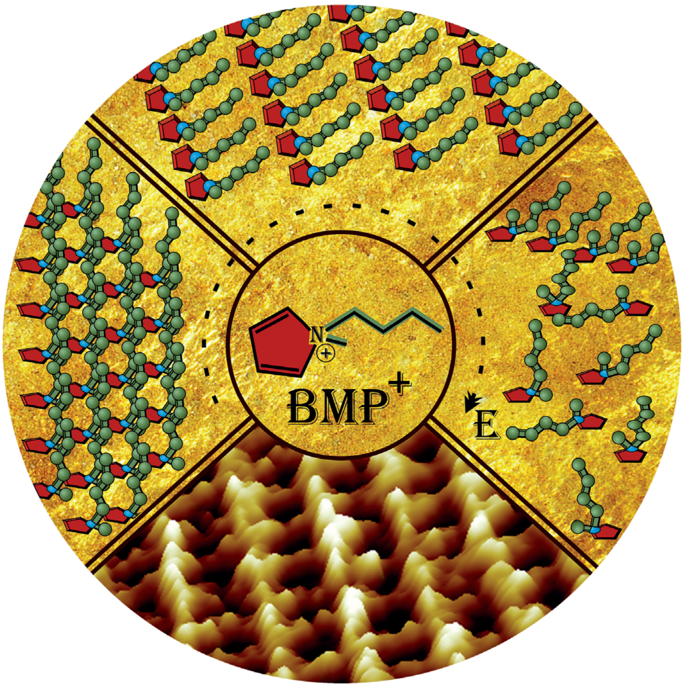
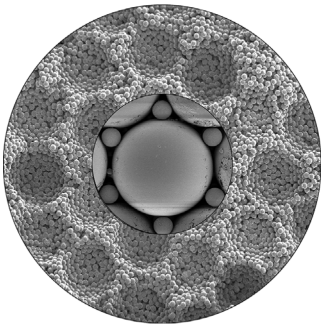
Shrouded in mystery, ...

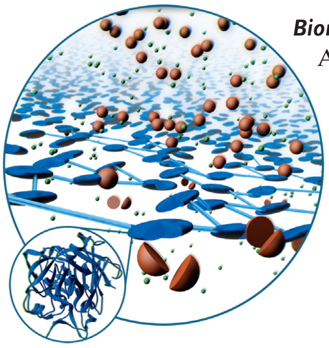


… the interface structure of ionic liquids is unclear despite their popularity for electrochemical applications. In their Communication on page 6062 ff., O. M. Magnussen et al. address the molecular arrangement and sub-second dynamics of these iconic compounds on gold electrodes by high-speed tunneling microscopy. With decreasing potential, distinct transitions in the structure and surface mobility of the innermost layer of 1-butyl-1-methylpyrrolidinium cations are found.

Colloidal Crystals

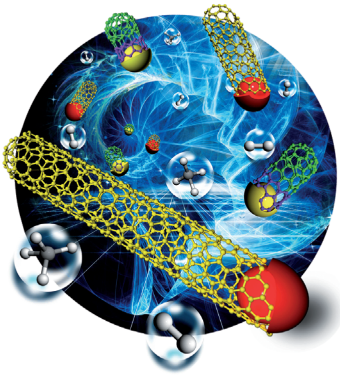
S. R. Little, J. J. McCarthy et al. show in their Communication on page 5854 ff. that by mimicking Brownian motion through agitation and tuning particle sizes and volume ratios, unique patterns are created as analogues to autonomously formed nanostructures.





Biomembranes

A method for the large-scale production of ultrathin cross-linked enzymes that allow simultaneous enzymatic conversion and selective removal of digestion products is described by N. E. Benes, M. Wessling et al. in their Communication on page 5910 ff.



Zigzag Carbon Nanotubes

The growth mechanism of zigzag carbon nanotubes (ZZ CNTs) is revealed by Q. Yuan and F. Ding in their Communication on page 5924 ff. allowing a method to maximize the yield of the rare ZZ CNTs to be proposed.

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Editorial

"... The challenge for chemistry is no longer just the synthesis of increasingly complex molecular structures, but to tailor functionalities. Chemistry is at the core of the molecular sciences, reaching out into many other areas. The Max Planck Society is committed to fostering progress in chemistry as one of the key fields of the future ..." Read more in the Editorial by Martin Stratmann and Christoph Ettl.

Service

Author Profile

"My favorite composer is Wolfgang Amadeus Mozart. I advise my students to work hard and be thoughtful ..." This and more about Xiao-Ming Chen can be found on page 5820.

News

J. Takaya

M. Rief

T. B. Marder

P. Levkin

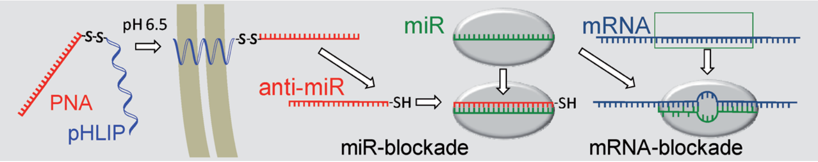
G. Gauglitz

D. Günther

Books

Highlights

RNA Interference

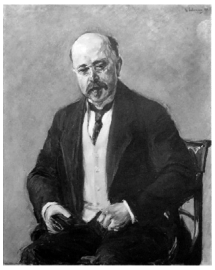


pHLIP opens the door to the cell: An improved cytosolic transfer of anti-microRNAs (anti-miRs) against onco-miRs paves the way for future cancer therapies. The employed anti-miR–peptide conjugates are based on peptide nucleic acids (PNAs), which are connected with the membrane translocation peptide pHLIP through a disulfide bond. The PNAs are thus transferred into the cell and released by the cleavage of the S–S bond (see scheme).

Essays

Science history

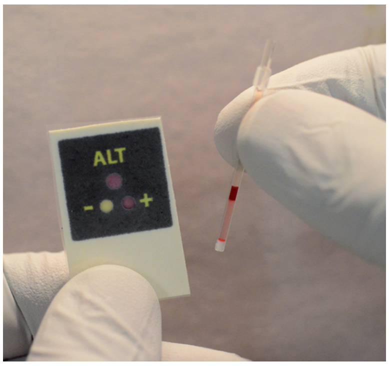
A commemorative symposium took place on the 16th June 2014 in the Magnus House in Berlin on the occasion of the 150th birthday of Walter Nernst. This Essay outlines the important stages in his life and consider the main features in the development of the discipline cofounded by him.



