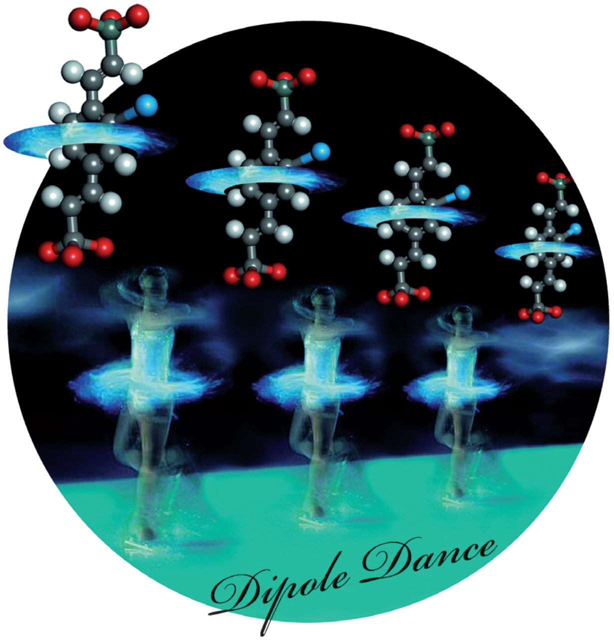
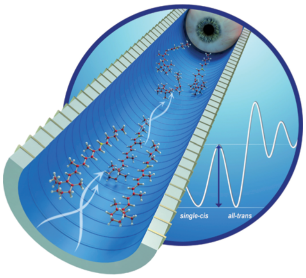
Like dancers on ice ...

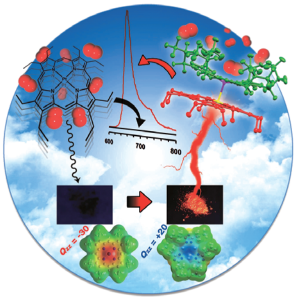


… performing pirouettes, dipolar molecular rotors have been programmed to spin in mesoporous fluorinated organosilica materials. In their Communication on page 4773 ff., A. Comotti, P. Sozzani, et al. report on the fast reorientation of the carbon–fluorine dipole. The relaxation rates obtained by NMR spectroscopy were modulated by the dipole dynamics, which in turn were regulated by I_2 vapor entering the pores.

Isomerization

In their Communication on page 4748 ff., Y. Toker and co-workers report the energy barrier for the isomerization of the retinal protonated Schiff base chromophore and show that it is significantly lower than that within opsin proteins.



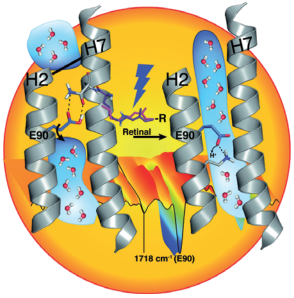


Supramolecular Chemistry

The formation of supramolecular octopus couples from cyclic Ag^I–triazolate trimers with fluorous octopus arms and free or Pt^{II} porphyrins with alkyl chains is described by C. Yang, M. A. Omary et al. in their Communication on page 4842 ff.

Channelrhodopsins

The light-gated ion channel channelrhodopsin-2 is the key protein in optogenetics. In their Communication on page 4953 ff., K. Gerwert et al. elucidate channel opening at a molecular level by using IR spectroscopy and simulations.



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Spotlight on Angewandte's Sister Journals — **4700–4703**

Author Profile

"My biggest motivation is exploring the world of chemistry. I lose track of time when I discuss with my students and 'travel' in the world of chemistry …"
This and more about Jin-Heng Li can be found on page 4704.

Jin-Heng Li — **4704**

News

W. Kunz

A. Company

S. van de Linde

S. Herres-Pawlis

S. M. Huber

Gay-Lussac-Humboldt Prize: W. Kunz — **4705**

Clara Immerwahr Award: A. Company — **4705**

Peter and Traudl Engelhorn Foundation Research Prize: S. van de Linde — **4705**

Bavarian Academy of Sciences and Humanities Prizes: S. Herres-Pawlis and S. M. Huber — **4705**

Books

Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis — Kálmán J. Szabó and Ola F. Wendt — *reviewed by K. Kirchner** — **4706**

Obituaries

Tsutomu Katsuki passed away on October 30, 2014, at the age of 68. His research career focused largely on asymmetric oxidation using metal complexes as catalysts. He developed the use of chiral (salen)manganese(III) catalysts, and also pioneered the use of molecular oxygen as oxidant to achieve high catalytic efficiency with complete stereo- and enantioselectivity.

Tsutomu Katsuki (1946–2014)

K. B. Sharpless,* M. G. Finn,
V. S. Martín ______ **4708**

Highlights

Genome Engineering

A. Rentmeister* ______ **4710 – 4712**

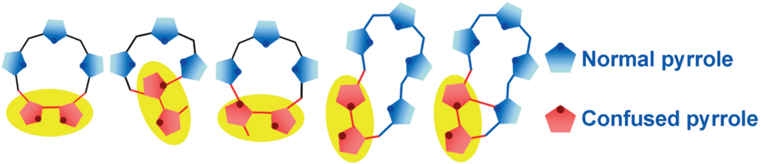
CRISPR Craze Conquers the RNA World: Precise Manipulation of DNA and RNA Based on a Bacterial Defense System

It cuts both ways: The CRISPR/Cas9 genome engineering system has been extended from DNA to RNA. The sequence-specific targeting and cleavage of RNA can be achieved with *S. pyogenes* Cas9–gRNA if an appropriate short single-stranded oligonucleotide, the "PAMmer", is added. This technique could lead to a general approach for sequence-specific RNA manipulation.

Porphyrinoids

F. D'Souza* ______ **4713 – 4714**

Expanded Porphyrins: More Confusion All the Time



Confusion leads to cooperative reactivity: Oxidative ring-closure reactions of oligopyrranes containing two terminal confused pyrroles yield expanded porphyrinoids, which show cooperative reactivity between the directly linked confused pyrroles. These transformations constitute a new method for the synthesis of novel porphyrinoids with unconventional pyrrole linking modes and unique properties.

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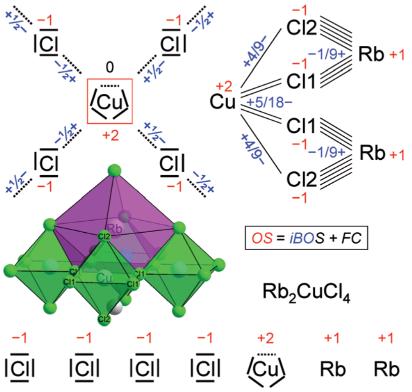
Essays

What is an oxidation state? Oxidation state has defining algorithms but lacks a comprehensive definition. Results of an IUPAC project to find such a definition have recently been published in an extensive Technical Report. A summary in this Essay is illustrated with applications on Lewis, bond-graph, and summary formulas of molecules, ions, or solids, together with the most recent information regarding tricky cases.

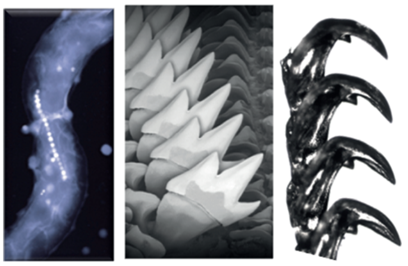


Oxidation State

P. Karen* ———— 4716 – 4726

Oxidation State, A Long-Standing Issue!

