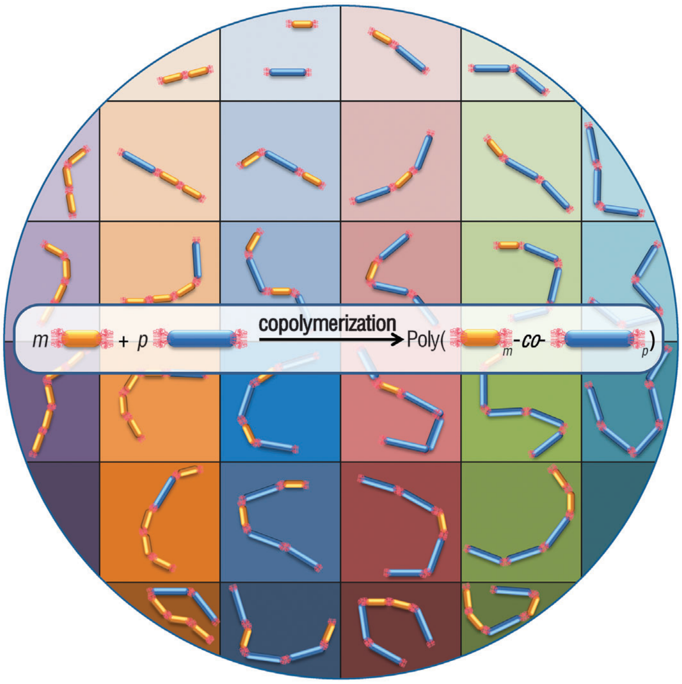
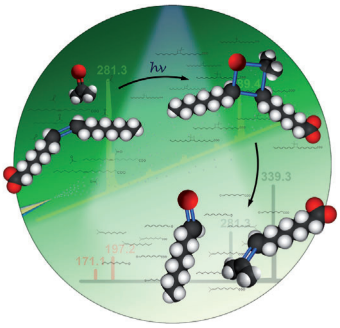
The self-assembly ...

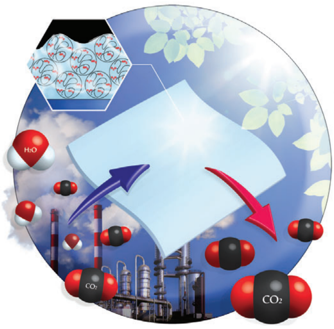


... of colloidal analogues of molecular copolymers can greatly benefit fundamental studies of molecular copolymerization and nanotechnology. In their Communication on page 2648 ff., K. Liu, E. Kumacheva, et al. present microscopy and spectroscopy analyses to develop design rules and a kinetic model for the growth of colloidal random and block copolymers made from plasmonic nanorods with different lengths and compositions.

Lipid Analysis

In their Communication on page 2592 ff. Y. Xia and X. Ma use tandem mass spectrometry for locating C=C bonds in lipids in complicated mixtures. The method exploits the Paternò-Büchi reaction.



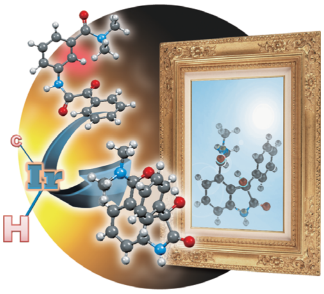


Carbon Dioxide Capture

Hydrogel films, composed of temperature-responsive microgel particles containing amine groups, that work as stimuli-responsive carbon dioxide absorbent are reported by Y. Hoshino et al. in their Communication on page 2654 ff.

Asymmetric C–H Functionalization

Y. Yamamoto et al. show in their Communication on page 2658 ff., that an asymmetric cationic iridium complex formed in situ can produce optically active oxindoles in high yields with complete regioselectivity and high enantioselectivities.



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Service

Author Profile

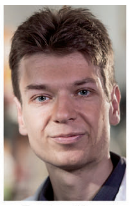
"My favorite time of day is sunrise.
I admire spontaneity …"
This and more about Dirk M. Guldi can be found on page 2534.

News

T. Junkers

J. Streuff

R. Marschall



S. Seiffert

M. Groß

G. S. Fischer

A. Doyle

J. A. Dumesic

F. Kraus

R. Eisenberg

C. J. Chang

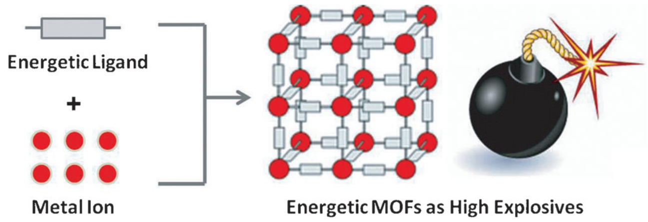
Books

Highlights

Energetic Materials

Q. Zhang, J. M. Shreeve* ___ **2540 – 2542**

Metal–Organic Frameworks as High Explosives: A New Concept for Energetic Materials

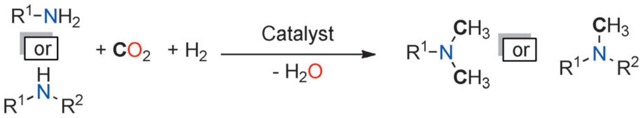


Energetic MOFs with 1D, 2D, or 3D structures were synthesized through a self-assembly strategy by using energetic organic linkers to bridge non-toxic metal ions. This new concept for energetic MOFs opens opportunities for developing new-generation primary explosives in the field of energetic materials.

CO_2 Activation

A. Tlili, X. Frogneux, E. Blondiaux, T. Cantat* ___ **2543 – 2545**

Creating Added Value with a Waste: Methylation of Amines with CO_2 and H_2



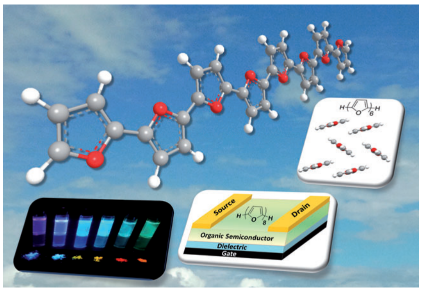
Unknown before 2013, a novel methodology utilizes CO_2 as a carbon source for the methylation of amines, with water as the by-product. This strategy offers a sustainable route to methylamines by converting CO_2 to value-added chemicals, using molecular hydrogen as a cheap and renewable reductant. The method may open novel applications for recycling CO_2 to bulk and fine chemicals.