Reviews

Patient Diagnostics

Fielding questions: This Review shares lessons from two case studies in the development of point-of-care tests: a colorimetric, paper-based liver function test using serum transaminases (left), and a test for sickle cell disease using aqueous multiphase systems and differences in the density of red blood cells characteristic of sickle cell disease (right).



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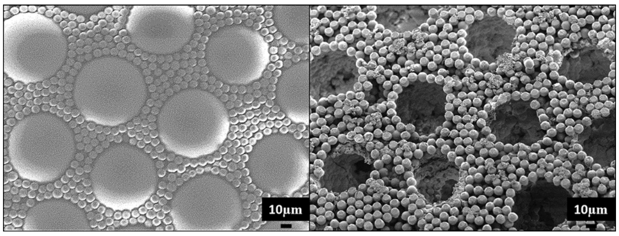
Communications

Colloidal Crystals

M. H. Lash, J. C. Jordan, L. C. Blevins,
M. V. Fedorchak, S. R. Little,*
J. J. McCarthy* ______ 5854 – 5858

Non-Brownian Particle-Based Materials with Microscale and Nanoscale Hierarchy

Frontispiece

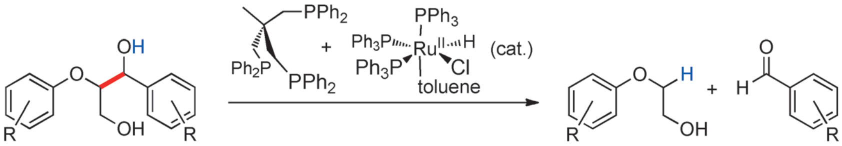


Non-Brownian microparticle mixtures are assembled into unique multicomponent colloidal crystals and their inverse structures. By mimicking the effects of Brownian motion through agitation and tuning of the particle sizes and volume ratios, unique stoichiometric patterns are created and can serve as an analogue to autonomously formed nanostructures.

Lignin Valorization

T. vom Stein, T. den Hartog, J. Buendia,
S. Stoychev, J. Mottweiler, C. Bolm,
J. Klankermayer,* W. Leitner 5859 – 5863

Ruthenium-Catalyzed C–C Bond Cleavage in Lignin Model Substrates

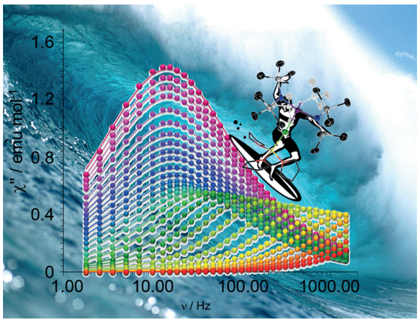


Sele-C-C-tivity! Highly selective C–C bond cleavage of model compounds for the lignin β-O-4 linkage was promoted by a catalyst formed in situ from [Ru(Cl)(H)(PPh$_3$)$_3$] and the ligand triphos (see scheme). Mechanistic investigations indicated a hydrogen-transfer-based retro-aldol pathway for this transformation.

Mononuclear Lanthanide SMMs

A. J. Brown, D. Pinkowicz, M. R. Saber,
K. R. Dunbar* ______ 5864 – 5868

A Trigonal-Pyramidal Erbium(III) Single-Molecule Magnet

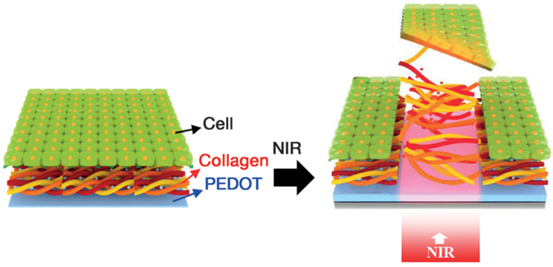


Riding the wave of erbium SMMs: The first trigonal pyramidal mononuclear erbium(III) single-molecule magnet (SMM) was synthesized and its magnetic properties investigated. Despite containing an axial Cl$^-$ ligand, which is expected to reduce the prolate nature of the erbium(III) ion, the molecule exhibits out-of-phase signals in the ac susceptibility data in the absence of an external field and hysteresis behavior up to 3 K.

Bionanotechnology

J. D. Kim, J. S. Heo, T. H. Park, C. H. Park,
H. O. Kim, E. K. Kim* ______ 5869 – 5873

Photothermally Induced Local Dissociation of Collagens for Harvesting of Cell Sheets

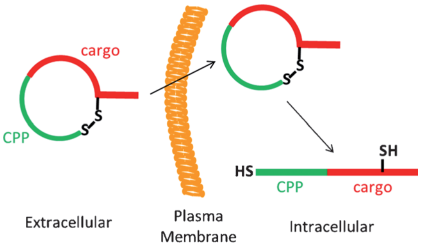


A live cell sheet is harvested by the dissociation of adsorbed collagens on a poly(3,4-ethylenedioxythiophene) (PEDOT) surface by a photothermal method employing near-IR (NIR) radiation. Irradiation with NIR light induces unfolding of the collagen triple helices leading to the spatially controlled detachment of a patterned cell sheet with intact cell morphology.

Cyclic Peptides

Z. Qian, X. Xu, J. F. Amacher,
D. R. Madden, E. Cormet-Boyaka,
D. Pei* ———— 5874 – 5878

Intracellular Delivery of Peptidyl Ligands by Reversible Cyclization: Discovery of a PDZ Domain Inhibitor that Rescues CFTR Activity

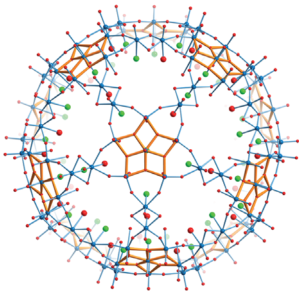


Roll in, unroll: Peptide cargoes were fused to cell-penetrating peptides (CPPs) and cyclized through a disulfide bond. This cyclization increases their proteolytic stability and cell permeability. Once they enter the cell, the disulfide bond is reduced by intracellular thiols, thus leading to regeneration of the functional linear peptides.

