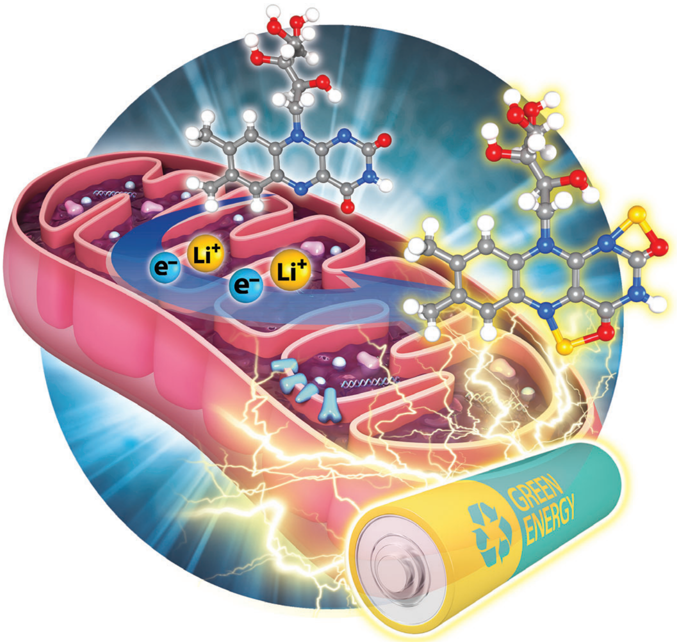
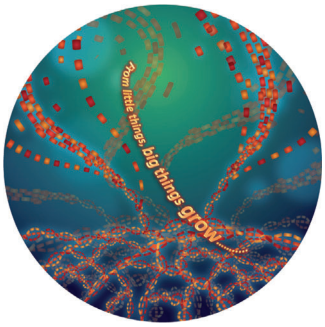
The cellular metabolism …

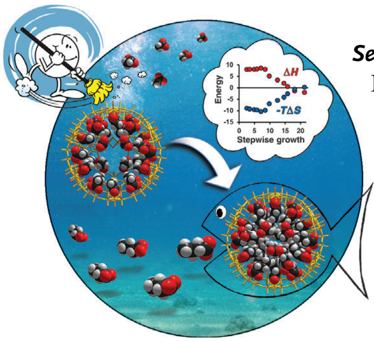


… comprises energy transduction machineries that operate by a series of redox-active components such as flavin molecules to store energy. In their Communication on page 8322 ff., C. B. Park, K. Kang, et al. present a biomimetic approach based on the analogy between energy-storage phenomena of mitochondria and rechargeable lithium batteries to design high-performance energy devices.

Self-Assembling Fibers

In their Communication on page 8266 ff., P. Perlmutter, A. I. Mechler, M.-I. Aguilar, and co-workers describe helical N-acetyl-β^3-peptides that spontaneously self-assemble to form nano- to macroscale fibers.



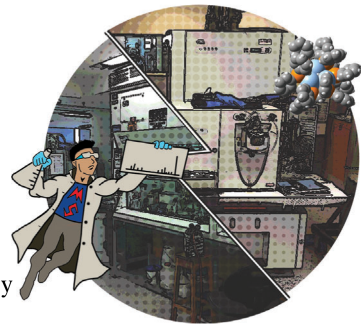


Self-Assembly Processes

In their Communication on page 8358 ff., A. Grego, A. Müller, and I. A. Weinstock describe a method that allows the study of the stepwise growth of structurally defined organic aggregates within a water-soluble porous metal-oxide nanocapsule.

Silver Hydrides

In their Communication on page 8391 ff., G. N. Khairallah, P. S. Donnelly, R. A. J. O'Hair et al. describe the synthesis, isolation, and characterization of $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-}H)(\mu_3\text{-}Cl)]BF_4\cdot 0.5\,CHCl_3$, in which mass spectrometry plays a key role.



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Service

Author Profile

“My favorite quote is ‘when the going gets tough, the tough get going’.
My favorite time of day is early morning …”
This and more about C. Oliver Kappe can be found on page 8198.

News

B. M. Weckhuysen

K. Nozaki

J. A. Lercher

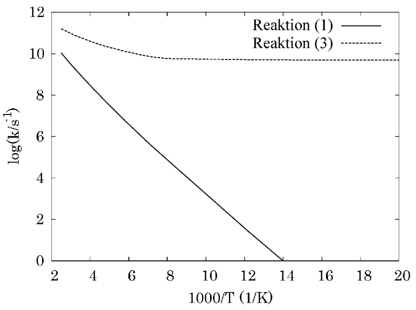
Books

Correspondence

Quantum Mechanics (1)

A. Fernández-Ramos* ______ **8204 – 8205**

Correct Interpretation of How Tunneling Proceeds at Low Temperatures in the Proton Transfer Reactions Involving Thiotropolone: A Comment

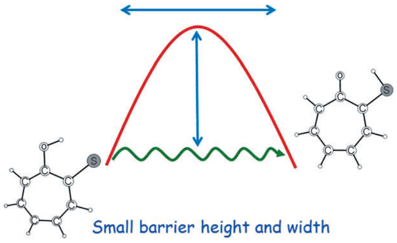


The correct interpretation is provided of how tunneling proceeds at low temperatures in the proton transfer Reactions (1) and (3) involving thiotropolone and tropolone (see the Arrhenius plots). It is also shown that the variational transition-state theory calculations carried out by Jose and Datta (*Angew. Chem.* **2012**, *124*, 9523; *Angew. Chem. Int. Ed.* **2012**, *51*, 9389), as well as their conclusions regarding these two processes are erroneous.

Quantum Mechanics (2)

A. Datta* ______ **8206 – 8207**

Pronounced Tunneling Effect of Proton Transfer in Thiotropolone at Room Temperature: A Reply



Quantum mechanical calculations can provide insight into the role of tunneling in many reactions. At room temperature a pronounced tunneling effect of proton transfer is found for thiotropolone (see picture).

Highlights

Flexible Minerals

D. Gebauer* ______ **8208 – 8209**

Bio-Inspired Materials Science at Its Best—Flexible Mesocrystals of Calcite

Minerals are the benchmark of hard and brittle materials. Self-assembled calcitic spicules were recently obtained utilizing a protein from silica biomineralization, silicatein-α. The synthetic spicules show remarkable material properties including extreme flexibility. Breakthroughs in bio-inspired materials science are highlighted. Will it be possible to obtain similar composites with truly artificial organic constituents?

For the USA and Canada:
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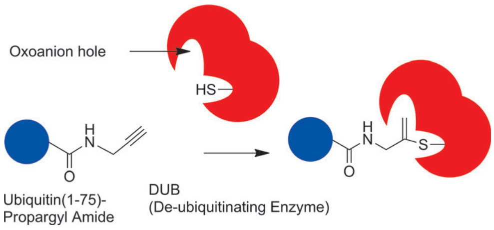


Are aliphatic alkynes truly bioorthogonal? In an attempt to prepare clickable ubiquitin derivatives bearing a C-terminal propargyl amide, two groups have now independently discovered propargylamides to be irreversible inhibitors of cysteine proteases. The unexpected findings demonstrate the unexpected reactivity of alkynes in protein-templated reactions and introduce a novel class of activity-based protein probes.