Minireviews

Organic Electronics

O. Gidron,* M. Bendikov ___ **2546 – 2555**

α-Oligofurans: An Emerging Class of Conjugated Oligomers for Organic Electronics



Long and short of it: A critical account of a new class of π-conjugated materials, long oligofurans, from the perspectives of their synthesis, molecular properties, chemical reactivity, and use in electronic devices is presented.

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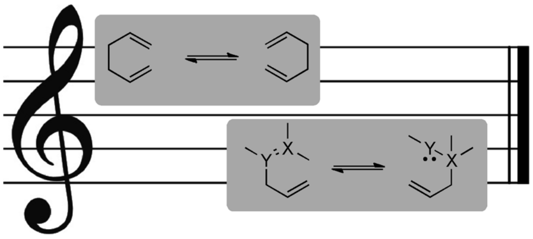
Reviews

Molecules and Music

A. C. Jones,* J. A. May, R. Sarpong,
B. M. Stoltz* ______ **2556 – 2591**

Toward a Symphony of Reactivity: Cascades Involving Catalysis and Sigmatropic Rearrangements



Unfinished Symphonies: The development of tandem processes has had a profound impact on organic synthesis. In this Review, catalyzed cascade transformations that involve sigmatropic rearrangements are discussed. To appeal to the musical sense of orchestration in chemical synthesis, we propose the descriptors duet, trio, quartet, etc. for defining transformations that involve more than one reaction in a cascade.

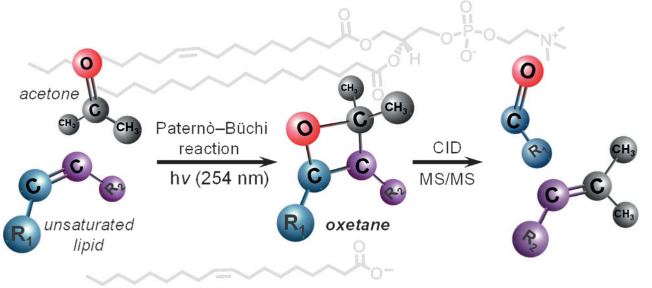
Communications

Lipid Analysis

X. Ma, Y. Xia* ______ **2592 – 2596**

Pinpointing Double Bonds in Lipids by Paternò-Büchi Reactions and Mass Spectrometry

Frontispiece

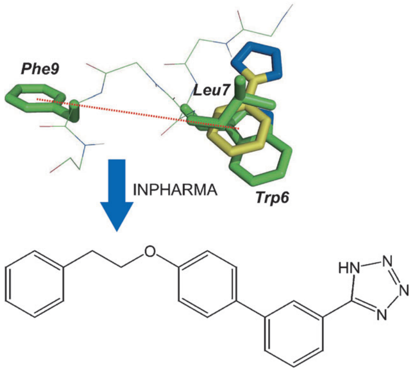


Where is the double bond? For the first time, the Paternò–Büchi (P-B) reaction has been exploited for double-bond localization in lipids. The P-B reaction is facilitated by UV irradiation of a nanoelectrospray plume entraining lipids and acetone. Tandem mass spectrometry of the online reaction products by collision activation leads to the rupture of oxetane rings and the formation of diagnostic ions specific to the double-bond location (see picture).

Structure-Based Drug Discovery

K. Ono, K. Takeuchi, H. Ueda, Y. Morita, R. Tanimura, I. Shimada,*
H. Takahashi* ______ **2597 – 2601**

Structure-Based Approach To Improve a Small-Molecule Inhibitor by the Use of a Competitive Peptide Ligand



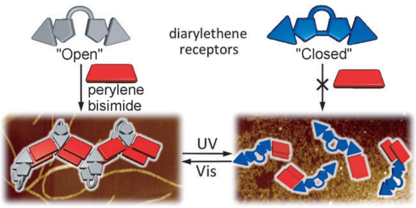
The best of both worlds: In a structure-based strategy to improve the affinity of a small-molecule inhibitor for its target protein, the interaction mode of a competitive peptide was constructively introduced. Thus, the discrimination of overlapping and non-overlapping peptide–compound pharmacophores by INPHARMA NMR spectroscopy enabled the design of a new compound (see structure) with improved affinity for the platelet receptor glycoprotein VI.

Photoresponsive Assemblies

S. Yagai,* K. Iwai, M. Yamauchi,
T. Karatsu, A. Kitamura, S. Uemura,
M. Morimoto, H. Wang,
F. Würthner **2602 – 2606**

Photocontrol Over Self-Assembled Nanostructures of π–π Stacked Dyes Supported by the Parallel Conformer of Diarylethene

Leading light: Photoresponsive dye aggregates exhibiting remarkable morphological changes were constructed through complexation of the parallel conformer of a diarylethene receptor with dimeric stacks of perylene bisimide through multiple hydrogen bonds. The aggregates can be reversibly transformed between helical nanofibers and granular nanoaggregates upon exposure to visible and UV light, respectively.

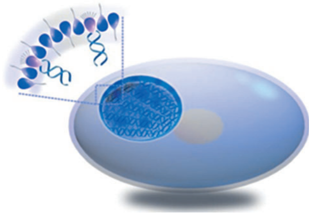


Vesicle Self-Assembly

Y. Dong, Y. Sun, L. Wang, D. Wang,
T. Zhou, Z. Yang, Z. Chen, Q. Wang,
Q. Fan, D. Liu* **2607 – 2610**

Frame-Guided Assembly of Vesicles with Programmed Geometry and Dimensions

Frame-filling: Discontinuous, pre-positioned leading hydrophobic groups (LHGs) have been introduced to a frame, outlining the fringe of its designed structure. The formed frame will guide other amphiphilic molecules to fill in the gap between LHGs, finally leading to the formation of heterovesicles with designed shape and size.

