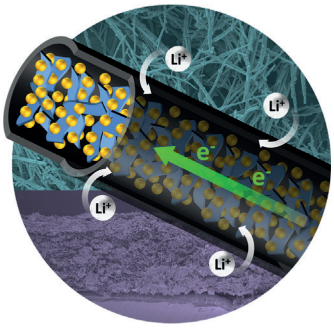
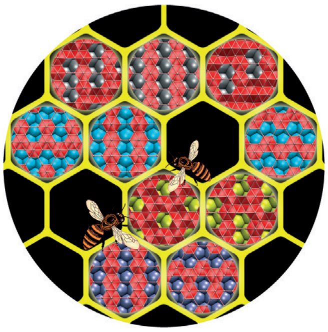
An energetic fused heterocycle …

… was synthesized in a two-step process described by D. E. Chavez and co-workers in their Communication on page 12973 ff. Firstly, a double N-amination of the bis(tetraethylammonium) salt of 3,3'-dinitro-5,5'-bi-1,2,4-triazole provides a thermally stable, di-N-aminated energetic material that is insensitive to impact, spark, and friction. A subsequent azo coupling reaction produces a fused, tricyclic 1,2,3,4-tetrazine ring system with excellent density and explosive performance properties.

Lithium–Sulfur Batteries

Hollow carbon nanofibers filled with MnO_2 nanosheets were synthesized by X. W. Lou and co-workers in their Communication on page 12886 ff., and shown to be a suitable sulfur host for lithium–sulfur batteries.



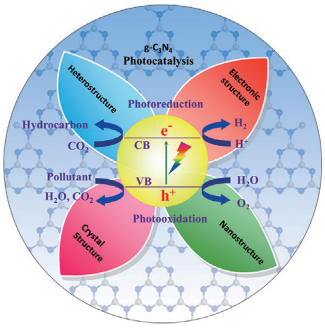


2D Materials

In their Communication on page 13022 ff. B. I. Yakobson et al. show theoretically that pure boron is the first 2D material that varies its structure depending on the metal substrate it is deposited on.

Photocatalysts

g-C_3N_4-Photocatalysts can be modified for specific tasks by varying four parameters: electronic structure, nanostructure, crystal structure, and heterostructure. In their Review on page 12868 ff. X. Wang et al. discuss these and the uses of such catalysts.



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Author Profile

"My science "heroes" are Gilbert Stork and Paul Wender. My favorite musicians are Frank Zappa, Jeff Beck, Donald Fagen, and Howlin' Wolf …"
This and more about Kevin I. Booker-Milburn can be found on page 12850.

News


J. L. Mascareñas


N. López


K. Muñiz


R. Martín


F. Zamora


R. Ponce Ortiz


M. Gulías

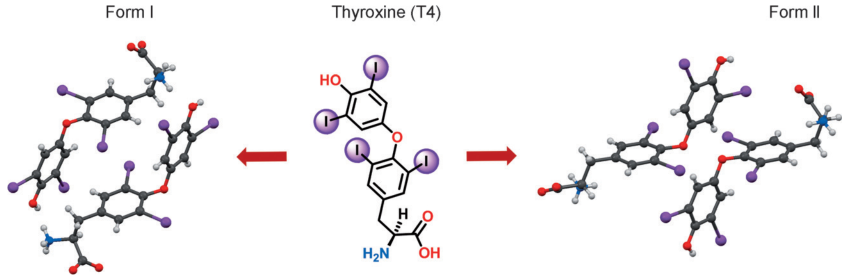

C. Martí-Gastaldo


F. Joó


J. Rocha

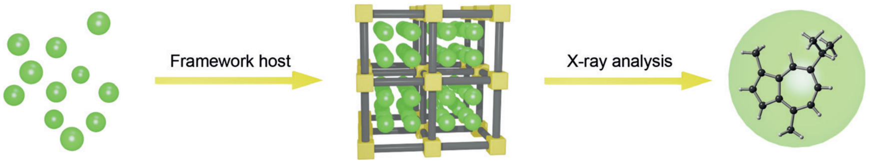
Books

Highlights



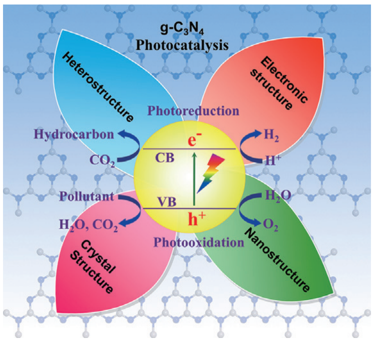
Form and substance: Through observation and careful follow-up on polymorphic forms of thyroxine (Forms I und II; black C, gray H, violet I, blue N, red O), Mondal and Mugesh have provided a stunningly simple answer to the apparent non-equivalence of thyroid hormone tablets. Their results further suggest control of deiodinase regioselectivity through the adjustment of torsional angles distant from the reactive bond.

Minireviews



Molecules made to order: Open-framework materials are typically studied for their gas-sorption properties. However, recent work has demonstrated that the crystalline architectures of such materials can be utilized to periodically order non-structural atoms and guest molecules. Recent examples where such framework materials have been utilized as a host matrix for crystallization are highlighted.

Reviews



Metal-free photocatalysis: Recent progress in g-C_3N_4 photocatalysis is highlighted. The four fundamental approaches for modification of g-C_3N_4 photocatalysts are discussed: electronic structure modulation, nanostructure design, crystal-structure engineering, and heterostructure construction. The application of g-C_3N_4 photocatalysts are briefly summarized and the opportunities and challenges in this field are discussed.

For the USA and Canada:
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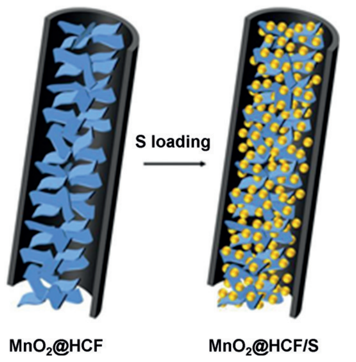
Communications



Keep the sulfur: Hollow carbon nanofibers filled with MnO$_2$ nanosheets (MnO$_2$@HCF) were synthesized and shown to be a suitable sulfur host for lithium–sulfur batteries. As the polysulfides are physically entrapped by the carbon shells and chemically bound by the MnO$_2$ nanosheets, this nanocomposite sulfur cathode displayed excellent specific/areal capacities and a good cycling stability.

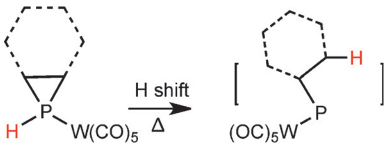
Lithium–Sulfur Batteries

Z. Li, J. T. Zhang,
X. W. Lou* ______ 12886 – 12890

Hollow Carbon Nanofibers Filled with MnO$_2$ Nanosheets as Efficient Sulfur Hosts for Lithium–Sulfur Batteries

Frontispiece

Caught in a trap: Secondary phosphirane complexes isomerize above 100 °C to give the corresponding terminal phosphinidene complexes, which can be trapped by alkenes and alkynes. This example is a rare instance of the isomerization of a P^{III} derivative into a P^{I} derivative. It appears to mimic the reductive elimination of alkanes from transition-alkylmetal hydrides.



