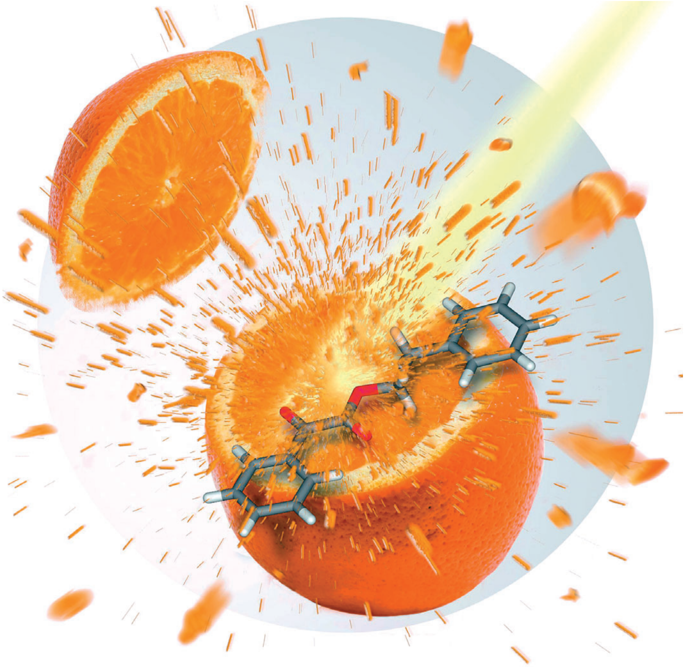
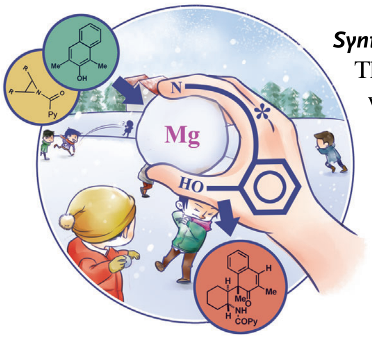
Like the peel of an orange ...



… the shell of core–shell capsules protects and encapsulates flavors and fragrances against premature degradation. To release the aroma in both cases, the peel or the shell has to be mechanically broken. In their Communication on page 2275 ff., D. L. Berthier, A. Herrmann, and co-workers report that co-encapsulation of 2-oxoacetates allows the light-triggered release of fragrances by photochemically generating a gas overpressure that ruptures the capsule wall without relying on additional mechanical pressure.

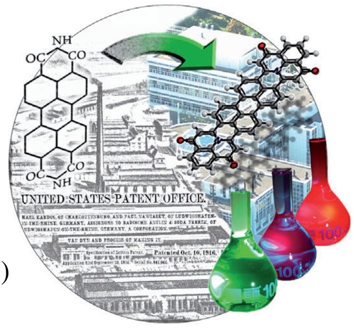
Isotope Effects

In their Communication on page 2052 ff., W. Ma, J. Zhao, and co-workers elucidated a proton-induced pathway for the TiO_2-mediated photochemical dehalogenation of non-adsorbable aromatic bromides with an inverse kinetic solvent isotope effect.



Synthetic Methods

The intermolecular dearomatization of β-naphthols with aziridines using a chiral Mg catalyst is reported by R. Wang et al. in their Communication on page 2185 ff. The products could be transformed into a polycyclic core skeleton and a polyhydroxylated compound.



Chromophores

K. Müllen and co-workers describe in their Communication on page 2285 ff. versatile synthetic methods to transform the long-established dye perylene-3,4:9,10-tetracarboxylic diimide (PDI) into novel chromophores.

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Service

Author Profile

"My favorite music is Tchaikovsky's ballet music. The most exciting thing about my research is directly observing the behavior of my favorite molecules …"
This and more about Masayuki Endo can be found on page 2002.

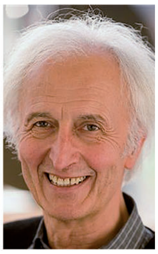
News

T. Bach

R. A. Shenvi

D. J. Weix

E. Giralt



H. Schwarz

Obituaries

Nico Nibbering, one of the European pioneers in gas-phase ion chemistry and mass spectrometry passed away on August 22nd 2014. He was one of the leading figures in the field of gas-phase uni- and bimolecular ion–molecule reactions, and his skills in solving reaction mechanisms were rivaled by only a few. Nibbering and his group were also pioneering scientists in ion cyclotron resonance mass spectrometry.

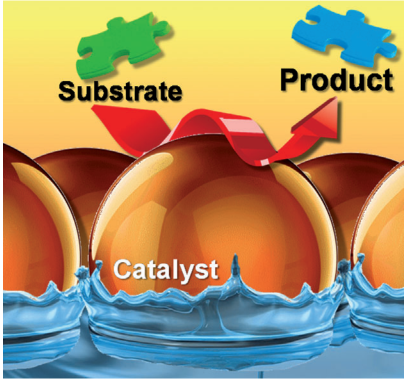
Minireviews

Biphasic Catalysis

M. Pera-Titus,* L. Leclercq, J.-M. Clacens, F. De Campo, V. Nardello-Rataj* ______ **2006 – 2021**

Pickering Interfacial Catalysis for Biphasic Systems: From Emulsion Design to Green Reactions

What a pick! Pickering emulsions are surfactant-free dispersions of two immiscible fluids which are kinetically stabilized by colloidal particles. This review describes recent examples of hybrid and composite amphiphilic materials for the design of interfacial catalysts in Pickering emulsions for industrially relevant biphasic reactions in fine chemistry, biofuel upgrading, and depollution.

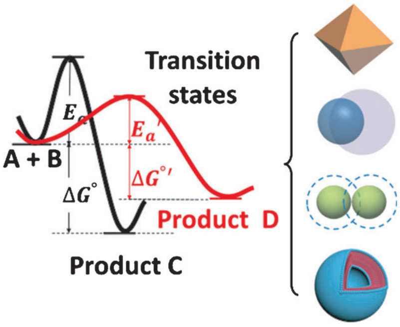


Reviews

Nanoparticle Synthesis

Y. Wang, J. He, C. Liu, W. H. Chong, H. Chen* ______ **2022 – 2051**

Thermodynamics versus Kinetics in Nanosynthesis



Understanding starts with distinction: Distinguishing between the thermodynamically and kinetically controlled scenarios is of critical importance when analyzing the complex phenomena in nanosynthesis, such as the growth of nanoparticles, their aggregation, and the shape evolution of polymer nanostructures. The processes are examined in detail in this Review and the mechanistic proposals are categorized in the common framework of thermodynamics and kinetics.

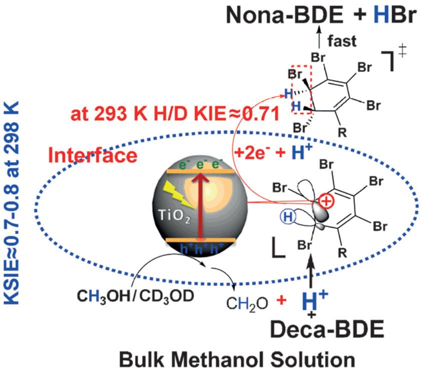
Communications

Surface Chemistry

W. Chang, C. Sun, X. Pang, H. Sheng, Y. Li, H. Ji, W. Song, C. Chen, W. Ma,* J. Zhao* ______ **2052 – 2056**

Inverse Kinetic Solvent Isotope Effect in TiO_2 Photocatalytic Dehalogenation of Non-adsorbable Aromatic Halides: A Proton-Induced Pathway

Frontispiece



A change up: Reported herein is an inverse kinetic solvent isotope effect (KSIE) for the reductive dehalogenation of decabromodiphenyl ethers (deca-BDEs). The transformation under TiO_2 photocatalysis involves a proton adduct intermediate which accompanies a hybridization change from sp^2 to sp^3 for an aromatic carbon atom. The protonation event leads to adsorption of the aromatic halides onto TiO_2 with a subsequent electron-transfer reaction to form dehalogenated products.