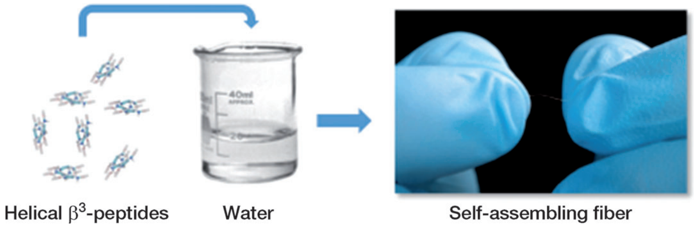
Activity-Based Protein Probes

Reviews

Although known for more than 100 years, fluorination still remains a challenge today. Recent advances, to a large extent enabled by catalysis, have resulted in more efficient methods to introduce fluorine and fluorine-containing functional groups into functionalized molecules. This Review focuses on new strategies for fluorination, with a brief introduction to conventional fluorination, so that the modern methods can be put into perspective.

Fluorine

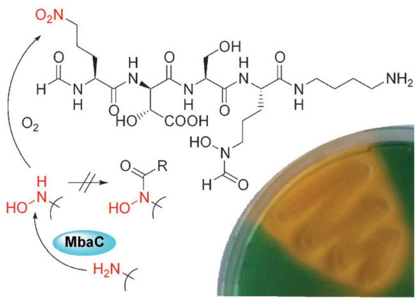
Communications



From little things big things grow: 14-Helical *N*-acetyl β^3-peptides spontaneously self-assemble in a unique head-to-tail fashion to form fibers from solution. The fiber size can be controlled from the nano- to the macroscale. The inherent flexibility in design and ease of synthesis provide powerful new avenues for the development of novel bio- and nanomaterials by supramolecular self-assembly.

Self-Assembling Fibers

Frontispiece

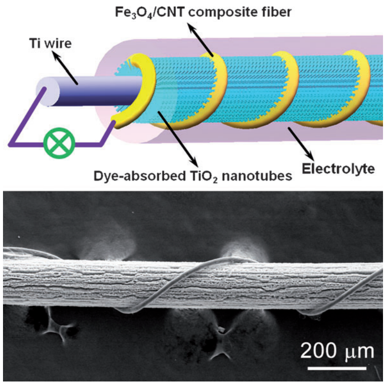


The elusive structure of malleobactin, a virulence factor of pathogens belonging to the *Burkholderia mallei* family, was finally unveiled by genetic and chemical analyses. The novel nitro-substituted siderophore is derived from an unusual, unprotected hydroxylamine, which undergoes spontaneous oxidation, as shown by in vitro assays and detection of analogues featuring hydroxylamino, nitroso, and azoxide groups.

Natural Products

J. Franke, K. Ishida, M. Ishida-Ito,
C. Hertweck* ______ 8271 – 8275

Nitro versus Hydroxamate in Siderophores of Pathogenic Bacteria: Effect of Missing Hydroxylamine Protection in Malleobactin Biosynthesis



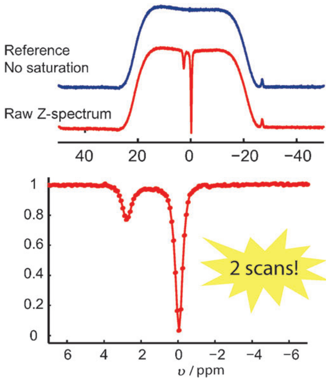
Post-it wire: Novel photovoltaic wires which can be easily attached onto a substrate by a magnetic field and then detached from the substrate after their use have been developed with a record energy conversion efficiency of 8.03 % (see picture; CNT = carbon nanotube). The photovoltaic wire is also lightweight, flexible, and can be interwoven.

Photovoltaics

H. Sun, Z. Yang, X. Chen, L. Qiu, X. You,
P. Chen, H. Peng* ______ 8276 – 8280

Photovoltaic Wire with High Efficiency Attached onto and Detached from a Substrate Using a Magnetic Field

Development of NMR methods: A fast method is reported to obtain Z-spectra for studying magnetization transfer and chemical exchange saturation transfer phenomena in homogeneous systems. The method exploits gradient fields to irradiate a given system and to acquire the *z* polarization of water protons simultaneously at many frequency offsets (see picture).

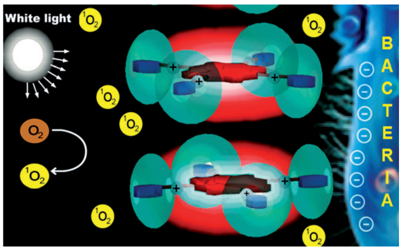


NMR Spectroscopy

X. Xu, J.-S. Lee,
A. Jerschow* ______ 8281 – 8284

Ultrafast Scanning of Exchangeable Sites by NMR Spectroscopy

Photodynamic therapy: A novel supramolecular photosensitizer is efficiently fabricated based on a strong host–guest interaction, which shows an enhanced singlet oxygen generation ability of the porphyrin units and has thus a greatly improved antibacterial efficiency (see picture). The supramolecular photosensitizer is an adaptive system with switchable photophysical properties.



Supramolecular Chemistry

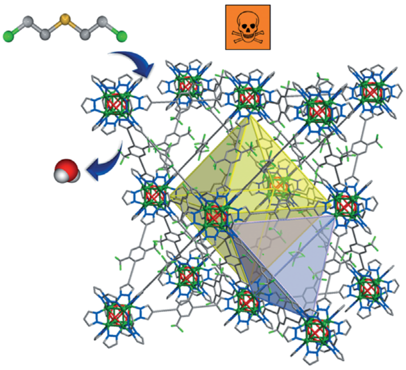
K. Liu, Y. L. Liu, Y. X. Yao, H. Yuan,
S. Wang, Z. Q. Wang,
X. Zhang* ______ 8285 – 8289

Supramolecular Photosensitizers with Enhanced Antibacterial Efficiency

Metal–Organic Frameworks

N. M. Padial, E. Quartapelle Procopio,
C. Montoro, E. López, J. E. Oltra,
V. Colombo, A. Maspero, N. Masciocchi,
S. Galli, I. Senkovska, S. Kaskel, E. Barea,*
J. A. R. Navarro* ______ **8290 – 8294**

Highly Hydrophobic Isoreticular Porous Metal–Organic Frameworks for the Capture of Harmful Volatile Organic Compounds

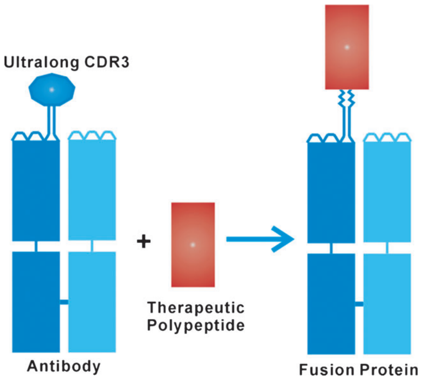


Tunable hydrophobicity: Efficient air filters for the protection against chemical warfare agents might be achieved by surface functionalization of the pores in robust metal–organic frameworks (MOFs) with fluoroalkyl residues and the precise control of their pore size (see picture). These MOFs capture harmful volatile organic compounds even under extremely moist conditions (80% relative humidity).

