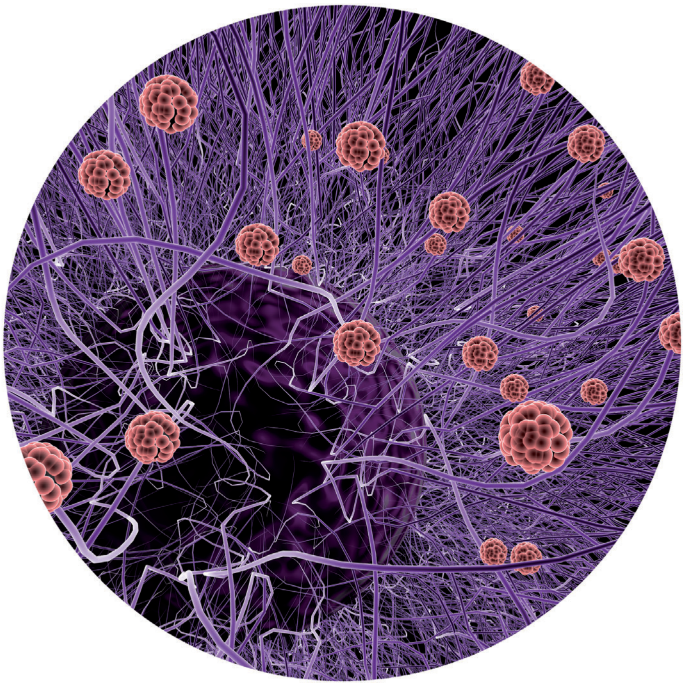
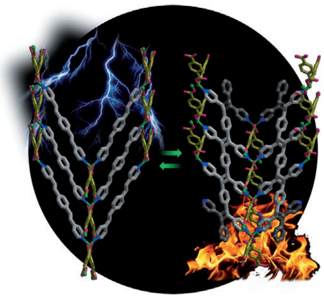
An enzymogel ...

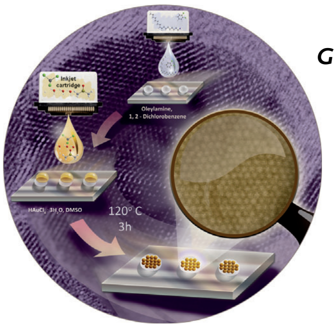


... that shows a novel type of phase-boundary biocatalysis is described by S. Minko, A. Voronov, et al. in their Communication on page 483 ff. The enzymogel particles combine biocatalysis involving enzymes in the particle, stimuli-triggered extracapsular biocatalysis, biocatalytic conversion of substrates contacting the enzymogel when the enzymes engulf the substrate, and stimuli-triggered reattachment of the released enzymes for their reuse (cover image courtesy of Ella Marushchenko).

Metal Organopolymeric Frameworks

In their Communication on page 414 ff., S. S. Lee, M. J. Zaworotko, J. J. Vittal et al. report a light- or heat-induced single-crystal-to-single-crystal interconversion of a Zn^{II} coordination polymer.



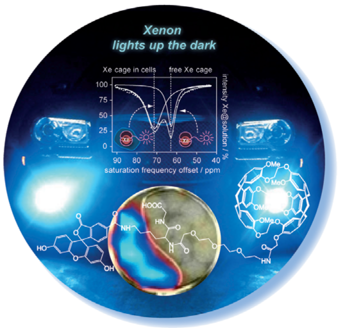


Gold Nanoparticles

The in situ synthesis of gold nanoparticles directly over a substrate surface by using inkjet printing followed by heating at 120°C is described by G. E. Jabbour et al. in their Communication on page 420 ff.

Imaging agents

In their Communication on page 493 ff., L. Schröder et al. demonstrate that sensitive MRI cell tracking with switchable contrast can be achieved using cryptophanes (CrA) as xenon hosts.



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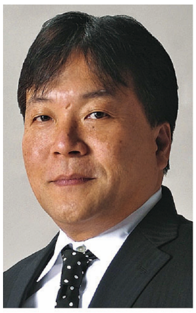
Spotlight on Angewandte's Sister Journals *352–355*

Author Profile

*"In a spare hour, I play the saxophone.
My favorite saying is: hmm, did you already try adding HMPA or AIBN? …"*
This and more about Adriaan J. Minnaard can be found on page 358.

Adriaan J. Minnaard ______ **356**

News



T. Aida

J. Caro

M. Tsapatsis

Van't Hoff Lecture:
T. Aida ______ **357**

Breck Prize:
J. Caro and M. Tsapatsis ______ **357**

Books

Handbook of Polymer Synthesis, Characterization and Processing

Enrique Saldívar-Guerra, Eduardo Vivaldo-Lima

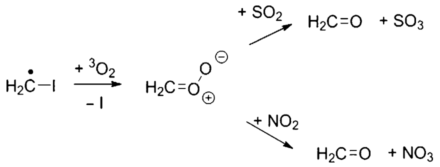
reviewed by A. Schmidt ______ **358**

Highlights

Criegee Intermediates

W. Sander* ———— 362–364

Carbonyl Oxides—Rising Stars in Tropospheric Chemistry



The X factor of tropospheric oxidation: Formaldehyde oxide, the smallest “Criegee intermediate”, has been observed spectroscopically in the gas phase. Field studies provide increasing evidence that Criegee intermediates play a key role in tropospheric oxidation (see scheme).

Light Harvesting

V. K. Praveen, C. Ranjith,
N. Armaroli* ———— 365–368

White-Light-Emitting Supramolecular Gels

Let there be light, let it be white: Recent developments in the use of chromophore-based gels as scaffolds for the assembly of white-light-emitting soft materials have been significant. The main advantage of this approach lies in the facile accommodation of selected luminescent components within the gel. Excitation-energy-transfer processes between these components ultimately generate the desired light output.

Essays

Bonding Models

D. Himmel, I. Krossing,*
A. Schnepf ———— 370–374

Dative Bonds in Main-Group Compounds: A Case for Fewer Arrows!

Risky business? The use of dative bonds to describe the electronic structure of main-group compounds has come into vogue in recent years. But where are the limits? When does the description as a dative bond make sense and when is this view misleading? This Essay develops the idea on the basis of current examples.

$D{:}\!\rightarrow A$ dative bond

or

${}^{\oplus}D{-}A^{\ominus}$ zwitterion?

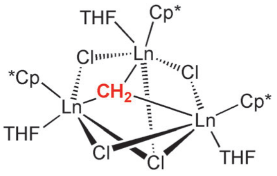
Minireviews

Carbene Chemistry

J. Kratsch, P. W. Roesky* ———— 376–383

Rare-Earth-Metal Methylidene Complexes

Rarely seen carbenes: Transition-metal carbenes have been known for about 50 years and have been widely applied as reagents and catalysts. In contrast, the carbene chemistry of the rare-earth metals is much less developed. Rare-earth-metal alkylidene, especially methylidene compounds (see picture) are an emerging class of compounds with a high synthetic potential.



