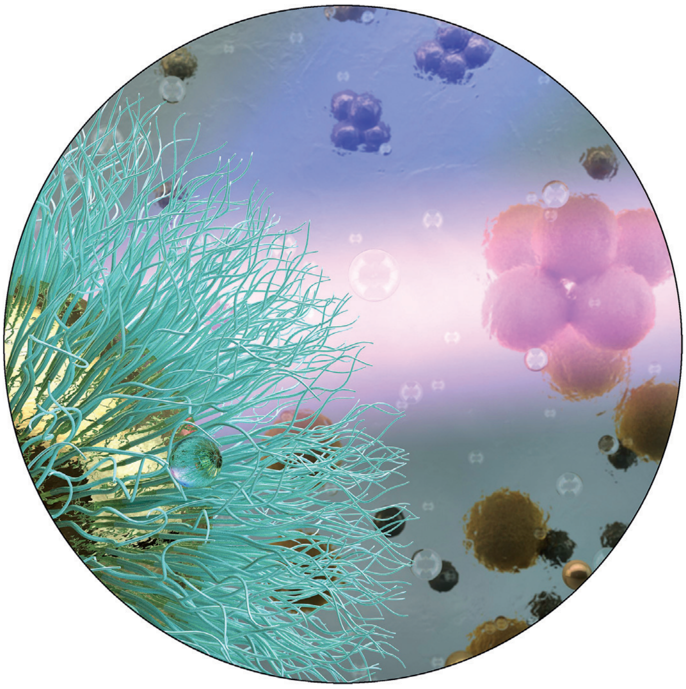
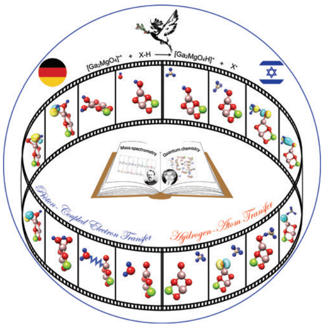
Precise control of the assembly ...

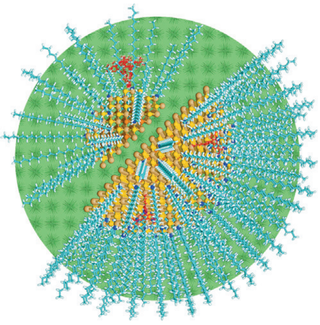


… of selected components within complex mixtures is a challenging task. In their Communication on page 12394 ff., R. Klajn et al. approach this challenge by decorating the surfaces of differently sized nanoparticles with two distinct azobenzenes that isomerize upon exposure to different wavelengths of light. The cover illustrates how ultraviolet and blue light can be used to selectively assemble large and small nanoparticles, respectively (Cover image: Ella Marushchenko).

Mechanistic Differences

In the gas phase, the heteronuclear oxide cluster $[Ga_2MgO_4]^{\bullet}$ reacts faster with water than with methane. In their Communication on page 12298 ff., H. Schwarz et al. explain this observation with different mechanisms of the two reactions.





Colloidal Nanocrystals

Size-dependent ligand-layer dynamics on the surface of colloidal nanocrystals were studied by using surface-bound dyes. In their Communication on page 12463 ff., U. Banin et al. show that the ligand-shell effective viscosity can be tuned by changing the surface geometry.

Reaction Mechanisms

In their Communication on page 12488 ff., M. Oestreich and T. Fallon describe a new stereochemical probe based on a constellation of deuterium-labeled silanes for determining the stereochemical outcome of reactions at silicon.

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Editorial

"... Fifty years ago, out of the ashes of the Second World War, the German Chancellor, Konrad Adenauer, and the Israeli Prime Minister, David Ben-Gurion, initiated the establishment of diplomatic relations between Germany and Israel. This special issue commemorates the fruitful and mutually enriching long-term collaborations between Israeli and German scientists ...
Read more in the Editorial by Helmut Schwarz, Itamar Willner, and Ilan Marek.

Service

Author Profile

"A good work day begins with some unexpected results from my group.
In restrospect I would never again refuse to use computers when I grew up ..."
This and more about Daniel B. Werz can be found on page 12206.

"My favorite food is Tfina Pkaila (a traditional Jewish Tunisian recipe).
The best advice I have ever been given is 'dream it, do it!' (Technion's axiom) ..."
This and more about Ilan Marek can be found on page 12206.

News


A. Brik


R. Klajn


I. Marek


L. S. Cederbaum


U. Diebold


C. Hertweck


F. Meyer

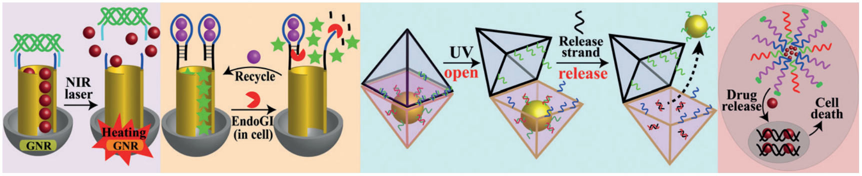

R. Weissleder


J. Troe


H. W. Roesky

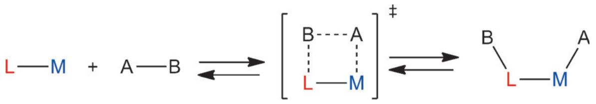
Reviews

Drug Carriers



DNA gates: Stimuli-responsive DNA-functionalized nano- and microcontainers composed of mesoporous SiO_2 nanoparticles, microcapsules, or micelles/vesicles act as drug carriers for targeted controlled release. Different stimuli such as chemical, photonic, thermal, and biocatalytic triggers are used to release the loaded drugs.

Homogeneous Catalysis



Together we're effective: Metal–ligand cooperation (MLC) implies that both the metal and the ligand are directly involved in bond activation processes, in contrast to "classical" transition metal catalysis where the ligand acts as a spectator, while all key transformations occur at the metal center. This Review discusses diverse modes of MLC in bond formation and bond cleavage reactions.