Porous capsules

S. Garai, M. Rubčić, H. Bögge,
E. T. K. Haupt, P. Gouzerh,
A. Müller* ———— 5879 – 5882

A Unique Fluoride Nanocontainer: Porous Molecular Capsules Can Accommodate an Unusually High Number of "Rather Labile" Fluoride Anions

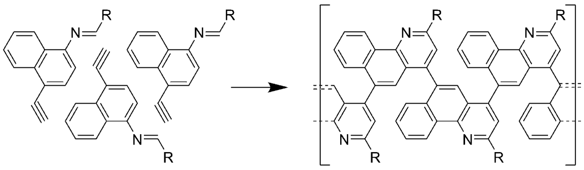


Overloaded: Porous molecular nanocontainers of the {Mo$_{132}$} Keplerate type can integrate a uniquely large number of fluorides. These F$^-$ ions (see structure, green) are partly as coordinated ligands at both the {(Mo^{VI})Mo$^{VI}_5$O$_{21}$(H$_2$O)$_5$(F)} pentagonal units (orange) and the linkers (blue), partly as a disordered water/fluoride assembly inside the cavity. The H$_2$O ligands are shown as red spheres (larger red spheres are for H$_2$O coordinated e.g. to the Mo^V centers of the linkers).

Organic Electronics

D. J. Dibble, Y. S. Park, A. Mazaheripour,
M. J. Umerani, J. W. Ziller,
A. A. Gorodetsky* ———— 5883 – 5887

Synthesis of Polybenzoquinolines as Precursors for Nitrogen-Doped Graphene Nanoribbons



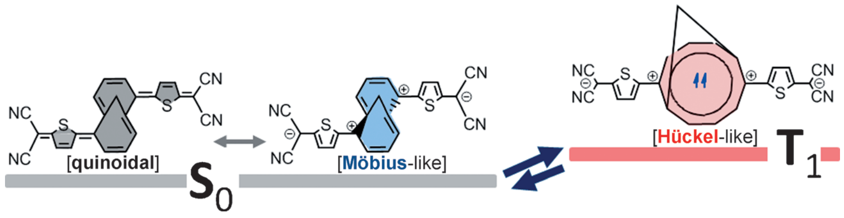
Towards nitrogen-doped nanoribbons: A previously unknown class of benzoquinoline-based materials was synthesized via the aza-Diels–Alder reaction. The reported straightforward and facile methodology provides ready access to a potentially diverse range of polybenzoquinolines. These materials hold promise as key intermediates for the synthesis of modular nitrogen-doped graphene nanoribbons.

Baird's Diradicals

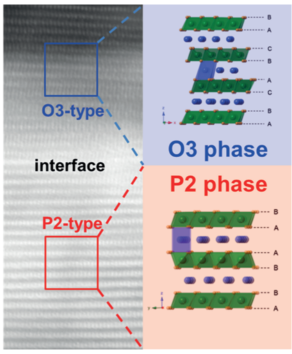
B. C. Streifel, J. L. Zafra, G. L. Espejo,
C. J. Gómez-García, J. Casado,*
J. D. Tovar* ———— 5888 – 5893

An Unusually Small Singlet–Triplet Gap in a Quinoidal 1,6-Methano[10]annulene Resulting from Baird's 4n π-Electron Triplet Stabilization

Inside Cover



Topological chameleon: A small ΔE_{ST} gap in a 1,6-methano[10]annulene-based tetracyanoquinodimethane results from an antiaromatic (but Möbius aromatic-like) singlet ground electronic state based on a [10]annulene dication and a Hückel aromatic-like triplet excited state. The small gap is a result of the net stabilization of the triplet excited state in accordance with Baird's rule.

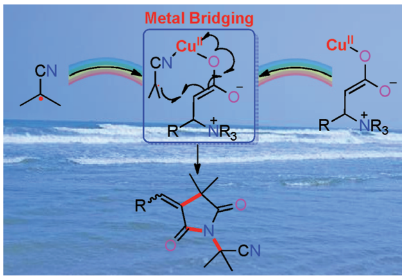


A layered composite with P2 and O3 integration is proposed for a sodium-ion battery with high energy density and long cycle life and characterized by XRD refinement, SAED and HAADF, and ABF-STEM. This layered composite can deliver a high reversible capacity with the largest energy density of 640 mAhg^{-1}, and it also presents good capacity retention over 150 times of sodium extraction and insertion.

Sodium-Ion Cathodes

S. Guo, P. Liu, H. Yu,* Y. Zhu, M. Chen, M. Ishida, H. Zhou* ______ **5894 – 5899**

A Layered P2- and O3-Type Composite as a High-Energy Cathode for Rechargeable Sodium-Ion Batteries



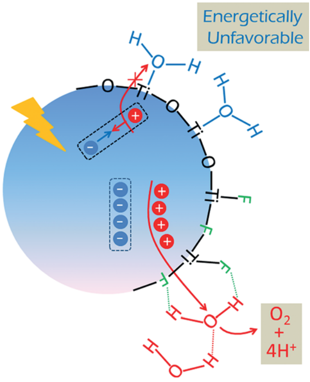
Electron bridge: An efficient strategy for improving the electron transfer between radicals and enolates has been developed. A redox-active copper species activates the free radical and brings the radical and enolate within proximity, which in turn facilitates the electron transfer. Thus, a cascade reaction for the synthesis of highly functionalized pyrrolidine-2,5-diones was developed.

Radical Cascades

Y. Xie, S. Guo, L. Wu, C. Xia, H. Huang* ______ **5900 – 5904**

Metal Bridging for Directing and Accelerating Electron Transfer as Exemplified by Harnessing the Reactivity of AIBN

Switching the water adsorption mode on TiO_2 to dual H-bonding by the presence of fluorine atoms at the surface not only thermodynamically enables the hole transfer to the water molecules, but also facilitates the proton-coupled electron transfer during water oxidation. This phenomenon is established by IR spectroscopy studies and calculations.

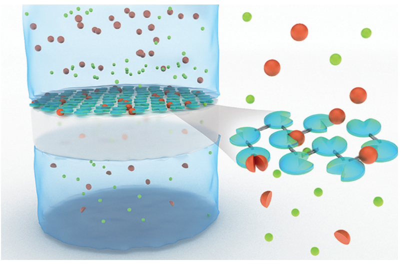


Photocatalysis

H. Sheng, H. Zhang, W. Song, H. Ji, W. Ma, C. Chen,* J. Zhao ______ **5905 – 5909**

Activation of Water in Titanium Dioxide Photocatalysis by Formation of Surface Hydrogen Bonds: An In Situ IR Spectroscopy Study

Ultrathin enzymatically active membranes are prepared by interfacial polymerization of pepsin with trimesoyl chloride. The high degree of covalent bonding between the pepsin molecules results in the formation of a homogenous film, while the pepsin retains the ability to degrade suitable substrates under acidic conditions. It is shown that the water-permeable membranes retain larger-molecular-weight components.