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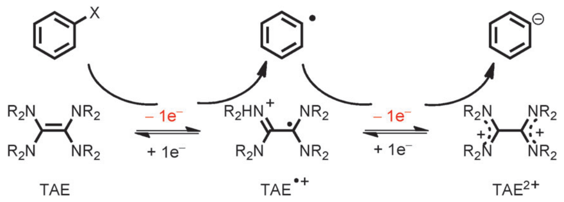
Reviews



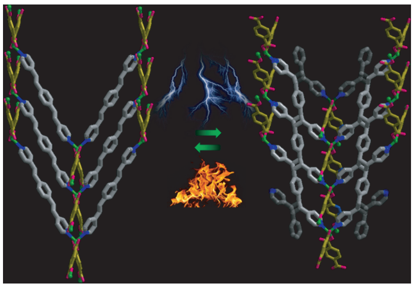
Among the different ways to effect radical formation, one-electron reduction involves the stepwise transfer of one or two electrons from a donor to an organic substrate. Besides metallic reagents, neutral organic molecules have emerged as an attractive novel source of reducing electrons.

Electron Transfer

J. Broggi,* T. Terme,*
P. Vanelle* ——— **384 – 413**

Organic Electron Donors as Powerful Single-Electron Reducing Agents in Organic Synthesis

Communications



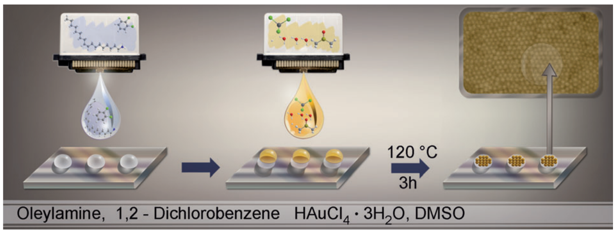
Make or break: A 3D structure consisting of an organic polymer containing cyclobutane rings blended with a Zn^{II} coordination polymer was obtained through a photochemical polymerization reaction. Monocrystalline metal complexes of organic polymer ligands are hitherto unknown. The organic polymer can be depolymerized by cleavage of the cyclobutane rings in a single-crystal-to-single-crystal manner.

Metal Organopolymeric Framework

I.-H. Park, A. Chanthapally, Z. Zhang,
S. S. Lee,* M. J. Zaworotko,*
J. J. Vittal* ——— **414 – 419**

Metal–Organic Organopolymeric Hybrid Framework by Reversible [2+2] Cycloaddition Reaction

Frontispiece



Midas touch: The use of low-cost manufacturing approaches in the synthesis of nanoparticles is critical for many applications. Reactive inkjet printing, along with a judicious choice of precursor/solvent system, was used to synthesize a relatively uniform assembly of crystalline gold nanoparticles, with diameters as small as (8 ± 2) nm, over a given substrate surface.

Nanofabrication

M. Abulikemu, E. H. Da'as, H. Haverinen,
D. Cha, M. A. Malik,
G. E. Jabbour* ——— **420 – 423**

In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing

Inside Back Cover


Angewandte Chemie
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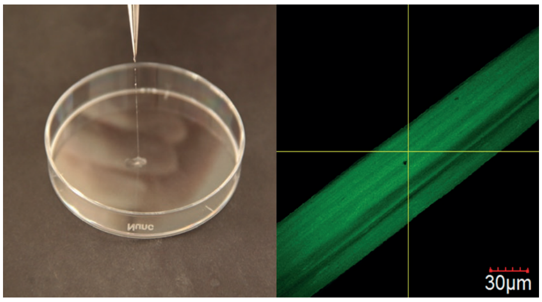
Communications
Molecular-Scale Diagnostics
Medication Detection by a Combinatorial Fluorescent Molecular Sensor
First published online: October 12, 2012
Authors: Dr. Bhimsen Rout1, Linor Unger1, Gad Armony1, Dr. Mark A. Iron2, Dr. David Margulies1,*
Keywords: analytical methods, combinatorial sensors, fluorescent probes, molecular devices, photophysics
DOI: 10.1002/anie.201206374
Working together to uncover the truth: A molecule-sized diagnostic system combining several recognition elements and four fluorescence-emission channels enabled the identification of a wide range of pharmaceuticals on the basis of distinct photophysical processes. The molecular sensor (see simplified representation; ID=identification) was also used to analyze drug concentrations and combinations in urine samples in a high-throughput manner.
There is wide interest in the development of fluorescent molecular sensors triggered by several input signals and their application as computation and analytical devices.[1] Such sensors can imitate the function of electronic
Input: Drug
Output: ID
Figures
References
Supporting Information
Search

Self-Assembled Fibers

F. Wang, Z. Liu, B. Wang, L. Feng, L. Liu,*
F. Lv, Y. Wang,* S. Wang* ____ 424 – 428

Multi-Colored Fibers by Self-Assembly of DNA, Histone Proteins, and Cationic Conjugated Polymers

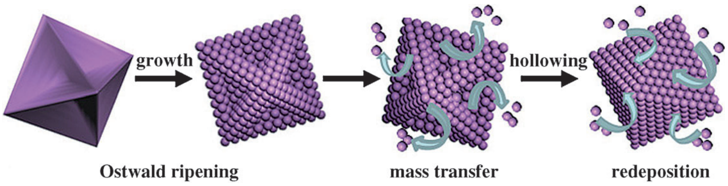


Artificial spider silk: Cationic conjugated polymers (CCPs) were used to construct inherent fluorescent microfibers (see picture) with DNA and histone proteins. The color of the fibers could be fine-tuned by changing the molar ratio of the three different CCPs.

Hollow Nanostructures

Z. C. Zhang, Y. F. Chen, X. B. Xu,
J. C. Zhang, G. L. Xiang, W. He,
X. Wang* ____ 429 – 433

Well-Defined Metal–Organic Framework Hollow Nanocages

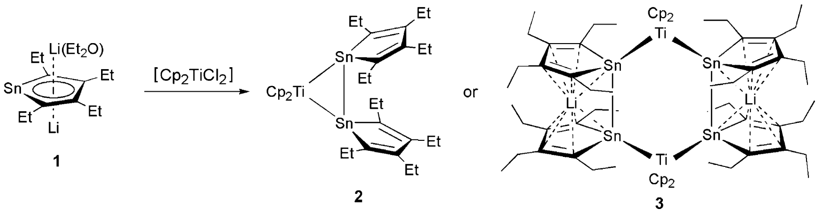


Inorganic–organic hybrids: A series of well-defined metal–organic frameworks and Fe^{III}-ICP hollow nanocages (see picture; ICP = infinite coordination polymer) were solvothermally prepared. A surface-energy-driven mechanism may be responsible for the formation of these hollow nanocages.

