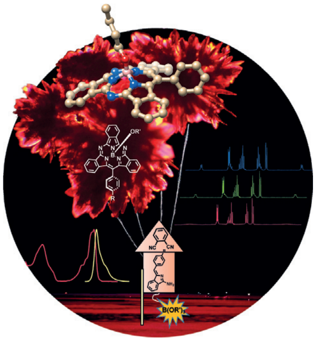
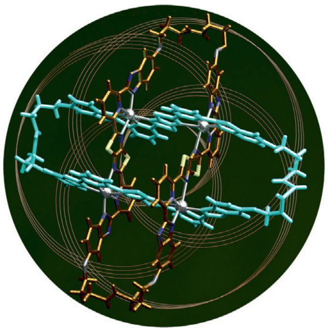
A half-century-old assertion ...

... about the structure of ceric ammonium nitrate (CAN) in solution is challenged. In their Communication on page 7534 ff., R. J. Ellis and co-workers show that in HNO_3, CAN is a dinuclear Ce–O–Ce complex. The bridging oxygen (the guy with the hat) would usually be attacked and devoured by the HNO_3 sharks. However, he is protected by the Ce "life rings" on either side, and so he is safe. The structure suggests that CAN can act as a two-electron-transfer reagent and not, as generally assumed, a one-electron-transfer reagent.

Porphyrinoids

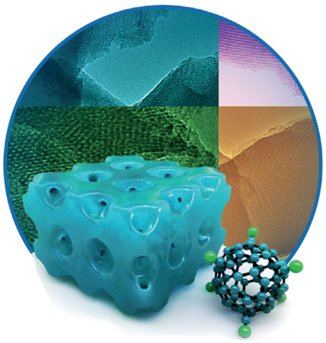
In their Communication on page 7510 ff., A. N. Cammidge et al. describe the synthesis of the first subphthalocyanine–subporphyrin hybrids and their characterization by NMR spectroscopy and X-ray crystallography.





Molecular Solomon Links

The self-assembly of four thiazole ligands and four transition-metal ions, followed by a ring-closing metathesis to a molecular Solomon link is described by D. A. Leigh et al. in their Communication on page 7555 ff.



Fullerene-Based Materials

In their Communication on page 7577 ff., T. Bein et al. report a highly ordered 3D covalent fullerene framework based on hexafunctionalized fullerene units, the mesoporosity of which is controlled by self-assembly with a block copolymer.

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Service

Author Profile

"My favorite time of day is the early morning.
I admire people who oppose violence …"
This and more about Ralf Ludwig can be found on page 7476.

News

R. G. Cooks

S. Granick

T. Ha

M. Head-Gordon

S. Mukamel

C. J. Murphy

D. M. Neumark

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R. A. Sheldon

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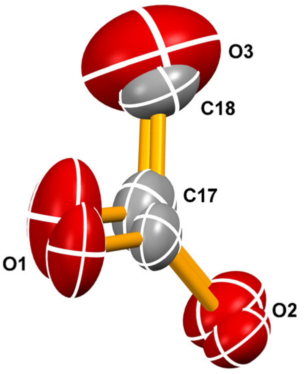
Books

Correspondence

Structure Elucidation

J. Hurmalainen, M. A. Land,
K. N. Robertson, C. J. Roberts,
I. S. Morgan, H. M. Tuononen,*
J. A. C. Clyburne* ________ **7484 – 7487**

Comment on “Crystallographic Snapshot of an Arrested Intermediate in the Biomimetic Activation of CO_2”



Out of focus: A recent Communication published in this journal describes the synthesis of $[n\mathrm{Bu_4N}]\mathrm{HCO_3}$. The authors performed a single-crystal X-ray study that revealed a putative species described as an incipient hydroxide ion engaging in a long, and presumably weak, interaction with CO_2. Our recent exploration of the coordination chemistry of CO_2 with small ions leads us to believe that such an exceptional bonding situation is unlikely. Instead, we argue that the crystal structure is that of $[n\mathrm{Bu_4N}]\mathrm{O_2CCH_3}$ and therefore not representative of the bulk powder from the synthesis.

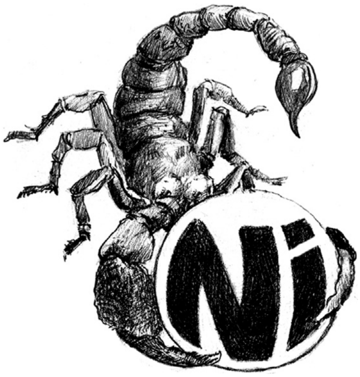
Highlights

Nickel(IV) Chemistry

R. Mitra, K.-R. Pörschke* ___ **7488 – 7490**

Organonickel(IV) Chemistry: A New Catalyst?

With scorpionate ligands finding their way into organonickel chemistry, the state of the art of present-day nickel(IV) chemistry is highlighted. Will rapid C–X coupling reactions emerge as a domain of higher-oxidation-state nickel chemistry?

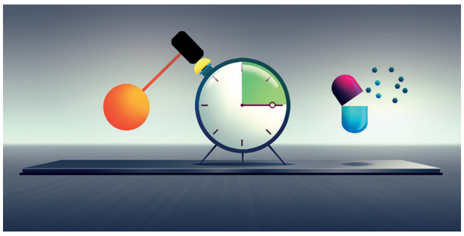


Reviews

Drug Release

A. Alouane, R. Labruère, T. Le Saux,
F. Schmidt,* L. Jullien* ___ **7492 – 7509**

Self-Immolative Spacers: Kinetic Aspects, Structure–Property Relationships, and Applications



Time to cleave: Self-immolative spacers are covalent assemblies tailored to ensure the temporally tailored cleavage of two chemical bonds on activation. Upon stimulation, a protective moiety is removed from one side of the spacer, which then triggers the release of a desired molecule. This Review deals with the kinetics of disassembly in self-immolative spacers and provides information for selecting a particular self-immolative motif for a specific demand.