Protein Engineering

Y. Zhang, D. Wang, L. de Lichtervelde,
S. B. Sun, V. V. Smider, P. G. Schultz,*
F. Wang* ______ **8295 – 8298**

Functional Antibody CDR3 Fusion Proteins with Enhanced Pharmacological Properties

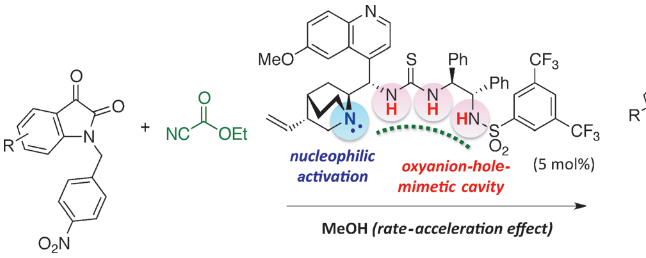


Real staying power: A subset of bovine antibodies (blue, see scheme) feature an ultralong CDR3 loop that forms an antiparallel β-sheet stalk, terminating in a folded, disulfide cross-linked knob domain. Fusion of a polypeptide (red) into this unique CDR3 motif provides a novel strategy for generating polypeptide therapeutics with enhanced pharmacokinetics and pharmacodynamics.

Asymmetric Catalysis

Y. Ogura, M. Akakura, A. Sakakura,*
K. Ishihara* ______ **8299 – 8303**

Enantioselective Cyanoethoxycarbonylation of Isatins Promoted by a Lewis Base–Brønsted Acid Cooperative Catalyst

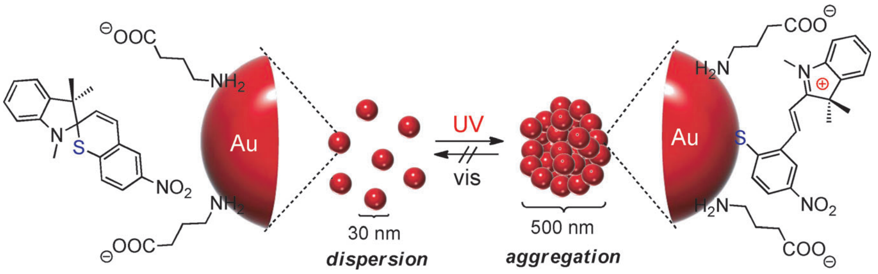


Teaming up to make it happen: In the title reaction, the Lewis basic site of the catalyst activated ethyl cyanoformate, and the deep and flexible Brønsted acidic cavity stabilized and selectively recognized the key reaction intermediate to promote asymmetric acylation (see scheme).

Nanoparticles

Y. Shiraishi,* K. Tanaka, E. Shirakawa,
Y. Sugano, S. Ichikawa, S. Tanaka,
T. Hirai ______ **8304 – 8308**

Light-Triggered Self-Assembly of Gold Nanoparticles Based on Photoisomerization of Spirothiopyran

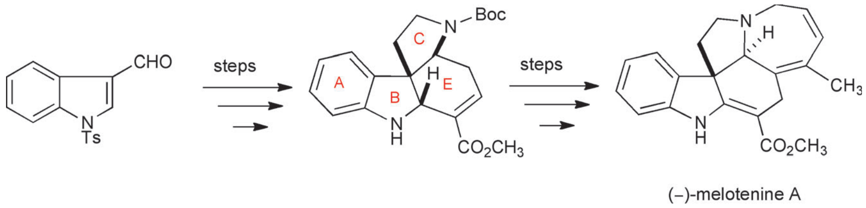


Give it some stick: UV irradiation of spirothiopyran in an aqueous solution of gold nanoparticles (AuNPs) gives AuNP aggregates. The aggregate size is tuned by the photoirradiation time and the aggregation is facilitated by the covalent binding of photoisomerized spirothiopyran to the surface of the AuNPs. This binding decreases the electrostatic repulsion between the AuNPs.

Natural Products

S. Zhao, G. Sirasani, S. Vaddypally, M. J. Zdilla, R. B. Andrade* **8309 – 8311**

Total Synthesis of (−)-Melotenine A

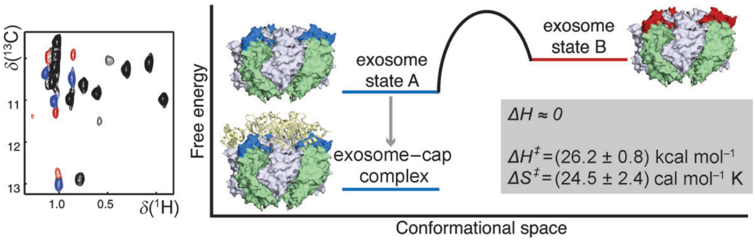


’Melo’ out: A concise asymmetric synthesis of (−)-melotenine A has been accomplished in fourteen steps and 1% overall yield from commercial *N*-tosylindole-3-carboxaldehyde. Key steps include a Piers annulation, an intermolecular vinylogous aldol reaction, and a novel one-pot sequence to prepare the ABCE tetracycle. Boc = *tert*-butoxycarbonyl, Ts = 4-toluenesulfonyl.

Molecular Machines

M. J. C. Audin, G. Dorn, S. A. Fromm, K. Reiss, S. Schütz, M. K. Vorländer, R. Sprangers* **8312 – 8316**

The Archaeal Exosome: Identification and Quantification of Site-Specific Motions That Correlate with Cap and RNA Binding



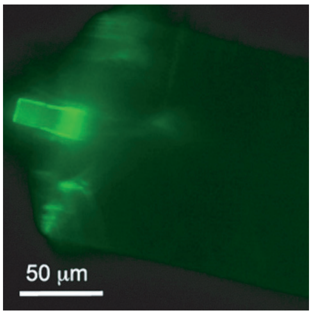
Big and unexpectedly flexible: The 173 kDa exosome core is unexpectedly dynamic in solution. The kinetic and thermodynamic properties connected with the identified exchange process were quantified. Both cap protein and RNA substrate binding significantly alter the identified motions, suggesting that these interactions occur through conformational selection.

Optochemical Sensing

X. A. Ton, B. Tse Sum Bui, M. Resmini, P. Bonomi, I. Dika, O. Soppera, K. Haupt* **8317 – 8321**

A Versatile Fiber-Optic Fluorescence Sensor Based on Molecularly Imprinted Microstructures Polymerized in Situ

Seeing molecules: A method using laser-induced photopolymerization was developed to generate highly selective fiber optic sensors in a few seconds that are based on molecularly imprinted polymer (MIP) microtips. The fluorescence detection signal was enhanced using gold nanoparticles. The sensor also detects nonfluorescent analytes when a fluorescent signaling monomer is incorporated into the MIP.