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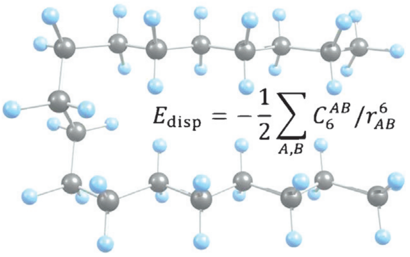
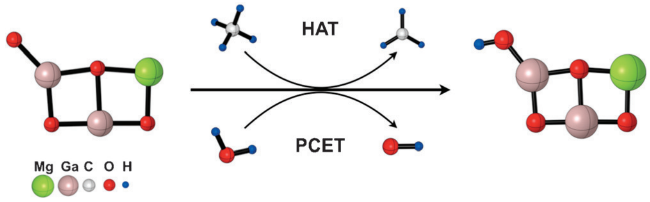
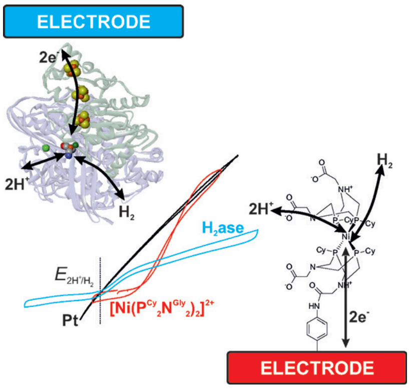


Center of attraction: Dispersion attraction makes all the difference in the stability of molecular structures, reactivity, and the design of catalysts. Although small for one pair of interactions, dispersion grows rapidly as the molecular size increases.

Communications

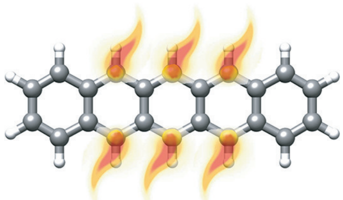


HAT trick: A combination of mass-spectrometry-based experiments and quantum chemical calculations reveals why the heteronuclear oxide cluster $[Ga_2MgO_4]^{\bullet+}$ unexpectedly reacts faster with water than with methane. HAT = hydrogen-atom transfer, PCET = proton-coupled electron transfer.



Inspirational performance: The H_2 oxidation performance of a surface-immobilized bio-inspired Ni-based complex is directly compared with [NiFe]-hydrogenase. The enzyme outperforms the Ni complex at high pH, while the Ni complex outperforms the enzyme at acidic pH and in the presence of CO. Both show competitive functionality compared to Pt. These results suggest benefits for both synthetic and natural catalysts in practical applications.

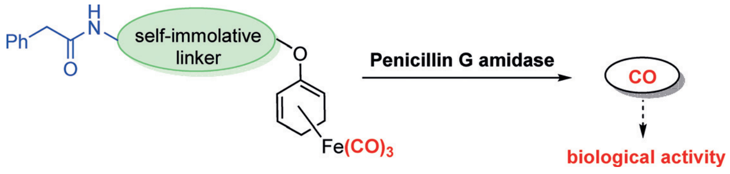
Hot FOD: The inclusion of static electron correlation (SEC) is mandatory for accurate quantum chemistry yet is particularly difficult to calculate. An analysis tool is developed based on a fractional occupation number weighted electron density (ρ^{FOD}) that is plotted as an isosurface and shows the "hot" (strongly correlated) electrons. Spatial integration of ρ^{FOD} yields a single number which can be used to globally quantify SEC.



CO-Releasing Molecules

N. S. Sitnikov, Y. Li, D. Zhang, B. Yard,
H.-G. Schmalz* ________ 12314 – 12318

Design, Synthesis, and Functional Evaluation of CO-Releasing Molecules Triggered by Penicillin G Amidase as a Model Protease

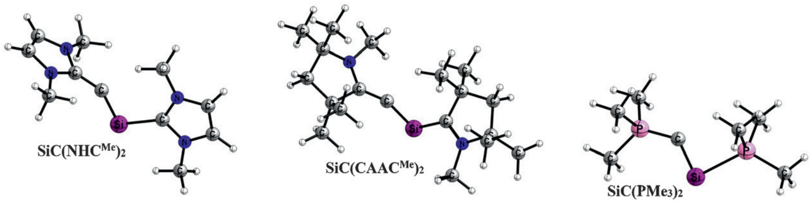


Please release me, let me CO: As an important step towards the development of protease-triggered CO-releasing molecules (CORMs), oxydiene–Fe(CO)$_3$ complexes bearing a penicillin G amidase (PGA)-cleavable side chain connected to the organometallic unit through a self-immolative linker were designed and synthesized. PGA-induced CO release was confirmed by headspace GC and by inhibition of VCAM-1 expression in a cell-based assay.

Silacarbon Complexes

D. M. Andrada,*
G. Frenking* ________ 12319 – 12324

Stabilization of Heterodiatomic SiC Through Ligand Donation: Theoretical Investigation of SiC(L)$_2$ (L = NHC^{Me}, CAAC^{Me}, PMe$_3$)



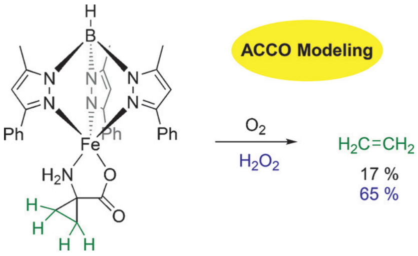
Planar or twisted? Quantum-chemical calculations have been carried out at the BP86/TZ2P+ level for the compounds SiC(L)$_2$ (L = NHC^{Me}, CAAC^{Me}, PMe$_3$; NHC = N-heterocyclic carbene, CAAC = cyclic (alkyl)aminocarbene). The optimized geometries exhibit a *trans* arrangement of the ligands L at SiC with a planar coordination when L = NHC^{Me} and PMe$_3$, while a twisted conformation is calculated when L = CAAC^{Me} (see structures; Si crimson, P pink, N blue).

Oxidase Mimetics

M. Sallmann, F. Oldenburg, B. Braun,
M. Réglier, A. J. Simaan,*
C. Limberg* ________ 12325 – 12328

A Structural and Functional Model for the 1-Aminocyclopropane-1-carboxylic Acid Oxidase

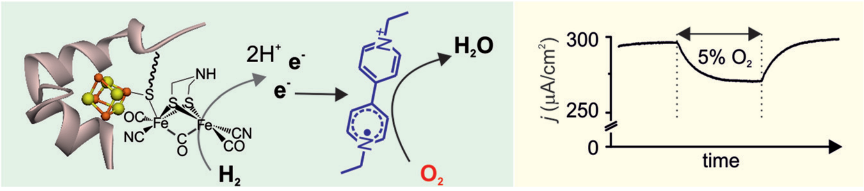
A ripening model: The depicted complex mimics the structure and the function of the aminocyclopropane-1-carboxylic acid oxidase (ACCO). It reacts with both O$_2$ and H$_2$O$_2$, respectively, to yield ethylene, which allows inferences with respect to the enzymatic mechanism.