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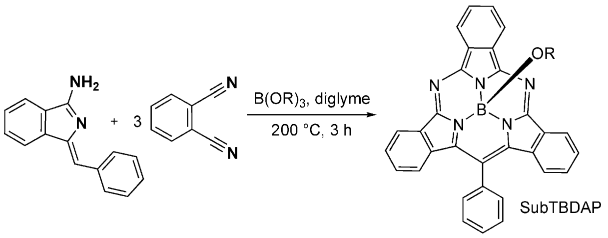
Communications

Porphyrinoids

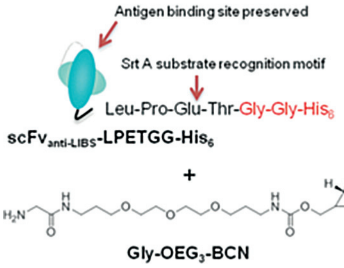


The first syntheses of subphthalocyanine–subporphyrin hybrid structures are reported. The new hybrids are isolated as robust, pure materials that display intense absorption and emission in the mid-visible region, and are further characterized in solution and solid state by variable-temperature NMR spectroscopy and X-ray crystallography, respectively.

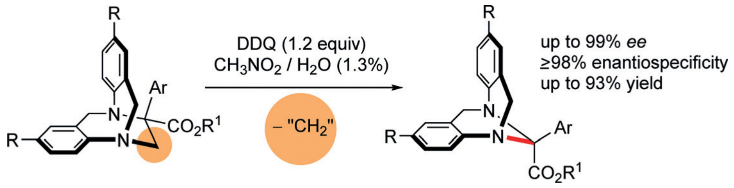
Frontispiece

Antibody Modification

A two-step modular system for site-specific antibody modification and conjugation is reported. The first step of this approach uses enzymatic bioconjugation with the transpeptidase Sortase A for site-specific incorporation of strained cyclooctyne functional groups into antibodies. The second step of this modular approach involves the copper-free azide–alkyne cycloaddition click reaction.



Asymmetric Synthesis

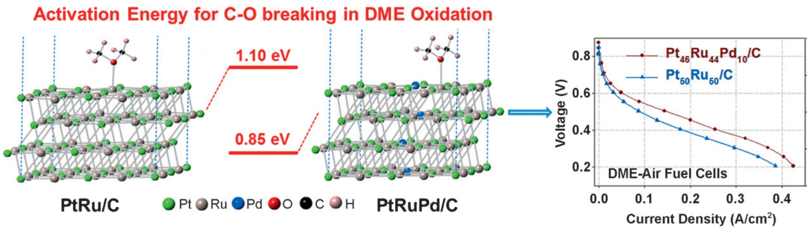


Against all odds: Simple treatment of ethano-Tröger bases with DDQ in wet nitromethane provokes a novel CH$_2$-extrusion reaction. Disubstituted methano-derivatives are formed in high yield and enantiospecificity despite undergoing two bond cleavages at stereogenic nitrogen and carbon centers, and a temporary rupture of the bicyclic structure. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Heterogeneous Catalysis

Q. Li, X. Wen, G. Wu, H. T. Chung, R. Gao,
P. Zelenay* ______ 7524 – 7528

High-Activity PtRuPd/C Catalyst for Direct Dimethyl Ether Fuel Cells

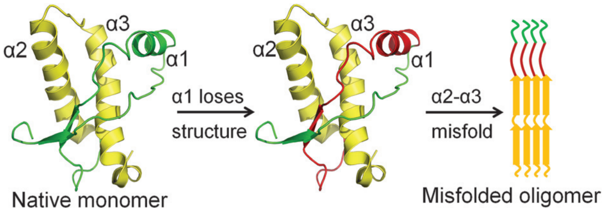


DME oxidation: Guided by DFT calculation, a ternary carbon-supported PtRuPd catalyst was designed and synthesized for dimethyl ether (DME) electrooxidation. The new $Pt_{46}Ru_{44}Pd_{10}/C$ led to a two-fold enhancement in the performance of a direct DME fuel cell (DDMEFC). This allowed the DDMEFC performance to slightly surpass the performance of the state-of-the-art direct methanol fuel cell (DMFC).

Protein Misfolding

J. Singh, J. B. Udgaonkar* __ 7529 – 7533

Structural Effects of Multiple Pathogenic Mutations Suggest a Model for the Initiation of Misfolding of the Prion Protein



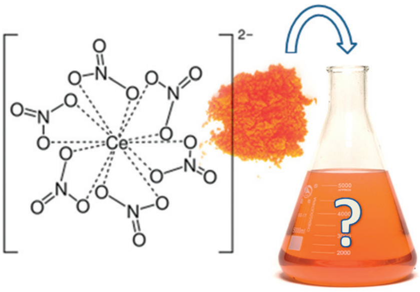
Prying on the prion: A molecular understanding of the prion diseases requires delineation of the origin of misfolding of the prion protein. Hydrogen–deuterium exchange mass spectrometry showed that several disease-linked mutant variants share a common structural perturbation in their native states. Two steps were identified for prion protein misfolding: loss of the structure of helix 1 and subsequent β-sheet formation by helices 2 and 3 (see picture).

Ceric Ammonium Nitrate (CAN)

T. J. Demars, M. K. Bera, S. Seifert,
M. R. Antonio, R. J. Ellis* __ 7534 – 7538

Revisiting the Solution Structure of Ceric Ammonium Nitrate

Front Cover

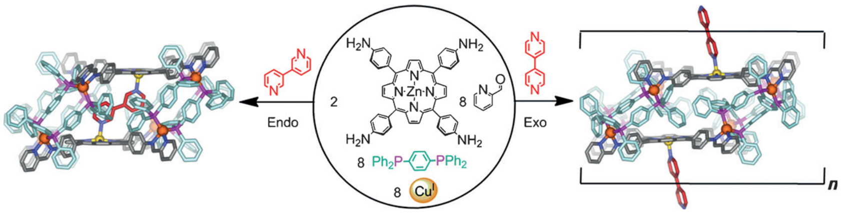


What CAN it be? The solution structure of ceric ammonium nitrate (CAN)—a vital chemical feedstock in organic synthesis—is revisited, challenging a half-century-old assertion with a radically different model. In nitric acid solutions a dinuclear oxo bridged structure is found, suggesting CAN is able to act as a two-electron transfer reagent, and not as generally assumed a one-electron transfer reagent.