Biomimetics

M. Lee, J. Hong, D.-H. Seo, D. H. Nam, K. T. Nam, K. Kang,* C. B. Park* **8322 – 8328**

Redox Cofactor from Biological Energy Transduction as Molecularly Tunable Energy-Storage Compound

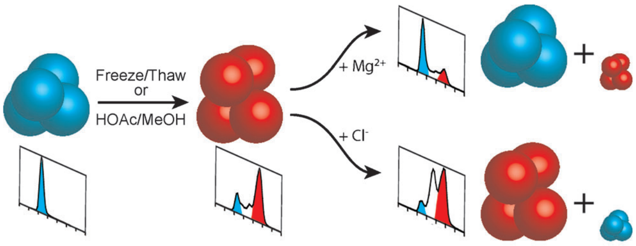
Flavin Battery: Flavins are used as a molecularly tunable cathode material that reversibly reacts with two lithium ions and two electrons per formula unit. Combined ex situ analyses and DFT calculations reveal that the redox reaction occurs using two successive single-electron transfer steps at nitrogen atoms of the diazabutadiene motif (see picture).

Front Cover

Protein Structure

L. Han, B. T. Ruotolo* ____ 8329–8332

Hofmeister Salts Recover a Misfolded Multiprotein Complex for Subsequent Structural Measurements in the Gas Phase

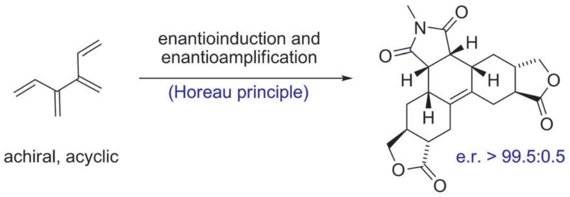


A misfolded protein complex (see picture, red tetramer), which exists both in solution and in the gas phase, can be recovered back to a native-like structure (blue) by the addition of salts prior to desorption/ionization into the gas phase using nano-electrospray ionization.

Synthetic Methods

N. J. Green, A. L. Lawrence, G. Bojase, A. C. Willis, M. N. Paddon-Row,* M. S. Sherburn* ____ 8333–8336

Domino Cycloaddition Organocascades of Dendralenes

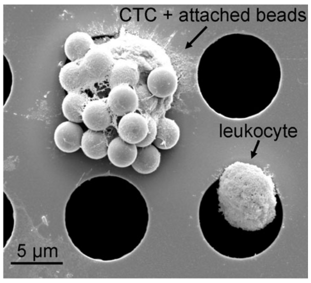


Hooray Horeau! Highly enantioselective organocatalyzed Diels–Alder reaction cascades are disclosed for the first time. The reaction enables the efficient and rapid construction of enantiopure polycycles from simple achiral, acyclic polyenes.

Cancer Cells

H. J. Lee, J. H. Oh, J. M. Oh, J. M. Park, J. G. Lee, M. S. Kim, Y. J. Kim, H. J. Kang, J. Jeong, S. I. Kim, S. S. Lee,* J. W. Choi,* N. Huh* ____ 8337–8340

Efficient Isolation and Accurate In Situ Analysis of Circulating Tumor Cells Using Detachable Beads and a High-Pore-Density Filter

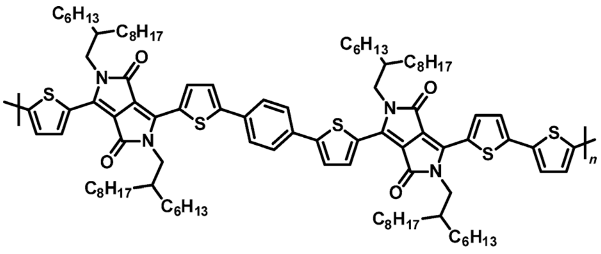


Analysis of cancer cells: A new technique isolates rare circulating tumor cells (CTCs) and analyzes their protein expression by the use of detachable beads and high-pore-density filters. This technique shows significantly improved efficiency in the isolation of rare CTCs from peripheral blood and enables accurate measurement of in situ protein-expression levels.

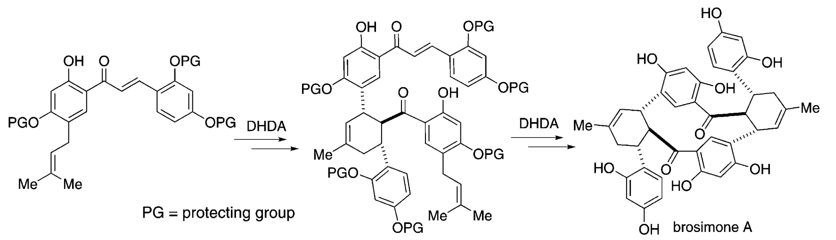
Organic Photovoltaics

K. H. Hendriks, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk, R. A. J. Janssen* ____ 8341–8344

High-Molecular-Weight Regular Alternating Diketopyrrolopyrrole-based Terpolymers for Efficient Organic Solar Cells



A regular alternating terpolymer design strategy is used to create a semiconducting polymer with tailored energy levels and optical band gap. Combined with a modified synthetic procedure for the polymerization reaction, high-molecular-weight polymers of the terpolymer as well as the parent co-polymers were obtained with high efficiencies (up to 8.0%) in organic solar cells when combined with [70]PCBM.

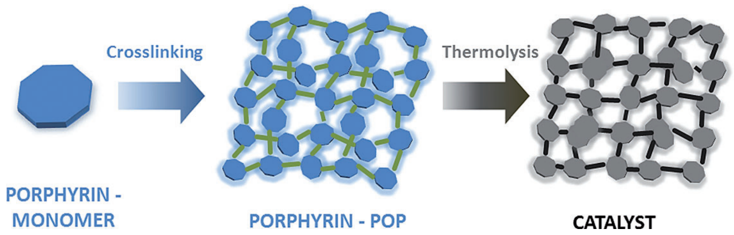


Passing (H_2) gas: Concise syntheses of the natural products brosimones A and B have been achieved using sequential dehydrogenative Diels–Alder (DHDA) cycloadditions. The syntheses employ either Pt/C-cyclopentene or DDQ to effect dehydrogenation of prenylchalcone substrates in combination with silver nanoparticles to promote subsequent Diels–Alder cycloadditions.

Natural Product Synthesis

C. Qi, H. Cong, K. J. Cahill, P. Müller,
R. P. Johnson,
J. A. Porco, Jr.* 8345 – 8348

Biomimetic Dehydrogenative Diels–Alder Cycloadditions: Total Syntheses of Brosimones A and B



An electrocatalyst for the oxygen reduction reaction that is free of precious metals was prepared by thermal activation of an ultrahigh-surface-area porous polyporphyrin. The PEM fuel cells made with such catalyst demonstrated excellent current and power densities.

