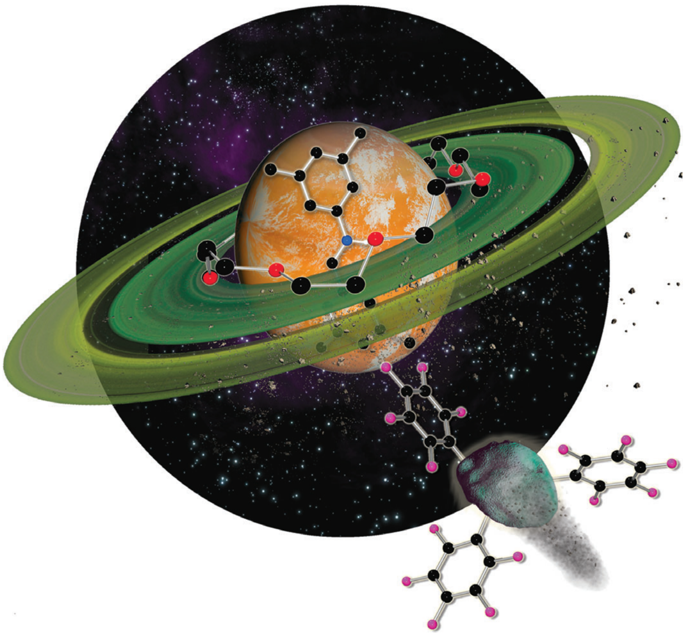
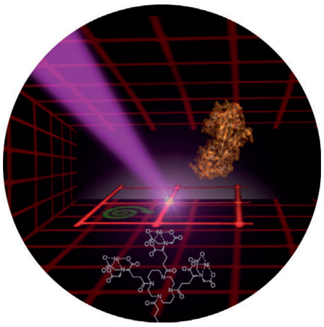
The reactivity of frustrated Lewis pairs ...

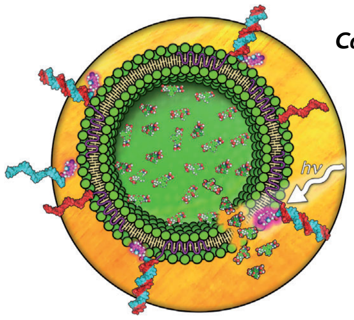


... is induced by the utilization of a sterically unencumbered aniline as the axle in a [2]rotaxane. In their Communication on page 960 ff., S. J. Loeb, D. W. Stephan, and co-workers show that the [2]rotaxane imparts enough steric bulk to the base to preclude adduct formation with $B(C_6F_5)_3$. This unique modification also shows frustrated Lewis pair reactivity in the activation of H_2 at room temperature.

Light-Triggered Chemical Biology

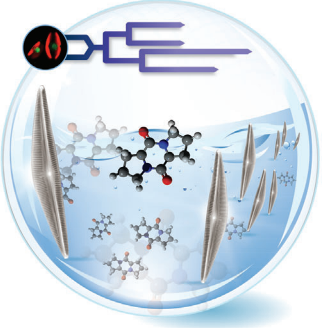
R. Tampé and co-workers describe in their Communication on page 848 ff. photoactivatable multivalent tetracysteine derivatives for the in situ labeling and assembly of His-tagged proteins in time and space.





Controlled Cargo Release

In their Communication on page 1008 ff., A. Herrmann and co-workers describe a method for sequence-specific cargo release from DNA-encoded lipid vesicles through the stable tagging of the liposome surface with amphiphilic DNA block copolymers.



Pheromones

A diatom species was found to employ sophisticated pheromone chemistry to locate mature sexual partners. In their Communication on page 854 ff., G. Pohnert et al. describe the metabolome of *Seminavis robusta*.

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Editorial


Jens K. Nørskov


Thomas Bligaard

"... The quest for the materials genome—the properties of a material that define its functional properties—has started. This signifies a transition to a new era of materials research where large amounts of materials data become available. The expectation is that this will significantly speed up the discovery of new materials ..."
Read more in the Editorial by J. K. Nørskov and T. Bligaard.

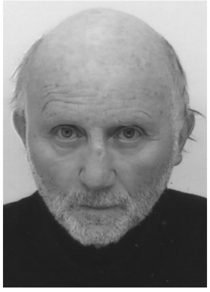
J. K. Nørskov,* T. Bligaard* ____ **776–777**

The Catalyst Genome

Service

Spotlight on Angewandte's Sister Journals ____ ***796–798***

Author Profile



*"I like refereeing because I can help to improve the quality of science.
My favorite place on earth is somewhere in the mountains ..."*
This and more about Achim Müller can be found on page 800.

Achim Müller ____ **800–802**

News


J. Kästner


W. Kunz


L. H. Gade

Hellmann Prize: J. Kästner ____ **803**

ECIS-Rhodia Prize: W. Kunz ____ **803**

Heidelberg Academy of Sciences and Humanities: L. H. Gade ____ **803**

Books

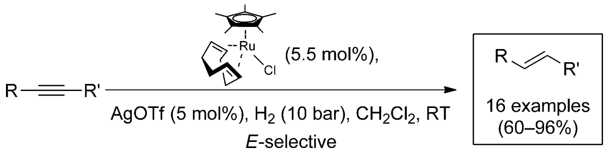
Chemistry in Theatre/The SciArtist — Carl Djerassi — *reviewed by S. Böschen* — **804**

Highlights

E-Alkenes

I. N. Michaelides, D. J. Dixon* **806 – 808**

Catalytic Stereoselective Semihydrogenation of Alkynes to *E*-Alkenes

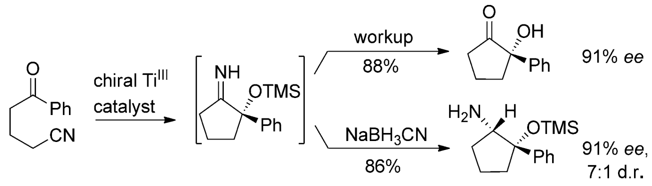


Less is more: Significant advancements have been made in recent years in the development of the *E*-selective, catalytic, functional-group-tolerant semihydrogenation of alkynes to *E*-alkenes through transition-metal catalysis (see scheme). For this type of catalysis, the use of mononuclear metal catalysts is superior to that of multinuclear metal catalysts.

Asymmetric Synthesis

S. Mondal, M. P. Bertrand,* M. Nechab* **809 – 811**

Enantioselective Synthesis of Carbocycles and Heterocycles by Radical/Polar and Polar/Radical Cascades



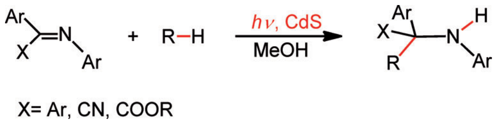
Radically efficient: New and appealing enantioselective cyclizations leading to highly functionalized carbocycles and heterocycles have been reported (see scheme; TMS = trimethylsilyl). These methodologies, based on the cascade combination of radical and polar steps, provide alternatives to conventional methodologies.