Reviews



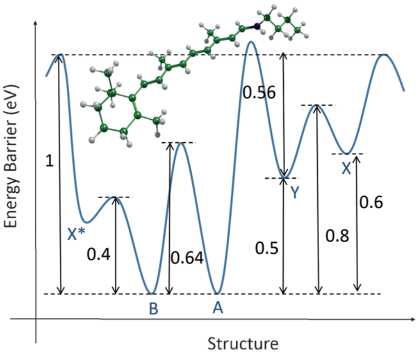
Mineral sorter: Various organisms have a genetic program that enables the controlled formation of a mineral ("biomineralization"). These biominerals offer properties and functionalities that abiotically formed materials, made of the same mineral, usually lack. Recent advances in the understanding iron oxide formation by bacteria and mollusks for their magnetic and mechanical properties are highlighted.

Magnetotactic Bacteria

D. Faivre,* T. U. Godec ———— 4728 – 4747

From Bacteria to Mollusks: The Principles Underlying the Biomineralization of Iron Oxide Materials

Communications



All the better to see you with: The primary step in animal vision is photoisomerization of the retinal protonated Schiff base chromophore. By using two stages of ion mobility spectroscopy (IMS-IMS), the energy barrier for isomerization of the isolated chromophore was measured, and it was shown that it is considerably smaller than the energy barrier within opsin proteins.

Isomerization

J. Dilger, L. Musbat, M. Sheves, A. V. Bochenkova, D. E. Clemmer, Y. Toker* ———— 4748 – 4752

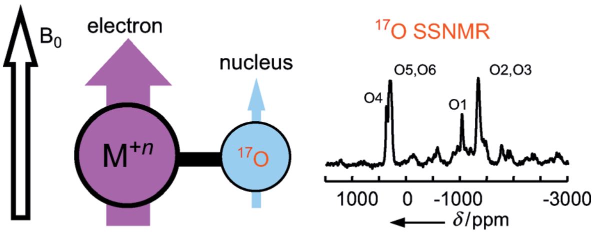
Direct Measurement of the Isomerization Barrier of the Isolated Retinal Chromophore

Frontispiece

NMR Spectroscopy

X. Kong, V. V. Terskikh, R. L. Khade, L. Yang, A. Rorick, Y. Zhang,* P. He, Y. Huang, G. Wu* ———— 4753 – 4757

Solid-State ^{17}O NMR Spectroscopy of Paramagnetic Coordination Compounds

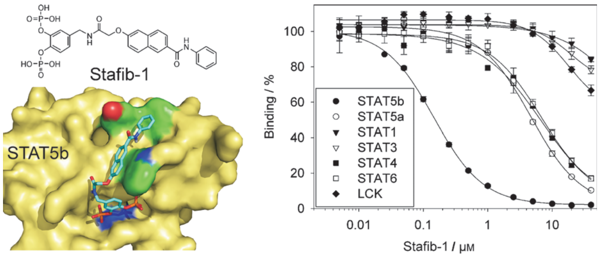


Going paramagnetic! High-quality ^{17}O solid-state NMR spectra were obtained for paramagnetic coordination complexes, even when the oxygen atoms of interest are directly bonded to the paramagnetic metal center.

Protein–Protein Interactions

N. Elumalai, A. Berg, K. Natarajan, A. Scharow, T. Berg* ———— 4758 – 4763

Nanomolar Inhibitors of the Transcription Factor STAT5b with High Selectivity over STAT5a



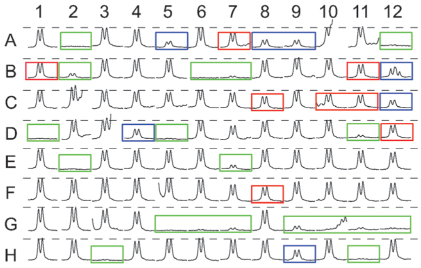
Can you tell them apart? Neither small molecules nor peptides have previously been reported to be able to distinguish between the highly homologous transcription factors STAT5a and STAT5b. Described herein is the natural product-inspired development of Stafib-1, as the first small molecule that can differentiate between STAT5a and STAT5b in vitro and in human tumor cells.

Whole-Cell Screening

J. Ma, Q. Cao, S. M. McLeod, K. Ferguson, N. Gao, A. L. Breeze,* J. Hu* ———— 4764 – 4767

Target-Based Whole-Cell Screening by ^1H NMR Spectroscopy

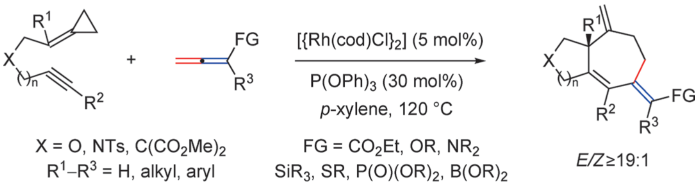
Screening a drug target in living cells can be monitored by ^1H NMR spectroscopy. This approach combines phenotypic and target-based screening technologies to find compounds inhibiting NDM-1 in living *Escherichia coli* cells. A strong NDM-1 inhibitor was identified with a cellular IC_{50} value of 0.51 µM.



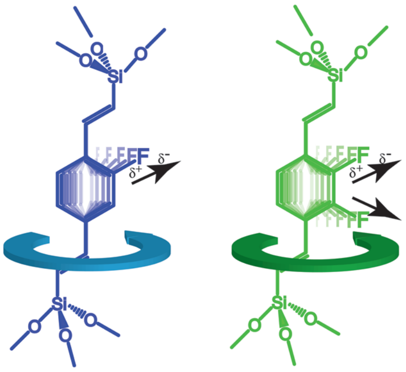
Synthetic Methods

P. A. Evans,* D. E. Negru, D. Shang ———— 4768 – 4772

Rhodium-Catalyzed [(3+2)+2] Carbocyclization of Alkynylidenecyclopropanes with Substituted Allenes: Stereoselective Construction of Tri- and Tetrasubstituted Exocyclic Olefins



At a distance: The development of the title reaction demonstrates that activated and unactivated allenes preferentially undergo carbometalation at the distal terminus to generate tri- and tetrasubstituted exocyclic olefins with a neutral rhodium catalyst. cod = 1,5-cyclooctadiene, Ts = 4-toluenesulfonyl.



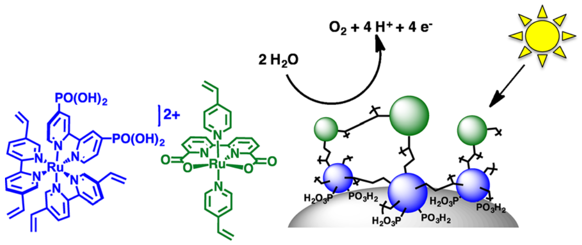
Oriented molecular rotors: Fluorinated molecular rotors (see picture) were engineered in mesoporous hybrid organosilica architectures with crystalline order in their walls. The rotor dynamics was established by magic angle spinning NMR and dielectric measurements, indicating a rotational correlation time as short as 10^{-9} s at 325 K. The dynamics were modulated by I_2 vapors entering the pores.

Porous Materials

S. Bracco, M. Beretta, A. Cattaneo, A. Comotti,* A. Falqui, K. Zhao, C. Rogers, P. Sozzani* ______ 4773 – 4777

Dipolar Rotors Orderly Aligned in Mesoporous Fluorinated Organosilica Architectures

Front Cover



Electropolymerization is used to prepare electrocatalytically and photocatalytically active electrodes for water oxidation. The catalyst studied shows a change in the water oxidation mechanism in the polymerized film as compared to solution. This approach establishes a new method for forming a chromophore–catalyst structure on mesoporous TiO_2 films for use in water-splitting dye-sensitized photoelectrosynthesis cells.

