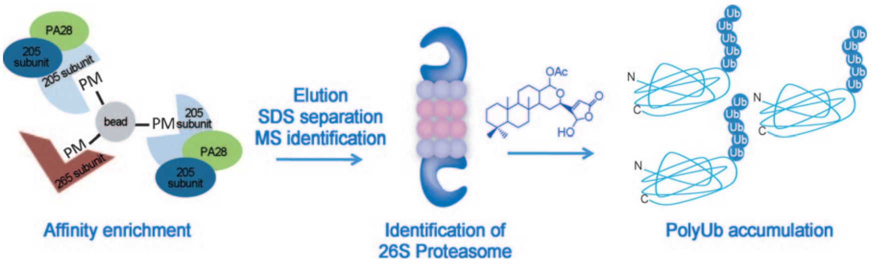


On display: A high-speed and high-quality passive-matrix electrochromic display (ECD) is constructed from a leuco dye and a TiO_2 nanoporous electrode (see picture). The vertical pores prevent the drifting of the colored dye molecules, leading to a clear image at high driving speeds. With full-color features, this kind of ECD promises to be a competitive candidate for a reflective electric display.

Chemical Biology

L. Margarucci, M. C. Monti, A. Tosco,
R. Riccio, A. Casapullo* ___ **3960–3963**

Chemical Proteomics Discloses Petrosaspongiolide M, an Anti-inflammatory Marine Sesterterpene, as a Proteasome Inhibitor

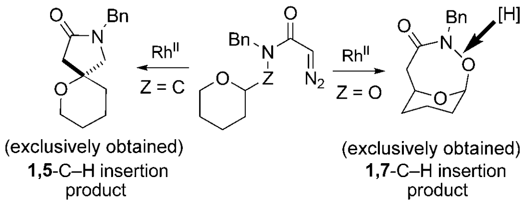


Gone fishing: Petrosaspongiolide M (PM), a marine γ-hydroxybutenolide sesterterpenoid, was efficiently immobilized on a solid support to selectively bind its macromolecular targets in a macrophage cell lysate. The proteasome machinery was identified as its most important partner.

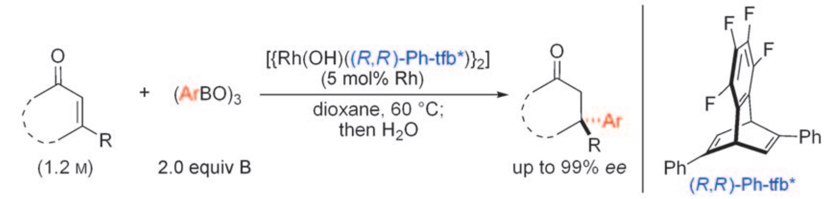
C–H Insertion

J. Wang, B. Stefane, D. Jaber, J. A. I. Smith,
C. Vickery, M. Diop,
H. O. Sintim* ______________ **3964–3968**

Remote C–H Functionalization: Using the N–O Moiety as an Atom-Economical Tether to Obtain 1,5- and the Rare 1,7-C–H Insertions



Dr. N–O: Rhodium-catalyzed intramolecular C–H insertion with diazocompounds, which are tethered by alkoxyamines, afforded 1,5- and the rare 1,7-insertion products (see scheme; Bn = benzyl). The resulting N–O tether is unaffected under the C–H insertion reaction conditions and it can be readily cleaved or transformed into various functionalities. The reduction of the N–O moiety controls acyclic stereochemistry.

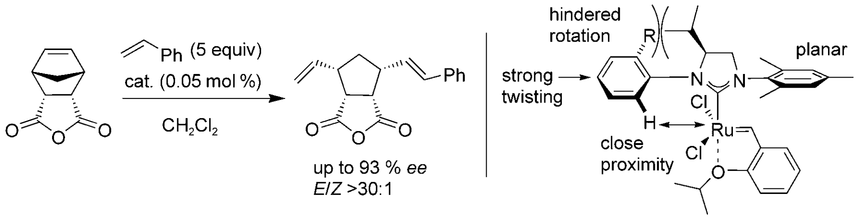


Lock, Stock and Two Smoking Barrelenes: The rhodium-catalyzed 1,4-addition of readily available arylboronic acid anhydrides to simple β,β-disubstituted α,β-unsaturated ketones creates quaternary carbon stereocenters with high enantiomeric excesses using a chiral tetrafluorobenzobarrelene ligand.