Fuel-Cell Catalysts

S. Yuan, J. Shui, L. Grabstanowicz,
C. Chen, S. Commet, B. Reprogle, T. Xu,
L. Yu,* D.-J. Liu* 8349 – 8353

A Highly Active and Support-Free Oxygen Reduction Catalyst Prepared from Ultrahigh-Surface-Area Porous Polyporphyrin

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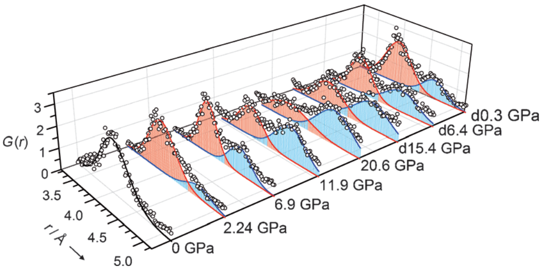


Pressed for time: Amorphous calcium carbonate (ACC) undergoes a reversible amorphous–amorphous phase transition at 10 GPa, adopting an aragonite-like local order. This result suggests a mechanism by which Mg^{2+}—a cation with smaller ionic radius than Ca^{2+}—modifies the local order of ACC to an aragonite-like order by helping to decrease the molar volume of the amorphous phase.

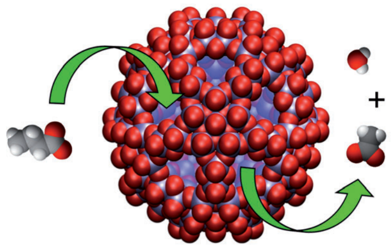
Polyamorphism

A. Fernandez-Martinez,* B. Kalkan,
S. M. Clark,
G. A. Waychunas 8354 – 8357

Pressure-Induced Polyamorphism and Formation of 'Aragonitic' Amorphous Calcium Carbonate

---

Unprecedented information concerning how the relative roles of different hydrophobic effects evolve during multistep hydrophobic assembly processes is provided by using a unique type of experiment to resolve the underlying energetics of individual growth steps in the formation of a structurally well-defined micelle-like organic aggregate of *n*-butyrate ions within a porous inorganic-oxide nanocapsule.



Supramolecular Chemistry

VIP

A. Grego, A. Müller,*
I. A. Weinstock* 8358 – 8362

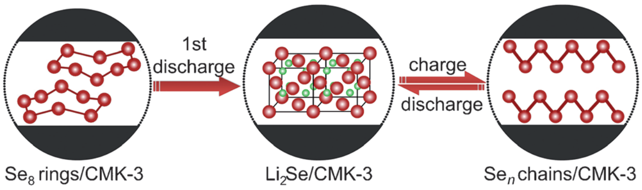
Stepwise-Resolved Thermodynamics of Hydrophobic Self-Assembly

Inside Back Cover

Li–Se Batteries

C.-P. Yang, S. Xin, Y.-X. Yin, H. Ye,
J. Zhang, Y.-G. Guo* ______ **8363 – 8367**

An Advanced Selenium–Carbon Cathode for Rechargeable Lithium–Selenium Batteries

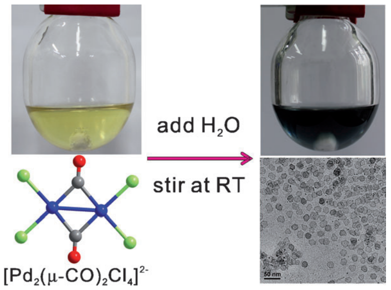


Selenium has been confined in the form of cyclic Se_8 molecules within ordered mesoporous carbon for use as a cathode material in Li–Se batteries. An ex situ study of the Se cathode reveals conversion from cyclic Se_8 molecules into chain-like Se_n molecules upon cycling. This effectively eliminates the shuttle effect of Se, resulting in superior electrochemical performance in terms of volumetric capacity density and cycling stability.

Pd Nanosheets

H. Li, G. X. Chen, H. Y. Yang, X. L. Wang,
J. H. Liang, P. X. Liu, M. Chen,
N. F. Zheng* ____________ **8368 – 8372**

Shape-Controlled Synthesis of Surface-Clean Ultrathin Palladium Nanosheets by Simply Mixing a Dinuclear Pd^{I} Carbonyl Chloride Complex with H_2O

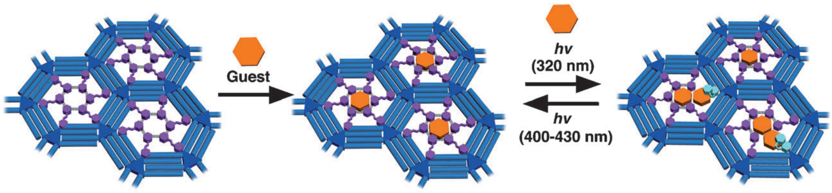


Simple shape control: Ultrathin Pd nanosheets are readily fabricated by simply mixing $[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$ with H_2O at ambient temperature. The as-prepared Pd nanosheets are surface clean and serve as an excellent platform to evaluate the effect of organic capping agents on the catalytic and electrocatalytic properties of Pd nanocrystals.

Tailored 2D Pores

K. Tahara,* K. Inukai, J. Adisoejoso,
H. Yamaga, T. Balandina, M. O. Blunt,
S. De Feyter,* Y. Tobe* _____ **8373 – 8376**

Tailoring Surface-Confined Nanopores with Photoresponsive Groups

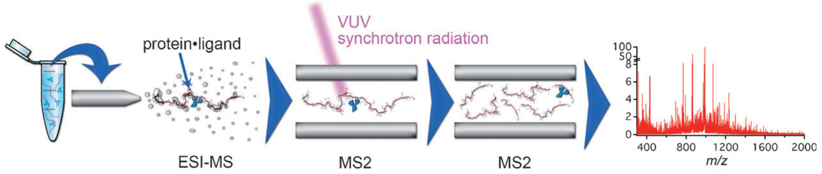


Opening light: Two-dimensional pores are formed by the self-assembly of azobenzene-functionalized triangular building blocks on graphite at the liquid–solid interface. These pores can selectively host a guest molecule. The pore size can be reversibly changed by irradiation at different wavelength which changes the number of guest molecules that are adsorbed (see scheme).

Mass Spectrometry of Proteins

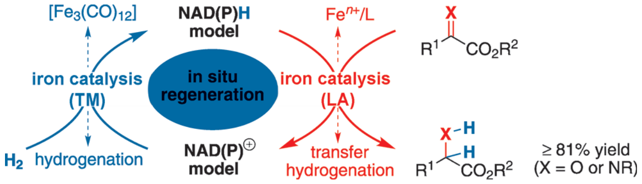
F. Canon, A. R. Milosavljević,
G. van der Rest, M. Réfrégiers, L. Nahon,
P. Sarni-Manchado, V. Cheynier,
A. Giuliani* ____________ **8377 – 8381**

Photodissociation and Dissociative Photoionization Mass Spectrometry of Proteins and Noncovalent Protein–Ligand Complexes



Weight of evidence: Using synchrotron radiation, photo-fragmentation of an intrinsically disordered protein is probed and compared with classical tandem mass-spectrometry activation techniques. It provides excellent sequence coverage allowing the identification of the protein noncovalent binding sites.

