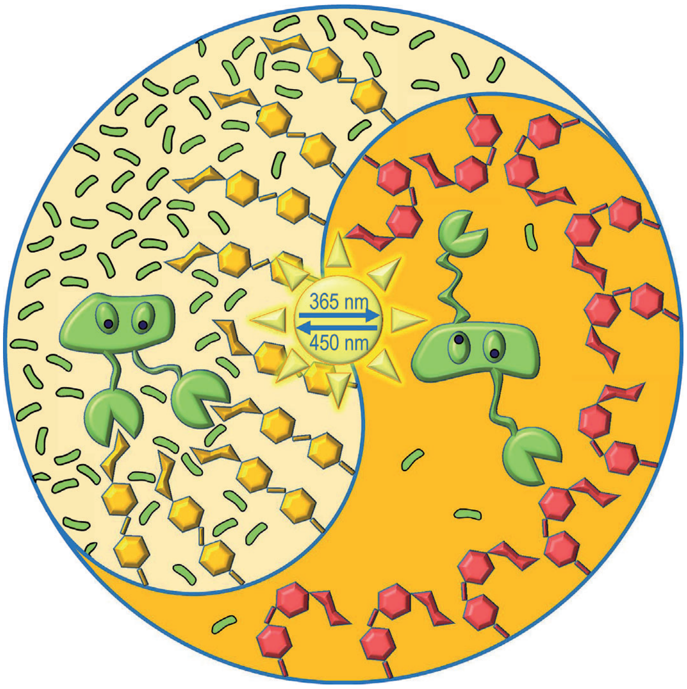
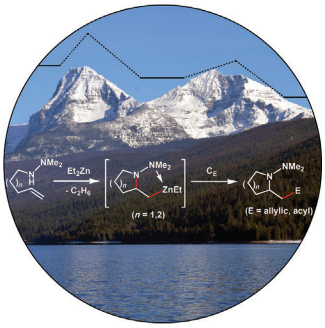
The Yin and Yang of carbohydrate recognition:

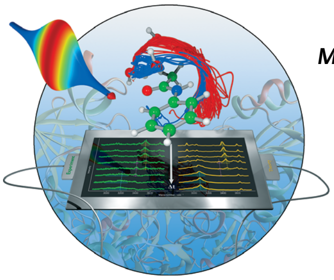


Bacteria (shown in green) have lectin-type appendages to adhere to glycosylated surfaces, such as the glycocalyx of host cells. In their Communication on page 14583 ff., A. Terfort, T. K. Lindhorst, and co-workers use a photoswitchable azobenzene glycoside monolayer as a glycocalyx model. The orientation of the carbohydrate ligands is controlled by photochemical *E*/*Z* isomerization of the azobenzene hinge. Thus, for bacterial cells, binding or not binding is a question of the orientation of the carbohydrate ligands.

Heterocycle Synthesis

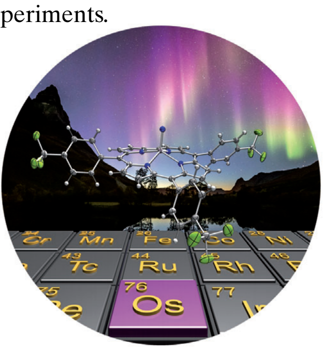
In their Communication on page 14352 ff., T. Livinghouse et al. describe the direct metalloamination/cyclization of hydrazinoalkenes by Et_2Zn. Electrophilic capture of the chelated organozinc intermediates drives the subsequent cascade.





Molecular Dynamics

O. Dopfer, M. Fujii, R. Mitric, and co-workers describe the water solvation dynamics in the acetanilide–water cluster in their Communication on page 14601 ff. Simulations can be verified by IR spectroscopy experiments.



Transition Metals

In their Communication on page 14411 ff., A. Ghosh et al. present oxidative metalation as a route to Os corroles. These complexes exhibit distinctive domed folded macrocycles and multiple Os–nitrido stretching frequencies.

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Miscellaneous

Author Profile

"My favorite saying is 'it is never too late to follow your dreams'.
If I were not a scientist, I would be a sketch artist ..."
This and more about Jagadese J. Vittal can be found on page 14302.

News

T. Schleid

C. Sanchez

R. Rinaldi

S. V. Ley

D. J. Procter

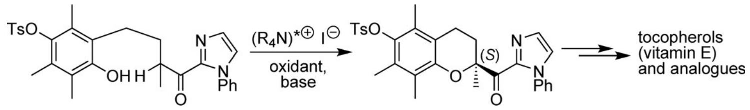
Books

Highlights

Click Chemistry

Organocatalytic click! Recent advances in the metal-free enamine/enolate-mediated azide–carbonyl [3+2] cycloaddition reaction are discussed. These approaches require neither a metal catalyst nor alkyne substrates. Owing to the ready availability of carbonyl compounds, these methods thus offer excellent alternatives for the synthesis of 1,4-/1,5-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles.

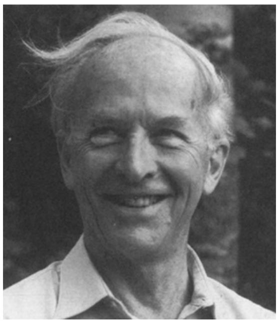
Asymmetric Catalysis



High-turnover catalysis offers a novel concept for the efficient chemo- and enantioselective preparation of chroman intermediates, which are useful for the synthesis of tocopherols (vitamin E components) and other biologically active compounds. A chiral ammonium iodide catalyst mediates the cycloetherification in combination with a cooxidant and an inorganic base in excellent yield and up to 93 % *ee*. OTs = *para*-toluenesulfonyl.

Essays

History of Science



A brilliant scientist and an outstanding personality who was one of the founders of modern photochemistry—Michael Kasha—is the subject of this Essay. Kasha's rule and the Kasha effect both bear his name, and he also discovered the chemical production of singlet molecular oxygen, and was a pioneer of excited-state proton transfer systems. Kasha combined his passion for chemistry and physics with that for music, photography, and botany.

For the USA and Canada:
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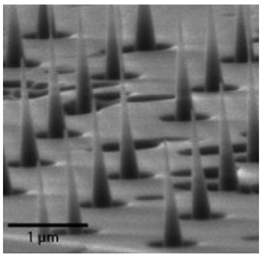
Reviews



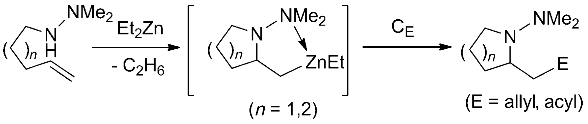
The other carbon 1D nanomaterials: The reproducible synthesis of crystalline diamond nanowires is possible, but has remained difficult. This Review gives an overview of nanowires as materials with exceptional properties, such as negative electron affinity, chemical inertness, high elastic modulus, hardness, and thermal conductivity at room temperature.

Nanomaterials

Y. Yu, L. Wu, J. Zhi* ______ **14326 – 14351**

Diamond Nanowires: Fabrication, Structure, Properties, and Applications

Communications



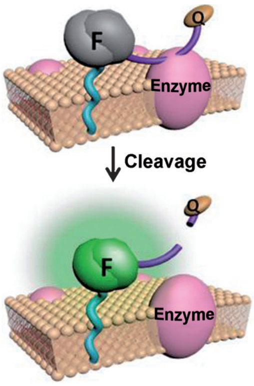
Zinc helps: An attractive way to nitrogen heterocycles uses organozinc intermediates which undergo facile allylation and acylation in situ (see scheme). In general, the products are obtained in excellent yields and diastereoselectivities. In some cases, reduction of the reaction temperature was necessary to reach diastereoselectivity.

Heterocycle Synthesis

B. Sunsdahl, A. R. Smith, T. Livinghouse* ______ **14352 – 14356**

Intramolecular Metalloamination of *N*,*N*-Dimethylhydrazinoalkenes: A Versatile Method to Access Functionalized Piperidines and Pyrrolidines

Frontispiece

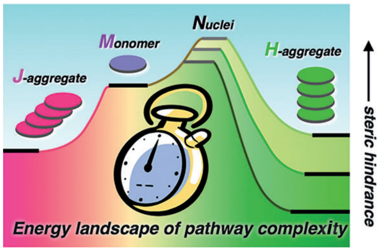


Cell-membrane imaging: A membrane-anchored small-molecule reporter containing a FRET pair (F–Q; F = fluorescein, Q = quencher) was prepared. This molecule is shown to be specifically cleaved by the membrane-localized proteolytic processing enzyme furin (see picture) and was employed in the real-time visualization of furin-like activity in living cells and tissues using one- and two-photon microscopic techniques.