Distannene Complex

T. Kuwabara, J. D. Guo, S. Nagase,
M. Saito* ____ 434 – 438

Diversity of the Structures in a Distannene Complex and its Reduction to Generate a Six-Membered Ti_2Sn_4 Ring Complex

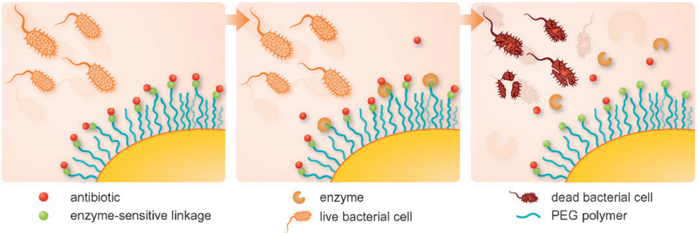


Various characters: Depending on the stoichiometry, the reaction of dilithiostannole **1** with $[Cp_2TiCl_2]$ yields either the three-membered $TiSn_2$ ring complex **2** or the six-membered Ti_2Sn_4 ring complex **3**. The novel distannene complex **2** can be regarded as a bis(stannylene) complex, as a Sn–Sn σ complex, and as an unprecedented resonance structure with delocalization of the σ orbital over the three-membered $TiSn_2$ ring.

Antimicrobial Surfaces

V. V. Komnatnyy, W.-C. Chiang,
T. Tolker-Nielsen, M. Givskov,
T. E. Nielsen* ____ 439 – 441

Bacteria-Triggered Release of Antimicrobial Agents

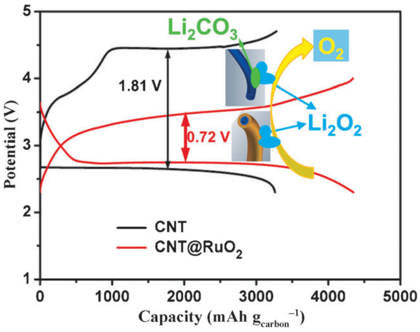


Bacteria-responsive materials: A new approach for the construction of antimicrobial polymeric materials is presented. Optimized solid-phase synthesis protocols provide access to drug hybrid constructs with lipase-labile chemical bonds. Upon cleavage of this labile bond by a cognate bacterial lipase, the release of antimicrobial compounds is triggered (see picture).

Lithium–Air Batteries

Z. L. Jian, P. Liu, F. J. Li, P. He, X. W. Guo, M. W. Chen, H. S. Zhou* ______ **442 – 446**

Core–Shell-Structured CNT@RuO_2 Composite as a High-Performance Cathode Catalyst for Rechargeable Li–O_2 Batteries

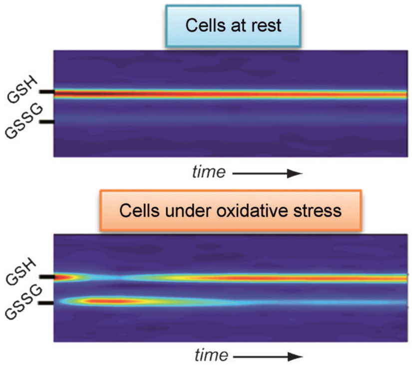


Get your battery going: Core–shell-structured CNT@RuO_2, a good catalyst for oxygen-reduction and oxygen-evolution reactions, was used to construct a Li–O_2 battery with a low overpotential (0.72 V) and thus a high round-trip efficiency (ca. 79 %). By preventing the direct contact of Li_2O_2 with the carbon nanotube (CNT), the uniform RuO_2 coating hinders the formation of Li_2CO_3 to improve round-trip efficiency and cycling performance (see picture).

In-Cell Redox Chemistry

S. Y. Rhieu,* A. A. Urbas, D. W. Bearden, J. P. Marino, K. A. Lippa, V. Reipa* ______ **447 – 450**

Probing the Intracellular Glutathione Redox Potential by In-Cell NMR Spectroscopy

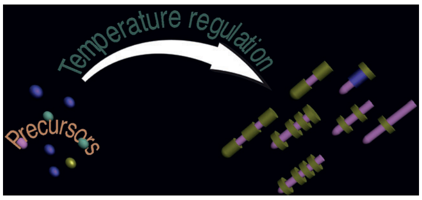


See the potential inside: Non-invasive and real-time analysis of cellular redox processes has been greatly hampered by the lack of suitable measurement techniques. An in-cell NMR-based method for measuring the intracellular glutathione redox potential was developed by direct and quantitative measurement of isotopically labeled glutathione introduced exogenously into living yeast (see figure; GSH and GSSG: reduced and oxidized forms of glutathione, respectively).

Colloid Growth

P. Datskos, J. Sharma* ______ **451 – 454**

Synthesis of Segmented Silica Rods by Regulation of the Growth Temperature

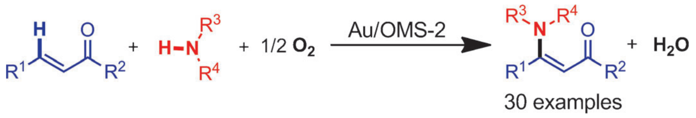


The control of the local diameter of segmented silica rods was possible by regulating the reaction temperature during growth. Segmented silica rods with controlled local thickness (such as thick-thin-thick, thin-thick-thin, or thin-thick-thicker) were thus obtained.

Heterogeneous Gold Catalysis

X. Jin, K. Yamaguchi, N. Mizuno* ______ **455 – 458**

Gold-Catalyzed Heterogeneous Aerobic Dehydrogenative Amination of α,β-Unsaturated Aldehydes to Enaminals

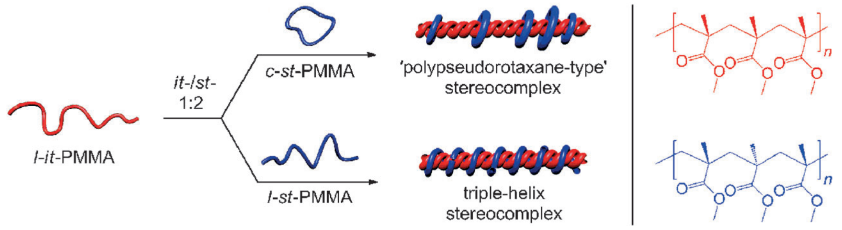


The man with the golden sieves: In the presence of gold nanoparticles supported on manganese-oxide-based octahedral molecular sieves OMS-2 (Au/OMS-2), dehydrogenative amination of α,β-unsaturated aldehydes with amines proceeded efficiently, with the corresponding enaminals isolated in moderate to high yields (50–97 %). The catalysis was truly heterogeneous, and Au/OMS-2 could be reused.

