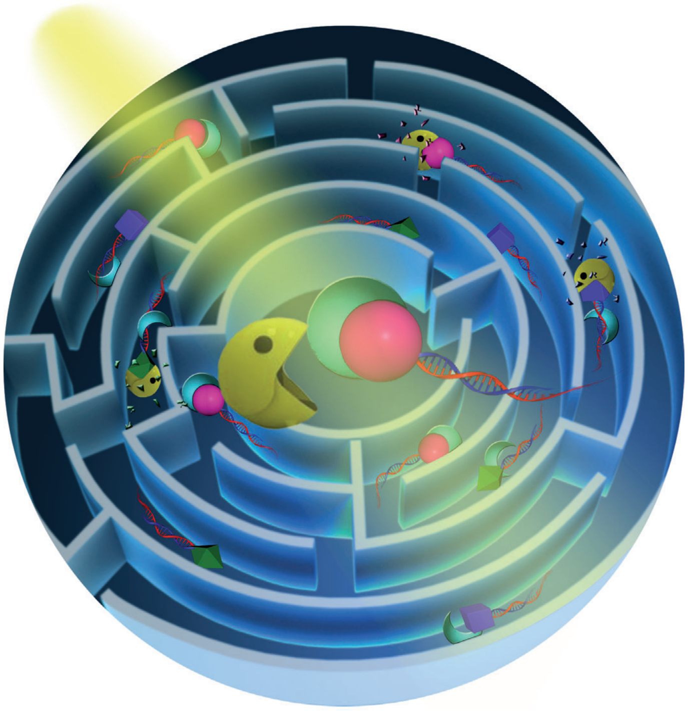
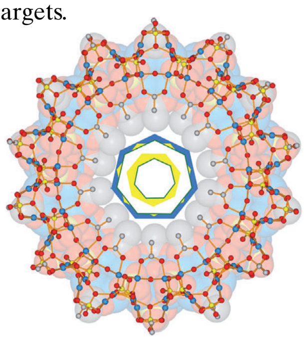
Selection of DNA-encoded libraries ...

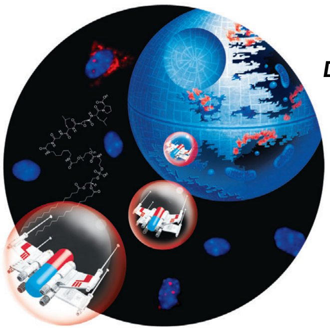


… (DELs) has become an important method to discover potent and specific binders against protein targets. In their Communication on page 10056 ff., Y. Huang, X. Li, and co-workers describe a new DEL selection method, in which ligand binding induces the formation of a stable complex that is resistant to nuclease digestion (Pac-Man) in order to achieve enrichment. Such iterated selections can be realized with completely unmodified and non-immobilized targets.

Polyoxometalates

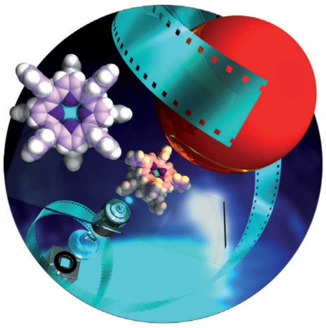
In their Communication on page 10032 ff., L. Cronin et al. investigate the self-assembly of a $\{Pd_{84}\}$ wheel from $\{Pd_6\}^-$ using electrophoresis, size-exclusion chromatography, and mass spectrometry.





Drug Delivery

A lipidated cathepsin B inhibitor was incorporated into the envelope of a liposomal nanocarrier, as reported by B. Turk, O. Vasiljeva, et al. in their Communication on page 10077 ff.



Synthetic Molecular Machines

The stepwise intramolecular rotation of a double-decker porphyrin was directly visualized with a relatively large bead probe by optical microscopy, as described by H. Noji et al. in their Communication on page 10082 ff.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
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Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
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Courier Services:
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Author Profile

"My favorite saying is "All roads lead to Rome" (but often not the one you expect to).
My biggest motivation is to find "terra incognita". ..."
This and more about Ingo Krossing can be found on page 9986 – 9987.

News

W. Kaim

E. F. Aziz

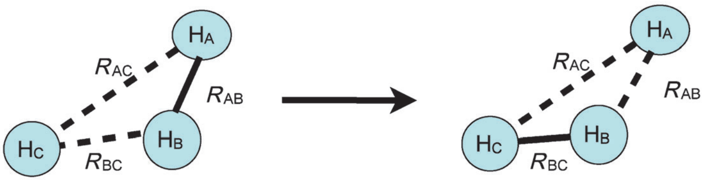
P. Levkin

M. Driess

Books

Reviews

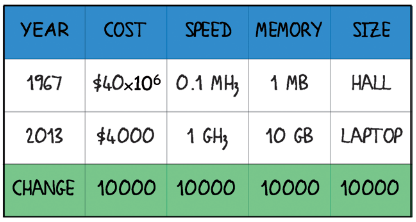
Molecular Modeling



Although the laws governing the motions of atoms are quantum mechanical, the key realization that made possible the simulation of the dynamics of complex systems, including biomolecules, was that a classical mechanical description of the atomic motions is adequate in most cases. From M. Karplus' own perspective, this realization was derived from calculations on the symmetric exchange reaction, $H + H_2 \rightarrow H_2 + H$.

Molecular Modeling

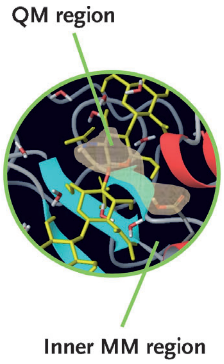
The computer industry should have received a share of the 2013 Nobel prize in chemistry as its massive research and development efforts led to unimaginable gains in computer speed (see table). This means that the cost of a particular calculation today is 100 000 000 less than it was at the beginning of Michael Levitt's scientific career as pointed out in his very personal account on the occasion of having received the Nobel prize.



YEAR	COST	SPEED	MEMORY	SIZE
1967	$40x10^6	0.1 MHz	1 MB	HALL
2013	$4000	1 GHz	10 GB	LAPTOP
CHANGE	10000	10000	10000	10000

Molecular Modeling

A detailed understanding of the action of biological molecules is a prerequisite for advances in health sciences, however, using a full quantum mechanical representation of large molecular systems is practically impossible. The solution to this has emerged from the realization that large systems can be spatially divided into a region where the quantum mechanical description is essential, with the remainder of the system being represented by empirical force fields.