For the USA and Canada:
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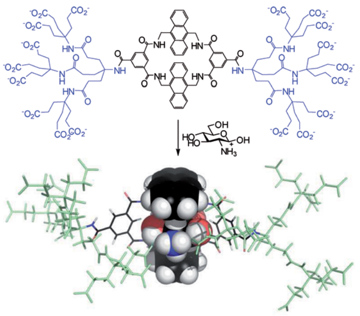
Molecular Recognition

H. Destecroix, C. M. Renney, T. J. Mooibroek, T. S. Carter, P. F. N. Stewart, M. P. Crump, A. P. Davis* ——— 2057 – 2061

Affinity Enhancement by Dendritic Side Chains in Synthetic Carbohydrate Receptors

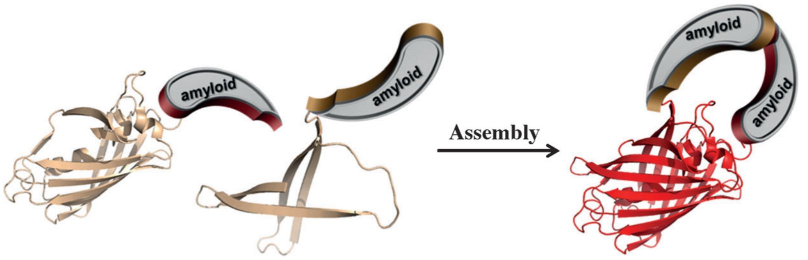


Sticky branches: The carboxylate-terminated side chains in a series of carbohydrate receptors contributed to binding if their length was just right. If they were too long, they blocked the cavity, but shorter variants could reach round to interact with polar groups on the substrate. Binding is favored by conformational degeneracy: if one carboxylate group moves away, another can take its place.

Amyloid Self-Assembly

Y. Bram, A. Lampel, R. Shaltiel-Karyo, A. Ezer, R. Scherzer-Attali, D. Segal, E. Gazit* ——— 2062 – 2067

Monitoring and Targeting the Initial Dimerization Stage of Amyloid Self-Assembly

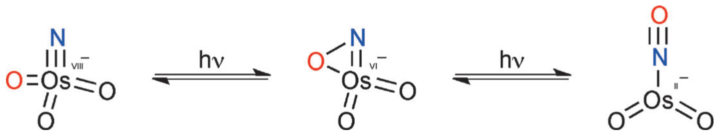


A bimolecular fluorescence complementation assay was employed to detect, monitor, and quantify the initial intermolecular interactions that lead to the amyloid self-assembly cascade. Several compounds that interfere with the dimerization process of the type 2 diabetes-associated islet amyloid polypeptide were identified. These compounds inhibit aggregation, shift the conformers equilibrium towards monomeric species, and ameliorate islet amyloid polypeptide cytotoxicity.

Photochemistry

W. A. Thornley, T. E. Bitterwolf* ——— 2068 – 2072

Photochemically Induced Intramolecular Six-Electron Reductive Elimination and Oxidative Addition of Nitric Oxide by the Nitridoosmate(VIII) Anion

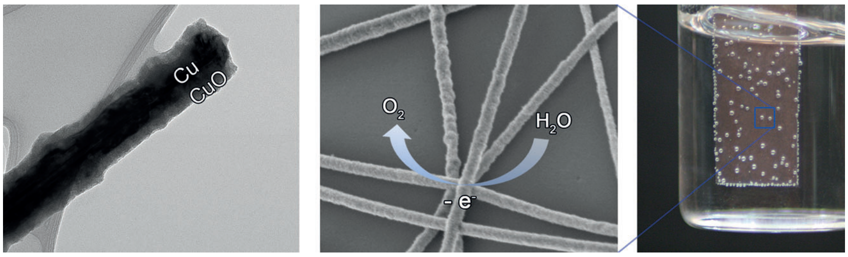


UV photolysis of the nitridoosmate(VIII) anion OsO_3N^- in low-temperature frozen matrices results in fully reversible nitrogen–oxygen bond formation to give the Os^{II} nitrosyl complex $OsO_2(NO)^-$ through a side-on nitroxyl Os^{VI} intermediate, $OsO_2(\eta^2\text{-}NO)^-$. Formally a reversible six-electron reductive elimination and oxidative addition, this represents the first reported example of such an intramolecular transformation.

Water Oxidation

J.-L. Du, Z.-F. Chen,* S.-R. Ye, B. J. Wiley, T. J. Meyer ——— 2073 – 2078

Copper as a Robust and Transparent Electrocatalyst for Water Oxidation



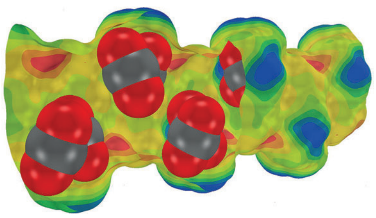
It's elementary! Copper can serve as a robust and transparent electrocatalyst for water oxidation in concentrated carbonate solutions. Formation of a compact layer of CuO intermediate from the underlying copper is found to prevent severe anodic corrosion, thus allowing sustained catalytic water oxidation.

Carbon Dioxide Sorption

C. X. Bezuidenhout, V. J. Smith,
P. M. Bhatt, C. Esterhuysen,
L. J. Barbour* ______________ 2079 – 2083

Extreme Carbon Dioxide Sorption Hysteresis in Open-Channel Rigid Metal–Organic Frameworks

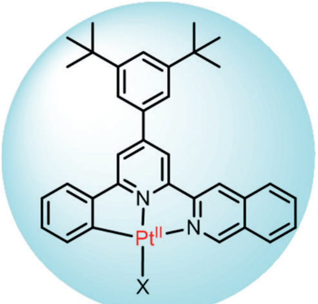
Extreme hysteresis: A systematic study has been carried out on CO_2 capture by three known metal–organic frameworks. These rigid and homeotypic MOFs display extreme hysteresis for CO_2 sorption/desorption, which can be explained in terms of electrostatic and steric topology.



Functional Materials

P.-K. Chow, G. Cheng, G. S. M. Tong,
W.-P. To, W.-L. Kwong, K.-H. Low,
C.-C. Kwok, C. Ma,
C.-M. Che* ______________ 2084 – 2089

Luminescent Pincer Platinum(II) Complexes with Emission Quantum Yields up to Almost Unity: Photophysics, Photoreductive C—C Bond Formation, and Materials Applications



1: X = $C\equiv CC_6F_5$

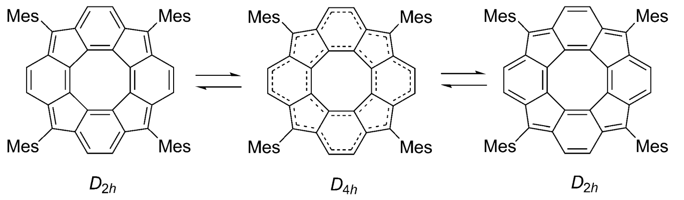
Multipurpose platinum: A phosphorescent Pt^{II} complex **1** with an emission quantum yield of 0.99 is employed as a catalyst for visible-light-induced reductive C—C bond formation and as a dopant in organic light-emitting diodes with an external quantum efficiency of 22.8%. Encapsulating **1** in mesoporous SiO_2 for two-photon-excited cellular imaging has been demonstrated.