Biomembranes

M. J. T. Raaijmakers, T. Schmidt, M. Barth, M. Tutus, N. E. Benes,* M. Wessling* ______ **5910 – 5914**

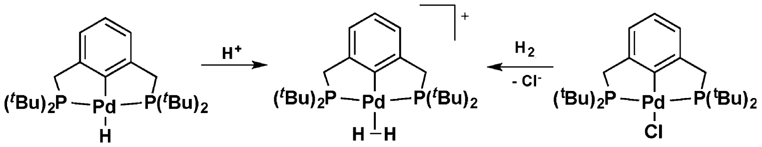
Enzymatically Active Ultrathin Pepsin Membranes

Inside Back Cover

Palladium Complexes

S. J. Connelly, A. G. Chanez, W. Kaminsky,
D. M. Heinekey* ———— **5915 – 5918**

Characterization of a Palladium Dihydrogen Complex

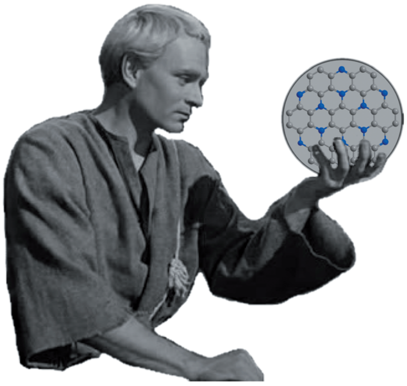


Palladium binds H_2: The first dihydrogen complex of palladium has been synthesized and characterized, employing a ^{tBu}PCP (κ^3-2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$) pincer ligand. The complex is investigated by X-ray crystallography and NMR spectroscopy, which reveals a very short H—H bond length.

Boron-Doped Graphite

T. C. King, P. D. Matthews, H. Glass,
J. A. Cormack, J. P. Holgado, M. Leskes,
J. M. Griffin, O. A. Scherman, P. D. Barker,
C. P. Grey, S. E. Dutton, R. M. Lambert,
G. Tustin, A. Alavi,*
D. S. Wright* ———— **5919 – 5923**

Theory and Practice: Bulk Synthesis of C_3B and its H_2- and Li-Storage Capacity



C_3B or not C_3B that is the question—Previous theoretical predictions suggest that the stoichiometrically doped graphite C_3B should be a promising H_2- and Li-storage material, with potentially important applications in power storage. The first experimental measurements of the real material indicate, however, that disorder is a limiting factor for the use of C_3B as an energy storage material.

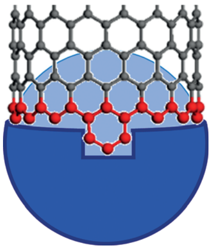
Carbon Nanotubes

Q. Yuan,* F. Ding* ———— **5924 – 5928**

How a Zigzag Carbon Nanotube Grows

Back Cover

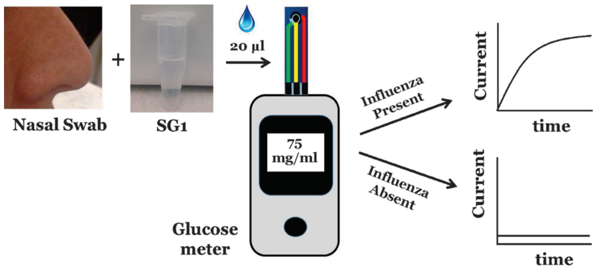
ZZ top: The mystery behind the ultra-slow growth of zigzag (ZZ) carbon nanotubes (CNTs) is investigated by exploring the unique kinetics of ZZ CNT growth. The underlying mechanism of their growth on a nanoparticle catalyst is revealed and for the first time a means to maximize the synthesis of ZZ CNTs, which to date are experimentally very rare, is proposed.



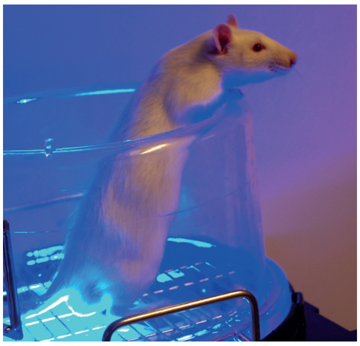
Biosensors

X. Zhang, A. N. Dhawane, J. Sweeney,
Y. He, M. Vasireddi,
S. S. Iyer* ———— **5929 – 5932**

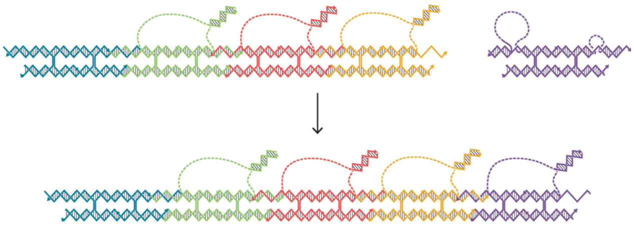
Electrochemical Assay to Detect Influenza Viruses and Measure Drug Susceptibility



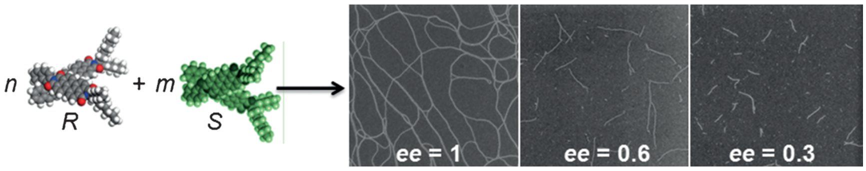
Flu finder: An electrochemical assay has been developed for the detection of influenza viruses using glucose-bearing substrates (SG1). By monitoring the release of glucose upon introduction of the virus, 19 different influenza strains have been successfully detected. The assay can also be used to rapidly measure drug susceptibility.



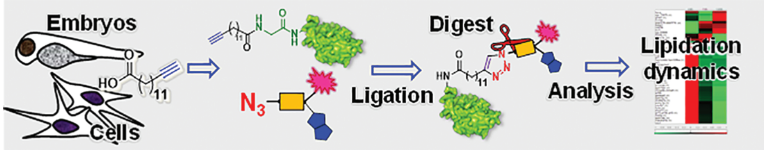
A bolt from the blue: A synthetic designer guanylate cyclase producing a blue-light-inducible surge of the second messenger cyclic guanosine monophosphate (cGMP) in mammalian cells was used as an erectile optogenetic stimulator (EROS). Blue-light-dependent penile erection associated with occasional ejaculation was triggered in male rats by simple illumination of EROS-transfected *corpus cavernosum* with a portable commercial light-therapy device.