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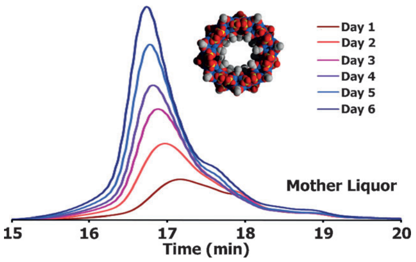
Communications

One ring to rule them all: The mechanism of self-assembly of a $\{Pd_{84}\}$ wheel was investigated by electrophoresis and size-exclusion chromatography (see picture). The latter was used in conjunction with electrospray mass spectrometry to probe directly the formation of the wheel, which forms over the course of six days through the aggregation of $\{Pd_6\}^-$ building blocks.

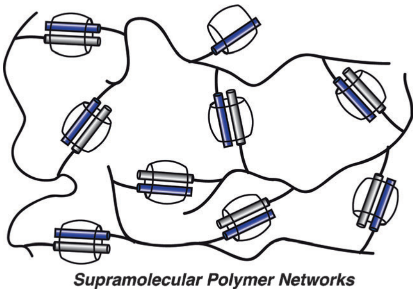


Polyoxometalates

R. A. Scullion, A. J. Surman, F. Xu, J. S. Mathieson, D.-L. Long, F. Haso, T. Liu, L. Cronin* ———— **10032 – 10037**

Exploring the Symmetry, Structure, and Self-Assembly Mechanism of a Gigantic Seven-Fold Symmetric $\{Pd_{84}\}$ Wheel

Frontispiece



Supramolecular hydrogels were obtained by utilizing the host–guest interactions of the macrocycle cucurbit[8]uril (CB[8]) with various guest molecules. The mechanical strength of these materials is directly correlated to the energetic barrier of the dissociation of the CB[8] ternary complex cross-links, whereas the self-healing requires a low energetic barrier for complex association.

Host–Guest Systems

E. A. Appel, R. A. Forster, A. Koutsioubas, C. Toprakcioglu, O. A. Scherman ———— **10038 – 10043**

Activation Energies Control the Macroscopic Properties of Physically Cross-Linked Materials

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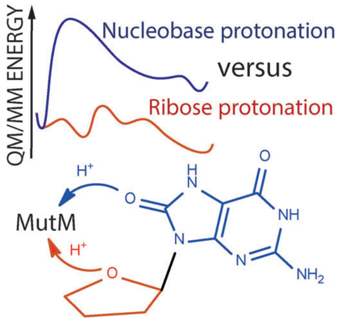

Sugar is the target: QM/MM (quantum mechanics/molecular mechanics) calculations with more than 1000 QM atoms for describing the catalytic pocket unravel the base excision repair mechanism of bacterial glycosylase, MutM. In contrast to conventional assumptions, MutM first attacks the ribose ring. Activity assays and a new crystal structure of the MutM lesion complex strongly support such a repair process with a higher involvement of the sugar ring.

DNA Repair

K. Sadeghian, D. Flaig, I. D. Blank, S. Schneider, R. Strasser, D. Stathis, M. Winnacker, T. Carell,* C. Ochsenfeld* ———— **10044 – 10048**

Ribose-Protonated DNA Base Excision Repair: A Combined Theoretical and Experimental Study

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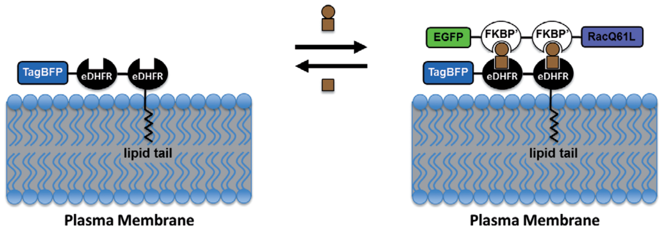


Hitching a ride: A novel bioorthogonal and reversible chemically induced dimerization system has been developed. Translocation of constitutively active Rac1 to the plasma membrane resulted in rapid and reversible lamellipodia formation in live cells.

Reversible Dimerization

P. Liu, A. Calderon, G. Konstantinidis, J. Hou, S. Voss, X. Chen, F. Li, S. Banerjee, J. Hoffmann, C. Theiss, L. Dehmelt, Y. Wu* ———— **10049 – 10055**

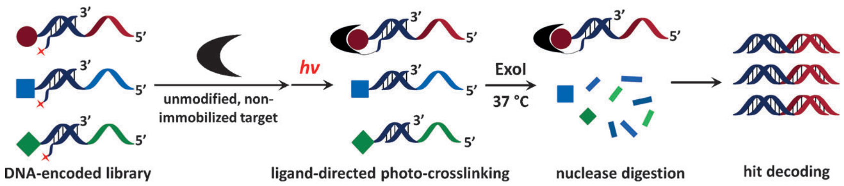
A Bioorthogonal Small-Molecule-Switch System for Controlling Protein Function in Live Cells

DNA-Encoded Library

P. Zhao, Z. Chen, Y. Li, D. Sun, Y. Gao, Y. Huang,* X. Li* ________ **10056 – 10059**

Selection of DNA-Encoded Small Molecule Libraries Against Unmodified and Non-Immobilized Protein Targets

Front Cover

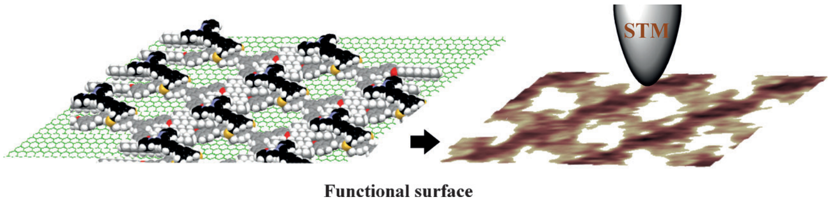


The requirement for modified and immobilized targets remains a significant disadvantage in the selection of DNA-encoded libraries against biological targets. By using a terminal protection strategy and ligand-induced target photo-crosslinking, iterated selections of DNA-encoded libraries can be realized with unmodified and non-immobilized target proteins.

Self-Assembly

P. Du, M. Jaouen, A. Bocheux, C. Bourgogne, Z. Han, V. Bouchiat, D. Kreher, F. Mathevet, C. Fiorini-Debuisschert, F. Charra,* A. J. Attias* ________ **10060 – 10066**

Surface-Confined Self-Assembled Janus Tectons: A Versatile Platform towards the Noncovalent Functionalization of Graphene

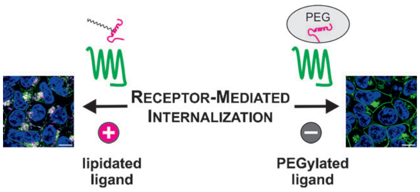


Built to order: A library of Janus tectons equipped with small chemical groups or functional moieties has been synthesized. The self-assembly on sp^2-hybridized carbon supports leads to the formation of well-organized adlayers with the same lattice parameters, as demonstrated by STM. The external exposed surface presents a wide range of functionalities positioned with a precise lateral order.