Photoelectrochemistry

D. L. Ashford, B. D. Sherman, R. A. Binstead, J. L. Templeton, T. J. Meyer* ______ 4778 – 4781

Electro-assembly of a Chromophore–Catalyst Bilayer for Water Oxidation and Photocatalytic Water Splitting

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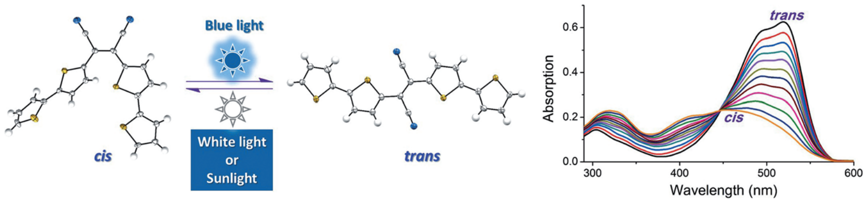

Light switch: A dicyanoethene-based molecular photoswitch operates only through *E*/*Z* photoisomerization that is triggered by visible light (100% *E*→*Z* conversion within minutes). The combination of favorable properties in a single photochromic switch makes it an attractive alternative to the frequently used azobenzenes in numerous photoswitching applications.

Molecular Switches

X. Guo, J. Zhou, M. A. Siegler, A. E. Bragg,* H. E. Katz* ______ 4782 – 4786

Visible-Light-Triggered Molecular Photoswitch Based on Reversible *E*/*Z* Isomerization of a 1,2-Dicyanoethene Derivative

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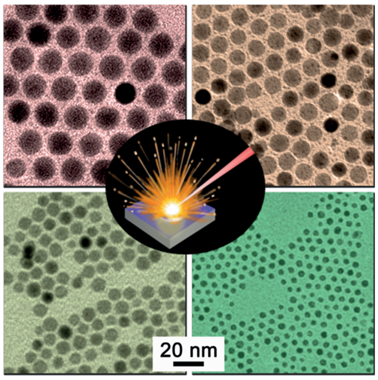


A robust conversion strategy that is free of reducing agents and precursors was developed. This method transforms bulk non-noble metals directly into ligand-protected, size-tailored, highly crystalline monodisperse spherical colloidal metal nanocrystals (NCs). The technique is based on near-IR laser-induced size-selective layer-by-layer surface vaporization. The monodisperse Cd NCs exhibit pronounced deep-UV localized surface plasmon resonance.

Metal Nanocrystals

R.-C. Luo, C. Li, X.-W. Du, J. Yang* ______ 4787 – 4791

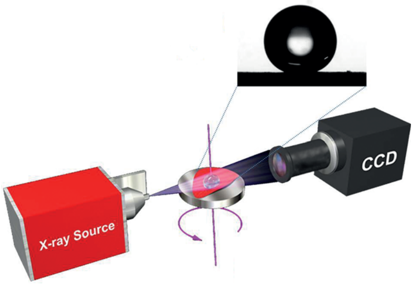
Direct Conversion of Bulk Metals to Size-Tailored, Monodisperse Spherical Non-Coinage-Metal Nanocrystals

Superhydrophobic Surfaces

S. Yang, J. Du, M. Cao, X. Yao, J. Ju, X. Jin, B. Su, K. Liu,* L. Jiang ______ **4792 – 4795**

Direct Insight into the Three-Dimensional Internal Morphology of Solid–Liquid–Vapor Interfaces at Microscale

Wetting behavior: In situ investigations of solid–liquid–vapor interfaces contribute to the improvement of theoretical wetting models and the development of surface and interface sciences. The wetting behavior of solid–liquid–vapor interfaces has been studied quantitatively by X-ray micro-computed tomography (Micro-CT; see picture) at microscale.

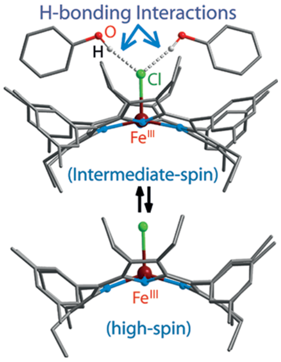


Spin-State Change

D. Sahoo, M. G. Quesne, S. P. de Visser,* S. P. Rath* ______ **4796 – 4800**

Hydrogen-Bonding Interactions Trigger a Spin-Flip in Iron(III) Porphyrin Complexes

Spin control: The electronic structure of a five-coordinate iron(III) porphinato chloride has been found to depend on the presence of hydrogen-bonding interactions, with the iron center switching reversibly between a high ($S=5/2$) and intermediate spin ($S=3/2$) state. Computational calculations clearly support the experimentally assigned spin state.

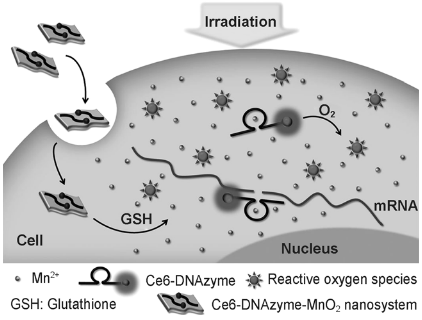


Cancer Therapy

H. Fan, Z. Zhao, G. Yan, X. Zhang, C. Yang, H. Meng, Z. Chen, H. Liu, W. Tan* ______ **4801 – 4805**

A Smart DNAzyme–MnO_2 Nanosystem for Efficient Gene Silencing

Multitasking: A smart carrier for DNAzymes has been developed in which MnO_2 nanosheets are able to enhance cellular uptake of DNAzymes, protect them from endogenous nuclease digestion, and self-generate in situ cofactors (Mn^{2+} ions) in the cell cytoplasm to maintain the catalytic activity of 10–23 DNAzyme for RNA cleavage and gene silencing. Ce6–DNAzyme = chlorin e6-labelled DNAzyme.

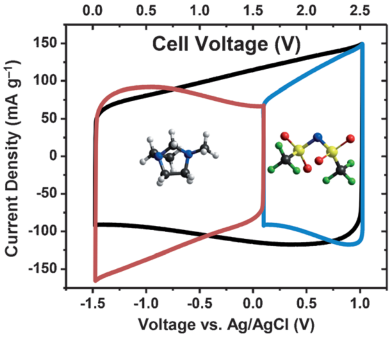


Electrochemistry

K. L. Van Aken, M. Beidaghi, Y. Gogotsi* ______ **4806 – 4809**

Formulation of Ionic-Liquid Electrolyte To Expand the Voltage Window of Supercapacitors

Asymmetric behavior: Using model electrochemical cells based on two identical onion-like carbon electrodes and two different ionic-liquid electrolytes and their mixtures, it was shown that the asymmetric behavior of the electrolyte cation and anion toward the two electrodes (see picture) limits the operating potential window of the cell and therefore its energy density.

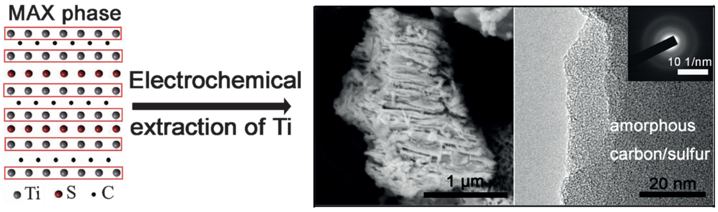


Layered Structures

M.-Q. Zhao, M. Sedran, Z. Ling, M. R. Lukatskaya, O. Mashtalir, M. Ghidiu, B. Dyatkin, D. J. Tallman, T. Djenizian, M. W. Barsoum, Y. Gogotsi* ______ **4810 – 4814**

Synthesis of Carbon/Sulfur Nanolaminates by Electrochemical Extraction of Titanium from Ti_2SC

Inside Cover

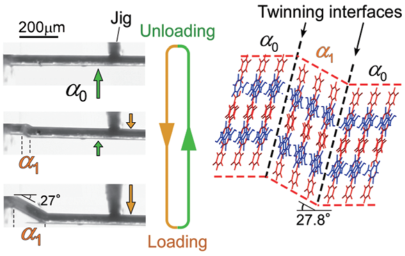


Carbon/sulfur nanolaminates composed of multilayered C/S flakes with predominantly amorphous, and some graphene-like, structures were synthesized by electrochemical extraction of Ti from a Ti_2SC MAX phase. This approach provides a novel method for the room-temperature synthesis of "AX" layered structures by the selective extraction of "M" from the MAX phases.

