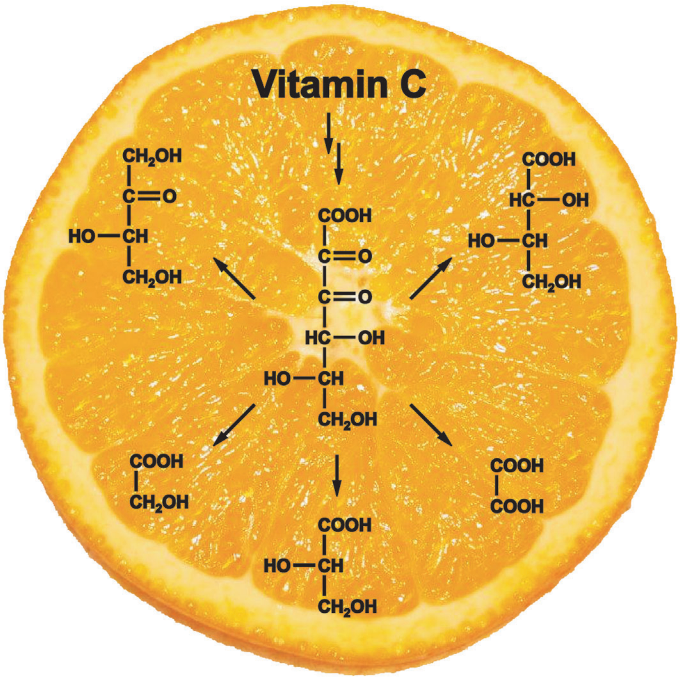
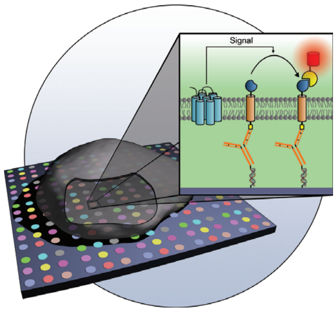
# Even 80 years after ...

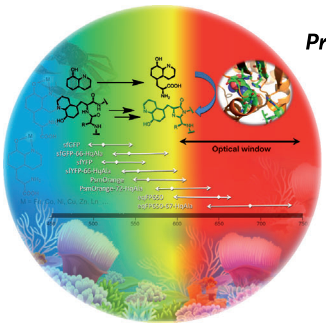


… the elucidation of the structure of L-threo-ascorbic acid (vitamin C), the chemistry of this reactive reducing carbohydrate remains exciting. In their Communication on page 4887 ff., M. A. Glomb and M. Smuda report on their investigations into the Maillard degradation pathway, which revealed three major fragmentation mechanisms that lead to carbonyl and dicarbonyl compounds, carboxylic acids, and amide advanced glycation endproducts.

### Protein Arrays in Cells

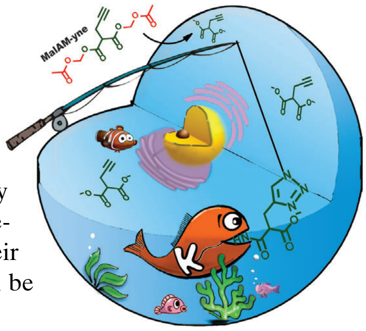
The protein-interaction arrays described by P. I. H. Bastiaens, L. Dehmelt et al. in their Communication on page 4790 ff. were used for the simultaneous monitoring of the interaction kinetics of a prey protein with two distinct bait proteins in individual living cells.





### Protein Engineering

In their Communication on page 4805 ff., J. Y. Wang and co-workers describe the synthesis and incorporation of an 8-hydroxyquinoline-modified amino acid into fluorescent proteins. This metal-chelating moiety causes the emission spectra of the proteins to be red-shifted.



### Posttranslational Modifications

A probe for malonylation of lysine, a newly discovered posttranslational modification, is described by Y. M. E. Fung, X. D. Li, et al. in their Communication on page 4883 ff. This probe can be used for detecting modifications in living cells.