Phosphorous Compounds

J. Wong, Y. Li, Y. Hao, R. Tian,*
F. Mathey* ______ 12891 – 12893

Isomerization of Secondary Phosphirane into Terminal Phosphinidene Complexes: An Analogy between Monovalent Phosphorus and Transition Metals

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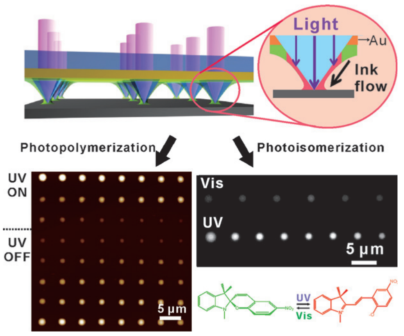


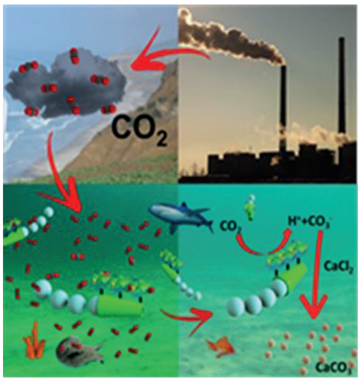
Nanolithography: An on-tip photo-modulated molecular printing concept is introduced to chemically regulate the nanoscale ink flow on cantilever-free scanning probe arrays. A photopolymerization can be effected to regulate the ink viscosity and therefore transport, resulting in a deliberate control over feature size from the micrometer to sub-50 nm length scales.

Molecular Printing

Z. Xie, Y. Zhou, J. L. Hedrick, P.-C. Chen,
S. He, M. M. Shahjamali, S. Z. Wang,
Z. J. Zheng,*
C. A. Mirkin* ______ 12894 – 12899

On-Tip Photo-Modulated Molecular Printing

Getting around: Modification of catalytic micromotors with carbonic anhydrase results in a scrubbing platform for accelerated "on-the-move" biomimetic sequestration of CO$_2$ (see figure). The ability of carbonic anhydrase to catalyze the hydration of CO$_2$ to form bicarbonate ions combined with the rapid movement of the micromotors as well as the corresponding fluid dynamics and mixing result in a highly efficient system.



Self-Propelled Devices

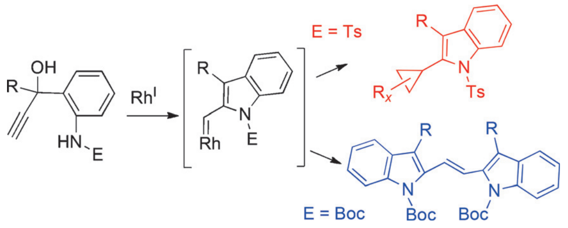
M. Uygun, V. V. Singh, K. Kaufmann,
D. A. Uygun, S. D. S. de Oliveira,
J. Wang* ______ 12900 – 12904

Micromotor-Based Biomimetic Carbon Dioxide Sequestration: Towards Mobile Microscrubbers

Heterocycles

X. Li, H. Li, W. Song, P.-S. Tseng, L.-y. Liu,* I. A. Guzei, W. Tang* —— **12905 – 12908**

Divergent Reactivity of Rhodium(I) Carbenes Derived from Indole Annulations



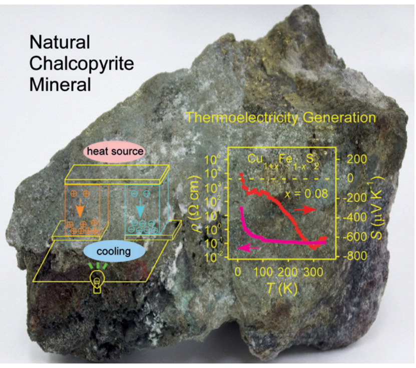
Two possibilities: An indole annulation can be coupled with stereoselective cyclopropanation or dimerization to form complex indole derivatives. The key intermediate is a putative rhodium(I) carbene derived from cycloisomerization of *ortho*-aniline-substituted propargylic alcohols. Boc = *tert*-butoxycarbonyl, Ts = 4-toluenesulfonyl.

Thermoelectrics

R. Ang,* A. U. Khan, N. Tsujii, K. Takai, R. Nakamura,* T. Mori* — **12909 – 12913**

Thermoelectricity Generation and Electron–Magnon Scattering in a Natural Chalcopyrite Mineral from a Deep-Sea Hydrothermal Vent

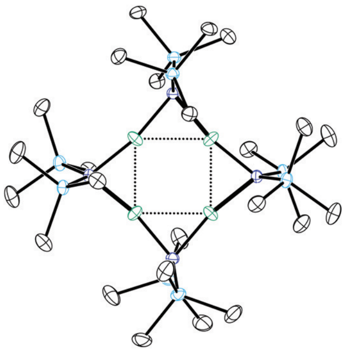
It came from the deep: A chalcopyrite mineral from a deep-sea hydrothermal vent has been found to have a large thermoelectric power and a high power factor, in which electron–magnon scattering and a large effective mass were detected. These findings highlight the feasibility of the generation of thermoelectric energy from natural materials that are abundant in the Earth's crust.



Silylamide Complexes

M. Faust, A. M. Bryan, A. Mansikkamäki, P. Vasko, M. M. Olmstead, H. M. Tuononen,* F. Grandjean, G. J. Long, P. P. Power* — **12914 – 12917**

The Instability of Ni{N(SiMe$_3$)$_2$}$_2$: A Fifty Year Old Transition Metal Silylamide Mystery



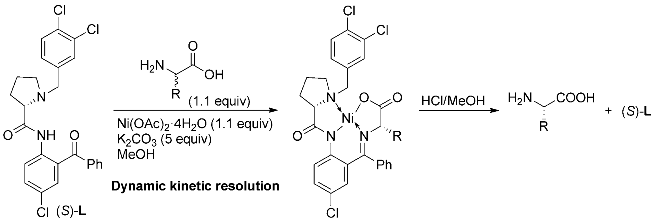
The singular instability of Ni{N(SiMe$_3$)$_2$}$_2$, one of the original transition metal silylamides of Bürger and Wannagat, was reinvestigated: it likely results from its tendency to undergo autoreduction into the dispersion force stabilized Ni^I tetramer [Ni{N(SiMe$_3$)$_2$}]$_4$ (see picture; Si light blue, N dark blue, Ni green), the first neutral homoleptic Ni^I amide.

Kinetic Resolution

Y. Nian, J. Wang, S. Zhou, S. Wang, H. Moriwaki, A. Kawashima, V. A. Soloshonok,* H. Liu* —————— **12918 – 12922**

Recyclable Ligands for the Non-Enzymatic Dynamic Kinetic Resolution of Challenging α-Amino Acids

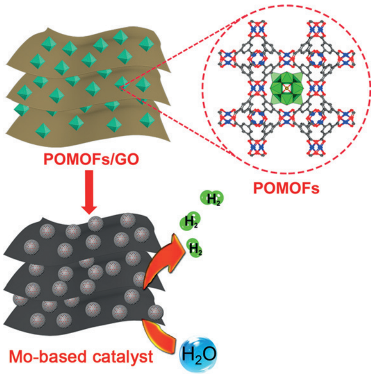
Inside Cover

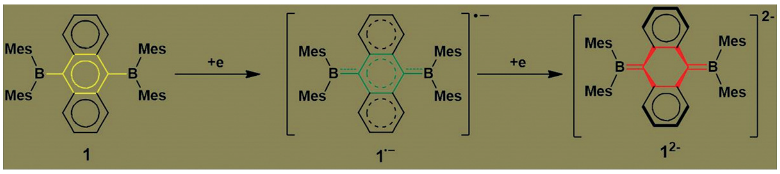


The non-enzymatic dynamic kinetic resolution of racemic α-amino acids bearing tertiary alkyl chains and multiple unprotected functional groups is based on the enantioselective formation of nickel(II) complexes and their hydrolysis under convenient conditions. The specially designed chiral ligands are inexpensive and can be quantitatively recycled.