Organosuperelasticity

S. Takamizawa,* Y. Takasaki **4815 – 4817**

Superelastic Shape Recovery of Mechanically Twinned 3,5-Difluorobenzoic Acid Crystals

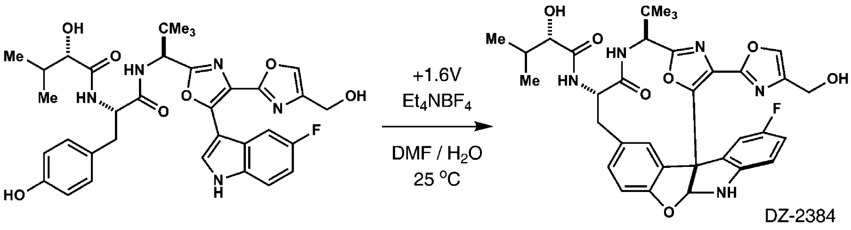


Organosuperelasticity is observed in single crystals of 3,5-difluorobenzoic acid. This elasticity is due to the molecular distortion on the twinning interface, suggesting a new mechanism for superelasticity in molecular materials.

Synthetic Methods

H. Ding, P. L. DeRoy, C. Perreault, A. Larivée, A. Siddiqui, C. G. Caldwell, S. Harran, P. G. Harran* ___ **4818 – 4822**

Electrolytic Macrocyclizations: Scalable Synthesis of a Diazonamide-Based Drug Development Candidate

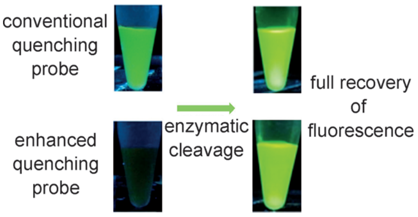


Electrifying chemistry! The core macrolactam of diazonamides can be synthesized electrochemically. This large ring forming dehydrogenation has enabled a concise preparation of DZ-2384, a refined analogue of diazonamide A slated for clinical development as a cancer therapeutic.

Self-Assembly

C. Ren, H. Wang, D. Mao, X. Zhang, Q. Fengzhao, Y. Shi, D. Ding, D. Kong, L. Wang, Z. Yang* ________ **4823 – 4827**

When Molecular Probes Meet Self-Assembly: An Enhanced Quenching Effect

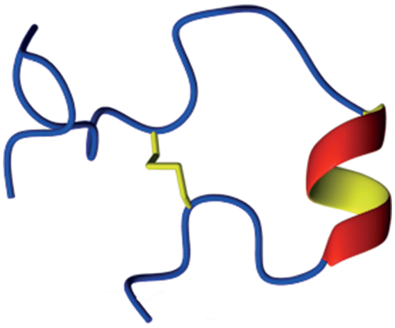


The incorporation of one or two fluoro phenylalanine groups (^{f}Fs) in conventional quenched probes can lead to the production of self-assembled probes with enhanced quenching effects. The self-assembled probes possess similar enzyme recognition and fluorescence recovery properties. This provides a useful strategy for the design of molecular probes with good fluorescence turn-on properties.

Glycopeptides

T. Reeks,* A. Jones, A. Brust, S. Sridharan,
L. Corcilius, B. L. Wilkinson,
M. Thaysen-Andersen, R. J. Payne,
R. M. Kini, N. L. Daly,
P. F. Alewood* ______ **4828 – 4831**

A Defined α-Helix in the Bifunctional *O*-Glycosylated Natriuretic Peptide TcNPa from the Venom of *Tropidechis carinatus*

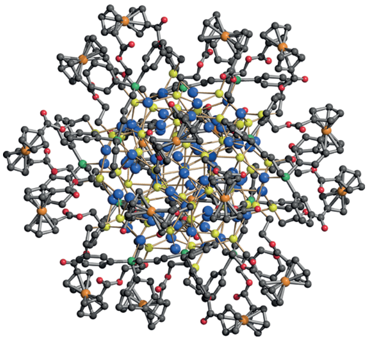


Snake toxin: A novel natriuretic peptide (NP) from *Tropidechis carinatus* contains an *O*-linked Gal-β(1-3)-GalNAc mucin-type glycan on the C-terminal threonine 27 residue. The secondary structure is in the form of an α-helix and has been identified for the first time from NMR analysis. Both synthesized glycosylated and nonglycosylated variants display bifunctional activity with NPR-A and NPR-B receptors.

Cluster Compounds

Y. Liu, B. Khalili Najafabadi,
M. Azizpoor Fard,
J. F. Corrigan* ______ **4832 – 4835**

A Functionalized Ag_2S Molecular Architecture: Facile Assembly of the Atomically Precise Ferrocene-Decorated Nanocluster $[Ag_{74}S_{19}(dppp)_6(fc(C\{O\}OCH_2CH_2S)_2)_{18}]$



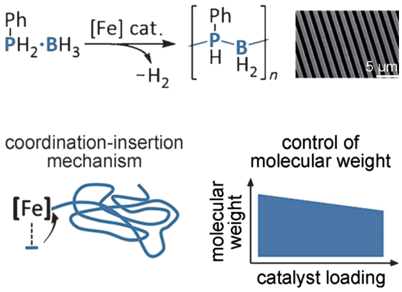
All wrapped up! A ferrocenyl-based dithiol reagent has been employed as a precursor for the preparation of a surface-functionalized $Ag_{74}S_{55}$ nanocluster $[Ag_{74}S_{19}(dppp)_6(fc(C\{O\}OCH_2CH_2S)_2)_{18}]$ (dppp = 1,3-bis(diphenylphosphino)propane, fc = $[Fe(\eta^5\text{-}C_5H_4)_2]$). The electrochemical properties and single-crystal X-ray structure of the cluster are reported (atom colors: Ag = blue, S = yellow, P = green, O = red, Fe = orange, C = gray).

Polymerization

A. Schäfer, T. Jurca, J. Turner, J. R. Vance,
K. Lee, V. A. Du, M. F. Haddow,
G. R. Whittell, I. Manners* _ **4836 – 4841**

Iron-Catalyzed Dehydropolymerization: A Convenient Route to Poly(phosphinoboranes) with Molecular-Weight Control

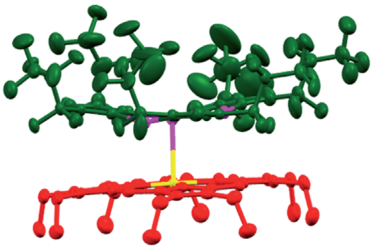
Loading matters: The catalyst loading is the key to control the molecular weight of the polymer in the iron-catalyzed dehydropolymerization of phosphine–borane adducts. Studies showed that the reaction proceeds through a chain-growth coordination–insertion mechanism.