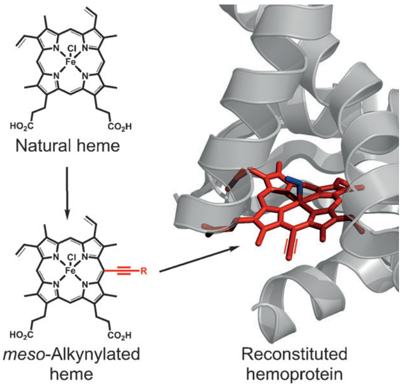


Hemoprotein Engineering

A. Nierth, M. A. Marletta* **2611 – 2614**

Direct *meso*-Alkynylation of Metalloporphyrins Through Gold Catalysis for Hemoprotein Engineering

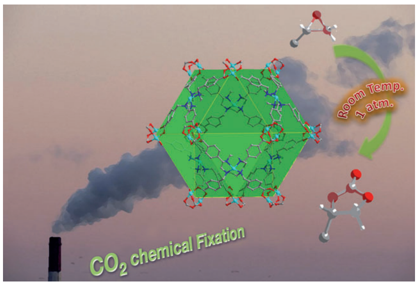
Golden trick: Metalloporphyrins can be directly functionalized at the methine protons (*meso* positions) to yield asymmetric alkynylated derivatives by using gold catalysis and hypervalent iodine reagents. This single-step procedure was applied to *b*-type heme and the product was incorporated into a gas-sensor heme protein. The terminal alkyne allows fluorophore labeling through copper(I)-catalyzed azide–alkyne cycloaddition.



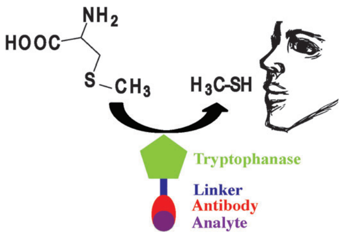
Crystal Engineering

W.-Y. Gao, Y. Chen, Y. Niu, K. Williams,
L. Cash, P. J. Perez, L. Wojtas, J. Cai,
Y.-S. Chen, S. Ma* **2615 – 2619**

Crystal Engineering of an nbo Topology Metal–Organic Framework for Chemical Fixation of CO_2 under Ambient Conditions



High catalytic activity for chemical fixation of CO_2 into cyclic carbonates under ambient conditions has been demonstrated in the metal–organic framework (MOF) MMCF-2 (see picture; C gray, O red, N blue, Cu pale blue). This MOF features a high density of well-oriented Lewis acid active sites within the cuboctahedral cage.



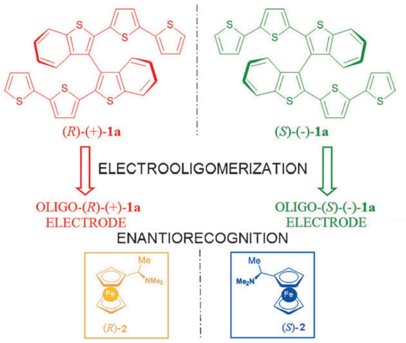
The nose knows: Tryptophanase (TPase), which converts *S*-methyl-L-cysteine into methyl mercaptan (smelly), was coupled to a molecular recognition element (such as an antibody) to create an odor-based biosensor. Biotinylated TPase could be combined with various biotin-labeled molecular recognition elements, thereby enabling a broad range of applications for this odor-based reporting system.

Biosensors

Y. Xu, Z. Zhang, M. M. Ali, J. Sauder, X. Deng, K. Giang, S. D. Aguirre, R. Pelton, Y. Li,* C. D. M. Filipe* ____ **2620 – 2622**

Turning Tryptophanase into Odor-Generating Biosensors

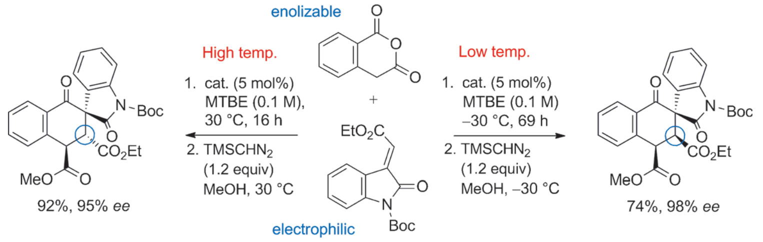
A jolt upon recognition: Torsion in the electroactive backbone endows poly-heterocycle films with high chiroptical activity, which is reversibly tunable by the electric potential, and outstanding enantiorecognition capability with about 100 mV between two enantiomeric ferrocenyl amino probes, in any order, in alternating sequences, and as a racemate.



Organic Chemistry

F. Sannicolò,* S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini, S. Rizzo ____ **2623 – 2627**

Potential-Driven Chirality Manifestations and Impressive Enantioselectivity by Inherently Chiral Electroactive Organic Films

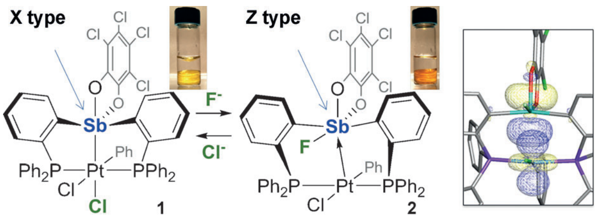


Squared away: The first strategy for bringing about enantioselective Tamura reactions is reported. In the presence of a squaramide-based catalyst, enolizable anhydrides react with alkylidene oxindoles to generate spirooxindole products with excellent enantio- and diastereocontrol. The methodology is of wide scope and leads to structurally diverse products.

Organocatalysis

F. Manoni, S. J. Connon* ____ **2628 – 2632**

Catalytic Asymmetric Tamura Cycloadditions



Picture of (non)innocence: A chloride–fluoride exchange reaction leads to the metamorphosis of a stiboranyl X ligand into a stiborane Z ligand. This phenomenon, which illustrates the coordination non-innocence of the antimony ligand, results from the cleavage of the covalent Sb–Pt bond of **1** and formation of a longer and weaker Pt→Sb interaction in **2**. This structural response is accompanied by a colorimetric one.

