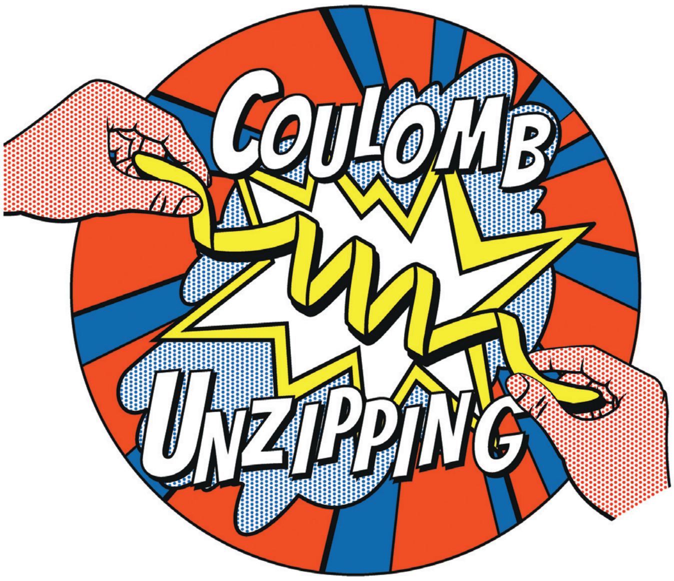
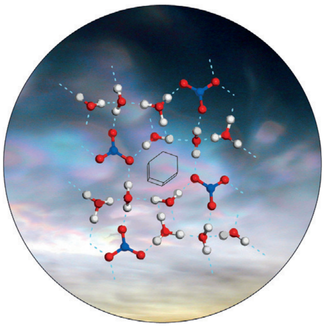
Charge-induced unzipping ...

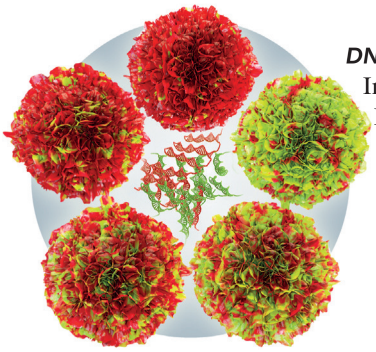


... of isolated proteins leads to a defined secondary structure characterized by intramolecular C_5 hydrogen bonds. The cover picture shows how Coulomb repulsion can pull apart helical elements to form an extended linear conformation similar to a single-strand β sheet. As G. von Helden and co-workers report in their Communication on page 3295 ff., this conformation is likely a universal form of secondary structure in highly charged protein ions.

Atmospheric Chemistry

The structure of nitric acid trihydrate, as determined by H. Grothe et al. and described in their Communication on page 3276 ff., provides information on the early stages of ice cloud formation in the stratosphere and upper troposphere.



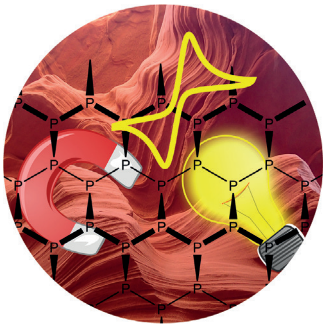


DNA/RNA Nanotechnology

In their Communication on page 3347 ff., P. T. Hammond et al. describe a modular platform for generating multiple polymeric RNAi molecules that self-assemble into composite sponge-like porous microstructures.

Anisotropy

The highly anisotropic electrical, magnetic, and electrochemical properties of layered black phosphorus are analyzed by Z. Sofer, M. Pumera, and co-workers in their Communication on page 3382 ff.



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Service

Author Profile

"The most important thing I learned from my students is to be prepared for everything.
The principal aspect of my personality is to tell things as they are …"
This and more about Stephan Schulz can be found on page 3260.

News

M. Grätzel

M. Kovalenko

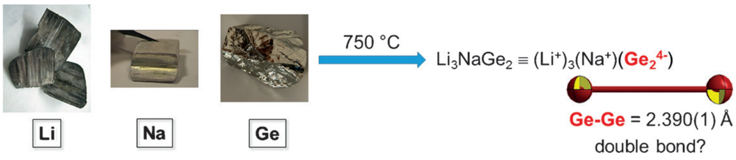
H. J. Jessen

B. Kräutler

Books

Highlights

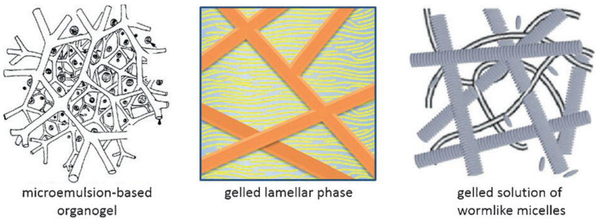
Germanides



Ge–Ge double bonds: The reaction of elemental lithium, sodium, and germanium at 750 °C results in the Zintl phase Li_3NaGe_2, which, according to the Zintl–Klemm concept, contains $[Ge{=}Ge]^{4-}$ dumbbells with unprecedented short Ge–Ge distances. Based on structural, spectroscopic, and theoretical considerations, convincing evidence is given that Ge–Ge double bonds are in fact present.

Reviews

Gels


microemulsion-based organogel

gelled lamellar phase

gelled solution of wormlike micelles

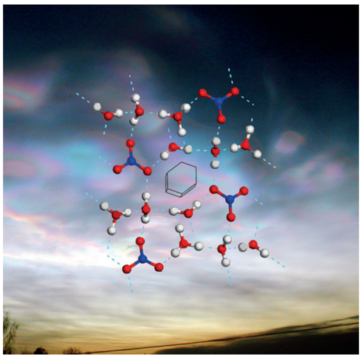
Going soft: Gelled complex fluids are soft materials in which the microstructure of the complex fluid is combined with the mechanical stability of a gel. This Review describes the structure and potential applications of such fluids and clarifies whether the respective system is formed through orthogonal self-assembly, that is, the independent but simultaneous formation of two coexisting self-assembled structures within one system.

Communications

Atmospheric Chemistry

Frontispiece

Unknown phase: The structure of nitric acid trihydrate was determined by a combination of X-ray and neutron diffraction experiments and sheds light on the early stages of ice cloud formation in the lower stratosphere and upper troposphere.



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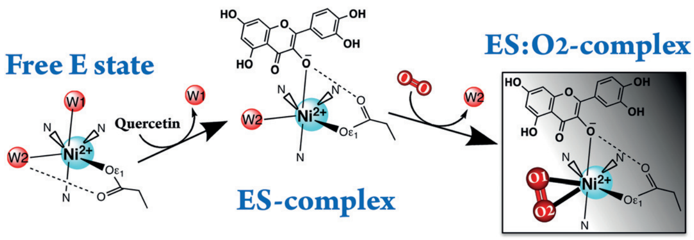

On side: Crystal structures of Ni-quercetinase in three different states (free E, ES-complex, and ES:O_2 complex) provide direct insight into how quercetin and O_2 are activated at the Ni^{2+} ion. The conformational change of a glutamate residue upon quercetin binding weakens the interaction between Ni and a water ligand (W), thereby priming Ni^{2+} to bind O_2 side-on and attack quercetin.