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## Editorial

*"... The Technische Universität München (TUM) Faculty Tenure Track involves the promotion of the best within the system; it means that at TUM, the road to full professorship stands open for talented young scientists through sustained achievement ..."*
Read more in the Editorial by Wolfgang A. Herrmann.

W. A. Herrmann* ______ 4700 – 4701

Tenure Track: The Royal Road to Professorship?

## Service

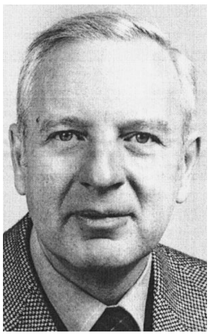
***Spotlight on Angewandte's*** Sister Journals ______ *4718 – 4720*

## Author Profile

*"I can never resist fresh sushi with a cup of green tea. My greatest achievement has been our three wonderful kids. ..."*
This and more about Thomas Ward can be found on page 4722.

Thomas Ward ______ 4722

## Obituaries



Rudolf Wiechert, the former Head of Chemical and Molecular Biology Research at Schering AG, and professor at the Technische Universität Berlin, passed away in January. He was known for his early work in organocatalysis, and in particular for his contribution to the Hajos–Parrish–Eder–Sauer–Wiechert reaction, a proline-catalyzed asymmetric aldol reaction.

Rudolf Wiechert (1928–2013)

E. Winterfeldt* ______ 4723

## Books

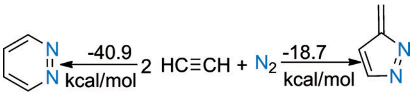
Applications of Supramolecular Chemistry — Hans-Jörg Schneider — *reviewed by U. Lüning* ______ **4724**

## Essays

### *Attacking $N_2$*

J. G. Andino, S. Mazumder, K. Pal, K. G. Caulton* ______ **4726–4732**

New Approaches to Functionalizing Metal-Coordinated $N_2$



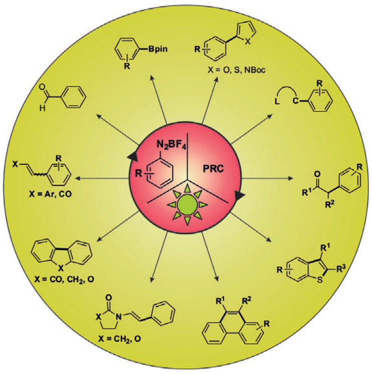
**$N_2$, can do**: Converting the refractory molecule $N_2$ into synthetic chemicals is thermodynamically preferred when the derivatizing reactant is a "high-energy molecule", one with a positive enthalpy of formation. Alkynes and allenes are thus targeted for this purpose (see scheme), and a range of likely products are identified, especially those with N–N bonds, including bipyrroles.

## Minireviews

### *Photocatalysis*

D. P. Hari, B. König* ______ **4734–4743**

The Photocatalyzed Meerwein Arylation: Classic Reaction of Aryl Diazonium Salts in a New Light



**Diazonium salts in the spotlight**: Photoredox catalysis is an excellent alternative to reactions with stoichiometric reducing reagents for the generation of aryl radicals. In this Minireview, early examples and recent advances of the photoredox chemistry of aryl diazonium salts are discussed.

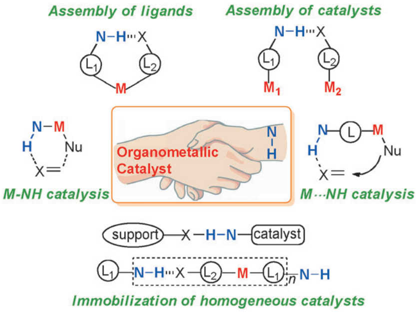
## Reviews

### *Organometallic Catalysis*

B. Zhao, Z. Han, K. Ding* ______ **4744–4788**

The N–H Functional Group in Organometallic Catalysis

**The "magic" effects** of N–H moieties in organometallic catalysis have been observed in various reaction systems. Recent advances are presented in the development of organometallic catalysts based on the concept of cooperative catalysis by taking the beneficial effect of the NH moiety in the catalyst by catalyst–substrate, ligand–ligand, and catalyst–catalyst interactions.