Stiboranyl Ligands

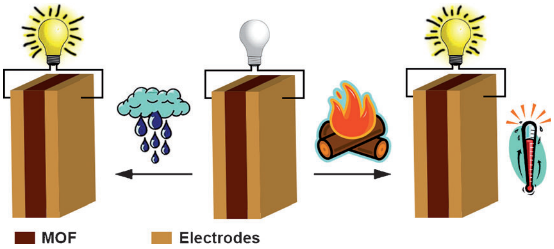
I.-S. Ke, J. S. Jones, F. P. Gabbaï* ____ **2633 – 2637**

Anion-Controlled Switching of an X Ligand into a Z Ligand: Coordination Non-innocence of a Stiboranyl Ligand

Proton-Conducting Materials

S. S. Nagarkar, S. M. Unni, A. Sharma,
S. Kurungot, S. K. Ghosh* — **2638 – 2642**

Two-in-One: Inherent Anhydrous and Water-Assisted High Proton Conduction in a 3D Metal–Organic Framework

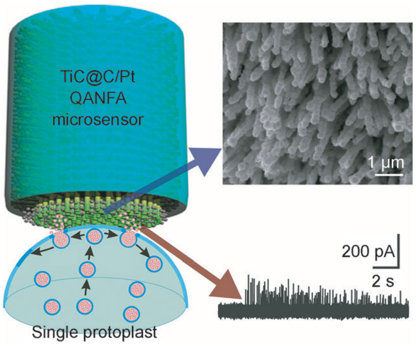


Two-in-one: A three-dimensional proton-conducting metal–organic framework (MOF) with acid–base pairs in its coordination space has been developed. Unlike other MOFs, which conduct protons either under anhydrous or under humid conditions, this compound shows high proton conductivity under both conditions.

Bioanalysis

J. T. Liu, L. S. Hu, Y. L. Liu, R. S. Chen,
Z. Cheng, S. J. Chen, C. Amatore,
W. H. Huang,* K. F. Huo* — **2643 – 2647**

Real-Time Monitoring of Auxin Vesicular Exocytotic Efflux from Single Plant Protoplasts by Amperometry at Microelectrodes Decorated with Nanowires



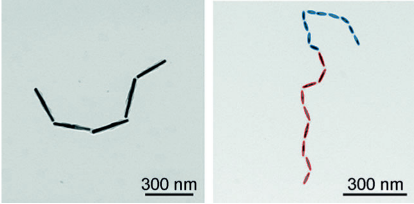
Auxin(IAA) efflux has been shown by recent biochemical results to be mediated by a vesicular cycling mechanism, but up to now there was no means for direct detection of IAA release from single plant cells in real-time. A novel TiC@C/Pt-QANFA micro-electrochemical sensor has high sensitivity in detection of IAA, and allows real-time monitoring and quantification of the quantal release of auxin from single plant protoplast by exocytosis.

Plasmonic Copolymers

K. Liu,* A. Lukach, K. Sugikawa, S. Chung,
J. Vickery, H. Therien-Aubin, B. Yang,
M. Rubinstein,
E. Kumacheva* — **2648 – 2653**

Copolymerization of Metal Nanoparticles: A Route to Colloidal Plasmonic Copolymers

Front Cover



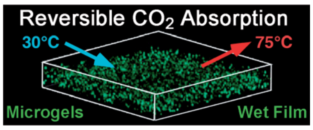
Golden chains (and some palladium too): Gold nanorods with different dimensions (see picture, red and blue rods) self-assemble into random and block colloidal copolymer structures, following the principles of molecular step-growth copolymerization. This approach was extended to the co-assembly of copolymers of gold and palladium nanorods.

Green Chemistry

M. Yue, Y. Hoshino,* Y. Ohshiro,
K. Imamura, Y. Miura — **2654 – 2657**

Temperature-Responsive Microgel Films as Reversible Carbon Dioxide Absorbents in Wet Environment

Inside Back Cover



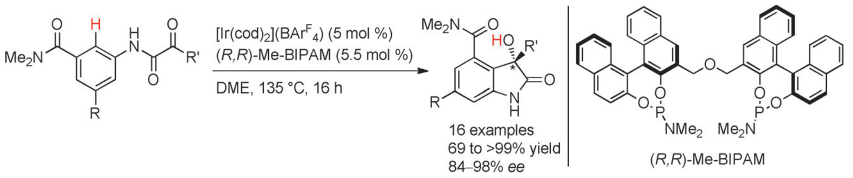
Carbon dioxide capture: Hydrogel films composed of temperature-responsive microgel particles (GP) containing amine groups reversibly absorbed carbon dioxide with a high capacity in response to the thermal stimuli (30–75 °C; see picture). A fast stimulus response rate of the GP films enabled the long-range and fast diffusion of bicarbonate ions into the films.

Asymmetric C–H Functionalization

T. Shirai, H. Ito,
Y. Yamamoto* ______ 2658 – 2661

Cationic Ir/Me-BIPAM-Catalyzed Asymmetric Intramolecular Direct Hydroarylation of α-Ketoamides

Back Cover

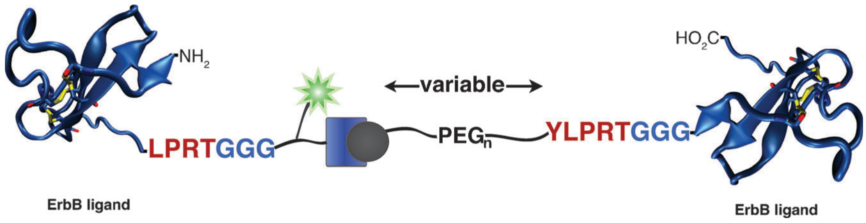


Carbon's got a brand new bond: Asymmetric intramolecular direct hydroarylation of α-ketoamides gives various optically active 3-substituted 3-hydroxy-2-oxindoles in high yields with complete regioselectivity and high enantioselectivities. This is realized by the use of an asymmetric cationic iridium complex formed in situ (see Scheme).

Proteins

A. T. Krueger, C. Kroll, E. Sanchez,
L. G. Griffith, B. Imperiali* _ 2662 – 2666

Tailoring Chimeric Ligands for Studying and Biasing ErbB Receptor Family Interactions

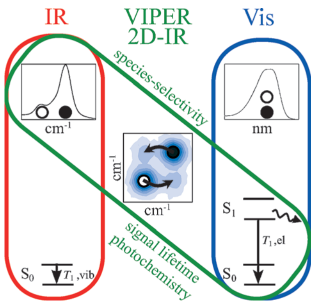


Signal tuning: A semisynthetic strategy for efficiently incorporating tunable functionality into chimeric recombinant proteins and application to a bivalent protein ligand tool for biasing signaling in the ErbB receptor family is described. Biasing away from an EGFR-HER2 dimerization with a bivalent EGF, reduced cell motility and intraligand spacing dependence, thus demonstrating the utility of this approach for potential structure–function studies.