Asymmetric Catalysis

R. Shintani,* M. Takeda, T. Nishimura,
T. Hayashi* ______________ **3969 – 3971**

Chiral Tetrafluorobenzobarrelenes as Effective Ligands for Rhodium-Catalyzed Asymmetric 1,4-Addition of Arylboroxines to β,β-Disubstituted α,β-Unsaturated Ketones



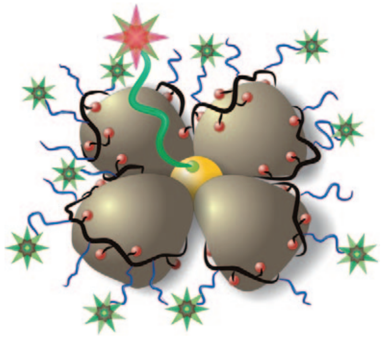
Single (substitution) is better: New chiral ruthenium metathesis (pre)catalysts with a monosubstituted carbon atom in the N-heterocyclic carbene ligand are highly stable in solution, initiate easily, show very high enantioselectivity and excellent *E* selectivity in asymmetric ring-opening cross-metathesis (see scheme).

Asymmetric Catalysis

S. Tiede, A. Berger, D. Schlesiger, D. Rost,
A. Lühl, S. Blechert* ________ **3972 – 3975**

Highly Active Chiral Ruthenium-Based Metathesis Catalysts through a Monosubstitution in the N-Heterocyclic Carbene

Flower power: A convenient strategy for preparing core-tunable multicomponent Au@MnO nanocrystals has been developed. The magnetic nanoflowers are not only efficient as cargo-specific carriers but also have excellent fluorescent properties resulting from fluorophors bound to the Au and MnO domains.

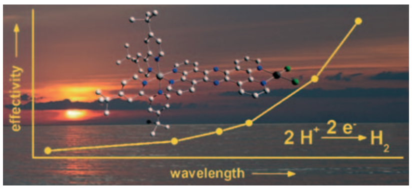


Functional Nanomaterials

T. D. Schladt, M. I. Shukoor, K. Schneider,
M. N. Tahir, F. Natalio, I. Ament, J. Becker,
F. D. Jochum, S. Weber, O. Köhler,
P. Theato, L. M. Schreiber, C. Sönnichsen,
H. C. Schröder, W. E. G. Müller,
W. Tremel* ______________ **3976 – 3980**

Au@MnO Nanoflowers: Hybrid Nanocomposites for Selective Dual Functionalization and Imaging

The color of the incident light determines the efficiency of the hydrogen evolution mediated by a supramolecular photocatalyst. This finding demonstrates the importance of the Franck–Condon point in artificial photosynthesis systems and should have an impact on their design.



Water Splitting

S. Tschierlei, M. Karnahl, M. Presselt,
B. Dietzek, J. Guthmuller, L. González,
M. Schmitt, S. Rau,*
J. Popp* ______________ **3981 – 3984**

Photochemical Fate: The First Step Determines Efficiency of H$_2$ Formation with a Supramolecular Photocatalyst

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

Corrigendum

A Single Residue Influences the Reaction Mechanism of Ammonia Lyases and Mutases

S. Bartsch
U. T. Bornscheuer* — **3362–3365**

Angew. Chem. Int. Ed. **2009**, *48*

DOI 10.1002/anie.200900337

While reanalyzing the data on a mutant of the phenylalanine ammonia lyase from *Petroselinum crispum* (*pc*PAL), the authors of this Communication (DOI: 10.1002/anie.200900337) observed confusion between sequence analysis and protein expression. Hence, the kinetic values provided for this *pc*PAL-Glu484Asn mutant are not correct. The corrected values are given in Table 1 of this Corrigendum.

Table 1 of this Corrigendum: Corrected kinetic constants for the *pc*PAL Glu484Asn mutant.

Enzyme	Substrate	K_M [mM]	$k_{cat.}$ [s^{-1}]	k_{cat}/K_M [$s^{-1}\,M^{-1}$]
*pc*PAL E484N	L-Phe	0.22 ± 0.07	0.10 ± 0.010	455
	L-*m*-Tyr	0.11 ± 0.01	0.04 ± 0.015	364
	L-Tyr	0.87 ± 0.39	0.004 ± 0.001	5

However, it must be emphasized, that this correction does not affect the conclusions made in the original Communication. Although the activity of this mutant is significantly lower than reported in the published article, the differences in the kinetic constants of the mutant towards L-*m*-Tyr and L-Phe is still significant (2.5-fold higher $k_{cat.}$ and an increased K_M value). Only very low activity towards L-Tyr was detected, thus explaining the inactivity of the tested double mutant Phe137His-Glu484Asn. This observation underlines the statement given in the article that the differences between PAL and TAL are not exclusively based on two residues but are also influenced by other factors.

Prof. Poppe suggested we cite the following publication instead of reference [13] given in the published Communication.

---

[13] S. Pilbák, A. Tomin, J. Rétey, L. Poppe, *FEBS J.* **2006**, *273*, 1004–1019.