Reviews

Photocatalysis with Visible Light

H. Kisch* **812 – 847**

Semiconductor Photocatalysis—Mechanistic and Synthetic Aspects



Photoinduced charge generation at semiconductor surfaces is currently the most promising method for the chemical utilization of visible light. These charges can be utilized for catalytic redox processes such as nitrogen fixation, functionalization of alkanes, and linear addition reactions of olefins to 1,2-diazenes and imines. Semiconductor photocatalysis combines aspects of classical photochemistry with electrochemistry, solid-state chemistry, and heterogeneous catalysis.

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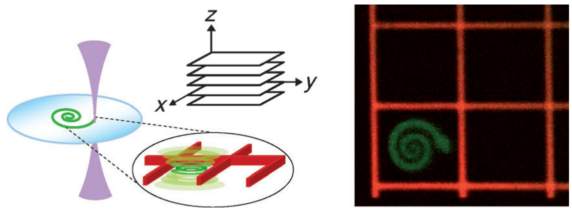
Communications

Light-Triggered Chemical Biology

N. Labòria, R. Wieneke,
R. Tampé* ________ 848 – 853

Control of Nanomolar Interaction and In Situ Assembly of Proteins in Four Dimensions by Light

Frontispiece



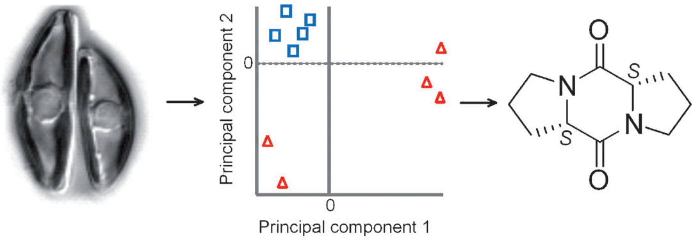
Making light work: Photoactivatable multivalent trisNTA compounds have been developed for the in situ labeling and assembly of His-tagged proteins in time and space (see picture). This small light-tunable lock-and-key system offers the opportunity to trigger nanomolar protein interactions, such as receptor clustering, or biotechnological applications, for example, multiprotein arrays.

Pheromones

J. Gillard, J. Frenkel, V. Devos, K. Sabbe,
C. Paul, M. Rempt, D. Inzé, G. Pohnert,*
M. Vuylsteke,* W. Vyverman* _ 854 – 857

Metabolomics Enables the Structure Elucidation of a Diatom Sex Pheromone

Back Cover

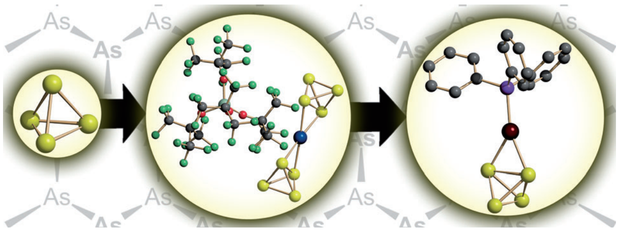


Finding a mate: Diatoms use chemical signals to sense the presence of and find their mating partners. When the metabolic profiles of sexually active and inactive cells were compared, a highly up-regulated metabolite generated in the attracting mating type was identified as di-L-prolyl diketopiperazine, the first diatom pheromone.

Complexes of Yellow Arsenic

C. Schwarzmaier, M. Sierka,
M. Scheer* ________ 858 – 861

Intact As_4 Tetrahedra Coordinated Side-On to Metal Cations



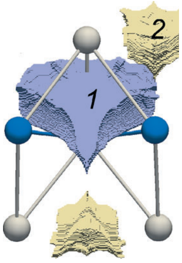
Extremely light sensitive yellow arsenic (As_4) reacts with a weakly coordinated silver cation to afford $[Ag(\eta^2\text{-}As_4)_2]^+[Al\{OC(CF_3)_3\}_4]^-$ as the first known homoleptic arsenic complex. DFT calculations and Raman spectroscopy clearly indicate the coordination of two intact As_4 tetrahedra. This unprecedented complex is used as an As_4 transfer agent, which is demonstrated by the synthesis of $[(PPh_3)Au(\eta^2\text{-}As_4)]^+[Al\{OC(CF_3)_3\}_4]^-$.

Structure and Bonding

K. Stolze, A. Isaeva, F. Nitsche,
U. Burkhardt, H. Lichte, D. Wolf,
T. Doert* ________ 862 – 865

CuTe: Remarkable Bonding Features as a Consequence of a Charge Density Wave

CuTe bonds! A delicate balance between polyanionic Te–Te bonds and multicenter Cu–Cu and Cu–Te interactions is found in the modulated structure of CuTe. Modulated CuTe is thus an alliance of typical bonding properties of polyanionic and metal-rich compounds.



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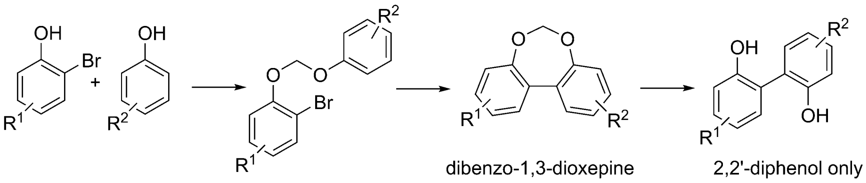
Diphenol Synthesis

K.-S. Masters,* S. Bräse* ——— **866 – 869**

The Acetal Concept: Regioselective Access to *ortho*,*ortho*-Diphenols via Dibenzo-1,3-dioxepines



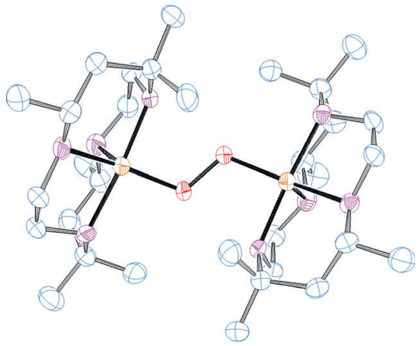
Traditional methods are ill-suited for the synthesis of *ortho*,*ortho*-biphenols, a structural motif found in many polyphenolic natural products, as well as synthetically useful compounds such as the chiral ligands binol, vapol, and vanol. The new route consists of a radical-based reaction of an acetal-tethered biphenyl ether substrate and subsequent hydrolytic cleavage of the dibenzo-1,3-dioxepine intermediate.

Copper Peroxido Complexes

T. Hoppe, S. Schaub, J. Becker, C. Würtele, S. Schindler* ——— **870 – 873**

Characterization of a Macrocyclic end-on Peroxido Copper Complex

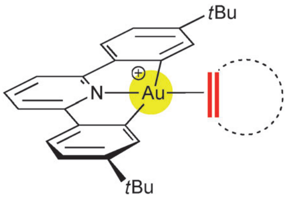
Thirty years on: The dinuclear copper peroxido complex [(tet b)CuO$_2$Cu(tet b)]$^{2+}$ has been structurally characterized (see picture: Cu yellow, O red, N pink; tet b = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). This complex is quite persistent in solution at room temperature and is the first example of a structurally characterized copper dioxygen adduct complex with a macrocyclic ligand based on earlier studies by Valentine et al.