2D-IR Spectroscopy

L. J. G. W. van Wilderen, A. T. Messmer,
J. Bredenbeck* ______ 2667 – 2672

Mixed IR/Vis Two-Dimensional Spectroscopy: Chemical Exchange beyond the Vibrational Lifetime and Sub-ensemble Selective Photochemistry

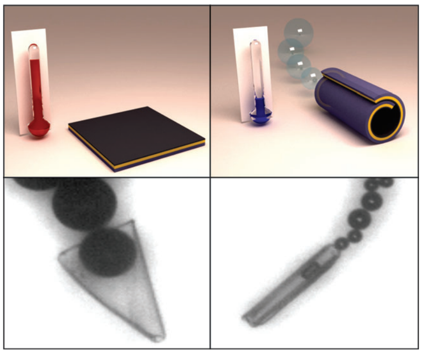


The VIPER (vibrationally promoted electronic resonance) 2D-IR experiment selects a species within a mixture according to its IR spectrum and electronically excites it. The relaxation barrier for 2D-IR exchange spectroscopy can thus be broken and chemical exchange tracked over long timescales. The photochemistry of the IR-selected species such as distinct conformers can be studied in the presence of other species with virtually identical UV/Vis spectra.

Micromotors

V. Magdanz, G. Stoychev, L. Ionov,*
S. Sanchez,* O. G. Schmidt 2673 – 2677

Stimuli-Responsive Microjets with Reconfigurable Shape

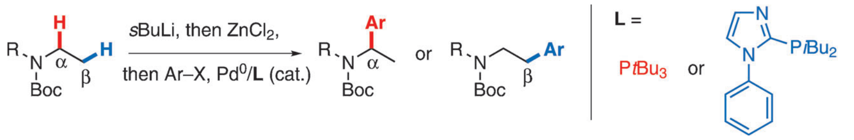


Micro jet boating: Flexible thermoresponsive polymer microjets can be fabricated. These self-propelled microjets can reversibly fold and unfold in an accurate manner by applying changes in temperature to the solution in which they are immersed. This effect allows them to start and stop multiple times by controlling the radius of curvature of the microtube.

Cross-Coupling

A. Millet, D. Dailler, P. Larini,
O. Baudoin* ______ 2678 – 2682

Ligand-Controlled α- and β-Arylation of Acyclic N-Boc Amines

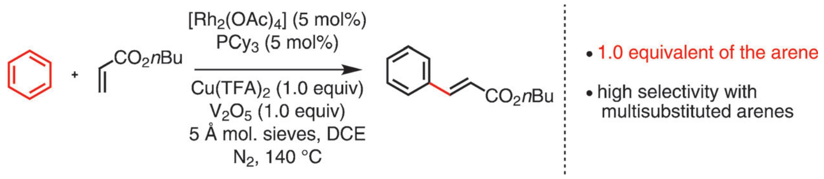


All manner of control: The arylation of α-zincated acyclic Boc-protected amines was selectively performed at the α- or β-position in a ligand-controlled manner. α-Arylation occurs by direct reductive elimination of the α-palladated intermediate whereas β-arylation involves palladium migration along the alkyl chain. Boc = *tert*-butoxycarbonyl.

C–H Functionalization

H. U. Vora, A. P. Silvestri, C. J. Engelin,
J.-Q. Yu* ______ 2683 – 2686

Rhodium(II)-Catalyzed Nondirected Oxidative Alkenylation of Arenes: Arene Loading at One Equivalent



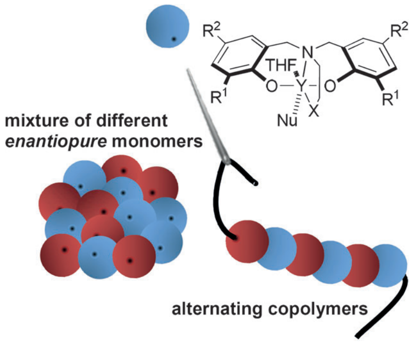
Down to one: A C–H alkenylation of simple arenes without the need for an excess amount of the arene was possible with a bimetallic Rh^{II} catalyst (see scheme). A phosphine ligand as well as a combination of the oxidants $Cu(TFA)_2$ and V_2O_5 proved essential for the efficient synthesis of monoalkenylated products with good selectivity, especially for di- and trisubstituted arene substrates.

Polymers

C. G. Jaffredo, Y. Chapurina,
S. M. Guillaume,*
J.-F. Carpentier* ______ 2687 – 2691

From Syndiotactic Homopolymers to Chemically Tunable Alternating Copolymers: Highly Active Yttrium Complexes for Stereoselective Ring-Opening Polymerization of β-Malolactonates

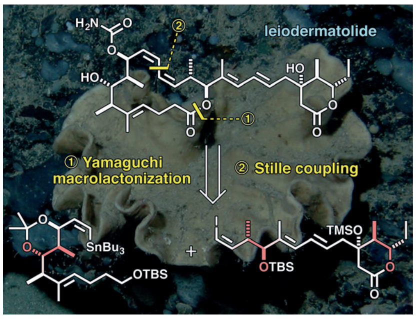
Alternating links: The first catalyst enabling the rapid, controlled, syndioselective polymerization of β-lactones with ester side-arms is described. With this catalyst, mixtures of β-lactones having opposite configurations are linked in an alternating fashion, thus affording a straightforward approach towards a new class of variously functionalized alternating copolymers.