Dioxygen Activation

J.-H. Jeoung, D. Nianios, S. Fetzner, H. Dobbek* ——— 3281 – 3284

Quercetin 2,4-Dioxygenase Activates Dioxygen in a Side-On O_2–Ni Complex

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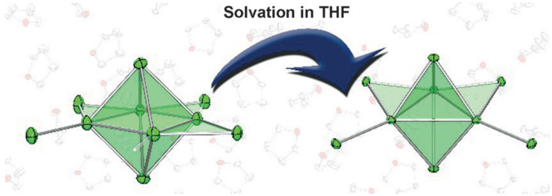
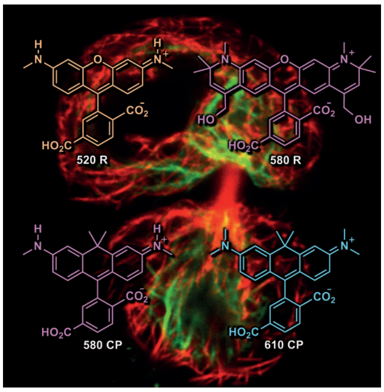


The bottom-up wet chemical synthesis of the ligand-protected oligonuclear clusters $\{[Zn_{10}](Cp^*)_6Me\}^+$, $\{[Zn_9](Cp^*)_6\}$, and $\{[Zn_8](Cp^*)_5({}^tBuNC)_3)\}^+$ is described. According to the Wade–Mingos rules, these zinc clusters are electron-deficient; quantum-chemical calculations reveal this to be due to the lack of π-type frontier orbitals on the apical ZnCp* units for cluster bonding.

Zinc Clusters

H. Banh, K. Dilchert, C. Schulz, C. Gemel, R. W. Seidel, R. Gautier, S. Kahlal, J.-Y. Saillard,* R. A. Fischer* 3285 – 3289

Atom-Precise Organometallic Zinc Clusters



Bright, photostable, and cell-permeant rhodamines, carbopyronines, and Si-rhodamines were designed as specific fluorescent markers for living cells. Cytoskeletal filaments, labeled by HaloTag fusion technology, were stained with 1 μM dye conjugates emitting green or red light. Light microscopy with stimulated emission depletion (STED) provided one- and two-color images with an optical resolution of 40–60 nm.

STED Microscopy

A. N. Butkevich,* G. Y. Mitronova, S. C. Sidenstein, J. L. Klocke, D. Kamin, D. N. H. Meineke, E. D'Este, P.-T. Kraemer, J. G. Danzl, V. N. Belov,* S. W. Hell* ——— 3290 – 3294

Fluorescent Rhodamines and Fluorogenic Carbopyronines for Super-Resolution STED Microscopy in Living Cells

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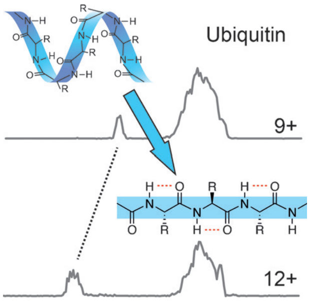
Ultracold gas-phase IR spectroscopy reveals that highly charged protein ions adopt highly ordered, regular secondary structures that are characterized by intramolecular C_5 hydrogen bonds. This transition in secondary structure is supported by a simple electrostatic model and is most likely universal for isolated proteins.



Protein Structure

A. I. González Flórez, E. Mucha, D.-S. Ahn, S. Gewinner, W. Schöllkopf, K. Pagel, G. von Helden* — 3295 – 3299

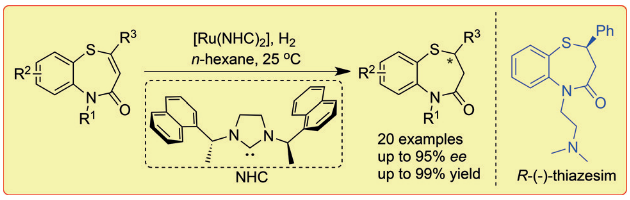
Charge-Induced Unzipping of Isolated Proteins to a Defined Secondary Structure

Front Cover

Asymmetric Hydrogenation

W. Li, C. Schlepphorst, C. Daniliuc,
F. Glorius* ———— 3300 – 3303

Asymmetric Hydrogenation of Vinylthioethers: Access to Optically Active 1,5-Benzothiazepine Derivatives

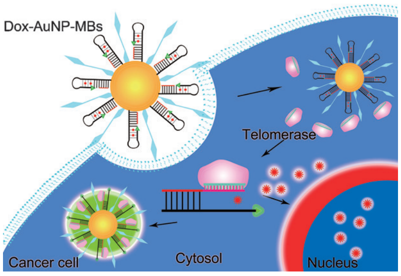


Popular heterocycles: A method for the asymmetric hydrogenation of vinylthioethers provides optically active 2,3-dihydro-1,5-benzothiazepinones. Excellent enantioselectivities (up to 95 % *ee*) and high yields (up to 99 %) were obtained for a variety of substrates using a ruthenium(II) NHC complex (NHC = N-heterocyclic carbene). This methodology was directly applied to the synthesis of the antidepressant drug *R*-(−)-thiazesim.

Drug Delivery

Y. Ma, Z. Wang, M. Zhang, Z. Han,
D. Chen, Q. Zhu, W. Gao, Z. Qian,*
Y. Gu* ———— 3304 – 3308

A Telomerase-Specific Doxorubicin-Releasing Molecular Beacon for Cancer Theranostics

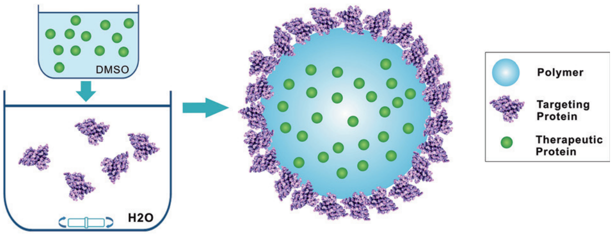


Telomerase beacons: A molecular-beacon-based drug delivery system was designed for both detection of telomerase activity in living cells and telomerase-triggered drug release. This molecular beacon (MB) could specifically distinguish tumor cells and normal cells on the basis of telomerase activity, release doxorubicin, and avoid toxicity in healthy organs.

Nanomedicine

X. Zhu, J. Wu, W. Shan, W. Tao, L. Zhao,
J.-M. Lim, M. D'Ortenzio, R. Karnik,
Y. Huang,* J. Shi,*
O. C. Farokhzad* ———— 3309 – 3312

Polymeric Nanoparticles Amenable to Simultaneous Installation of Exterior Targeting and Interior Therapeutic Proteins

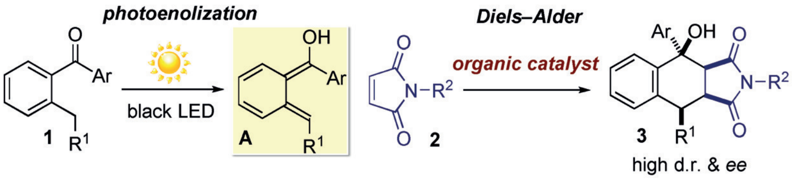


Drug delivery: A novel polymeric nanoparticle platform that is capable of installing protein ligands on the particle surface and simultaneously carrying therapeutic proteins inside was developed by self-assembly. The surface coating with transferrin drastically changed the cellular behavior of the nanoparticles and enhanced the transepithelial transport by transcytosis.