Gold(III) Alkene Complexes

N. Savjani, D.-A. Roşca, M. Schormann, M. Bochmann* ——— **874 – 877**

Gold(III) Olefin Complexes

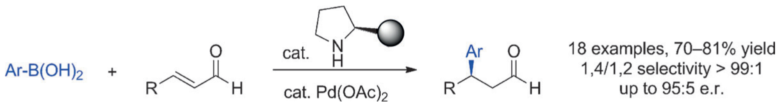


Zeise's salt gets company: 185 years after the report of the well-known platinum(II) ethylene compound, examples of isolable olefin complexes of its isoelectronic neighbor in the periodic table, gold(III), have been prepared (see picture). The complexes are very susceptible towards nucleophilic attack; there is also structural evidence for Au^{III}–Ag interactions.

Asymmetric Catalysis

I. Ibrahem,* G. Ma, S. Afewerki, A. Córdova* ——— **878 – 882**

Palladium/Chiral Amine Co-catalyzed Enantioselective β-Arylation of α,β-Unsaturated Aldehydes

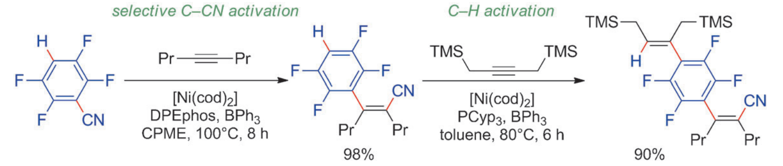


Palladium and a simple chiral amine are used as co-catalysts for the enantioselective conjugate addition of aryl boronic acids to α,β-unsaturated aldehydes (see scheme). The synthetic utility of this co-catalyzed reaction was demonstrated in the short total syntheses of (*R*)-(−)-curcumene and 4-aryl-2-ones.

C—C Activation

Y. Minami,* H. Yoshiyasu, Y. Nakao,*
T. Hiyama* ______ 883 – 887

Highly Chemoselective Carbon—Carbon σ-Bond Activation: Nickel/Lewis Acid Catalyzed Polyfluoroarylcyanation of Alkynes



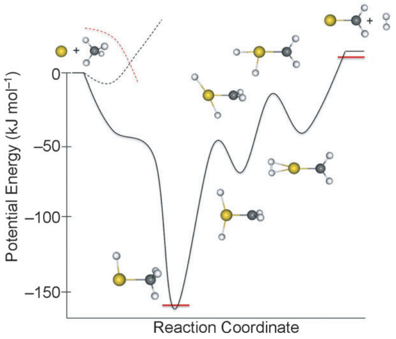
Selective C—C bond cleavage: A catalyst consisting of nickel(0)/DPEphos and BPh_3 is highly effective for the addition of polyfluorobenzonitriles to alkynes through selective activation of the C—CN bond over the C—H or C—F bonds. The addition reaction is applicable to the sequential insertion of two different alkynes into C—CN and C—H bonds (see scheme).

Methane Activation

M. Perera, R. B. Metz,* O. Kostko,
M. Ahmed ______ 888 – 891

Vacuum Ultraviolet Photoionization Studies of $PtCH_2$ and H-Pt-CH_3: A Potential Energy Surface for the Pt+CH_4 Reaction

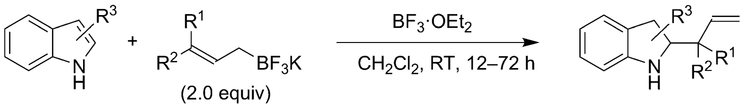
Does Charge Matter? Direct vacuum UV measurement of ionization energies reveals that C–H insertion by Pt to form H-Pt-CH_3 is highly exoergic, while production of $PtCH_2+H_2$ is slightly endoergic. Experiments and spin-orbit DFT calculations reveal surprisingly similar energetics for dehydrogenation of methane by neutral and cationic platinum. Red lines in the picture indicate experimentally determined energies.



Indole Functionalization

F. Nowrouzi, R. A. Batey* ______ 892 – 895

Regio- and Stereoselective Allylation and Crotylation of Indoles at C2 Through the Use of Potassium Organotrifluoroborate Salts



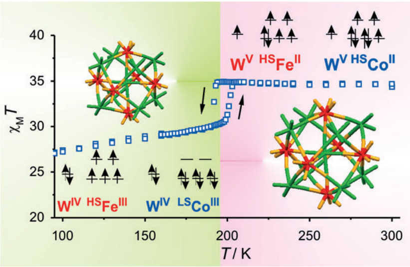
A practical method for the allylation, prenylation, propargylation, and diastereoselective crotylation of indoles has been developed using air- and moisture-stable potassium organotrifluoroborate reagents (see scheme). Lewis acids such as $BF_3{\cdot}Et_2O$ promote addition to afford 2-allyl- and 2-crotylindolines in high yields and diastereoselectivities.

Switchable Materials

R. Podgajny,* S. Chorazy, W. Nitek,
M. Rams, A. M. Majcher, B. Marszałek,
J. Żukrowski, C. Kapusta,
B. Sieklucka* ______ 896 – 900

Co–NC–W and Fe–NC–W Electron-Transfer Channels for Thermal Bistability in Trimetallic $\{Fe_6Co_3[W(CN)_8]_6\}$ Cyanido-Bridged Cluster

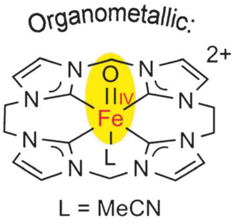
Which way to choose? The trimetallic cyanide-bridged $Fe_6Co_3W_6$ cluster serves as a molecular platform for two cooperating electron-transfer channels, W^{V}–CN–$^{HS}Co^{II}\rightleftarrows W^{IV}$–CN–$^{LS}Co^{III}$ and W^{V}–CN–$^{HS}Fe^{II}\rightleftarrows W^{IV}$–CN–$^{HS}Fe^{III}$. $\{Co^{II}_3Fe^{II}_6[W^{V}(CN)_8]_6(MeOH)_{24}\}{\cdot}x\,MeOH$ has a first-order unique spin transition with thermal charge-transfer-induced spin transition and spin bistability that is due to a specific distribution of Co and Fe sites.



Bioinorganic Chemistry

S. Meyer, I. Klawitter, S. Demeshko, E. Bill,
F. Meyer* ——— 901 – 905

A Tetracarbene–Oxoiron(IV) Complex

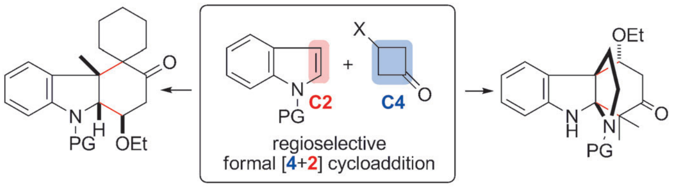


Bioinspired organometallic chemistry: An oxoiron(IV) unit has been trapped within a macrocyclic tetracarbene ligand, merging a key bioinorganic intermediate with a popular organometallic scaffold (see picture). The stability of the new complex has allowed its characterization by a variety of methods, which show a strong σ-donating tetracarbene coordination leading to an $S=1$ ground state and unusual properties of the oxoiron(IV) species.