Host–Guest Systems

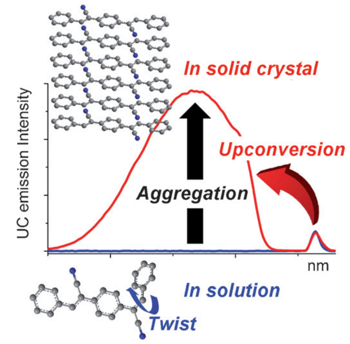
G. Jayamurugan, D. A. Roberts,
T. K. Ronson,
J. R. Nitschke* ______ 7539 – 7543

Selective *Endo* and *Exo* Binding of Mono- and Ditopic Ligands to a Rhomboidal Diporphyrin Prism

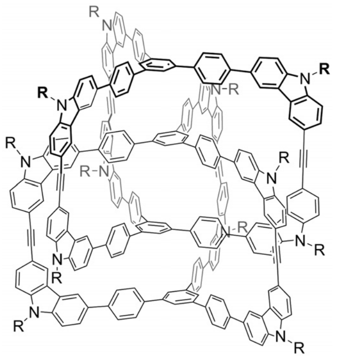


In or out: A slipped-cofacial rhomboidal diporphyrin prism was synthesized using mixed tetratopic iminopyridyl and ditopic phosphine ligands. This receptor exhibits selective *endo* and *exo* binding properties to the positional isomers of bipyridine (2,2′, 3,3′, and 4,4′) and quinuclidine. The differences in binding nature and strength between different ligands have enabled network transformations to be demonstrated.

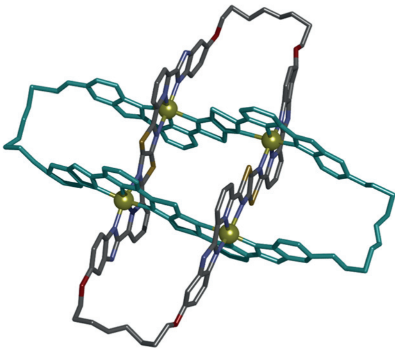
Affairs of state: Whereas a cyano-substituted 1,4-distyrylbenzene derivative shows no upconverted (UC) emission in solution, a clear upconverted emission is observed for solution-cast crystals (see picture). The difference is attributed to immediate decay of excited triplets through conformational twisting and isomerization being possible in solution but not in the solid state.

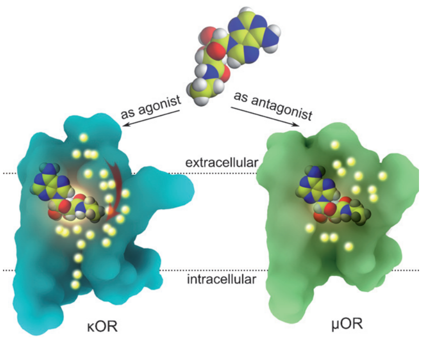


All knotted up: Permanently interlocked aryleneethynylene cages were prepared through thermodynamically controlled alkyne metathesis from simple monomers in solution. This template-free approach favors at equilibrium the formation of the interlocked complexes (see picture) over that of independent cages, despite the unfavorable entropy loss associated with catenation.



Gridlocked: A molecular Solomon link was obtained in 72 % yield through the self-assembly of a 2×2 interwoven molecular grid consisting of four thiazole ligands and four transition-metal cations, followed by ring-closing olefin metathesis. Interwoven grids should prove to be useful intermediates in the synthesis to higher-order molecular knots and links.



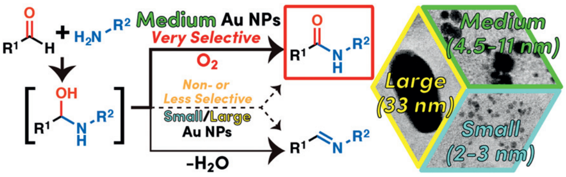


One rule to link them all: The same ligand can act as an agonist for the κ-opioid receptor (κOR) and as an antagonist for the μ-opioid receptor (μOR). Long-timescale MD simulations reveal that antagonist binding diminishes the solvent-accessible surface area (SASA) of the binding pocket, which consequently blocks the entrance of water into the receptor, whereas agonist binding leads to comparatively larger SASA values.

Heterogeneous Catalysis

H. Miyamura, H. Min, J.-F. Soulé,
S. Kobayashi* __________ 7564 – 7567

Size of Gold Nanoparticles Driving Selective Amide Synthesis through Aerobic Condensation of Aldehydes and Amines

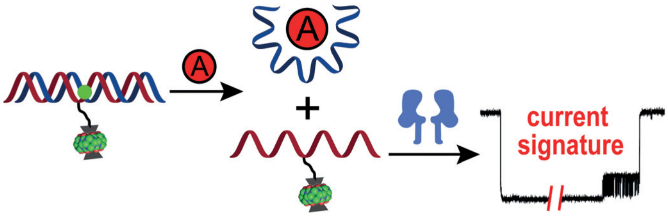


Superior activity and selectivity of gold nanoparticles (Au–NPs) of medium size (4.5–11 nm) were found for the direct and selective aerobic oxidative amide synthesis from various combinations of aldehydes and amines. This is an example of an unusual correlation between the size of NPs and their activity/selectivity. These catalysts could be recovered and reused several times without loss of activity.

Host–Guest Systems

T. Li, L. Liu, Y. Li, J. Xie,
H.-C. Wu* __________ 7568 – 7571

A Universal Strategy for Aptamer-Based Nanopore Sensing through Host–Guest Interactions inside α-Hemolysin



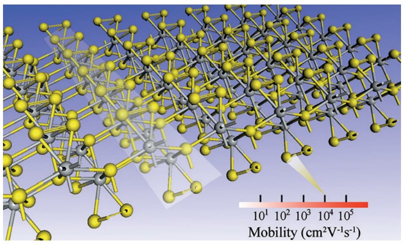
The presence of analytes causes the aptamer–probe duplex to unwind and release the DNA probe which can quantitatively produce signature current events when translocated through an α-hemolysin nanopore. This strategy should be universally applicable in sensing different types of analytes with nanopore sensors.

Semiconductors

J. Dai, X. C. Zeng* __________ 7572 – 7576

Titanium Trisulfide Monolayer: Theoretical Prediction of a New Direct-Gap Semiconductor with High and Anisotropic Carrier Mobility

New semiconductor: A titanium trisulfide monolayer is predicted to be a direct-gap semiconductor with ultrahigh electron mobility ($\approx 10^4$ cm^{2}V^{-1}s^{-1}), which is higher than that of MoS$_2$ and phosphorene. The monolayer can be exfoliated from its bulk phase due to the lower exfoliation energy compared to graphite.