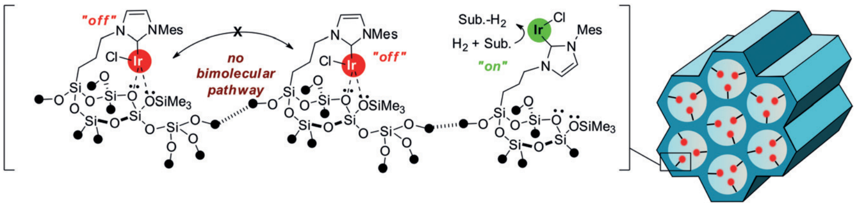
Four at once: The regio- and stereoselective concomitant addition of trifluoromethyl and trifluoromethanesulfonate groups to alkynes is enabled by a photocatalyst. Combining this process with palladium-catalyzed cross-couplings provides access to various tetrasubstituted trifluoromethylated alkenes from simple alkynes in a facile one-pot process.

Nanocomposite catalyst: A novel Mo-based catalyst for the hydrogen-evolution reaction has been synthesized by directly carbonizing a composite obtained from polyoxometalate-based metal–organic frameworks and graphene oxide at a relatively low temperature. The Mo-based catalyst exhibits a positive onset potential, low Tafel slope, high exchange current density, and long-term stability for the hydrogen-evolution reaction in acidic media.





Pucker up: 9,10-Bis(dimesitylboryl)anthracene (**1**), having a planar conjugated π-system, can be reduced stepwise to the radical anion $\mathbf{1}^{\bullet-}$ and dianion $\mathbf{1}^{2-}$, accompanied by stepwise changes of the aromaticity of the anthracene moiety. $\mathbf{1}^{\bullet-}$ has a planar semiquinoidal structure, whereas $\mathbf{1}^{2-}$ has a puckered quinoidal structure.

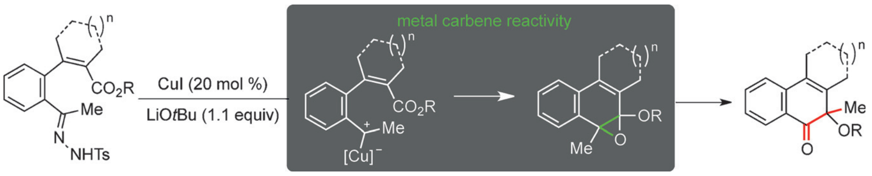


Lending support: Homogeneous positioning of Ir$^{\text{I}}$ complexes within the pore-channels of a silica framework stabilizes a low-valent Ir$^{\text{I}}$ species and leads to drastically improved catalyst efficiency. Catalyst decomposition by formation of iridium-hydride clusters is prevented by the attachment to the support. Mes = 2,4,6-trimethylphenyl.

Carbenes

N. Su, J. A. Theorell, D. J. Wink,
T. G. Driver* ______ **12942 – 12946**

Copper-Catalyzed Formation of α-Alkoxycycloalkenones from *N*-Tosylhydrazones



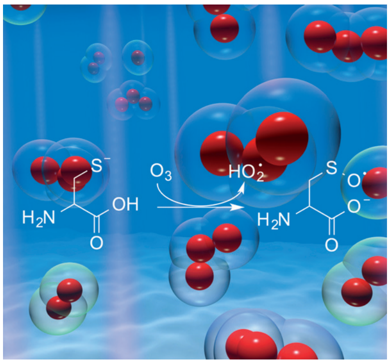
The combination of 20 mol% of copper iodide and lithium *tert*-butoxide triggers the formation of a broad range of substituted, functionalized α-alkoxy 2*H*-naphthalenones from readily available *N*-tosylhydrazones. The reaction proceeds by the cycloaddition of a copper carbenoid with an ester, and a subsequent Lewis acid-catalyzed [1,2] alkyl shift of the in situ generated alkoxyepoxide intermediate.

Radical Chemistry

G. N. Khairallah, A. T. Maccarone,
H. T. Pham, T. M. Benton, T. Ly,
G. da Silva, S. J. Blanksby,*
R. A. J. O'Hair* ______ **12947 – 12951**

Radical Formation in the Gas-Phase Ozonolysis of Deprotonated Cysteine

Gas-phase reactions: Deprotonated cysteine reacted with ozone to give a rich set of products including sequential oxygen atom abstraction reactions to yield cysteine sulfenate, sulfonate, and sulfonate anions, and significantly sulfenate radical anions formed by ejection of a hydroperoxy radical (see picture). The free-radical pathway occurred only when both thiol and carboxylate moieties were available.

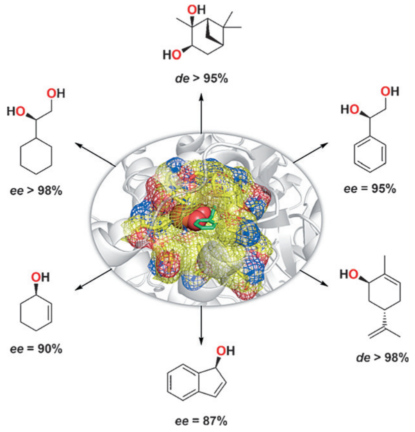


Biocatalysis

C. Gally, B. M. Nestl,
B. Hauer* ______ **12952 – 12956**

Engineering Rieske Non-Heme Iron Oxygenases for the Asymmetric Dihydroxylation of Alkenes

Modulation by mutation: Rieske non-heme iron oxygenases can be used as efficient biocatalysts for the selective oxyfunctionalization of various olefins yielding vicinal *cis*-diols and allylic alcohols. Introduction of a single amino acid substitution in the active sites of two selected oxygenases resulted in variants with improved stereoselectivities and product formations.

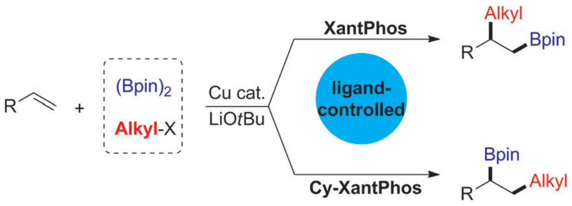


Cross-Coupling

VIP

W. Su, T.-J. Gong, X. Lu, M.-Y. Xu, C.-G. Yu,
Z.-Y. Xu, H.-Z. Yu, B. Xiao,*
Y. Fu* ______ **12957 – 12961**

Ligand-Controlled Regiodivergent Copper-Catalyzed Alkylboration of Alkenes

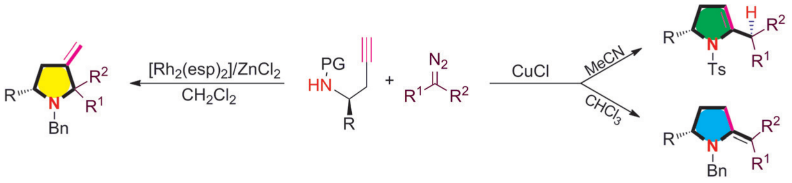


One way or another: The copper-catalyzed regiodivergent alkylboration of alkenes with bis(pinacolato)diboron and alkyl halides is described. The regioselectivity of the carboboration can be controlled by fine-tuning the ligand structure.