Cycloaddition

M. Kawano, T. Kiuchi, S. Negishi,
H. Tanaka, T. Hoshikawa
J. Matsuo,* H. Ishibashi ——— 906 – 910

Regioselective Inter- and Intramolecular Formal [4+2] Cycloaddition of Cyclobutanones with Indoles and Total Synthesis of (±)-Aspidospermidine

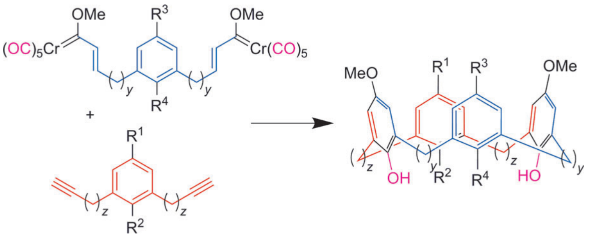


This way and that way: A formal [4+2] cycloaddition between various cyclobutanones and indoles proceeded efficiently under Lewis acid catalysis (see scheme; PG = protecting group). The regioselectivity of the reaction could be controlled in such a way that each of the two possible regioisomers of a cycloaddition product could be synthesized selectively. The usefulness of this reaction for the total synthesis of hydrocarbazole natural products was demonstrated.

Synthetic Methods

A. V. Predeus, V. Gopalsamuthiram,
R. J. Staples, W. D. Wulff* ——— 911 – 915

Rational Synthesis for All *All*-Homocalixarenes

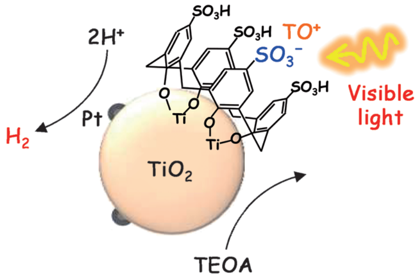


Have it all: The synthesis of homocalixarenes of all sizes has been demonstrated using the triple annulation of bis(carbene) complexes with diynes (see scheme). This strategy in principle should allow access to all homocalixarenes. The generality of the synthetic approach is also demonstrated by the preparation of a pyrrole-containing calixarene.

Photocatalysis

T. Kamegawa, S. Matsuura, H. Seto,
H. Yamashita* ——— 916 – 919

A Visible-Light-Harvesting Assembly with a Sulfocalixarene Linker between Dyes and a Pt-TiO_2 Photocatalyst

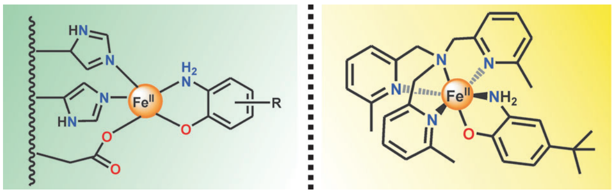


Successful anchoring of cationic dye molecules (thiazole orange, TO) on Pt-TiO_2 for a visible-light-harvesting assembly was achieved by surface modification of Pt-TiO_2 with 4-sulfocalix[4]arene as a linker, leading to formation of surface complexes (see picture). This heterogeneous system can act as an efficient photocatalyst for production of hydrogen in the presence of a sacrificial reagent (TEOA = triethanolamine).

Biomimetic Model

B. Chakraborty, T. K. Paine* 920–924

Aromatic Ring Cleavage of 2-Amino-4-*tert*-butylphenol by a Nonheme Iron(II) Complex: Functional Model of 2-Aminophenol Dioxygenases

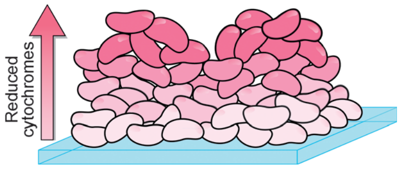


Biomimetic aromatic ring cleavage: An iron(II)-2-aminophenolate complex (see picture, right) with a tetradentate ligand reacts with dioxygen to cleave the aromatic C—C bond of 2-amino-4-*tert*-butylphenolate to form 4-*tert*-butyl-2-picolinate. This complex represents a functional model of 2-aminophenol-1,6-dioxygenase (APD) and 3-hydroxyanthranilate-3,4-dioxygenase (HAD).

Conduction in Bacterial Films

L. Robuschi, J. P. Tomba, G. D. Schrott, P. S. Bonanni, P. M. Desimone, J. P. Busalmen* 925–928

Spectroscopic Slicing to Reveal Internal Redox Gradients in Electricity-Producing Biofilms



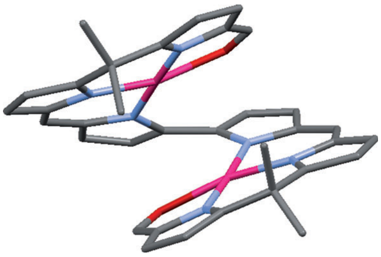
Wired-up bacteria: Confocal Raman microscopy in combination with 3D structural analysis is used in the measurement of redox gradients in electricity-producing biofilms in vivo. The approach provides new relevant information for the understanding of electron conduction mechanisms in these systems.

Helical Structures

C. Eerdun, S. Hisanaga, J. Setsune* 929–932

Single Helicates of Dipalladium(II) Hexapyrroles: Helicity Induction and Redox Tuning of Chiroptical Properties

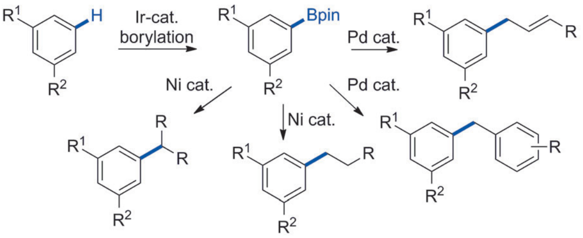
Hexapyrrole-α,ω-dialdehyde, which has eight donor atoms, afforded a dipalladium(II) single helicate (see picture; Pd pink, O red, N blue). A rapid interchange of the helical screw was slowed down by imine formation at the terminal aldehyde units with (*R*)-(−)-1-cyclohexylethylamine, leading to an overwhelming excess of a *P*-helical screw. This stable dinuclear single helicate has a redox-driven reversible change in chiroptical properties.



Arene Alkylation

D. W. Robbins, J. F. Hartwig* 933–937

Sterically Controlled Alkylation of Arenes through Iridium-Catalyzed C–H Borylation

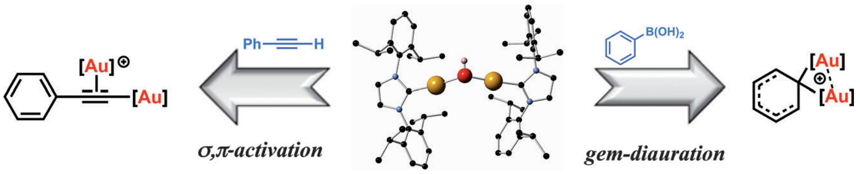


Complementary chemistry: A one-pot method for the site-selective alkylation of arenes controlled by steric effects is reported. The process occurs through Ir-catalyzed C–H borylation, followed by Pd- or Ni-catalyzed coupling with alkyl electrophiles. This selectivity complements that of the typical Friedel–Crafts alkylation; *meta*-selective alkylation of a broad range of arenes with various electronic properties and functional groups occurs in good yield with high site selectivity.