Bioimaging

J. Mu, F. Liu,* M. S. Rajab, M. Shi, S. Li, C. Goh, L. Lu, Q. H. Xu, B. Liu, L. G. Ng, B. G. Xing* ______ **14357 – 14362**

A Small-Molecule FRET Reporter for the Real-Time Visualization of Cell-Surface Proteolytic Enzyme Functions



Finding the right balance: The energy landscape of a supramolecular polymerization in which the supramolecular assembly transforms from a J-aggregate to an H-aggregate over time has been modulated by a rational molecular design. Based on this, kinetic control over pathway complexity was achieved through adjusting the balance between the coupled equilibria.

Systems Chemistry

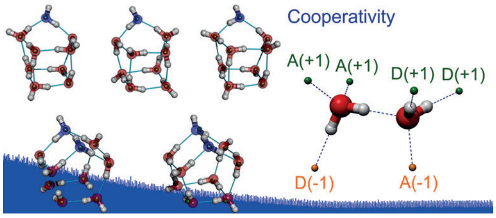
S. Ogi, T. Fukui, M. L. Jue, M. Takeuchi,* K. Sugiyasu* ______ **14363 – 14367**

Kinetic Control over Pathway Complexity in Supramolecular Polymerization through Modulating the Energy Landscape by Rational Molecular Design

Water Clusters

C. Pérez, D. P. Zaleski, N. A. Seifert,
B. Temelso, G. C. Shields,* Z. Kisiel,*
B. H. Pate* ____________ **14368 – 14372**

Hydrogen Bond Cooperativity and the Three-Dimensional Structures of Water Nonamers and Decamers

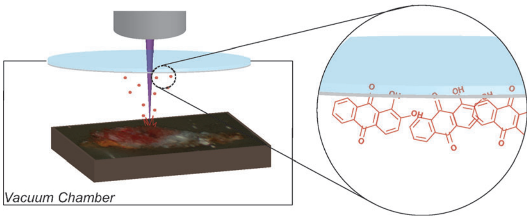


Broadband rotational spectroscopy enabled the observation of three isomers of the water nonamer and two isomers of the water decamer. The distinctive O–O distance patterns allow a conclusive identification. The observed cooperativity effects are consistent with a simple model for hydrogen bonding in water that takes the cooperative and anticooperative bonding effects of nearby water molecules into account.

Analysis of Paintings

A. Cesaratto, M. Leona,* J. R. Lombardi,
D. Comelli, A. Nevin,
P. Londero* ____________ **14373 – 14377**

Detection of Organic Colorants in Historical Painting Layers Using UV Laser Ablation Surface-Enhanced Raman Microspectroscopy



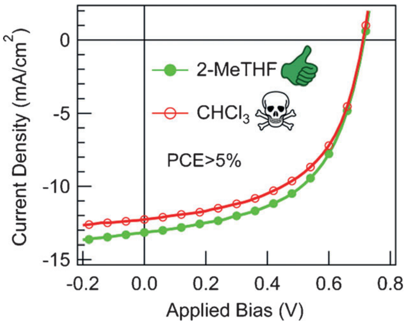
UV-LA-SERS of paintings: The UV-laser ablation SERS technique can be used for the study of organic paint layers when the sample is properly pretreated and the ablation parameters are carefully controlled. UV-LA-SERS permitted the sampling of cross-sections from selected thin layers, avoiding contamination from adjacent layers.

Sustainable Chemistry

X. Chen, X. Liu, M. A. Burgers, Y. Huang,
G. C. Bazan* ____________ **14378 – 14381**

Green-Solvent-Processed Molecular Solar Cells

Inside Cover

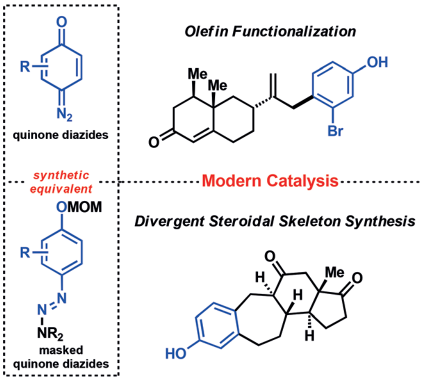


Molecular solar cells with high efficiencies can be fabricated from the green solvent 2-MeTHF. The light-harvesting semiconducting layer comprises a molecular donor with intermediate dimensions and a soluble fullerene derivative. No specific structural modifications are required on the semiconductors in order to use sustainable resources. PCE = power conversion efficiency.

Olefin Functionalization

H. T. Dao, P. S. Baran* __ **14382 – 14386**

Quinone Diazides for Olefin Functionalization

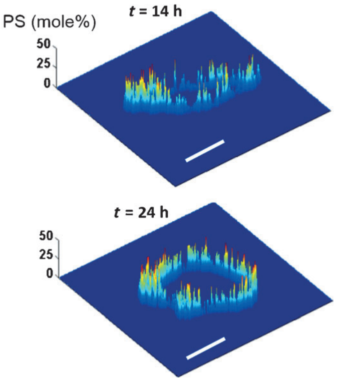


Teaching an old dog new tricks: The combination of modern catalysis and free quinone diazides allows classic diazo compounds to be utilized for both inter- and intramolecular olefin cyclopropanation reactions with a variety of different olefin classes (see example). The use of suitably masked quinone diazides also provides a fundamentally new approach to steroid skeletons (MOM = methoxymethyl).

Lipid Membranes

S.-L. Liu, R. Sheng, M. J. O'Connor, Y. Cui, Y. Yoon, S. Kurilova, D. Lee,* W. Cho* —— **14387 – 14391**

Simultaneous In Situ Quantification of Two Cellular Lipid Pools Using Orthogonal Fluorescent Sensors

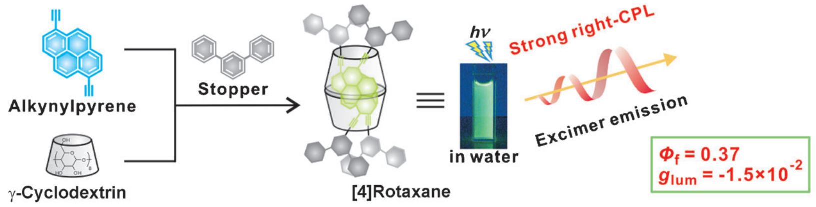


Same time, same place: The time-resolved quantification of multiple lipids in a lipid membrane provides insight into the complex mechanisms of lipid-mediated cell signaling and regulation. Sensors were prepared by incorporating two environmentally sensitive fluorophores with minimal spectral overlap into engineered lipid-binding proteins.

Rotaxanes

M. Inouye,* K. Hayashi, Y. Yonenaga, T. Itou, K. Fujimoto, T. Uchida, M. Iwamura, K. Nozaki — **14392 – 14396**

A Doubly Alkynylpyrene-Threaded [4]Rotaxane That Exhibits Strong Circularly Polarized Luminescence from the Spatially Restricted Excimer

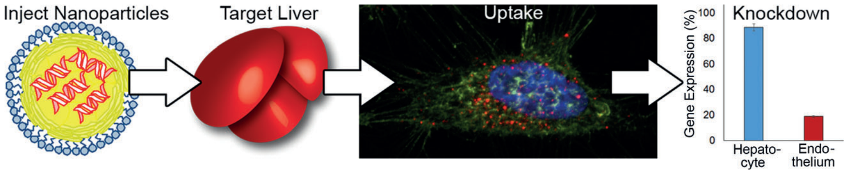


Facing facts: A pyrene-based [4]rotaxane has been formed by encapsulating two highly emissive alkynylpyrene molecules in two γ-cyclodextrins, followed by stoppering. The pyrene cores exist near the two wider rims of two γ-CD molecules and face each other, thereby generating a spatially restricted, asymmetrically twisted alkynylpyrene excimer that emits circularly polarized luminescence (CPL) with a large dissymmetry factor (g_{lum}) in water.