Modified Peptides

V. Mäde, S. Babilon, N. Jolly, L. Wanka, K. Bellmann-Sickert, L. E. Diaz Gimenez, K. Mörl, H. M. Cox, V. V. Gurevich, A. G. Beck-Sickinger* ____ **10067 – 10071**

Peptide Modifications Differentially Alter G Protein-Coupled Receptor Internalization and Signaling Bias

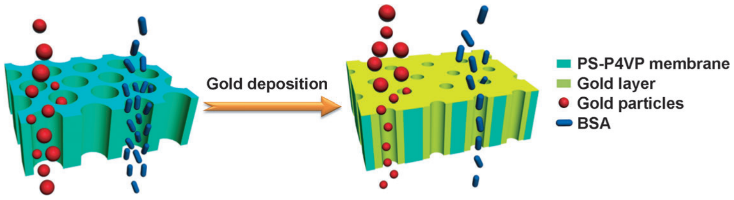


PEGylation and lipidation have been found to enhance ligand preference for anorexigenic G protein-coupled human Y receptors. Lipidation biased the agonist towards arrestin recruitment and internalization, whereas PEGylation precluded receptor internalization and prolonged signaling independently of the cell system and modified residue, thus indicating novel modes of action.

Block Copolymer Membrane

H. Z. Yu, X. Y. Qiu, S. P. Nunes, K. V. Peinemann* ________ **10072 – 10076**

Self-Assembled Isoporous Block Copolymer Membranes with Tuned Pore Sizes



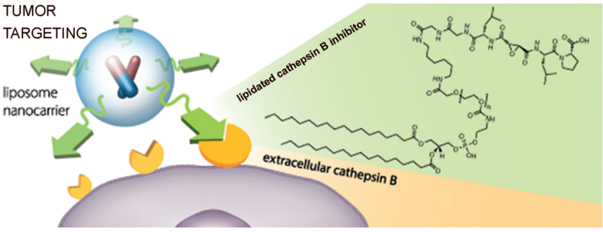
Golden pores: Membranes with tunable cylindrical pore diameters between 3 and 20 nm were manufactured and tested for nanoparticle separation and controlled delivery of proteins. The pore size was regulated by electroless gold deposition. The precise size discrimination, facile and scalable fabrication processes, and biocompatible characteristics favor potential uses in the purification of nanoscale materials and drug delivery.

Drug Delivery

G. Mikhaylov, D. Klimpel, N. Schaschke, U. Mikac, M. Vizovisek, M. Fonovic, V. Turk, B. Turk,* O. Vasiljeva* ______ 10077 – 10081

Selective Targeting of Tumor and Stromal Cells By a Nanocarrier System Displaying Lipidated Cathepsin B Inhibitor

Inside Back Cover



On target: A lipidated cathepsin B (CtsB) inhibitor was incorporated into the envelope of a liposomal nanocarrier. The resulting CtsB-targeted drug delivery system, which can be loaded with diagnostic or therapeutic agents, was selectively internalized by tumor and stromal cells, thus validating CtsB targeting as a promising approach to cancer diagnosis and treatment.

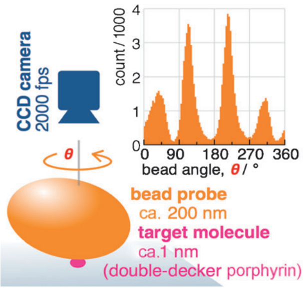
Synthetic Molecular Machines

T. Ikeda, T. Tsukahara, R. Iino, M. Takeuchi, H. Noji* __ 10082 – 10085

Motion Capture and Manipulation of a Single Synthetic Molecular Rotor by Optical Microscopy

Back Cover

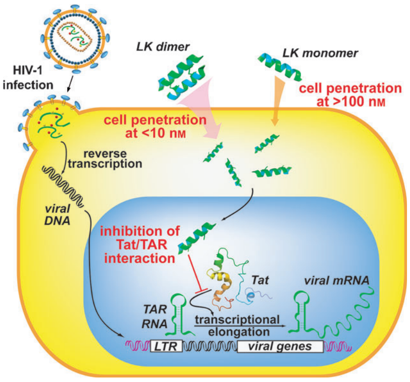
Single-molecule optical microscopy was applied to study the rotation of a double-decker porphyrin. With a magnetic bead as the probe, the rotary diffusion of this synthetic nanorotor with 90° steps was visualized; it is consistent with the four-fold structural symmetry of this molecule.



Peptide Antivirals

S. Jang, S. Hyun, S. Kim, S. Lee, I.-S. Lee, M. Baba, Y. Lee,* J. Yu* _ 10086 – 10089

Cell-Penetrating, Dimeric α-Helical Peptides: Nanomolar Inhibitors of HIV-1 Transcription



Going viral: Nearly quantitative penetration into eukaryotic cells and effective inhibition of the elongation of the short hairpin RNA transcript TAR at low nanomolar concentrations has been achieved by using dimeric α-helical peptide bundles based on leucine (L) and lysine (K). The effective inhibition of HIV-1 replication strongly suggests that these dimers have strong potential as anti-HIV-1 drugs.

Carbonylation

K. Natte, A. Dumrath, H. Neumann, M. Beller* ______ 10090 – 10094

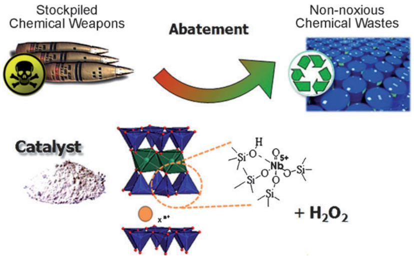
Palladium-Catalyzed Carbonylations of Aryl Bromides using Paraformaldehyde: Synthesis of Aldehydes and Esters

Outsourcing CO: Novel protocols have been developed for conducting palladium-catalyzed reductive carbonylations and alkoxycarbonylations of aryl bromides using paraformaldehyde as an external CO source. The advantage of these methods: gaseous carbon monoxide is not needed.

Heterogeneous Catalysis

F. Carniato, C. Bisio,* R. Psaro,
L. Marchese,
M. Guidotti* ________ **10095 – 10098**

Niobium(V) Saponite Clay for the Catalytic Oxidative Abatement of Chemical Warfare Agents



Heterogeneous catalysis against chemical weapons: A bifunctional Nb^V-containing saponite clay was prepared and found to be an optimal catalyst for the oxidative abatement of chemical warfare agents (CWA). In comparison to parent samples and a conventional commercial decontamination powder, a remarkable activity and high selectivity were obtained for the oxidation of (2-chloroethyl)ethyl sulfide (CEES), a simulant of sulfur mustard, at room temperature.