Synthetic Methods

A. Gómez-Suárez, S. Dupuy,
A. M. Z. Slawin, S. P. Nolan* ___ 938 – 942

Straightforward Synthetic Access to *gem*-Diaurated and Digold σ,π-Acetylide Species

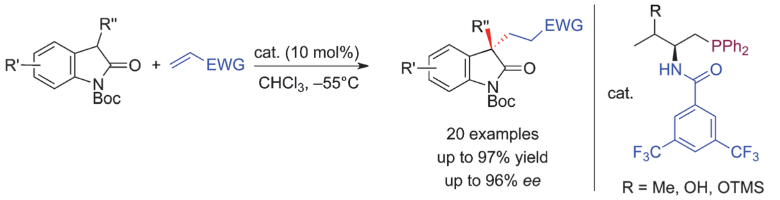


The more the merrier: Following previous investigations on the synthesis of organogold complexes by using [Au(IPr)(OH)], a high-yielding straightforward methodology for the synthesis of *gem*-diaurated and σ,π-acetylide species via a dinuclear gold hydroxide complex [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (see scheme) has now been developed.

Asymmetric Catalysis

F. Zhong, X. Dou, X. Han, W. Yao, Q. Zhu,
Y. Meng, Y. Lu* ___ 943 – 947

Chiral Phosphine Catalyzed Asymmetric Michael Addition of Oxindoles

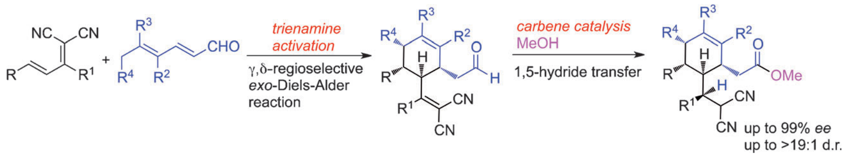


Bifunctional phosphines derived from amino acids mediate the asymmetric Michael addition of 3-substituted oxindoles to activated alkenes (see scheme). Biologically relevant chiral 3,3-disubstituted oxindoles were thus prepared in high yields and with excellent enantioselectivities from 3-aryl- and 3-alkyl-substituted oxindoles and various activated alkenes.

Asymmetric Synthesis

C. Ma, Z.-J. Jia, J.-X. Liu, Q.-Q. Zhou,
L. Dong, Y.-C. Chen* ___ 948 – 951

A Concise Assembly of Electron-Deficient 2,4-Dienes and 2,4-Dienals: Regio- and Stereoselective *exo*-Diels–Alder and Redox Reactions through Sequential Amine and Carbene Catalysis

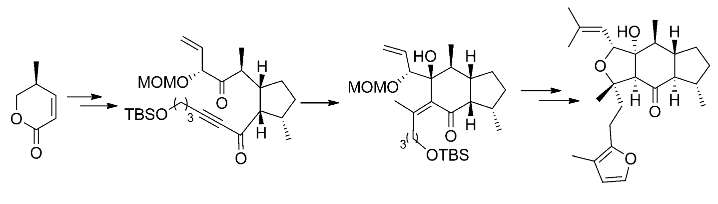


Ideal relay catalysis: A γ,δ-regioselective anomalous *exo*-Diels–Alder reaction with electron-deficient β-substituted 2,4-dienes and 2,4-dienals has been developed by using trienamine activation. The resulting multifunctional cycloadducts contain perfectly positioned functional groups, thereby facilitating a 1,5-hydride transfer from the C–H group of an aldehyde to an activated alkene under sequential catalysis of a carbene (see scheme).

Natural Products

X. Huang, L. Song, J. Xu, G. Zhu,
B. Liu* ___ 952 – 955

Asymmetric Total Synthesis of Leucosceptroid B

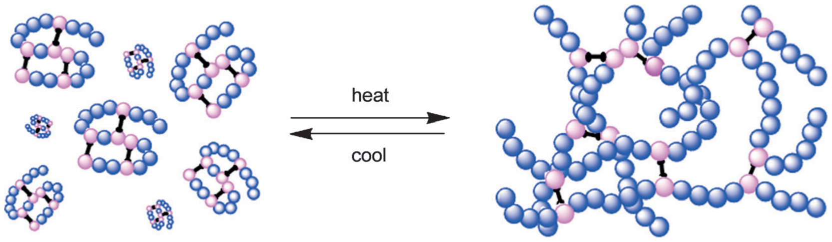


Less stable, but natural: The asymmetric total synthesis of leucosceptroid B (see scheme) has been accomplished in 19 steps. Thermodynamically, this natural product proved to be less stable than its C11 epimer, a synthetic intermediate. This synthesis features a high degree of flexibility, facilitating its application to the preparation of a broad range of other natural derivatives.

Constitutional Dynamic Materials

D. E. Whitaker, C. S. Mahon,
D. A. Fulton* ______ 956–959

Thermoresponsive Dynamic Covalent Single-Chain Polymer Nanoparticles Reversibly Transform into a Hydrogel



To gel and back: Polymer nanoparticles can be reversibly transformed into a chemically cross-linked hydrogel. This transformation is triggered by the application of heat, which causes the polymer chains to aggregate, and the dynamic nature of the covalent cross-linking serves to reorganize the polymer chains into a hydrogel network.

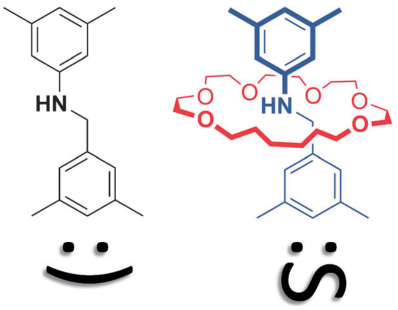
Rotaxanes

C. B. Caputo, K. Zhu, V. N. Vukotic,
S. J. Loeb,* D. W. Stephan* __ 960–963

Heterolytic Activation of H_2 Using a Mechanically Interlocked Molecule as a Frustrated Lewis Base

Front Cover

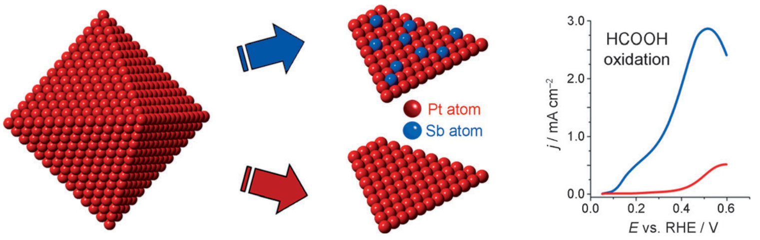
Frustrating: A sterically unencumbered aniline base (see picture, left) can be transformed into a bulky Lewis base by converting it into a [2]rotaxane (right). This Lewis base donor, which is surrounded by a protective macrocyclic ring, exhibits the reactivity of a frustrated Lewis pair (e.g. activation of H_2(g)) without the need for direct covalent modification to increase its bulk.