Asymmetric Photoorganocatalysis

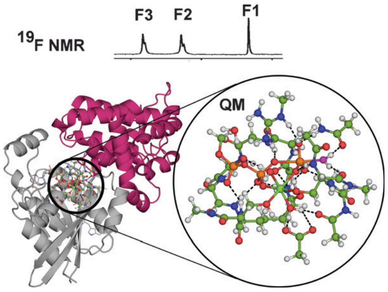
L. Dell'Amico, A. Vega-Peñaloza,
S. Cuadros, P. Melchiorre* 3313 – 3317

Enantioselective Organocatalytic Diels–Alder Trapping of Photochemically Generated Hydroxy-*o*-Quinodimethanes



Caught it! The excitation of 2-alkyl benzophenones **1** with light affords transient hydroxy-*o*-quinodimethanes **A**. Because of their high reactivity and fleeting nature, dienes **A** had not been trapped previously in a stereoselective catalytic fashion. A simple organocatalytic strategy to control the stereochemical outcome of the Diels–Alder trapping of **A** with maleimides **2** to give stereochemically dense products **3** is now reported (see scheme).

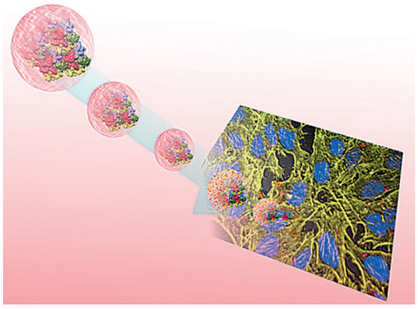
Reaction Mechanisms



Guanosine 5′-triphosphate hydrolysis by the small G protein, RhoA, was analyzed by combining X-ray, ^{19}F NMR, and DFT calculations. A transition-state model based on ^{19}F NMR spectra is proposed for nucleophilic attack of water on GTP, founded on an extensive network of 20 hydrogen bonds. This network disrupts inhibitory hydrogen bonds that stabilize an unreactive ground state conformation.

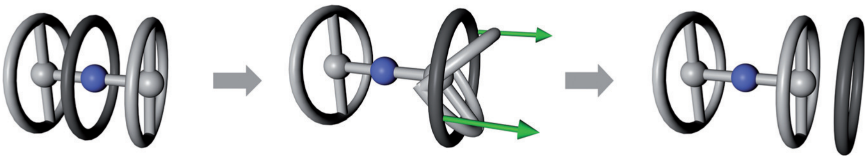
Hybrid Materials

Inside Cover



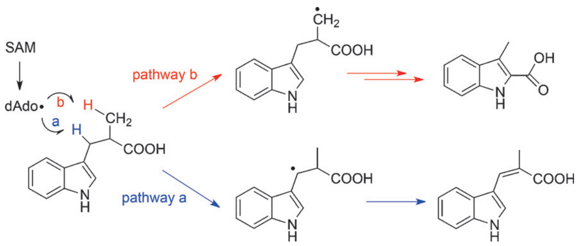
Speshell delivery: The construction of a breakable shell around proteins can be used for encapsulation and delivery of functional proteins. The shell comprises silica units that are held together with disulfide bridges. These stimulus-responsive containers break into very small pieces upon contact with the cell environment, and the proteins retain their activity during encapsulation.

Interlocked Systems



Escape artist extraordinaire: How shape-persistent is “shape-persistent”? Novel phenylene–ethynylene–butadiynylene rotaxanes synthesized by a covalent-template approach were found to undergo unthreading of the wheel from the axis (see picture). The detailed unthreading mechanism was investigated theoretically by state-of-the-art DFT-based molecular mechanics and a string method for the simulation of rare events.

Biosynthesis

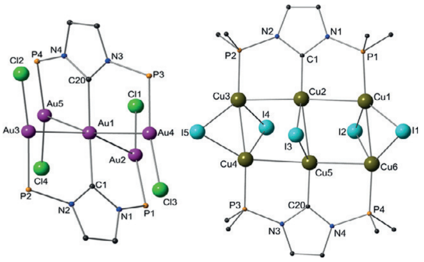


Two roads diverged: The radical *S*-adenosyl-L-methionine enzyme NosL, which catalyzes the transformation of L-tryptophan into 3-methyl-2-indolic acid (MIA), was investigated with the substrate analogue 2-methyl-3-(indol-3-yl)propanoic acid (MIPA). Radical-mediated hydrogen abstraction was found to be from the amino group of L-tryptophan and occurs at two different sites of MIPA, thus partitioning the substrate into different reaction pathways.

Polynuclear Complexes

P. Ai, M. Mauro, L. De Cola,
A. A. Danopoulos,*
P. Braunstein* ________ 3338–3341

A Bis(Diphosphanyl N-Heterocyclic Carbene) Gold Complex: A Synthon for Luminescent Rigid $AuAg_2$ Arrays and Au_5 and Cu_6 Double Arrays



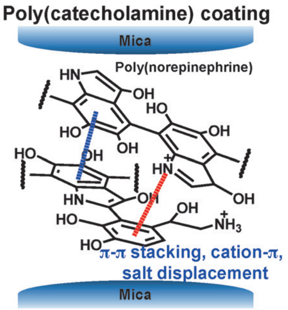
Crossing paths: A mononuclear bis(NHC)/Au^I (NHC = N-heterocyclic carbene) cationic complex with a rigid bis(phosphane)-functionalized NHC ligand ($PC_{NHC}P$) provides access to unique Au, Au/Ag, and Cu arrays. These arrays display metallophilicity-based photoluminescence.

Adhesive Coatings

C. Lim, J. Huang, S. Kim, H. Lee,*
H. Zeng,* D. S. Hwang* __ 3342–3346

Nanomechanics of Poly(catecholamine) Coatings in Aqueous Solutions

Give it some stick: The adhesive strength of self-polymerized catecholic coating layers was measured with a surface forces apparatus. The adhesive strength between poly(catecholamine) layers is 30-times higher than that between poly(catechol) layers. The origin of the strong attraction between poly(catecholamine) layers is possibly due to surface salt displacement, π–π stacking, and cation–π interactions involving the primary amine moiety.

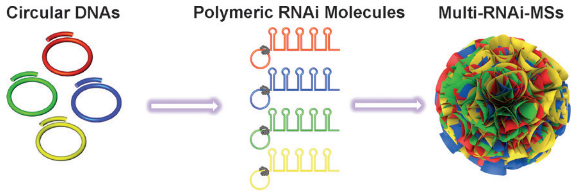


DNA/RNA Nanotechnology

Y. H. Roh, J. Z. Deng, E. C. Dreaden,
J. H. Park, D. S. Yun, K. E. Shopsowitz,
P. T. Hammond* ________ 3347–3351

A Multi-RNAi Microsponge Platform for Simultaneous Controlled Delivery of Multiple Small Interfering RNAs

Inside Back Cover

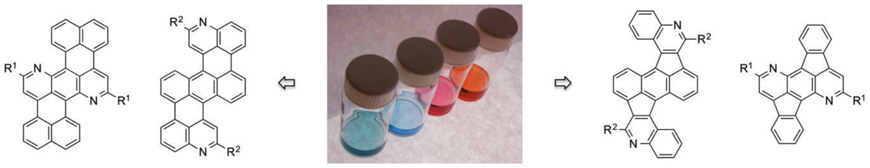


Multiple small interfering RNA (siRNA) molecules were self-assembled and densely packed into composite sponge-like porous microstructures (Multi-RNAi-MSs) by rolling circle transcription. Within each singular microstructure, the stoichiometry of the various polymeric siRNA molecules was precisely controlled by manipulating the types and ratios of the circular DNA templates.