Antiaromaticity

S. Nobusue, H. Miyoshi, A. Shimizu,
I. Hisaki, K. Fukuda, M. Nakano,
Y. Tobe* ______________ 2090 – 2094

Tetracyclopenta[*def,jkl,pqr,vwx*]tetraphenylene: A Potential Tetraradicaloid Hydrocarbon

Inside Cover

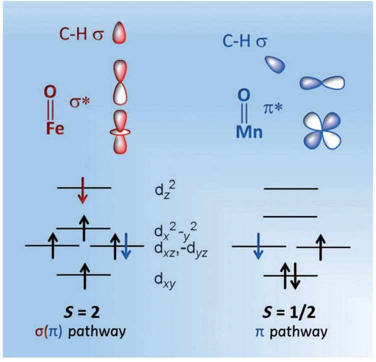


Aromatic? A tetramesityl derivative of hitherto unknown tetracyclopenta[*def,jkl,pqr,vwx*]tetraphenylene, a potential tetraradicaloid hydrocarbon, was synthesized. It exhibits remarkable antiaromaticity as a result of the peripheral 20-π-electron circuit. In solution, it adopts closed-shell D_{2h} structures that rapidly equilibrate via the D_{4h} structure, and in crystals, it adopts an approximate D_{2h} structure.

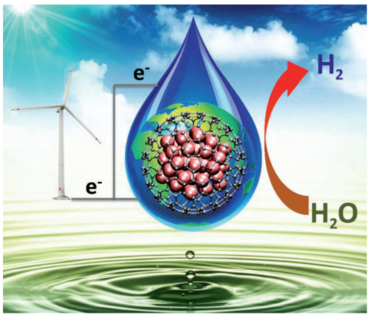
Reactive Intermediates

P. Barman, A. K. Vardhaman, B. Martin,
S. J. Wörner, C. V. Sastri,*
P. Comba* ______________ 2095 – 2099

Influence of Ligand Architecture on Oxidation Reactions by High-Valent Nonheme Manganese Oxo Complexes Using Water as a Source of Oxygen



Choosing a path: Two isomers of mononuclear nonheme Mn^{IV}=O complexes have been synthesized and characterized. Interestingly, one of the isomers is significantly more reactive than the other, while in the corresponding Fe^{IV}=O-based oxidation reactions the opposite reactivity is observed. Theoretical calculations indicate that the order of reactivity is primarily due to a switch in reaction pathways (σ versus π) with concomitant steric effects.



An advanced electrocatalyst consists of uniform CoNi nanoalloys that are encapsulated by ultrathin graphene shells (1–3 layers) and exhibits high activity and stability in the hydrogen evolution reaction (HER) in acidic media. This study paves the way for the design of high-performance, low-cost HER electrocatalysts and other catalysts that can be employed under harsh conditions.

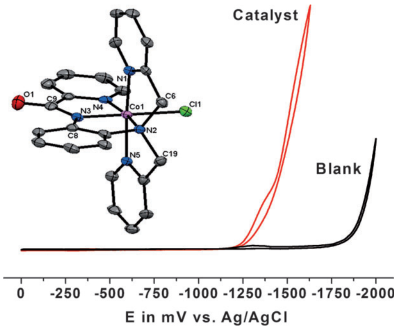
Hydrogen Evolution Reaction

J. Deng, P. Ren, D. Deng,*
X. Bao* ———— **2100 – 2104**

Enhanced Electron Penetration through an Ultrathin Graphene Layer for Highly Efficient Catalysis of the Hydrogen Evolution Reaction

---

Pyridine and cobalt: A series of cobalt complexes with pentadentate pyridine-rich ligands is studied both for their ligand transformations as well as for their catalytic activity toward proton and water reduction. Turnover numbers of up to 7000 after 18 h were observed.



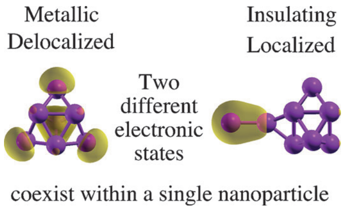
Water Reduction

D. Basu, S. Mazumder, X. Shi,
H. Baydoun, J. Niklas, O. Poluektov,
H. B. Schlegel,*
C. N. Verani* ———— **2105 – 2110**

Ligand Transformations and Efficient Proton/Water Reduction with Cobalt Catalysts Based on Pentadentate Pyridine-Rich Environments

---

For some sizes of zinc clusters, metallic and insulating electronic states coexist within a single nanoparticle; for others, the coexistence of two weakly interacting metallic phases localized at the shell and the core is found. These features are due to an anomalously long core–shell separation that equips those regions with largely independent structural, vibrational, and thermal properties.

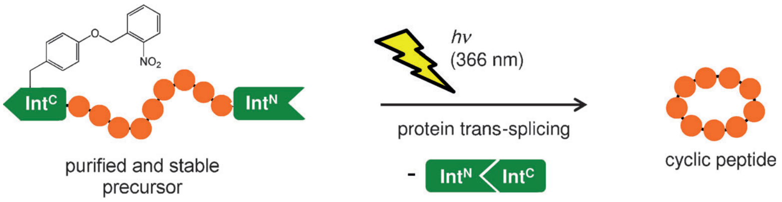


Metallic States

A. Aguado,* A. Vega, A. Lebon,
B. von Issendorff ———— **2111 – 2115**

Insulating or Metallic: Coexistence of Different Electronic Phases in Zinc Clusters

---



Split inteins provide a powerful approach to cyclic peptides and libraries thereof, but the spontaneous nature of the protein splicing reaction prevents a convenient purification from cellular mixtures. A novel photoactivatable intein that can be purified from *E. coli* cells to produce the cyclic product in a controlled fashion is now reported and expected to facilitate screening and lead identification.

Protein Engineering

J. K. Böcker, K. Friedel, J. C. J. Matern,
A.-L. Bachmann,
H. D. Mootz* ———— **2116 – 2120**

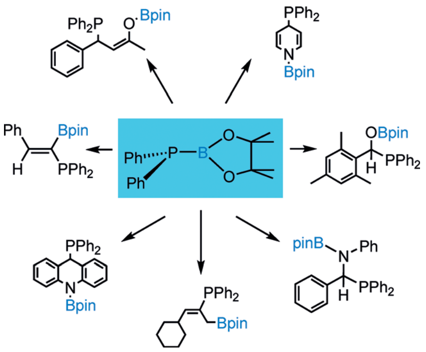
Generation of a Genetically Encoded, Photoactivatable Intein for the Controlled Production of Cyclic Peptides

Synthetic Methods

E. N. Daley, C. M. Vogels, S. J. Geier, A. Decken, S. Doherty,* S. A. Westcott* ______ **2121 – 2125**

The Phosphinoboration Reaction

Phosphine machine: Phosphinoboronate esters containing a reactive P–B bond were synthesized. These compounds add to aldehydes, ketones, aldimines, and α,β-unsaturated ketones in the absence of a catalyst or strong base and to C–C multiple bonds in the first examples of transition-metal-catalyzed phosphinoboration reactions.