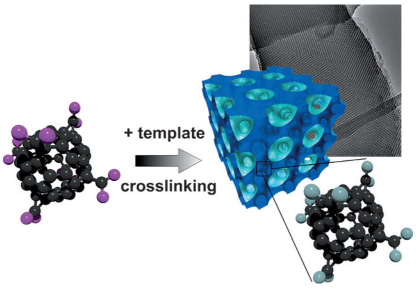


Fullerene-Based Materials

N. K. Minar, K. Hou, C. Westermeier, M. Döblinger, J. Schuster, F. C. Hanusch, B. Nickel, G. A. Ozin,
T. Bein* __________ 7577 – 7581

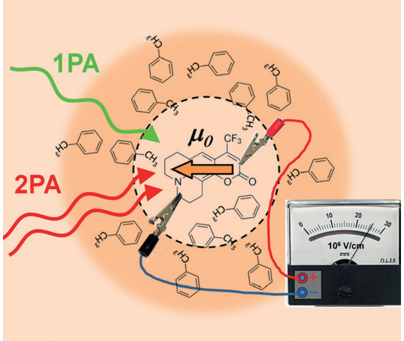
A Highly-Ordered 3D Covalent Fullerene Framework

Back Cover



Self-assembling C$_{60}$: A highly ordered 3D fullerene framework is prepared with a structure based on octahedrally functionalized fullerene building blocks. The C$_{60}$ building blocks coassemble with a liquid-crystalline block copolymer to produce a covalent fullerene framework with orthorhombic *Fmmm* symmetry and 7.5 nm pores.

Solvent effects: The strength of the dipolar solute-induced reaction field, along with the ground- (μ_0) and excited-state electrostatic dipole moments and polarizability of a solvated chromophore, were determined using one-photon (1PA) and two-photon (2PA) absorption measurements. The approach was verified on two benchmark chromophores *N*,*N*-dimethyl-6-propionyl-2-naphthylamine and coumarin 153.



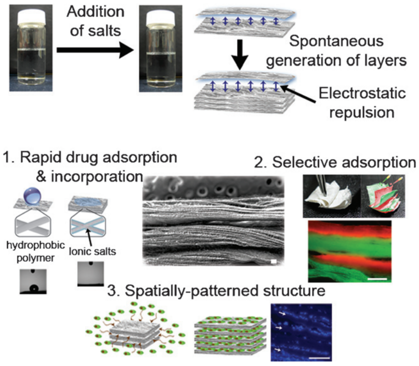
Solvatochromism

A. Rebane,* G. Wicks, M. Drobizhev, T. Cooper, A. Trummal, M. Uudsemaa ______ 7582 – 7586

Two-Photon Voltmeter for Measuring a Molecular Electric Field

---

Multilayered, self-assembled, and volume-expanded nanofibrous structures can be formulated by a novel process referred to as the spontaneous organization of numerous-layer generation by electrospray (SpONGE). The SpONGE matrix possesses the unique ability to split multiple individual fibrous layers by manual separation and spatially position biomolecules.



Nanofiber Self-Assembly

G. Jin, M. Shin, S. Kim, H. Lee,* J. H. Jang* ______ 7587 – 7591

SpONGE: Spontaneous Organization of Numerous-Layer Generation by Electrospray

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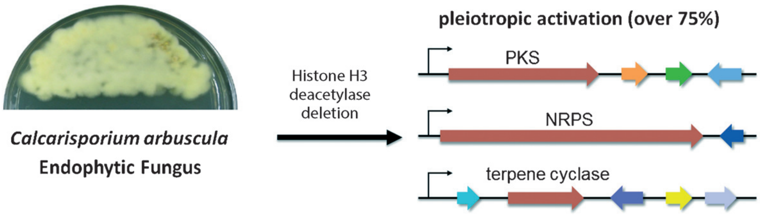


The endophytic fungus *Calcarisporium arbuscula* is rich in cryptic gene clusters for natural product biosynthesis. Removal of a global epigenetic repressor HdaA, the histone H3 deacetylase, activates the expression of over 75% of the silenced gene clusters and enables the isolation of new natural products.

Epigenetics

X. M. Mao, W. Xu, D. Li, W. B. Yin, Y. H. Chooi, Y. Q. Li, Y. Tang,* Y. Hu* ______ 7592 – 7596

Epigenetic Genome Mining of an Endophytic Fungus Leads to the Pleiotropic Biosynthesis of Natural Products

---

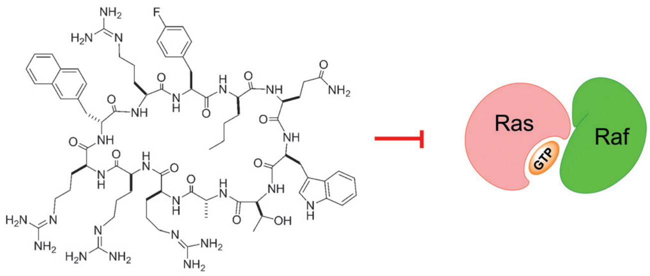
Ironing out any difficulties: Unlike complexes of other transition metals, an iron catalyst enabled the synthesis of phosphabenzenes from 1,6-diynes and phosphaalkynes (see scheme). A variety of phosphabenzene derivatives were formed in good to high yield by FeI_2-catalyzed [2+2+2] cycloaddition reactions of these substrates in *m*-xylene.

Synthetic Methods

K. Nakajima, S. Takata, K. Sakata,* Y. Nishibayashi* ______ 7597 – 7601

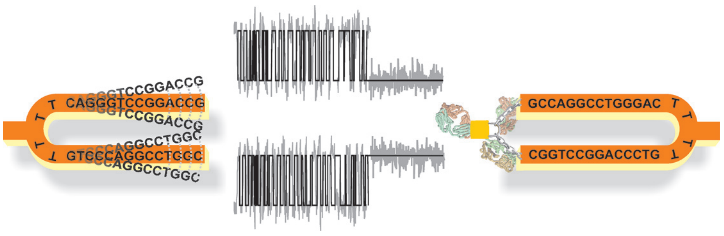
Synthesis of Phosphabenzenes by an Iron-Catalyzed [2+2+2] Cycloaddition Reaction of Diynes with Phosphaalkynes

Drug Discovery



Round, round, get around: Cell-permeable cyclic peptides were developed that act as direct Ras inhibitors by blocking Ras–effector protein interactions. These peptides, named cyclorasins, cause growth inhibition and apoptosis in cancer cells.