Heterocycles

K. Liu, C. Zhu, J. Min, S. Peng, G. Xu, J. Sun* ———— **12962 – 12967**

Stereodivergent Synthesis of N-Heterocycles by Catalyst-Controlled, Activity-Directed Tandem Annulation of Diazo Compounds with Amino Alkynes

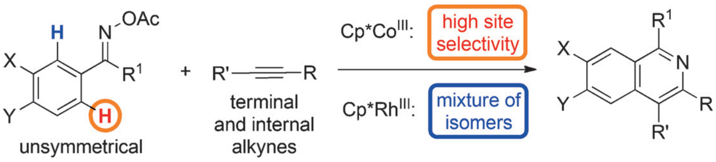


Different paths: A stereodivergent synthesis of five-membered N-heterocycles has been developed and involves trapping of the in situ formed intermediates. The copper-catalyzed annulation proceeds by allenoate formation and subsequent intramolecular hydroamination. The rhodium-catalyzed route features a carbenoid insertion into the N–H bond and subsequent Conia-ene cyclization. PG = protecting group.

C–H Activation

B. Sun, T. Yoshino, M. Kanai,* S. Matsunaga* ———— **12968 – 12972**

Cp*Co^{III} Catalyzed Site-Selective C–H Activation of Unsymmetrical *O*-Acyl Oximes: Synthesis of Multisubstituted Isoquinolines from Terminal and Internal Alkynes



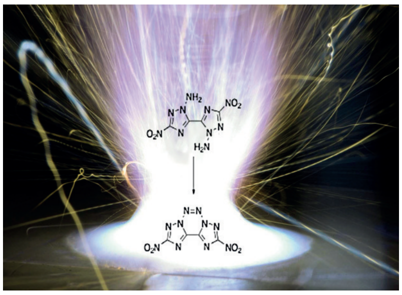
Isoquinolines are obtained by the C–H activation of *O*-acyl oximes with a Cp*Co^{III} catalyst. Whereas the reactions catalyzed by the Cp*Co^{III} system proceed with high site selectivity favoring C–H activation at the sterically less hindered site, the use of the corresponding Cp*Rh^{III} catalyst leads to low selectivities and/or yields when unsymmetrical *O*-acyl oximes and terminal alkynes are used.

Energetic Materials

D. E. Chavez,* J. C. Bottaro, M. Petrie, D. A. Parrish ———— **12973 – 12975**

Synthesis and Thermal Behavior of a Fused, Tricyclic 1,2,3,4-Tetrazine Ring System

Front Cover

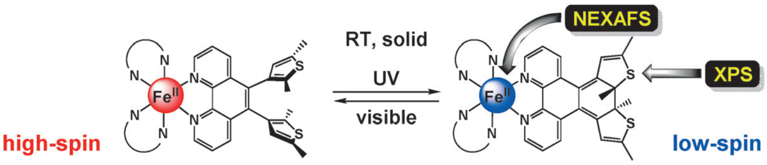


Ring of fire: Double N-amination of the bis(tetraethylammonium) salt of 3,3′-dinitro-5,5′-bi-1,2,4-triazole results in a thermally stable di-N-aminated energetic material that is insensitive to impact, spark, and friction. Subsequent oxidation leads to a fused, tricyclic 1,2,3,4-tetrazine ring system (see figure) with excellent density and explosive performance properties.

Molecular Switches

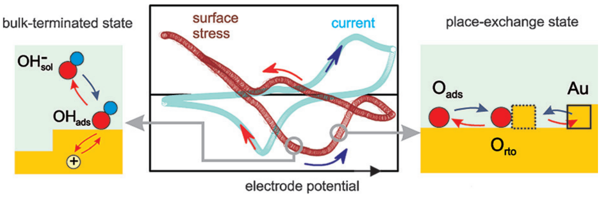
B. Rösner, M. Milek, A. Witt, B. Gobaut, P. Torelli, R. H. Fink,* M. M. Khusniyarov* ———— **12976 – 12980**

Reversible Photoswitching of a Spin-Crossover Molecular Complex in the Solid State at Room Temperature



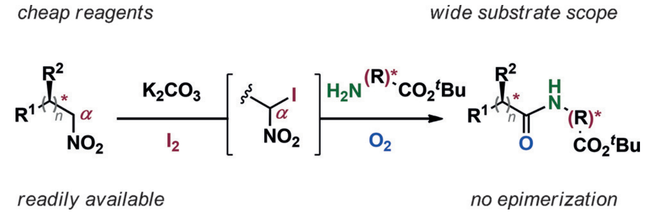
Make the cycle: A photochromic organic moiety integrated into a bistable spin-crossover iron(II) complex underwent reversible cyclization in the solid state upon irradiation with light of different wavelengths (see scheme). The ligand-based photoreaction triggered a reversible spin transition at the coordinated metal ion at room temperature.

Surface Reactions



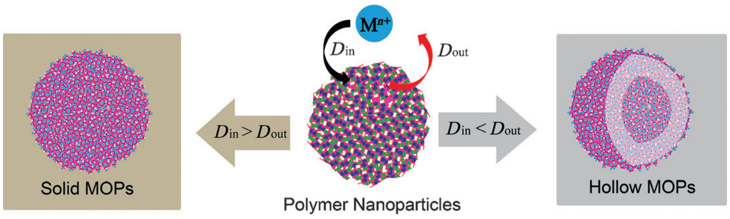
Less noble or more noble?: The different oxygen electrosorption processes, and specifically oxygen species adsorption on the bulk-terminated surface versus the formation of a mixed oxygen–gold surface layer by the replacement-turnover process, exhibit fundamentally different coupling between the chemistry and the mechanics of the surface.

Peptide Coupling



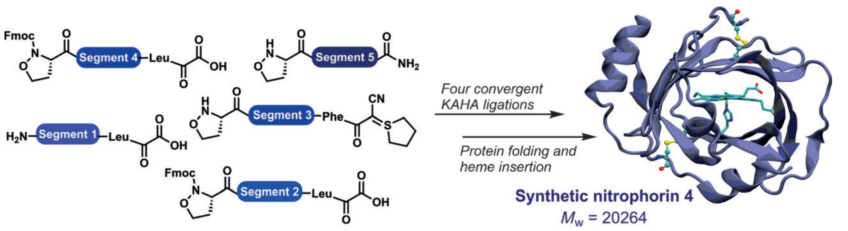
An odd couple: A mild oxidative entry into amide formation between readily available nitroalkanes and amines is disclosed involving iodine, molecular oxygen, and solid potassium carbonate. As well as halogen bonding of amines by the iodonium source, amidation is shown to proceed via α-iodo nitroalkanes with complete stereochemical integrity and high functional-group tolerance.