Drug Delivery

O. F. Khan, E. W. Zaia, H. Yin, R. L. Bogorad, J. M. Pelet, M. J. Webber, I. Zhuang, J. E. Dahlman, R. Langer, D. G. Anderson* —— **14397 – 14401**

Ionizable Amphiphilic Dendrimer-Based Nanomaterials with Alkyl-Chain-Substituted Amines for Tunable siRNA Delivery to the Liver Endothelium In Vivo

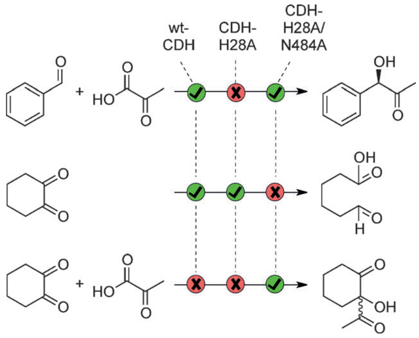


Formulation control: Dendrimer derivatives for in vivo siRNA delivery to liver endothelial cells, hepatocellular carcinoma cells, and/or hepatocytes are prepared from poly(amido amine) and poly(propylenimine) dendrimers substituted with alkyl chains of different lengths. Through formulation changes, these materials have the ability to broaden or narrow their targeted cellular subpopulation within the liver.

Enzyme Catalysis

S. Loschonsky, T. Wacker, S. Waltzer, P. P. Giovannini, M. J. McLeish, S. L. A. Andrade, M. Müller* —— **14402 – 14406**

Extended Reaction Scope of Thiamine Diphosphate Dependent Cyclohexane-1,2-dione Hydrolase: From C–C Bond Cleavage to C–C Bond Ligation

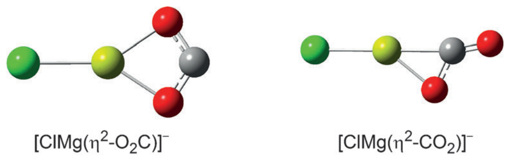


The ThDP-dependent enzyme CDH catalyzes an asymmetric benzoin condensation and the C–C bond cleavage of cyclohexane-1,2-dione. Mutation experiments resulted in the selective knockdown of one of these reactivities; CDH-H28A/N484A catalyzes the addition of pyruvate to cyclohexane-1,2-dione. This variant is one of the few ThDP-dependent enzymes that uses ketones as substrates in a C–C bond-forming reaction.

CO₂ Activation

G. B. S. Miller, T. K. Esser, H. Knorke,
S. Gewinner, W. Schöllkopf, N. Heine,
K. R. Asmis,*
E. Uggerud* ———— **14407 – 14410**

Spectroscopic Identification of a Bidentate Binding Motif in the Anionic Magnesium–CO_2 Complex ($[ClMgCO_2]^-$)



Bidentate coordination of CO_2: An anionic complex of $MgCl^-$ and CO_2, $[ClMgCO_2]^-$, is formed upon electrospray ionization followed by collision-induced dissociation. With the help of infrared photodissociation spectroscopy it is shown that the complex exists solely in the double oxygen-bound $[ClMg(\eta^2\text{-}O_2C)]^-$ form, a type of CO_2 coordination not previously seen in unimetallic complexes.

Transition Metals

A. B. Alemayehu, K. J. Gagnon, J. Terner,
A. Ghosh* ———— **14411 – 14414**

Oxidative Metalation as a Route to Size-Mismatched Macrocyclic Complexes: Osmium Corroles

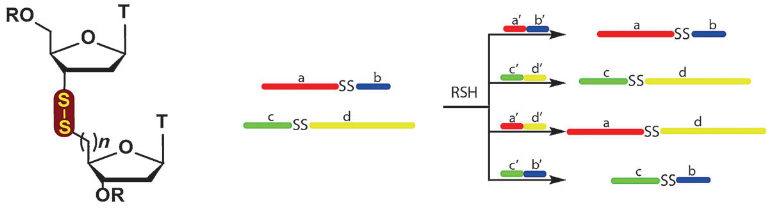
Back Cover

Last man standing! After the synthesis of platinum corroles, osmium was the last remaining middle and late 5d metal to be inserted into the contracted porphyrin analogue. Oxidative metalation has now provided a moderately high-yielding route to osmium corroles. DEGME = diethylene glycol monomethyl ether.

Reversible DNA Ligation

D. J. Hansen, I. Manuguerra,
M. B. Kjelstrup,
K. V. Gothelf* ———— **14415 – 14418**

Synthesis, Dynamic Combinatorial Chemistry, and PCR Amplification of 3′–5′ and 3′–6′ Disulfide-linked Oligonucleotides



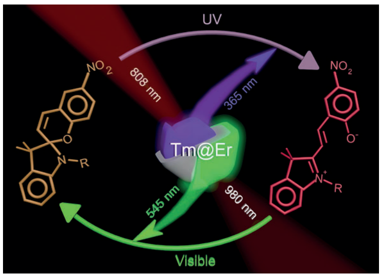
Internucleosidic 3′–5′ and 3′–6′ disulfide linkages allows cleavage and template-directed formation of desired disulfides in the presence of mercaptoethanol. The artificial disulfide backbone is tolerated by polymerases and the sequences can be amplified by polymerase chain reaction.

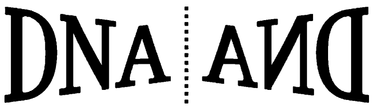
Core–Shell Nanoparticles

J. Lai, Y. Zhang, N. Pasquale,
K.-B. Lee* ———— **14419 – 14423**

An Upconversion Nanoparticle with Orthogonal Emissions Using Dual NIR Excitations for Controlled Two-Way Photoswitching

Spiropyran photoswitching: A single-crystal core–shell-structured upconversion nanoparticle (Tm@Er) is capable of orthogonal UV (365 nm) and visible (545 nm) emissions in response to two distinct NIR excitations at 808 and 980 nm. It was applied in NIR-light-based two-way photoswitching of spiropyran.



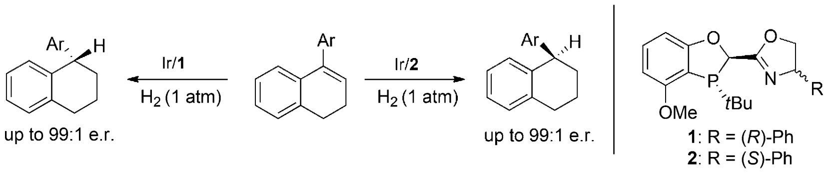


DNA, proteins, and small molecules all alike: When mixed in a racemate, DNA D- and L-enantiomers invariably crystallize as a racemate regardless of the sequence and of the folding motif.

DNA Crystallography

P. K. Mandal, G. W. Collie, B. Kauffmann, I. Huc* ______ **14424 – 14427**

Racemic DNA Crystallography



Air-stable P-chiral dihydrobenzooxaphosphole oxazoline ligands were designed and synthesized. When they were used in the iridium-catalyzed asymmetric hydrogenation of unfunctionalized 1-aryl-3,4-dihydronaphthalenes under one atmosphere pressure of H_2, up to 99:1 e.r. was obtained. High enantioselectivities were also observed in the reduction of the exocyclic imine derivatives of 1-tetralones.

P,N Ligands

B. Qu,* L. P. Samankumara, S. Ma, K. R. Fandrick, J.-N. Desrosiers, S. Rodriguez, Z. Li, N. Haddad, Z. S. Han, K. McKellop, S. Pennino, N. Grinberg, N. C. Gonnella, J. J. Song, C. H. Senanayake ______ **14428 – 14432**

A Mild Dihydrobenzooxaphosphole Oxazoline/Iridium Catalytic System for Asymmetric Hydrogenation of Unfunctionalized Dialins

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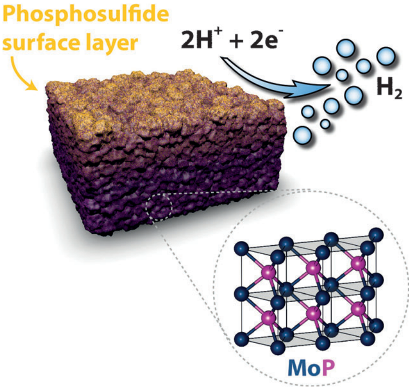


Introducing sulfur into the surface of molybdenum phosphide produces a molybdenum phosphosulfide catalyst with outstanding activity and stability for the hydrogen evolution reaction (HER) in acidic environments. Synergistic effects between sulfur and phosphorus produce an electrode that is more active than those based on either the pure sulfide or the pure phosphide.

