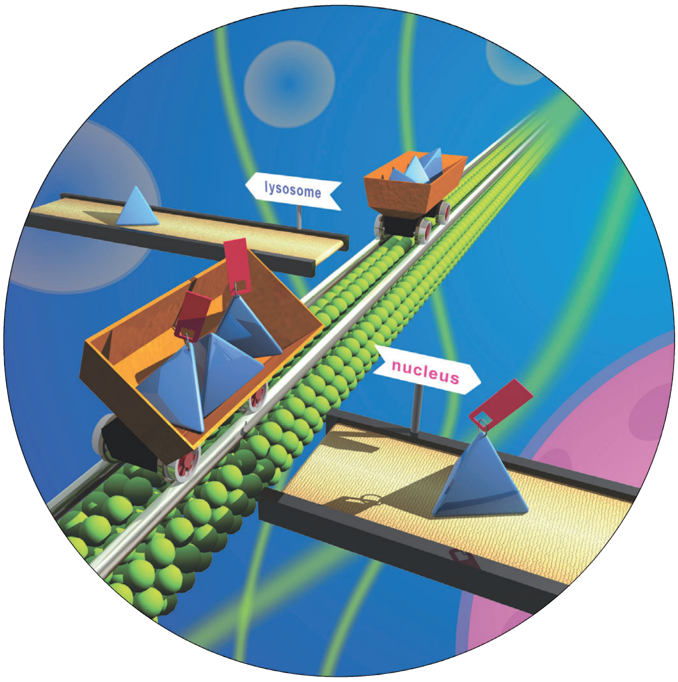
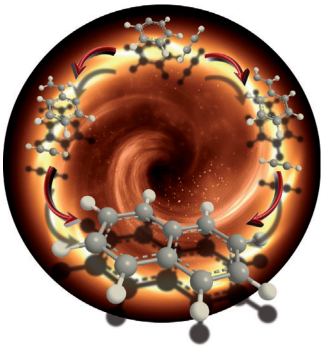
Tetrahedral DNA nanostructures ...

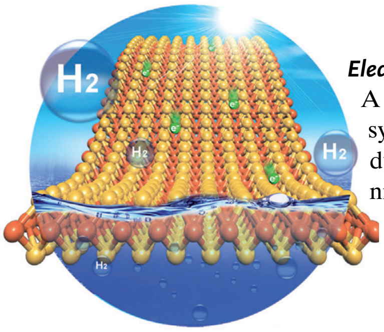


… can be readily taken up by cells. In their Communication on page 7745 ff., C. Fan, Q. Huang, and co-workers investigate the endocytotic internalization into mammalian cells and subsequent transport of these self-assembled DNA nanostructures by single-particle tracking. These results constitute the next step toward the development of novel drug-delivery systems based on nucleic acids.

Gas-Phase Chemistry

In their Communication on page 7740 ff., R. I. Kaiser, M. Ahmed et al. use photo-ionization mass spectrometry to show the formation of naphthalene in the gas phase through the reaction of a phenyl radical with two acetylene molecules.





Electrocatalysis

A high-temperature solution-phase method for the synthesis of ultrathin WS_2 nanoflakes is introduced by Z. Liu, Y. G. Li et al. in their Communication on page 7860 ff.

Lithium-Ion Batteries

In their Communication on page 7864 ff., Y. Wang, H. Peng et al. describe a wire-shaped lithium-ion battery that consists of two composite yarns, made from aligned multi-walled carbon nanotubes and lithium oxides, as the anode and cathode.

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Editorial

"… Future generations of chemists will increasingly contribute to solving complex biology problems. For many subjects in the life sciences, chemistry is already essential today. The more that chemists are willing to look into biological questions, the closer we get to true interdisciplinarity. An institute for basic-science research in biology such as EMBL is a fantastic host for such projects and indeed for chemists …"
Read more in the Editorial by Carsten Schultz.

Service

Author Profile

"My favorite place on earth is under water. Guaranteed to make me laugh is a good pun. …"
This and more about Alexander Heckel can be found on page 7704.

News


J.-F. Carpentier


G. Dantelle


R. Nicolaÿ


Y. Pellegrin


F. Pointillart


D. Touboul


R. Lill


P. R. Wich

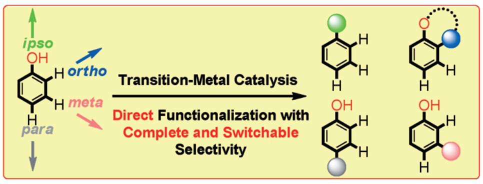

F. M. Bickelhaupt

Books

Highlights

Switchable Selectivity

Direct Functionalization with Complete and Switchable Positional Control: Free Phenol as a Role Model



PhenAll: Recent breakthroughs in site-selective and direct functionalization of free phenols by transition-metal-catalyzed C–O or C–H bond activation are highlighted here as role models for the complete and switchable positional control of transformations of important core structures.

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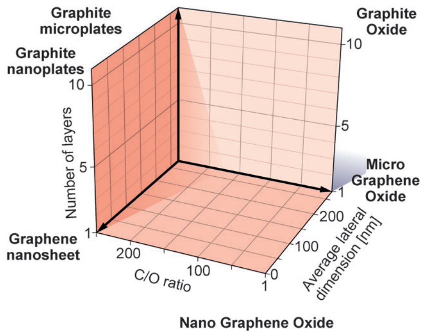
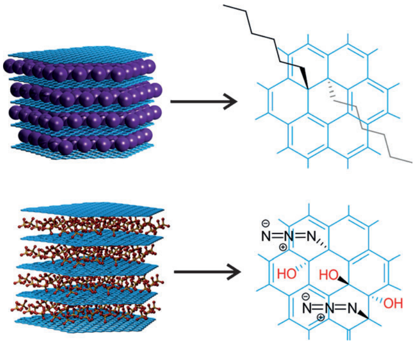
Essays

Graphing graphene: Because the naming of graphene-based materials (GBMs) has led to confusion and inconsistency, a classification approach is necessary. Three physical-chemical properties of GBMs have been defined by the GRAPHENE Flagship Project of the European Union for the unequivocal classification of these materials (see grid).



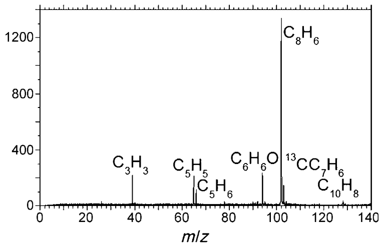
Reviews

The well-controlled synthesis of new graphene and graphene oxide derivatives as well as determination of the atomic structure are key challenges for synthetic chemists. Structure–property relationships must be exploited to use the full potential of graphene derivatives in upcoming applications. This Review focuses on concepts in the chemistry of graphene and graphene oxide with the aim of encouraging chemists to enhance the field of research.



Communications

Formation of naphthalene: The prototype polycyclic aromatic hydrocarbon naphthalene is shown by photo-ionization mass spectrometry to be formed in the gas phase through the reaction of a phenyl radical with two acetylene molecules (see picture). The first direct experimental evidence of the existence of the hydrogen abstraction–acetylene addition mechanism is given which so far had only been speculated theoretically.