Natural Product Synthesis

I. Paterson,* K. K.-H. Ng, S. Williams,
D. C. Millican, S. M. Dalby ___ 2692 – 2695

Total Synthesis of the Antimitotic Marine Macrolide (−)-Leiodermatolide

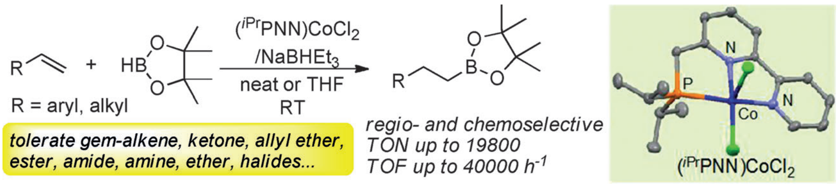


Supply to meet the demand: The tubulin-targeting mechanism of action of the marine macrolide leiodermatolide makes it a novel lead for anticancer drug discovery. With the aim of ensuring a sustainable supply and enabling structure–activity-relationship studies, a convergent synthetic route based on palladium-mediated fragment assembly and macrolactonization was developed (see scheme). Boron-mediated aldol reactions set six of the nine stereocenters.

Synthetic Methods

L. Zhang, Z. Zuo, X. Leng, Z. Huang* ______ **2696 – 2700**

A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane

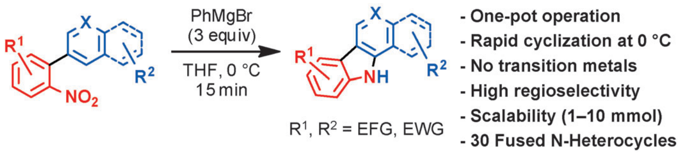


A PNN pincer cobalt complex (see picture) has been developed for catalytic hydroboration of alkenes with pinacolborane. The system displays high activity and functional-group compatibility and the regio- and chemoselectivity of the hydroboration of α-olefins is excellent.

Heterocycles

H. Gao, Q.-L. Xu, M. Yousufuddin, D. H. Ess,* L. Kürti* ______ **2701 – 2705**

Rapid Synthesis of Fused N-Heterocycles by Transition-Metal-Free Electrophilic Amination of Arene C–H Bonds

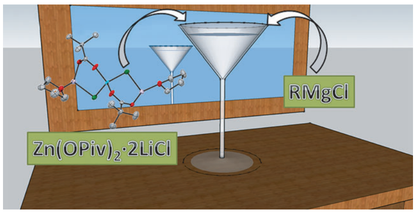


Controlled fusion: A transition-metal-free, low-temperature, and regioselective intramolecular amination of aromatic C(sp^2)–H bonds provides fused N-heterocycles. This reaction is operationally simple and scalable (1–10 mmol) and the scope of substrates is wide (see scheme). Density functional calculations indicate that a stepwise electrophilic aromatic cyclization mechanism may be operative.

Organozinc Reagents

A. Hernán-Gómez, E. Herd, E. Hevia, A. R. Kennedy, P. Knochel,* K. Koszinowski, S. M. Manolikakes, R. E. Mulvey,* C. Schnegelsberg ______ **2706 – 2710**

Organozinc Pivalate Reagents: Segregation, Solubility, Stabilization, and Structural Insights

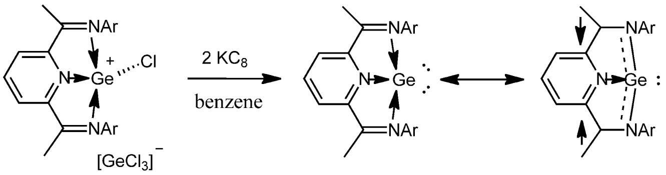


(un)Mixing cocktails: The secret ingredient in complicated multicomponent organozinc solution mixtures is magnesium pivalate, which enhances the air stability of Zn–C bonds by cleaning up OH^- or O^{2-} antagonists and capturing H_2O molecules, thus making these contaminants less accessible to carry out hydrolysis.

Germanium(0) Compounds

T. Chu, L. Belding, A. van der Est, T. Dudding, I. Korobkov, G. I. Nikonov* ______ **2711 – 2715**

A Coordination Compound of Ge^0 Stabilized by a Diiminopyridine Ligand

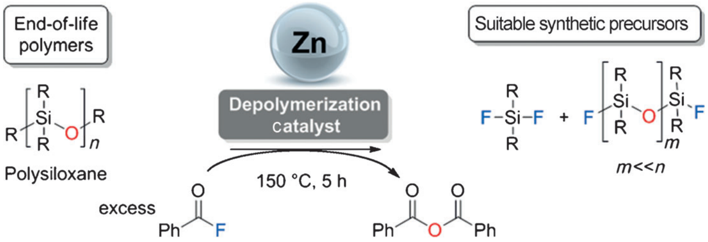


Putting the e back into Ge: A cationic Ge^{II} complex was reduced to give a complex composed of a neutral germanium atom with a tridentate diiminopyridinate ligand. The Ge^0 complex was found to have a singlet ground state and partial multiple-bond character between the Ge atom and the imine nitrogen atoms according to NMR, IR, and EPR spectroscopy, as well as X-ray analysis and DFT calculations.

Depolymerization

S. Enthaler* 2716–2721

Zinc-Catalyzed Depolymerization of End-of-Life Polysiloxanes

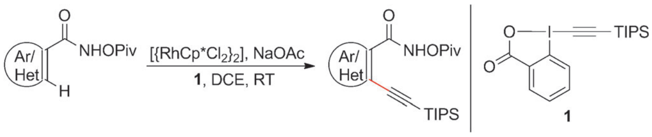


Reclaiming resources: Straightforward zinc-catalyzed depolymerization of a range of polysiloxanes produced difluorodimethylsilanes and 1,3-difluoro-1,1,3,3-tetramethyldisiloxanes, which are appropriate starting materials for new polymers. In the presence of simple zinc salts, extraordinary catalytic activity and selectivity were feasible at low temperature (see scheme).

Cross-coupling

C. Feng, T.-P. Loh* 2722–2726

Rhodium-Catalyzed C–H Alkynylation of Arenes at Room Temperature

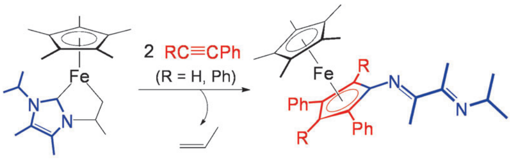


Hot rhod: A rhodium-catalyzed, electronically reversed Sonogashira reaction between unbiased arenes and the hypervalent iodine reagent **1** proceeds through C–H activation. This reaction displays excellent functional-group tolerance and high efficiency, and thus opens a new synthetic pathway to access functionalized alkynes. Cp* = C_5Me_5, DCE = 1,2-dichloroethane, Piv = pivaloyl, TIPS = triisopropylsilyl.