Organic Electronics

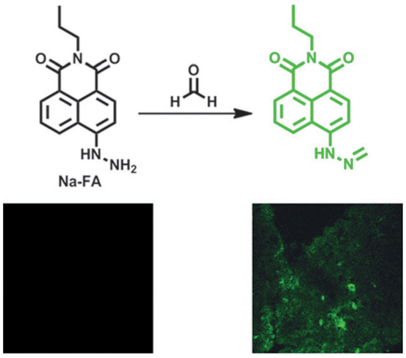
Y. S. Park, D. J. Dibble, J. Kim, R. C. Lopez,
E. Vargas,
A. A. Gorodetsky* ________ 3352–3355

Synthesis of Nitrogen-Containing Rubicene and Tetrabenzopentacene Derivatives

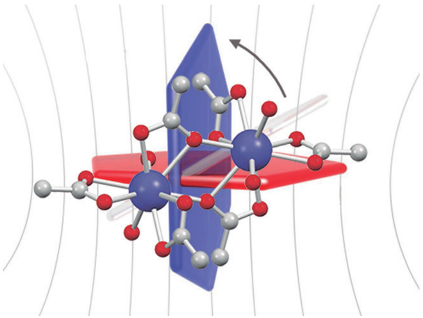


Variants of classic polycyclic aromatic hydrocarbons: Nitrogen-containing rubicenes and tetrabenzopentacenes were prepared by using a straightforward approach. The reported synthetic method may enable the development of electron-transporting organic semiconductors and the eventual construction of larger carbonaceous systems.

Shine a little light: The first two-photon fluorescent formaldehyde probe, **Na-FA**, was engineered by condensation of a hydrazine moiety with FA. This unique strategy grants the probe highly favorable properties: a very large turn-on signal, a low detection limit, and a very fast onset, which collectively enable tracking of endogenous FA in living tissues for the first time.

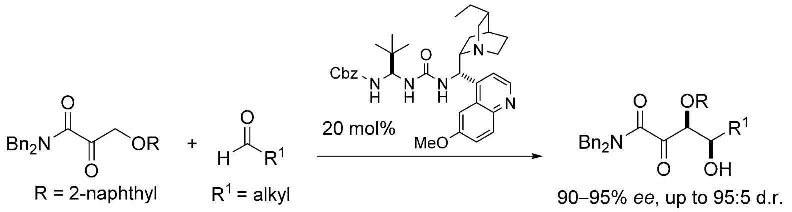


Fluorescent Probes



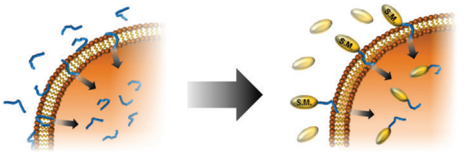
Molecular refrigerants: The magnetocaloric effect of anisotropic hydrated dysprosium acetate was studied. Possible applications as molecular refrigerants are discussed. Cooling is attained by rotating aligned single-crystal samples in a constant applied magnetic field (see picture).

Molecular Magnetism



New players in town: The enantioselective direct cross-aldol reaction of α-keto amides with aldehydes was accomplished using ureidopeptide-based Brønsted base catalysts. The reaction provides stereodefined *syn*-aldol adducts without self-condensation, competitive aldehyde enolization, aldol dehydration, and lactonization products, which are usually observed when using α-keto esters as donor partners. Cbz = benzyloxycarbonyl.

Asymmetric Catalysis



Intrinsic peptide disorder mediates cytoplasmic delivery of cell-impermeable small molecules

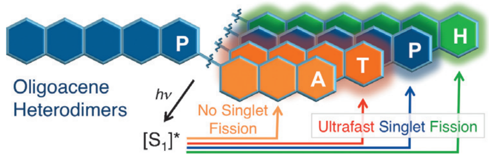
Disorder imparts order: CLIP6, an intrinsically disordered peptide, mediates cellular entry through non-endosomal physical translocation across the membrane. This activity, defined by its unstructured state, facilitates the delivery of membrane-impermeable cargo to the interior of cells.

Cell-Penetrating Peptides

Singlet Fission in Oligoacenes

S. N. Sanders, E. Kumarasamy, A. B. Pun, M. L. Steigerwald, M. Y. Sfeir,* L. M. Campos* **3373 – 3377**

Intramolecular Singlet Fission in Oligoacene Heterodimers

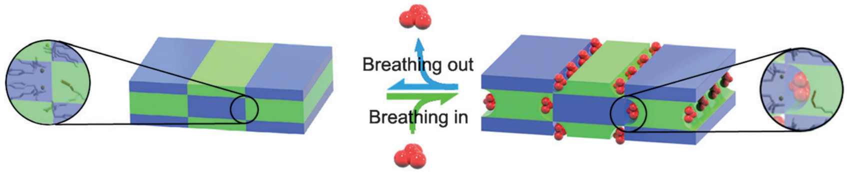


Organic electronics: A series of oligoacene heterodimers was synthesized to test the energetic requirements for singlet fission—a photophysical process that yields two triplet excitons from a single photon. Thus a possibility is offered to tune this process.

Host–Guest Systems

Y. Sheng, Q. Chen,* J. Yao, Y. Lu, H. Liu,* S. Dai* **3378 – 3381**

Guest-Induced Breathing Effect in a Flexible Molecular Crystal



The Age of Gemini: A breathing effect is realized by cell expansion and alkyl transformation of a flexible molecular crystal containing Gemini units. This breath-like transition endows the crystal with preferential chloroform adsorption.

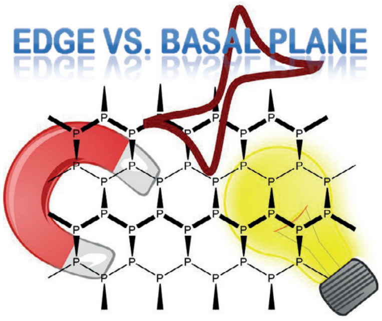
Anisotropy

Z. Sofer,* D. Sedmidubský, Š. Huber, J. Luxa, D. Bouša, C. Boothroyd, M. Pumera* **3382 – 3386**

Layered Black Phosphorus: Strongly Anisotropic Magnetic, Electronic, and Electron-Transfer Properties

Back Cover

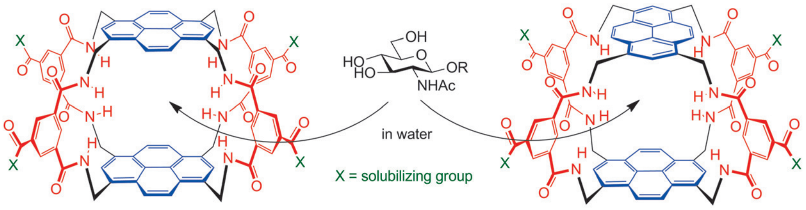
A shift in direction: The electrical, magnetic, and electrochemical properties of black phosphorus display an anomalous anisotropy. These unusual observations were interpreted by means of calculations, which manifested the metallic character of the edge plane and the semiconductivity of the basal plane, indicating that black phosphorus belongs to a group of materials known as topological insulators.