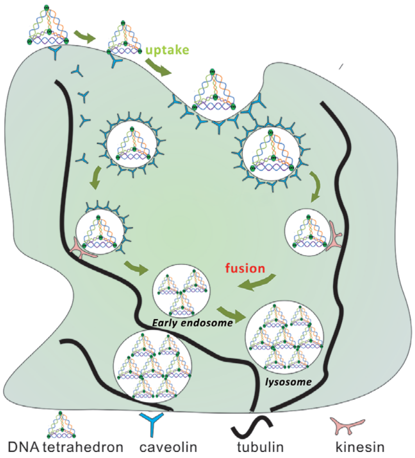


DNA Nanostructures

L. Liang, J. Li, Q. Li, Q. Huang,* J. Shi, H. Yan, C. Fan* ______ **7745 – 7750**

Single-Particle Tracking and Modulation of Cell Entry Pathways of a Tetrahedral DNA Nanostructure in Live Cells

Front Cover



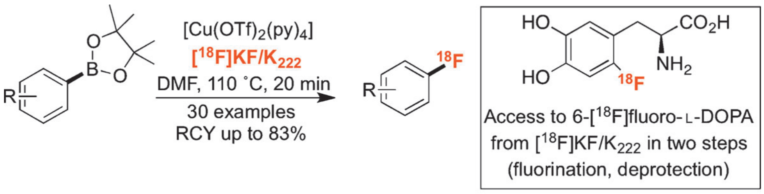
Transported to a better place: The endocytotic internalization of tetrahedral DNA nanostructures (TDNs) into cells by a caveolin-dependent pathway was investigated through single-particle tracking. The subsequent microtubule-dependent transport of the TDNs to the lysosomes for digestion (see figure) could be redirected to the nucleus by functionalization of the TDNs.

Radiochemistry

M. Tredwell, S. M. Preshlock, N. J. Taylor, S. Gruber, M. Huiban, J. Passchier, J. Mercier, C. Génicot, V. Gouverneur* ______ **7751 – 7755**

A General Copper-Mediated Nucleophilic ^{18}F Fluorination of Arenes

Inside Cover

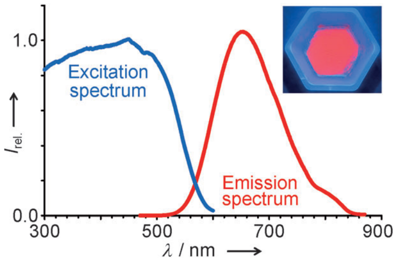


^{18}F-labeling for PET: The nucleophilic ^{18}F fluorination of pinacol-derived aryl boronic esters is achieved with [^{18}F]KF/K$_{222}$ in the presence of [Cu(OTf)$_2$(py)$_4$] (OTf = trifluoromethanesulfonate, py = pyridine); this unprecedented method can produce a clinical dose of 6-[^{18}F]fluoro-L-DOPA in two steps (fluorination followed by deprotection) from a readily available shelf-stable arylBPin precursor (see scheme). RCY = decay-corrected radiochemical yield

Red Phosphors

Y. Sato,* H. Kato, M. Kobayashi, T. Masaki, D. H. Yoon, M. Kakihana* ______ **7756 – 7759**

Tailoring of Deep-Red Luminescence in Ca_2SiO_4:Eu^{2+}

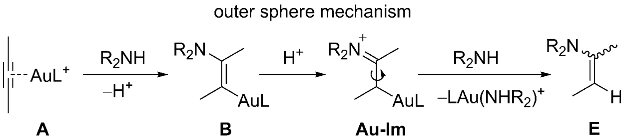


A dicalcium silicate phosphor, $Ca_{2-x}Eu_xSiO_4$, emits red light in response to blue-light excitation. When excited at 450 nm, deep-red emission at 650 nm was clearly observed in $Ca_{1.2}Eu_{0.8}SiO_4$. The picture shows a photograph of the corresponding $Ca_{1.20}Eu_{0.80}SiO_4$ phosphor upon excitation with blue LEDs. The external and internal quantum efficiencies were 44% and 50%, respectively.

Gold Catalysis

A. Zhdanko,* M. E. Maier* _ **7760 – 7764**

Mechanistic Study of Gold(I)-Catalyzed Hydroamination of Alkynes: Outer or Inner Sphere Mechanism?



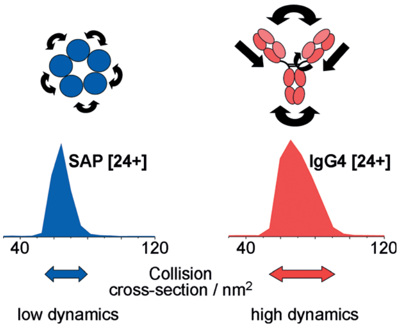
Which way is right? Experimental mechanistic study of hydroamination reveals the formation of conformationally flexible auro-iminium salts **Au-Im**, which originate from protonation of the vinyl gold species **B**. Rotation around the C–CAu bond is the reason for the loss of stereospecificity of protodeauration, which explains earlier stereochemical results. This shows that the reaction proceeds through the outer sphere mechanism.

Conformation Analysis

K. J. Pacholarz, M. Porrini, R. A. Garlish,
R. J. Burnley, R. J. Taylor, A. J. Henry,
P. E. Barran* ________ **7765 – 7769**

Dynamics of Intact Immunoglobulin G Explored by Drift-Tube Ion-Mobility Mass Spectrometry and Molecular Modeling

Dancing antibodies: Collision cross-sections of immunoglobulins G1 and G4 have been determined using linear drift-tube ion-mobility mass spectrometry. Intact antibodies and Fc hinge fragments possess far higher intrinsic flexibility than proteins of comparable size. This is rationalized with MD simulations, which reveal dynamics between linked folded domains. The IgG1 subclass is less dynamic than the IgG4 subclass in the absence of solvent.

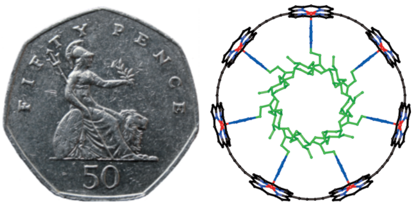


Template-Directed Synthesis

P. Liu, P. Neuhaus, D. V. Kondratuk,
T. S. Balaban,
H. L. Anderson* ________ **7770 – 7773**

Cyclodextrin-Templated Porphyrin Nanorings

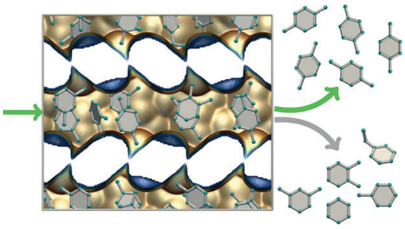
Floppy yet effective: Cyclodextrins have been decorated with pyridine legs to create chiral templates for directing the synthesis of nanorings consisting of six or seven zinc porphyrin macrocycles. The flexibility of these cyclodextrin derivatives does not make them less effective as templates, and it only slightly reduces the cooperativity of their interactions with the nanorings.