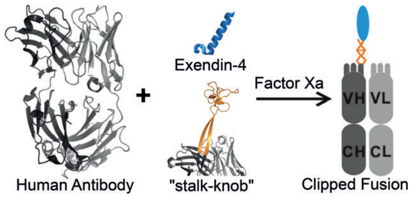


Protein Engineering

Y. Zhang, H. Zou, Y. Wang, D. Caballero, J. Gonzalez, E. Chao, G. Welzel, W. Shen, D. Wang, P. G. Schultz,* F. Wang* ______ **2126 – 2130**

Rational Design of a Humanized Glucagon-Like Peptide-1 Receptor Agonist Antibody

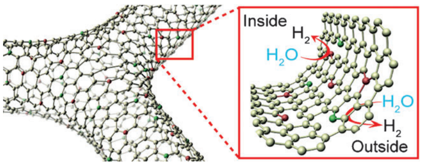
A humanized glucagon-like peptide-1 receptor agonist antibody was generated through genetic fusion of the exendin-4 peptide into CDR3H of the humanized monoclonal antibody herceptin with a heterodimeric coiled-coil "stalk". The resulting clipped herceptin–Ex-4 fusion protein shows excellent biological and pharmacological properties.



Hydrogen Evolution Reaction

Y. Ito, W. Cong, T. Fujita, Z. Tang, M. W. Chen* ______ **2131 – 2136**

High Catalytic Activity of Nitrogen and Sulfur Co-Doped Nanoporous Graphene in the Hydrogen Evolution Reaction

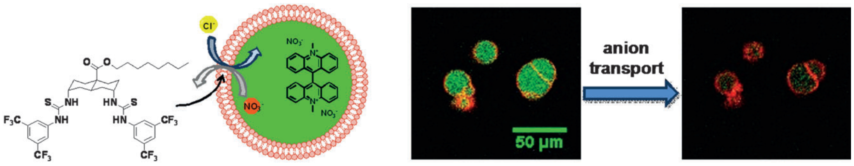


Together they're strong: Nitrogen and sulfur co-doped nanoporous graphene displays high catalytic activity in the hydrogen evolution reaction (HER) at low operating potential. The interplay between the chemical dopants and geometric lattice defects is crucial for the superior HER performance by minimizing the Gibbs free energy of H* absorption.

Ion Transport

H. Valkenier, N. López Mora, A. Kros,* A. P. Davis* ______ **2137 – 2141**

Visualization and Quantification of Transmembrane Ion Transport into Giant Unilamellar Vesicles

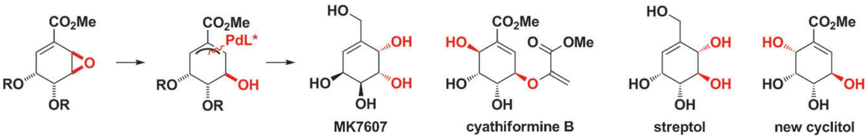


Seeing is believing: Transmembrane ion transport is commonly studied in vesicles that are too small for examination by routine microscopy. A method is presented that employs giant unilamellar vesicles that permits direct visualization of the phenomenon. The technique was applied to chloride/nitrate exchange by a powerful anionophore, allowing quantification of anion transport into single cell-sized membrane compartments.

Carbasugars

M. J. Moschitto, D. N. Vaccarello,
C. A. Lewis* ______________ 2142 – 2145

Regiodivergent Addition of Phenols to Allylic Oxides: Control of 1,2- and 1,4-Additions for Cyclitol Synthesis

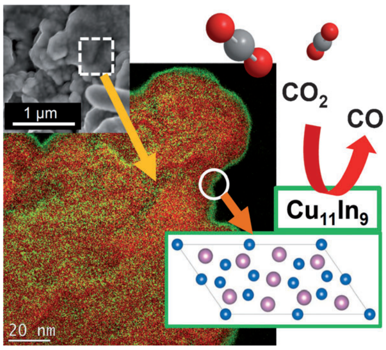


Controlling π: A catalyst-controlled regiodivergent resolution of allylic oxides is achieved by interception of chiral palladium π-allyl complexes. This method tolerates complex, fully substituted cyclohexenoates to provide access to the enantiomers of carbasugar natural products as is shown with the total syntheses of MK 7607, cyathiformine B type, streptol, and a new cyclitol.

Electrocatalysis

S. Rasul, D. H. Anjum, A. Jedidi,
Y. Minenkov, L. Cavallo,
K. Takanabe* ______________ 2146 – 2150

A Highly Selective Copper–Indium Bimetallic Electrocatalyst for the Electrochemical Reduction of Aqueous CO_2 to CO



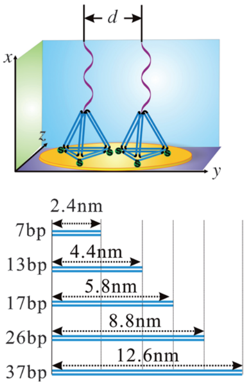
A non-noble metal electrocatalyst based on a copper–indium (Cu–In) alloy has been developed for the selective conversion of CO_2 into CO with a low overpotential. Combined experimental and theoretical approaches address the electronic and geometric arrangement of the catalyst surface, thus guiding the design of the electrochemical surfaces for improved energy conversion efficiency.

Surface Chemistry

VIP

M. Lin, J. Wang, G. B. Zhou, J. Wang,
N. Wu, J. Lu, J. Gao, X. Q. Chen, J. Shi,
X. Zuo,* C. Fan* ______________ 2151 – 2155

Programmable Engineering of a Biosensing Interface with Tetrahedral DNA Nanostructures for Ultrasensitive DNA Detection

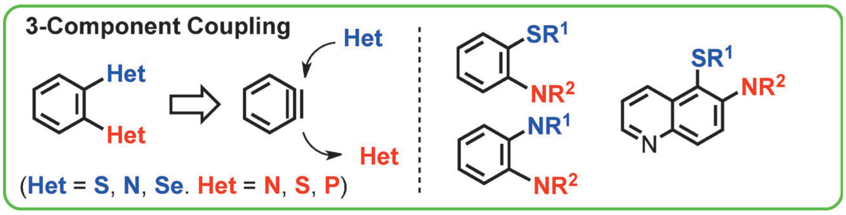


Self-assembled DNA nanostructures with precise sizes allowed a programmable “soft lithography” approach to engineer the interfaces of electrochemical DNA sensors. Using millimeter-sized gold electrodes modified with several types of tetrahedral DNA nanostructures of different sizes, it was shown that both the kinetics and thermodynamics of DNA hybridization were profoundly affected.

Multicomponent Reactions

J.-A. García-López, M. Çetin,
M. F. Greaney* ______________ 2156 – 2159

Double Heteroatom Functionalization of Arenes Using Benzyne Three-Component Coupling

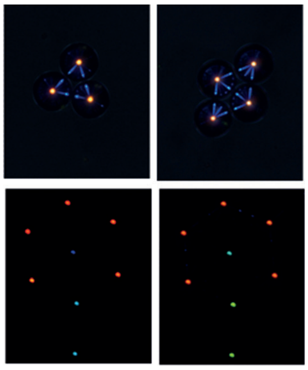


Three components, two C−X bonds: Magnesiated heteroatom nucleophiles effectively add to the strained triple bond of benzyne to form an incipient aryl Grignard. In the same pot, electrophilic N, S, or P reagents can capture this intermediate under copper(I) catalysis to produce a variety of 1,2-difunctionalized arenes.