Biomimetic Hosts

P. Rios, T. S. Carter, T. J. Mooibroek,* M. P. Crump, M. Lisbjerg, M. Pittelkow, N. T. Supekar, G.-J. Boons, A. P. Davis* **3387 – 3392**

Synthetic Receptors for the High-Affinity Recognition of O-GlcNAc Derivatives

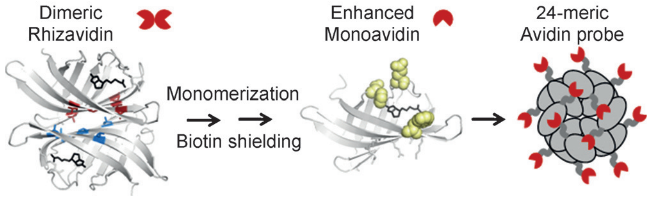


Two carbohydrate receptors (see scheme) were prepared directly from a pyrenyl tetraamine and an isophthaloyl derivative. With extended aromatic surfaces linked by polar spacers, they are well suited to binding all-equatorial monosaccharides, showing especially high affinities for β-linked *N*-acetylglucosamine (GlcNAc).

Protein Engineering

J. M. Lee, J. A. Kim, T. C. Yen, I. H. Lee, B. Ahn, Y. Lee, C. L. Hsieh, H. M. Kim, Y. Jung* ________ **3393 – 3397**

A Rhizavidin Monomer with Nearly Multimeric Avidin-Like Binding Stability Against Biotin Conjugates

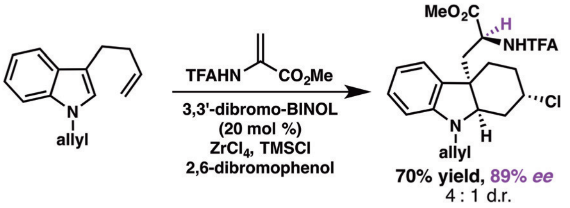


Extremely high binding stability against various biotin conjugates has been observed in a monomeric avidin-like protein—enhanced monoavidin—that was developed from naturally dimeric rhizavidin by minimally disturbing the protein rigidity and additionally shielding the bound biotin. This stable monomeric biotin linker protein was further engineered to generate an unprecedented 24-meric avidin probe.

Heterocycle Synthesis

B. E. Daniels, J. Ni, S. E. Reisman* ________ **3398 – 3402**

Synthesis of Enantioenriched Indolines by a Conjugate Addition/Asymmetric Protonation/Aza-Prins Cascade Reaction



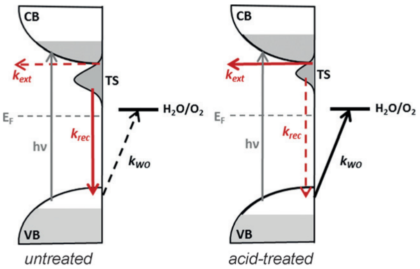
The artist formerly known as Prins: The title cyclization reaction has been developed and is catalyzed by a zirconium-derived Lewis-acid-assisted Brønsted acid. The protocol enables the synthesis of a range of polycyclic indolines in good yields and with high enantioselectivity.

Photoelectrochemistry

Y. Yang, M. Forster, Y. Ling, G. Wang, T. Zhai, Y. Tong, A. J. Cowan,* Y. Li* ________ **3403 – 3407**

Acid Treatment Enables Suppression of Electron–Hole Recombination in Hematite for Photoelectrochemical Water Splitting

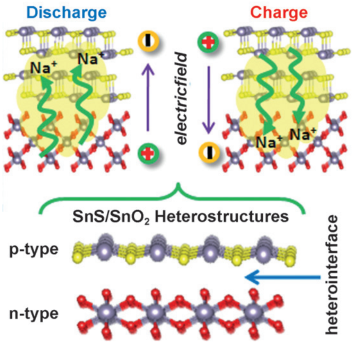
A simple acid treatment method is reported to increase the photoelectrochemical activity of hematite photoanodes. The enhanced photocurrent was due to the combination of improved efficiency of charge separation and suppressed electron–hole recombination, resulting in a greater yield of trapped photoelectrons being extracted to the external circuit.



Sodium-Ion Batteries

Y. Zheng, T. F. Zhou, C. F. Zhang, J. F. Mao, H. K. Liu, Z. P. Guo* ________ **3408 – 3413**

Boosted Charge Transfer in SnS/SnO$_2$ Heterostructures: Toward High Rate Capability for Sodium-Ion Batteries



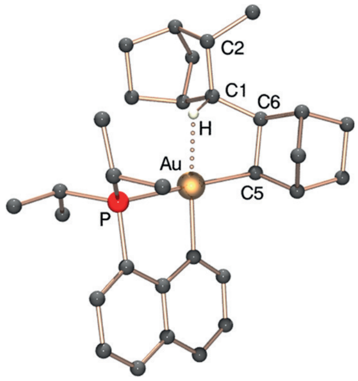
Tin anodes: Ultrafine SnS/SnO$_2$ heterostructures were fabricated and applied as anodes for sodium-ion batteries. The as-prepared material shows excellent performance and outstanding cycling stability at high rates, which can be ascribed to the charge-transfer driving force, good structural stability, and excellent electrical conductivity.

Agostic Interactions

F. Rekhroukh, L. Estévez, C. Bijani,
K. Miqueu,* A. Amgoune,*
D. Bourissou* ________ 3414 – 3418

Experimental and Theoretical Evidence for an Agostic Interaction in a Gold(III) Complex

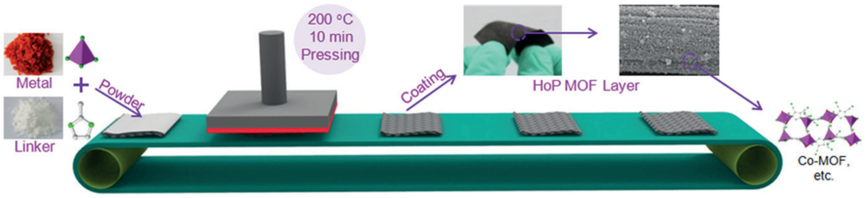
Striking gold: The first direct evidence for an agostic interaction in a gold complex is reported. Low-temperature NMR spectroscopy is used to characterize a tricoordinate gold(III) alkyl complex featuring a C–H⋯Au agostic interaction. Theoretical analyses confirmed the presence of an attractive interaction between the C–H bond and the gold center.



Metal–Organic Frameworks

Y. Chen, S. Li, X. Pei, J. Zhou, X. Feng,
S. Zhang, Y. Cheng, H. Li, R. Han,
B. Wang* ________ 3419 – 3423

A Solvent-Free Hot-Pressing Method for Preparing Metal–Organic-Framework Coatings

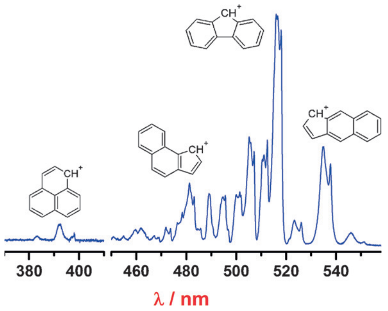


Hot off the press: A solvent-free approach for producing stable MOF coatings through a hot-pressing (HoP) method is presented. In the HoP method, temperature and pressure are applied simultaneously to facilitate the rapid growth of MOF nanocrystals onto desired substrates. This strategy was proven to be applicable to various MOFs and substrates.