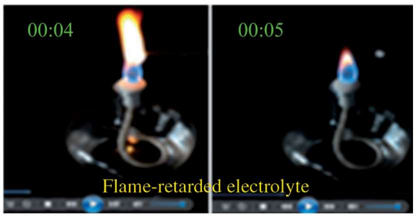
Li-S Batteries

J. L. Wang,* F. J. Lin, H. Jia, J. Yang,
C. W. Monroe, Y. N. NuLi **10099 – 10104**

Towards a Safe Lithium–Sulfur Battery with a Flame-Inhibiting Electrolyte and a Sulfur-Based Composite Cathode

Fire away: A nonflammable sulfur composite cathode has been shown to maintain extremely stable electrochemical activity over 750 cycles and exhibit a discharge capacity greater than 800 $mAh^{-1}g^{-1}$(sulfur) at a high rate of 10 C in a flame-inhibiting electrolyte. The safe electrolyte was generated from a phosphite additive that participates in interfacial reactions on the cathode and accelerates Li-ion diffusion more than tenfold.

Nonflammable cathode

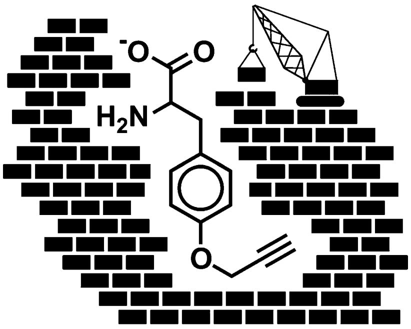


Biosynthetic Engineering

H. Kries, R. Wachtel, A. Pabst, B. Wanner,
D. Niquille, D. Hilvert* __ **10105 – 10108**

Reprogramming Nonribosomal Peptide Synthetases for “Clickable” Amino Acids

Pocketed: A single active site mutation reprograms the substrate specificity of nonribosomal peptide synthetase adenylation domains, enabling efficient incorporation of non-natural aromatic amino acids containing unique chemical functionality for bioorthogonal labeling.

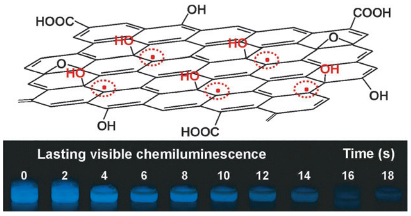


Graphene Oxide Radicals

L. Yang, R. Zhang, B. Liu, J. Wang,
S. Wang, M. Han,
Z. Zhang* ________ **10109 – 10113**

π-Conjugated Carbon Radicals at Graphene Oxide to Initiate Ultrastrong Chemiluminescence

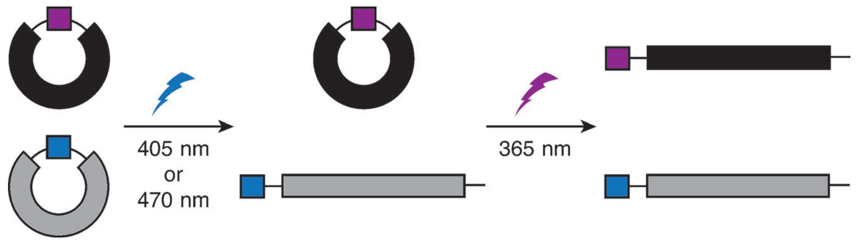
GO chemiluminescence: Freshly prepared graphene oxide exhibits a large number of π-conjugated carbon radicals at its π-network plane. These radicals result from the addition of hydroxyl radicals from hydrogen peroxide onto the conjugated double bonds of graphene oxide and can directly initiate a long-lasting visible chemiluminescence of luminol.



Optochemical Biology

S. Yamazoe, Q. Liu, L. E. McQuade,
A. Deiters,* J. K. Chen* ____ **10114 – 10118**

Sequential Gene Silencing Using Wavelength-Selective Caged Morpholino Oligonucleotides

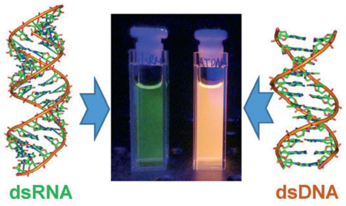


Not on the same wavelength: Sequential gene silencing in zebrafish embryos has been achieved using caged morpholino oligonucleotides with spectrally distinct triggers (see picture). These optochemical tools have allowed the examination of genetic interactions that dynamically regulate mesoderm patterning.

Platinum DNA Intercalators

T. Zou, J. Liu, C. T. Lum, C. Ma,
R. C.-T. Chan, C.-N. Lok, W.-M. Kwok,
C.-M. Che* ____________ **10119 – 10123**

Luminescent Cyclometalated Platinum(II) Complex Forms Emissive Intercalating Adducts with Double-Stranded DNA and RNA: Differential Emissions and Anticancer Activities



Making light of DNA: The luminescent Pt^{II} pincer complex $[Pt(C{\wedge}N{\wedge}N)(C{\equiv}NtBu)]ClO_4$ intercalates into DNA and forms an unconventional emissive exciplex. The emission profile and excited-state lifetime are sensitive to nucleic acid structure, which is used to differentiate between dsRNA and dsDNA. The complex shows strong in vitro cytotoxicity and suppresses tumor growth in an animal model.

Chemical Genomics

G. S. Erwin, D. Bhimsaria, A. Eguchi,
A. Z. Ansari* ____________ **10124 – 10128**

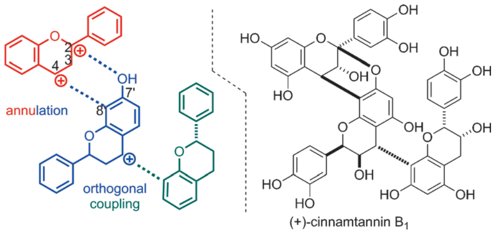
Mapping Polyamide–DNA Interactions in Human Cells Reveals a New Design Strategy for Effective Targeting of Genomic Sites

Siteseeing: The first mapping of pyrrole/imidazole polyamides across several genomic sites with distinct chromatin characteristics in live cells is reported. Bioinformatic analysis of the data shows that clustered binding sites best predict binding in cells. The results point to a new design principle to deploy polyamides and perhaps other synthetic molecules to effectively target desired genomic sites in vivo.