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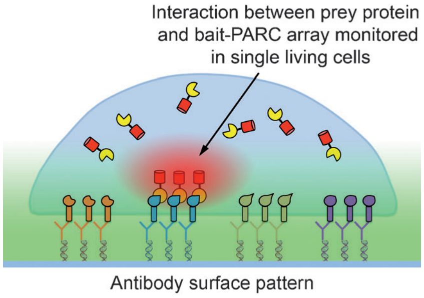
# Communications

## Protein Array in Cells

S. Gandor, S. Reisewitz,
M. Venkatachalapathy, G. Arrabito,
M. Reibner, H. Schröder, K. Ruf,
C. M. Niemeyer, P. I. H. Bastiaens,*
L. Dehmelt* ________ **4790 – 4794**

A Protein-Interaction Array Inside a Living Cell

**Taking the bait**: Protein-interaction arrays were generated in living cells by the interaction of bait-presenting artificial receptor constructs (bait-PARCs) with micrometer-scaled antibody surface patterns (see figure). This method was applied to simultaneously monitor the interaction kinetics of a prey protein with two distinct bait proteins in individual living cells.



**Frontispiece**

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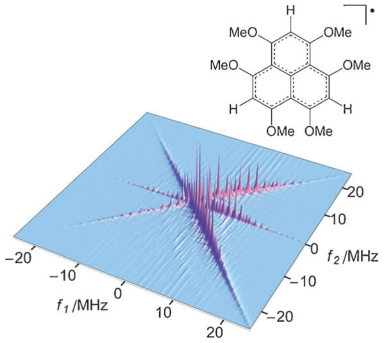
## Quantum Simulator

A. Ueda, S. Suzuki, K. Yoshida, K. Fukui,
K. Sato, T. Takui,* K. Nakasuji,
Y. Morita* ________ **4795 – 4799**

Hexamethoxyphenalenyl as a Possible Quantum Spin Simulator: An Electronically Stabilized Neutral π Radical with Novel Quantum Coherence Owing to Extremely High Nuclear Spin Degeneracy

**A phenalenyl radical** with six methoxy groups, which were introduced symmetrically, has been synthesized. The extensively delocalized and highly symmetric electronic-spin system was studied with advanced cw-/pulsed-ESR techniques, thereby giving an experimental model to explore molecular quantum spin simulators with novel quantum coherence attributable to the extremely high degeneracy of the nuclear spin states owing to the eighteen equivalent protons.