Electronic Spectroscopy

J. Fulara, A. Chakraborty,
J. P. Maier* ________ 3424 – 3427

Electronic Characterization of Reaction Intermediates: The Fluorenylium, Phenalenylium, and Benz[*f*]indenylium Cations and Their Radicals

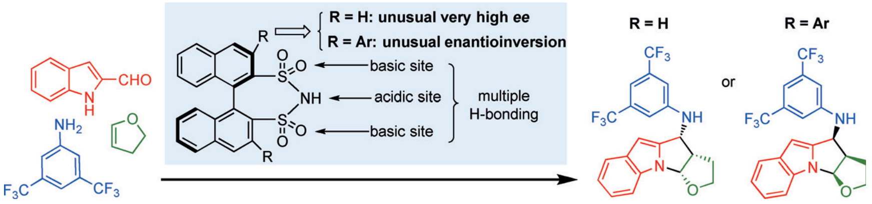


The fluorenylium, phenalenylium, and benz[*f*]indenylium cations and their radicals, which are key intermediates in organic reactions, were electronically characterized in 6 K neon matrices after mass-selected deposition of $C_{13}H_9^+$ ions. The structural assignments were based on calculated excitation energies.

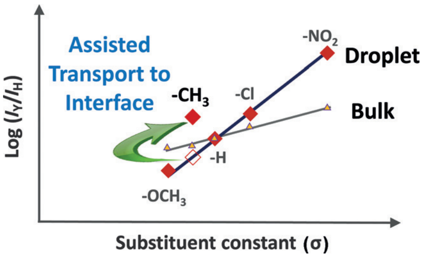
Asymmetric Organocatalysis

A. Galván, A. B. González-Pérez,
R. Álvarez,* A. R. de Lera, F. J. Fañanás,*
F. Rodríguez* ________ 3428 – 3432

Exploiting the Multidentate Nature of Chiral Disulfonimides in a Multicomponent Reaction for the Asymmetric Synthesis of Pyrrolo[1,2-*a*]indoles: A Remarkable Case of Enantioinversion

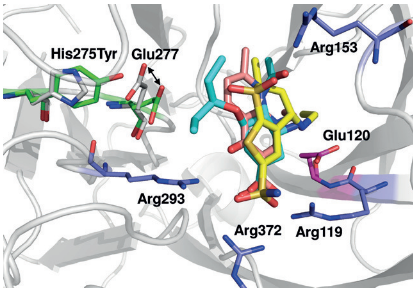


One way or the other: Some exceptional features of chiral disulfonimide organocatalysts are demonstrated in the context of a new highly selective synthesis of pyrrolo[1,2-*a*]indoles. A three-point coordination model explains the high enantioselectivity observed. An unusual switch of enantioselectivity was observed upon simple structural modification of the catalyst (see scheme).



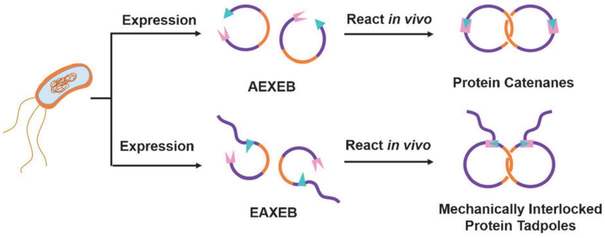
On the face of it: A series of competitive substituent effect studies on a Claisen–Schmidt reaction reveal that interfacial processes play an important role in accelerating reaction rates in thin films and droplets. The additional acceleration of the methyl-substituted reagent and the changes of the Hammett ρ values for bulk and droplet-based reactions suggest that transport to the interface controls reaction rates.

Mass Spectrometry



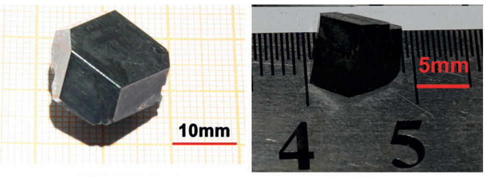
Finding a new purpose: A structure-based computational screen identified the FDA-approved drugs nalidixic acid and dorzolamide as potent inhibitors of the influenza H275Y neuraminidase mutant, but not the wild-type enzyme. H275Y is the most common drug-resistance mutation in neuraminidase, and this screening method enables rapid identification of inhibitors for newly emerging mutations.

Drug Discovery



Let's get together: The combination of a protein dimerization domain and genetically encoded SpyTag–SpyCatcher protein chemistry enables the cellular synthesis of topologically complex protein catenanes and mechanically interlocked protein "tadpoles" through programmed posttranslational modification.

Protein Catenanes



$CH_3NH_3SnI_3$ $CH(NH_2)_2SnI_3$

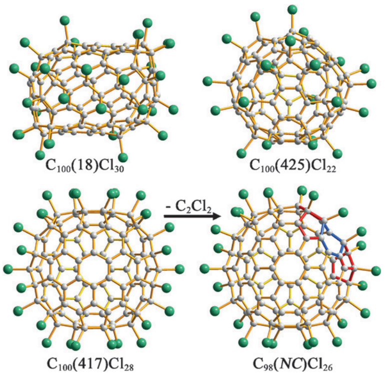
Unleaded: Bulk single crystals of lead-free perovskites $CH_3NH_3SnI_3$ and $CH(NH_2)_2SnI_3$ can be obtained by top-seeded solution growth under an ambient atmosphere. $CH_3NH_3SnI_3$ acts as a p-type semiconductor, while $CH(NH_2)_2SnI_3$ behaves as an n-type semiconductor. $CH(NH_2)_2SnI_3$ was found to be more stable than $CH_3NH_3SnI_3$ after storage under an ambient atmosphere for one month.

Crystal Growth

Fullerenes

S. Wang, S.-F. Yang,* E. Kemnitz,*
S. I. Troyanov* ______________ **3451 – 3454**

New Isolated-Pentagon-Rule and Skeletally Transformed Isomers of C_{100} Fullerene Identified by Structure Elucidation of their Chloro Derivatives

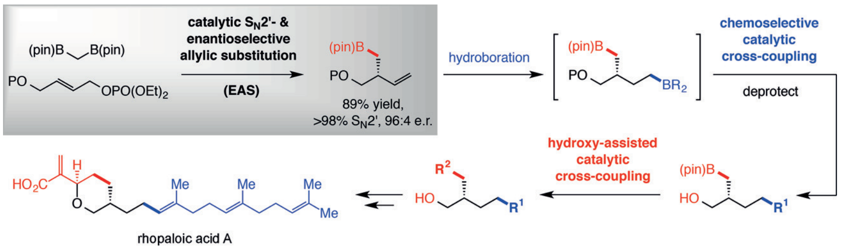


Chloride is key: Three isomers of C_{100} fullerene which obey the isolated pentagon rule (IPR) have been isolated and characterized by X-ray structure determination of their chloro derivatives. Although the IPR cages in C_1-$C_{100}(425)Cl_{22}$ and C_2-$C_{100}(18)Cl_{28/30}$ retain cage connectivities, C_s-$C_{100}(417)Cl_{28}$ transforms into the nonclassical (*NC*) isomer C_1-C_{98}-$(NC)Cl_{26}$ by loss of a C_2 fragment (see picture; C = gray; Cl = green).