Electrochemical Biocatalysis

A. A. Oughli, F. Conzuelo, M. Winkler,
T. Happe, W. Lubitz, W. Schuhmann,
O. Rüdiger,* N. Plumeré* 12329 – 12333

A Redox Hydrogel Protects the O$_2$-Sensitive [FeFe]-Hydrogenase from *Chlamydomonas reinhardtii* from Oxidative Damage

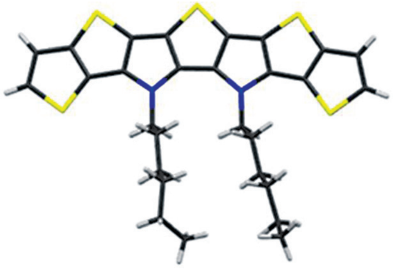


Reactivation is optional: [FeFe]-hydrogenase in a redox hydrogel can be exposed to O$_2$ under turnover conditions for H$_2$ oxidation. A stable catalytic current is maintained, which indicates that the protection mechanism is based only on O$_2$ reduction at the hydrogel surface.

Heteroacenes

C. Wetzel, E. Brier, A. Vogt, A. Mishra, E. Mena-Osteritz, P. Bäuerle* ________ **12334 – 12338**

Fused Thiophene-Pyrrole-Containing Ring Systems up to a Heterodecacene

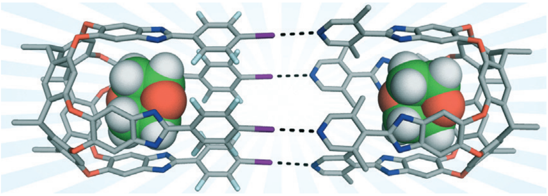


A bunch of fives: A new family of fused thiophene-pyrrole-containing S,N-heteroacenes with extended π-conjugation was synthesized (S yellow, N blue, C gray, H white). The characterization of optical and redox properties showed valuable structure–property relationships.

Host–Guest Systems

O. Dumele, N. Trapp, F. Diederich* ________ **12339 – 12344**

Halogen Bonding Molecular Capsules

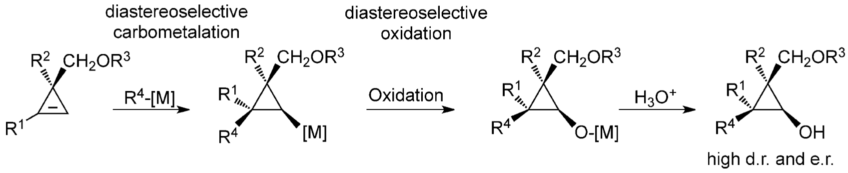


Time for halogens: Self-assembly of supramolecular capsules solely by halogen bonding (XB) is realized on the platform of resorcin[4]arene cavitands. The halogenated donor hemisphere binds in a 180° fashion through tetradentate XB to the acceptor hemisphere for capsule formation in solution. Guest inclusion inside the XB capsule is demonstrated and quantified.

Synthetic Methods

M. Simaan, P.-O. Delaye, M. Shi, I. Marek* ________ **12345 – 12348**

Cyclopropene Derivatives as Precursors to Enantioenriched Cyclopropanols and *n*-Butenals Possessing Quaternary Carbon Stereocenters

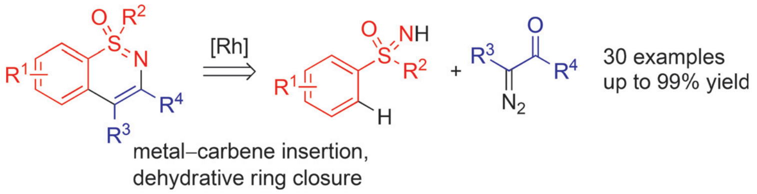


Make it two: The diastereoselective carbocupration reaction of cyclopropenylmethyl ethers followed by addition of oxenoid leads to the formation of diastereo- and enantiomerically enriched 2,2,3,3-tetrasubstituted cyclopropanol derivatives (see scheme). The ring fragmentation of the copper cyclopropanolate leads to acyclic butenal derivatives possessing enantiomerically enriched α-quaternary carbon stereocenters.

Heterocycles

Y. Cheng, C. Bolm* ________ **12349 – 12352**

Regioselective Syntheses of 1,2-Benzothiazines by Rhodium-Catalyzed Annulation Reactions



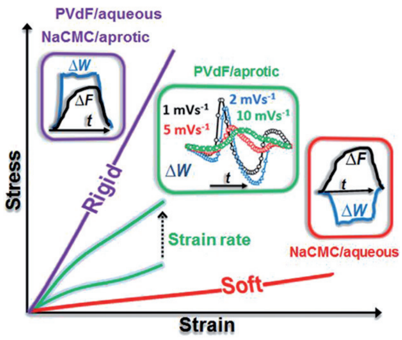
Domino effect: Rhodium-catalyzed annulation reactions provide 1,2-benzothiazines in excellent yields starting from S-aryl sulfoximines and diazo compounds. The catalysis shows a high functional-group tolerance and the process demonstrates excellent regioselectivity.

Lithium-Ion Batteries

N. Shpigel, M. D. Levi,* S. Sigalov,
O. Girshevitz, D. Aurbach,* L. Daikhin,
N. Jäckel, V. Presser ______ 12353 – 12356

Non-Invasive In Situ Dynamic Monitoring of Elastic Properties of Composite Battery Electrodes by EQCM-D

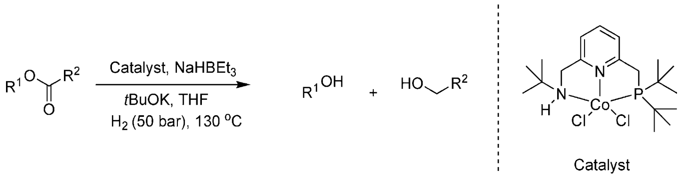
Intercalation-induced frequency (ΔF) and resonance width (ΔW) changes of composite Li-ion battery electrodes during their charge/discharge processes can be measured by electrochemical quartz-crystal microbalance with dissipation monitoring (EQCM-D). This visualizes in situ the dynamic character of the viscoelastic properties of the polymeric binders. PVdF = polyvinylidene fluoride, CMC = carboxymethylcellulose.