Hollow Nanoparticles



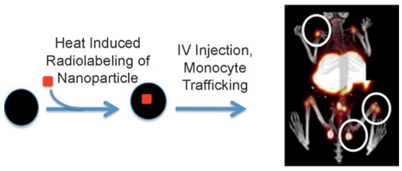
Hollow metal–organic particles (MOPs) are prepared by simply adding metal ions into solutions of polymeric organic nanoparticles. The size and shell thickness of the MOPs can be easily tuned. Evidence for the generality of the method is provided by its application to a variety of metal ions with different coordination geometries.

Protein Synthesis



It's all coming together! The 20 kDa heme protein nitrophorin 4 was synthesized by sequential KAHA ligations using a convergent strategy. The folded synthetic protein readily coordinates the heme cofactor, and the holoprotein shows identical biological properties to the wild-type protein for NO binding and nitrite dismutase reactivity.

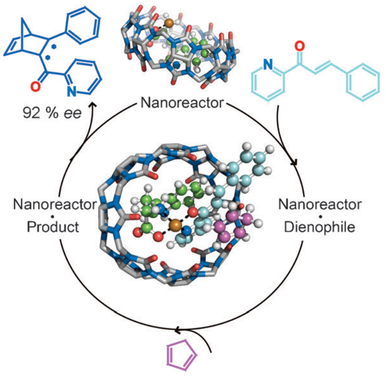
Heat-induced radiolabeling yields ^{89}Zr-Feraheme nanoparticles, which are taken up by blood monocytes and carried to the lymph nodes (white circles), as shown in a PET/CT image of a normal mouse.



In Vivo Nanoparticle Imaging

M. D. Normandin, H. Yuan, M. Q. Wilks, H. H. Chen, J. M. Kinsella, H. Cho, N. J. Guehl, N. Absi-Halabi, S. M. Hosseini, G. El Fakhri, D. E. Sosnovik, L. Josephson* ________ **13002 – 13006**

Heat-Induced Radiolabeling of Nanoparticles for Monocyte Tracking by PET



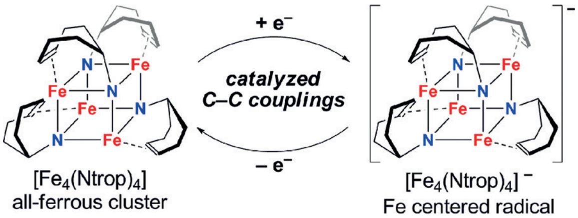
Chiral CB[*n*] catalysis: A supramolecular CB[8]-based catalyst system forms a chiral nanoreactor in the presence of a single, natural L-amino acid as the chiral source for an asymmetric Lewis acid catalyzed Diels–Alder reaction. Both a substantial rate acceleration (up to 9.5 times) and high enantioselectivity up to 92% *ee* were achieved. The nanoreactor assembly was also investigated through spectroscopic measurements and isothermal calorimetry.

Host–Guest Catalysis

L. Zheng, S. Sonzini, M. Ambarwati, E. Rosta, O. A. Scherman,* A. Herrmann* ________ **13007 – 13011**

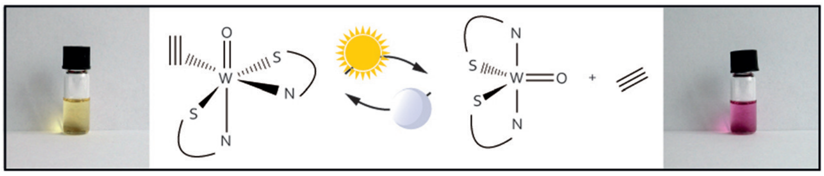
Turning Cucurbit[8]uril into a Supramolecular Nanoreactor for Asymmetric Catalysis

Iron Heterocubanes



A iron heterocubane cluster, $[Fe_4(Ntrop)_4]$, with an unprecedented all-ferrous Fe_4N_4 core was synthesized and fully characterized (trop = 5*H*-dibenzo[*a*,*d*]cyclo-hepten-5-yl). This compound can reversibly store up to four electrons at remarkably negative potentials. The $[Fe_4(Ntrop)_4]/[Fe_4(Ntrop)_4]^-$ system catalyzes the oxidative coupling of allyl anions and the reductive coupling of acridinium cations in a one-pot reaction.

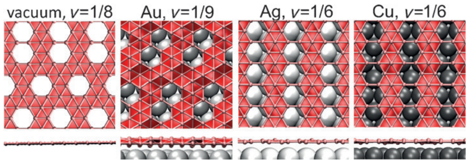
Bioinorganic Chemistry



On and off relationship: A structural-functional model has been designed to mimic the tungstoenzyme acetylene hydratase. The S-Phoz ligand (2-(4′,4′-dimethyloxazolin-2′-yl)thiophenolate) is used to generate a bioinspired environment around the W center, which can stabilize $W–C_2H_2$ adducts and can also reversibly activate ethyne.

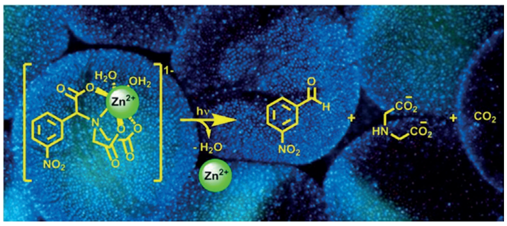
Boron Monolayers

Inside Back Cover



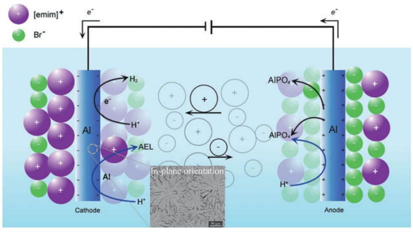
Concerto in B flat: 2D materials usually have a specific lattice structure that is independent of external conditions. In contrast, the structure of 2D boron (red, see picture) depends on the metal substrate. On weakly interacting metals, 2D boron shows significant off-plane buckling but on more reactive metals, it strongly favors a planar structure.

Photocage Compounds



Light-driven metal release: A photodecarboxylation reaction has been exploited to design a photocaged complex for Zn^{2+} with superior properties compared to other caged metal complexes. The photocage has been used to control the uptake of Zn^{2+} in frog oocytes expressing a human zinc transport protein.

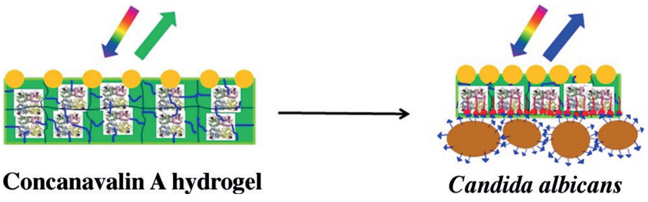
Al be back: An in situ electrochemical ionothermal method allows highly oriented and defect-free $AlPO_4$-11 molecular-sieve films to be synthesized using an Al electrode as the Al source. The $AlPO_4$-11 film shows excellent corrosion resistance.