Metal–Organic Frameworks

A. Torres-Knoop, R. Krishna,
D. Dubbeldam* ________ **7774 – 7778**

Separating Xylene Isomers by Commensurate Stacking of *p*-Xylene within Channels of MAF-X8

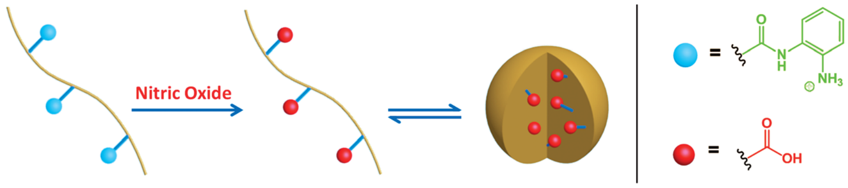


Think inside the box: By viewing the channels of metal–organic frameworks as “bookshelves”, we can exploit the concept of commensurate stacking to design highly *para*-xylene selective structures. A screening study reveals the metal–organic framework MAF-X8 possesses this property and is found to be superior to currently used technology such as BaX zeolite.

NO-Responsive Polymers

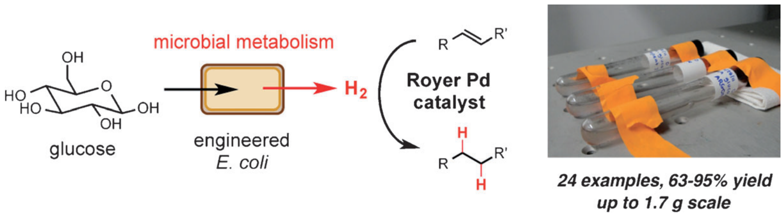
J. Hu, M. R. Whittaker, H. Duong, Y. Li,
C. Boyer,* T. P. Davis* ________ **7779 – 7784**

Biomimetic Polymers Responsive to a Biological Signaling Molecule: Nitric Oxide Triggered Reversible Self-assembly of Single Macromolecular Chains into Nanoparticles



NO problem: Polymerization of NO-responsive monomers containing *o*-phenylenediamine functional groups has led to the formation of NO-responsive macromolecular chains that act as truly biomimetic polymers. Exposure to NO results in the thermoresponsive copolymers undergoing self-assembly into micellar structures (see example). The NO-triggered self-assembly process with turn on fluorescence was further used to image endogenous NO.

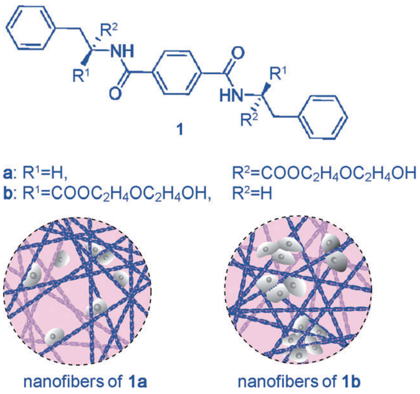
Biotransformations



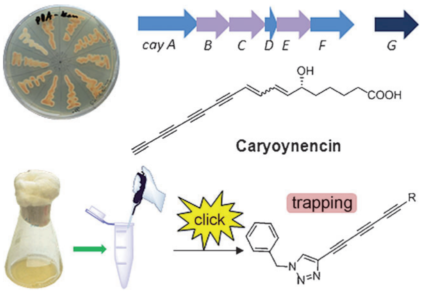
Reduction to practice: A hydrogenation reaction has been developed that employs hydrogen generated in situ by a microorganism and a biocompatible palladium catalyst to reduce alkenes on a synthetically useful scale. This type of transformation, which directly combines tools from organic chemistry with the metabolism of a living organism for small-molecule production, represents a new strategy for chemical synthesis.

Chiral Hydrogels

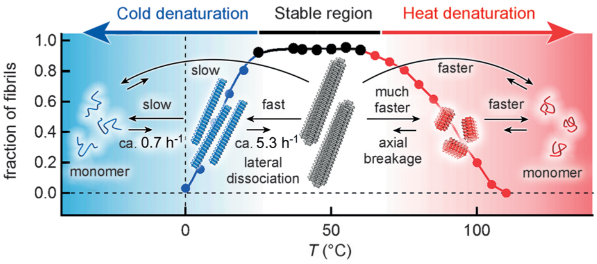
A blockbuster in 3D: Cell behavior in a 3D environment was greatly influenced by the chirality of nanofibers created by supramolecular hydrogelators. Only one enantiomer of a 1,4-benzenedicarboxamide phenylalanine derivative **1** formed nanofibers that led to high cell-adhesion and cell-proliferation densities (bottom right). Models of the extracellular matrix designed by this strategy could provide the desirable cell density for tissue engineering.



Biosynthesis



Triple trouble: The genes for a bacterial polyyne biosynthesis pathway were discovered in the plant pathogen *Burkholderia caryophylli*. Caryoynencin biosynthesis involves bacteria-specific desaturases/acetylenases and a cytochrome P450 monooxygenase. Highly fragile polyynes were successfully trapped and isolated from a crude metabolite mixture by an in situ click reaction. Homologous polyyne gene clusters were found in various bacterial genomes.

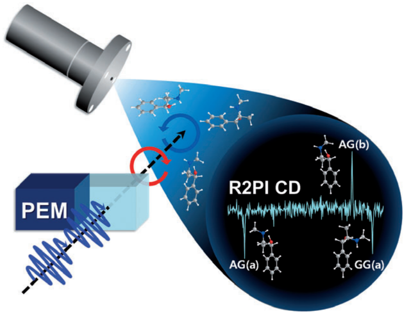


Chilling stress causes stable α-synuclein fibrils to dissociate into monomers. Monomers detach directly from the fibril ends. Amyloid-specific charge repulsion caused by the burial of charged residues in fibril cores induces cold denaturation of α-synuclein fibrils. At elevated temperatures, the dissociation of monomers from fibril ends also takes place, which is further amplified by fibril breakage.

Amyloid Fibrils

T. Ikenoue, Y.-H. Lee, J. Kardos, M. Saiki, H. Yagi, Y. Kawata, Y. Goto* **7799 – 7804**

Cold Denaturation of α-Synuclein Amyloid Fibrils

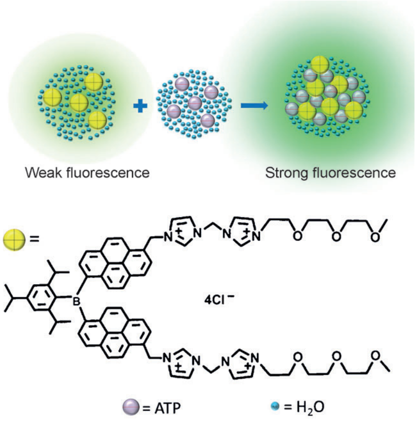


Taking the pulse: Conformation-specific circular dichroism spectra of cold chiral molecules in a supersonic jet were obtained using circularly polarized laser pulses generated by synchronizing the firing of nanosecond laser pulses to the oscillation of a photoelastic modulator (PEM). Reported herein is the first resonant two-photon ionization (R2PI) CD spectra of ephedrine using the method.