Homogeneous Catalysis

D. Srimani, A. Mukherjee,
A. F. G. Goldberg, G. Leitus,
Y. Diskin-Posner, L. J. W. Shimon,
Y. Ben David,
D. Milstein* ______ 12357 – 12360

Cobalt-Catalyzed Hydrogenation of Esters to Alcohols: Unexpected Reactivity Trend Indicates Ester Enolate Intermediacy

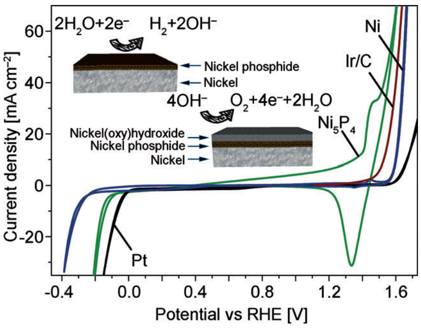


Getting involved: The atom-efficient and environmentally benign catalytic hydrogenation of carboxylic acid esters to alcohols has been accomplished in recent years mainly with precious-metal-based catalysts. Presented here is the first cobalt-catalyzed hydrogenation of esters to alcohols. Unexpectedly, the evidence indicates the unprecedented involvement of ester enolate intermediates.

Water Splitting

M. Ledendecker, S. Krick Calderón,
C. Papp, H.-P. Steinrück, M. Antonietti,
M. Shalom* ______ 12361 – 12365

The Synthesis of Nanostructured Ni_5P_4 Films and their Use as a Non-Noble Bifunctional Electrocatalyst for Full Water Splitting

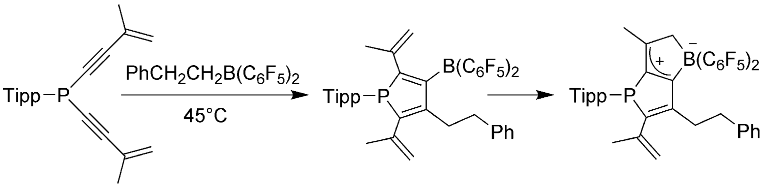


Doubling up: 3D hierarchical structured nickel phosphide (Ni_5P_4) shows excellent performance as a hydrogen evolution catalyst. The formation of a NiOOH/Ni_5P_4 heterojunction results in high activity towards the oxygen evolution reaction, thereby making the catalyst one of the best bifunctional catalysts for the overall water splitting reaction.

Phospholes

J. Möbus, G. Kehr, C. G. Daniliuc,
C. Mück-Lichtenfeld,
G. Erker* ______ 12366 – 12369

Observation of a Thermally Induced Bora-Nazarov Cyclization at a Phosphole Framework

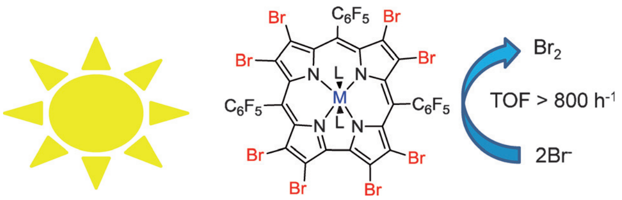


Ringing the changes: 2,5-Alkenyl-substituted phospholes bearing an adjacent electrophilic borane can undergo a thermally induced bora-Nazarov type ring closure. Tipp = 2,4,6-triisopropylphenyl.

Photocatalysis

A. Mahammed,
Z. Gross* ——— 12370 – 12373

Metallocorroles as Photocatalysts for Driving Endergonic Reactions, Exemplified by Bromide to Bromine Conversion

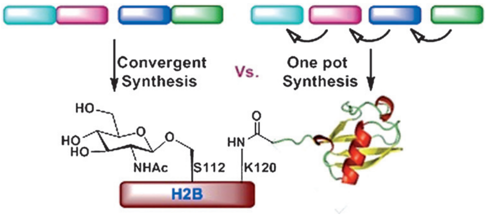


Brominated corroles that form post-transition-metal complexes are very efficient catalysts for the photocatalyzed transformation of bromide to bromine. They are very stable under the reaction conditions and the energy levels of their oxidizing and reducing half-filled MOs are easily tuned. TOF = turnover frequency.

Convergent Synthesis

M. Seenaiah, M. Jbara, S. M. Mali,
A. Brik* ——— 12374 – 12378

Convergent Versus Sequential Protein Synthesis: The Case of Ubiquitinated and Glycosylated H2B

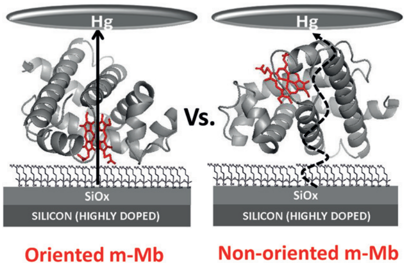


Choose your strategy: Comparison of convergent and one-pot synthetic approaches to singly or doubly post-translationally modified H2B protein enables the selection of the most efficient approach to obtain the target proteins in high purity and workable quantities.

Bioelectronics

S. Raichlin, I. Pecht,* M. Sheves,*
D. Cahen* ——— 12379 – 12383

Protein Electronic Conductors: Hemin–Substrate Bonding Dictates Transport Mechanism and Efficiency across Myoglobin

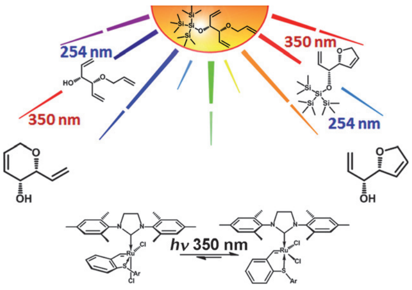


ETp in wired myoglobin: Electron transport (ETp) across myoglobin (Mb), measured in a solid-state-like configuration between two electronic contacts, increased up to 20-fold once Mb was bound to one of the contacts in an oriented manner by its hemin group. The oriented behavior of Mb is due to both the strong protein–substrate electronic coupling and the direct access to a highly efficient transport path through the hemin chromophore.