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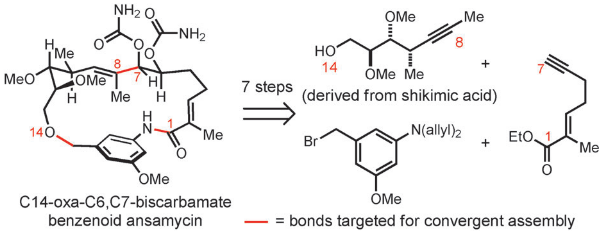
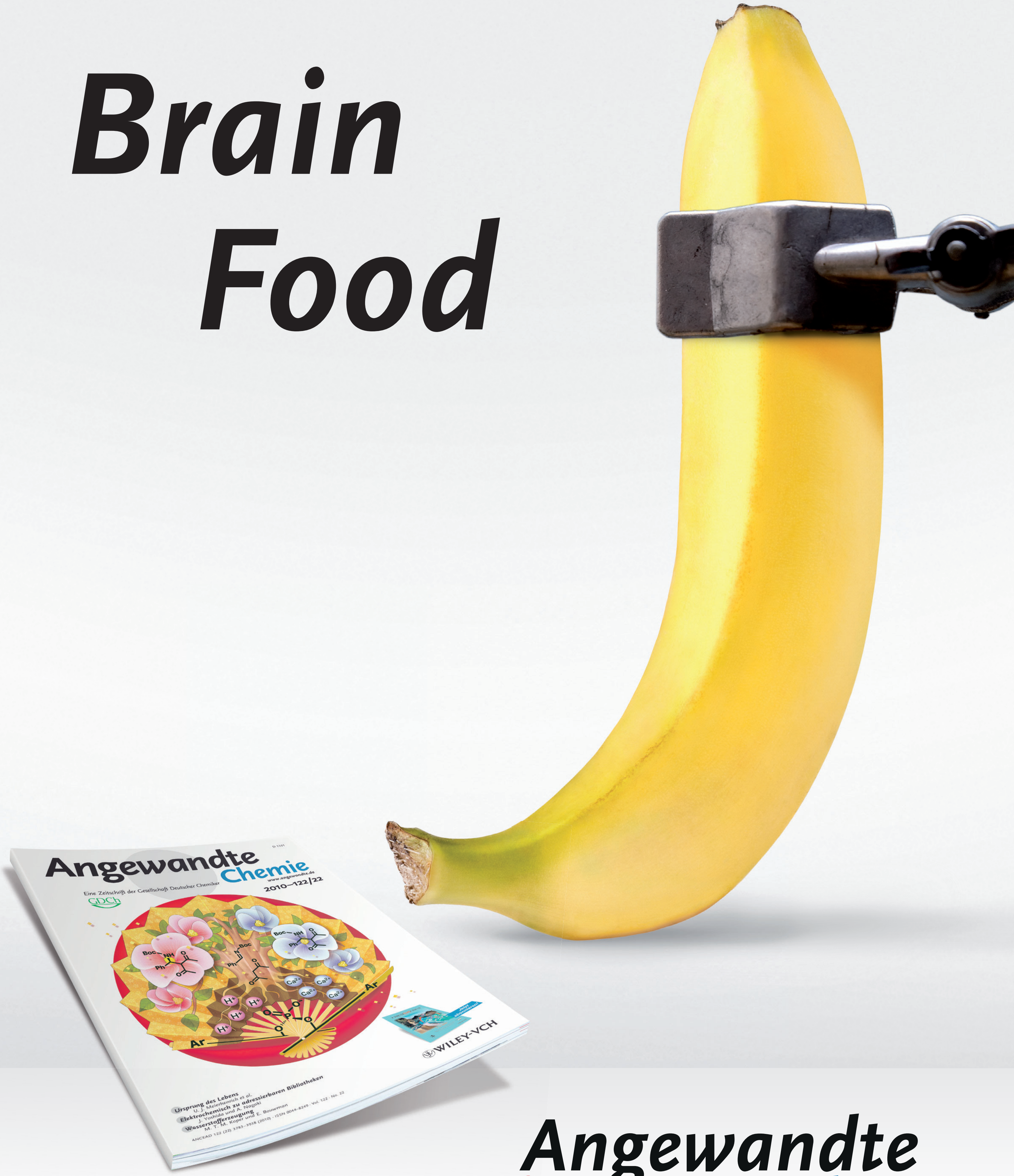
## Natural Product Synthesis

V. Jeso, S. Iqbal, P. Hernandez,
M. D. Cameron, H. Park, P. V. LoGrasso,*
G. C. Micalizio* ________ **4800 – 4804**

Synthesis of Benzoquinone Ansamycin-Inspired Macrocyclic Lactams from Shikimic Acid



**One is not like the other**: The title approach proceeds by stepwise coupling of three relatively simple substrates. Three natural product-inspired agents are described, one of which has natural product-like toxicity for HeLa and MCF7 cells. It is isoform-selective, thus targeting Hsp90α/β over Grp94, and adopts a conformation similar to that of geldanamycin when complexed with Hsp90.