Molecular-Sieve Films

T. Yu, W. Chu, R. Cai,* Y. Liu, W. Yang* ——— **13032 – 13035**

In Situ Electrochemical Synthesis of Oriented and Defect-Free AEL Molecular-Sieve Films Using Ionic Liquids



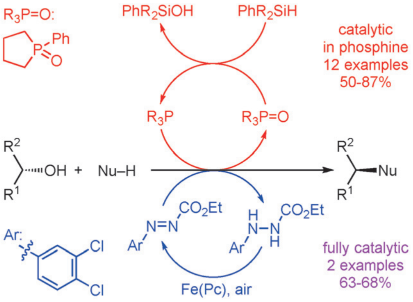
A con trick: Two-dimensional arrays of photonic crystals (PCs) embedded on Concanavalin A protein hydrogel surfaces can be used to selectively detect *Candida albicans* by multivalently and selectively binding to mannan on the cell surface. The resulting crosslinking shrinks the protein hydrogel to reduce the 2D particle spacing, and blue-shift the light diffracted from the PC (see figure). The sensor can distinguish between *C. albicans* and *E. coli*.

Sensors

Z. Cai, D. H. Kwak, D. Punihaole, Z. Hong, S. S. Velankar, X. Liu,* S. A. Asher* ——— **13036 – 13040**

A Photonic Crystal Protein Hydrogel Sensor for *Candida albicans*

Make it catalytic: A catalytic Mitsunobu reaction using innocuous reagents to recycle the stoichiometric phosphine oxide and hydrazine by-products was developed. The reported method is catalytic in 1-phenylphospholane and uses phenylsilane to recycle the catalyst. Integration of this phosphine catalytic cycle with Taniguchi's azocarboxylate catalytic system provided the first fully catalytic Mitsunobu reaction.

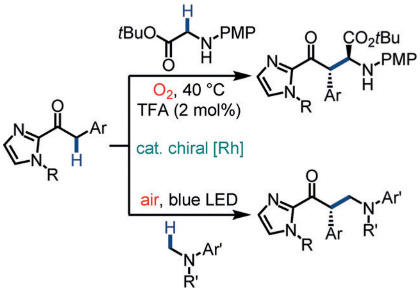


Organocatalysis

J. A. Buonomo, C. C. Aldrich* ——— **13041 – 13044**

Mitsunobu Reactions Catalytic in Phosphine and a Fully Catalytic System

Green stuff: A sustainable C–C bond formation is merged with the catalytic asymmetric generation of one or two stereocenters by combining asymmetric enolate chemistry with either autoxidation or visible-light photosensitized oxidation. The robustness of a chiral-at-metal rhodium(III) catalyst serves to facilitate the reaction. PMP = *para*-methoxyphenyl, TFA = trifluoroacetic acid.



C–H Activation

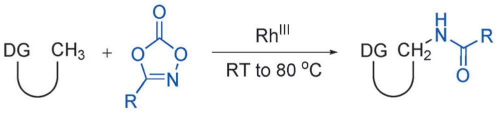
Y. Tan, W. Yuan, L. Gong,* E. Meggers* ——— **13045 – 13048**

Aerobic Asymmetric Dehydrogenative Cross-Coupling between Two C_{sp^3}–H Groups Catalyzed by a Chiral-at-Metal Rhodium Complex

C–H Activation

H. Wang, G. Tang, X. Li* **13049 – 13052**

Rhodium(III)-Catalyzed Amidation of Unactivated C(sp^3)–H Bonds

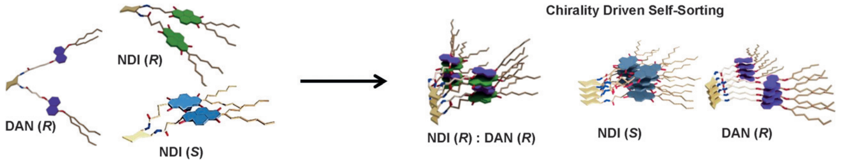


Rhodium(III) catalysts can effect the mild amidation of a broad scope of methyl and methylene C(sp^3)–H bonds. Quinoline and oxime ether directing groups (DGs) facilitate the reaction with high efficiency by using 3-substituted 1,4,2-dioxazol-5-ones as the amide source.

Chiral Polymerization

B. Narayan, K. K. Bejagam,
S. Balasubramanian,
S. J. George* **13053 – 13057**

Autoresolution of Segregated and Mixed p-n Stacks by Stereoselective Supramolecular Polymerization in Solution



Chiral stacking: A chirality-driven self-sorting strategy has been introduced for the construction of mixed and segregated donor-acceptor supramolecular arrays in solution.

DOI: 10.1002/anie.201584414

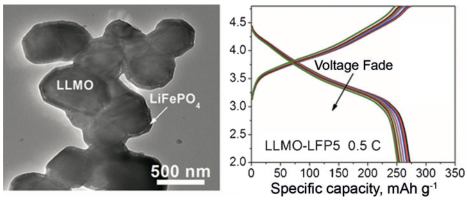
Flashback: 50 Years Ago . . .

The preparation of new elements by bombarding samples with heavy ions was a field that had already taken off: neptunium (atomic number 93) was first reported in 1940, and elements with atomic numbers 102, 103, and 104 were reported in 1957, 1961, and 1964, respectively. In a Review, C. Keller discussed the synthesis of transcurium elements. He postulated "…the next few years may witness the discovery of isotopes of elements up to atomic number 109 …". He was certainly correct: element 109 (meitnerium) was first created in 1982.

Hellmut Bredereck, Rolf Gleiter, and co-workers published two Communications. The first report was on the reactions of N,N-disubstituted formamides with alkali metals, which proceeded with the evolution of hydrogen to form the metal formamide. The salt then either decomposed with loss of carbon monoxide to form the metal dialkylamide, or reacted with the starting formamide to produce the salt of the substituted glyoxylamide. The second report described the reaction of *N,N*-dimethyl-3-dimethylaminoprop-1-enylideneammonium salts. Treatment with potassium methoxide resulted in the formation of *N,N,N′,N′*-tetramethyl-1-propene-1,3-diamine, and treatment with sodium dimethylamide resulted in the formation of *N,N,N′,N′,N″,N″*-hexamethyl-3-propene-1,1,3-triamine. Reaction of these products with CH-acidic compounds resulted in the formation of butadiene derivatives.

Adolf Krebs outlined the occurrence of 1,2-didehydrocyclooctatetraene as an intermediate in the reaction of bromocyclooctatetraene with potassium *tert*-butoxide. The presence of the intermediate was confirmed by identifying the products of trapping experiments.

Read more in Issue 11/1965.



Lithium-rich layered oxides, $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ (LLMO), were modified with a nanoscale $LiFePO_4$ (LFP) surface according to a facile sol–gel method. This surface modification combines the advantages of bulk doping and surface coating as the LLMO crystal structure is stabilized by cationic doping and the LLMO cathode is protected from corrosion processes induced by organic electrolytes.

Cathode Materials

F. Zheng, C. Yang,* X. Xiong, J. Xiong, R. Hu, Y. Chen, M. Liu* ___ 13058 – 13062

Nanoscale Surface Modification of Lithium-Rich Layered-Oxide Composite Cathodes for Suppressing Voltage Fade

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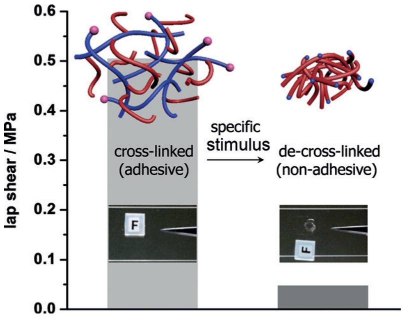
The depolymerization of < 1 mol% of a macro-cross-linker gives rise to an amplified response in stimuli-responsive cross-linked adhesives. This amplified response enables rapid and sensitive debonding in response to specific stimuli, as well as pre-programmed debonding of layers in composite materials. The use of depolymerizable macro-cross-linkers transforms an inexpensive monomer into a highly stimuli-responsive adhesive.