Photochemistry

E. Levin, S. Mavila, O. Eivgi, E. Tzur,
N. G. Lemcoff* ——— 12384 – 12388

Regioselective Chromatic Orthogonality with Light-Activated Metathesis Catalysts

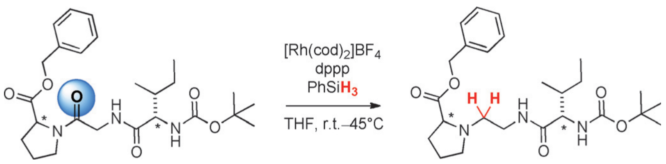


A guiding light: By the combination of a light-activated sulfur-chelated olefin-metathesis catalyst with a photocleavable bulky silyl protecting group, two orthogonal pathways enabled the selective synthesis of five- or six-membered heterocycles according to the order in which the starting material was irradiated with light of different wavelengths. Thus, protecting-group removal and metathesis gave either a dihydropyran or a dihydrofuran.

Peptide Modification

S. Das, Y. Li, C. Bornschein, S. Pisiewicz, K. Kiersch, D. Michalik, F. Gallou, K. Junge, M. Beller* ______ **12389 – 12393**

Selective Rhodium-Catalyzed Reduction of Tertiary Amides in Amino Acid Esters and Peptides



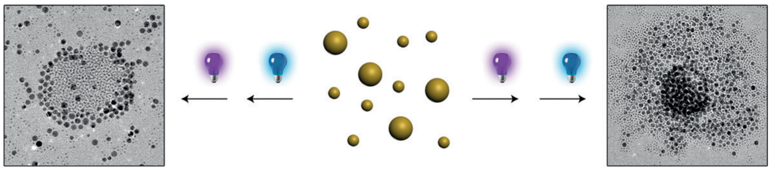
Peptide modification: Application of a commercially available rhodium precursor and bis(diphenylphosphino)propane (dppp) ligand together with phenyl silane as a reductant allows specific reductive derivatization of biologically interesting peptides.

Nanoparticles

D. Manna, T. Udayabhaskararao, H. Zhao, R. Klajn* ______ **12394 – 12397**

Orthogonal Light-Induced Self-Assembly of Nanoparticles using Differently Substituted Azobenzenes

Front Cover



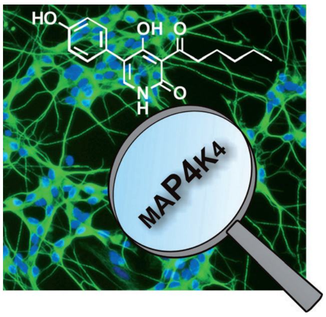
A guiding light: Nanoparticles functionalized with variously substituted azobenzenes self-assemble into aggregates in response to different wavelengths of light. Exposing a mixture of differently sized nanoparticles, each functionalized with a different azobenzene, to light of a specific color (ultraviolet or blue) induces the selective self-assembly of only one type of the nanoparticles. Irradiation with the other wavelength triggers the disassembly of the aggregates and the simultaneous self-assembly of nanoparticles of the other type.

Biological Activity

P. Schröder, T. Förster, S. Kleine, C. Becker, A. Richters, S. Ziegler, D. Rauh, K. Kumar, H. Waldmann* ______ **12398 – 12403**

Neuritogenic Militarinone-Inspired 4-Hydroxypyridones Target the Stress Pathway Kinase MAP4K4

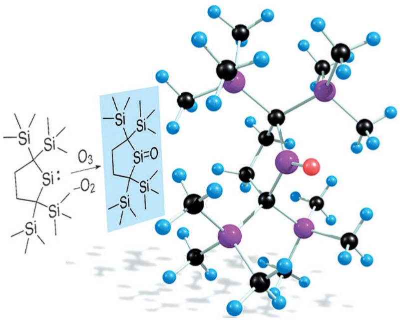
No stress: Reported herein is the synthesis of a militarinone-inspired 4-hydroxy-2-pyridone collection, its investigation for enhancement of neurite outgrowth, and the discovery of the stress pathway kinase MAP4K4 as a target of the discovered neuritogenic pyridones. The findings support the notion that MAP4K4 may be a new target for the treatment of neurodegenerative diseases.



Silicon Compounds

M. M. Linden, H. P. Reisenauer, D. Gerbig, M. Karni, A. Schäfer, T. Müller, Y. Apeloig,* P. R. Schreiner* ______ **12404 – 12409**

Preparation of a Silanone through Oxygen Atom Transfer to a Stable Cyclic Silylene

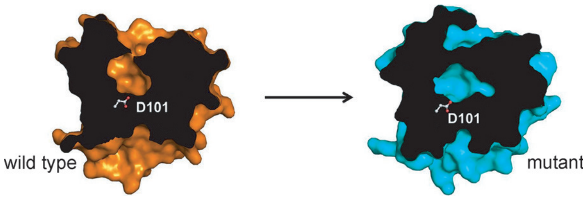


One atom at a time: Oxygen atom transfer from ozone to a stable silylene provides access to a new cyclic silanone. This bimolecular atom transfer reaction was achieved under matrix isolation conditions through co-deposition of the silylene and ozone. Conclusive evidence for the silanone is provided by comparison of experimental and computed IR spectra, including isotopological $^{16}O/^{18}O$ replacements. Atom colors: Si = purple, C = black, O = red, H = blue.

Enzyme Catalysis

Z. Sun, R. Lonsdale, X. D. Kong, J. H. Xu, J. Zhou,* M. T. Reetz* ____ 12410 – 12415

Reshaping an Enzyme Binding Pocket for Enhanced and Inverted Stereoselectivity: Use of Smallest Amino Acid Alphabets in Directed Evolution

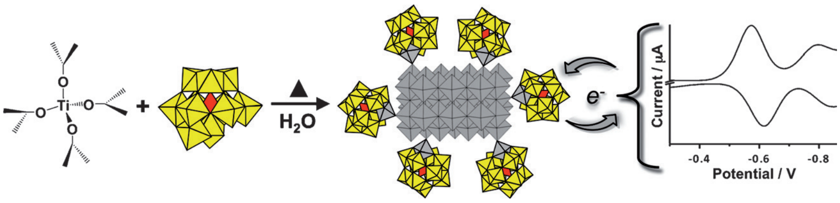


Emil Fischer's lock-and-key hypothesis has been revisited in experiments to reshape the binding pocket of limonene epoxide hydrolase (see picture) by using a single amino acid building block in the saturation mutagenesis of a 10-residue site. Catalytic variants selective for the formation of both (*R*,*R*)- and (*S*,*S*)-1,2-cyclohexanediol in the hydrolytic desymmetrization of cyclohexene oxide were identified in one and the same mutant library.