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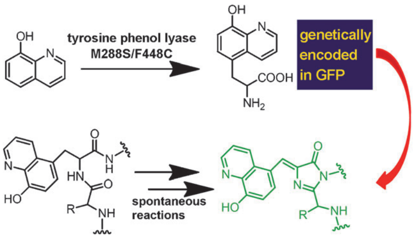
2010–122/22
WILEY-VCH
Ursprung des Lebens
Elektrochemisch zu adressierbaren Bibliotheken
Wasserstofferzeugung

## Protein Engineering

X. H. Liu, J. S. Li, C. Hu, Q. Zhou,
W. Zhang, M. R. Hu, J. Z. Zhou,
J. Y. Wang* ——— 4805 – 4809

Significant Expansion of the Fluorescent Protein Chromophore through the Genetic Incorporation of a Metal-Chelating Unnatural Amino Acid

Inside Back Cover



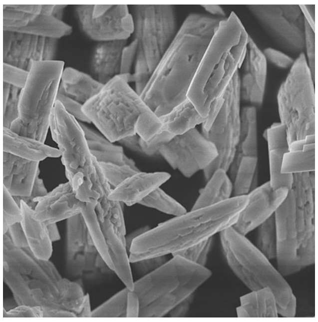
**Caught red-shifted**: A novel metal-chelating unnatural amino acid with an 8-hydroxyquinoline group (HqAla) can be enzymatically incorporated into GFP (see scheme). Substituting a Tyr residue in the chromophore of FPs with HqAla results in significantly red-shifted excitation and emission maxima. The crystal structure of superfolder GFP bearing HqAla in its chromophore shows the structural basis for these red shifts.

---

## Photocatalysis

G. Wang, B. Huang,* X. Ma, Z. Wang,
X. Qin, X. Zhang, Y. Dai,
M.-H. Whangbo ——— 4810 – 4813

$Cu_2(OH)PO_4$, a Near-Infrared-Activated Photocatalyst



**Crystal power!** Libethenite, $Cu_2(OH)PO_4$ (see 4–5 μm × 1.5 μm image), absorbs strongly in the near-infrared (NIR) region and is an effective photocatalyst for the decomposition of 2,4-dichlorophenol in aqueous solution under NIR irradiation. This NIR activation of the photocatalyst is due to a facile transfer of photogenerated electrons from the trigonal bipyramidal $Cu^{II}$ sites to the adjacent octahedral $Cu^{II}$ sites.

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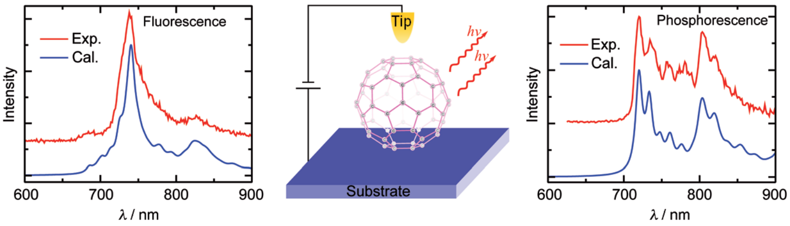
## Molecular Electroluminescence

G. Tian, Y. Luo* ——— 4814 – 4817

Fluorescence and Phosphorescence of Single $C_{60}$ Molecules as Stimulated by a Scanning Tunneling Microscope



**Glow-in-the-dark buckyballs**: Reproduction of the fluorescence and phosphorescence spectra of single $C_{60}$ molecules in a scanning tunneling microscope by simulations according to first principles (see picture) revealed the underlying mechanisms and enabled the correct assignment of the spectra.