Natural Products

Y. Ito, K. Ohmori,*
K. Suzuki* ____________ **10129 – 10133**

Annulation Approach to Doubly Linked (A-type) Oligocatechins: Syntheses of (+)-Procyanidin A_2 and (+)-Cinnamtannin B_1

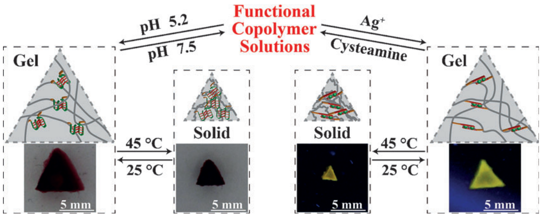


Sweet oligocatechins: The first stereoselective and high-yielding syntheses of doubly linked (A-type) procyanidins, (+)-procyanidin A_2 and (+)-cinnamtannin B_1, have been achieved by exploiting dual activation of the electrophilic flavan units at C2 and C4, thus allowing catechin annulation with nucleophilic flavan units in a regio- and stereoselective manner.

Thermosensitive Polymers

W. Guo, C. H. Lu, X. J. Qi, R. Orbach,
M. Fadeev, H. H. Yang,
I. Willner* ______ **10134 – 10138**

Switchable Bifunctional Stimuli-Triggered Poly-*N*-Isopropylacrylamide/DNA Hydrogels



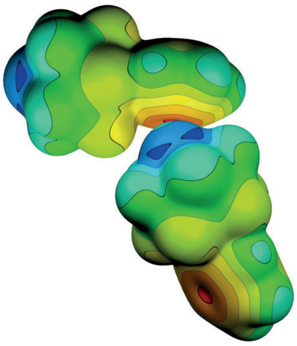
All change! Nucleic acid-functionalized pNIPAM copolymers undergo bi-triggered phase transitions. In the presence of H^+/OH^- or Ag^+/cysteamine, the polymers undergo cyclic and reversible gel-to-solution transitions. The hydrogels undergo further cyclic and reversible hydrogel/solid-phase transitions upon heating and cooling the systems.

Chalcogen Bonding

J. Fanfrlík, A. Přáda, Z. Padělková,
A. Pecina, J. Macháček, M. Lepšík,
J. Holub, A. Růžička,* D. Hnyk,*
P. Hobza* ______ **10139 – 10142**

The Dominant Role of Chalcogen Bonding in the Crystal Packing of 2D/3D Aromatics

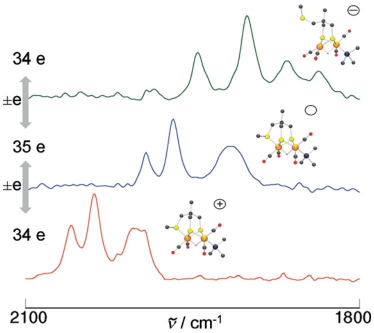
Chalcogen bonds of thiaboranes were found to be considerably stronger than σ-hole bonds in organic compounds. The reason is the highly positive belt of σ-holes on the positively charged sulfur atom. The charge distribution is the driving force for chalcogen bonding of thiaboranes.



Electrochemistry

A. Jablonskytė, J. A. Wright, S. A. Fairhurst,
L. R. Webster,
C. J. Pickett* ______ **10143 – 10146**

[FeFe] Hydrogenase: Protonation of {2Fe3S} Systems and Formation of Super-reduced Hydride States

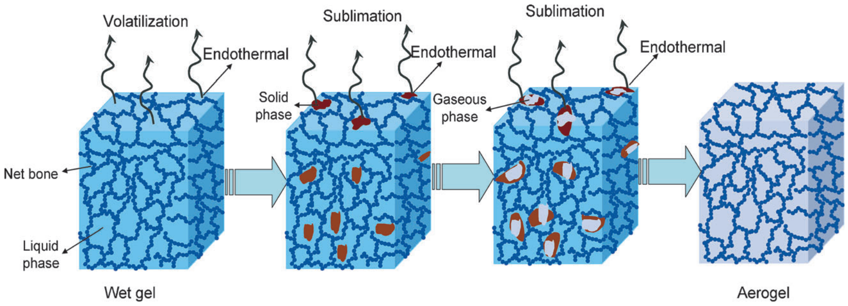


Out of thin layers: The synthesis and crystallographic characterization of a complex possessing a well-defined {2Fe3S(μ-H)} core gives access to a paramagnetic bridging hydride with retention of the core geometry. The chemistry of this 35-electron species within the confines of a thin-layer FTIR spectro-electrochemistry cell provides evidence for an unprecedented super-reduced $Fe^I(\mu\text{-}H)Fe^I$ intermediate (see scheme).

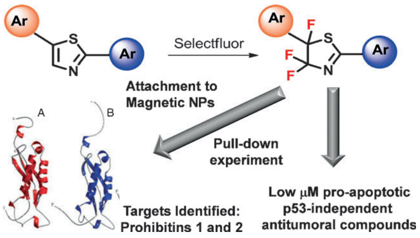
Aerogels

L. Ren,* S. Cui, F. Cao,
Q. Guo ______ **10147 – 10149**

An Easy Way To Prepare Monolithic Inorganic Oxide Aerogels



Not cracking up: A drying method based on the sublimation of organic solvent allows the rapid synthesis of the monolithic inorganic oxide aerogels without cracks from wet gels. The method proceeds by endothermic evaporation of organic solvent at the outer surface followed by sublimation of solidified solvent (see picture).



Not one, not two, but three: A novel fluorination of thiazoles selectively yields a trifluorinated heterocyclic scaffold. Robust chemistry leads, in short sequences, to a family of potent p53-independent pro-apoptotic antitumor compounds. Pull-down experiments show that these derivatives are selective ligands of prohibitins. NP = nanoparticle.

Drug Discovery

A. Pérez-Perarnau, S. Preciado, C. M. Palmeri, C. Moncunill-Massaguer, D. Iglesias-Serret, D. M. González-Gironès, M. Miguel, S. Karasawa, S. Sakamoto, A. M. Cosialls, C. Rubio-Patiño, J. Saura-Esteller, R. Ramón, L. Caja, I. Fabregat, G. Pons, H. Handa, F. Albericio,* J. Gil,* R. Lavilla* ———— **10150 – 10154**

A Trifluorinated Thiazoline Scaffold Leading to Pro-apoptotic Agents Targeting Prohibitins

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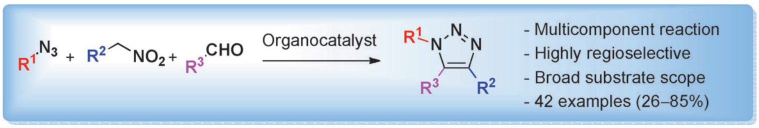


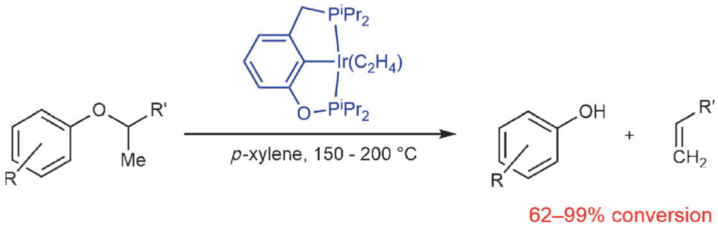
Fully functionalized 1,2,3-triazoles were obtained by a metal-free three-component reaction. Simple and readily available building blocks were employed in this organocatalytic transformation, which gave the desired products in good yield and with high regioselectivity. Most of the synthesized triazoles were previously inaccessible.