Iron Carbene Chemistry

T. Hatanaka, Y. Ohki,*
K. Tatsumi* 2727–2729

Coupling of an N-Heterocyclic Carbene on Iron with Alkynes to Form η^5-Cyclopentadienyl-Diimine Ligands

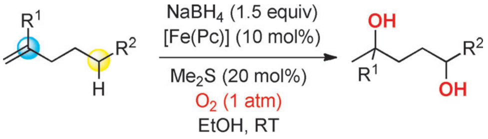


Iron sandwich with a side of diimines: A cyclometalated N-heterocyclic carbene ligand in a half-sandwich iron complex was found to couple with alkynes, leading to a unique type of ring opening of the carbene ligand and the formation of ferrocenyl–diimine complexes.

Synthetic Methods

T. Hashimoto, D. Hirose,
T. Taniguchi* 2730–2734

Direct Synthesis of 1,4-Diols from Alkenes by Iron-Catalyzed Aerobic Hydration and C–H Hydroxylation



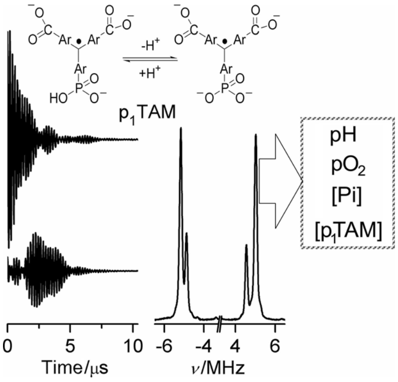
One more hydroxy group: A method for the synthesis of 1,4-diols from simple alkenes has been developed. This unusual transformation entails an iron-catalyzed aerobic hydration and is achieved with convenient reagents, such as molecular oxygen. The formation of an intermediary alkoxy radical, which undergoes a [1,5] hydrogen shift, is likely to be essential for $C(sp^3)$–H hydroxylation. Pc = phthalocyanine.

EPR Spectroscopy

A. A. Bobko, I. Dhimitruka, J. L. Zweier, V. V. Khramtsov* ______ **2735 – 2738**

Fourier Transform EPR Spectroscopy of Trityl Radicals for Multifunctional Assessment of Chemical Microenvironment

Inside Cover

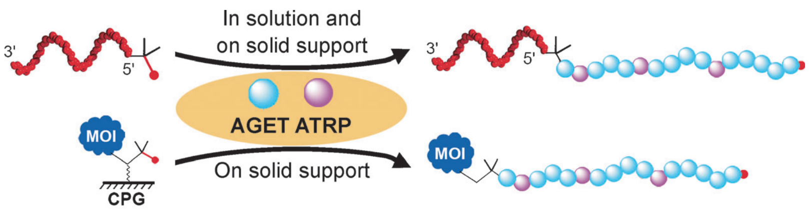


Examination of tissue by EPR: Fourier transform EPR spectroscopy using a phosphonated trityl probe (p_1TAM) makes possible the concurrent measurement of four parameters of the microenvironment related to the physiology of living tissue, namely pO_2, pH, and the concentrations of inorganic phosphate (Pi) and the probe (see picture). The trityl radical possesses long relaxation times.

Solid-Phase ATRP

S. E. Averick, S. K. Dey, D. Grahacharya, K. Matyjaszewski,*
S. R. Das* ______ **2739 – 2744**

Solid-Phase Incorporation of an ATRP Initiator for Polymer–DNA Biohybrids

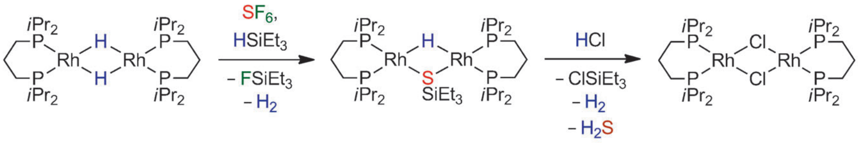


Solid-phase polymer biohybrids: An atom-transfer radical polymerization (ATRP) initiator was incorporated onto DNA or biotin using solid-phase phosphoramidite chemistry, providing well-defined (co)polymers both in solution and on solid support. MOI = molecule of interest; AGET = activators generated by electron transfer.

S–F Activation

L. Zámostná, T. Braun,*
B. Braun ______ **2745 – 2749**

S–F and S–C Activation of SF_6 and SF_5 Derivatives at Rhodium: Conversion of SF_6 into H_2S

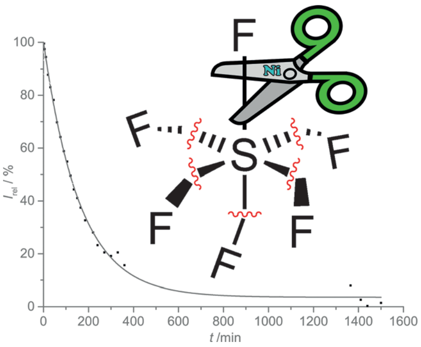


Activation of the stable greenhouse gas SF_6: The rhodium hydrido complex [{Rh(μ-H)(dippp)}$_2$] effected defluorination at the sulfur atom of SF_6 and organic SF_5 compounds under mild conditions. The reduction of SF_6 in the presence of $HSiEt_3$ led exclusively to the thiolato complex $[Rh_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dippp})_2]$ and $FSiEt_3$ (see Scheme). A cyclic process was developed for the conversion of SF_6 into H_2S.