Electrocatalysis

F. J. Vidal-Iglesias, A. López-Cudero,
J. Solla-Gullón, J. M. Feliu* __ 964–967

Towards More Active and Stable Electrocatalysts for Formic Acid Electrooxidation: Antimony-Decorated Octahedral Platinum Nanoparticles

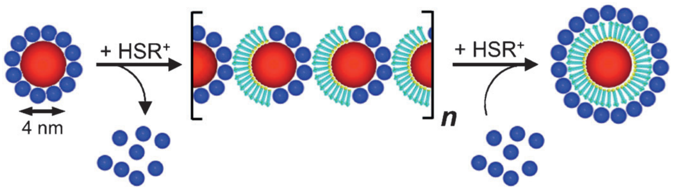


Antimony has it covered: Sb-decorated octahedral Pt nanoparticles have been prepared, and their electrocatalytic properties evaluated for formic acid electrooxidation. When tested at 0.2 V, these nanoparticles displayed high and stable current densities, as well as 35, five, and eight-fold current oxidation increases over bare octahedral and Sb-decorated spherical and cubic nanoparticles, respectively.

Nanoparticles

O. Zeiri, Y. Wang, A. Neyman, F. Stellacci,
I. A. Weinstock* ______ 968–972

Ligand-Shell-Directed Assembly and Depolymerization of Patchy Nanoparticles

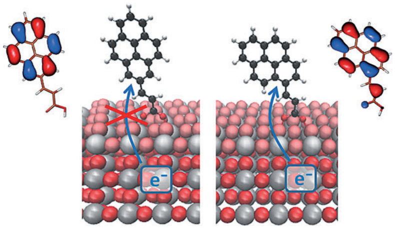


Unprecedented insertions of cationic alkanethiols, $HS(CH_2)_{11}N(CH_3)_3^+$ (see scheme; cyan-colored rods), between polyoxometalate protecting ligands, α-$AlW_{11}O_{39}^{9-}$ (blue circles), and the surfaces of gold nanoparticles, give “zwitterionic” patchy nanoparticles (PNs). Their shell structures and assembly properties vary with particle size during rational in situ modifications that lead to three-component core–shell aggregates never observed before in PNs.

Dye-Sensitized Solar Cells

E. Maggio, N. Martsinovich,
A. Troisi* ——— **973 – 975**

Using Orbital Symmetry to Minimize Charge Recombination in Dye-Sensitized Solar Cells

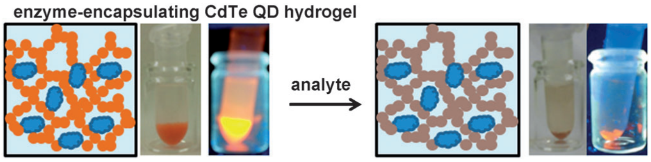


Suitably designed symmetric dyes can be used in dye-sensitized solar cells to reduce the charge recombination rate by two to three orders of magnitude. If the electron coupling between the electrode and the dye is mediated by a conjugated linker, it is possible to design dyes for which the HOMO of the dye is not coupled to the semiconductor.

Biosensors

J. P. Yuan, D. Wen, N. Gaponik,
A. Eychmüller* ——— **976 – 979**

Enzyme-Encapsulating Quantum Dot Hydrogels and Xerogels as Biosensors: Multifunctional Platforms for Both Biocatalysis and Fluorescent Probing

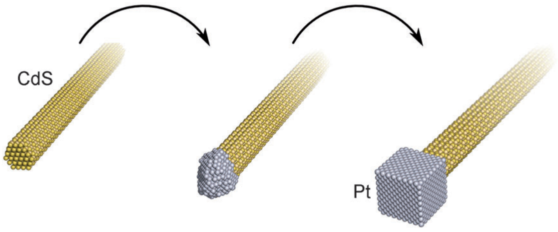


Trapped: Enzymes (blue in picture) were encapsulated into CdTe quantum dot (QD) hydrogels during the self-assembly of CdTe QDs (orange) in phosphate buffer solution. The as-prepared enzyme-encapsulating QD hydrogel incorporating both a biocatalysis unit and a fluorescence signaling unit was further explored as a multifunctional platform in the development of optical biosensors.

Nanocrystals

H. Schlicke, D. Ghosh, L.-K. Fong,
H. L. Xin, H. Zheng,
A. P. Alivisatos* ——— **980 – 982**

Selective Placement of Faceted Metal Tips on Semiconductor Nanorods

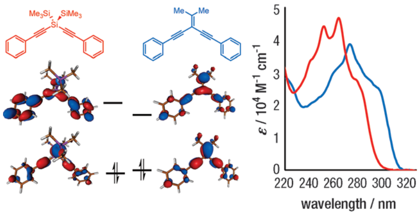


Squaring the circle: Carbon monoxide was used to grow faceted cube-like platinum tips on semiconductor nanorods (see scheme). These novel hybrid structures reveal a new degree of synthetic control and might allow control over the catalytic activity of nanoscale photocatalysts by adding defined faceting.

Conjugation

R. Emanuelsson, A. Wallner, E. A. M. Ng,
J. R. Smith, D. Nauroozi, S. Ott,
H. Ottosson* ——— **983 – 987**

Cross-Hyperconjugation: An Unexplored Orbital Interaction between π-Conjugated and Saturated Molecular Segments



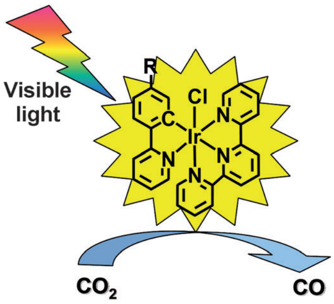
Crossing a barrier: Molecules with saturated ER_2 units (E = C or Si, R = electron-releasing group) inserted between two π-conjugated segments have electronic and optical properties that resemble those of cross-conjugated molecules (see figure). This cross-hyperconjugation provides a deeper understanding of the conjugation phenomenon, and is an alternative to cross-conjugation in the design of molecules for nano and materials applications.

Photocatalysis

S. Sato,* T. Morikawa, T. Kajino,
O. Ishitani ______ 988 – 992

A Highly Efficient Mononuclear Iridium Complex Photocatalyst for CO_2 Reduction under Visible Light

Mononuclear iridium(III) terpyridine (tpy) 2-phenylpyridine (ppy) complexes [Ir(tpy)(R-ppy)Cl] (R = H, Me, CF_3) can act as efficient and selective CO_2 reduction photocatalysts. The reaction is driven using visible light in a homogeneous solution, and even in a H_2O mixed solution. The most efficient photocatalyst is [Ir(tpy)(Me-ppy)Cl], for which the turnover in CO was over 50 and the quantum yield was 0.21 at 480 nm.