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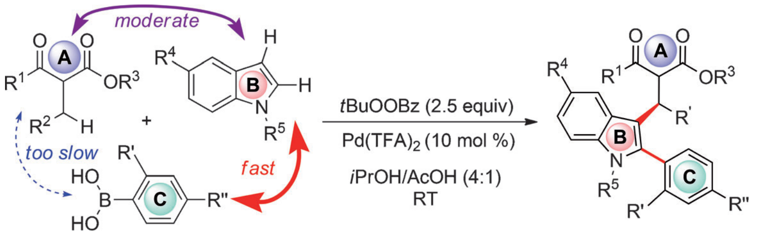
## Multicomponent Reactions

R. Y. Nimje, M. V. Leskinen,
P. M. Pihko* ——— 4818 – 4822

A Three-Component Palladium-Catalyzed Oxidative C–C Coupling Reaction: A Domino Process in Two Dimensions

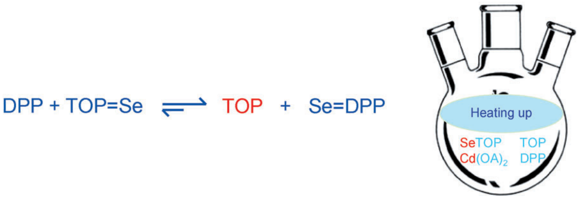


**Easy as ABC... or CBA!** Indoles can be selectively functionalized twice by a catalytic oxidative three-component coupling of arylboronates and β-ketoesters. The difference in the rates (see scheme) of the competing processes are amplified under the conditions of the three-component reaction.

## Nanocrystal Formation

K. Yu,* X. Liu, Q. Zeng, D. M. Leek,
J. Ouyang, K. M. Whitmore,
J. A. Ripmeester, Y. Tao,
M. Yang* ________________ **4823 – 4828**

Effect of Tertiary and Secondary Phosphines on Low-Temperature Formation of Quantum Dots



**Getting to the TOP of things**: The coordination of tri-*n*-octylphosphine (TOP) instead of diphenylphosphine (DPP) to cadmium oleate ($Cd(OA)_2$) reveals how tertiary and secondary phosphines enhance the yield and reproducibility of the synthesis of nanocrystals by shifting the equilibrium of the reaction to the right (see picture). High Cd-to-Se and Se-to-TOP feed molar ratios facilitate the formation of Se=DPP by way of Se exchange from TOP to DPP.

---

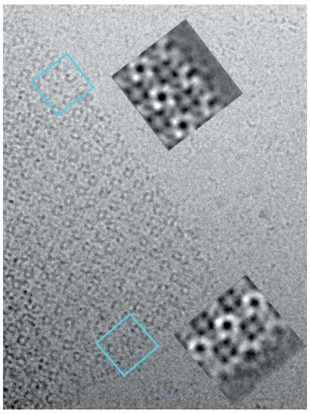
## Self-Assembly

L. R. Comolli,* C. E. Siegerist, S.-H. Shin,
C. Bertozzi, W. Regan, A. Zettl,
J. De Yoreo ________________ **4829 – 4832**

Conformational Transitions at an S-Layer Growing Boundary Resolved by Cryo-TEM

**Inside Cover**

**Snapshots of growth**: The use of a single graphene layer as the support for S-layer self-assembly of proteins provides an ideal, robust flat surface to image the expanding boundary by flash freezing and cryo-TEM, capturing the conformational states present at the expanding boundary (see figure). Image alignment and averaging provide a view of the steps leading to subunit recruitment and maturation in the self-assembly process.