Supramolecular Chemistry

C. Yang,* R. K. Arvapally, S. M. Tekarli,
G. A. Salazar, O. Elbjeirami, X. Wang,
M. A. Omary* ______ **4842 – 4846**

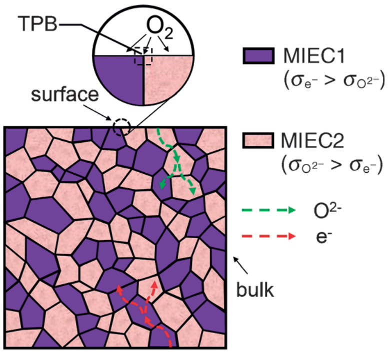
Formation of a Fluorous/Organic Biphasic Supramolecular Octopus Assembly for Enhanced Porphyrin Phosphorescence in Air



Glowing supramolecular octopi: A fluorous/organic biphasic supramolecular octopus pair with two nanoscopic cavities was constructed by coupling of a fluorous Ag_3 macrocycle with a metalloporphyrin through strong quadrupole–quadrupole interactions. The unique configuration of this system enhances the phosphorescence of the metalloporphyrin under ambient conditions.

Inside Back Cover

A dual-phase membrane made of two different mixed ionic–electronic conductors (MIEC) is presented. This composite mechanism enhances the rate of surface exchange and bulk diffusion for oxygen permeation at the same time. TPB = triple phase boundary.



Conducting Membranes

W. Fang,* F. Y. Liang, Z. W. Cao, F. Steinbach, A. Feldhoff **4847 – 4850**

A Mixed Ionic and Electronic Conducting Dual-Phase Membrane with High Oxygen Permeability

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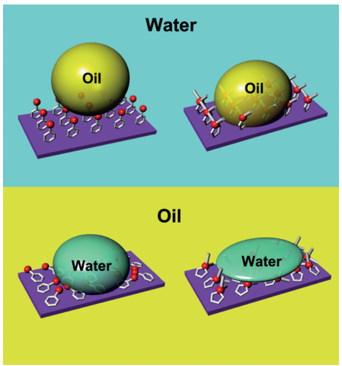

Wet surfaces: Liquid wetting on charged surfaces is well correlated with the molecular nature of surface ionic groups. The orientation change of surface ionic groups either hardly affects water wetting if their configuration is isotropic, or markedly transforms poor water wetting in oil to poor water de-wetting in water if their configuration is anisotropic, thus leading to excellent underwater oil repellency.

Interfaces

X. Liu, C. Leng, L. Yu, K. He, L. J. Brown, Z. Chen, J. Cho, D. Wang* **4851 – 4856**

Ion-Specific Oil Repellency of Polyelectrolyte Multilayers in Water: Molecular Insights into the Hydrophilicity of Charged Surfaces

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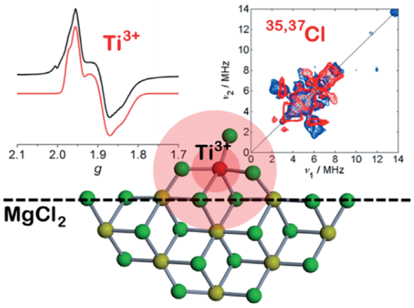

Advanced EPR experiments reveal the coordination environment and chemical accessibility of Ti^{3+} sites in an activated $MgCl_2$-supported industrial Ziegler–Natta (ZN) catalyst. These results provide the first detailed characterization of potential catalytically active sites in industrial ZN catalysts. Sphere colors: green = Cl^-, yellow = Mg^{2+}.

Heterogeneous Catalysis

E. Morra, E. Giamello, S. Van Doorslaer, G. Antinucci, M. D'Amore, V. Busico, M. Chiesa* **4857 – 4860**

Probing the Coordinative Unsaturation and Local Environment of Ti^{3+} Sites in an Activated High-Yield Ziegler–Natta Catalyst

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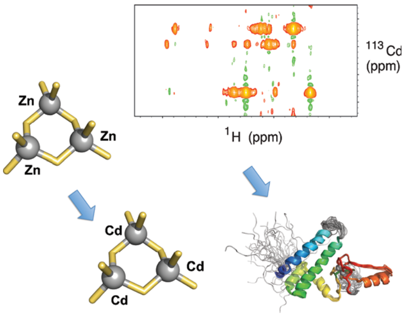


Cadmium finds the links: Replacing zinc with the spin $^1/_2$ isotope cadmium-113 makes it possible to trace metal–ligand bonding networks in zinc-finger proteins using NMR spectroscopy. Previously this approach was restricted to very small domains, but the structure determination of Bud31p, a 157-residue splicing protein from yeast, shows that recently introduced hardware advances have turned this into a widely useful method.

Zinc-Finger Proteins

A.-M. M. van Roon, J.-C. Yang, D. Mathieu, W. Bermel, K. Nagai, D. Neuhaus* **4861 – 4864**

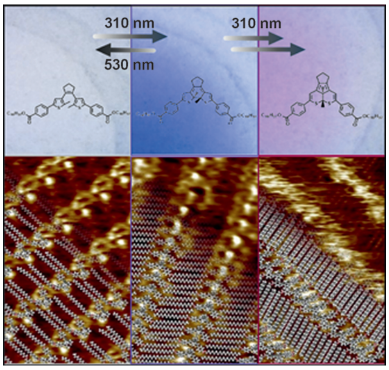
^{113}Cd NMR Experiments Reveal an Unusual Metal Cluster in the Solution Structure of the Yeast Splicing Protein Bud31p

Self-Assembly

S. Bonacchi, M. El Garah, A. Ciesielski,
M. Herder, S. Conti, M. Cecchini,*
S. Hecht,* P. Samorì* ______ **4865 – 4869**

Surface-Induced Selection During In Situ Photoswitching at the Solid/Liquid Interface

A diarylethene derivative exhibits pronounced affinity for the graphite surface in all its isomeric forms. The photoswitch between its two isomers, that is, the open and closed form, at the solid/liquid interface was investigated by submolecularly resolved scanning tunneling microscopy and atomistic modeling. Prolonged irradiation leads to the in situ irreversible formation of another isomer as by-product of the reaction.

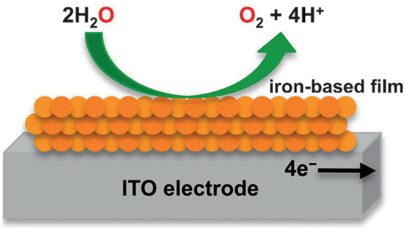


Water Splitting

Y. Z. Wu, M. X. Chen, Y. Z. Han, H. X. Luo,
X. J. Su, M.-T. Zhang, X. H. Lin, J. L. Sun,
L. Wang, L. Deng, W. Zhang,
R. Cao* ______ **4870 – 4875**

Fast and Simple Preparation of Iron-Based Thin Films as Highly Efficient Water-Oxidation Catalysts in Neutral Aqueous Solution

A catalyst with iron strength: Iron-based films were deposited onto electrodes by cyclic voltammetry within a minute, thus minimizing the time and energy input for potential large-scale applications. The films, which had a very low iron loading, catalyzed water oxidation in neutral aqueous media with a high turnover frequency and showed remarkable catalytic stability (see picture; ITO = indium tin oxide).

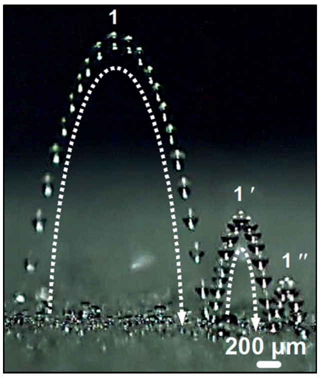


Superhydrophobic Surfaces

Y. Luo, J. Li, J. Zhu, Y. Zhao,
X. Gao* ______ **4876 – 4879**

Fabrication of Condensate Microdrop Self-Propelling Porous Films of Cerium Oxide Nanoparticles on Copper Surfaces

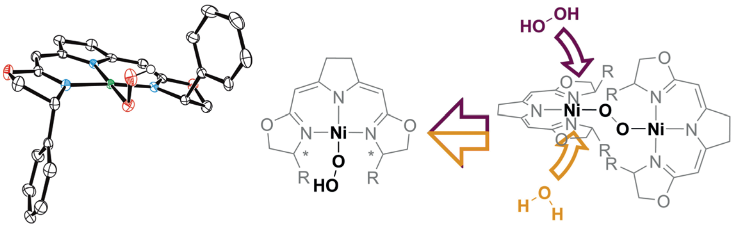
Water-drop ejector seat: A facile, cheap, and scalable electrodeposition approach gives copper surfaces coated with porous films made of cerium oxide nanoparticles. The films have condensate microdrop self-propelling (CMDSP) properties, that is, droplets move across and even jump from the surface (see time-lapse photo). The key to the film preparation is the control over preferential growth of isotropic nanoparticles and the synergistic use of the hydrogen-evolution reaction releasing tiny bubbles as pore-making templates.