Signal passing in DNA: A triggered self-assembly process of DNA nanostructured tiles is demonstrated. The DNA-strand-exchange mechanism sends a signal across a tile leading to a binding event by activation of a second binding site 18 nm away. Five unique DNA tiles self-assemble sequentially in a domino-like cascade.

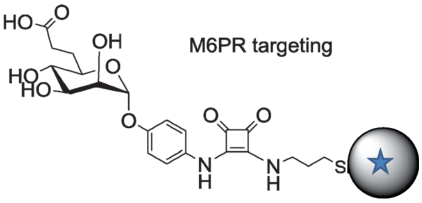


Going to great lengths: The length of chiral supramolecular polymers was precisely controlled through varying the enantiomeric excess. The homochiral assembly favors fibrous growth whereas heterochiral assembly preferentially leads to nanoparticles. The stronger heterochiral bindings at the growing ends of fibers effectively terminate the elongation of the fibers.



Catch and release: Multifunctional capture reagents were developed that enable enzymatically-triggered release and direct detection of lipid-modified peptides by mass spectrometry. Dynamic proteome lipidation was visualized, enriched, and identified on an unprecedented scale, both in cells and in a developing zebrafish embryo.

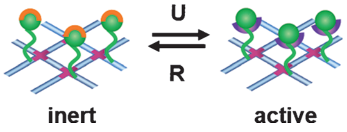
Nanoparticles



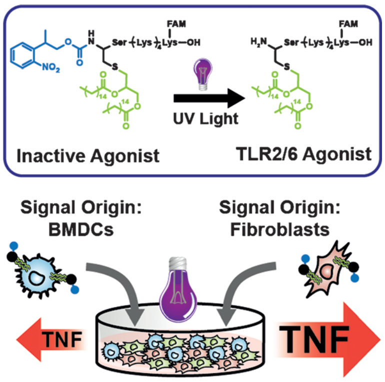
On target: The over-expression of a mannose-6-phosphate receptor was demonstrated in prostate tissues and cancer cell lines. This receptor was targeted with a mannose-6-phosphate analogue grafted onto the surface of mesoporous silica nanoparticles (MSNs). MSNs were efficient for cancer imaging and therapy, thus demonstrating the potential of M6PR targeting for prostate cancer theranostics.

Cell Adhesion

Reversible encryption: Dynamic materials for regulation of cell adhesion are important to a variety of biological and biomedical applications. This study demonstrates an encrypted ligand and hydrogel with the capability of inducing and inhibiting cell adhesion, which is controlled by hybridization reaction-driven molecular reconfiguration. U = unblocking sequence, R = recovering sequence.

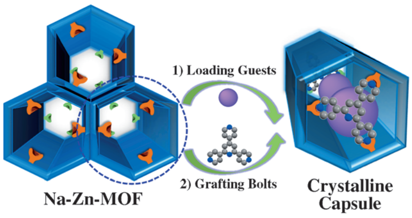


Peptidomimetics



The origin of inflammation in cell culture is commonly obscured by paracrine and autocrine signaling. A small-molecule immunopotentiator was developed that tags cells and initiates inflammation of the tagged cells using light. BMDCs = bone-marrow-derived dendritic cells, TNF = tumor necrosis factor.

Metal–Organic Frameworks

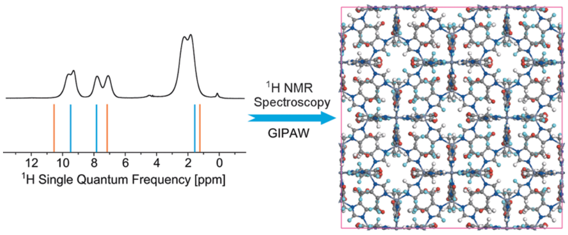


Lock, stock, and barrel: A two-step "loading-locking" process has been developed to encapsulate target guest molecules in porous metal–organic frameworks (MOFs). In this approach, size-matching organic ligands are preselected and deliberately grafted onto open metal sites to lock the pores of the MOFs to prevent the leaching of guests. Rapid release of the encapsulated guests can be achieved by application of an external stimulus.

Structure Elucidation

M. Baias, A. Lesage, S. Aguado, J. Canivet,
V. Moizan-Basle, N. Audebrand,
D. Farrusseng,* L. Emsley* **5971 – 5976**

Superstructure of a Substituted Zeolitic Imidazolate Metal–Organic Framework Determined by Combining Proton Solid-State NMR Spectroscopy and DFT Calculations

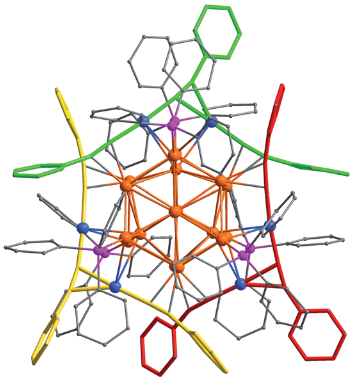


The superstructure of a substituted zeolitic imidazolate metal–organic framework was determined from a combination of experimental NMR chemical shifts and DFT-calculated shifts (see picture). The study indicates the presence of two different environments for each type of functional group in the metal–organic framework.

Cluster Compounds

X.-K. Wan, S.-F. Yuan, Q. Tang, D. Jiang,*
Q.-M. Wang* **5977 – 5980**

Alkynyl-Protected Au_{23} Nanocluster: A 12-Electron System

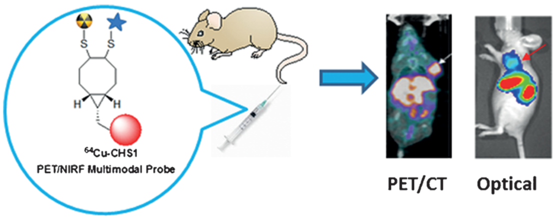


A heart of gold: Gold nanocluster $[Au_{23}(PhC{\equiv}C)_9(Ph_3P)_6]^{2+}$ has an unprecedented Au_{17} kernel protected by three PhC_2-Au-C_2(Ph)-Au-C_2Ph motifs (see picture; green, yellow, and red) and six Ph_3P units. DFT electronic structure analysis suggests that the stability of the 12-electron cluster is due to the splitting of the superatomic 1D orbitals under the D_{3h} symmetry of the Au_{17} core. Atom colors: Au = orange/blue; P = purple; C = gray.