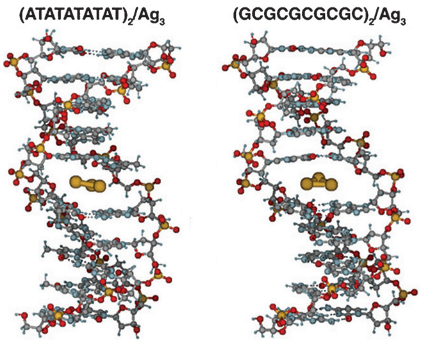
Mechanochemical Sensing



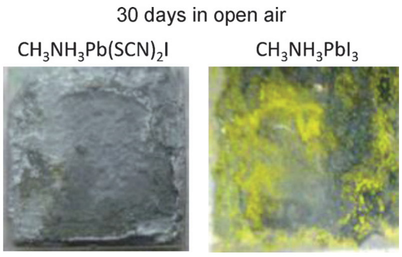
Like the vibration of prongs in a tuning fork: A DNA hairpin acts as a molecular tuning fork (MTF) by rapidly switching between unfolded and folded states (mechanoescence). Similar to fluorescence that needs a fluorophore, mechanoescence requires a MTF mechanophore. This biosensor has a picomolar detection limit for antibodies in human serum.

Silver Clusters

Sandwiching silver in DNA: Subnanometric silver clusters (Ag_2 and Ag_3) were synthesized using a kinetic control procedure. Interaction studies of the clusters with DNA have demonstrated that Ag_2 clusters interact only by covalent binding, whereas Ag_3 clusters intercalate between the base pairs in DNA (see picture) and induce strong conformational changes.



Solar Cells

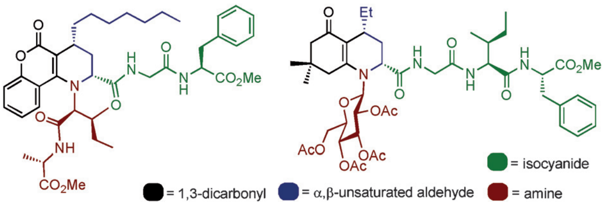


The replacement of two iodides by two pseudohalide thiocyanate ions in $CH_3NH_3PbI_3$ results in a perovskite material with superior tolerance to moisture when used as the active material of a solar cell. For the $CH_3NH_3Pb(SCN)_2I$ perovskite films, no significant degradation was observed after the film had been exposed to air with a relative humidity of 95% for over four hours, whereas the $CH_3NH_3PbI_3$ films degraded in less than 1.5 hours.

Synthetic Methods

R. Echemendía, A. F. de La Torre,
J. L. Monteiro, M. Pila, A. G. Corrêa,
B. Westermann, D. G. Rivera,*
M. W. Paixão* ——— 7621–7625

Highly Stereoselective Synthesis of Natural-Product-Like Hybrids by an Organocatalytic/Multicomponent Reaction Sequence

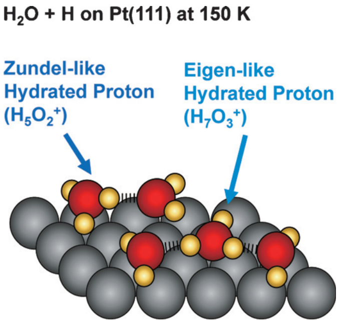


One shot complexity: The combination of an organocatalytic conjugate addition with a stereoselective multicomponent reaction (MCR) enables the one-pot synthesis of enantiomerically pure natural product hybrids. Such interplay between organocatalysis and MCRs allows the tunable diversification of up to four structural elements, thus facilitating the rapid exploration of a large chemical space.

Surface Chemistry

Y. Kim, S. Shin, H. Kang* ——— 7626–7630

Zundel-like and Eigen-like Hydrated Protons on a Platinum Surface



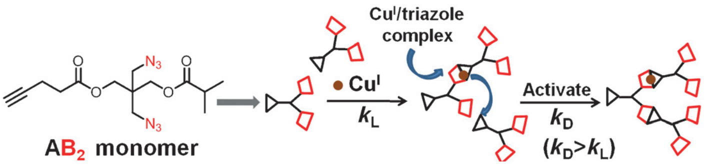
Hydrated protons on a Pt surface: Adsorbed atomic hydrogen on a Pt(111) surface is ionized to protons with the assistance of adsorbed water, resulting in the formation of protonated water clusters of certain preferential forms ($H_5O_2^+$ and $H_7O_3^+$). These surface-bound ions could play an important role in Pt electrode surface reactions.

Hyperbranched Polymers

Y. Shi, R. W. Graff, X. Cao, X. Wang,
H. Gao* ——— 7631–7635

Chain-Growth Click Polymerization of AB_2 Monomers for the Formation of Hyperbranched Polymers with Low Polydispersities in a One-Pot Process

Inside Cover

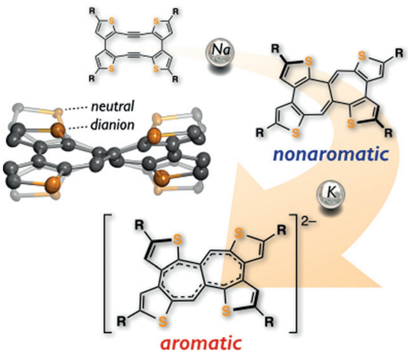


A chain-growth polymerization method that uses copper-catalyzed azide–alkyne cycloaddition (CuAAC) reactions of trifunctional AB_2 monomers produces hyperbranched polymers in a one-pot solution process. Polymers with high molecular weight, low polydispersity, and a high degree of branching are thus obtained.

Aromatic Systems

H. Oshima, A. Fukazawa,* T. Sasamori,
S. Yamaguchi* ——— 7636–7639

A Nonaromatic Thiophene-Fused Heptalene and Its Aromatic Dianion

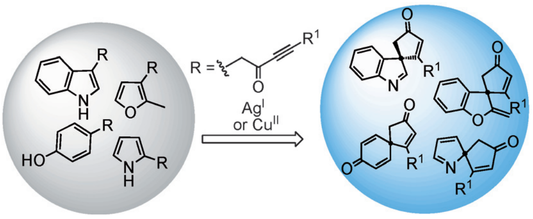


Evolution: Reductive transannular cyclization of an arene-fused bisdehydro[12]annulene granted access to a π-extended heptalene skeleton. The tetrathieno-fused heptalene exhibits a highly twisted, nonaromatic saddle structure. X-ray crystallography shows that chemical reduction transforms this nonplanar system into a more planar heptalene dianion with lesser degrees of bond alternation, reflecting high levels of Hückel aromaticity.