Inside Cover



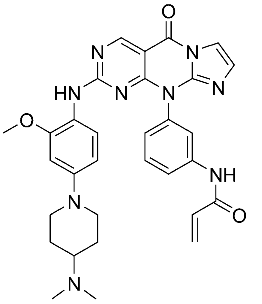
Two irons for a smoother finish: An NAD(P)H model was regenerated readily in situ by iron-catalyzed reduction with molecular hydrogen. The subsequent biomimetic reduction of α-keto-/α-iminoesters proceeded smoothly in the presence of an iron-based Lewis acid (LA) to provide α-hydroxyesters and amino acid esters in good to excellent yields (see scheme; NAD(P)$^+$ = nicotinamide adenine dinucleotide (phosphate), TM = transition metal).

Iron Catalysis

L.-Q. Lu, Y. Li, K. Junge,
M. Beller* **8382–8386**

Iron-Catalyzed Hydrogenation for the In Situ Regeneration of an NAD(P)H Model: Biomimetic Reduction of α-Keto-/α-Iminoesters

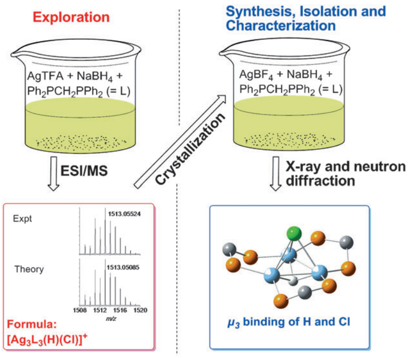
Catching the mutants: Pyrimido[4,5-*d*]pyrimidin-4(1*H*)-one derivatives (see example) were identified as specific inhibitors of $EGFR^{T790M}$ mutants. The compounds bound with T790M or L858R/T790M mutants with significantly lower K_d values than that with $EGFR^{WT}$. They also selectively inhibited EGFR signal transduction and proliferation of NSCLC cells harboring $EGFR^{L858R/T790M}$ mutation, but were significantly less potent to cells with $EGFR^{WT}$.



Drug Design

T. Xu, L. Zhang, S. Xu, C.-Y. Yang, J. Luo, F. Ding, X. Lu,* Y. Liu, Z. Tu, S. Li, D. Pei, Q. Cai, H. Li, X. Ren, S. Wang,
K. Ding* **8387–8390**

Pyrimido[4,5-*d*]pyrimidin-4(1*H*)-one Derivatives as Selective Inhibitors of EGFR Threonine^{790} to Methionine^{790} (T790M) Mutants



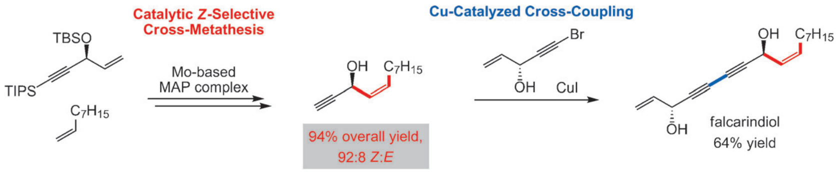
Mass spectrometry shows the way! MS analysis of silver salts treated with sodium borohydride in the presence of a bis(phosphino) ligand revealed the formation of novel silver hydride nanocluster cations instead of all silver nanocluster cations. This serendipitous discovery prompted the condensed-phase synthesis, isolation, and characterization of $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-}H)(\mu_3\text{-}Cl)]BF_4\cdot 0.5\,CHCl_3$.

Silver Hydrides

A. Zavras, G. N. Khairallah,* T. U. Connell, J. M. White, A. J. Edwards, P. S. Donnelly,* R. A. J. O'Hair* **8391–8394**

Synthesis, Structure and Gas-Phase Reactivity of a Silver Hydride Complex $[Ag_3\{(PPh_2)_2CH_2\}_3(\mu_3\text{-}H)(\mu_3\text{-}Cl)]BF_4$

Back Cover



Get me a *Z* (olefin): Efficient catalytic cross-metathesis reactions that afford *Z*-disubstituted allylic silyl or benzyl ethers are reported (see scheme, MAP = monoalkoxide pyrrolide). The approach, in combination with catalytic cross-coupling, provides a general entry to otherwise difficult-to-access alkyne-containing *Z* olefins.

Cross-Metathesis

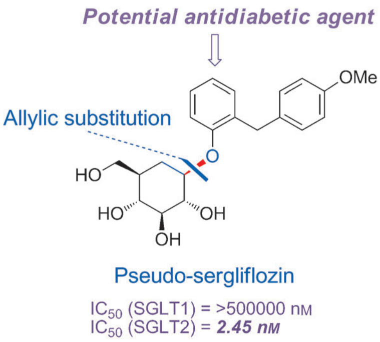
T. J. Mann, A. W. H. Speed, R. R. Schrock,
A. H. Hoveyda* **8395–8400**

Catalytic *Z*-Selective Cross-Metathesis with Secondary Silyl- and Benzyl-Protected Allylic Ethers: Mechanistic Aspects and Applications to Natural Product Synthesis

Drug Design

T. K. M. Shing,* W.-L. Ng, J. Y.-W. Chan, C. B.-S. Lau ——— **8401 – 8405**

Design, Syntheses, and SAR Studies of Carbocyclic Analogues of Sergliflozin as Potent Sodium-Dependent Glucose Cotransporter 2 Inhibitors

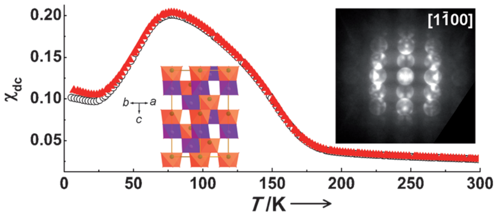


Combating diabetes: A small-molecule carbohydrate mimic, pseudo-sergliflozin, was synthesized effectively by a regio- and stereoselective allylic substitution reaction. It was found to be a potent and selective inhibitor of a transporter protein—sodium-dependent glucose cotransporter 2 (SGLT2)—which is responsible for glucose reabsorption in the human body. It could be a lead compound for further development into an antidiabetic agent.

Polar Magnetic Oxides

M. R. Li, D. Walker, M. Retuerto, T. Sarkar, J. Hadermann, P. W. Stephens, M. Croft, A. Ignatov, C. P. Grams, J. Hemberger, I. Nowik, P. S. Halasyamani, T. T. Tran, S. Mukherjee, T. S. Dasgupta, M. Greenblatt* ——— **8406 – 8410**

Polar and Magnetic Mn_2FeMO_6 (M = Nb, Ta) with $LiNbO_3$-type Structure: High-Pressure Synthesis

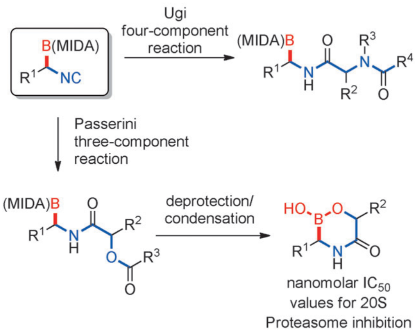


Polar $LiNbO_3$-type magnetic oxides have been extended, for the first time, to the $A_2BB'O_6$ family. $Mn^{2+}{}_2Fe^{3+}M^{5+}O_6$ (M = Nb, Ta), synthesized at high pressure, adopt a polar structure, as demonstrated by electron diffraction and the second harmonic generation effect, and they have interesting magnetic properties.