Hybrid Materials

M. Raula, G. Gan Or, M. Saganovich, O. Zeiri, Y. Wang, M. R. Chierotti, R. Gobetto, I. A. Weinstock* ________ 12416 – 12421

Polyoxometalate Complexes of Anatase-Titanium Dioxide Cores in Water

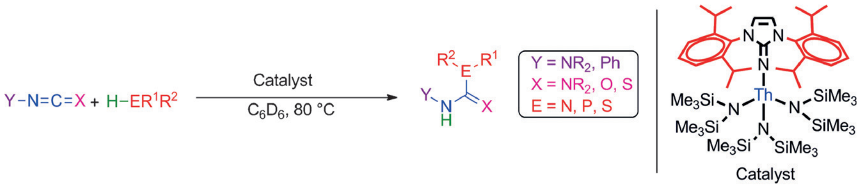


Redox-active ligands for TiO_2: Polyoxometalate (POM) electron acceptors serve as covalently coordinated inorganic ligands for anatase-TiO_2 nanocrystals, giving assemblies positioned between molecular macroanions and traditional colloidal nanoparticles. The POM ligands have tunable redox potentials, providing options for controlling reactions of soluble metal oxide semiconductor nanocrystals.

Actinide Catalysis

I. S. R. Karmel, M. Tamm,* M. S. Eisen* ____________ 12422 – 12425

Actinide-Mediated Catalytic Addition of E−H Bonds (E = N, P, S) to Carbodiimides, Isocyanates, and Isothiocyanates

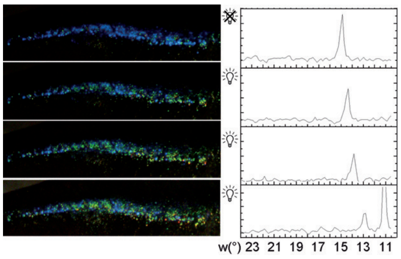


New reactivity: The mono(imidazolin-2-iminato) thorium complex [Th(Im$^{\mathrm{Dipp}}$N)-{N(SiMe$_3$)$_2$}$_3$] was successfully applied as an active catalyst for the addition of E−H (E = N, P, S) bonds across the central Y=N=C=X linkage of carbodiimides, isocyanates and isothiocyanates, yielding the respective insertion products in high yields and under mild reaction conditions.

Photonic Crystals

D. Gur, B. A. Palmer, B. Leshem, D. Oron, P. Fratzl, S. Weiner, L. Addadi* ____________ 12426 – 12430

The Mechanism of Color Change in the Neon Tetra Fish: a Light-Induced Tunable Photonic Crystal Array



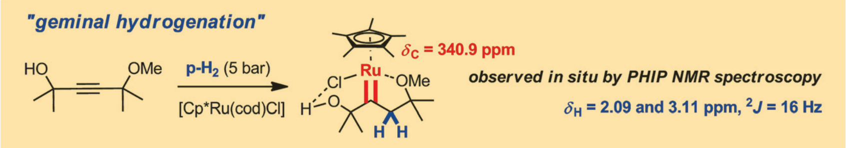
Color switch: The physical mechanism of the light-triggered color change in the lateral stripe of the neon tetra is controlled by changing the tilt angle of the guanine crystal arrays. It is shown that the color change can be described by the "Venetian blinds" model.

Ruthenium Carbenes

M. Leutzsch, L. M. Wolf, P. Gupta,
M. Fuchs, W. Thiel, C. Farès,
A. Fürstner* ________ **12431 – 12436**

Formation of Ruthenium Carbenes by *gem*-Hydrogen Transfer to Internal Alkynes: Implications for Alkyne *trans*-Hydrogenation

Inside Cover

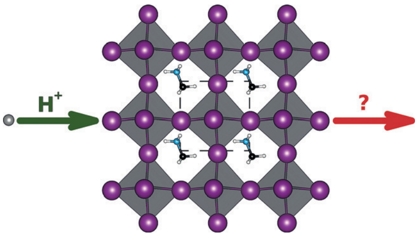


Let's stay together: Certain ruthenium complexes are able to catalyze the stereochemically highly unusual *trans*-hydrogenation of internal alkynes, but can also effect a geminal hydrogenation, during which both H atoms of a single H_2 precursor are delivered to the very same alkyne C atom whilst the neighboring C atom is converted into a metal carbene. The significance of this finding is analyzed by PHIP NMR spectroscopy (PHIP = para-hydrogen-induced polarization transfer) and density functional calculations.

Hybrid Perovskites

D. A. Egger,* L. Kronik,*
A. M. Rappe* ________ **12437 – 12441**

Theory of Hydrogen Migration in Organic–Inorganic Halide Perovskites



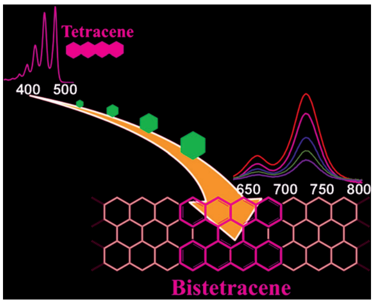
On the move: An examination of the pathways for hydrogen migration in organic–inorganic halide perovskites has shown that hydrogen defects are likely mobile in these materials. These findings may bear important consequences for the hysteresis, stability, and ionic conductivity of hybrid perovskites and related solar cells.

Perylenes

J. Liu, P. Ravat, M. Wagner,
M. Baumgarten, X. Feng,*
K. Müllen* ________ **12442 – 12446**

Tetrabenzo[a,f,j,o]perylene: A Polycyclic Aromatic Hydrocarbon With An Open-Shell Singlet Biradical Ground State

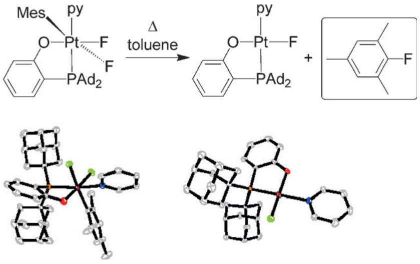
"Bistetracene", in which two tetracenes are connected side by side with two bonds, was synthesized and characterized. Based on the experimental work and theoretical calculations, bistetracene exhibits a remarkable singlet biradical feature in the ground state, which can be considered as a short segment of infinite zigzag-edged graphene nanoribbons.