Autoxidation

C. A. Rettenmeier, H. Wadepohl,
L. H. Gade* ______ **4880 – 4884**

Structural Characterization of a Hydroperoxo Nickel Complex and Its Autoxidation: Mechanism of Interconversion between Peroxo, Superoxo, and Hydroperoxo Species

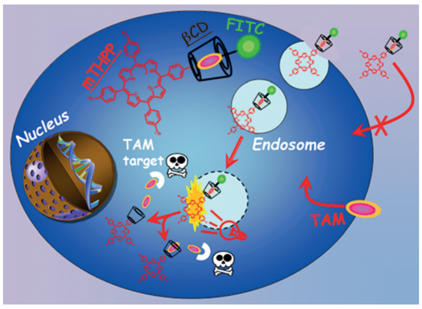


Pincer-stabilized nickel(I) complexes readily react with molecular oxygen to form dinuclear 1,2-µ-peroxo-bridged nickel(II) complexes, which are the major components of a dynamic equilibrium with the corresponding mononuclear superoxo species. The peroxo complexes further react with hydrogen peroxide to give the corresponding nickel(II) hydroperoxides.

Targeted Drug Delivery

T. A. Theodossiou,* A. R. Gonçalves, K. Yannakopoulou, E. Skarpen, K. Berg ——— 4885 – 4889

Photochemical Internalization of Tamoxifens Transported by a “Trojan-Horse” Nanoconjugate into Breast-Cancer Cell Lines

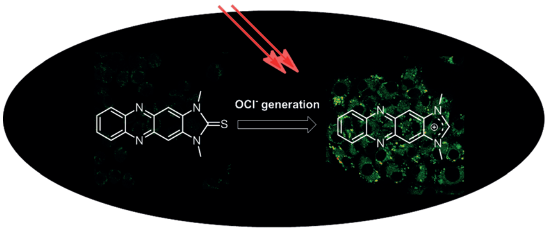


Smuggled within enemy walls: A porphyrin–β-cyclodextrin (mTHPP–βCD) conjugate was used to “smuggle” small tamoxifen (TAM) molecules into cells by endocytosis on the command of light (see picture; FITC = fluorescein isothiocyanate). Upon irradiation with red light, the porphyrin ruptured the endosomal membranes, and the large tamoxifen payload that was released caused substantial and permanent cytotoxicity to tamoxifen-sensitive MCF7 cells.

Fluorescence Probes

Q. Xu, C. H. Heo, G. Kim, H. W. Lee, H. M. Kim,* J. Yoon* ——— 4890 – 4894

Development of Imidazoline-2-Thiones Based Two-Photon Fluorescence Probes for Imaging Hypochlorite Generation in a Co-Culture System

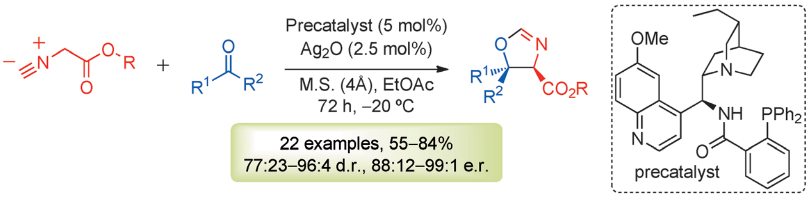


Imaging in a co-culture system: The first two-photon fluorescence probes for hypochlorite were developed. The imidazoline-2-thione probes operate through specific reactions with OCl^- that produce fluorescent products. Using the probes, imaging OCl^- generation in macrophages in a co-culture system was demonstrated.

Asymmetric Catalysis

R. de la Campa, I. Ortín, D. J. Dixon* ——— 4895 – 4898

Direct Catalytic Enantio- and Diastereoselective Ketone Aldol Reactions of Isocyanoacetates

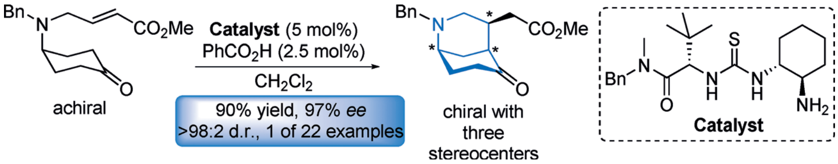


A stereoselective aldol reaction of unactivated ketones and isocyanoacetate pronucleophiles is catalyzed by a binary catalyst system consisting of an aminophosphine precatalyst and silver(I) oxide and affords oxazoline products with a fully substituted β-carbon atom. The reaction is efficient and broad in scope and proceeds with high diastereo- and enantioselectivity.

Enantioselective Organocatalysis

A. D. Gammack Yamagata, S. Datta, K. E. Jackson, L. Stegbauer, R. S. Paton,* D. J. Dixon* ——— 4899 – 4903

Enantioselective Desymmetrization of Prochiral Cyclohexanones by Organocatalytic Intramolecular Michael Additions to α,β-Unsaturated Esters

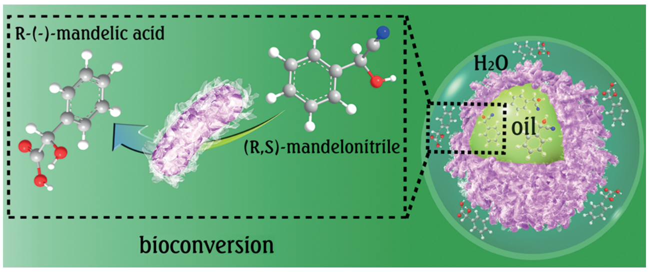


Enantioenriched derivatives of 2-azabicyclo[3.3.1]nonane, a key motif common to many alkaloids, are obtained by a catalytic asymmetric desymmetrization reaction with a cyclohexanediamine-derived primary-amine organocatalyst. A range of prochiral cyclohexanone derivatives with an α,β-unsaturated ester moiety linked to the 4-position afford the bicyclic products as single diastereoisomers in high enantioselectivity and good yields.

Biocatalysis

Z. Chen, H. Ji, C. Zhao, E. Ju, J. Ren,*
X. Qu* ________ 4904 – 4908

Individual Surface-Engineered Microorganisms as Robust Pickering Interfacial Biocatalysts for Resistance-Minimized Phase-Transfer Bioconversion

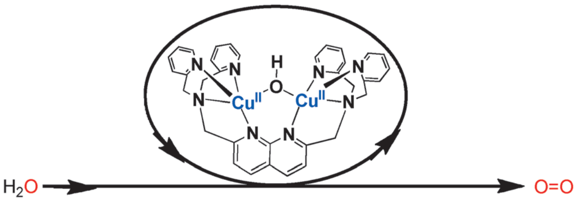


Whole-cell biocatalysis in biphasic systems was achieved by using individually encapsulated bacteria as robust recyclable Pickering interfacial biocatalysts. By minimizing diffusional resistance, enhanced bioconversion efficiencies were obtained, for example for the conversion of hydrophobic (*R*,*S*)-mandelonitrile into hydrophilic (*R*)-(−)-mandelic acid.