Triazole Synthesis

J. Thomas, J. John, N. Parekh, W. Dehaen* ———— **10155 – 10159**

A Metal-Free Three-Component Reaction for the Regioselective Synthesis of 1,4,5-Trisubstituted 1,2,3-Triazoles

Inside Cover



A catalyst for ether direction: Cleavage of the alkyl C–O bond of aryl ethers is catalyzed by pincer Ir catalysts, without the need for additional reagents, including H_2. The corresponding phenols are generated in up to 99% conversion, with reaction times as short as 1 hour.

C–O Bond Cleavage

M. C. Haibach, N. Lease, A. S. Goldman* ———— **10160 – 10163**

Catalytic Cleavage of Ether C–O Bonds by Pincer Iridium Complexes

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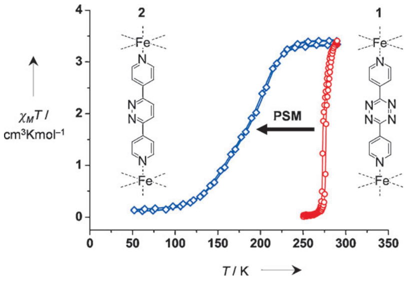
Changing the switch: Covalent postsynthetic modification (PSM; see picture) of a pillaring ligand in a new porous Fe^{II} spin crossover framework occurs with retention of single crystallinity to generate a closely related framework phase that exhibits markedly different switching behaviors (see picture). This conversion establishes covalent modification as a new method for controlling spin crossover in this emerging class of porous multifunctional materials.



Metal–Organic Frameworks

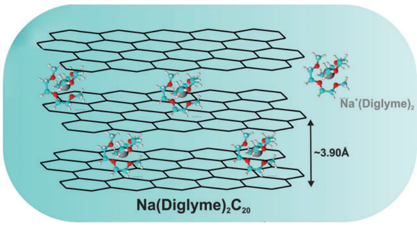
J. E. Clements, J. R. Price, S. M. Neville, C. J. Kepert* ———— **10164 – 10168**

Perturbation of Spin Crossover Behavior by Covalent Post-Synthetic Modification of a Porous Metal–Organic Framework

Batteries

B. Jache, P. Adelhelm* ___ 10169 – 10173

Use of Graphite as a Highly Reversible Electrode with Superior Cycle Life for Sodium-Ion Batteries by Making Use of Co-Intercalation Phenomena

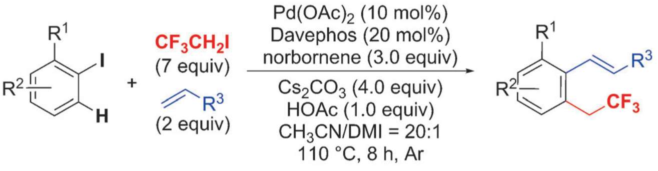


In contrast to the general view, graphite can be used as an electrode material in sodium-ion batteries by taking advantage of the formation of ternary graphite intercalation compounds. The important features of this electrode reaction are the small irreversible capacity, the low overpotentials, and the superior cycle life. With a capacity close to 100 mAh g^{-1}, the electrode is attractive for stationary applications.

Trifluoroethylation

H. Zhang, P. Chen,
G. Liu* ___ 10174 – 10178

Palladium-Catalyzed Cascade C–H Trifluoroethylation of Aryl Iodides and Heck Reaction: Efficient Synthesis of *ortho*-Trifluoroethylstyrenes



C–H trifluoroethylation, 37 examples

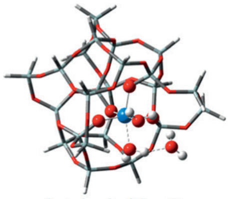
The palladium-catalyzed selective C–H bond trifluoroethylation of aryl iodides allows for an efficient synthesis of a variety of *ortho*-trifluoroethyl-substituted styrenes. Preliminary mechanistic studies indicate that the reaction might proceed through rate-determining oxidative addition of CF_3CH_2I to a palladacycle.

Active Sites in Sn-*β*

P. Wolf, M. Valla, A. J. Rossini,
A. Comas-Vives, F. Núñez-Zarur,
B. Malaman, A. Lesage, L. Emsley,
C. Copéret,* I. Hermans* 10179 – 10183

NMR Signatures of the Active Sites in Sn-β Zeolite

Open and closed: The Sn-β zeolite spectroscopic signatures obtained from ^{119}Sn Mössbauer and DNP-SENS NMR spectroscopy combined with DFT calculations on a T site model indicate that the active sites correspond to two types of octahedral Sn^{IV} sites: one with two water molecules coordinated to the framework Sn atom (closed site) and one where an Sn-O-Si bridge was opened by one of the water molecules (open site).

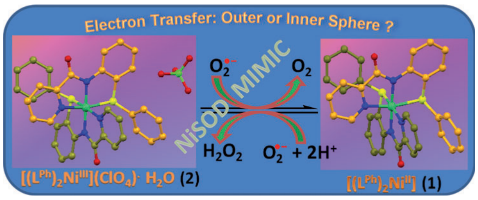


Octahedral Sn site

Enzyme Models

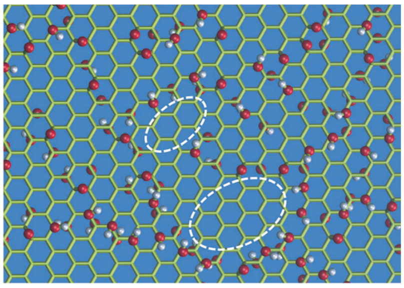
S. K. Chatterjee, R. C. Maji, S. K. Barman,
M. M. Olmstead,
A. K. Patra* ___ 10184 – 10189

Hexacoordinate Nickel(II)/(III) Complexes that Mimic the Catalytic Cycle of Nickel Superoxide Dismutase



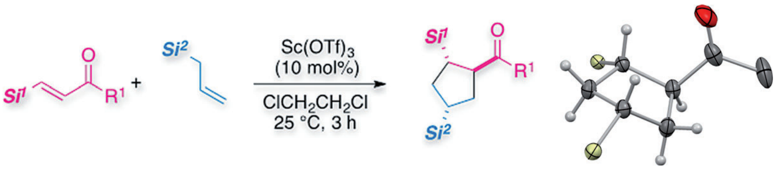
Copy cat: Hexacoordinate nickel(II)/(III) complexes are prepared which mimic the catalytic cycle of nickel superoxide dismutase (NiSOD) by an outer-sphere electron-transfer mechanism. The complexes employ a bis-tridentate N_2S donor carboxamide ligand, *N*-2-phenylthiophenyl-2′-pyridinecarboxamide (HL^{Ph}), and have been structurally characterized and their SOD activities examined.