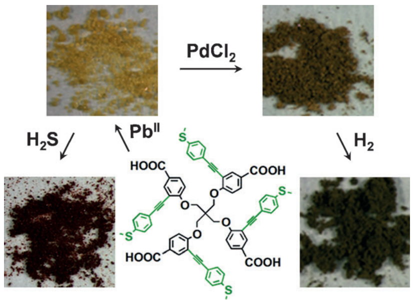
Catalyst Design

J. Kibsgaard, T. F. Jaramillo* ______ **14433 – 14437**

Molybdenum Phosphosulfide: An Active, Acid-Stable, Earth-Abundant Catalyst for the Hydrogen Evolution Reaction

---

Yin and yang: A system incorporating both rigid and flexible components has been prepared in which traditional configuration has been reversed by installing rigid side arms onto a soft core (see picture). After binding to Pb^{II} ions, the dynamic hard–soft (carboxy–thioether) metal–organic framework has distinct amphoteric character, with the donor-acceptor properties enabling uptake of $PdCl_2$ and a sensitive colorimetric response to H_2S.



Metal–Organic Frameworks

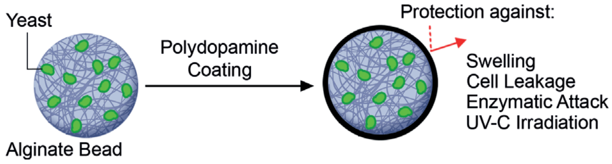
J. Cui, Y.-L. Wong, M. Zeller, A. D. Hunter, Z. Xu* ______ **14438 – 14442**

Pd Uptake and H_2S Sensing by an Amphoteric Metal–Organic Framework with a Soft Core and Rigid Side Arms

Cytoprotection

B. J. Kim, T. Park, H. C. Moon, S.-Y. Park, D. Hong, E. H. Ko, J. Y. Kim, J. W. Hong, S. W. Han, Y.-G. Kim,* I. S. Choi* ______ 14443 – 14446

Cytoprotective Alginate/Polydopamine Core/Shell Microcapsules in Microbial Encapsulation



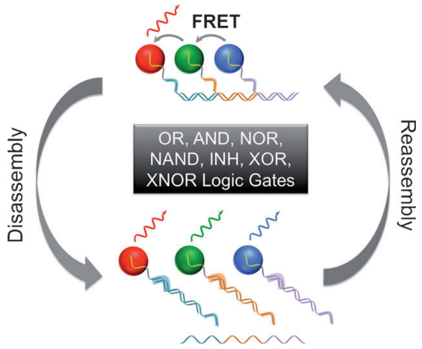
All wrapped up: Alginate/polydopamine core/shell microcapsules that encapsulate yeast *Saccharomyces cerevisiae* cells prevent gel swelling because of the mechanical durability of the polydopamine shell. Encapsulation enhances cell resistance against external stresses, such as enzymatic attack and UV-C irradiation, and effectively prevents cell growth and leakage.

Biocomputing

X. He, Z. Li, M. Chen, N. Ma* ______ 14447 – 14450

DNA-Programmed Dynamic Assembly of Quantum Dots for Molecular Computation

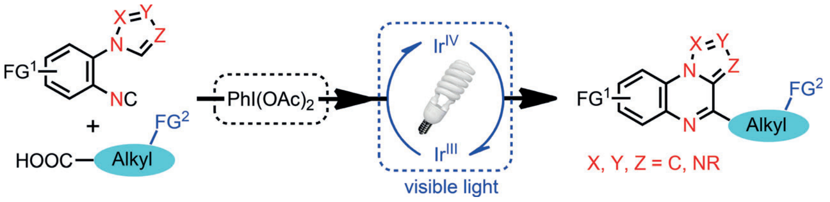
It's only logical: A quantum dot (QD)-based molecular computing system is constructed based on the DNA-programmed dynamic assembly of multicolor QDs. A complete set of seven elementary logic gates and a half-adder is realized for QD biocomputing.



Heterocycles

Z. He, M. Bae, J. Wu, T. F. Jamison* ______ 14451 – 14455

Synthesis of Highly Functionalized Polycyclic Quinoxaline Derivatives Using Visible-Light Photoredox Catalysis

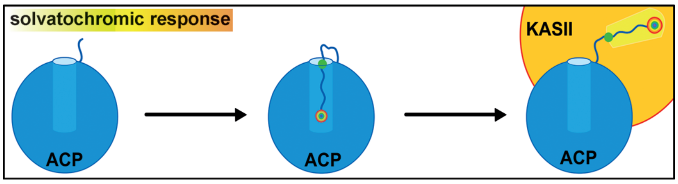


Full of nitrogen: Highly functionalized pyrrolo[1,2-*a*]quinoxalines and other nitrogen-rich polycyclic quinoxaline analogues have been obtained by a visible-light-induced decarboxylative radical cyclization of arylisocyanides using phenyliodine(III) dicarboxylate reagents under mild reaction conditions. A telescoped preparation of these polycyclic compounds has been established by using a three-step continuous-flow system.

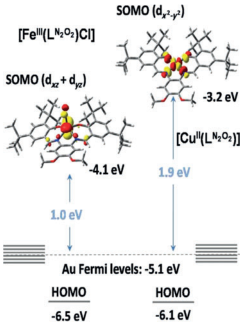
Solvatochromism

J. Beld, H. Cang, M. D. Burkart* ______ 14456 – 14461

Visualizing the Chain-Flipping Mechanism in Fatty-Acid Biosynthesis



Flipping out in style: Protein–protein interactions with the partner protein ketoacyl synthase II (KASII) cause fatty-acid-intermediate cargo sequestered by the acyl carrier protein (ACP) to flip from the hydrophobic core of the carrier protein into the active site of the partner protein. Solvatochromic pantetheine probes were used to visualize this event (see picture).



Current rectification: Iron(III) and copper(II) metallosurfactants were used to study current rectification in Au|molecule|Au devices. An asymmetric mechanism of rectification seems favorable when the energies of the molecular complex orbitals are comparable with the Fermi levels of the gold electrode (see picture).

Coordination Chemistry

L. D. Wickramasinghe, S. Mazumder, S. Gonawala, M. M. Perera, H. Baydoun, B. Thapa, L. Li, L. Xie, G. Mao, Z. Zhou, H. B. Schlegel, C. N. Verani* ______ **14462 – 14467**

The Mechanisms of Rectification in Au|Molecule|Au Devices Based on Langmuir–Blodgett Monolayers of Iron(III) and Copper(II) Surfactants

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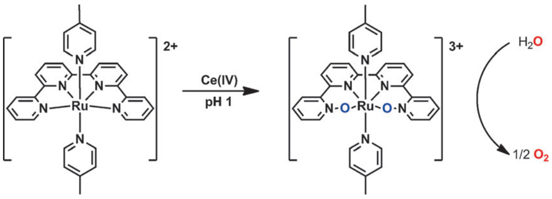

What is the real catalyst? A series of ruthenium(II) complexes $[Ru(qpy)(L)_2]^{2+}$ (qpy = 2,2′:6′,2″:6″,2‴-quaterpyridine; L = substituted pyridine) function as precatalysts for water oxidation using $(NH_4)_2Ce(NO_3)_6$ (CAN) as the terminal oxidant. In the presence of CAN, they are readily oxidized to the qpy-*N*,*N*‴-dioxide complexes $[Ru(ONNO)(L)_2]^{3+}$, which are the real catalysts for water oxidation.

Water Oxidation

Y. Liu, S. M. Ng, S. M. Yiu, W. W. Y. Lam, X. G. Wei, K. C. Lau, T. C. Lau* ______ **14468 – 14471**

Catalytic Water Oxidation by Ruthenium(II) Quaterpyridine (qpy) Complexes: Evidence for Ruthenium(III) qpy-*N*,*N*‴-dioxide as the Real Catalysts

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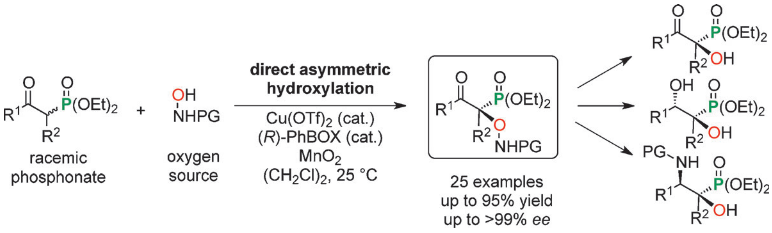

Go for oxygen: The copper-catalyzed direct α-oxidation of racemic β-ketophosphonates using nitrosocarbonyl compounds as an electrophilic oxygen source is a new method for the asymmetric synthesis of biogenic tertiary α-hydroxy phosphonic acid derivatives. Highly efficient asymmetric hydroxylations could thus be achieved at room temperature under mild conditions.