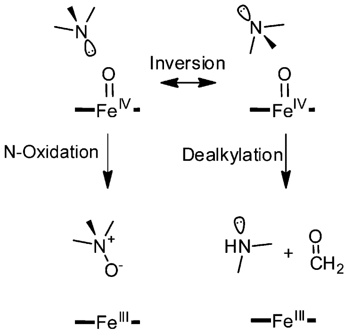


Density Functional Calculations

P. Rydberg, M. S. Jørgensen,
T. A. Jacobsen, A.-M. Jacobsen,
K. G. Madsen, L. Olsen* ______ 993 – 997

Nitrogen Inversion Barriers Affect the N-Oxidation of Tertiary Alkylamines by Cytochromes P450

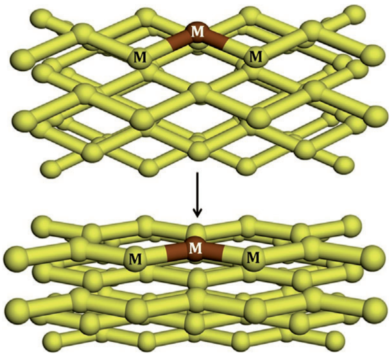
Calculations: Cytochrome P450 enzymes facilitate a number of chemically different reactions. For example, amines can be either N-dealkylated or N-oxidized, but it is complex to rationalize which of these competing reactions occurs. It is shown that the barrier for inversion of the alkylamine nitrogen atom seems to be of vital importance for the amount of N-oxidized product formed relative to dealkylation and hydroxylation products.



Dynamic Frameworks

B. Manna, A. K. Chaudhari, B. Joarder,
A. Karmakar, S. K. Ghosh* ______ 998 – 1002

Dynamic Structural Behavior and Anion-Responsive Tunable Luminescence of a Flexible Cationic Metal–Organic Framework

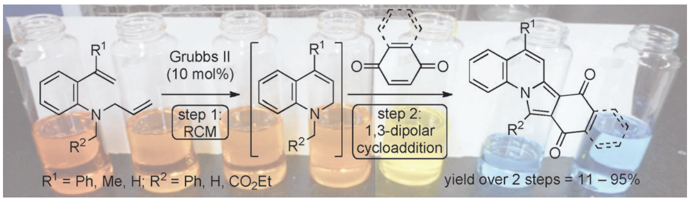


Guest and anion dependent: Structural dynamism and luminescence of a cationic porous framework (see picture) are investigated by different analytical techniques, such as single-crystal-to-single-crystal structural transformation. The compound shows size-selective sorption of hydrophobic guest molecules, easy exchange of anions of the framework, and interesting anion-responsive luminescence.

Ruthenium Catalysis

M. Arisawa,* Y. Fujii, H. Kato, H. Fukuda,
T. Matsumoto, M. Ito, H. Abe, Y. Ito,
S. Shuto* ______ 1003 – 1007

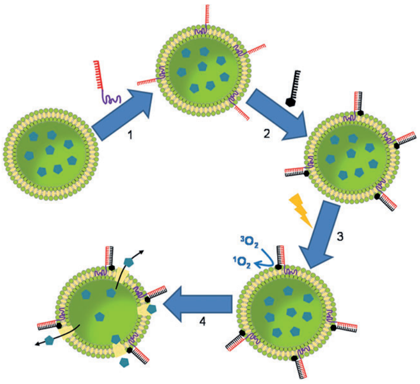
One-Pot Ring-Closing Metathesis/1,3-Dipolar Cycloaddition through Assisted Tandem Ruthenium Catalysis: Synthesis of a Dye with Isoindolo[2,1-*a*]quinoline Structure



The one-pot tandem reaction of *N*-alkyl-*N*-allyl-2-vinylaniline derivatives with benzo- or naphthoquinones and a ruthenium–alkylidene catalyst leads to isoindolo[2,1-*a*]quinolines in a variety of colors, which can be altered by exchanging the substituent on the core heterocycle (see scheme). This reaction offers a new synthetic method for π-conjugated small molecules from simple aniline derivatives.

Controlled Cargo Release

Vesicle buster: Versatile functionalized nanocontainers, based on the stable incorporation of 22 mer DNA-*b*-PPO block copolymers (DBCs) into lipid vesicles, are presented (see picture). The study shows effective and sequence-specific cargo release from the DBC–lipid vesicles. Hybridization of these vesicles with an oligonucleotide photosensitizer allows for singlet oxygen generation upon irradiation, which induces cargo release.

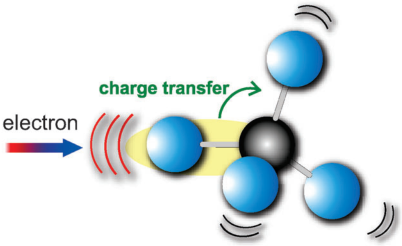


A. Rodríguez-Pulido, A. I. Kondrachuk, D. K. Prusty, J. Gao, M. Loi, A. Herrmann* ——— 1008 – 1012

Light-Triggered Sequence-Specific Cargo Release from DNA Block Copolymer–Lipid Vesicles

Inside Back Cover

Stereodynamics



Electron capture at the carbon–fluorine σ* antibonding orbital accounts for the vector correlations between fragments F^- and CF_3 or F and CF_3^- in two complementary dissociation pathways after electron attachment to CF_4. An orientation effect in the low-energy electron attachment is observed by velocity mapping (see picture; C black, F blue).

L. Xia, X.-J. Zeng, H.-K. Li, B. Wu, S. X. Tian* ——— 1013 – 1016

Orientation Effect in the Low-Energy Electron Attachment to the Apolar Carbon Tetrafluoride Molecule

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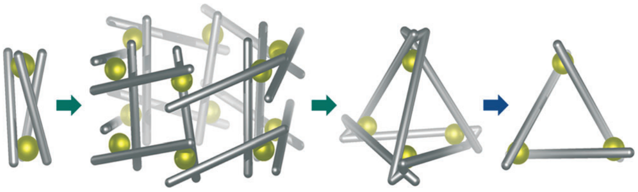
Systems Chemistry



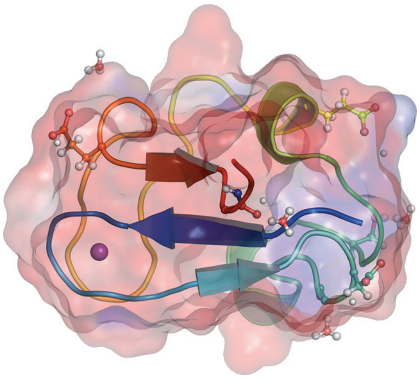
Cd^{II} transformer: By using a linear dialdehyde, Cd^{II} ions, and different amines, different architectures were constructed, including an $M_2L_3^{4+}$ triple helicate, an $M_3L_3^{6+}$ triangle, an M_4L^{8+} cryptate, as well as an $M_{12}L_{18}^{24+}$ hexagonal prism. These structures could be interconverted in a complex network by dynamic imine exchange, the addition of a template, or a change in the pH value of the solution.

W. Meng, T. K. Ronson, J. K. Clegg, J. R. Nitschke* ——— 1017 – 1021

Transformations within a Network of Cadmium Architectures

Protein Perdeuteration

Neutron crystallographic analyses at near-atomic resolution are presented for both reduced and oxidized forms of perdeuterated *Pyrococcus furiosus* rubredoxin, a small iron–sulfur redox protein with remarkable thermostability. Hydronium ions may play a key role in the protonation and charge-transfer processes associated with the oxidized and reduced forms of the protein. Picture: overall structure showing D_3O^+ ions (red and gray molecules).