Stereocomplexes

J. M. Ren, K. Satoh, T. K. Goh, A. Blencowe, K. Nagai, K. Ishitake, A. J. Christofferson, G. Yiapanis, I. Yarovsky, M. Kamigaito,* G. G. Qiao* ——— **459 – 464**

Stereospecific Cyclic Poly(methyl methacrylate) and Its Topology-Guided Hierarchically Controlled Supramolecular Assemblies



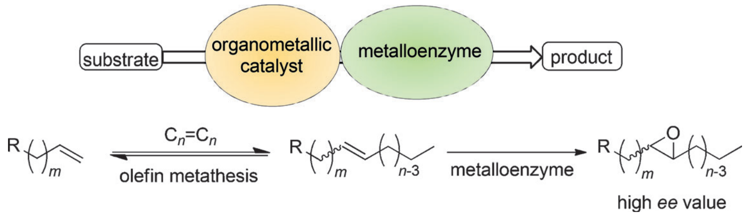
Hierarchy of controls: A cyclic syndiotactic poly(methyl methacrylate) (*c*-*st*-PMMA, blue in the picture) was synthesized with simultaneous control over molecular weight, tacticity, and topology. This meticulous microstructural control made the *c*-*st*-PMMA able to undergo stereocomplexation with complementary linear isotactic (*l*-*it*-) PMMA (red) to form an unprecedented supramolecular assembly with a distinct crystallization mode.

Enzyme catalysis

VIP

C. A. Denard, H. Huang, M. J. Bartlett, L. Lu, Y. Tan, H. Zhao,* J. F. Hartwig* ——— **465 – 469**

Cooperative Tandem Catalysis by an Organometallic Complex and a Metalloenzyme

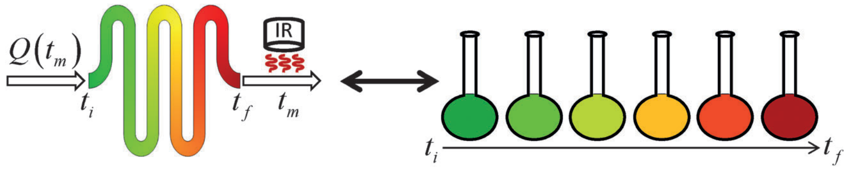


Working together: An organometallic catalyst and a metalloenzyme react cooperatively to produce epoxides with high substrate specificity and regioselectivity through a dynamic equilibrium of alkenes. Yields obtained are higher in the one-pot reaction than that from the sequential reactions.

Kinetics in Flow

J. S. Moore, K. F. Jensen* ——— **470 – 473**

“Batch” Kinetics in Flow: Online IR Analysis and Continuous Control

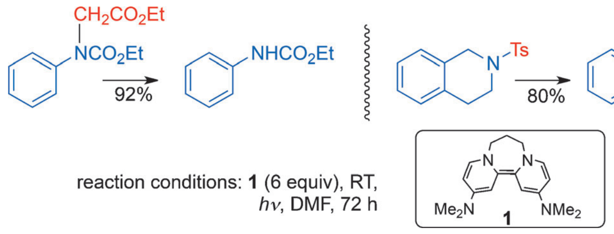


Go with the flow: By continuously manipulating the flow rate and temperature, classical batch-reactor time-series data were obtained with microreactors under conditions of low dispersion with inline IR analysis. The approach requires significantly less time and a smaller amount of starting material compared to one-at-a-time flow experiments, which allows for the rapid generation of kinetic data.

Radical Ions

S. O’Sullivan, E. Doni, T. Tuttle,* J. A. Murphy* ——— **474 – 478**

Metal-Free Reductive Cleavage of C—N and S—N Bonds by Photoactivated Electron Transfer from a Neutral Organic Donor



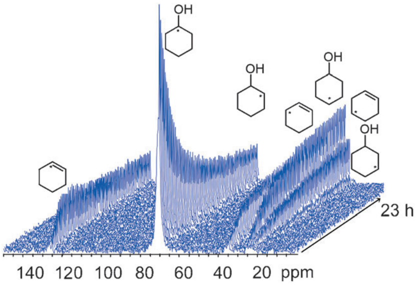
Radical fragmentations: Electron transfer from the photoactivated neutral electron donor **1** delivers high yields of S—N and C—N cleavage products for a range of nitrogen-containing species. These reactions proceed at room temperature and under mild reaction conditions in the absence of any metal reagents. DMF = *N*,*N*-dimethylformamide, Ts = 4-toluenesulfonyl.

Heterogeneous Catalysis

A. Vjunov, M. Y. Hu, J. Feng,
D. M. Camaioni, D. Mei, J. Z. Hu, C. Zhao,
J. A. Lercher* ______ 479–482

Following Solid-Acid-Catalyzed Reactions by MAS NMR Spectroscopy in Liquid Phase—Zeolite-Catalyzed Conversion of Cyclohexanol in Water

Hot analysis: The catalytic conversion of cyclohexanol on zeolite HBEA in hot liquid water leads to dehydration as well as alkylation products. A novel microautoclave suitable for application in magic angle spinning (MAS) NMR at high temperatures has been successfully applied to obtain new insight into the mechanistic pathway leading to an understanding of the reactions under selected experimental conditions.

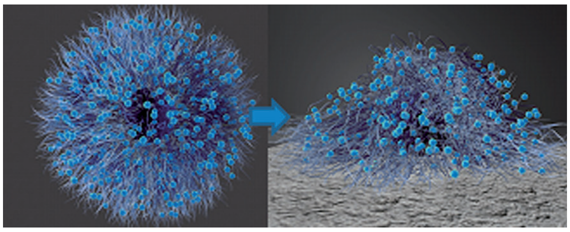


Biocatalysis

O. Kudina, A. Zakharchenko,
O. Trotsenko, A. Tokarev, L. Ionov,
G. Stoychev, N. Puretskiy, S. W. Pryor,
A. Voronov,* S. Minko* ______ 483–487

Highly Efficient Phase Boundary Biocatalysis with Enzymogel Nanoparticles

Front Cover



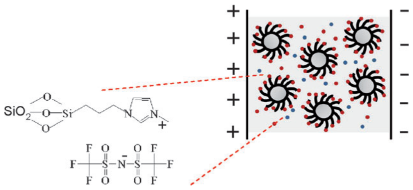
Mobile enzymes: An enzymogel, in which an enzyme is incorporated into a core–shell nanoparticle bearing a polymer brush, demonstrates a novel type of phase-boundary biocatalysis that involves remotely directed binding to and engulfing insoluble substrates (see picture). The brush-like architecture favors the efficient interfacial interaction when the enzymogel spreads over the substrate and extends the reaction area.