Asymmetric Synthesis

B. Maji,* H. Yamamoto* . **14472 – 14475**

Copper-Catalyzed Asymmetric Synthesis of Tertiary α-Hydroxy Phosphonic Acid Derivatives with In Situ Generated Nitrosocarbonyl Compounds as the Oxygen Source

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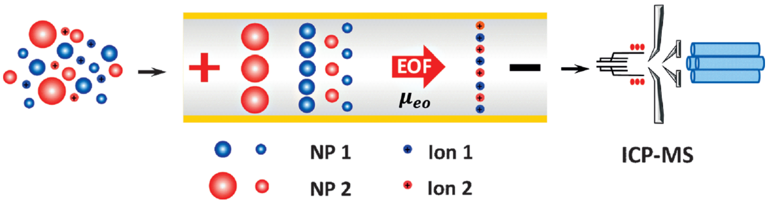


(Nano)size matters: Capillary electrokinetic separation and inductively coupled plasma mass spectrometry (ICP-MS) were combined in a method that allows the identification and accurate size determination of nanoparticles in complex media (see picture). This method provides a powerful tool for investigating polydisperse multiple NP systems and rapid screening of NP-containing products.

Nanoparticles

VIP

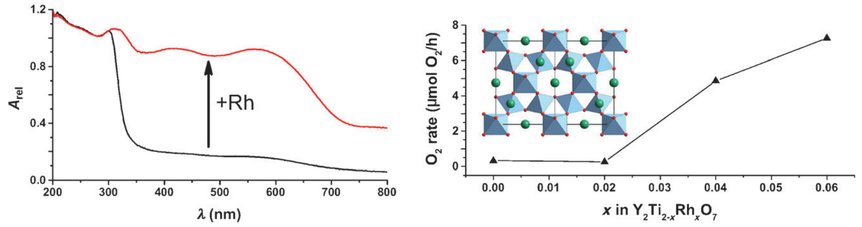
L. H. Liu, B. He, Q. Liu,* Z. J. Yun, X. T. Yan, Y. M. Long, G. B. Jiang* ______ **14476 – 14479**

Identification and Accurate Size Characterization of Nanoparticles in Complex Media

Water Oxidation

B. Kiss, C. Didier, T. Johnson,
T. D. Manning, M. S. Dyer, A. J. Cowan,
J. B. Claridge, J. R. Darwent,
M. J. Rosseinsky* ________ **14480 – 14484**

Photocatalytic Water Oxidation by a Pyrochlore Oxide upon Irradiation with Visible Light: Rhodium Substitution Into Yttrium Titanate

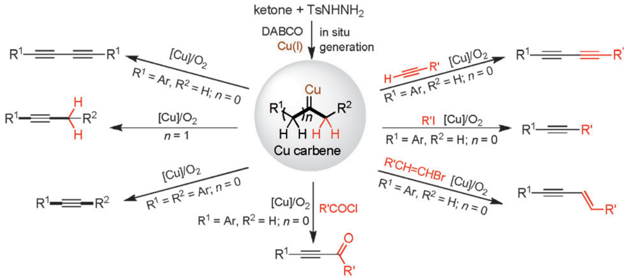


Splitting water: Visible-light-activated water oxidation was achieved using rhodium-substituted pyrochlore yttrium titanate, $Y_2Ti_{2-x}Rh_xO_7$ ($0 \leq x \leq 0.2$). When $x \leq 0.06$, the material absorbs visible light up to $\lambda = 700$ nm. Materials with composition $0.04 \leq x \leq 0.06$ showed stable oxygen evolution without the need for a co-catalyst.

Synthetic Methods

X. Li, X. Liu, H. Chen, W. Wu, C. Qi,
H. Jiang* ________ **14485 – 14489**

Copper-Catalyzed Aerobic Oxidative Transformation of Ketone-Derived *N*-Tosyl Hydrazones: An Entry to Alkynes

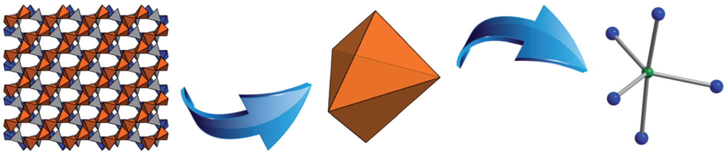


The ynes: The title reaction leads to synthetically valuable internal alkynes and diynes. This method features an inexpensive catalyst, O_2 as the oxidant, good functional-group tolerance, high regioselectivity, and readily available starting materials. DABCO = 1,4-diazabicyclo[2.2.2]octane, Ts = 4-toluenesulfonyl.

Phosphorus Nitrides

D. Baumann,
W. Schnick* ________ **14490 – 14493**

Pentacoordinate Phosphorus in a High-Pressure Polymorph of Phosphorus Nitride Imide $P_4N_6(NH)$



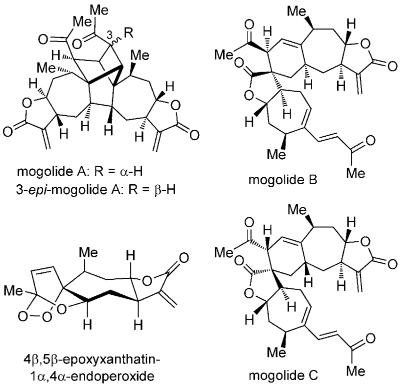
Give me five: Pentacoordinate phosphorus is detected for the first time in a high-pressure polymorph of phosphorus nitride imide $P_4N_6(NH)$. This phase exhibits a new very dense network structure composed of chains of edge-sharing trigonal PN_5 bipyramids (see picture) connected by P_2N_7 double tetrahedra.

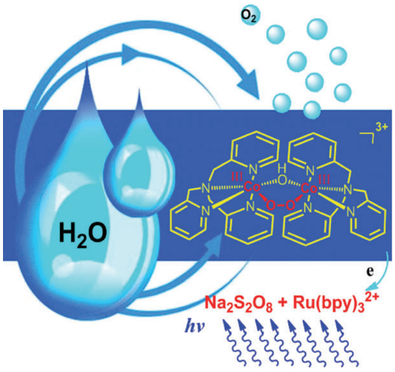
Natural Products Synthesis

H. Shang, J. Liu, R. Bao, Y. Cao, K. Zhao,
C. Xiao, B. Zhou, L. Hu,*
Y. Tang* ________ **14494 – 14498**

Biomimetic Synthesis: Discovery of Xanthanolide Dimers

It takes two: The first biomimetic synthesis of 4β,5β-epoxyxanthatin-1α,4α-endoperoxide has been achieved. Moreover, four unprecedented xanthanolide dimers were synthesized from xanthatin by three different types of dimerizations. Although these dimers were first identified as artifacts in the lab, two of them, mogolides A and B, proved to be naturally occurring substances.



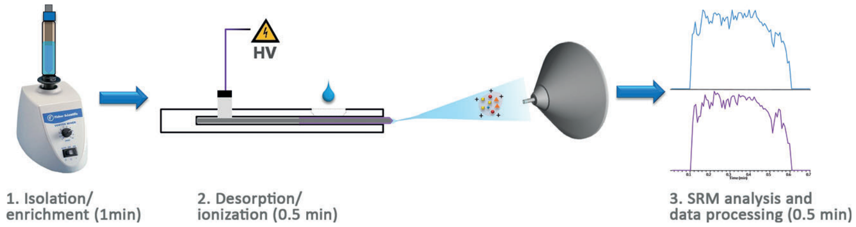


Light-driven oxygen evolution: A dinuclear cobalt complex has been synthesized as a molecular and homogeneous catalyst for light-driven and electrochemical water oxidation. The catalyst can efficiently promote oxygen evolution under visible-light irradiation at near neutral pH in the presence of a ruthenium-based photosensitizer and an electron acceptor.

Water Oxidation

H.-Y. Wang,* E. Mijangos, S. Ott,
A. Thapper* ———— **14499–14502**

Water Oxidation Catalyzed by a Dinuclear Cobalt–Polypyridine Complex

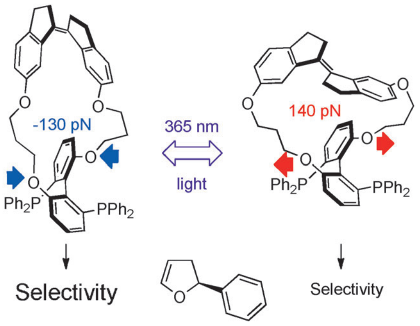


There's no hiding now: Coated blade spray is a technique based on solid-phase microextraction that has been designed for the quick extraction/cleanup of analytes from complex matrices and direct desorption/ionization under ambient MS conditions. The entire analytical process can be completed within 3 min (see picture; HV = high voltage, SRM = selected reaction monitoring) with limits of quantitation in the low picogram-per-millimeter region.