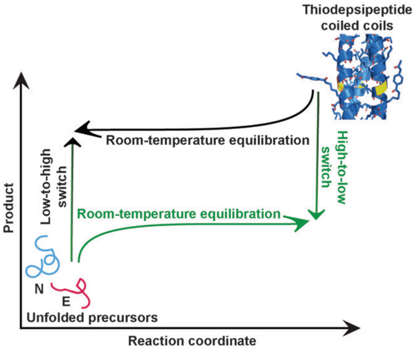
Electrophilic Fluorination

I. Dubinsky-Davidchik, I. Goldberg,
A. Vigalok,*
A. N. Vedernikov* ________ **12447 – 12451**

Selective Aryl–Fluoride Reductive Elimination from a Platinum(IV) Complex

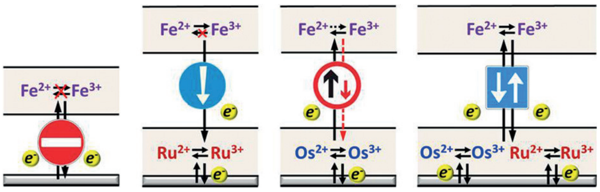


F fluors the competition: A difluoro(mesityl)platinum(IV) complex underwent highly selective reductive elimination of 2-fluoromesitylene upon heating in toluene (see scheme). The potentially competitive C(sp^2)—O reductive elimination is disfavored by the bulky chelating P,O ligand. Experimental and theoretical studies indicate that the C—F coupling takes place from an unsaturated neutral Pt^{IV} center.



Remember where you come from: Dynamic thioester peptide equilibration led to one of two distinct steady states, depending on the initial precursor and product concentrations. This rare non-enzymatic bistable system could be switched from one state to the other by applying physical or chemical stimuli (see picture).

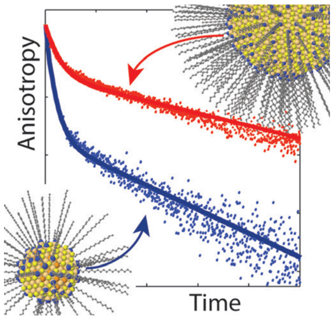
Systems Chemistry



Alternative routes: Variation of the positioning of redox-active metal complexes with respect to a conductive surface leads to molecular materials with unique electron-transfer properties. Restricted, unidirectional, and bidirectional charge transfer is obtained with the correct combination of metal complexes in well-defined orientations (see picture).

Electrochemistry

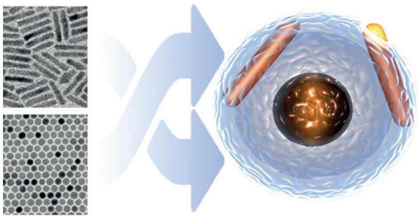
Dynamic properties of a ligand shell: The size-dependent dynamic properties of an organic ligand shell, capping the surface of colloidal nanocrystals, have been studied by probing polarized emission of surface-bound organic dyes (see picture). These properties affect the synthesis, dispersibility, and optoelectronic features of colloidal nanocrystals.



Surface Chemistry

Inside Back Cover

Matching unlikely pairs: In a two-step procedure, iron oxide nanocrystals were initially encapsulated in a polystyrene (PS) shell and subsequently used as beads for a controlled assembly of elongated quantum dots/quantum rods (QDQRs) The fluorescence of the QDQRs and magnetism of iron oxide were perfectly preserved in the resulting nanohybrids.

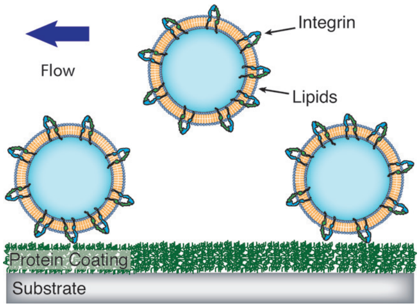


Functional Nanostructures

Cell Adhesion

J. P. Frohnmayer, D. Brüggemann, C. Eberhard, S. Neubauer, C. Mollenhauer, H. Boehm, H. Kessler, B. Geiger, J. P. Spatz* —— **12472 – 12478**

Minimal Synthetic Cells to Study Integrin-Mediated Adhesion

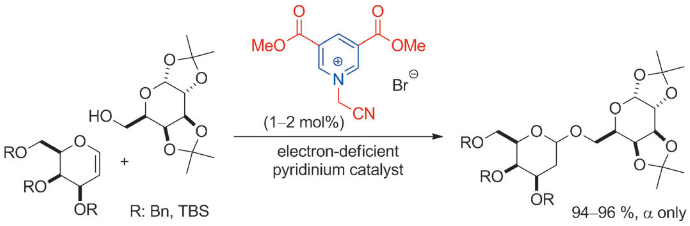


A well-controlled model system that mimics integrin-mediated adhesion has been developed. The interactions of these synthetic cells with various extracellular matrix proteins were analyzed using a quartz crystal microbalance with dissipation monitoring, which confirmed that the integrin had been functionally incorporated into the lipid vesicles.

Organocatalytic Glycosylation

S. Das, D. Pekel, J.-M. Neudörfl, A. Berkessel* —— **12479 – 12483**

Organocatalytic Glycosylation by Using Electron-Deficient Pyridinium Salts

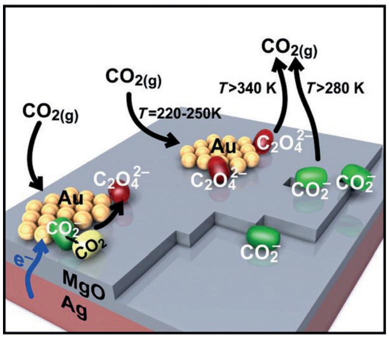


Less is more! Electron-deficient pyridinium cations efficiently catalyze the glycosylation of benzyl- and silyl-protected glycals. Both primary and secondary alcohols can act as glycosyl acceptors. The glycosylation shown proceeds at RT and affords exclusively the α-galactoside. The 1,2-addition product of the alcohol component to the pyridinium cation most likely acts as crucial catalysis intermediate.

CO_2 Activation

F. Calaza,* C. Stiehler, Y. Fujimori, M. Sterrer, S. Beeg, M. Ruiz-Oses, N. Nilius, M. Heyde, T. Parviainen, K. Honkala, H. Häkkinen, H.-J. Freund —— **12484 – 12487**

Carbon Dioxide Activation and Reaction Induced by Electron Transfer at an Oxide–Metal Interface



Electrons are shuttled back and forth between CO_2 and a metal–insulator–metal model system, enabling the activation of CO_2 and its reaction to oxalate. This may either react further or reversibly decompose to CO_2.