Fluorescent Probes

Y. Sun, X. W. Ma, K. Cheng, B. Y. Wu,
J. L. Duan, H. Chen, L. H. Bu, R. P. Zhang,
X. M. Hu, Z. X. Deng, L. Xing,
X. C. Hong,* Z. Cheng* **5981 – 5984**

Strained Cyclooctyne as a Molecular Platform for Construction of Multimodal Imaging Probes

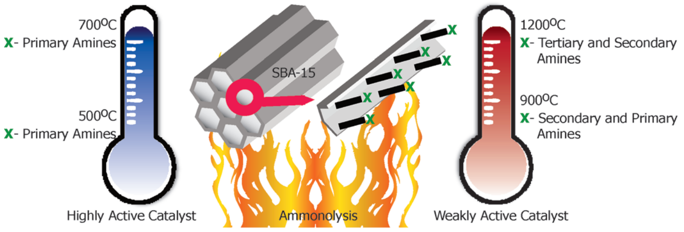


Spitting image: The products of the base-catalyzed addition of various functional molecules to bicyclo[6.1.0]nonyne-based scaffolds provided precursors for novel dual-modality (PET and NIRF) uPAR-targeted imaging probes. The probes were evaluated in U87MG cells and tumor-bearing mice models, thus demonstrating excellent imaging characteristics.

Heterogeneous Catalysis

B. Singh, K. R. Mote, C. S. Gopinath,
P. K. Madhu,*
V. Polshettiwar* **5985 – 5989**

SBA-15-Oxynitrides as a Solid-Base Catalyst: Effect of Nitridation Temperature on Catalytic Activity



Oxynitride solid: Solid bases, such as SBA-15-oxynitrides, have attracted considerable interest for potential applications as catalysts in important industrial processes. It is shown that tuning the temperature of nitridation (ammonolysis) leads to enhanced catalytic activity of these solid bases. Detailed studies are discussed to explain this change in activity.

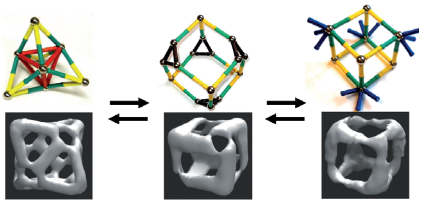
DNA Nanocages

VIP

Y. Li, C. Tian, Z. Liu, W. Jiang, C. Mao* ______ **5990 – 5993**

Structural Transformation: Assembly of an Otherwise Inaccessible DNA Nanocage

One way or another: A strategy has been developed for the assembly of DNA nanocages that can not be assembled directly. In this approach a precursor DNA nanocage is assembled first and is then isothermally transformed into a desired, complicated nanocage. Dramatic changes in the 3D structures and topologies accompany the transformation, as shown by native polyacrylamide gel electrophoresis and cryogenic electron microscopy imaging.

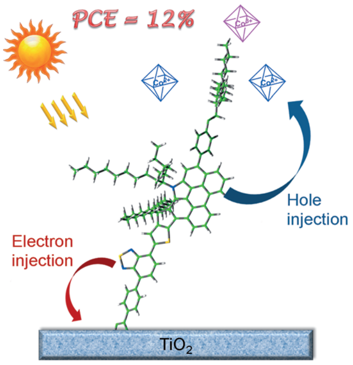


Polycycles

Z. Yao, M. Zhang, R. Li, L. Yang, Y. Qiao, P. Wang* ______ **5994 – 5998**

A Metal-Free N-Annulated Thienocyclopentaperylene Dye: Power Conversion Efficiency of 12% for Dye-Sensitized Solar Cells

Power trip: A perylene dye derived from N-annulated thienocyclopentaperylene, which is characterized by a low-energy gap and a high electron injection yield, was synthesized for dye-sensitized solar cells. A high power conversion efficiency of 12%, at an irradiance of the AM1.5G sunlight, was achieved. This efficiency is the highest achieved thus far by using just a metal-free organic dye.

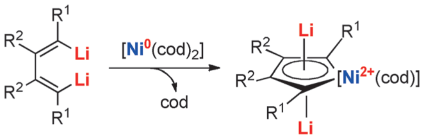


Organolithium Compounds

J. Wei, W.-X. Zhang, Z. Xi* _ **5999 – 6002**

Dianions as Formal Oxidants: Synthesis and Characterization of Aromatic Dilithionickeloles from 1,4-Dilithio-1,3-butadienes and [Ni(cod)$_2$]

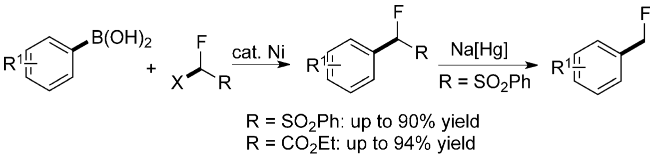
A formal event: Organolithium compounds can behave as reductants but never as oxidants in redox reactions. This work discloses that conjugated dilithio butadienyldianions can react with zero-valent [Ni(cod)$_2$] to afford divalent aromatic dilithionickeloles. In this redox reaction, the dilithio butadienyldianions behave as formal oxidants, thus oxidizing Ni^0 into Ni^{2+}.



Monofluoromethylation

Y.-M. Su, G.-S. Feng, Z.-Y. Wang, Q. Lan, X.-S. Wang* ______ **6003 – 6007**

Nickel-Catalyzed Monofluoromethylation of Aryl Boronic Acids

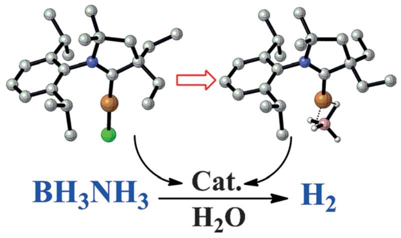


Aryl boronic acids can be monofluoromethylated under nickel catalysis. The utility of this method is demonstrated by the monofluoromethylation of a borylated and acyl-protected derivative of the statin drug ezetimibe. Mechanistic investigations indicate that a fluoromethyl radical is involved in the Ni^{I}/Ni^{III} catalytic cycle.