Stimuli-Responsive Materials

H. Kim, H. Mohapatra, S. T. Phillips* ___ 13063 – 13067

Rapid, On-Command Debonding of Stimuli-Responsive Cross-Linked Adhesives by Continuous, Sequential Quinone Methide Elimination Reactions

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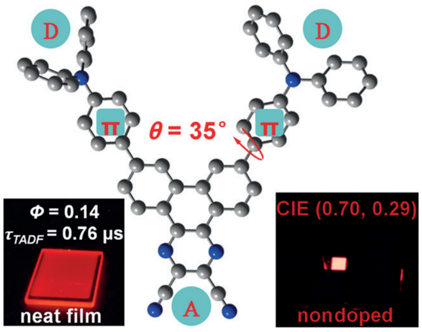
Seeing red: A V-shaped molecule (TPA-DCPP), which undergoes thermally activated delayed fluorescence (TADF) to emit in the near-IR region, has been synthesized. The molecule incorporates triphenylamine (TPA) as the donor (D) and 2,3-dicyanopyrazino phenanthrene (DCPP) as the acceptor (A). A nondoped OLED prepared using TPA-DCPP exhibited a maximum external quantum efficiency (EQE) of 2.1%, whereas the doped device had an EQE of almost 10%.



Organic Light-Emitting Diodes

S. Wang, X. Yan, Z. Cheng, H. Zhang, Y. Liu, Y. Wang* ___ 13068 – 13072

Highly Efficient Near-Infrared Delayed Fluorescence Organic Light Emitting Diodes Using a Phenanthrene-Based Charge-Transfer Compound

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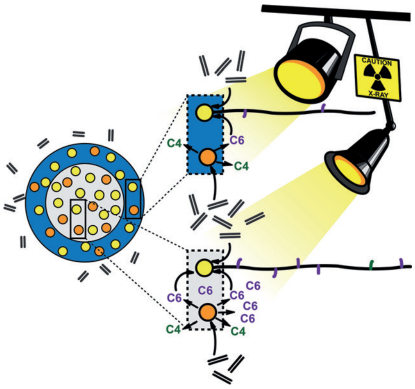


Two-in-one: A novel triethylaluminium-modified Phillips $Cr/Ti/SiO_2$ ethylene polymerisation catalyst with two distinct active regions has been developed. STXM was used as a micro-spectroscopy method to discriminate between the active sites producing low molecular weight linear chain and high molecular weight short-chain branched polyethylene within a single catalyst particle.

Phillips Catalyst

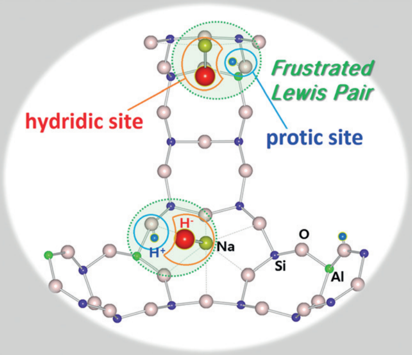
D. Cicmil, J. Meeuwissen, A. Vantomme, J. Wang, I. K. van Ravenhorst, H. E. van der Bij, A. Muñoz-Murillo, B. M. Weckhuysen* ___ 13073 – 13079

Polyethylene with Reverse Co-monomer Incorporation: From an Industrial Serendipitous Discovery to Fundamental Understanding

Zeolites

H. Lee, Y. N. Choi,* D.-W. Lim,
M. M. Rahman, Y.-I. Kim, I. H. Cho,
H. W. Kang, J.-H. Seo, C. Jeon,
K. B. Yoon* ______ **13080 – 13084**

Formation of Frustrated Lewis Pairs in Pt$_x$-Loaded Zeolite NaY



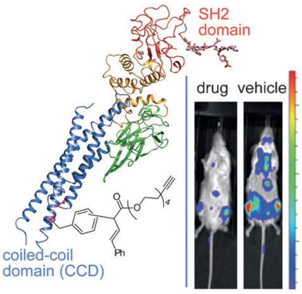
Poring over zeolites: Frustrated Lewis pairs (FLPs), consisting of sodium hydride (Na$^+$H$^-$) and a framework-bound hydroxy proton O(H$^+$), form inside the nanopores of zeolite NaY loaded with platinum nanoparticles after treatment of the material with H$_2$ at circa 400 K. FLP-containing zeolites may be applicable to size- and shape-selective ionic hydrogenation reactions.

Leukemia Therapy

M. B. Minus, W. Liu, F. Vohidov,
M. M. Kasembeli, X. Long, M. J. Krueger,
A. Stevens, M. I. Kolosov, D. J. Tweardy,*
E. A. R. Sison,* M. S. Redell,*
Z. T. Ball* ______ **13085 – 13089**

Rhodium(II) Proximity-Labeling Identifies a Novel Target Site on STAT3 for Inhibitors with Potent Anti-Leukemia Activity

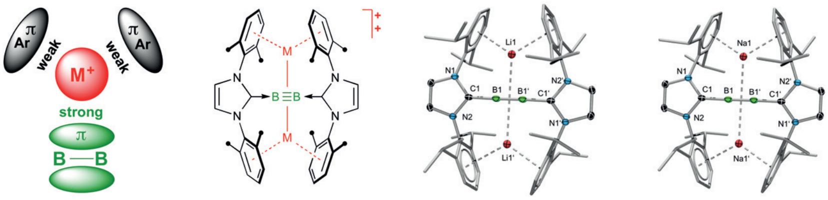
Touching from a distance: Small molecules block STAT3 SH2 phosphotyrosine recognition by binding to the distal coiled-coil domain (CCD). Inhibition of this new CCD target site, which was identified by catalytic rhodium labeling, blocks tumor progression in a leukemia mouse model.



Cation–π Interactions

R. Bertermann, H. Braunschweig,*
P. Constantinidis, T. Dellermann,
R. D. Dewhurst, W. C. Ewing, I. Fischer,
T. Kramer, J. Mies, A. K. Phukan,
A. Vargas ______ **13090 – 13094**

Exclusive π Encapsulation of Light Alkali Metal Cations by a Neutral Molecule



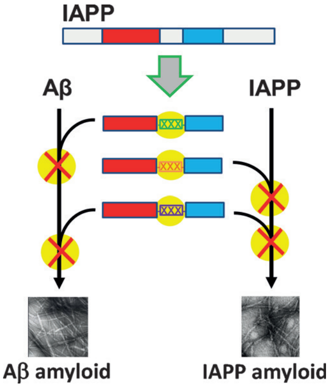
No help required: Cation–π interactions are one of the most important classes of noncovalent bonding; however, examples of exclusive cation–π bonding are exceedingly rare. A neutral diboryne molecule has been found to encapsulate Li$^+$ and Na$^+$ in the absence of a net charge, covalent bonds, or lone-pair donor groups. In the resulting encapsulation complexes, a neutral molecule binds the light alkali metals exclusively through cation–π interactions.