Reflection Colors

J. Fan, Y. Li, H. K. Bisoyi, R. S. Zola,
D. Yang, T. J. Bunning, D. A. Weitz,
Q. Li* ________________ **2160 – 2164**

Light-Directing Omnidirectional Circularly Polarized Reflection from Liquid-Crystal Droplets

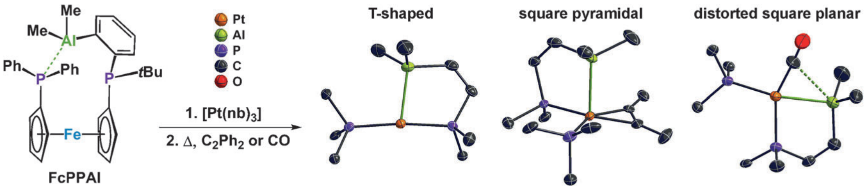


Blue rays: Photoirradiation of self-organized, phototunable 3D photonic superstructures of monodisperse droplets of a cholesteric liquid crystal (CLC) containing a photosensitive chiral molecular switch gives dynamic reflection colors. The colors can be tuned reversibly upon light irradiation, and in groups of droplets blue-ray patterns arise from photonic cross-communication between neighboring droplets.

Coordination Chemistry

B. E. Cowie, F.-A. Tsao,
D. J. H. Emslie* ____________ **2165 – 2169**

Synthesis and Platinum Complexes of an Alane-Appended 1,1′-Bis(phosphino)ferrocene Ligand



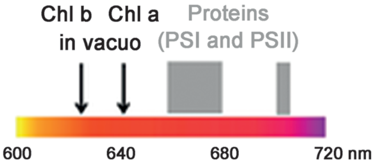
[{Pt(FcPPAl}$_2$], [PtL$_x$(FcPPAl)] (L$_x$ = norbornene(nb), C_2H_4, C_2Ph_2, and H_2), and [Pt(CO)(FcPPAl)] featuring T-shaped, square-pyramidal, and distorted square-planar geometries were synthesized from an alane-appended bis(phosphino)ferrocene ligand, FcPPAl. In all cases, the FcPPAl ligand coordinates through both phosphine donors and the alane, and the hydride and carbonyl complexes feature unusual multicenter bonding involving Pt, Al, and an H or CO ligand.

Photosynthesis

B. F. Milne,* Y. Toker, A. Rubio,
S. B. Nielsen* ____________ **2170 – 2173**

Unraveling the Intrinsic Color of Chlorophyll

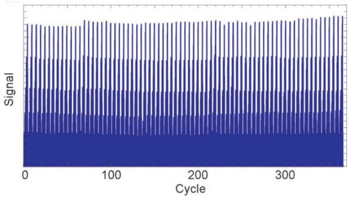
Taking chlorophylls out of leaves: From a combination of gas-phase spectroscopy and theoretical calculations, the intrinsic colors of chlorophyll a and b reveal themselves. The two molecules isolated in vacuo absorb further to the blue than when in a solution or located within a protein pocket of photosynthetic systems, unequivocally demonstrating redshifting effects of the microenvironment.



Reversible Biosensors

R. A. Potyrailo,* A. J. Murray, N. Nagraj,
A. D. Pris, J. M. Ashe,
M. Todorovic ____________ **2174 – 2178**

Towards Maintenance-Free Biosensors for Hundreds of Bind/Release Cycles

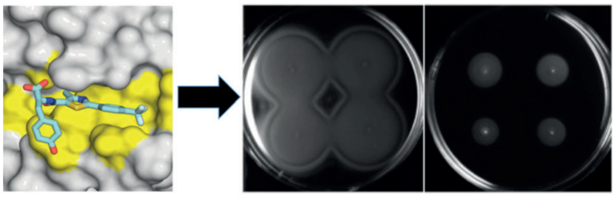


Reversible biosensors based on a single immobilized aptamer layer were developed and employed for 100–365 bind/release cycles with less than 5% variation in the binding affinity. These biosensors that operate for multiple sensing cycles may find applications in distributed sensor networks, in resource-limited settings, and as wearable sensors.

Drug Discovery

L. A. Adams, P. Sharma, B. Mohanty, O. V. Ilyichova, M. D. Mulcair, M. L. Williams, E. C. Gleeson, M. Totsika, B. C. Doak, S. Caria, K. Rimmer, J. Horne, S. R. Shouldice, M. Vazirani, S. J. Headey, B. R. Plumb, J. L. Martin, B. Heras,* J. S. Simpson,* M. J. Scanlon* ______ **2179 – 2184**

Application of Fragment-Based Screening to the Design of Inhibitors of *Escherichia coli* DsbA



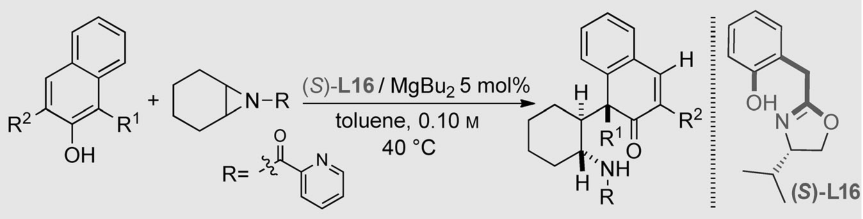
Combating bacterial virulence: DsbA is an oxidoreductase enzyme and a key mediator of virulence in *Escherichia coli*. Using fragment-based screening, compounds were developed that inhibit DsbA activity in vitro and *E. coli* motility in a cell-based assay. Crystal structures of the compounds in complex with DsbA provide a rationale for their activity.

Synthetic Methods

D. Yang, L. Wang, F. Han, D. Li, D. Zhao, R. Wang* ______ **2185 – 2189**

Intermolecular Enantioselective Dearomatization Reaction of β-Naphthol Using *meso*-Aziridine: A Bifunctional In Situ Generated Magnesium Catalyst

Inside Back Cover



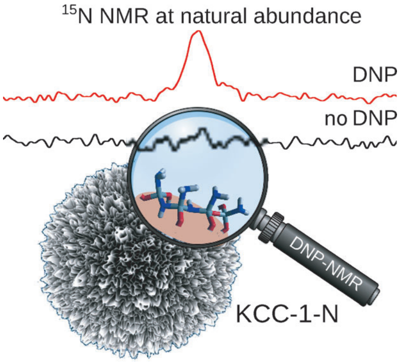
All in a box: The intermolecular dearomatization reactions of β-naphthols with aziridines have been realized using the title catalyst. A newly designed Box–OH ligand [(*S*)-**L16**] was employed and proved to be efficient. The corresponding dearomatization product was transformed into a polycyclic core skeleton and a polyhydroxylated compound.