Laser Spectroscopy

A. Hong, C. M. Choi, H. J. Eun, C. Jeong, J. Heo,* N. J. Kim* ______ **7805 – 7808**

Conformation-Specific Circular Dichroism Spectroscopy of Cold, Isolated Chiral Molecules



Tracking device: The triarylboron compound in the scheme displays an apparent ATP-dependent fluorescence enhancement. The analyte, ATP, induces finite aggregation and endows the indicator with appreciable photostability and superior tolerance to environmental electrolytes, thus leading to its successful application to the monitoring of ATP levels in vitro and in vivo. ATP = adenosine 5′-triphosphate.

Fluorescence Probes

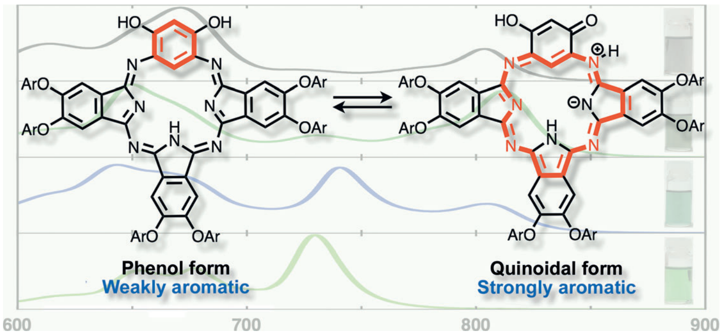
X. Y. Li, X. D. Guo, L. X. Cao, Z. Q. Xun, S. Q. Wang, S. Y. Li,* Y. Li,* G. Q. Yang* ____________ **7809 – 7813**

Water-Soluble Triarylboron Compound for ATP Imaging In Vivo Using Analyte-Induced Finite Aggregation

Phthalocyanine Analogues

N. Toriumi, A. Muranaka,* K. Hirano,
K. Yoshida, D. Hashizume,
M. Uchiyama* ____________ **7814 – 7818**

18π-Electron Tautomeric Benziphthalocyanine: A Functional Near-Infrared Dye with Tunable Aromaticity

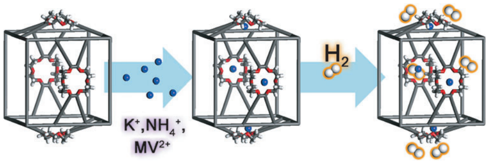


Controlling tautomerism: An 18π-electron aromatic benziphthalocyanine consists of two 18π-electron tautomers, a weakly aromatic phenol form, and a strongly aromatic quinoidal form. This equilibrium can be controlled by chemical modification and by solvent effects, enabling tuning of the aromaticity and near-infrared absorption.

Metal–Organic Frameworks

D.-W. Lim, S. A. Chyun,
M. P. Suh* ____________ **7819 – 7822**

Hydrogen Storage in a Potassium-Ion-Bound Metal–Organic Framework Incorporating Crown Ether Struts as Specific Cation Binding Sites

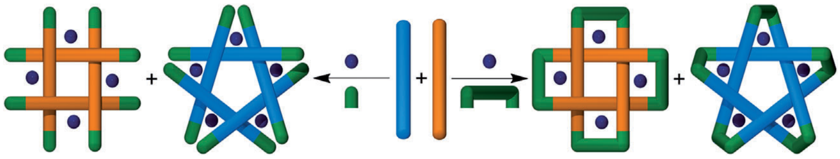


Crown ethers strut their stuff: The metal–organic framework SNU-200 incorporates 18-crown-6 moieties as a cation binding site. SNU-200 binds K^+, NH_4^+, and methyl viologen^{2+} (MV^{2+}) and their counterions. Its gas sorption properties depend on the bound cation. The K^+/SCN^- bound SNU-200 shows the highest isosteric heat (9.92 kJ mol^{-1}) of H_2 adsorption, a result of the open metal sites on the K^+ ions.

Supramolecular Chemistry

J.-F. Ayme, J. E. Beves, C. J. Campbell,
D. A. Leigh* ____________ **7823 – 7827**

The Self-Sorting Behavior of Circular Helicates and Molecular Knots and Links



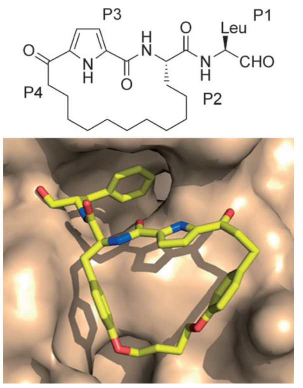
It takes all sorts: Tris(bidentate) ligand strands that differ in length by just two atoms self-sort into circular helicates of different sizes with a monoamine and into different molecular topologies—a molecular Solomon link and a pentafoil knot—with a diamine (see picture).

β-Strand Templates

K. C. H. Chua, M. Pietsch, X. Zhang,
S. Hautmann, H. Y. Chan, J. B. Bruning,
M. Gütschow, A. D. Abell* _ **7828 – 7831**

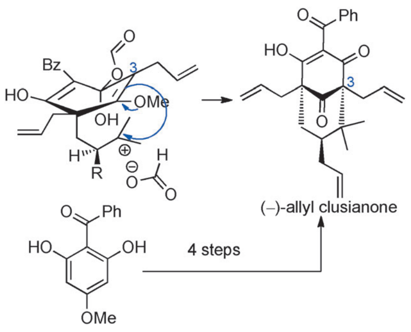
Macrocyclic Protease Inhibitors with Reduced Peptide Character

The incorporation of a pyrrole into a peptide backbone generates simple macrocycles that adopt a β-strand geometry. The attachment of a P1 amino aldehyde to these templates then gives rise to potent protease inhibitors (see example, top, which has K_i values of 440 pM and 920 pM against the cysteine cathepsins L and S, respectively). A crystal structure of a related derivative bound to chymotrypsin (see picture, bottom) confirms the design.



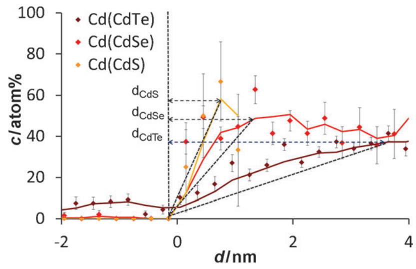
Natural Product Synthesis

Aim for selectivity: (−)-Clusianone was produced by a stereodivergent asymmetric total synthesis in six steps from commercial materials. The synthesis utilizes a challenging formic acid-mediated cationic cyclization forging a bond between two sterically encumbered quaternary carbon atoms.

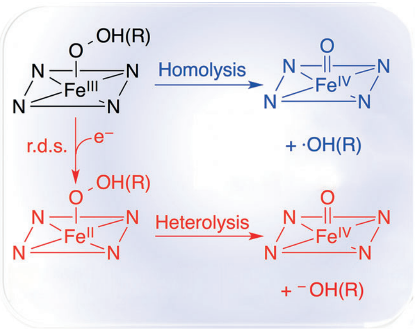


Heterojunction-Mediated Catalysis

That's a (quantum dot) wrap! A series of highly active semiconductor photocatalysts have been synthesized by growing wurtzite-ZnO tetrahedrons around preformed CdS, CdSe, and CdTe quantum dots. The resulting heterostructured CdX/ZnO nanocrystals with extensive type-II nanojunctions exhibit rapid photocatalytic decomposition of organic molecules in aqueous media.