Hydrides

X. Hu,* M. Soleilhavoup, M. Melaimi, J. Chu, G. Bertrand* ______ **6008 – 6011**

Air-Stable (CAAC)CuCl and (CAAC)CuBH$_4$ Complexes as Catalysts for the Hydrolytic Dehydrogenation of BH$_3$NH$_3$

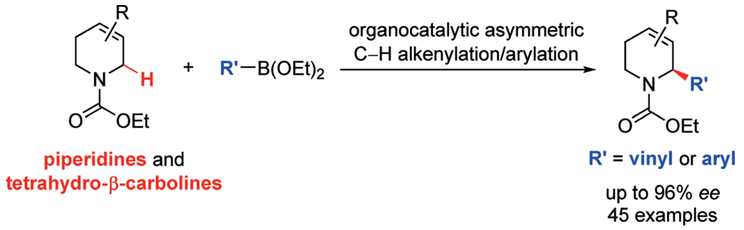


Copper works! [(CAAC)CuCl] reacts with both NaBH$_4$ and BH$_3$NH$_3$ to afford [(CAAC)CuBH$_4$] as a thermally and air-stable complex. Both complexes efficiently promote the hydrolytic dehydrogenation of ammonia borane at room temperature, with a turnover frequency of up to 8400 mol$_{H_2}$ mol$_{cat}^{-1}$ h^{-1}. In addition, these air-stable catalysts are readily recyclable. CAAC = cyclic (alkyl)(amino)carbene.

Synthetic Methods

X. Liu, Z. Meng, C. Li, H. Lou, L. Liu* ______ **6012 – 6015**

Organocatalytic Enantioselective Oxidative C−H Alkenylation and Arylation of *N*-Carbamoyl Tetrahydropyridines and Tetrahydro-β-carbolines

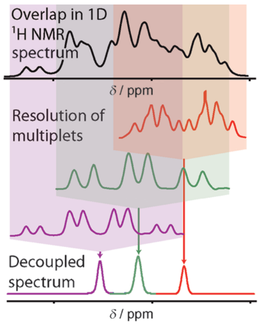


Without a metal: A large variety of N-heterocycles and boronates were subjected to the title reactions, which proceeded with high efficiency and excellent regio- and enantioselectivity. The new method was applied in complex molecule synthesis.

NMR Spectroscopy

A. Cotte, D. Jeannerat* ______ **6016 – 6018**

1D NMR Homodecoupled ^{1}H Spectra with Scalar Coupling Constants from 2D *NemoZS*-DIAG Experiments

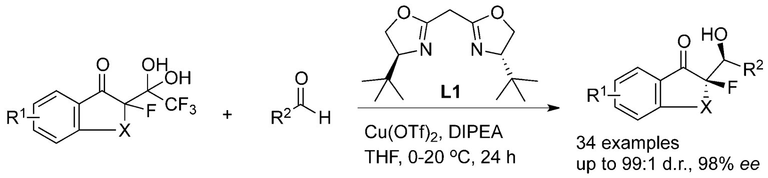


Clear separation: The overlapping ^{1}H multiplets of a 1D NMR spectrum are easily resolved in a 2D *nemoZS*-DIAG spectrum. An automatic analysis can extract the scalar coupling constants and produce a homodecoupled 1D ^{1}H spectrum.

Asymmetric Catalysis

C. Xie, L. Wu, J. Han,* V. A. Soloshonok, Y. Pan ______ **6019 – 6023**

Assembly of Fluorinated Quaternary Stereogenic Centers through Catalytic Enantioselective Detrifluoroacetylative Aldol Reactions

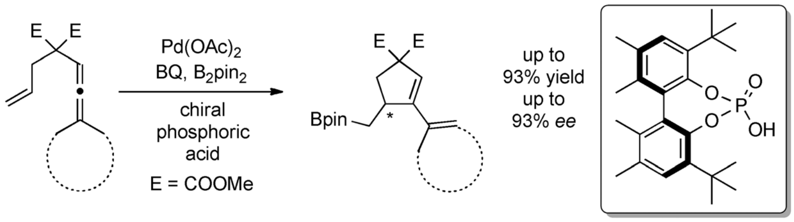


High selectivity: Asymmetric catalytic detrifluoroacetylative aldol addition reactions between 2-fluoro-1,3-diketones/hydrates and aldehydes afford α-fluoro-β-hydroxyketone products containing C−F quaternary stereogenic centers in good yields, high diastereo-, and enantioselectivities.

Synthetic Methods

T. Jiang, T. Bartholomeyzik, J. Mazuela, J. Willersinn, J.-E. Bäckvall* **6024 – 6027**

Palladium(II)/Brønsted Acid-Catalyzed Enantioselective Oxidative Carbocyclization–Borylation of Enallenes

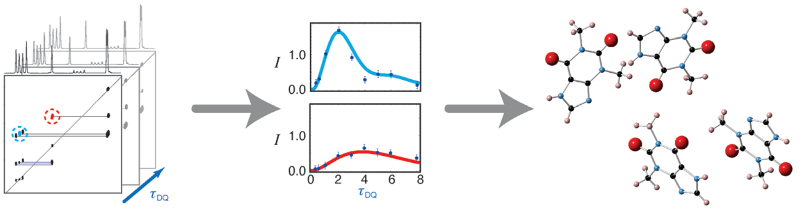


Biphenol-type chiral phosphoric acids serve as co-catalysts to induce enantioselectivity in the palladium(II)-catalyzed oxidative carbocyclization–borylation of enallenes. The method was used to prepare a number of enantioenriched borylated carbocycles in high yields and enantioselectivities (up to 93 %). BQ = benzoquinone, pin = pinacolato.

NMR Spectroscopy

G. Mollica, M. Dekhil, F. Ziarelli, P. Thureau,* S. Viel* ______ **6028 – 6031**

Quantitative Structural Constraints for Organic Powders at Natural Isotopic Abundance Using Dynamic Nuclear Polarization Solid-State NMR Spectroscopy

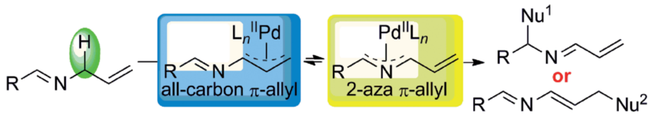


Structure elucidation: ^{13}C–^{13}C double-quantum (DQ) build-up curves (see picture, center) are recorded using dynamic nuclear polarization solid-state NMR spectroscopy. Structural constraints based on these curves are quantitatively related to the crystal structures of organic microcrystalline powders at natural isotopic abundance, as shown for theophylline. τ_{DQ} = DQ excitation time.