Spirocycles

M. J. James, J. D. Cuthbertson, P. O'Brien, R. J. K. Taylor,* W. P. Unsworth* ______ **7640 – 7643**

Silver(I)- or Copper(II)-Mediated Dearomatization of Aromatic Ynones: Direct Access to Spirocyclic Scaffolds

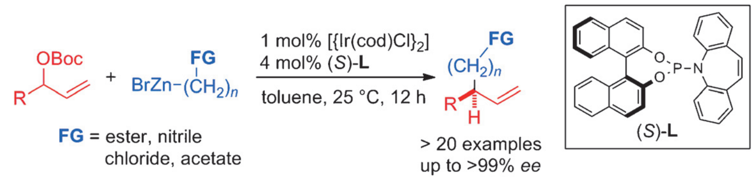


Dearomatization: Simple achiral aromatic compounds that contain ynone substituents, including indole, anisole, pyrrole, and benzofuran derivatives, can be converted into complex chiral spirocyclic scaffolds. The silver(I)-catalyzed dearomatizing spirocyclization typically provides the products in more than 95 % yield and up to 89:11 e.r.

Synthetic Methods

J. Y. Hamilton, D. Sarlah, E. M. Carreira* ______ **7644 – 7647**

Iridium-Catalyzed Enantioselective Allylic Alkylation with Functionalized Organozinc Bromides

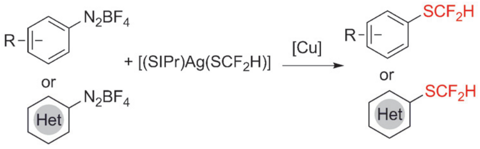


An Ir/(P,olefin) complex catalyzes the title reaction and the method provides a variety of allylated products with excellent regio- and stereoselectivities. The utility of the coupling is demonstrated in a catalytic enantioselective synthesis of a preclinical drug (−)-preclamol. Boc = *tert*-butyloxycarbonyl, cod = 1,5-cyclooctadiene.

Synthetic Methods

J. Wu, Y. Gu, X.-B. Leng, Q. Shen* ______ **7648 – 7652**

Copper-Promoted Sandmeyer Difluoromethylthiolation of Aryl and Heteroaryl Diazonium Salts

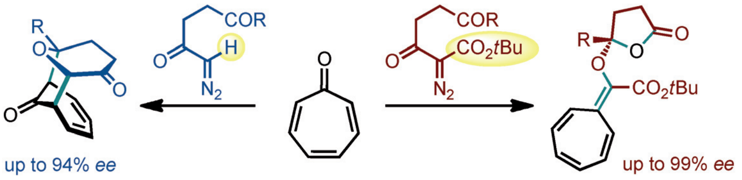


A dose of salt: The title reaction is conducted under mild reaction conditions and various functional groups are compatible. (Hetero)aryl diazonium salts reacted smoothly to afford the medicinally important difluoromethylthiolated (hetero)arenes. A practical one-pot direct diazotization and difluoromethylthiolation protocol was developed for aniline derivatives to generate difluoromethylthiolated arenes.

Asymmetric Cycloaddition

S. Murarka, Z.-J. Jia, C. Merten, C.-G. Daniliuc, A. P. Antonchick,* H. Waldmann* ______ **7653 – 7656**

Rhodium(II)-Catalyzed Enantioselective Synthesis of Troponoids

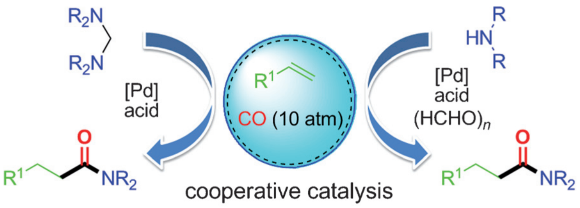


Decisive dipoles: In the rhodium(II)-catalyzed asymmetric 1,3-dipolar cycloaddition of tropone with carbonyl ylides, a programmable chemoselective reaction with the keto group or the 6π system of tropone was controlled by the substrate (see scheme). The developed method enables the synthesis of complex products in highly enantiomerically enriched form.

Synthetic Methods

G. Zhang, B. Gao,
H. Huang* ———— 7657 – 7661

Palladium-Catalyzed Hydroaminocarbonylation of Alkenes with Amines: A Strategy to Overcome the Basicity Barrier Imparted by Aliphatic Amines

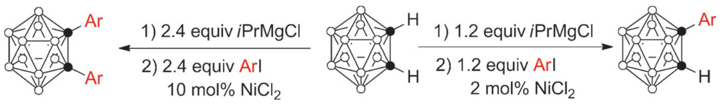


Back to basics: The basicity of aliphatic amines precludes their use in the palladium-catalyzed hydroaminocarbonylation. This issue was overcome by using aminals as surrogates of aliphatic amines. A cooperative catalytic system was discovered to operate by the synergistic combination of palladium, paraformaldehyde, and acid for promotion of the hydroaminocarbonylation of alkenes with both aromatic and aliphatic amines.

Carboranes

C. Tang, Z. Xie* ———— 7662 – 7665

Nickel-Catalyzed Cross-Coupling Reactions of *o*-Carboranyl with Aryl Iodides: Facile Synthesis of 1-Aryl-*o*-Carboranes and 1,2-Diaryl-*o*-Carboranes

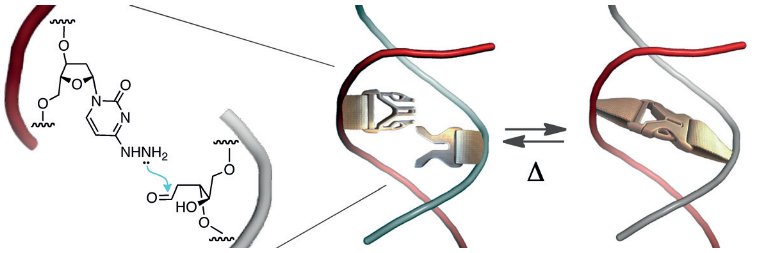


Rattling the cage: Cross-coupling of hypervalent cage carbon atoms with sp^2-carbon centers has been achieved under nickel catalysis. A series of 1-aryl-*o*-carboranes and 1,2-diaryl-*o*-carboranes can be synthesized and the methods also offer a facile and direct route for the incorporation of an *o*-carborane unit into conjugated π systems.