Water Oxidation

X.-J. Su, M. Gao, L. Jiao, R.-Z. Liao,*
P. E. M. Siegbahn, J.-P. Cheng,
M.-T. Zhang* ________ 4909 – 4914

Electrocatalytic Water Oxidation by a Dinuclear Copper Complex in a Neutral Aqueous Solution

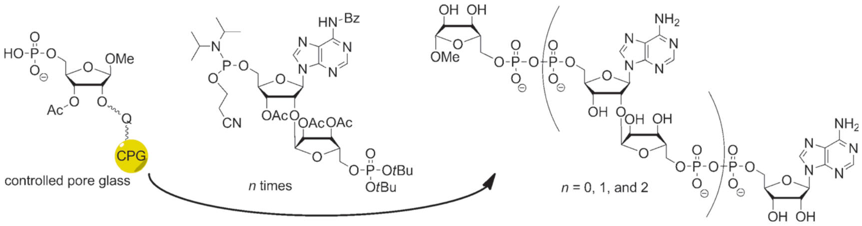


Cu^{III} not Cu^{IV}: A robust dinuclear Cu^{II} complex catalyzed water oxidation in a neutral aqueous solution. The O—O bond formation was proceeded by an intramolecular interaction between two Cu^{III} centers rather than by the high-oxidation-state Cu^{IV}=O moiety as previously reported.

Solid-Phase Synthesis

H. A. V. Kistemaker, L. N. Lameijer,
N. J. Meeuwenoord, H. S. Overkleeft,
G. A. van der Marel,*
D. V. Filippov* ________ 4915 – 4918

Synthesis of Well-Defined Adenosine Diphosphate Ribose Oligomers

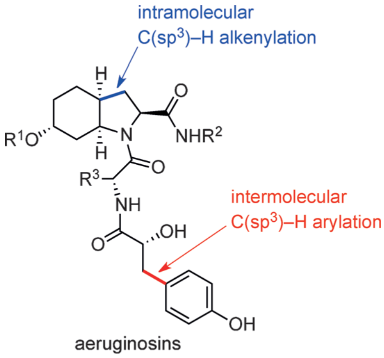


In twos and threes: A general solid-phase synthetic methodology was developed for the preparation of ADP-ribose oligomers (see scheme; Bz = benzoyl). A dimeric and a trimeric fragment of poly-ADP-ribose were synthesized by this completely chemical approach in milligram quantities.

Total Synthesis

D. Dailler, G. Danoun,
O. Baudoin* ________ 4919 – 4922

A General and Scalable Synthesis of Aeruginosin Marine Natural Products Based on Two Strategic C(sp^3)—H Activation Reactions

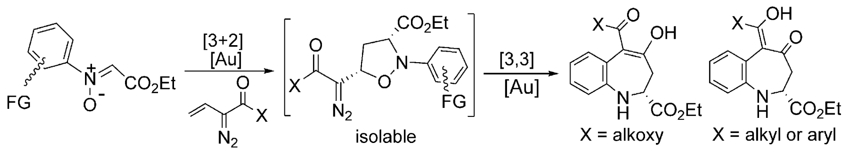


Family ties: An efficient access to the aeruginosin family of marine natural products, which exhibit potent inhibitory activity against serine proteases, was achieved. The strategic use of two different C(sp^3)—H activation reactions led to the synthesis of aeruginosins 98B and 298 A, with the latter being obtained on an unprecedentedly large scale.

Heterocycle Synthesis

V. V. Pagar, R.-S. Liu* ______ **4923 – 4926**

Gold-Catalyzed Cycloaddition Reactions of Ethyl Diazoacetate, Nitrosoarenes, and Vinyldiazo Carbonyl Compounds: Synthesis of Isoxazolidine and Benzo[*b*]azepine Derivatives

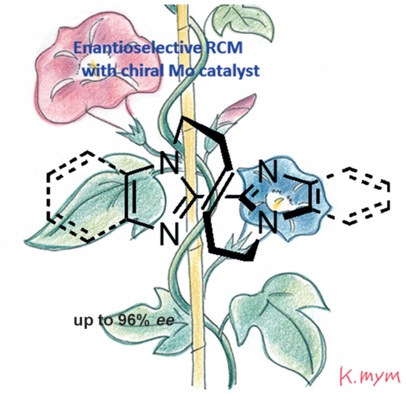


A little shifty: The title reaction yields isoxazolidine derivatives stereoselectively. Treatment of these isoxazolidine products with the same catalyst results in a novel 1,2-H shift/[3,3] rearrangement to give benzo[*b*]azepine compounds. The mechanism of this skeletal rearrangement is elucidated with deuterium-labeling experiments. FG = functional group.

Asymmetric Catalysis

Y. Okayama, S. Tsuji, Y. Toyomori, A. Mori,* S. Arae, W.-Y. Wu, T. Takahashi, M. Ogasawara* ______ **4927 – 4931**

Enantioselective Synthesis of Macrocyclic Heterobiaryl Derivatives of Molecular Asymmetry by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis

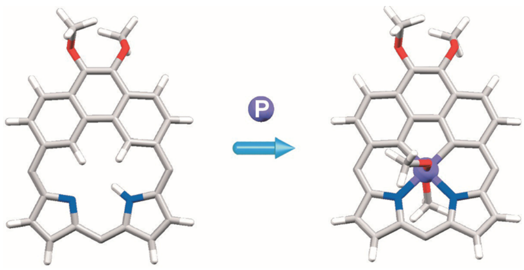


Winding-vine-shaped molecular asymmetry is induced by enantioselective ring-closing metathesis with a chiral molybdenum catalyst. The reaction proceeds under mild reaction conditions through an *E*-selective ring-closing metathesis leading to macrocyclic bisazoles with enantioselectivities of up to 96% *ee*.

Porphyrinoids

B. Szyszko, A. Białońska, L. Szterenberg, L. Latos-Grażyński* ______ **4932 – 4936**

Phenanthriporphyrin: An Antiaromatic Aceneporphyrinoid as a Ligand for a Hypervalent Organophosphorus(V) Moiety

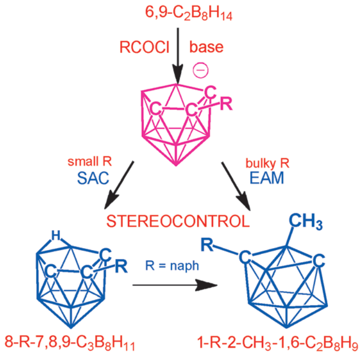


PAH–porphyrins: Phenanthriporphyrin, an antiaromatic hybrid macrocycle, merges structural facets of polycyclic aromatic hydrocarbons and porphyrins. The {CCNN} core of this aceneporphyrinoid involves phenanthrene carbon atoms which coordinate a hypervalent organophosphorus(V) center. Atom colors: C = gray; N = blue; O = red; H = white; P = purple.

Stereocontrol

M. Bakardjiev, J. Holub, J. Macháček, D. Hnyk, B. Štíbr,* Z. Růžičková, A. Růžička ______ **4937 – 4940**

Unique Stereocontrol in Carborane Chemistry: Skeletal Alkylcarbonation (SAC) versus Exoskeletal Alkylmethylation (EAM) Reactions

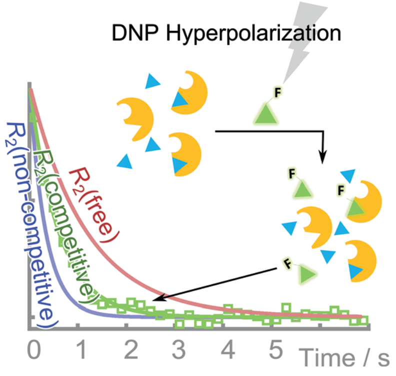


Demand and deliver: Reactions between *arachno*-6,9-$C_2B_8H_{14}$ and acyl chlorides are uniquely stereocontrolled. Sterically undemanding chlorides give tricarbollides 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (skeletal alkylcarbonation = SAC products), while bulky chlorides produce entirely different 1-R-2-CH_3-*closo*-1,6-$C_2B_8H_8$ dicarbaboranes (exoskeletal alkylmethylation = EAM products).