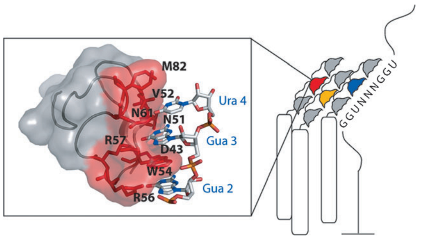


Enzyme Models



Ironed out: One-electron reduction of mononuclear nonheme Fe^{III}–OOH and Fe^{III}–OOR complexes by ferrocene derivatives resulted in the formation of the corresponding $Fe^{IV}O$ complexes. Reduction of the Fe^{III} to Fe^{II} species is the rate-determining step (r.d.s.), followed by the heterolytic O–O bond cleavage to give the $Fe^{IV}O$ complexes. The results provide the first example of this pathway to form $Fe^{IV}O$ intermediates which occur in nonheme iron enzymatic and Fenton reactions.

Protein Design

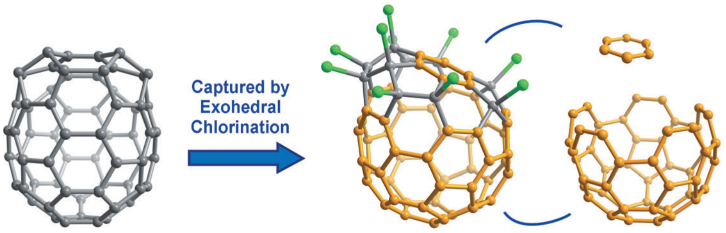


Variation on a theme: A combinatorial library of RanBP2-type zinc finger (ZF) domains has been engineered in an effort to select variants with distinct RNA-binding preferences. One variant was shown to successfully discriminate the sequence GCC over GGU and AAA, but only in the context of a three-ZF polypeptide. This study provides proof of principle that the specificity of RNA-binding modules based on ZF domains can be successfully altered.

Fullerenes

C. L. Gao, X. Li, Y. Z. Tan, X. Z. Wu,
Q. Y. Zhang, S. Y. Xie,*
R. B. Huang ——— 7853 – 7855

Synthesis of Long-Sought C_{66} with Exohedral Stabilization

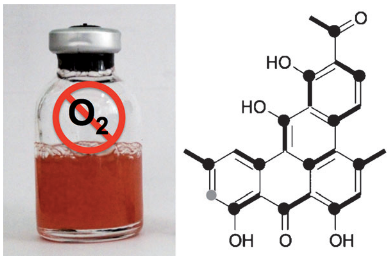


Captured at last! Elusive $^{\#4348}C_{66}$ was stabilized exohedrally to give a fullerene derivative identified as $^{\#4348}C_{66}Cl_{10}$ by X-ray single-crystal diffraction (see picture). The isolation of this chlorofullerene supports the existence of $^{\#4348}C_{66}$ in the carbon arc.

Natural Products

S. Pidot, K. Ishida, M. Cyrulies,
C. Hertweck* ——— 7856 – 7859

Discovery of Clostrubin, an Exceptional Polyphenolic Polyketide Antibiotic from a Strictly Anaerobic Bacterium



Hold your breath: Genomics-based metabolic profiling of *Clostridium beijerinckii* led to the discovery of clostrubin, the first polyketide isolated from an obligate anaerobe. The unusual polyphenolic compound demonstrates pronounced antibiotic activity against a variety of bacterial pathogens. Isotope labeling revealed that the novel ring topology results from noncanonical chain folding that deviates from the pathways used by aerobic microorganisms.

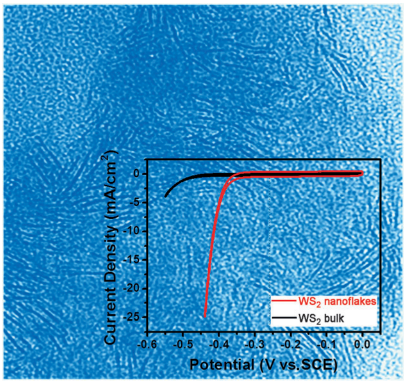
Electrocatalysis

L. Cheng, W. J. Huang, Q. F. Gong,
C. H. Liu, Z. Liu,* Y. G. Li,*
H. J. Dai ——— 7860 – 7863

Ultrathin WS_2 Nanoflakes as a High-Performance Electrocatalyst for the Hydrogen Evolution Reaction

Inside Back Cover

Ultrathin WS_2 nanoflakes were synthesized according to a new high-temperature solution-phase method. These nanoflakes may be used as efficient catalysts for the electrocatalytic hydrogen evolution reaction and represent an attractive alternative to the expensive platinum benchmark catalysts.

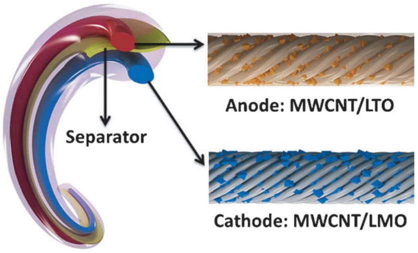


Lithium-Ion Batteries

J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang,
X. Fang, W. Weng, Y. Wang,*
H. Peng* ——— 7864 – 7869

Elastic and Wearable Wire-Shaped Lithium-Ion Battery with High Electrochemical Performance

Back Cover

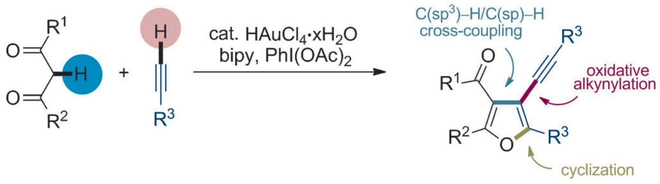


Super-stretchy: A novel and safe wire-shaped lithium-ion battery consists of two composite yarns, which were made from aligned multi-walled carbon nanotubes (MWCNT) and lithium titanium oxide (LTO) or lithium manganese oxide (LMO), as the anode and cathode. These wire-shaped batteries were woven into light, flexible, and stretchable battery textiles.

Homogeneous Catalysis

Y. Ma, S. Zhang, S. Yang, F. Song,*
J. You* ________________ 7870 – 7874

Gold-Catalyzed C(sp^3)−H/C(sp)−H Coupling/Cyclization/Oxidative Alkynylation Sequence: A Powerful Strategy for the Synthesis of 3-Alkynyl Polysubstituted Furans

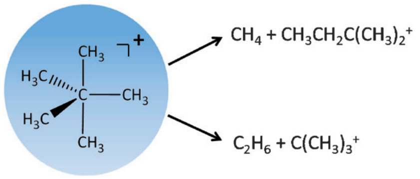


Pure and simple: The first gold-catalyzed C(sp^3)−H/C(sp)−H cross-coupling/cyclization/oxidative alkynylation sequence of 1,3-dicarbonyl compounds reacting with terminal alkynes has been achieved under mild reaction conditions by taking advantage of the unique redox property and carbophilic π acidity of gold. Ultimately, 3-alkynyl polysubstituted furans are synthesized concisely and regiospecifically from simple starting materials.