DNA Cross-Links

J. Gamboa Varela,
K. S. Gates* ———— 7666 – 7669

A Simple, High-Yield Synthesis of DNA Duplexes Containing a Covalent, Thermally Cleavable Interstrand Cross-Link at a Defined Location

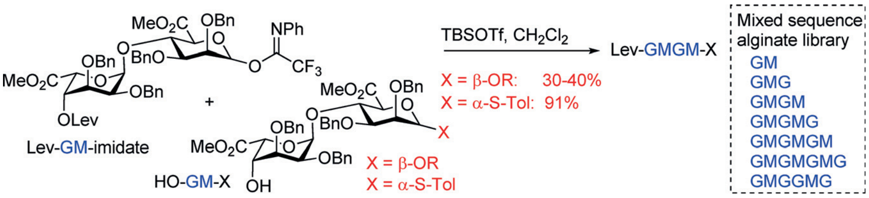


Reversibly linked: Simple post-synthetic modifications of commercially available 2′-deoxyoligonucleotides were employed to generate covalent, but thermally cleavable interstrand cross-links. The hydrazone cross-link was formed in a high yield at a single site in duplex DNA.

Oligosaccharides

Q. Zhang, E. R. van Rijssel,
M. T. C. Walvoort, H. S. Overkleeft,
G. A. van der Marel,
J. D. C. Codée* ———— 7670 – 7673

Acceptor Reactivity in the Total Synthesis of Alginate Fragments Containing α-L-Guluronic Acid and β-D-Mannuronic Acid

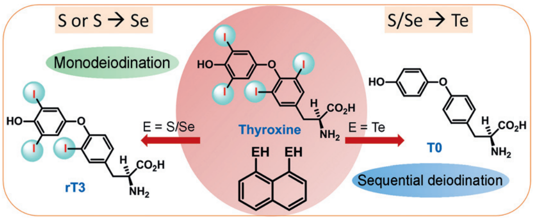


Mix it up: The first, fully stereoselective synthesis of a small library of mixed-sequence alginates, containing both α-L-guluronic and β-D-mannuronic acid residues, is reported. Key to the successful assembly of the oligomers is the use of conformationally flexible disaccharide acceptor building blocks. TBSOTf = *tert*-butyldimethylsilyl trifluoromethanesulfonate.

Bioorganic Chemistry

K. Raja, G. Mugesh* ______ 7674 – 7678

Remarkable Effect of Chalcogen Substitution on an Enzyme Mimetic for Deiodination of Thyroid Hormones

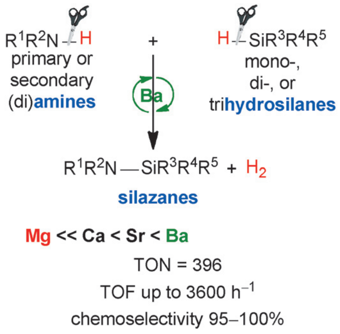


It's hormonal: The replacement of sulfur/selenium atoms in deiodinase mimetics by tellurium atoms remarkably alters the reactivity as well as regioselectivity toward thyroxine (T4). Sequential deiodinations of T4 by tellurium compounds produce all the thyroid hormone derivatives.

Synthetic Methods

C. Bellini, J.-F. Carpentier,* S. Tobisch,* Y. Sarazin* ______ 7679 – 7683

Barium-Mediated Cross-Dehydrocoupling of Hydrosilanes with Amines: A Theoretical and Experimental Approach

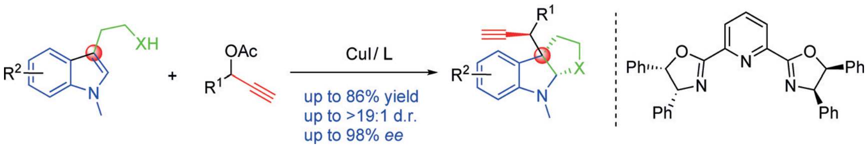


Raising the bar(ium): Alkaline-earth complexes of the type $[Ae\{N(SiMe_3)_2\}_2\cdot(THF)_x]$ and $[\{N^\wedge N\}Ae\{N(SiMe_3)_2\}\cdot(THF)_x]$ are very active, productive, and chemoselective precatalysts for the N–H/H–Si cross-dehydrocoupling of (di)amines with (di)hydrosilanes. The mechanisms have been elucidated by combining DFT and experimental data. THF = tetrahydrofuran, TOF = turnover frequency, TON = turnover number.

Asymmetric Catalysis

W. Shao, H. Li, C. Liu, C.-J. Liu,* S.-L. You* ______ 7684 – 7687

Copper-Catalyzed Intermolecular Asymmetric Propargylic Dearomatization of Indoles

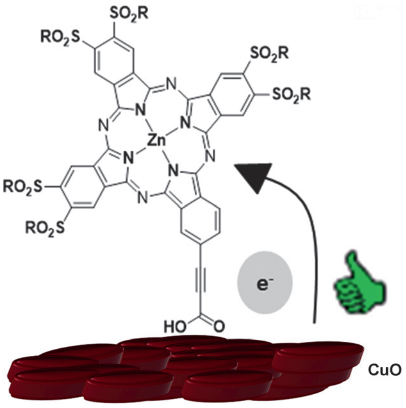


New sub: The title reaction provides a highly efficient synthesis of versatile furoindoline and pyrroloindoline derivatives containing a quaternary carbon stereogenic center and a terminal alkyne moiety with up to 86 % yield and 98 % *ee* by an asymmetric propargylic substitution reaction.

Photosensitizers

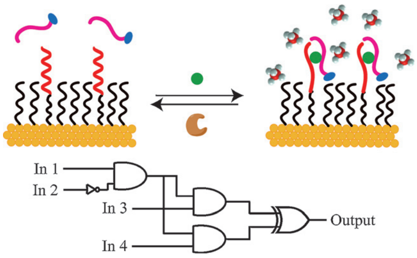
O. Langmar, C. R. Ganivet, A. Lennert, R. D. Costa,* G. de la Torre, T. Torres,* D. M. Guldi* ______ 7688 – 7692

Combining Electron-Accepting Phthalocyanines and Nanorod-like CuO Electrodes for p-Type Dye-Sensitized Solar Cells



The longer the better: Novel electron-accepting zinc phthalocyanines with different linker lengths performed well in combination with nanorod-like CuO electrodes in p-type dye-sensitized solar cells. A particularly high efficiency of 0.191 % was observed with a photosensitizer containing a carboxyethynyl anchor (see picture; R is a branched alkyl group).