NMR Spectroscopy

Y. Kim, C. Hilty* ____________ **4941 – 4944**

Affinity Screening Using Competitive Binding with Fluorine-19 Hyperpolarized Ligands

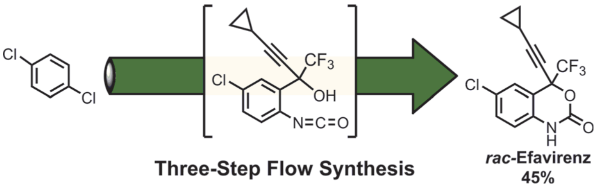


Just one scan: Screening for protein–ligand interactions is achieved efficiently using a competitive binding experiment with hyperpolarized ^{19}F NMR spectroscopy. The binding of any non-fluorinated ligand is detected through a change in relaxation rate of a fluorinated reporter ligand. Enhanced by dynamic nuclear polarization, a single NMR scan enables the binding affinity of a ligand of interest to be accurately determined.

Synthetic Methods

C. A. Correia, K. Gilmore, D. T. McQuade, P. H. Seeberger* ____________ **4945 – 4948**

A Concise Flow Synthesis of Efavirenz

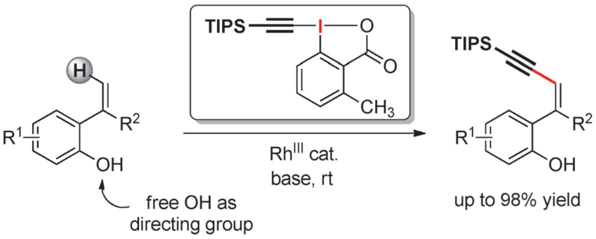


As fast as you can: Efavirenz is an essential medicine for the treatment of HIV, but is inaccessible to millions of people worldwide. A proof-of-principle, semi-continuous, three-step synthesis that is based on the intramolecular cyclization of an aryl isocyanate provides *rac*-Efavirenz in three steps and 45% overall yield.

C–H Activation

P. Finkbeiner, U. Kloeckner, B. J. Nachtsheim* ____________ **4949 – 4952**

OH-Directed Alkynylation of 2-Vinylphenols with Ethynyl Benziodoxolones: A Fast Access to Terminal 1,3-Enynes



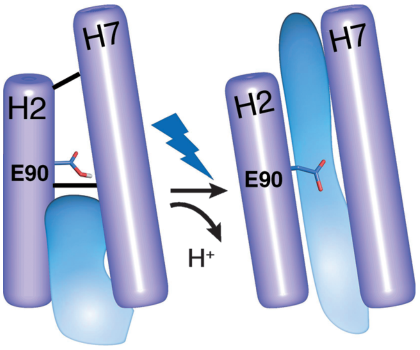
TIPS and tricks for alkynylation: The first direct alkynylation of 2-vinylphenols was developed. The rationally optimized hypervalent iodine reagent TIPS-EBX* (see scheme) in combination with [(Cp*RhCl$_2$)$_2$] as a C–H-activating transition-metal catalyst enables the construction of a variety of highly substituted 1,3-enynes in high yield under mild conditions and with excellent chemo- and stereoselectivity.

Channelrhodopsin

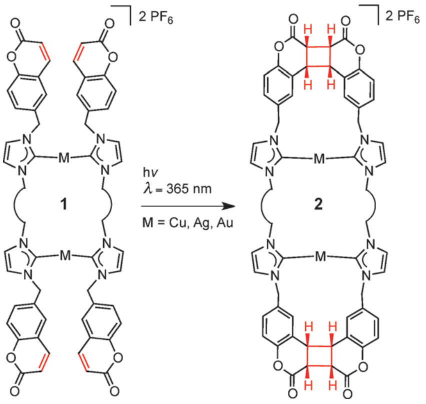
J. Kuhne, K. Eisenhauer, E. Ritter, P. Hegemann,* K. Gerwert,* F. Bartl ____________ **4953 – 4957**

Early Formation of the Ion-Conducting Pore in Channelrhodopsin-2

Back Cover



Pore preformation of the ion-conducting channelrhodopsin-2 is triggered by downward movement of the highly conserved E90. Upon light-induced isomerization, the retinal E90 undergoes a conformational change and deprotonation, which leads to water influx and Helix 2 movement.



Tying up loose ends: The synthesis and characterization of a series of dinuclear molecular rectangles (**1**) containing Cu^I, Ag^I, or Au^I ions and coumarin pendants is described. Photochemically induced [2+2] cycloaddition reactions were performed with these complexes to give new complexes (**2**) featuring a macrocyclic coordinated tetracarbene ligand and two cyclobutane rings.

Tetracarbene Ligands

Y.-F. Han,* G.-X. Jin, C. G. Daniliuc,
F. E. Hahn* ______ **4958 – 4962**

Reversible Photochemical Modifications in Dicarbene-Derived Metallacycles with Coumarin Pendants

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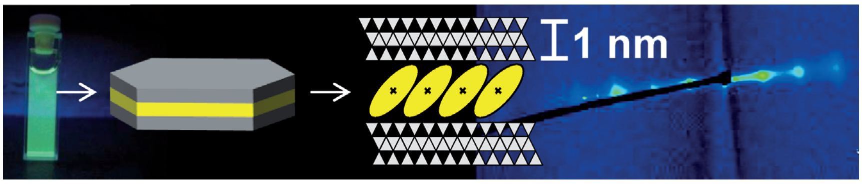

Under glass: The encapsulation of functional molecules between two sheets of transparent and chemically stable 1 nm thin silicate layers is presented. The new technique can be used to mask hydrophobic functional molecules and render them completely dispersible in water. The combination of structural anisotropy and a preferred orientation of the functional molecules lead to optically anisotropic films.

Layered Materials

M. Stöter, B. Biersack, S. Rosenfeldt,
M. J. Leitl, H. Kalo, R. Schobert, H. Yersin,
G. A. Ozin, S. Förster,
J. Breu* ______ **4963 – 4967**

Encapsulation of Functional Organic Compounds in Nanoglass for Optically Anisotropic Coatings

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

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

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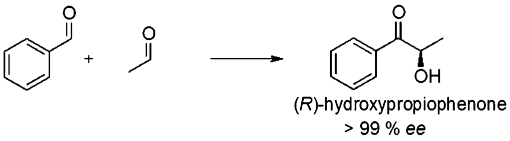
This article is accompanied by a cover picture (front or back cover, and inside or outside).

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

In Figure 1 B of this Communication a wrong chemical formula was given for (*R*)-hydroxypropiophenone, the product of the top equation. The correct equation is shown below.



Furthermore, in Table 1, entry 6, the correct name of the *Ap*PDC variant is E469G/T384G/I468A/W543F (and not E469G/T384G/I468V/W543F).

A Tailor-Made Chimeric Thiamine Diphosphate Dependent Enzyme for the Direct Asymmetric Synthesis of (*S*)-Benzoins

R. Westphal, C. Vogel, C. Schmitz,
J. Pleiss, M. Müller, M. Pohl,*
D. Rother ______ **9376–9379**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201405069