Multicomponent Reactions

A. Zajdlik, Z. Wang, J. L. Hickey, A. Aman, A. D. Schimmer, A. K. Yudin* ——— **8411 – 8415**

α-Boryl Isocyanides Enable Facile Preparation of Bioactive Boropeptides



Entry to bioactive boropeptides: MIDA-containing α-boryl isocyanides are isolable molecules which allow one-step access to boroalkyl-functionalized heterocycles as well as biologically active boropeptides through a multicomponent approach. Among these derivatives are 6-boromorpholinones, novel borocycles with nanomolar IC_{50} values for 20S proteasome inhibition. MIDA = N-methyliminodiacetyl.

Asymmetric Hydrogenation

T.-L. Liu, C.-J. Wang,* X. Zhang* ——— **8416 – 8419**

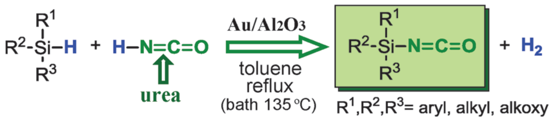
Synthesis of Chiral Aliphatic Amines through Asymmetric Hydrogenation

The direct route: A Rhodium-catalyzed asymmetric hydrogenation method for the efficient synthesis of a broad range of chiral allylic amines and aliphatic amines from readily available materials was developed. A chiral Z-allylic amine was obtained for the first time through a Rhodium–DuanPhos-catalyzed asymmetric hydrogenation. TMS = Trimethylsilyl, cod = cyclooctadiene, TON = turnover number.

Cross-Coupling

K. Taniguchi, S. Itagaki, K. Yamaguchi, N. Mizuno* ______ **8420 – 8423**

Heterogeneous-Gold-Catalyzed Acceptorless Cross-Dehydrogenative Coupling of Hydrosilanes and Isocyanic Acid Generated in situ from Urea

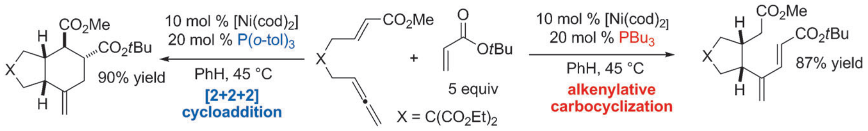


Support structure: In the presence of gold nanoparticles supported on alumina (Au/Al_2O_3), various hydrosilanes can be converted into the corresponding silyl isocyanates using urea as an isocyanate source. The observed catalysis is truly heterogeneous, and the retrieved Au/Al_2O_3 catalyst can be reused several times without any loss of its high catalytic performance.

Multicomponent Cycloadditions

N. N. Noucti, E. J. Alexanian* ______ **8424 – 8427**

Stereoselective Nickel-Catalyzed [2+2+2] Cycloadditions and Alkenylative Cyclizations of Ene-Allenes and Alkenes

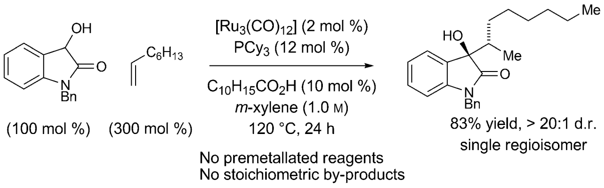


[2+2+2] = 4 (stereocenters)? Nickel-catalyzed multicomponent cycloadditions and alkenylative cyclizations involving two alkenes and one allene are described. The [2+2+2] cycloaddition provides rapid access to stereochemically complex, *cis*-fused hydrindanes. By exchanging P(*o*-tol)$_3$ for PBu_3 as ligand, the reaction pathway can be diverted to an alkenylative cyclization process.

Transfer Hydrogenation

E. Yamaguchi, J. Mowat, T. Luong, M. J. Krische* ______ **8428 – 8431**

Regio- and Diastereoselective C–C Coupling of α-Olefins and Styrenes to 3-Hydroxy-2-oxindoles by Ru-Catalyzed Hydrohydroxyalkylation

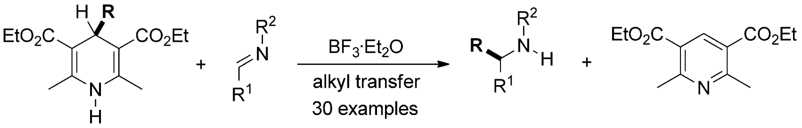


The direct approach: Ruthenium(0)-catalyzed hydrohydroxyalkylation of α-olefins and styrenes with 3-hydroxy-2-oxindoles forms branched products of C–C coupling with high levels of diastereocontrol. A mechanism involving diene–olefin oxidative coupling and a subsequent carboxylic acid co-catalyzed transfer hydrogenolysis of the resulting oxaruthenacycle intermediate is postulated.

Alkylation

G.-X. Li, R. Chen, L. Wu, Q. Fu, X.-M. Zhang, Z. Tang* ______ **8432 – 8436**

Alkyl Transfer from C–C Cleavage



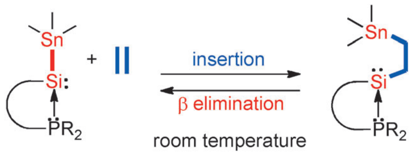
Hydrogenation was only the beginning: Hantzsch esters have now been used to transfer alkyl groups to imines under mild catalytic conditions to provide a variety of amines (see scheme). Benzyl, secondary alkyl, and tertiary alkyl groups containing ether, ester, and hydroxy functionalities were transferred successfully. The use of Hantzsch esters as alkylation reagents offers a practical and complementary alternative to organometallic processes.

Alkene Insertion

R. Rodriguez, Y. Contie, D. Gau,
N. Saffon-Merceron, K. Miqueu,
J.-M. Sotiropoulos, A. Baceiredo,*
T. Kato* ________ 8437 – 8440

Reversible Insertion of Unactivated Alkenes into Silicon(II)–Tin Bonds

Insertion without assertion: Alkenes reacted reversibly under mild conditions (25–85 °C) with phosphine–silylene complexes containing a Si^{II}–Sn bond to give alkyl silylene complexes (see scheme). Theoretical studies indicated that the insertion reaction proceeds through oxidative addition and migratory insertion in a two-step process and thus revealed that silicon(II)–phosphine complexes can behave like transition-metal complexes.

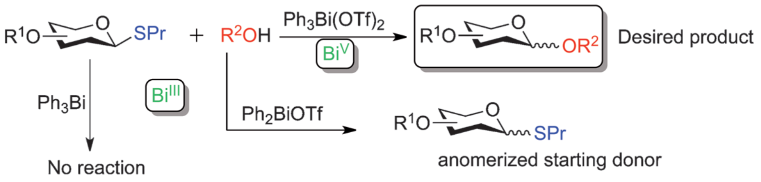


Glycosylation

VIP

M. Goswami, A. Ellern,
N. L. B. Pohl* ________ 8441 – 8445

Bismuth(V)-Mediated Thioglycoside Activation

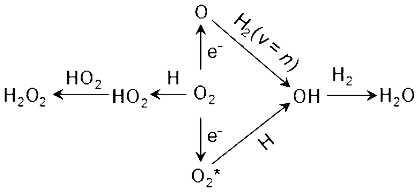


A straightforward method utilizing a bismuth(V) compound was developed for the activation of thiopropylglycosides for coupling to various acceptors; good to excellent yields were obtained without applying additional additives/co-promoters. The method does not require low temperatures, is applicable to a wide variety of carbohydrates, and tolerates different functional groups including alkenes.