Enantioselective Catalysis

Y. Shi, A. H. Hoveyda* ______ **3455 – 3458**

Catalytic S_N2'- and Enantioselective Allylic Substitution with a Diborylmethane Reagent and Application in Synthesis

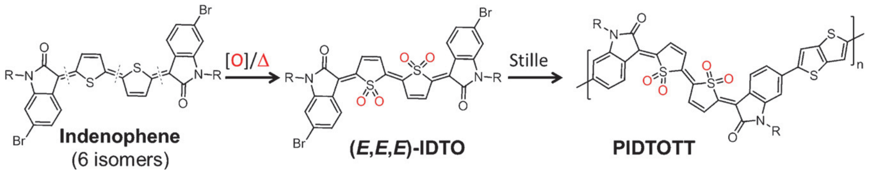


Combination catalysis: The first examples of catalytic enantioselective allylic substitution reactions that introduce a CH_2–B(pin) unit are described (pin = pinacolato). In combination with various catalytic cross-coupling processes, a range of important organic molecules are now readily accessible.

Polymers

Y. Deng, B. Sun, Y. He, J. Quinn, C. Guo,
Y. Li* ______________ **3459 – 3462**

Thiophene-*S*,*S*-dioxidized Indophenine: A Quinoid-Type Building Block with High Electron Affinity for Constructing n-Type Polymer Semiconductors with Narrow Band Gaps

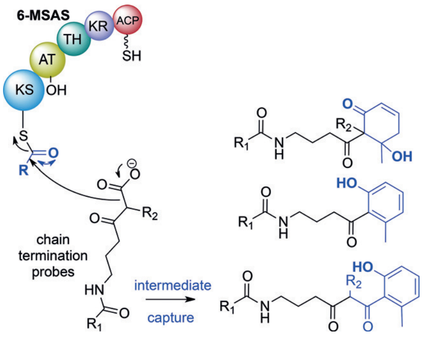


Three isomers of thiophene-*S*,*S*-dioxidized indophenine (IDTO) were conveniently synthesized through oxidation of an indophenine compound. Two of the three isomers could be converted into the most stable isomer, (*E*,*E*,*E*)-IDTO, by heating at 110 °C. The conjugated polymer PIDTOTT based on (*E*,*E*,*E*)-IDTO displayed unipolar n-type semiconductor characteristics with surprisingly high electron mobility (up to $0.14\ cm^2V^{-1}s^{-1}$).

Chemical Probes

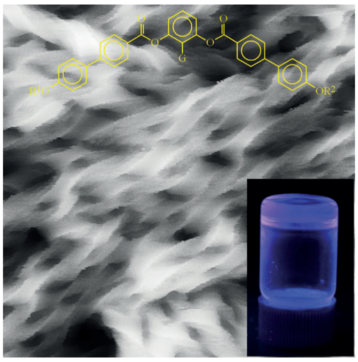
J. S. Parascandolo, J. Havemann,
H. K. Potter, F. Huang, E. Riva, J. Connolly,
I. Wilkening, L. Song, P. F. Leadlay,
M. Tosin* ______________ **3463 – 3467**

Insights into 6-Methylsalicylic Acid Bio-assembly by Using Chemical Probes



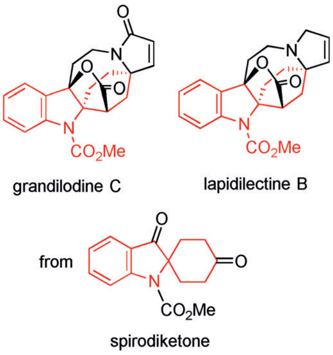
Chemical probes capable of reacting with KS (ketosynthase)-bound biosynthetic intermediates were utilized for the investigation of the model type I iterative polyketide synthase 6-methylsalicylic acid synthase (6-MSAS) in vivo and in vitro. From the fermentation of fungal and bacterial 6-MSAS hosts in the presence of chain termination probes, a full range of biosynthetic intermediates was isolated (see examples) and characterized.

Bent on being different: When lamellar crystals (B4 phase) of bent-core molecules were dissolved in organic solvents, gels composed of helical ribbons built up of molecular monolayers and bilayers were formed (see picture). Spontaneous chiral symmetry breaking occurred at the microscale in the B4 phase and the gels but only led to optical activity in the B4 phase. A dramatic increase in fluorescence was observed upon the transition to the gel state.

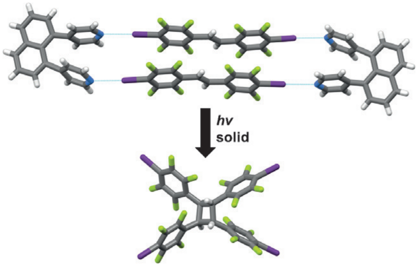


Chirality

Enantioselective total syntheses and determination of the absolute stereochemistry of the *Kopsia* alkaloids (+)-grandilodine C and (+)-lapidilectine B were accomplished. A key intermediate, spirodiketone, was synthesized in 3 steps and following enantioselective deprotonation, lactone formation, vinylation, allylic amination, and ring-closing metathesis, gave the above alkaloids in optically active form.



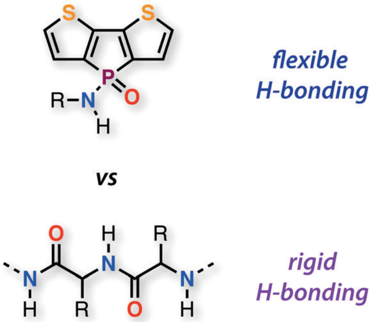
Natural Product Synthesis



This way, please: A ditopic halogen-bond acceptor organizes a halogenated stilbene for a stereoselective [2+2] photodimerization reaction to take place between two stilbenes in the solid state. The resultant halogen-functionalized cyclobutane product self-assembles to form a host–guest compound that exhibits a very rare form of self-inclusion. Atom colors: C = gray; I = purple; N = blue; F = green.

Self-Assembly

New HOPe: Dithienophosphole-based phosphinamides (see structure) display rotationally flexible hydrogen bonding that contrasts with that of their carboxamide cousins. Besides the novel hydrogen-bonding motif, these compounds also demonstrated unique photophysical and amphiphilic properties as a result of hydrogen-bond-directed self-assembly.



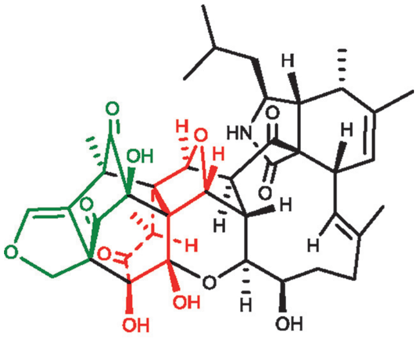
Hydrogen Bonding

Natural Product Synthesis

H. Zhu, C. Chen, Q. Tong, X. N. Li, J. Yang, Y. Xue, Z. Luo, J. Wang, G. Yao, Y. Zhang* ______ 3486 – 3490

Epicochalasines A and B: Two Bioactive Merocytochalasans Bearing Caged Epicoccine Dimer Units from *Aspergillus flavipes*

Adamantly original: Two bioactive merocytochalasans isolated from the liquid culture broth of *Aspergillus flavipes* represent a new class of cytochalasans with unexpected scaffolds consisting of fused aspochalasin and epicoccine dimer moieties. Epicochalasines A (**1**) and B both possess a hendecacyclic 5/6/11/5/6/5/6/5/6/6/5 ring system with an adamantyl cage but have different carbon skeletons.