Electrochemistry

Y. Lu, K. Korf, Y. Kambe, Z. Tu,
L. A. Archer* ______ 488–492

Ionic-Liquid–Nanoparticle Hybrid Electrolytes: Applications in Lithium Metal Batteries

Hybrid electrolytes made of ionic-liquid-tethered nanoparticles (see picture) outperform their corresponding untethered ionic-liquid electrolytes in terms of electrochemical stability and full-cell applications in Li/Li$_4$Ti$_5$O$_{12}$. When employing lithium metal as the anode, they provide 10000-fold or more dendrite suppression than one might anticipate based on their mechanical modulus alone.

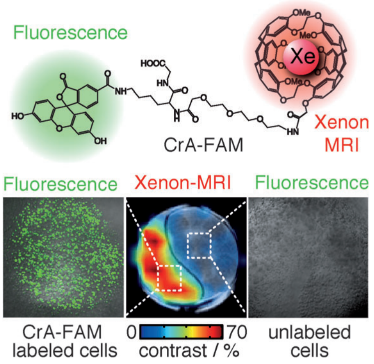


Imaging agents

S. Klippel, J. Döpfert, J. Jayapaul,
M. Kunth, F. Rossella, M. Schnurr,
C. Witte, C. Freund,
L. Schröder* ______ 493–496

Cell Tracking with Caged Xenon: Using Cryptophanes as MRI Reporters upon Cellular Internalization

Back Cover

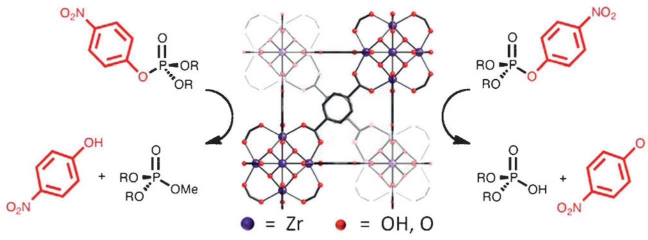


Xenon, the crypt keeper: Cryptophanes (CrA) are introduced as xenon hosts for live-cell MRI with fluorescence co-registration. Cellular uptake of the lipophilic cages, as identified by a unique chemical shift, is read-out using hyperpolarized ^{129}Xe and chemical exchange saturation transfer. Localization of labeled cells is achieved with a single acquisition at low micromolar CrA concentrations, thus demonstrating very sensitive MRI cell tracking with switchable contrast.

Heterogeneous Catalysis

M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen,* O. K. Farha,* J. T. Hupp* ______ 497 – 501

Simple and Compelling Biomimetic Metal–Organic Framework Catalyst for the Degradation of Nerve Agent Simulants

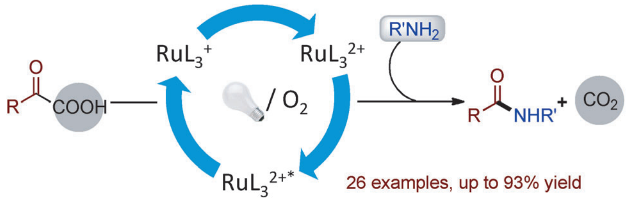


Nervous breakdown: UiO-66, a biomimetic metal–organic framework based on a zirconium oxo cluster, is capable of rapidly catalyzing the breakdown of phosphate-based nerve agent simulants. UiO-66 catalyzes both methanolysis and hydrolysis of the nerve agent simulant methyl paraoxon (shown in the graphic, R = CH_3) with high catalytic efficiency.

Photochemistry

J. Liu, Q. Liu, H. Yi, C. Qin, R. Bai, X. Qi, Y. Lan,* A. Lei* ______ 502 – 506

Visible-Light-Mediated Decarboxylation/Oxidative Amidation of α-Keto Acids with Amines under Mild Reaction Conditions Using O_2

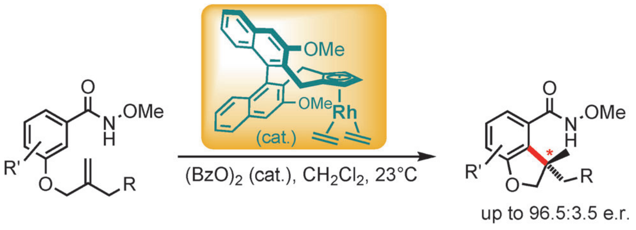


Bring to light: A new approach to oxidative decarboxylation under visible light using O_2 as the oxidant has been developed. A variety of functional groups were well-tolerated in this reaction and insights into the mechanism were investigated with the assistance of EPR spectroscopy, cyclic voltammetry, and theoretical studies.

C–H Activation

B. Ye, P. A. Donets, N. Cramer* ______ 507 – 511

Chiral Cp-Rhodium(III)-Catalyzed Asymmetric Hydroarylations of 1,1-Disubstituted Alkenes



Dihydrofurans that bear methyl-substituted quaternary stereocenters were obtained by rhodium(III)-catalyzed enantioselective hydroarylation and C–H functionalization at mild conditions. The use of chiral cyclopentadienyl ligands with a biaryl backbone led to excellent enantioselectivities.

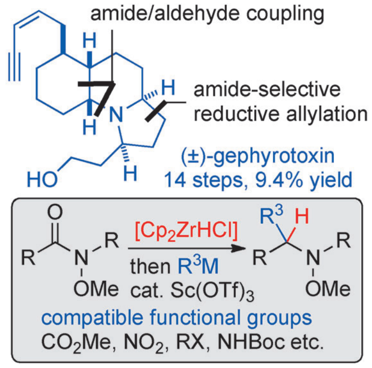
Total Synthesis

VIP

K. Shirokane, T. Wada, M. Yoritate, R. Minamikawa, N. Takayama, T. Sato,* N. Chida* ______ 512 – 516

Total Synthesis of (±)-Gephyrotoxin by Amide-Selective Reductive Nucleophilic Addition

Aim for selectivity: A chemoselective approach that utilizes *N*-methoxyamides has been developed for the total synthesis of (±)-gephyrotoxin. The *N*-methoxy group enabled the direct coupling of the amide with an aldehyde and amide-selective reductive allylation in the presence of a more electrophilic methyl ester, which resulted in the most concise and efficient total synthesis of (±)-gephyrotoxin described to date.