Bond Theory

W. C. McKee, J. Agarwal,
H. F. Schaefer, III,
P. von R. Schleyer* ________ 7875 – 7878

Covalent Hypercoordination: Can Carbon Bind Five Methyl Ligands?



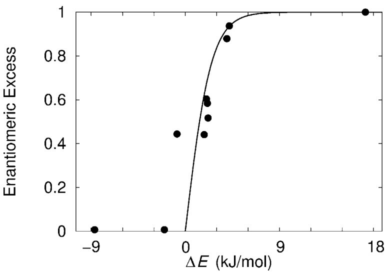
$C(CH_3)_5^+$ is the first example of a five-coordinate carbon atom bound only to separate (monodentate) carbon ligands. This species illustrates the limits of carbon bonding, exhibiting Lewis-violating "electron-deficient bonds" between the hypercoordinate carbon and its methyl groups. Though not kinetically persistent under standard laboratory conditions, its dissociation activation barriers may permit $C(CH_3)_5^+$ fleeting existence near 0 K.

Solubility Determination

A. Otero-de-la-Roza, B. H. Cao, I. K. Price,
J. E. Hein, E. R. Johnson* __ 7879 – 7882

Predicting the Relative Solubilities of Racemic and Enantiopure Crystals by Density-Functional Theory

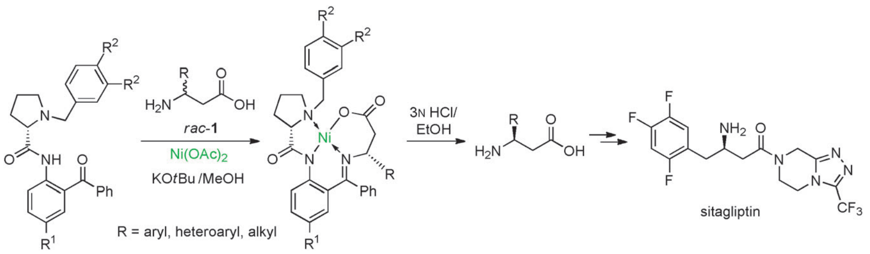
Solubility forecasting: Using a simple thermodynamic model and first-principles density-functional calculations, it is possible to predict the difference in solubility between the enantiopure and racemic solid phases. This approach uses dispersion-corrected density functionals and on average it is capable of accurately predicting the solution-phase enantiomeric excess to within about 10% of experimental measurements (see picture).



Enantioselectivity

S. B. Zhou, J. Wang, X. Chen, J. L. Aceña,
V. A. Soloshonok,* H. Liu* _ 7883 – 7886

Chemical Kinetic Resolution of Unprotected β-Substituted β-Amino Acids Using Recyclable Chiral Ligands



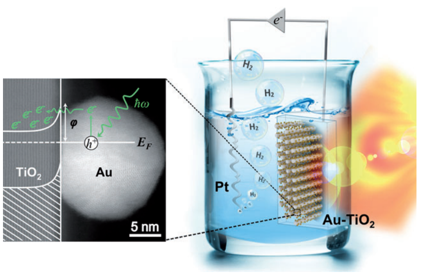
The nick of time: A chemical method for resolution of unprotected β-amino acids *rac*-**1** was developed through enantioselective formation and disassembly of nickel(II) complexes to deliver the target β-substituted β-amino acids in good yields and excellent enantioselectivity. The chiral ligands are inexpensive and can be quantitatively recycled. The procedure was used for the preparation of anti-diabetic drug sitagliptin.

Plasmonic Photoelectrochemistry

J. S. DuChene, B. C. Sweeny,
A. C. Johnston-Peck, D. Su, E. A. Stach,
W. D. Wei* ______________ **7887 – 7891**

Prolonged Hot Electron Dynamics in Plasmonic-Metal/Semiconductor Heterostructures with Implications for Solar Photocatalysis

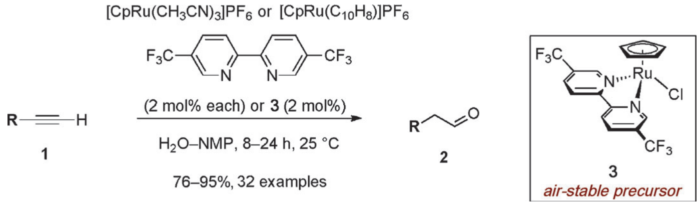
Harvesting hot electrons: Plasmon-mediated electron transfer (PMET) in plasmonic (Au/TiO_2) photoanodes provides a unique pathway for procuring excited-state electrons that exhibit lifetimes commensurate with the prolonged timescales required for solar photochemistry. These long-lived electrons were harnessed for visible-light-driven hydrogen evolution from water (see picture).



Homogeneous Catalysis

L. Li, M. Zeng,
S. B. Herzon* ______________ **7892 – 7895**

Broad-Spectrum Catalysts for the Ambient Temperature Anti-Markovnikov Hydration of Alkynes

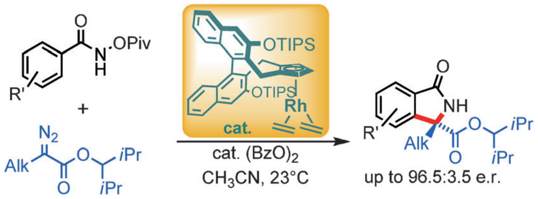


Alkyne hydration: Half-sandwich ruthenium complexes derived from 5,5′-bis(trifluoromethyl)-2,2′-bipyridine show a high activity for the anti-Markovnikov hydration of terminal alkynes (see picture). A wide array of alkynes are efficiently hydrated to aldehydes using 2 mol% metal loadings at 25 °C within 8–24 h.

C–H Activation

B. Ye, N. Cramer* ______________ **7896 – 7899**

Asymmetric Synthesis of Isoindolones by Chiral Cyclopentadienyl-Rhodium(III)-Catalyzed C–H Functionalizations



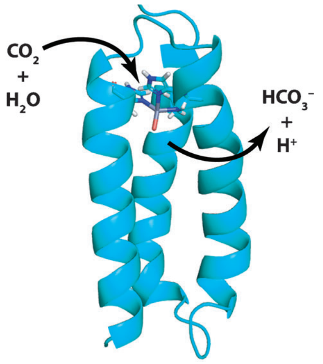
Heterocycle synthesis: Chiral isoindolones are obtained by rhodium(III)-catalyzed enantioselective reactions of aryl hydroxamates with alkyl-substituted diazo esters through C–H functionalization under mild conditions. Chiral cyclopentadienyl ligands with a biaryl backbone lead to excellent enantioselectivities.