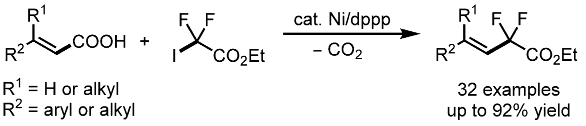


1

Synthetic Methods

G. Li, T. Wang, F. Fei, Y.-M. Su, Y. Li, Q. Lan, X.-S. Wang* ______ 3491 – 3495

Nickel-Catalyzed Decarboxylative Difluoroalkylation of α,β-Unsaturated Carboxylic Acids

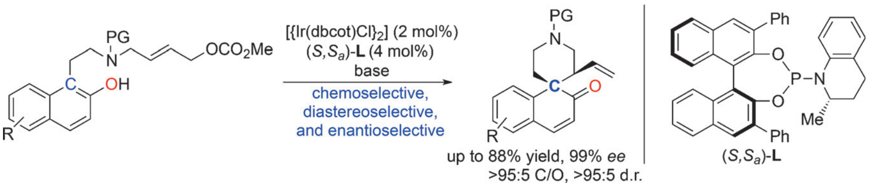


Nickel and F: The title reaction has been developed using commonly available fluoroalkyl halides. This novel transformation demonstrates broad substrate scope, excellent functional-group tolerance, mild reaction conditions, and excellent stereoselectivity. Mechanistic investigations indicate that a fluoroalkyl radical is involved in the catalytic cycle. dppp = 1,3-bis(diphenylphosphino)propane.

Asymmetric Catalysis

Q. Cheng, Y. Wang, S.-L. You* ______ 3496 – 3499

Chemo-, Diastereo-, and Enantioselective Iridium-Catalyzed Allylic Intramolecular Dearomatization Reaction of Naphthol Derivatives

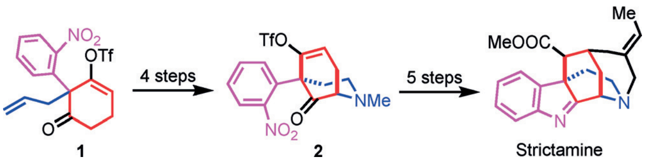


Triple challenge: The challenges addressed in the title reaction include chemoselectivity between C and O as nucleophiles, diastereoselectivity when contiguous chiral centers are generated, and enantioselective control for constructing an all-carbon quaternary stereocenter. The [{Ir(dbcot)Cl}$_2$]/(*S*,*S*$_a$)-**L** system leads to a general method for the dearomatization of naphthols. dbcot = dibenzocyclooctatetraene.

Natural Product Synthesis

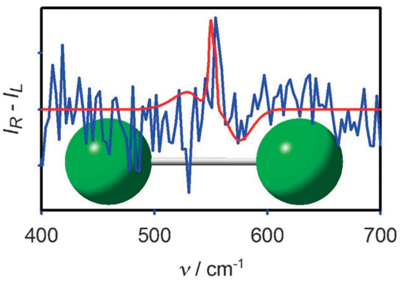
W. Ren, Q. Wang, J. Zhu* __ 3500 – 3503

Total Synthesis of (±)-Strictamine



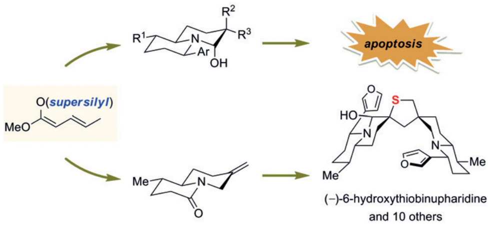
Strictly business: Strictamine, containing an unusual methanoquinolizidine core, was synthesized in nine steps from cyclohexenone **1**. The method involved: a) build-up of the functionalized 2-azabicyclo[3.3.1]nonan-9-one skeleton **2** from **1**, b) late-stage construction of the indolenine unit, and c) a Ni-promoted cyclization.

Diamagnetic Raman Optical Activity



Rotating diamagnetic molecules are supposed not to interact much with external magnetic fields because their magnetic dipole moment is small. However, a strong magnetic Raman optical activity of Cl_2, Br_2 and I_2 gases was measured. This activity was rationalized by paramagnetic excited electronic states participating in the Raman scattering.

Alkaloids



From Supersilyl to Super Killers: Enantiopure monomeric nuphar alkaloids having apoptotic activity were discovered (see example), and concise enantioselective formal syntheses of 11 nuphar alkaloids were achieved. The syntheses featured the unprecedented use of supersilyl groups to control the regio-, diastereo-, and enantioselectivity of vinylogous Mukaiyama–Mannich reactions.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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Angewandte Corrigendum

The authors of this Communication were kindly informed by Dr. A. M. Beauchemin that some alkyl ketone derived nitrones can be prepared in *tert*-butyl alcohol with special cautions. Therefore, the second sentence in the introduction part (page 14924, left column) must be changed to: “Unfortunately, nitrones (I′) cannot be generated from the intermolecular reactions of aryl ketones (R^2 or R^3 = aryl)[3,4] with nitrosoamines, rendering their [3+2]-cycloadditions infeasible.”
One new reference (J. Y. Pfeiffer, A. M. Beauchemin, *J. Org. Chem.* **2009**, *74*, 8381–8383) should be cited in Ref. [3] although it is not relevant to the reactions reported in this Communication. The main text and Supporting Information remain unchanged and its scientific merit is unaffected by this correction.

Alkene-Directed N-Attack Chemoselectivity in the Gold-Catalyzed [2+2+1]-Annulations of 1,6-Enynes with *N*-Hydroxyanilines

D. B. Huple, B. D. Mokar,
R.-S. Liu* ______ 14924–14928

Angew. Chem. Int. Ed. **2015**, *54*

DOI: 10.1002/anie.201507946

Angewandte Corrigendum

Tetrazole Photoclick Chemistry: Reinvestigating Its Suitability as a Bioorthogonal Reaction and Potential Applications

Z. Li, L. Qian, L. Li, J. C. Bernhammer, H. V. Huynh, J.-S. Lee, S. Q. Yao* ______________ **2002–2006**

Angew. Chem. Int. Ed. **2016**, *55*

DOI: 10.1002/anie.201508104

The authors of this Communication have been alerted to an erroneous statement regarding the reactivity of tetrazoles at physiological pH (page 2004, 1st paragraph "Interestingly, of all functional groups tested, CO_2H appeared most reactive at physiological pH, better than other common nucleophiles including thiols, amines, and alcohols"). This statement was made on the basis of results obtained between the reaction of **1** and pent-4-enoic acid (Figure 1 A) in a 1:1 CH_3CN/PBS buffer (pH 7.4). Although the experiment was done and results were obtained as exactly described in the manuscript, the final pH of this reaction, due to the addition of excess pent-4-enoic acid (10 mм), was inadvertently lowered to pH 5.90. Consequently, in order to more accurately describe results from the above and other related experiments in Figure 1 A, the phrase "at physiological pH" must be removed from the above statement. Apart from this, all experimental results, other statements, and conclusions made in this manuscript remain valid. Based on preliminary studies carried out at pH 7.4, tetrazole **1** indeed reacted with a variety of biological nucleophiles (acids, alcohols, amines, thiols, etc.) faster than simple terminal alkenes. Under similar conditions, selective cycloaddition of **1** only occurred when highly activated alkenes (e.g. acrylates/acrylamides) were used. These findings will be reported in due course.