Mass Spectrometry

G. A. Gómez-Ríos,
J. Pawliszyn* ———— **14503–14507**

Development of Coated Blade Spray Ionization Mass Spectrometry for the Quantitation of Target Analytes Present in Complex Matrices

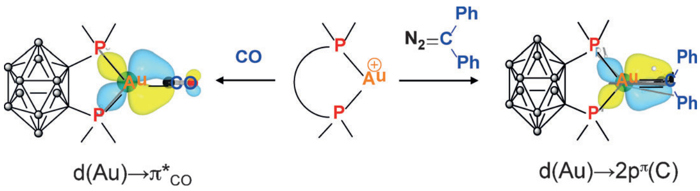


Make the switch: A molecular switch mechanically distorts a chiral ligand, thus generating forces on the order of 100 pN and leading to measureable changes in the enantioselectivities of asymmetric Heck arylations and Trost allylic alkylations.

Ligand Design

Z. S. Kean, S. Akbulatov, Y. Tian,
R. A. Widenhoefer,* R. Boulatov,*
S. L. Craig* ———— **14508–14511**

Photomechanical Actuation of Ligand Geometry in Enantioselective Catalysis



A gift from gold: Bending was shown to significantly enhance π-backdonation in gold(I) complexes. This strategy gives access to the first classical carbonyl complex of gold and allows the isolation of a diphenyl carbene complex that is stabilized by the gold fragment rather than the carbene substituents. The structures of these new complexes were thoroughly analyzed by spectroscopic, crystallographic, and computational means.

Gold Complexes

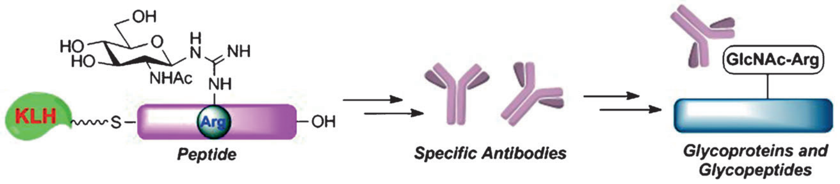
M. Joost, L. Estévez, S. Mallet-Ladeira,
K. Miqueu,* A. Amgoune,*
D. Bourissou* ———— **14512–14516**

Enhanced π-Backdonation from Gold(I): Isolation of Original Carbonyl and Carbene Complexes

Protein Glycosylation

M. Pan, S. Li, X. Li, F. Shao,* L. Liu,* H.-G. Hu* ____ 14517 – 14521

Synthesis of and Specific Antibody Generation for Glycopeptides with Arginine *N*-GlcNAcylation

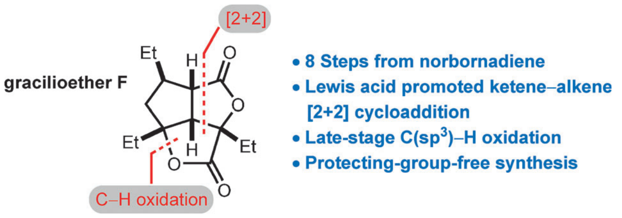


Arginine *N*-GlcNAcylation: Chemical synthesis and specific antibody generation of glycopeptides with *N*-GlcNAcyl groups was accomplished. This enables the generation of highly reactive and specific antibodies for the enrichment and detection of arginine *N*-GlcNAcylated glycoproteins.

Total Synthesis

C. M. Rasik, M. K. Brown* ____ 14522 – 14526

Total Synthesis of Gracilioether F: Development and Application of Lewis Acid Promoted Ketene–Alkene [2+2] Cycloadditions and Late-Stage C−H Oxidation

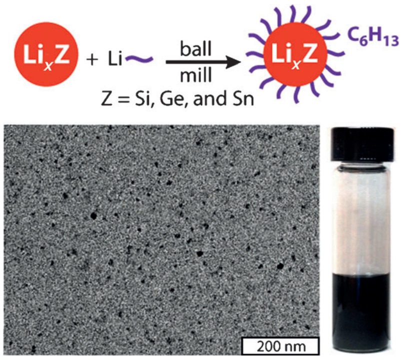


Controlled oxidation: Gracilioether F can be synthesized from norbornadiene in only eight steps while avoiding the use of protecting groups. Key steps of the synthesis include a Lewis acid promoted [2+2] cycloaddition of a ketene with an olefin and a late-stage carboxylic acid directed C(sp^3)−H oxidation.

Lithiated Nanocrystals

J. E. Cloud, Y. Wang, T. S. Yoder, L. W. Taylor, Y. Yang* ____ 14527 – 14532

Colloidal Nanocrystals of Lithiated Group 14 Elements



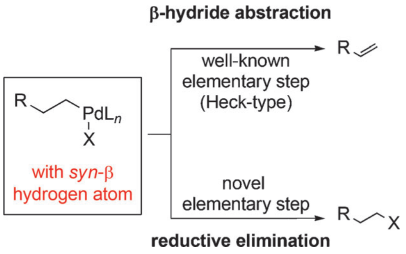
Anode materials: An unconventional method has been successfully developed for synthesizing four types of colloidal nanocrystals of lithiated group 14 elements, specifically, Li$_{4.4}$Si, Li$_{3.75}$Si, Li$_{4.4}$Ge, and Li$_{4.4}$Sn (together denoted as Li$_x$Z; see picture). The success was the result of overcoming the challenge of incompatibility of Li$_x$Z compounds with all conventional passivating ligands.

Synthetic Methods

W. Hao, J. Wei, W. Geng, W.-X. Zhang, Z. Xi* ____ 14533 – 14537

Transfer of Aryl Halide to Alkyl Halide: Reductive Elimination of Alkylhalide from Alkylpalladium Halides Containing *syn*-β-Hydrogen Atoms

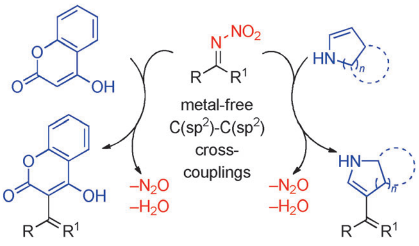
Elimination vs. abstraction: Usually, alkylpalladium halides containing *syn*-β-hydrogen atoms will undergo β-hydride abstraction to afford the Heck-type products. However, this general knowledge is only conditionally correct. Experimental results show that reductive elimination of alkylhalides from alkylpalladium halides containing *syn*-β-hydrogen atoms may surpass the β-hydride abstraction or even become exclusive in certain cases.



Synthetic Methods

V. V. Angeles-Dunham, D. M. Nickerson, D. M. Ray, A. E. Mattson* ______ 14538 – 14541

Nitrimines as Reagents for Metal-Free Formal C(sp^2)–C(sp^2) Cross-Coupling Reactions

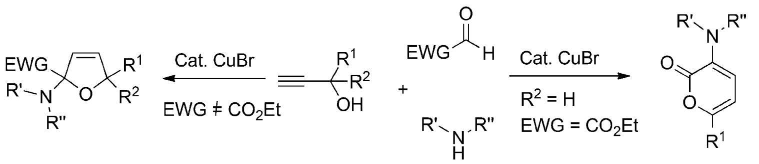


No metal needed: Nitrimines are employed as powerful reagents for metal-free formal C(sp^2)–C(sp^2) cross-coupling reactions. This process is tolerant of a wide array of nitrimine and heterocyclic coupling partners giving rise to the corresponding di- or trisubstituted alkenes, typically in high yield and with high stereoselectivity. This method is ideal for the metal-free construction of heterocycle-containing drug targets, such as phenprocoumon.

Heterocycles

W. Fan, S. Ma* ______ 14542 – 14545

Copper(I)-Catalyzed Three-Component Reaction of Terminal Propargyl Alcohols, Aldehydes, and Amines: Synthesis of 3-Amino-2-pyrones and 2,5-Dihydrofurans

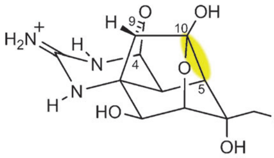


Magic trio: The title reaction proceeds under mild reaction conditions. The reaction involves a sequential A^3-coupling, alkyne–allene isomerization, and cycloisomerization to generate α-amino 2,5-dihydrofurans (see scheme; EWG = electron-withdrawing group). In case of using ethyl glyoxalate as the aldehyde, a ring-opening, lactonization, and isomerization process affords the 3-amino-2-pyrones.