M. G. Cuypers, S. A. Mason, M. P. Blakeley, E. P. Mitchell, M. Haertlein, V. T. Forsyth* 1022 – 1025

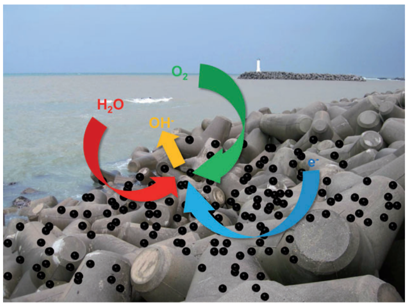
Near-Atomic Resolution Neutron Crystallography on Perdeuterated *Pyrococcus furiosus* Rubredoxin: Implication of Hydronium Ions and Protonation State Equilibria in Redox Changes

Oxygen-Reduction Catalysts

J. Lee, G. Park, S. Kim, M. Liu,*
J. Cho* ________________ 1026 – 1030

A Highly Efficient Electrocatalyst for the Oxygen Reduction Reaction: N-Doped Ketjenblack Incorporated into Fe/Fe$_3$C-Functionalized Melamine Foam

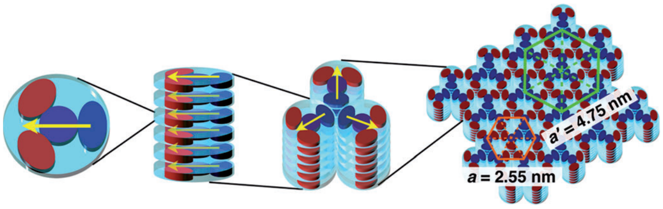
Inspired by the tetrapod structures of a breakwater, a highly efficient electrocatalyst for oxygen reduction reaction (ORR) in alkaline solution has been created from low-cost, commercial melamine foam and ketjenblack. The unique porous architecture greatly facilitates rapid mass transport, while the N-doped ketjenblack and Fe/Fe$_3$C-functionalized surface of the framework dramatically enhance the ORR activity.



Liquid Crystals

M.-C. Yeh, Y.-L. Su, M.-C. Tzeng,
C. W. Ong,* T. Kajitani,* H. Enozawa,
M. Takata, Y. Koizumi, A. Saeki, S. Seki,
T. Fukushima ________________ 1031 – 1034

Amphiphilic Design of a Discotic Liquid-Crystalline Molecule for Dipole Manipulation: Hierarchical Columnar Assemblies with a 2D Superlattice Structure

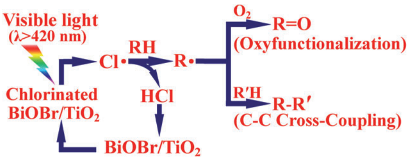


A liquid-crystalline dibenzophenazine that was forced to adopt a head-to-head stacking arrangement to generate a large dipole moment adapted to this stacking by hierarchical assembly into a 2D hexagonal superlattice (see picture). Thus, the net dipole and the contact area between immiscible side chains were minimized. Homeotropic alignment of the assembly on glass gave rise to directional charge transport.

Photocatalysis

R. S. Yuan,* S. L. Fan, H. X. Zhou,
Z. X. Ding, S. Lin, Z. H. Li,* Z. Z. Zhang,
C. Xu, L. Wu, X. X. Wang,
X. Z. Fu ________________ 1035 – 1039

Chlorine-Radical-Mediated Photocatalytic Activation of C–H Bonds with Visible Light



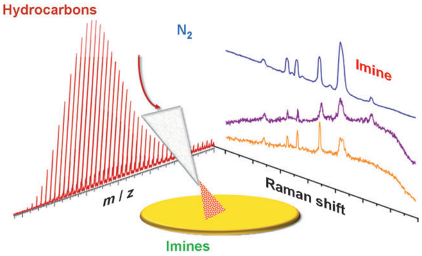
Going green on the cheap: A highly effective photocatalytic reaction mode involving chlorine radicals generated on chlorinated BiOBr/TiO$_2$ upon irradiation with visible light enabled selective transformations of alkanes into functionalized products through the formation of C–O and C–C bonds (see scheme). This process provides a sustainable strategy for direct C–H functionalization under mild conditions.

Metal-Free Alkane Transformation

G. Li, X. Li, Z. Ouyang,
R. G. Cooks* ________________ 1040 – 1043

Carbon–Carbon Bond Activation in Saturated Hydrocarbons by Field-Assisted Nitrogen Fixation

Functionalization of alkanes: Waxes present on electrically charged surfaces undergo C–C bond functionalization with N$_2$ to give imines. The products are characterized on-line by mass spectrometry or collected and characterized off-line by Raman spectroscopy (see picture).

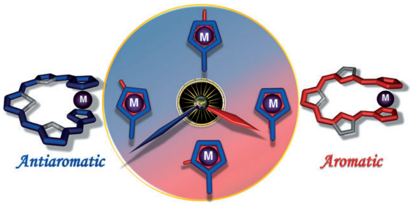


Aromaticity

I. Grocka, L. Latos-Grażyński,* M. Stępień ________ 1044 – 1048

Ruthenocenoporphyrinoids: Conformation Determines Macrocyclic π Conjugation Transmitted Across a d-Electron Metallocene

Hinges upon Ru: The hingelike flexibility of ruthenocene plays the critical role as a determinant of aromaticity as exemplified by its aromatic synperiplanar and antiaromatic anticlinal(eclipsed) conformers of ruthenocenoporphyrinoids (see figure).

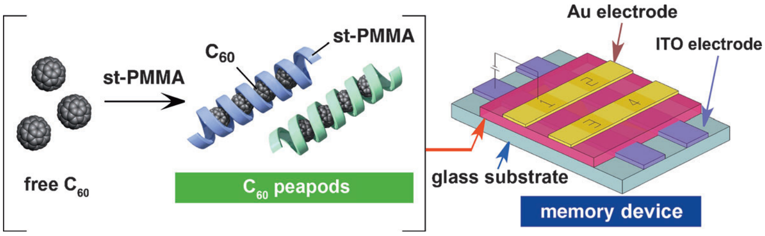


Molecular Wires

S. Qi,* H. Iida, L. Liu, S. Irle,* W. Hu, E. Yashima* ________ 1049 – 1053

Electrical Switching Behavior of a [60]Fullerene-Based Molecular Wire Encapsulated in a Syndiotactic Poly(methyl methacrylate) Helical Cavity

Inside Cover



Exploding peapods? A helical syndiotactic poly(methyl methacrylate) encapsulates C_{60} molecules within its helical cavity to form a supramolecular peapod-like molecular wire. Sandwich devices using these molecular wires in the active layer exhibit an irreversible electrical switching effect. Calculations predict a violent Coulomb explosion in the peapod C_{60} wires during the charge injection process, which would account for the observed irreversible electrical switching.

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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