Amyloid Inhibitors

E. Andreetto, E. Malideli, L.-M. Yan,
M. Kracklauer, K. Farbiarz,
M. Tatarek-Nossol, G. Rammes, E. Prade,
T. Neumüller, A. Caporale,
A. Spanopoulou, M. Bakou, B. Reif,
A. Kapurniotu* ______ **13095 – 13100**

A Hot-Segment-Based Approach for the Design of Cross-Amyloid Interaction Surface Mimics as Inhibitors of Amyloid Self-Assembly

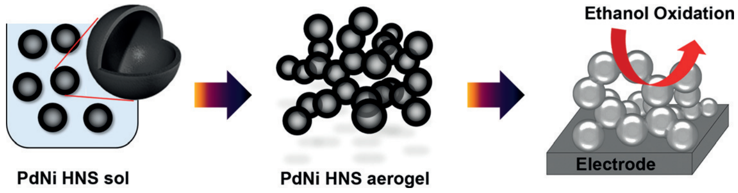
Inhibitors of amyloid self-assembly are difficult to design because of the dynamic nature of the structures involved. A hot-segment-linking approach has led to highly potent inhibitors of the cytotoxic self-assembly of the Aβ peptide (Alzheimer's disease), the islet amyloid polypeptide in type 2 diabetes, or both polypeptides. This strategy should be applicable to inhibiting pathogenic interactions of other proteins as well.



Electrocatalysis

B. Cai, D. Wen, W. Liu, A.-K. Herrmann, A. Benad, A. Eychmüller* **13101 – 13105**

Function-Led Design of Aerogels: Self-Assembly of Alloyed PdNi Hollow Nanospheres for Efficient Electrocatalysis



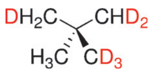
Function follows form: Aerogel electrocatalysts consisting of alloyed PdNi hollow nanospheres (HNS) were prepared. Their chemical composition and shell thickness can be controlled based on the ratio of the Ni/Pd precursors. The mass activity of the $Pd_{83}Ni_{17}$ HNS aerogel is 5.6 times higher than that of the commercial Pd/C catalyst.

Chiral Discrimination

A. Masarwa, D. Gerbig, L. Oskar, A. Loewenstein, H. P. Reisenauer, P. Lesot,* P. R. Schreiner,* I. Marek* **13106 – 13109**

Synthesis and Stereochemical Assignment of Crypto-Optically Active $^2H_6$-Neopentane

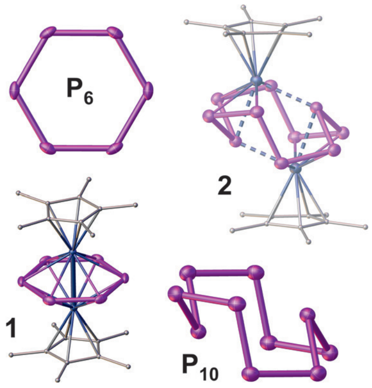
The spectroscopic limits for chiral discrimination with NMR spectroscopy in chiral aligned media and with vibrational circular dichroism spectroscopy have been studied with sixfold-deuterated chiral neopentane. Since the stereogenicity of this compound is only due to small mass differences, the determination of its structure is particularly difficult.



Polyphosphorus Complexes

M. Fleischmann, F. Dielmann, L. J. Gregoriades, E. V. Peresypkina, A. V. Virovets, S. Huber, A. Y. Timoshkin, G. Balázs, M. Scheer* **13110 – 13115**

Redox and Coordination Behavior of the Hexaphosphabenzene Ligand in $[(Cp^*Mo)_2(\mu,\eta^6{:}\eta^6\text{-}P_6)]$ Towards the "Naked" Cations Cu^+, Ag^+, and Tl^+

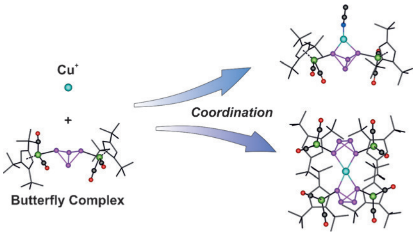


One ring to bind them all! The reactivity of the long-known hexaphosphabenzene complex **1** has been studied for the first time. The coordination of **1** to Cu^+, Ag^+, and Tl^+ affords layered compounds as supramolecular analogues of graphene, while oxidation leads to a bisallylic distortion of the P_6 ring. A *cyclo*-P_{10} complex **2** was also characterized, which is the largest known cyclic polyphosphorus complex.

Butterfly Complexes

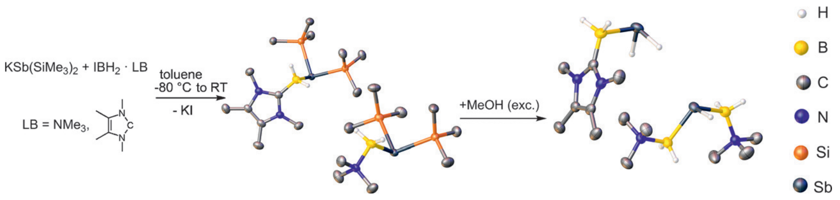
C. Schwarzmaier, S. Heinl, G. Balázs, M. Scheer* **13116 – 13121**

E_4 Butterfly Complexes (E = P, As) as Chelating Ligands



The butterfly has landed: The first examples of the coordination of E_4 butterfly complexes (E = P, As) are presented. It is shown that the "wing-tip" E atoms are capable of acting as ligands towards Cu^+ cations. The E_4 moieties act as bidentate ligands with a very narrow bite-angle, which is comparable to that of dppm (bis(diphenylphosphino)methane).

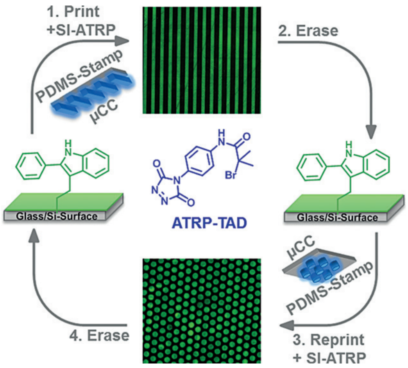
Main-Group Chemistry



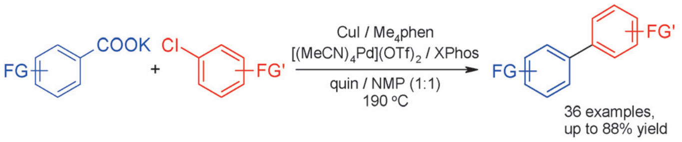
Getting heavier! The monomeric parent compound of the stibanylboranes, "H_2Sb-BH_2", which is only stabilized by a Lewis base, was isolated and completely characterized. DFT calculations give further insight into the stability of these unique compounds.

Rewritable Materials

Write and erase: The click reaction between a triazolinedione (TAD)-conjugated ATRP initiator and indole was used for the patterning of glass and silicon wafers employing microcontact chemistry. The reversibility of the click reaction enabled the writing, erasing, and rewriting of surfaces with polymer brush micropatterns for the first time.



Decarboxylative Cross-Coupling



Lifting the restriction: A combination of a CuI/Me$_4$phen decarboxylation catalyst and a [(MeCN)$_4$Pd](OTf)$_2$/XPhos cross-coupling catalyst enables the synthesis of biaryls from inexpensive aryl chlorides and potassium benzoates regardless of their substitution pattern (see scheme; FG = functional group). This approach lifts the restriction of decarboxylative cross-coupling reactions to *ortho*-substituted or heterocyclic carboxylate substrates.

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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