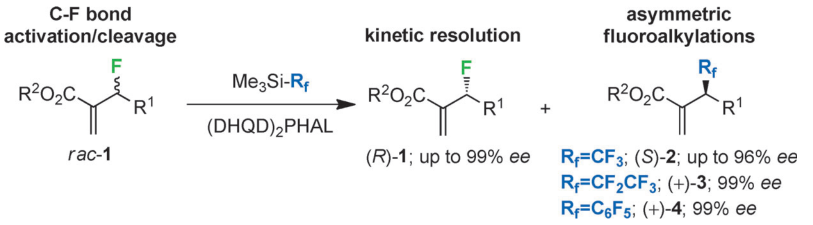


C–F Bond Activation

T. Nishimine, K. Fukushi, N. Shibata,
H. Taira, E. Tokunaga, A. Yamano,
M. Shiro, N. Shibata* ________ **517–520**

Kinetic Resolution of Allyl Fluorides by Enantioselective Allylic Trifluoromethylation Based on Silicon-Assisted C–F Bond Cleavage

Inside Cover

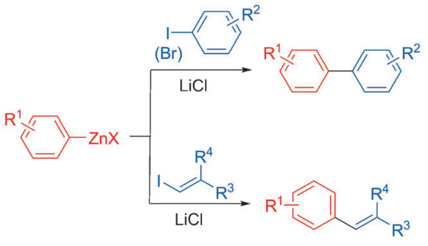


Two birds, one stone! The first kinetic resolution of allyl fluorides was achieved by the development of an organocatalyzed enantioselective allylic trifluoromethylation. Two kinds of chiral fluorinated compounds, which incorporate C*–F and C*–CF_3 units, respectively, can thus be accessed by a single transformation.

C–C Coupling

E. Shirakawa,* F. Tamakuni, E. Kusano,
N. Uchiyama, W. Konagaya, R. Watabe,
T. Hayashi ________ **521–525**

Single-Electron-Transfer-Induced Coupling of Arylzinc Reagents with Aryl and Alkenyl Halides



Arylzinc reagents were found to undergo coupling with aryl and alkenyl halides to give biaryl and styrene derivatives, respectively. The cross-coupling, which features high functional-group tolerance, proceeds through a single-electron-transfer mechanism and thus does not require the aid of transition-metal catalysis.

Structure Elucidation

L. Zhong, P. R. Savoie, A. S. Filatov,
J. T. Welch* ________ **526–529**

Preparation and Characterization of Alkenyl Aryl Tetrafluoro-λ^6-sulfanes

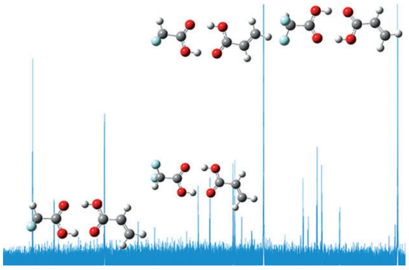
Something to that effect: The title compounds have been prepared by the direct addition of readily accessible chlorotetrafluorosulfanyl arenes to primary alkynes. Substitution of the apical fluorine of the pentafluorosulfanyl group enables modulation of the reactivity of this functional group, while at the same time facilitating the direct investigation of effects of the aryl substituent on the aryl tetrafluorosulfanyl-substituted products.

Rotational Spectroscopy

G. Feng, Q. Gou, L. Evangelisti,
W. Caminati* ________ **530–534**

Frontiers in Rotational Spectroscopy: Shapes and Tunneling Dynamics of the Four Conformers of the Acrylic Acid—Difluoroacetic Acid Adduct

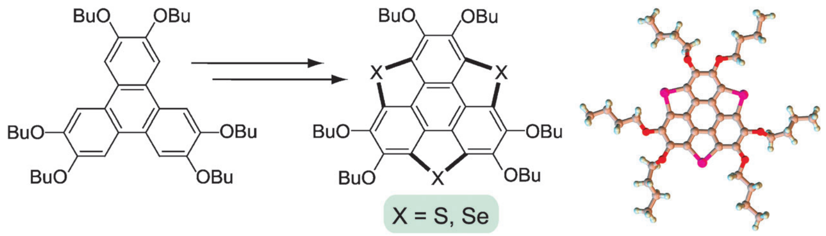
Conformers of molecular adducts: The Fourier-transform microwave spectrum of the acrylic acid–difluoroacetic acid adduct revealed four conformers (see picture). The spectrum supplied information on Ubbelohde effect, dissociation energies, potential-energy functions, and transmission of information through the π system of the eight-atom assembly of the two carboxylic groups.



Synthetic Methods

X. Li, Y. Zhu, J. Shao, B. Wang, S. Zhang, Y. Shao, X. Jin, X. Yao, R. Fang, X. Shao* ________ 535 – 538

Non-Pyrolytic, Large-Scale Synthesis of Trichalcogenasumanene: A Two-Step Approach

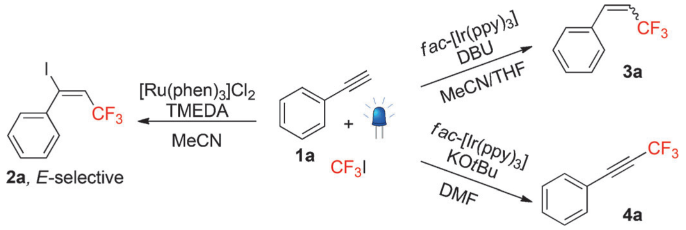


Dancing the two-step: Trichalcogenasumanenes were synthesized on a multigram scale through a two-step approach that takes advantage of non-pyrolytic cyclization and solventless ring contraction. Solid-state structure and photophysical investigations demonstrate that these compounds are promising candidates for electronic materials.

Trifluoromethylation

N. Iqbal, J. Jung, S. Park, E. J. Cho* ________ 539 – 542

Controlled Trifluoromethylation Reactions of Alkynes through Visible-Light Photoredox Catalysis

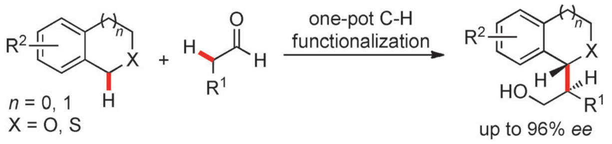


Variety through selectivity: Highly valuable trifluoromethylated alkenyl iodides, alkenes, and alkynes were selectively generated from alkynes and CF_3I by environmentally benign and efficient visible-light photoredox catalysis. A suitable choice of catalyst, base, and solvent was crucial for the reactivity and selectivity of these processes.