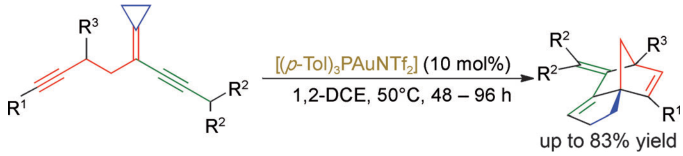
Metalloenzyme Design

V. M. Cangelosi, A. Deb,
J. E. Penner-Hahn,
V. L. Pecoraro* ______________ **7900 – 7903**

A De Novo Designed Metalloenzyme for the Hydration of CO_2

Chasing down the cheetah: A synthetic metalloenzyme was created that is capable of catalyzing the hydration of carbon dioxide with an efficiency within 1400-fold of carbonic anhydrase II, one of the most efficient enzymes known. This designed zinc enzyme performs better than small-molecule models of carbonic anhydrase. Picture: Zn purple, N dark blue, O red, C cyan.



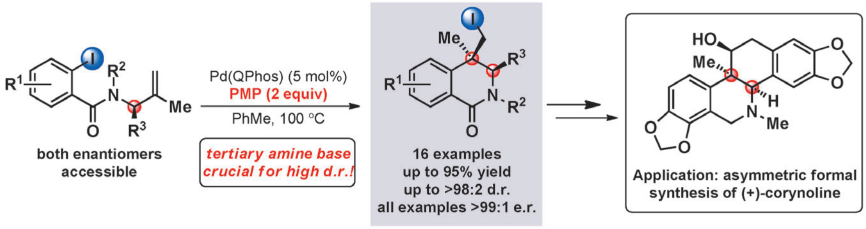


When gold met alkylidenecyclopropane: Cationic gold catalysts can mediate the highly exothermic (≈60 kcal mol^{-1}) cycloisomerization of 1,6-diynes bearing an alkylidene cyclopropane moiety. This diastereoselective methodology efficiently generates 1,2-trimethylenenorbornanes, an important building block for abiotic targets and sesquiterpene natural products. DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl, Tol = Tolyl.

Gold Catalysis

H. Zheng, L. L. Adduci, R. J. Felix, M. R. Gagné* ______ **7904 – 7907**

Gold-Catalyzed Diastereoselective Cycloisomerization of Alkylidene-Cyclopropane-Bearing 1,6-Diynes



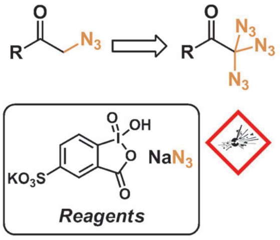
A-mean combination: A general and efficient synthesis of chiral dihydroisoquinolinones by a highly diastereoselective Pd⁰-catalyzed carboiodination is reported. As an additive, the bulky tertiary amine base PMP (1,2,2,6,6-pentamethylpiperidine) is presumed to act as a weakly coordinating ligand, leading to a significant and general increase in diastereoselectivity. The utility of the method was applied to the asymmetric formal synthesis of (+)-corynoline.

Carboiodination

D. A. Petrone, H. Yoon, H. Weinstabl, M. Lautens* ______ **7908 – 7912**

Additive Effects in the Palladium-Catalyzed Carboiodination of Chiral *N*-Allyl Carboxamides

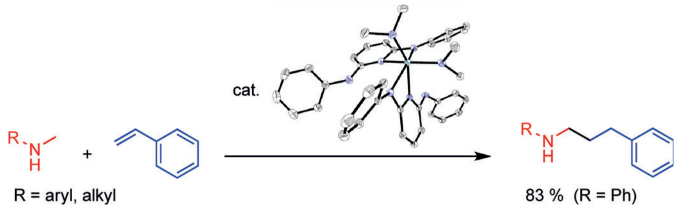
Either/or: Geminal triazides are rapidly constructed with broad scope by the use of oxocarboxylic acids, iodomethyl ketones, or terminal olefins as starting substrates in oxidative azidations with a mild derivative of 2-iodoxybenzoic acid and sodium azide. Along with this little-studied class of organic azides, α-azidoesters were also synthesized.



Organic Azides

P. Klahn, H. Erhardt, A. Kotthaus, S. F. Kirsch* ______ **7913 – 7917**

The Synthesis of α-Azidoesters and Geminal Triazides



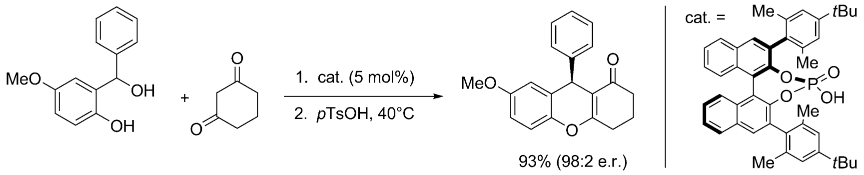
Linear progress: A new Ti complex with 2,6-bis(phenylamino)pyridinato ligands catalyzes highly regioselective hydroaminoalkylation reactions of styrenes. The process that directly gives access to the corresponding linear hydroaminoalkylation products offers a new and flexible synthetic approach towards pharmaceutically important 3-arylpropylamines. It is also possible to convert (*E*)-1-phenyl-1,3-butadienes into the corresponding linear products.

C–H Activation

J. Dörfler, T. Preuß, A. Schischko, M. Schmidtmann, S. Doye* 7918 – 7922

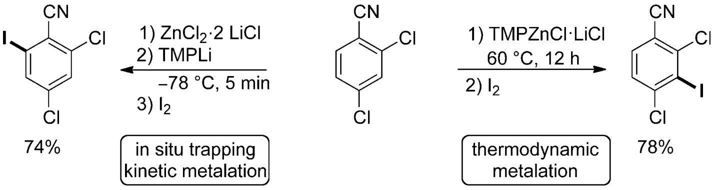
A 2,6-Bis(phenylamino)pyridinato Titanium Catalyst for the Highly Regioselective Hydroaminoalkylation of Styrenes and 1,3-Butadienes

Asymmetric Catalysis



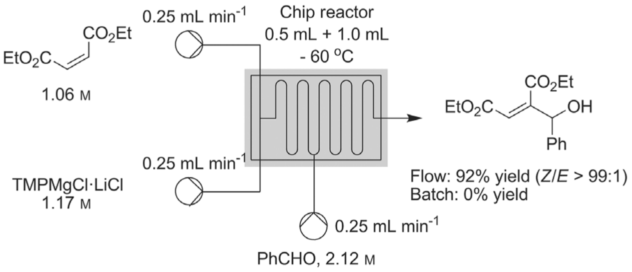
Chiral phosphoric acids permit the in situ generation of hydrogen-bonded *ortho*-quinone methides which react with β-diketones and β-keto esters with excellent enantioselectivity and furnish valuable 4-aryl-4*H*-chromenes and related heterocycles upon subsequent cyclodehydration. These observations extend the substrate scope of enantioselective phosphoric acid catalysis towards an important additional class of compounds.