Graphene Oxide



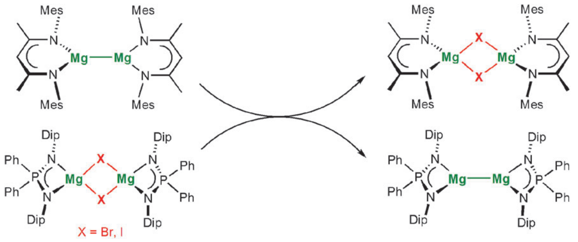
A reaction mechanism and a kinetic profile for graphene oxidation are proposed. Graphene oxidation proceeds with high correlation between oxidation loci, which is due to three crucial factors: 1) breaking of delocalized π bonds, 2) steric hindrance, and 3) hydrogen-bond formation.

Synthetic Methods



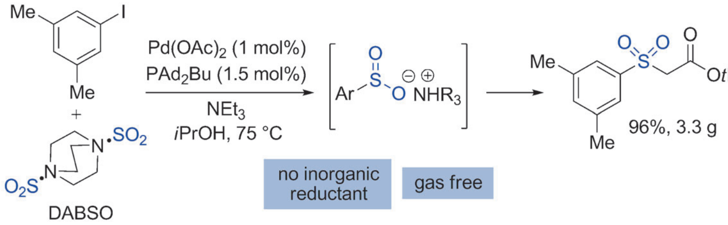
Two silicon atoms collaborate: The Sc(OTf)$_3$-catalyzed stereoselective [3+2] cycloaddition of allylsilanes to β-silylenones with migration of one silyl group has been developed. The electronic effect of two silyl groups plays a key role for selective cycloaddition. Two silyl groups of the obtained cycloadduct can be regioselectively oxidized into hydroxy groups. X-ray crystal structure: C gray, H white, Si yellow, O red.

Metal–Metal Bonds



The new switcheroo: A dimeric magnesium(I) complex has been prepared by a simple redox reaction using a known magnesium(I) complex. The new complex is stabilized by a high-oxidation-state phosphorane-based ligand and undergoes a C–C coupling reaction with *tert*-butylisocyanate.

Synthetic Methods

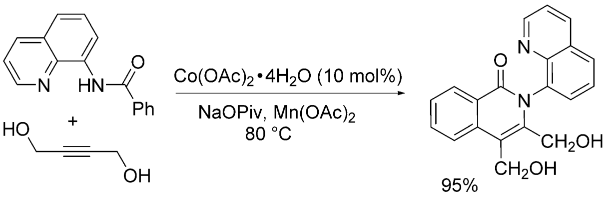


’SO’$_2$ versatile: The combination of an aryl halide, the SO$_2$ surrogate DABSO, a Pd^0 catalyst, isopropyl alcohol, and triethylamine delivers the corresponding ammonium sulfinate salts. Isopropyl alcohol serves as both the solvent and formal reductant, thus allowing the efficient formation of sulfinate intermediates in a process free of gaseous reagents and inorganic reductants. The salts can be converted into sulfones, sulfonamides, and sulfonyl chlorides.

C–H Activation

L. Grigorjeva,
O. Daugulis* ———— **10209 – 10212**

Cobalt-Catalyzed, Aminoquinoline-Directed C(sp^2)–H Bond Alkenylation by Alkynes

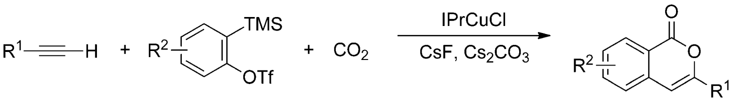


In the air: Excellent functional-group tolerance is observed in the title reaction, and both internal and terminal alkynes are competent substrates for the coupling. The reaction employs $Co(OAc)_2 \cdot 4H_2O$ as the catalyst, $Mn(OAc)_2$ as the co-catalyst, and oxygen (from air) as the terminal oxidant. Piv = pivalate.

Synthetic Methods

W.-J. Yoo, T. V. Q. Nguyen,
S. Kobayashi* ———— **10213 – 10217**

Synthesis of Isocoumarins through Three-Component Couplings of Arynes, Terminal Alkynes, and Carbon Dioxide Catalyzed by an NHC–Copper Complex



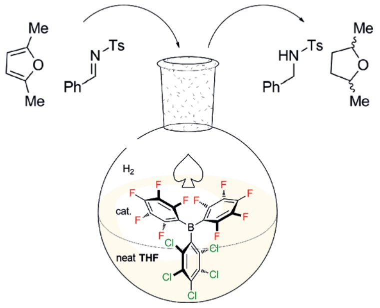
A facile synthetic protocol to isocoumarins consists of a three-component coupling reaction between 1-alkynes, 2-(trimethylsilyl)aryl triflates, and CO_2 (see scheme). The key to this reaction was the use of a versatile N-heterocyclic carbene/copper complex that was able to catalyze multiple transformations within the three-component reaction.

H_2 Activation

D. J. Scott, M. J. Fuchter,
A. E. Ashley* ———— **10218 – 10222**

Metal-Free Hydrogenation Catalyzed by an Air-Stable Borane: Use of Solvent as a Frustrated Lewis Base

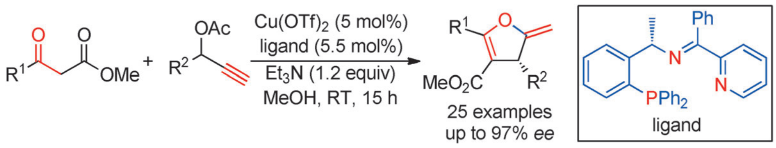
Reduced frustration: THF solutions of the boranes $B(C_6Cl_5)_x(C_6F_5)_{3-x}$ ($x = 0$–3) activate H_2 and effect catalytic hydrogenation of unsaturated substrates through a mechanism in which the solvent acts as a "frustrated" Lewis base. In particular, weakly basic substrates, such as *N*-tosyl imines, and pyrrole and furan derivatives (a new substrate family for frustrated Lewis pair (FLP) hydrogenations), are reduced under relatively mild conditions using air-stable $B(C_6Cl_5)(C_6F_5)_2$.