Synthetic Methods

Z. Meng, S. Sun, H. Yuan, H. Lou,* L. Liu* ________ 543 – 547

Catalytic Enantioselective Oxidative Cross-Coupling of Benzylic Ethers with Aldehydes

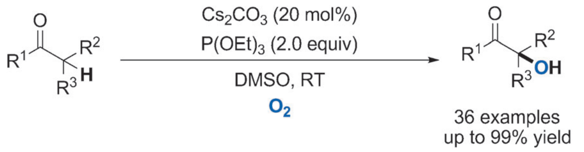


In one go: The first one-pot enantioselective oxidative coupling of cyclic benzylic ethers with aldehydes has been developed. A variety of benzylic ethers could be functionalized with this method, and the corresponding oxygen heterocycles were obtained with high enantioselectivity.

Hydroxylation with Dioxygen

Y.-F. Liang, N. Jiao* ________ 548 – 552

Highly Efficient C–H Hydroxylation of Carbonyl Compounds with Oxygen under Mild Conditions

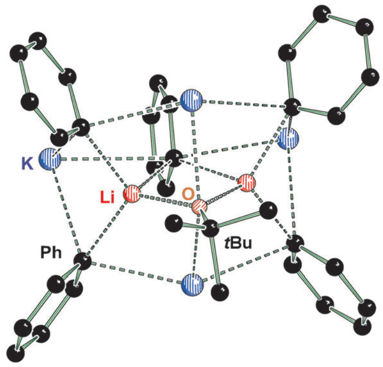


OH, so simple! A transition-metal-free Cs_2CO_3-catalyzed α-hydroxylation of carbonyl compounds with O_2 provided a variety of tertiary α-hydroxycarbonyl compounds (see scheme; DMSO = dimethyl sulfoxide), which are widely used in the chemical and pharmaceutical industry. The simple conditions and the use of molecular oxygen as both the oxidant and the oxygen source make this protocol very efficient and practical.

Metalation Reactions

C. Unkelbach, D. F. O'Shea,
C. Strohmann* ______________ 553 – 556

Insights into the Metalation of Benzene and Toluene by Schlosser's Base: A Superbasic Cluster Comprising PhK, PhLi, and *t*BuOLi

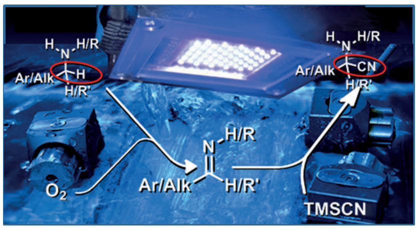


A discrete mixed-metal Li_2K_4 cluster that contains phenyl anions and *tert*-butoxide is formed smoothly by the metalation of benzene by Schlosser's base (*n*BuLi/*t*BuOK) in THF at low temperatures (see picture). The aggregate itself exhibits superbasic behavior by metalating toluene. The delocalized benzyl anion obtained this way π bonds to potassium counterions, thereby creating a 2D coordination polymer.

Photooxidative Cyanation

D. B. Ushakov, K. Gilmore, D. Kopetzki,
D. T. McQuade,
P. H. Seeberger* ______________ 557 – 561

Continuous-Flow Oxidative Cyanation of Primary and Secondary Amines Using Singlet Oxygen

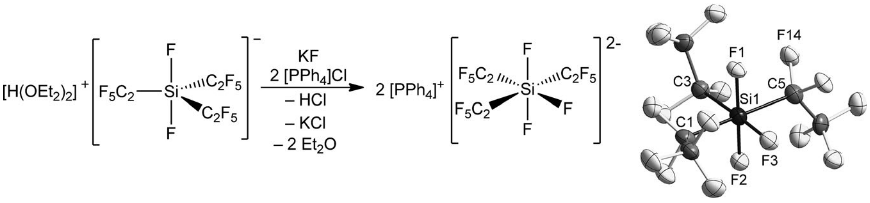


The mild synthesis of imines paves the way to aminonitriles and amino acids. Aerobic oxidation of primary and secondary amines in a continuous photoreactor with singlet oxygen generated in situ led to the rapid formation of imines, which were quantitatively trapped as α-aminonitriles (see scheme; TMS = trimethylsilyl). Benzylic and primary α-aminonitriles, precursors for amino acids, could be efficiently produced in three minutes.

Perfluoroalkyl Silicon Compounds

S. Steinhauer, H.-G. Stammler,
B. Neumann, N. Ignat'ev,
B. Hoge* ______________ 562 – 564

Synthesis of Five- and Six-Coordinate Tris(pentafluoroethyl)fluorosilicates

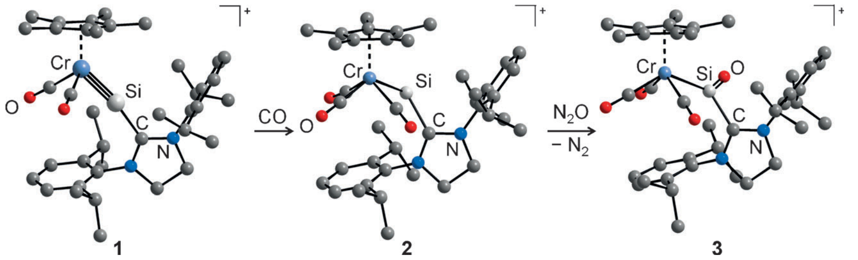


Child's play: The chemistry of perfluoroalkyl silanes is still at its infancy. The preparation and full characterization has now been achieved for $[PPh_4]_2[Si(C_2F_5)_3F_3]$ (see scheme and structure) and $[PPh_4][Si(C_2F_5)_3F_2]$ and their precursor $[H(OEt_2)_2][Si(C_2F_5)_3F_2]$ from $SiCl_4$ and LiC_2F_5 as starting materials.

Main-Group Chemistry

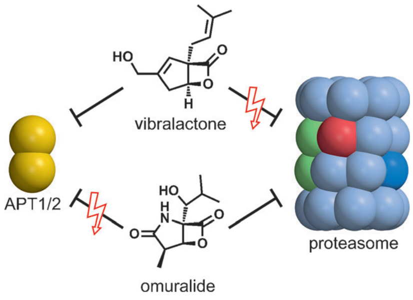
A. C. Filippou,* B. Baars, O. Chernov,
Y. N. Lebedev,
G. Schnakenburg ______________ 565 – 570

Silicon–Oxygen Double Bonds: A Stable Silanone with a Trigonal-Planar Coordinated Silicon Center



Si=O in a complex: The first silanone that is stable at room temperature (**3**) is reported. The two-step synthesis involves carbonylation of the silylidyne complex **1** to give the chromiosilylene **2**, followed by oxidation of **2** with N_2O. Silanone **3** features a polar, short Si=O bond (1.526(3) Å) to a trigonal-planar-coordinated silicon center and reacts with water to give the dihydroxysilyl complex.