Hydrogen Peroxide Synthesis

Y. H. Yi, J. C. Zhou, H. Guo,* J. L. Zhao,
J. Su, L. Wang, X. S. Wang,
W. M. Gong ________ 8446 – 8449

Safe Direct Synthesis of High Purity H_2O_2 through a H_2/O_2 Plasma Reaction

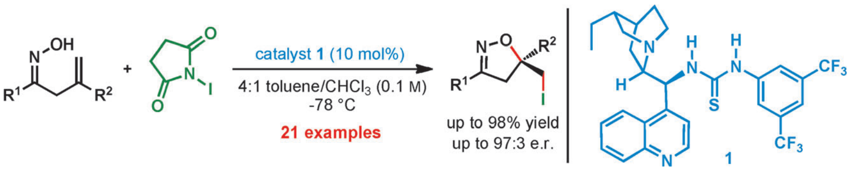


Plasma makes it safer: A gaseous H_2/O_2 plasma reaction has been developed for the safe direct synthesis of H_2O_2. Low electron density favors the generation of H_2O_2 by a chain termination path. This plasma method is promising for the direct synthesis of neutral, high concentration (ca. 60 wt %), and high purity (electronic grade) H_2O_2.

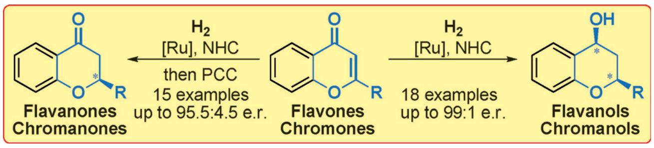
Asymmetric Catalysis

C. B. Tripathi,
S. Mukherjee* ________ 8450 – 8453

Catalytic Enantioselective Iodoetherification of Oximes



Organocatalysis: The first catalytic enantioselective iodoetherification of oximes is developed using commercially available *N*-iodosuccinimide. In the presence of a dihydrocinchonidine-derived thiourea (10 mol %), β,γ-unsaturated oximes undergo facile iodoetherification to produce Δ^2-isoxazolines containing a quaternary stereogenic center generally in high yield with good to excellent enantioselectivity.



Two to four! Readily available flavones and chromones were efficiently converted into four valuable chiral classes of O-heterocycles—flavanones, chromanones, flavanols, and chromanols—by means of an enantioselective Ru/NHC-catalyzed hydrogenation process (see scheme; NHC = N-heterocyclic carbene, PCC = pyridinium chlorochromate).

Asymmetric Hydrogenation

D. Zhao, B. Beiring,
F. Glorius* ______ 8454 – 8458

Ruthenium–NHC-Catalyzed Asymmetric Hydrogenation of Flavones and Chromones: General Access to Enantiomerically Enriched Flavanones, Flavanols, Chromanones, and Chromanols

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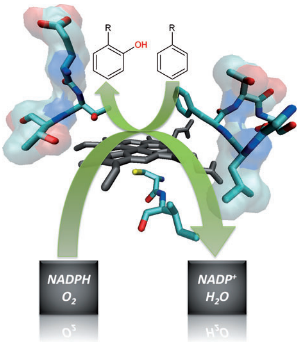
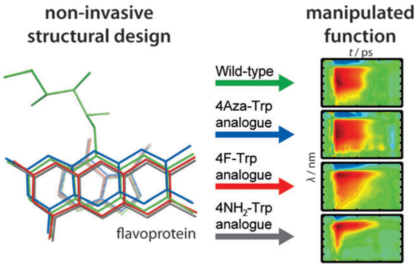


Dream come true: A new monooxygenase catalyst shows excellent activity for the hydroxylation of halogenated benzenes, anisole, and toluene with almost complete *ortho* regioselectivity (see scheme; R = F, Cl, Br, I, CH_3, OCH_3). The substrates were hydroxylated at room temperature in water without cosolvent using molecular oxygen as oxidant.

Aromatic Hydroxylation

A. Dennig, N. Lülsdorf, H. Liu,
U. Schwaneberg* ______ 8459 – 8462

Regioselective *o*-Hydroxylation of Monosubstituted Benzenes by P450 BM3

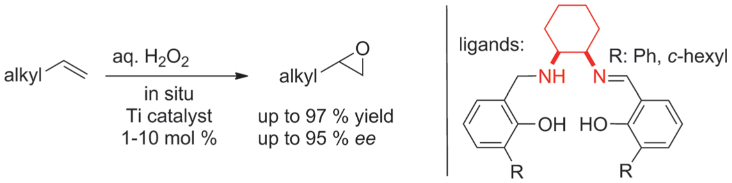


Tamed electrons: To manipulate a protein photocycle in a directed manner, the flavoprotein dodecin was endoscopically modified at its key amino acid tryptophan with substituents carefully selected by their structural and electronic influence. The approach is ideal in the precision of rational protein engineering, and allows correlating tryptophan ionization potentials and electron transfer rates in a Marcus model.

Reaction Control in Proteins

H. Staudt, M. G. Hoesl, A. Dreuw,
S. Serdjukow, D. Oesterhelt, N. Budisa,
J. Wachtveitl,*
M. Grininger* ______ 8463 – 8466

Directed Manipulation of a Flavoprotein Photocycle



Help for the neglected: Terminal, non-conjugated olefins, such as 1-octene, are difficult to epoxidize asymmetrically. Ti salalen complexes based on *cis*-1,2-diaminocyclohexane catalyze this demanding reaction giving high yields and enantioselectivities (up to 95 % *ee*), with H_2O_2 as the oxidant. The X-ray structures of the μ-oxo and peroxo complexes shed light on the coordination behavior of this novel class of ligands.

Asymmetric Catalysis

A. Berkessel,* T. Günther, Q. Wang,
J.-M. Neudörfl ______ 8467 – 8471

Titanium Salalen Catalysts Based on *cis*-1,2-Diaminocyclohexane: Enantioselective Epoxidation of Terminal Non-Conjugated Olefins with H_2O_2

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).

Angewandte Corrigendum

Biomimetic Surface Engineering of Lanthanide-Doped Upconversion Nanoparticles as Versatile Bioprobes

L.-L. Li, R. Zhang, L. Yin, K. Zheng, W. Qin, P. R. Selvin, Y. Lu* **6121–6125**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201109156

The acknowledgment section of this Communication contained an incorrect CPLC grant number. This section should read as follows:

“This work was supported by the Beckman Institute of the University of Illinois through a Seed Grant, and the US National Science Foundation (CMMI 0749028 and DMR-0117792 to Y.L., 0968976 and 0822613 to P.S.) and National Institute of Health (AR044420 and GM068625 to P.S.).”