Nanocatalysis

A. S. Lilly Thankamony, C. Lion, F. Pourpoint, B. Singh, A. J. Perez Linde, D. Carnevale, G. Bodenhausen, H. Vezin, O. Lafon,* V. Polshettiwar* **2190 – 2193**

Insights into the Catalytic Activity of Nitridated Fibrous Silica (KCC-1) Nanocatalysts from ^{15}N and ^{29}Si NMR Spectroscopy Enhanced by Dynamic Nuclear Polarization

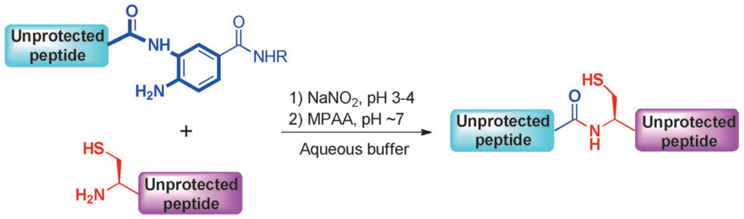
Running a temperature: Solid-state NMR spectroscopy, enhanced by dynamic nuclear polarization, was used to study the mechanism of nitridation of silica. Experiments performed on oxynitrides produced from fibrous silica nanospheres (KCC-1) provide detailed information about the surface structure and its modification as a function of nitridation temperature. This study allows understanding the influence of the nitridation temperature on the activity of these solid-base nanocatalysts.



Native Chemical Ligation

J.-X. Wang, G.-M. Fang, Y. He, D.-L. Qu, M. Yu, Z.-Y. Hong, L. Liu* **2194 – 2198**

Peptide *o*-Aminoanilides as Crypto-Thioesters for Protein Chemical Synthesis

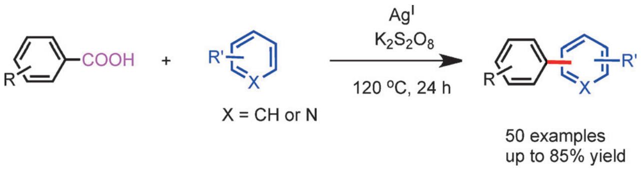


Making it easier to make the link: The activation of fully unprotected peptide *o*-aminoanilides with $NaNO_2$ in an aqueous buffer enabled their use as peptide crypto-thioesters in native chemical ligation (see scheme; MPAA = 4-mercaptophenylacetic acid). The practicability and unique advantages of this method were demonstrated by the total chemical synthesis of histone H2B and lactocyclicin Q.

Cross-Coupling

J. Kan, S. Huang, J. Lin, M. Zhang, W. Su* **2199 – 2203**

Silver-Catalyzed Arylation of (Hetero)-arenes by Oxidative Decarboxylation of Aromatic Carboxylic Acids

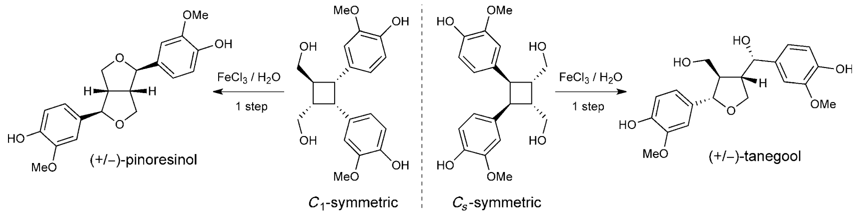


Silver hammer: The silver-catalyzed decarboxylative arylation of electron-deficient (hetero)arenes has been successfully developed using aromatic carboxylic acids as arylating reagents. For most of the aromatic carboxylic acids evaluated, 5 mol % of the silver(I) salt was enough for the oxidative decarboxylation. An *ortho* substituent was not necessary for this decarboxylative cross-coupling procedure.

Total Synthesis

A. K. F. Albertson, J.-P. Lumb* **2204 – 2208**

A Bio-Inspired Total Synthesis of Tetrahydrofuran Lignans

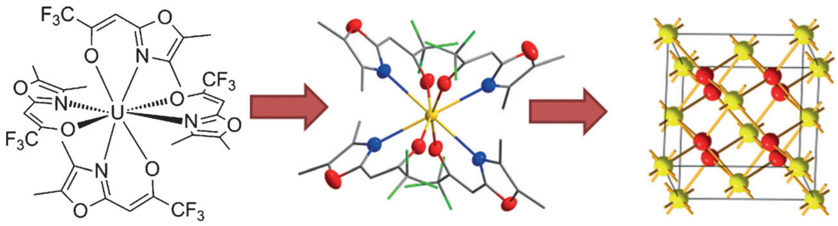


Ringing the changes: A bio-inspired synthesis of furanolignan natural products that hinges on the oxidative ring opening of diarylcyclobutane diols is reported. The resulting bis-*para*-quinone methides participate in a complex cascade to complete the first total synthesis of tanegool. Modification of the cyclobutane prior to oxidation affords the structurally distinct lignan pinoresinol, thus demonstrating the flexibility of this synthetic strategy.

Nanostructured Materials

L. Appel, J. Leduc, C. L. Webster, J. W. Ziller, W. J. Evans,* S. Mathur* **2209 – 2213**

Synthesis of Air-Stable, Volatile Uranium(IV) and (VI) Compounds and Their Gas-Phase Conversion To Uranium Oxide Films

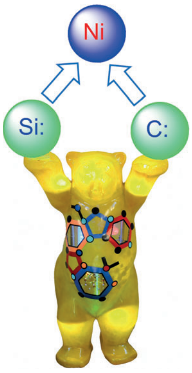


Soft chemical processing: Volatile and air-stable complexes of uranium(IV) were obtained by a special ligand design. One of the complexes was a precursor for the chemical vapor phase deposition of uranium oxide thin films and the resulting nanostructured thin films were fully characterized by scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

Carbene Complexes

G. Tan, S. Enthaler, S. Inoue, B. Blom, M. Driess* ______ 2214 – 2218

Synthesis of Mixed Silylene–Carbene Chelate Ligands from N-Heterocyclic Silylcarbenes Mediated by Nickel

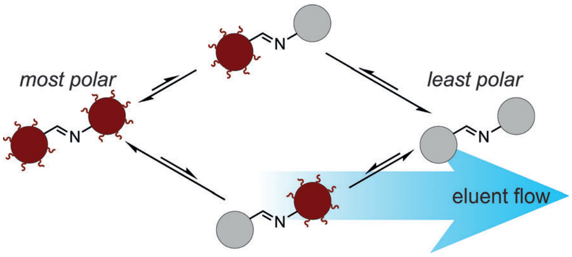


Two of a perfect pair: A chelate ligand combining N-heterocyclic silylene (NHSi) and N-heterocyclic carbene (NHC) donor subunits could be realized through Ni^{II}-mediated tautomerization reactions of a hydrosilyl-substituted N-heterocyclic carbene. The unexpected coordination features of the two ligands leads to the isolation of unprecedented Ni^{II} and Ni^{0} complexes, including a complex with agostic Si–H→Ni interaction.

Dynamic Combinatorial Chemistry

C.-W. Hsu, O. Š. Miljanić* __ 2219 – 2222

Adsorption-Driven Self-Sorting of Dynamic Imine Libraries

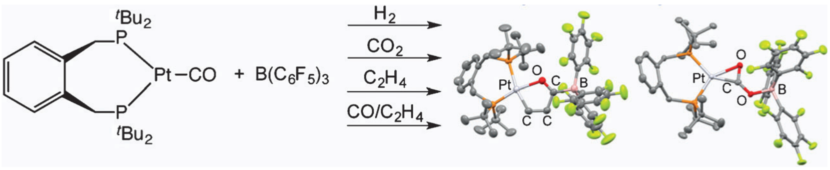


Mix and match: Complex and dynamic imine libraries with n^2 members can be sorted into just n final products during the course of column chromatography on silica gel. Through a cascade of disproportionation reactions, the most and least polar imines in the mixture are amplified at the expense of their counterparts of intermediate polarity.