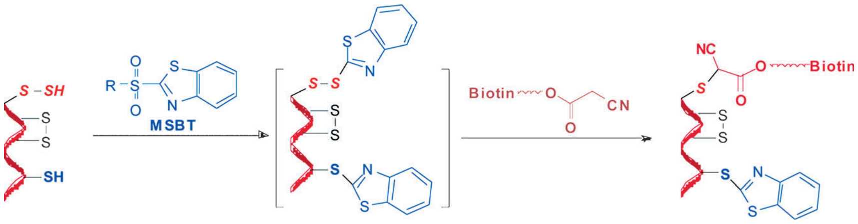
Yin and Yang of β-lactones: Despite their structural similarity, the natural products omuralide and vibralactone have different biological targets. While omuralide blocks the chymotrypsin-like activity of the proteasome with an IC_{50} value of 47 nm, vibralactone does not have any effects at this protease up to a concentration of 1 mm. Activity-based protein profiling in HeLa cells revealed that the major targets of vibralactone are APT1 and APT2.



Target Identification

A. List, E. Zeiler, N. Gallastegui, M. Rusch,
C. Hedberg, S. A. Sieber,*
M. Groll* ________ 571 – 574

Omuralide and Vibralactone: Differences in the Proteasome-β-Lactone-γ-Lactam Binding Scaffold Alter Target Preferences

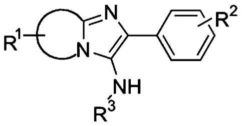


Selective detection: The first selective tag-switch method can be used to directly label protein persulfide units (sites of S-sulfhydration) in the form of stable thioether conjugates. It is thought that H_2S alone cannot lead to S-sulfhydration and that the two possible physiological mechanisms include reaction with protein sulfenic acids (P-SOH) and the involvement of metal centers, which would facilitate the oxidation of H_2S to $HS^{\bullet}$.

Protein S-Sulfhydration

D. Zhang, I. Macinkovic,
N. O. Devarie-Baez, J. Pan, C.-M. Park,
K. S. Carroll, M. R. Filipovic,*
M. Xian* ________ 575 – 581

Detection of Protein S-Sulfhydration by a Tag-Switch Technique



Imidazopyridine

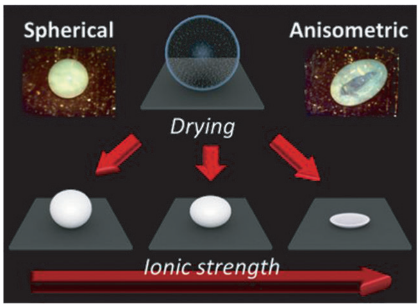
Creative combo: Microfluidic combinatorial synthesis was used along with computational target prediction to afford novel imidazopyridines with potent activity as adenosine $A_{1/2B}$ and adrenergic $\alpha_{1A/B}$ receptor antagonists. The polypharmacology-driven design of molecular librarys and miniaturized flow synthesis hold great potential for drug discovery and chemical biology.

Combinatorial Chemistry

M. Reutlinger, T. Rodrigues, P. Schneider,
G. Schneider* ________ 582 – 585

Combining On-Chip Synthesis of a Focused Combinatorial Library with Computational Target Prediction Reveals Imidazopyridine GPCR Ligands

Getting out of shape: Anisometric SiO_2 supraparticles are produced by the simple evaporation of a suspension of sessile droplets containing fumed silica deposited on a superhydrophobic substrate. Their shape is directly controlled by the initial NaCl concentration of the suspension. This process is easily extended to supraparticles containing further functional colloidal components.



Asymmetric Supraparticles

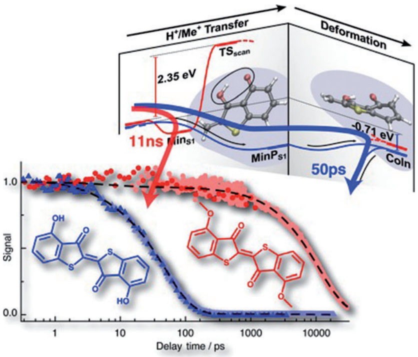
M. Sperling, O. D. Velev,*
M. Gradzielski* ________ 586 – 590

Controlling the Shape of Evaporating Droplets by Ionic Strength: Formation of Highly Anisometric Silica Supraparticles

Indigo Mimetic

M. Dittmann, F. F. Graupner, B. Maerz,
S. Oesterling, R. de Vivie-Riedle,
W. Zinth,* M. Engelhard,*
W. Lüttke **591 – 594**

Photostability of 4,4′-Dihydroxythioindigo, a Mimetic of Indigo

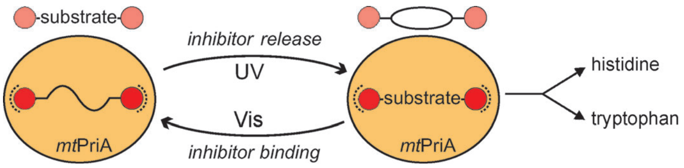


Beyond the blue: The vastly different photochemical properties of 4,4′-dihydroxythioindigo and its dimethoxy derivative demonstrate that excited-state proton transfer within the rigid ring system of only one hemithioindigo moiety improves photostability. This promoting mechanism is the same as that in indigo and in many UV stabilizers. This concept may serve as an interesting strategy towards new photostable dyes for the visible part of the spectrum.

Light-Regulated Enzyme Activity

B. Reisinger, N. Kuzmanovic, P. Löffler,
R. Merkl, B. König,*
R. Sterner* **595 – 598**

Exploiting Protein Symmetry To Design Light-Controllable Enzyme Inhibitors



Light switch: The activity of the metabolic branch-point enzyme PriA from *Mycobacterium tuberculosis* (*mt*PriA) can be controlled reversibly by light. Two-pronged inhibitors based on the dithienylethene scaffold were designed utilizing *mt*PriA's natural rotational symmetry. Switching from the flexible, ring-open to the rigid, ring-closed isomer reduces inhibition activity by one order of magnitude.

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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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

Enantioselective Allylic Thioetherification: The Effect of Phosphoric Acid Diester on Iridium-Catalyzed Enantioconvergent Transformations

M. Roggen, E. M. Carreira* **8652–8655**

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

DOI: 10.1002/anie.201202092

After consultation with the authors, the editorial office has been made aware of incongruities in the spectra in the Supporting Information for this Communication in which ethical standards were not adhered to by the first author. A revised version of the Supporting Information is provided that is in compliance. The changes do not affect any of the conclusions of the Communication.