Yes or no? A novel split aptamer-based multi-level logic gate, which is built from INHIBIT and AND gates, performs a net XOR analysis, with an electrochemical signal as output. This work reveals a new route for the design of bioelectronic logic circuits that can realize multi-level logic operations and which simplify an otherwise complex diagnosis to a yes/no decision.



Logic Gates

L. Feng, Z. Lyu, A. Offenhäusser,
D. Mayer* ______ **7693 – 7697**

Multi-Level Logic Gate Operation Based on Amplified Aptasensor Performance

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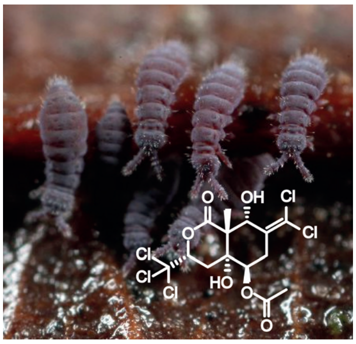
Inedible: The snow flea *Ceratophysella sigillata* produces unique polychlorinated octahydroisocoumarins to repel predators. The structure of the major representative, sigillin A, was elucidated through isolation, spectroscopic analysis, and X-ray crystallography. A promising synthetic approach for the total synthesis of this class of compounds was developed, in which α-vinylation of a lactone and ring-closing metathesis are the key steps. (Image: F. Kohl)

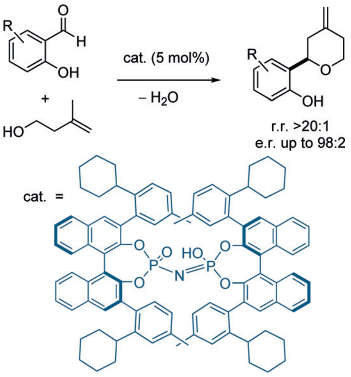


Chlorinated Repellents

W. Schmidt, T. M. Schulze, G. Brasse,
E. Nagrodzka, M. Maczka, J. Zettel,
P. G. Jones, J. Grunenberg, M. Hilker,
U. Trauer-Kizilelma, U. Braun,
S. Schulz* ______ **7698 – 7702**

Sigillin A, a Unique Polychlorinated Arthropod Deterrent from the Snow Flea *Ceratophysella sigillata*

A bulky cat.: In an organocatalytic asymmetric Prins cyclization, salicylaldehydes react with 3-methyl-3-buten-1-ol in the presence of a chiral imidodiphosphoric acid catalyst to afford highly functionalized 4-methylenetetrahydropyrans in excellent regio- and enantioselectivities (see scheme).

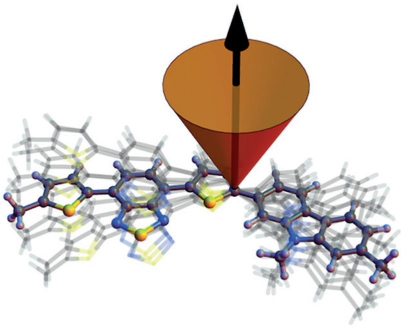


Organocatalysis

G. C. Tsui, L. Liu, B. List* ______ **7703 – 7706**

The Organocatalytic Asymmetric Prins Cyclization

Probing polymer morphology through triplet excitons: Controlling morphology is crucial for the development of efficient organic solar cells. PCDTBT, a promising conjugated polymer in organic photovoltaics, is oriented face-on when cast on PET film. Time-resolved electron paramagnetic resonance spectroscopy of its triplet excitons reveals both the orientation with respect to the surface and the degree of ordering (see picture).



Molecular Ordering in the Solid State

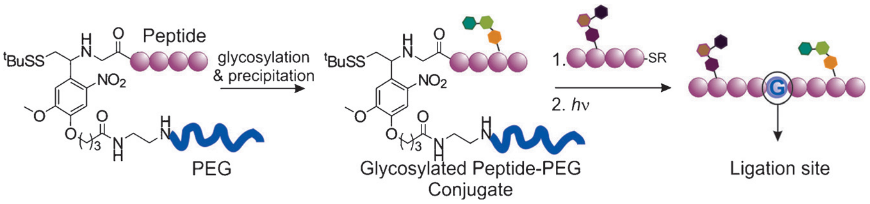
T. Biskup,* M. Sommer, S. Rein,
D. L. Meyer, M. Kohlstädt, U. Würfel,
S. Weber ______ **7707 – 7710**

Ordering of PCDTBT Revealed by Time-Resolved Electron Paramagnetic Resonance Spectroscopy of Its Triplet Excitons

Peptide Linkage

C. Bello, S. Wang, L. Meng,
K. W. Moremen,
C. F. W. Becker* ———— **7711–7715**

A PEGylated Photocleavable Auxiliary Mediates the Sequential Enzymatic Glycosylation and Native Chemical Ligation of Peptides



Two in one: An efficient approach for the preparation of modified peptides has been applied to the synthesis of O-glycosylated MUC1 repeats. A photocleavable PEGylated auxiliary mediates the sequential O-glycosylation and subsequent ligation of MUC1 peptides.

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

Crystallographic Snapshot of an Arrested Intermediate in the Biomimetic Activation of CO_2

S. L. Ackermann, D. J. Wolstenholme,*
C. Frazee, G. Deslongchamps,
S. H. M. Riley, A. Decken,
G. S. McGrady* ———— **164–168**

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

DOI: 10.1002/anie.201407165

The authors of this Communication now believe that a single crystal of a $[(n\text{-}C_4H_9)_4N]^+[CH_3CO_2]^-$ impurity in their bulk sample was misidentified as $[(n\text{-}C_4H_9)_4N]^+[O_2C\cdots OH]^-$ in their original report. This was interpreted as an arrested intermediate in the base-mediated activation of CO_2, indicating an egregiously long C—O(H) bond that is in fact the C—C bond of the $[CH_3CO_2]^-$ salt. However, the biomimetic nature of the hydrophobic pockets in $[(n\text{-}C_4H_9)_4N]^+[CH_3CO_2]^-$ still offers valuable insights into the substrate binding sites in human carbonic anhydrase II, since the geometry of the weak hydrogen bonding is identical to the interactions that tether CO_2 to the pockets of this metalloenzyme. Moreover, the computational component of the original study revealed a three-stage process for the base-mediated activation of CO_2, which is independent of the experimental structural study.