Frustrated Lewis Pairs

S. J. K. Forrest, J. Clifton, N. Fey, P. G. Pringle,* H. A. Sparkes, D. F. Wass* ______ 2223 – 2227

Cooperative Lewis Pairs Based on Late Transition Metals: Activation of Small Molecules by Platinum(0) and $B(C_6F_5)_3$

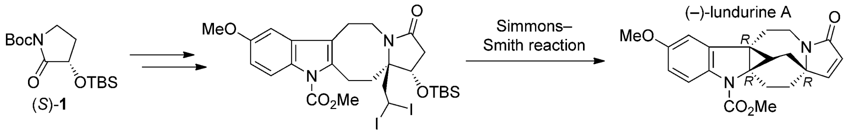


Better together: A combination of a platinum(0)–diphosphine complex with $B(C_6F_5)_3$ behaves cooperatively to activate and couple small molecules, such as H_2, CO, CO_2, and ethene. This behavior is reminiscent of frustrated Lewis pair chemistry, with the Pt^0 complex acting as a transition metal Lewis base.

Total Synthesis

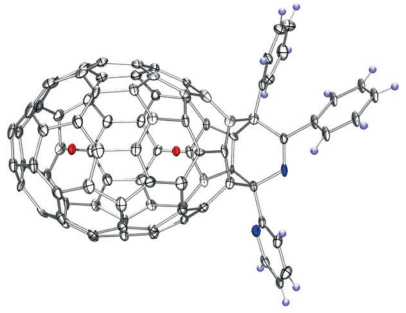
S.-J. Jin, J. Gong, Y. Qin* __ 2228 – 2231

Total Synthesis of (−)-Lundurine A and Determination of its Absolute Configuration



Five in one blow: The total synthesis of (−)-lundurine A (**1**) succeeded in 15 steps from easily accessible (*S*)-pyrrolidinone **1**. A Simmons–Smith reaction allows the efficient, simultaneous assembly of the cyclopropyl C ring, the six-membered D ring, the seven-membered E ring, and the quaternary carbon stereocenters at C2 and C7.

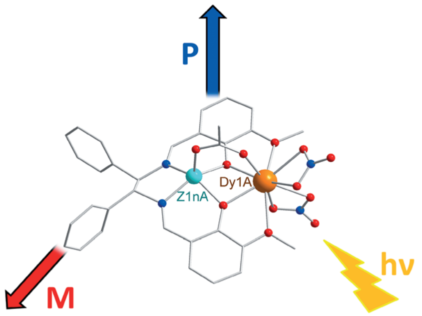
Metallofullerenes



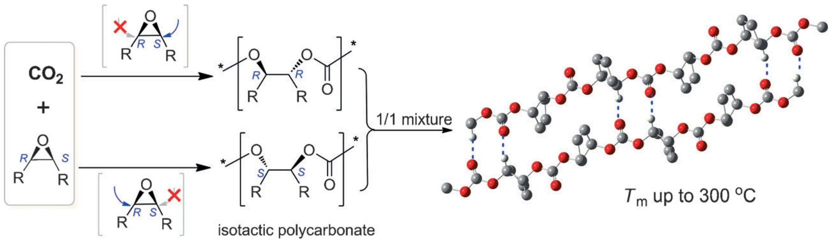
Molecular surgery on fullerenes: The thermal reaction of the endohedral metallofullerene $La_2@D_2(10611)$-C_{72} with 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine proceeded selectively to afford only two bisfulleroid isomers. X-ray crystallographic analysis of one isomer (see picture) clearly shows the formation of an open-cage derivative having three seven-membered ring orifices on the cage and a significantly elongated cage geometry.

Molecular Ferroelectrics

An attractive glow: A high-temperature ferroelectric material based on a chiral Zn^{2+}/Dy^{3+} complex exhibits Dy^{3+} luminescence, optical activity, and magnetism. Remarkably, this molecular material remains crystallized in a polar structure. This leads to a ferroelectric behavior, making it one of the highest-temperature working molecular ferroelectrics.

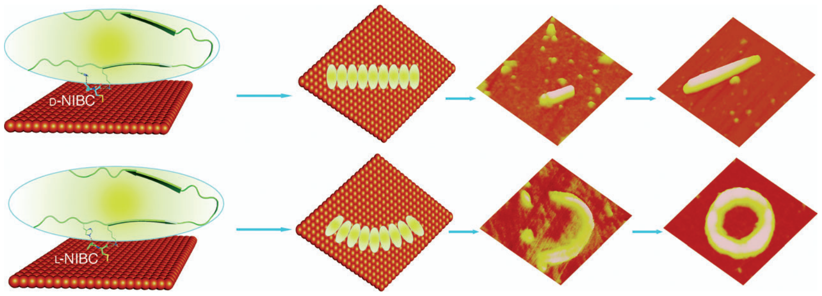


Polymer Stereocomplexes



Mixed tactics: Mixing of crystalline or amorphous isotactic (*R*)- and (*S*)-polycarbonates affords crystalline stereocomplexed polymers which have a high melting temperature of up to 300 °C, and provides higher thermal properties for CO_2-based polycarbonate materials.

Chirality-Guided Assembly

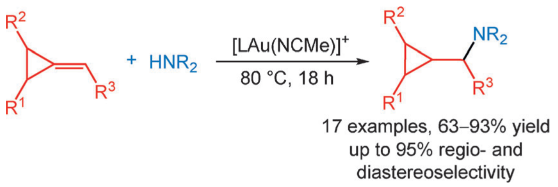


Stereoselective surfaces: Molecular chirality on a surface induces ring-like aggregates of amyloid Aβ(1–40) on *N*-isobutyryl-L-cysteine (L-NIBC)-modified gold surface at low concentration, whereas D-NIBC results in rod-like aggregates. The different alignment modes of the β-hairpin are guided by surface chirality through stereoselective recognition enhanced by electrostatic interactions.

Gold Catalysis

J. C. Timmerman, B. D. Robertson, R. A. Widenhoefer* ________ 2251 – 2254

Gold-Catalyzed Intermolecular Anti-Markovnikov Hydroamination of Alkylidenecyclopropanes

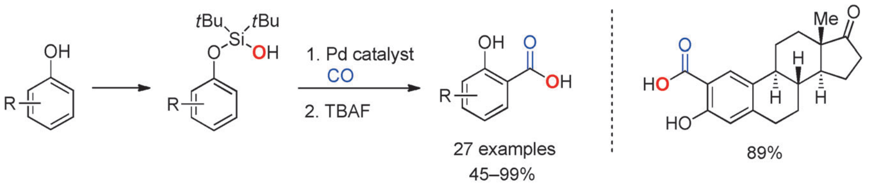


A golden opportunity: 1-cyclopropyl alkylamine derivatives are prepared in high yield and with high regio- and diastereoselectivity by the gold-catalyzed hydroamination of alkylidenecyclopropanes (ACPs). From NMR spectroscopic analysis, sp hybridization of the ACP internal alkene carbon atom is suggested to control the regiochemistry of the reaction.