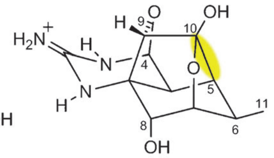
Biosynthesis

Y. Kudo, Y. Yamashita, D. Mebs, Y. Cho, K. Konoki, T. Yasumoto, M. Yotsu-Yamashita* ______ 14546 – 14549

C5–C10 Directly Bonded Tetrodotoxin Analogues: Possible Biosynthetic Precursors of Tetrodotoxin From Newts



4,9-anhydro-10-hemiketal-5-deoxytetrodotoxin (**2**)



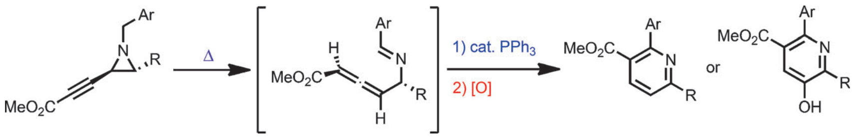
4,9-anhydro-8-*epi*-10-hemiketal-5,6,11-trideoxytetrodotoxin (**3**)

Breaking newt ground: Two tetrodotoxin analogues (**2** and **3**) were discovered in toxic newts. Their bicyclic carbon skeletons consist of ten carbons, thus suggesting a possible monoterpene origin for tetrodotoxin (TTX, **1**). Based on their structural features, Baeyer–Villiger-like oxidation or cleavage of the C5–C10 bond was proposed for the final stage of the biosynthesis of tetrodotoxin.

Organocatalysis

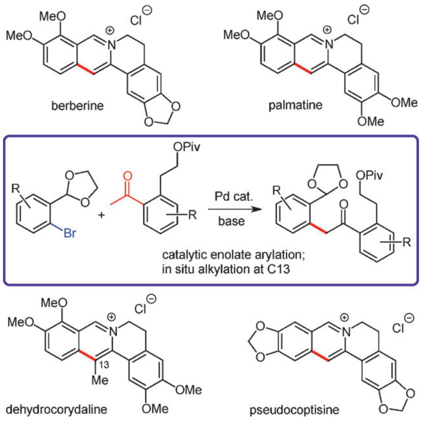
M. Yoshida,* T. Mizuguchi, K. Namba ______ 14550 – 14554

One-Pot Synthesis of Tri- and Tetrasubstituted Pyridines by Sequential Ring-Opening/Cyclization/Oxidation of N-Arylmethyl 3-Aziridinylpropiolate Esters



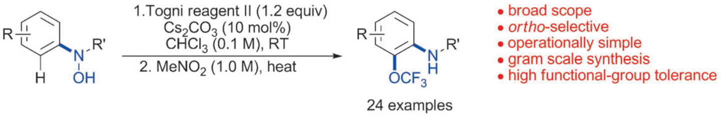
Small ring, big ring: A novel strategy for the one-pot synthesis of substituted pyridines from N-arylmethyl 3-aziridinylpropiolate esters is described. The method employs a three-step procedure including the formation of allenyl imines, phosphine-catalyzed cyclization, and subsequent oxidation of the dihydropyridines. Depending on the reaction conditions of the final oxidation step, tri- and tetrasubstituted pyridines can be selectively produced.

Natural Product Synthesis



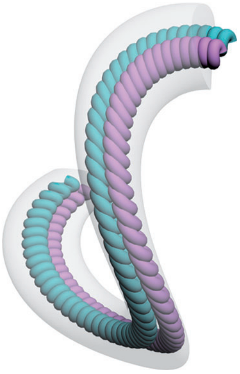
All in the family: A concise synthesis of the biologically active alkaloid berberine is reported, and a versatile palladium-catalyzed enolate arylation is used to form the isoquinoline core. This modular route allows the rapid synthesis of other members of the protoberberine family (pseudocoptisine and palmatine) by using different coupling partners. Moreover, substituents can be rapidly and regioselectively introduced at the C13 position (dehydrocorydaline). Piv = pivaloyl.

Synthetic Methods



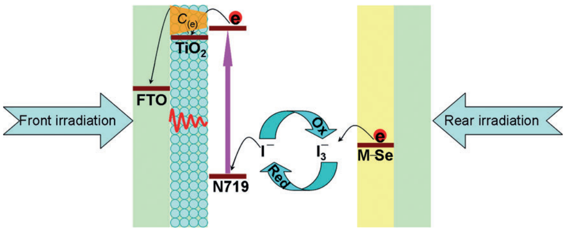
What a move: Trifluoromethoxylation of arenes has been achieved through a thermally induced intramolecular OCF_3 migration. This operationally simple protocol, which is amenable to gram-scale synthesis, affords various synthetically useful trifluoromethoxylated aniline derivatives in good yields and with high levels of *ortho* selectivity.

Energy Storage Devices

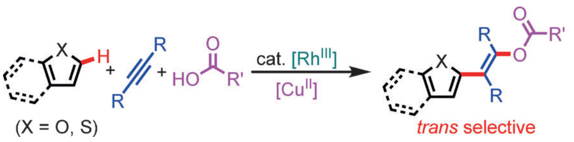


My flexible friend: Springlike electrodes with remarkable electrochemical properties have been used to create flexible and stretchable fiber-shaped supercapacitors and lithium-ion batteries. The electrodes, which are made from twisted aligned multiwalled carbon nanotubes (see picture), can be stretched by over 300%, and the devices show stable performance under bending and stretching deformations.

Energy Conversion



Transparent counter electrodes consisting of metal selenide binary alloys (Co, Ni, Cu, Fe, Ru) were synthesized and applied in bifacial dye-sensitized solar cells (DSSCs). These solar cells exhibit good energy conversion efficiencies regardless of whether the solar cell is irradiated from the front or from the rear.

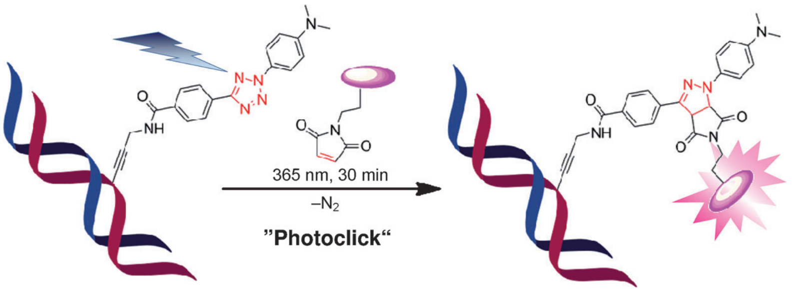


What a pair: A Rh^{III}/Cu^{II}-promoted process is reported to provide tetrasubstituted enol esters in a *trans*-selective fashion. This three-component reaction uses a rhodium(III) catalyst for the C2-selective activation of electron-rich heteroarenes and the addition across the alkyne. Copper(II) then takes over to forge the vinyl ester bond. The method was also used for the functionalization of bioactive furocoumarin natural products.

C–H Activation

M. V. Pham, N. Cramer* _ **14575–14579**

Rhodium(III)/Copper(II)-Promoted *trans*-Selective Heteroaryl Acyloxylation of Alkynes: Stereodefined Access to *trans*-Enol Esters

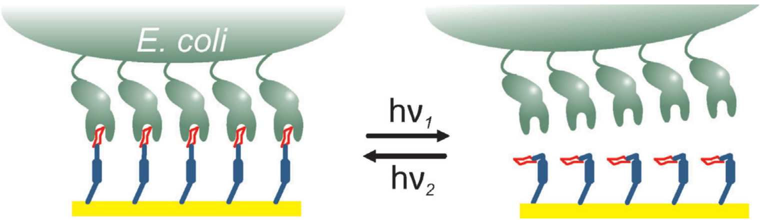


A light click away: The diaryltetrazole group at the 5-position of 2′-deoxyuridine allows the photoinduced postsynthetic modification with maleimide-functionalized sulfo-Cy3 dye.

Click Chemistry

S. Arndt,
H.-A. Wagenknecht* ____ **14580–14582**

“Photoclick” Postsynthetic Modification of DNA



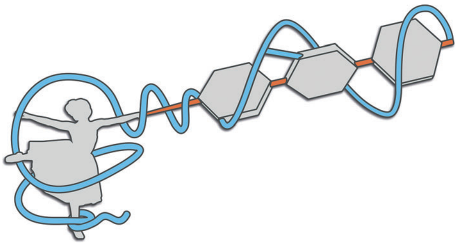
To bind or not to bind: Although azobenzene α-mannosides are good ligands for the bacterial adhesins in both isomeric forms (*E* and *Z*), photochemical reorientation of the α-mannosyl moieties within a biorepulsive monolayer (as a glycocalyx model) can reversibly alter the adhesion of bacterial cells to the surface.