Reaction Mechanisms

T. Fallon,* M. Oestreich* **12488 – 12491**

A Constellation of Deuterium-Labeled Silanes as a Simple Mechanistic Probe not Requiring Absolute Configuration Determination

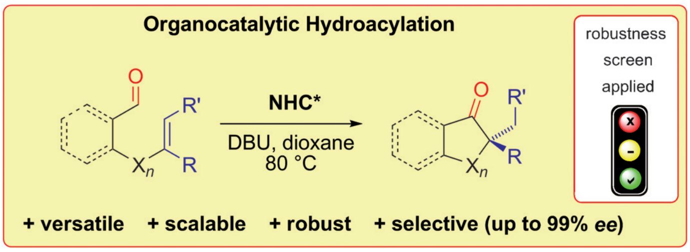
Back Cover

Silicon stargazing: A new type of mechanistic probe is designed and evaluated. A cocktail of deuterium-labeled hydrosilanes provides a "silent" stereochemical relationship between the silicon atom and the probe's backbone as the basis of the analysis. This technique does not suffer from the biases of traditional methods, nor does it require the determination of the absolute configuration.

Enantioselective Organocatalysis

D. Janssen-Müller, M. Schedler, M. Fleige,
C. G. Daniliuc,
F. Glorius* ——— **12492 – 12496**

Enantioselective Intramolecular Hydroacylation of Unactivated Alkenes: An NHC-Catalyzed Robust and Versatile Formation of Cyclic Chiral Ketones

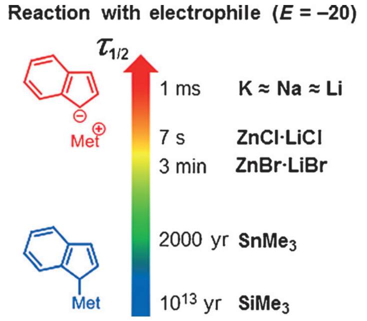


100 % Organic: A highly enantioselective N-heterocyclic carbene (NHC)-catalyzed intramolecular hydroacylation of aromatic and, more interestingly, aliphatic aldehydes with unactivated olefins offers access to a range of cyclic α-chiral ketones bearing quaternary centers. The reaction was found to be highly robust and proceeds with excellent yield in the presence of a diverse range of functional groups.

Nucleophilicity

F. Corral-Bautista, L. Klier, P. Knochel,
H. Mayr* ——— **12497 – 12500**

From Carbanions to Organometallic Compounds: Quantification of Metal Ion Effects on Nucleophilic Reactivities

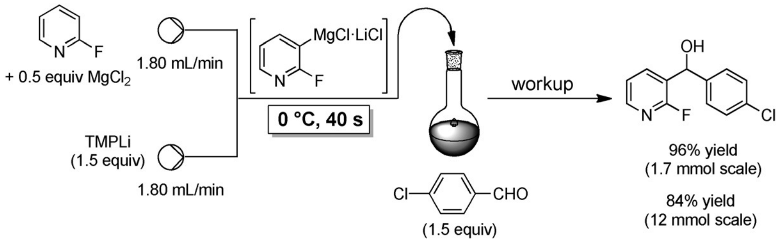


Different worlds: Kinetic investigations with reference electrophiles show that a reaction with an electrophile, which would proceed within milliseconds with indenyl lithium, would require much more than the age of the universe with the corresponding organosilicon compound. Met = metal.

Synthetic Methods

M. R. Becker, P. Knochel* **12501 – 12505**

Practical Continuous-Flow Trapping Metalations of Functionalized Arenes and Heteroarenes Using TMPLi in the Presence of Mg, Zn, Cu, or La Halides

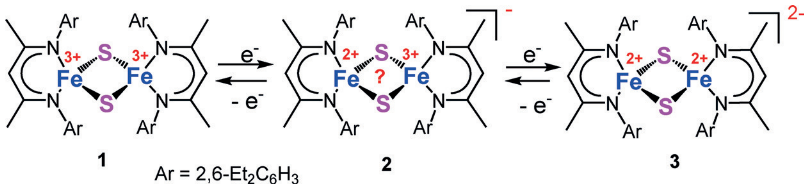


Flow makes the difference: In situ trapping transmetalations in which functionalized arenes or heterocycles are mixed with metal salts proceed at 0 °C within 40 s in a continuous flow apparatus. Subsequent batch quenching of the resulting Mg, Zn, Cu, or La organic species with various electrophiles proceeds in high yields (see example).

Rieske Clusters

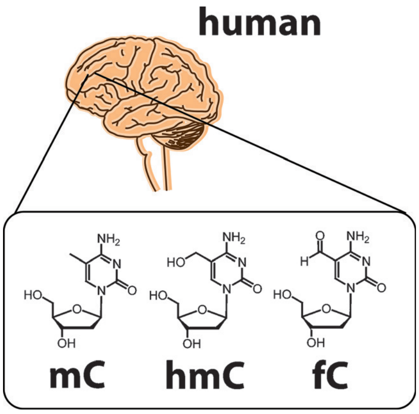
S. Yao, F. Meier, N. Lindenmaier,
R. Rudolph, B. Blom, M. Adelhardt,
J. Sutter, S. Mebs, M. Haumann, K. Meyer,
M. Kaupp, M. Driess* ——— **12506 – 12510**

Biomimetic [2Fe-2S] Clusters with Extensively Delocalized Mixed-Valence Iron Centers



Great sharing: The facile formation of the complete redox series of biomimetic [2Fe-2S] clusters **1** to **3** supported by β-diketiminato ligands is reported. The reduced mixed-valence [2Fe-2S] cluster **2** represents a unique biomimetic [2Fe-2S] cluster anion with an extensively delocalized Fe^{2+}Fe^{3+} pair as evidenced by ^{57}Fe Mössbauer and XAS/XES spectroscopy and supported by DFT calculations.

Epigenetics



Brain teaser: Age-dependent global levels of 5-methyl- (mC), 5-hydroxymethyl- (hmC), and 5-formylcytosine (fC) were quantified in human and mouse brain tissues. While the hmC content increases sharply with age to reach a high steady-state level of 1.2% in the adult human brain, fC levels rapidly decline during early developmental stages.

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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