C–H Activation

Y. Wang, V. Gevorgyan* ____ 2255 – 2259

General Method for the Synthesis of Salicylic Acids from Phenols through Palladium-Catalyzed Silanol-Directed C–H Carboxylation

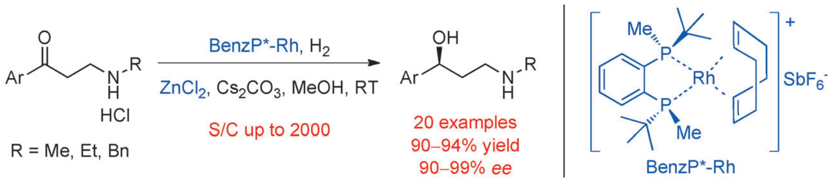


A strict director: The title reaction produced a wide range of salicylic acid derivatives with high efficiency and selectivity. The scope of this method was demonstrated by the carboxylation of estrone (see scheme; TBAF = tetrabutylammonium fluoride) and by the unsymmetrical bisfunctionalization of a phenolic compound through sequential C–H functionalization reactions.

Asymmetric Catalysis

Q. Hu, Z. Zhang, Y. Liu, T. Imamoto, W. Zhang* ______________ 2260 – 2264

$ZnCl_2$-Promoted Asymmetric Hydrogenation of β-Secondary-Amino Ketones Catalyzed by a P-Chiral Rh–Bisphosphine Complex

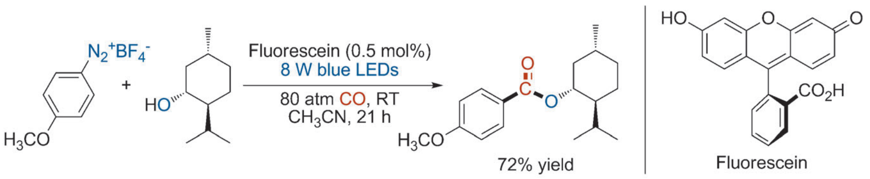


Competitive coordination: Chiral γ-secondary-amino alcohols were obtained in high yields and with excellent enantioselectivities by hydrogenation of β-secondary-amino ketones. NMR spectroscopy and HRMS are used to investigate the mechanism for the activation effect of $ZnCl_2$ on the bisphosphine–rhodium catalyst.

Synthetic Methods

W. Guo, L.-Q. Lu,* Y. Wang, Y.-N. Wang, J.-R. Chen, W.-J. Xiao* _____ 2265 – 2269

Metal-Free, Room-Temperature, Radical Alkoxycarbonylation of Aryldiazonium Salts through Visible-Light Photoredox Catalysis

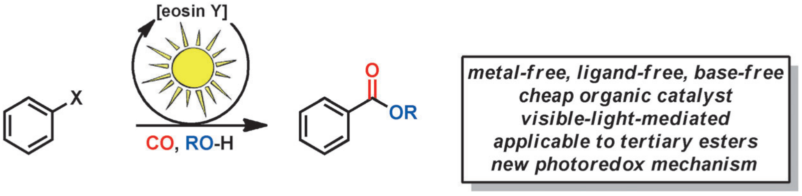


All lit up: The radical alkoxycarboxylation of aryldiazonium salts using CO gas was accomplished through visible-light-induced photoredox catalysis. The reaction is metal-free, and proceeds at room temperature with a low loading of organic photocatalyst. A wide range of esters were conveniently synthesized in moderate to good yields. Importantly, this strategy can be further applied to other carboxylation reactions.

Photocatalysis

M. Majek,
A. Jacobi von Wangelin* ____ 2270–2274

Metal-Free Carbonylations by Photoredox Catalysis



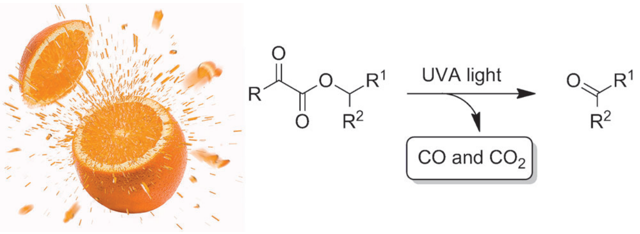
A metal-free and base-free carbonylation has been developed which affords primary, secondary, and tertiary alkyl benzoates under irradiation with visible light in the presence of eosin Y as a photocatalyst. The mechanism has been studied by spectroscopic, theoretical, and preparative methods, and appears to involve intermediate aryl and aroyl radical species as well as a light-driven one-electron redox cycle without any sacrificial redox partner.

Stimuli-Responsive Materials

N. Paret, A. Trachsel, D. L. Berthier,*
A. Herrmann* ____________ 2275–2279

Controlled Release of Encapsulated Bioactive Volatiles by Rupture of the Capsule Wall through the Light-Induced Generation of a Gas

Front Cover

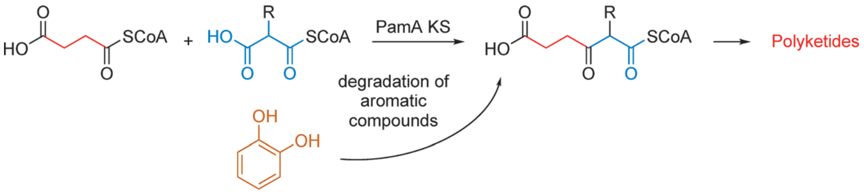


A burst of aroma: Bioactive compounds, such as fragrances, can be efficiently released from core–shell microcapsules by the light-induced decomposition of encapsulated 2-oxoacetates, generating an overpressure of gas that expands or even breaks the capsule wall.

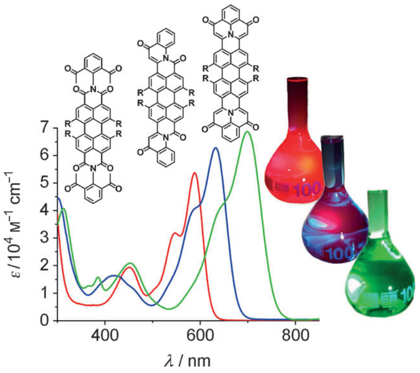
Polyketide Biosynthesis

Y. Rebets, E. Brötz, N. Manderscheid,
B. Tokovenko, M. Myronovskyi, P. Metz,*
L. Petzke,* A. Luzhetskyy* _ 2280–2284

Insights into the Pamamycin Biosynthesis



A pamamycin biosynthesis gene cluster was identified by the genome alignment of two pamamycin-producing strains. Genetic and biochemical studies allowed the complete delineation of pamamycin biosynthesis. The pathway proceeds through 3-oxoadipyl-CoA, a key intermediate in the primary metabolism of the degradation of aromatic compounds.



Color control: Novel π-extended naphthalenes and perylenes containing 3*a*-aza-1,6-phenalenedione-, 4-oxoquinoline-, or 4-hydroxyquinoline-based chromophores were synthesized by a facile imidization of acetyl anilines with anhydrides and intramolecular aldol condensation. They show a strong red shift of the absorption bands relative to the parent imides, as well as fluorescence in the visible/NIR range.

Dyes

D. Jänsch, C. Li, L. Chen, M. Wagner, K. Müllen* **2285 – 2289**

Versatile Colorant Syntheses by Multiple Condensations of Acetyl Anilines with Perylene Anhydrides

Back Cover

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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