Asymmetric Catalysis

F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, J. Xu,
X.-P. Hu* ———— **10223 – 10227**

Enantioselective Synthesis of Highly Functionalized Dihydrofurans through Copper-Catalyzed Asymmetric Formal [3+2] Cycloaddition of β-Ketoesters with Propargylic Esters

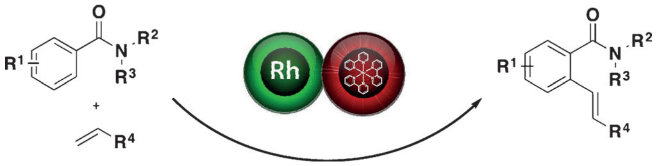


The combination of $Cu(OTf)_2$ and a chiral tridentate P,N,N ligand as the catalyst enabled the title reaction, giving a variety of 2-methylene-2,3-dihydrofurans in good yields and with good to high enantioselectivities. Furthermore, the exocyclic methylene group can be hydrogenated in a highly diastereoselective fashion to give unusual *cis*-2,3-dihydrofuran derivatives.

C–H Functionalization

D. C. Fabry, J. Zoller, S. Raja,
M. Rueping* ———— 10228 – 10231

Combining Rhodium and Photoredox Catalysis for C–H Functionalizations of Arenes: Oxidative Heck Reactions with Visible Light

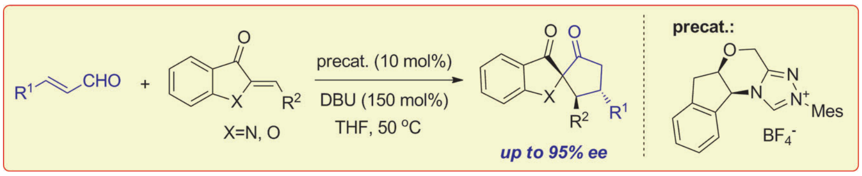


Much milder and environmentally friendly reaction conditions can be used for oxidative Heck reactions through the combined use of rhodium and redox catalysis. This allows the rhodium complex to be catalytically regenerated. A broad range of substrates was tolerated in the reaction and afforded different amides in good to very good yields.

Asymmetric Organocatalysis

C. Guo, M. Schedler, C. G. Daniliuc,
F. Glorius* ———— 10232 – 10236

N-Heterocyclic Carbene Catalyzed Formal [3+2] Annulation Reaction of Enals: An Efficient Enantioselective Access to Spiro-Heterocycles

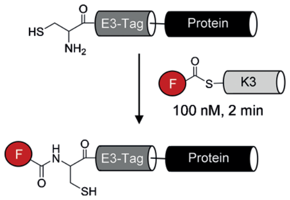


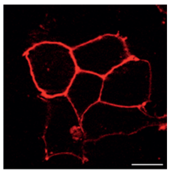
Ring, ring: A highly enantioselective formal [3+2] annulation of α,β-unsaturated aldehydes with azaaurones or aurone is catalyzed by an N-heterocyclic carbene (NHC) and generates spiro-heterocycles. The protocol represents a unique NHC activation-based approach to access spiro-heterocyclic derivatives bearing a quaternary stereogenic center with high optical purity.

Protein Labeling

U. Reinhardt, J. Lotze, S. Zernia, K. Mörl,
A. G. Beck-Sickinger,
O. Seitz* ———— 10237 – 10241

Peptide-Templated Acyl Transfer: A Chemical Method for the Labeling of Membrane Proteins on Live Cells





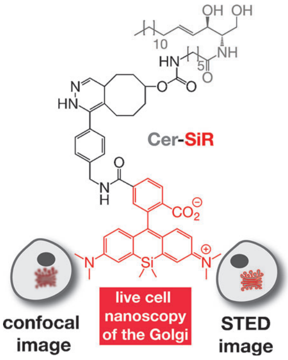
A glossy kiss: Coiled-coil formation brings a thioester-linked reporter K3 peptide into proximity to an E3-tagged membrane protein. This triggers a rapid transfer of the reporter from the labeling reagent to the protein of interest. High target specificity, speed, low concentrations of labeling agent, and minimal mass increase are noteworthy features which facilitated the fluorescence microscopic imaging of the human Y_2 receptor on living cells.

Visualizing the Golgi Apparatus

R. S. Erdmann, H. Takakura,
A. D. Thompson, F. Rivera-Molina,
E. S. Allgeyer, J. Bewersdorf, D. Toomre,*
A. Schepartz* ———— 10242 – 10246

Super-Resolution Imaging of the Golgi in Live Cells with a Bioorthogonal Ceramide Probe

Seeing is believing: A new lipid-based strategy to visualize Golgi structure and dynamics at super-resolution in live cells is presented. The method is based on two reagents: a *trans*-cyclooctene-containing ceramide lipid and a highly reactive, tetrazine-tagged, near-IR dye. These reagents assemble to give Cer-SiR, which enables prolonged live-cell imaging of the Golgi apparatus by 3D confocal and stimulated emission depletion (STED) microscopy.

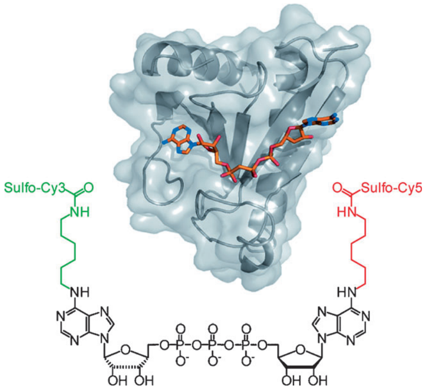


Signaling Molecules

S. M. Hacker, F. Mortensen, M. Scheffner, A. Marx* ______________ **10247 – 10250**

Selective Monitoring of the Enzymatic Activity of the Tumor Suppressor Fhit

F(h)it and light up: The fragile histidine triade protein (Fhit) is a diadenosine triphosphate hydrolase that is frequently inactivated during cancer development. Now a fluorogenic probe has been synthesized and used to study the enzymatic activity of endogenous Fhit in cell lysates. This probe was applied to study Fhit effectors in this biologically relevant setup; in-depth insights into the mechanisms involved in regulating Fhit are expected.



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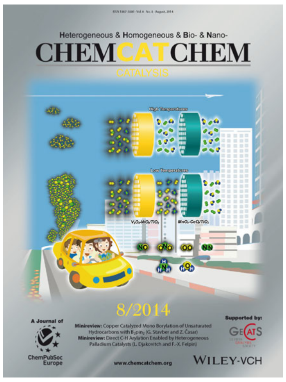

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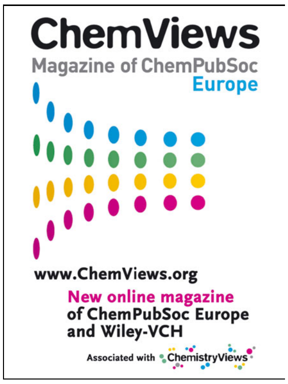

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