Synthetic Methods

B. M. Trost,* S. Mahapatra, M. Hansen ______ **6032 – 6036**

Palladium-Catalyzed C–H Activation of N-Allyl Imines: Regioselective Allylic Alkylations to Deliver Substituted Aza-1,3-Dienes

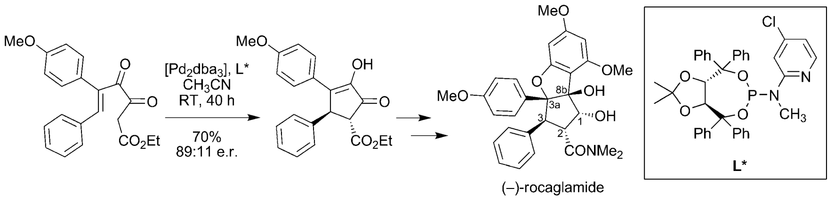


Making one into two: Palladium-catalyzed direct C(sp^3)–H activation of an N-allyl imine led to the generation of an all-carbon π-allyl complex which presumably remains in equilibrium with a rare 2-aza π-allyl species. Nucleophilic attack on the π-allyl intermediates gave either a 1-aza-1,3-diene or 2-aza-1,3-diene in a completely regioselective manner.

Total Synthesis

Z. Zhou, M. A. Tius* ______ **6037 – 6040**

Synthesis of Each Enantiomer of Rocaglamide by Means of a Palladium(0)-Catalyzed Nazarov-Type Cyclization

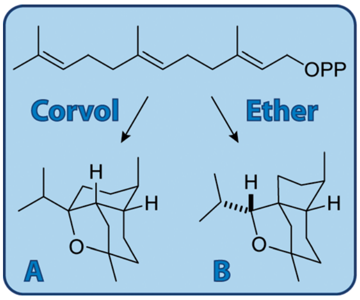


Start to finish: A recently reported Pd^0-catalyzed asymmetric Nazarov-type cyclization was applied in the key step of the first catalytic asymmetric total synthesis of (–)-rocaglamide (natural) and (+)-rocaglamide. The stereochemistry at the C3 position controls the stereochemistry of all other stereocenters and is determined in the cyclization step. dba = dibenzylidene acetone.

Terpene Biosynthesis

P. Rabe, K. A. K. Pahirulzaman,
J. S. Dickschat* ———— **6041 – 6045**

Structures and Biosynthesis of Corvol Ethers—Sesquiterpenes from the Actinomycete *Kitasatospora setae*

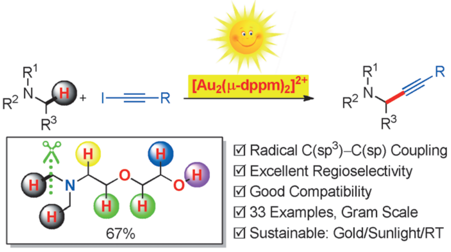


Ether way: Two new sesquiterpene ethers were obtained by incubation of farnesyl diphosphate with a recombinant terpene cyclase from *Kitasatospora setae*. The structures of both terpenes were elucidated by NMR spectroscopic methods. Incubation experiments with isotopically labeled precursors gave detailed insight into the mechanism of the bacterial sesquiterpene cyclase.

Gold Photocatalysis

J. Xie, S. Shi, T. Zhang, N. Mehrkens,
M. Rudolph,
A. S. K. Hashmi* ———— **6046 – 6050**

A Highly Efficient Gold-Catalyzed Photoredox α-C(sp^3)—H Alkynylation of Tertiary Aliphatic Amines with Sunlight

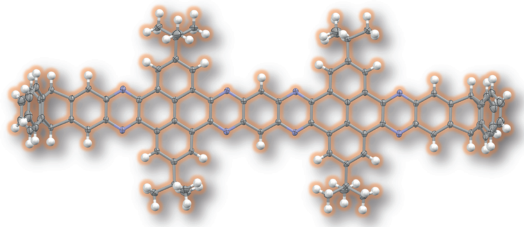


Golden sunshine: With 1-iodoalkynes as radical alkynylation reagents, unactivated tertiary aliphatic amines react in the presence of $[Au_2(\mu\text{-dppm})_2]^{2+}$ (dppm = bis(diphenylphosphanyl)methane) in sunlight to afford propargylamines. A C—C coupling of an α-aminoalkyl radical and an alkynyl radical was proposed as the mechanism.

Polycyclic π Systems

B. Kohl, F. Rominger,
M. Mastalerz* ———— **6051 – 6056**

A Pyrene-Fused *N*-Heteroacene with Eleven Rectilinearly Annulated Aromatic Rings

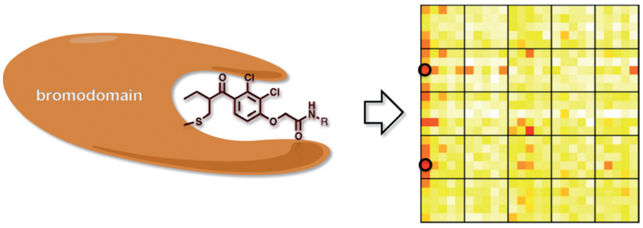


Acenes eleven: A highly soluble pyrene-fused undecacene is prepared by adding end-capping triptycenylene units to the linear π system (see structure, N blue). The new compound shows a high tendency to crystallize; two polymorphs from dichlorobenzene and chloroform solutions could be obtained.

Proteome Analysis

J.-P. Daguer, C. Zambaldo, D. Abegg,
S. Barluenga, C. Tallant, S. Müller,
A. Adibekian,
N. Winssinger* ———— **6057 – 6061**

Identification of Covalent Bromodomain Binders through DNA Display of Small Molecules



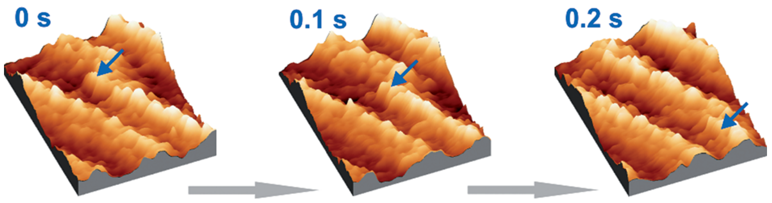
Covalent trap: Probes that broadly react with cysteine residues conserved across the bromodomain family were identified by using a DNA microarray displaying libraries of small molecules. The utility of the probe to enrich bromodomains from crude lysates was demonstrated through pull-down assays.

Ionic Liquids

R. Wen, B. Rahn,
O. M. Magnussen* ________ **6062 – 6066**

Potential-Dependent Adlayer Structure and Dynamics at the Ionic Liquid/Au(111) Interface: A Molecular-Scale In Situ Video-STM Study

Front Cover



Potentially structured: Au (111) electrodes were studied in the room-temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide by high-speed scanning tunneling microscopy. Two distinct transitions in the molecular arrangement of cations at the interface and their sub-second dynamic behavior are observed with decreasing potential.

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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