S-F Activation

P. Holze, B. Horn, C. Limberg,*
C. Matlachowski, S. Mebs __ **2750 – 2753**

The Activation of Sulfur Hexafluoride at Highly Reduced Low-Coordinate Nickel Dinitrogen Complexes

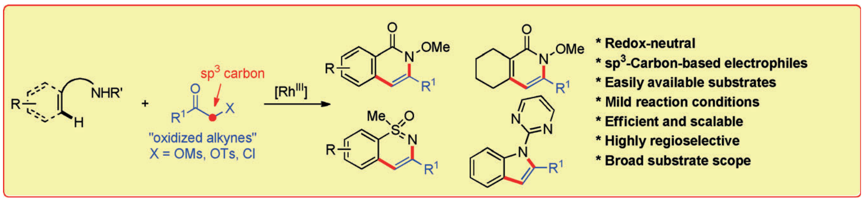


SF_6 taken into pieces: Reduced β-diketiminate nickel species are capable of converting SF_6, which is used as an inert gaseous dielectric medium for high-voltage switches, into sulfide and fluoride compounds. The fluoride product complex features an unprecedented $[NiF]^+$ unit, where the Ni atom is only three-coordinate. The low-coordinate sulfide product exhibits an almost linear $[Ni(\mu\text{-S})Ni]^{2+}$ moiety.

C–H Activation

D.-G. Yu, F. de Azambuja,
F. Glorius* ____________ 2754 – 2758

α-MsO/TsO/Cl Ketones as Oxidized Alkyne Equivalents: Redox-Neutral Rhodium(III)-Catalyzed C–H Activation for the Synthesis of N-Heterocycles

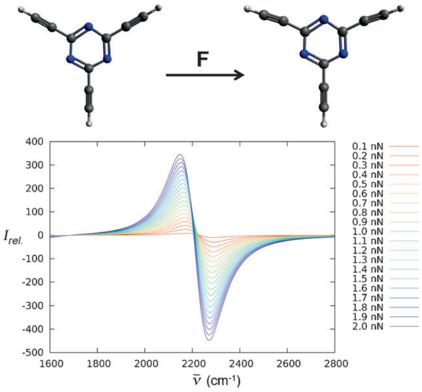


Who needs alkynes? α-Halo and pseudohalo ketones (as C(sp^3)-based electrophiles) are utilized as oxidized alkyne equivalents in Rh^{III}-catalyzed redox-neutral annulations to efficiently generate diverse N-heterocycles. Owing to the mild reaction conditions, a variety of functional groups are tolerated.

Molecular Dynamics

T. Stauch, A. Dreuw* ______ 2759 – 2761

Force–Spectrum Relations for Molecular Optical Force Probes



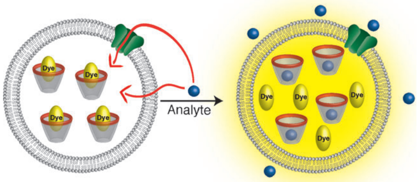
Using the force: Molecules whose symmetry decreases on deformation are studied by state-of-the-art theoretical methods. A direct quantitative relationship between their spectroscopic properties and the mechanical force acting on them is established. This result allows for the computational design of unique molecular force probes.

Supramolecular Chemistry

G. Ghale, A. G. Lanctôt, H. T. Kreissl,
M. H. Jacob, H. Weingart,
M. Winterhalter,
W. M. Nau* ____________ 2762 – 2765

Chemosensing Ensembles for Monitoring Biomembrane Transport in Real Time

Pass and release: Direct and real-time monitoring of analyte transport through the lipid bilayer is possible by the selective co-encapsulation of a macrocycle and a fluorescent dye inside liposomes. Once the analyte passes through the membrane, the dye is displaced from the macrocycle, and can be monitored by fluorescence. Tracking the translocation of an arginine-rich peptide across a bacterial membrane protein shows the applicability of the new method.

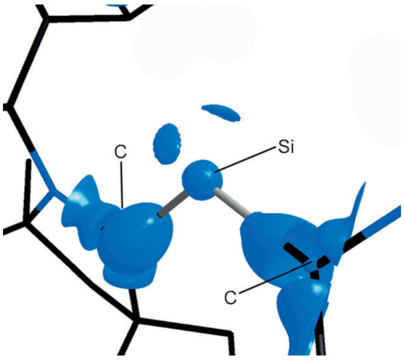


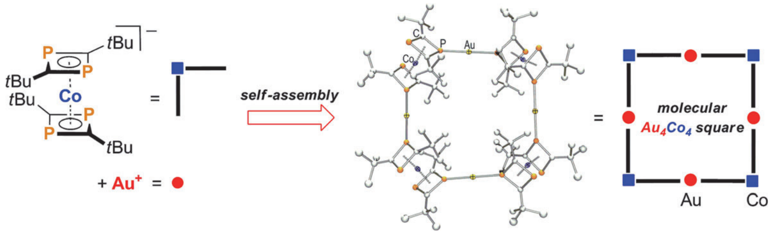
Silylones

B. Niepötter, R. Herbst-Irmer, D. Kratzert,
P. P. Samuel, K. C. Mondal,
H. W. Roesky,* P. Jerabek, G. Frenking,*
D. Stalke* ____________ 2766 – 2770

Experimental Charge Density Study of a Silylone

Two non-bonding VSCCs found in a silylone: An experimental and theoretical charge-density study confirms the interpretation of (cAAC)$_2$Si as a silylone to be valid. The two separated VSCCs present in the non-bonding region of the central silicon are indicative for two lone pairs. The nitrogen–carbene-carbon bond seems to have a significant double bond character, indicating a singlet state for the carbene carbon atom.





A square of gold: $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ is formed by the self-assembly of gold(I) cations and anions comprising a cobalt center sandwiched by phosphorus-containing moieties. X-ray diffraction and NMR spectroscopy investigations confirm that the metal atoms form a C_4 symmetrical arrangement. The results show the potential of phospha-organometallic sandwich complexes as building blocks in supramolecular assemblies.

Metallostructures

J. Malberg, M. Bodensteiner, D. Paul,
T. Wiegand, H. Eckert,
R. Wolf* ______________ **2771 – 2775**

Preparation of an Organometallic Molecular Square by Self-Assembly of Phosphorus-Containing Building Blocks

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

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

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Angewandte Corrigendum

The Supporting Information for this Communication contains an incorrect ^1H NMR spectrum and tabulation for compound **21**. A corrected version of the Supporting Information is provided online along with this Corrigendum.

A Concise Synthesis of (−)-Aplyviolene Facilitated by a Strategic Tertiary Radical Conjugate Addition

M. J. Schnermann,
L. E. Overman* __________ **9576–9580**

Angew. Chem. Int. Ed. **2012**, *51*

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