Bacterial Adhesion

T. Weber, V. Chandrasekaran, I. Stamer,
M. B. Thygesen, A. Terfort,*
T. K. Lindhorst* ________ **14583–14586**

Switching of Bacterial Adhesion to a Glycosylated Surface by Reversible Reorientation of the Carbohydrate Ligand

Front Cover



A molecular dance ribbon: Similar to a dance ribbon pirouetting around its handling stick, an elongated second oligomer wraps itself around the oligophenyl backbone, thereby inducing chirality, in a new type of “Geländer” structure. The new helical molecule was fully characterized and the racemization behavior elucidated.

Helical Structures

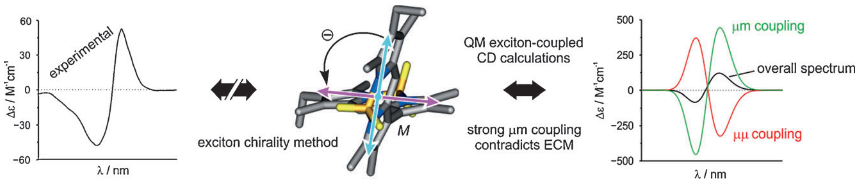
M. Rickhaus, L. M. Bannwart,
M. Neuburger, H. Gsellinger,
K. Zimmermann, D. Häussinger,
M. Mayor* __________ **14587–14591**

Inducing Axial Chirality in a “Geländer” Oligomer by Length Mismatch of the Oligomer Strands

Configuration Determination

T. Bruhn,* G. Pescitelli,* S. Jurinovich, A. Schaumlöffel, F. Witterauf, J. Ahrens, M. Bröring, G. Bringmann* ________ 14592 – 14595

Axially Chiral BODIPY DYEmers: An Apparent Exception to the Exciton Chirality Rule

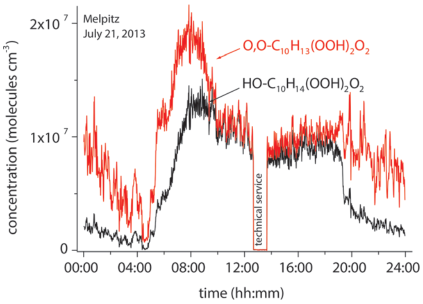


The strong magnetic transition dipole moment of the first π–π* transition of the BODIPY chromophore has a high impact on the chiroptical properties of BODIPY dimers. The μm coupling overcomes the μμ coupling and thus the exciton chirality method is no longer applicable for this biaryl system.

Atmospheric Chemistry

T. Jokinen, M. Sipilä, S. Richters, V.-M. Kerminen, P. Paasonen, F. Stratmann, D. Worsnop, M. Kulmala, M. Ehn, H. Herrmann, T. Berndt* ________ 14596 – 14600

Rapid Autoxidation Forms Highly Oxidized RO_2 Radicals in the Atmosphere



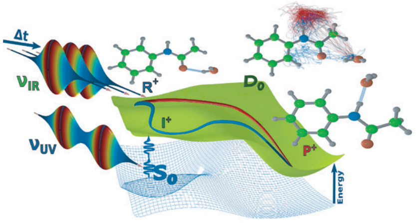
Not only in the solution phase: Highly oxidized RO_2 radicals in the atmosphere are rapidly formed by autoxidation initiated by the reaction of O_3 and OH radicals with biogenic emissions such as limonene and α-pinene. Field measurements (see picture) confirm experimental findings from a flow-tube study. The closed-shell products from this process represent important aerosol constituents influencing aerosol–cloud–climate interactions.

Solvation Dynamics

M. Wohlgemuth, M. Miyazaki, M. Weiler, M. Sakai, O. Dopfer,* M. Fujii,* R. Mitrić* ________ 14601 – 14604

Solvation Dynamics of a Single Water Molecule Probed by Infrared Spectra—Theory Meets Experiment

Migration routes: Following a new, generally applicable strategy, simulations of water solvation dynamics around biomolecular structures can be verified reliably by experimental time-resolved infrared spectroscopy. Quantitative details of solvent motion (timescale and reaction path) can thus be obtained at the molecular level.

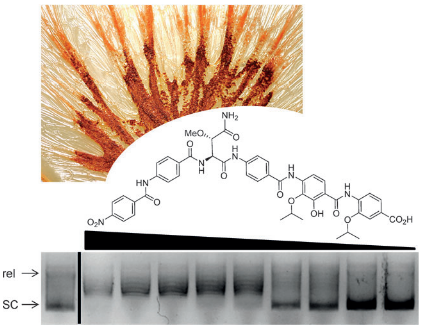


Inside Back Cover

Antibiotics

S. Baumann, J. Herrmann, R. Raju, H. Steinmetz, K. I. Mohr, S. Hüttel, K. Harmrolfs, M. Stadler, R. Müller* ________ 14605 – 14609

Cystobactamids: Myxobacterial Topoisomerase Inhibitors Exhibiting Potent Antibacterial Activity



Against multidrug resistance: A novel chemical scaffold with very pronounced activity against bacterial topoisomerases has been isolated from myxobacteria. Cystobactamid 919-2, as the most active derivative, is a potent antibacterial agent against numerous pathogens, including some Gram-negative species, such as *E. coli* and *A. baumannii* (see Scheme; rel and SC denote relaxed and supercoiled *E. coli* DNA, respectively).

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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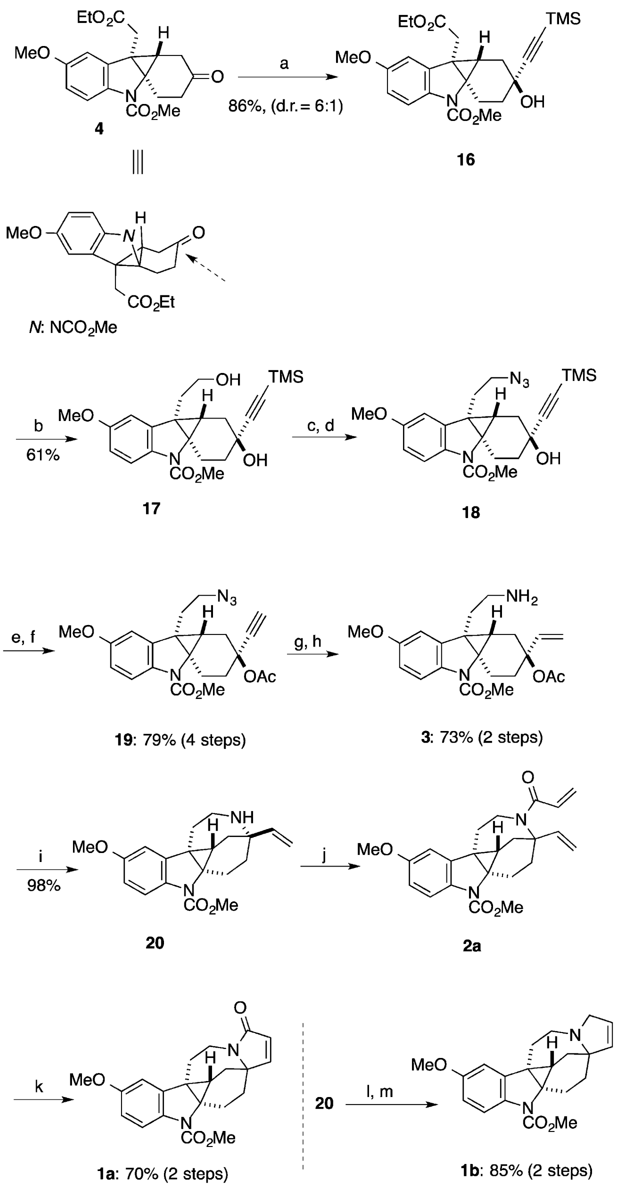
Angewandte Corrigendum

In this communication, the structure of compound **16** in Scheme 3 was incorrect. The revised Scheme 3, including the correct structures of compounds **16**–**19** and **3**, is shown below.



Scheme 3. Total synthesis of **1a** and **1b**.

A Concise and Versatile Synthesis of Alkaloids from *Kopsia tenuis*: Total Synthesis of (±)-Lundurine A and B

S. Arai, M. Nakajima,
A. Nishida* ______________ **5569–5572**

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