Regioselective Metalations



Fast, faster, the fastest: Aromatic and heterocyclic substrates, when treated with TMPLi (TMP = 2,2,6,6-tetramethylpiperidyl), undergo a kinetic lithiation and then a transmetalation with a metal salt such as $MgCl_2$, $ZnCl_2$, or CuCN. This allows an expedited metalation of sensitive pyridines bearing a nitro, ester, or cyano group and allows the preparation of kinetic regioisomers of functionalized aromatic compounds or heterocycles.

Flow Metalation

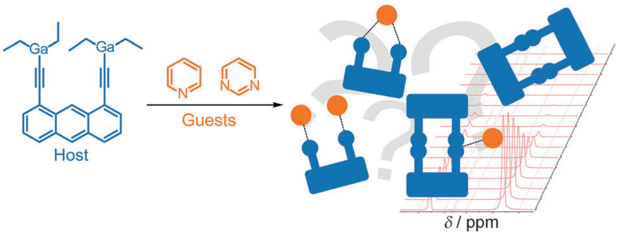


Go with the flow: Flow conditions allow a practical metalation of functionalized heterocycles and various acrylates in the presence of the base TMPMgCl·LiCl (TMP = 2,2,6,6-tetramethylpiperidyl). More convenient temperatures and very fast reaction times can usually be achieved by applying the flow conditions. Sensitive acrylic derivatives can be magnesiated under flow conditions. Furthermore, the flow reactions are readily scalable without further optimization.

Host–Guest Chemistry

J.-H. Lamm, P. Niermeier, A. Mix,
J. Chmiel, B. Neumann, H.-G. Stammler,
N. W. Mitzel* ____________ **7938 – 7942**

Mechanism of Host–Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy

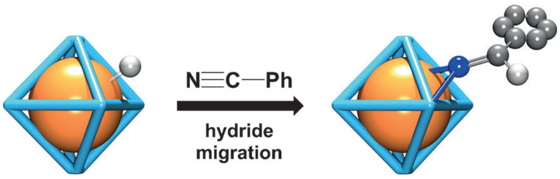


Dynamic host–guest complexation was studied using a new combination of NMR titration and diffusion NMR experiments. The host is the bidentate 1,8-bis[(diethylgallanyl)ethynyl]anthracene, the guests are pyrimidine and pyridine. The analysis of the diffusion NMR experiments requires tailor-made reference compounds of the same shape for comparison.

Metalloid Clusters

C. Ganesamoorthy, J. Weßing, C. Kroll,
R. W. Seidel, C. Gemel,
R. A. Fischer* ____________ **7943 – 7947**

The Intermetalloid Cluster $[(\mathrm{Cp^*AlCu})_6\mathrm{H}_4]$, Embedding a Cu_6 Core Inside an Octahedral Al_6 Shell: Molecular Models of Hume–Rothery Nanophases

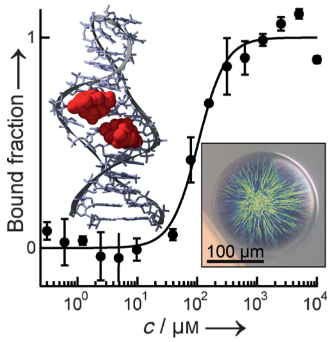


Aluminum–copper cluster: The novel intermetallic cluster $[(\mathrm{Cp^*AlCu})_6\mathrm{H}_4]$ was selectively obtained from the reaction of $[\mathrm{Cp^*Al}]_4$ and $[\mathrm{Ph_3PCuH}]_6$. The stronger affinity of Cp*Al towards Cu sweeps the phosphine ligands from the hydride derivative and furnishes an octahedral Al_6 cage to encapsulate the Cu_6 core. The hydrido cluster $\mathrm{M}_{12}\mathrm{H}_4$ reacts with benzonitrile to give the stoichiometric insertion product $[(\mathrm{Cp^*AlCu})_6\mathrm{H}_3(\mathrm{N{=}CHPh})]$.

Biomolecule Interaction Analysis

S. A. I. Seidel, N. A. Markwardt,
S. A. Lanzmich, D. Braun* _ **7948 – 7951**

Thermophoresis in Nanoliter Droplets to Quantify Aptamer Binding

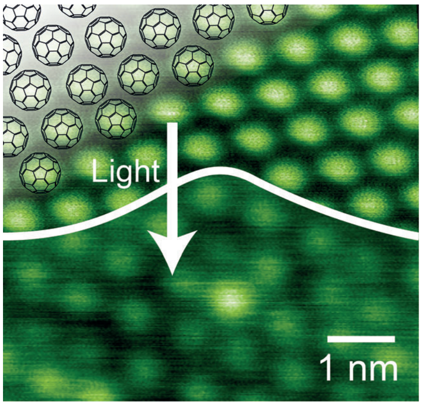


In 10 nL droplets, AMP-aptamer affinity, cooperativity, and buffer dependence were quantified by thermophoresis. Compared to established capillary measurements, sample consumption was cut down by a factor of 50. In locally heated nL samples, temperature, Marangoni flow, and concentration were analyzed by fluorescence microscopy and numerical simulation. Miniaturization and the 1536-well plate format make the method high-throughput and automation friendly.

Guided Covalent Networks

R. Lindner, P. Rahe, M. Kittelmann,
A. Gourdon, R. Bechstein,
A. Kühnle* ______________ **7952 – 7955**

Substrate Templating Guides the Photoinduced Reaction of C_{60} on Calcite



Reactions on insulators: C_{60} fullerenes undergo a photochemical reaction on calcite, a bulk insulator. The irradiated structures are investigated by non-contact atomic force microscopy. Domains of covalently linked molecules form along specific substrate directions. The observed directional reaction is readily explained by a model based on lattice mismatch minimization.

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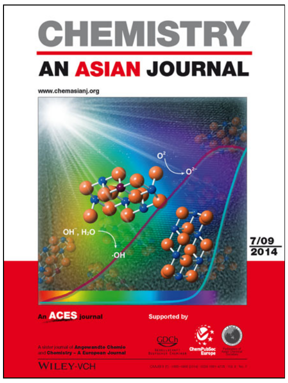

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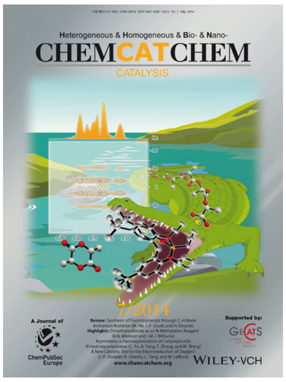

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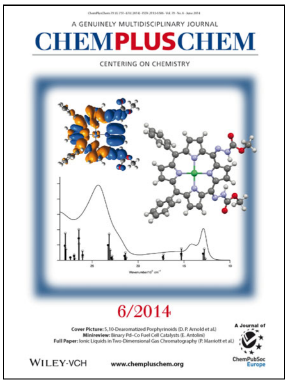

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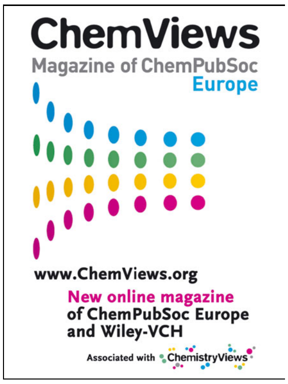

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