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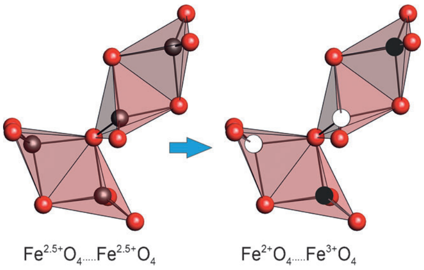
## $Fe^{II}/Fe^{III}$ Charge Order

M. F. Lü, J. C. Waerenborgh,
C. Greaves* ________________ **4833 – 4836**

$Sr_4Fe_6O_{12}$: Low-Temperature $Fe^{2+}$–$Fe^{3+}$ Charge Order within Pairs of Edge-Linked Tetrahedra

**Mix and match**: Topotactic hydride reduction allows the first synthesis of the fully reduced parent phase, $Sr_4Fe_6O_{12}$, of the important family $Sr_4Fe_6O_{13\pm\delta}$. The structure provides a rare example of pairs of edge-linked tetrahedra, in this case containing a random arrangement of $Fe^{II}$ and $Fe^{III}$ centers at 300 K. On cooling, charge order occurs so that each pair of tetrahedra has one $Fe^{II}$ (white) and one $Fe^{III}$ (black) center.



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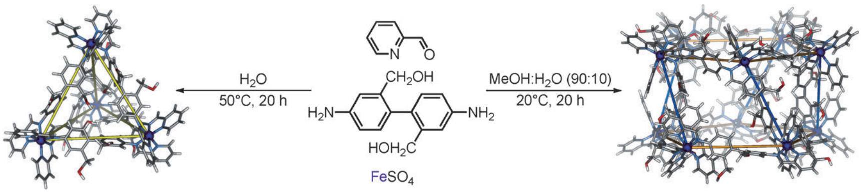
## Systems Chemistry

S. Zarra, J. K. Clegg,
J. R. Nitschke* ________________ **4837 – 4840**

Selective Assembly and Disassembly of a Water-Soluble $Fe_{10}L_{15}$ Prism



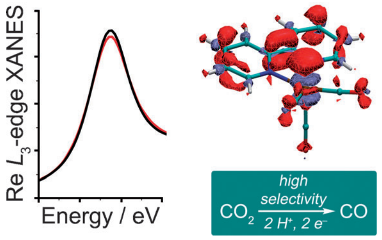
**Survival of the fittest**: Two water-soluble metal–organic architectures, a tetrahedron and a pentagonal prism, were selectively assembled from the same building blocks under different reaction conditions. In a mixture of the two, the prism was disassembled upon addition of 4-methoxyaniline to form a mononuclear complex, while leaving the more stable tetrahedral structure intact.

## Sustainable Catalysis

E. E. Benson, M. D. Sampson, K. A. Grice, J. M. Smieja, J. D. Froehlich, D. Friebel, J. A. Keith, E. A. Carter, A. Nilsson, C. P. Kubiak* ______ **4841 – 4844**

The Electronic States of Rhenium Bipyridyl Electrocatalysts for $CO_2$ Reduction as Revealed by X-ray Absorption Spectroscopy and Computational Quantum Chemistry

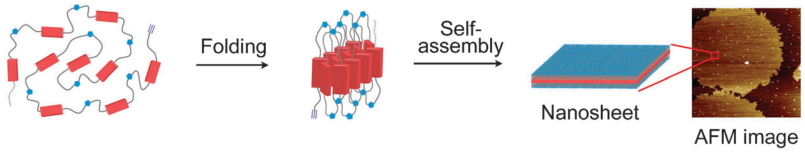
**Where are the electrons** that allow a highly reduced rhenium bipyridyl catalyst to attack $CO_2$, but not $H^+$? XAS and computational quantum chemistry indicate that the negative charge in $[Re(bpy)(CO)_3]^-$ and $[Re(bpy\text{-}tBu)(CO)_3]^-$ is not stored in a localized Re 5d state, but rather in the bipyridine ligand . The active states of this family of catalysts possess formally $Re^0$ metal centers with singly reduced bipyridine ligands.



## Self-Assembly

Y. Zheng, H. Zhou, D. Liu, G. Floudas, M. Wagner, K. Koynov, M. Mezger, H.-J. Butt, T. Ikeda* ______ **4845 – 4848**

Supramolecular Thiophene Nanosheets

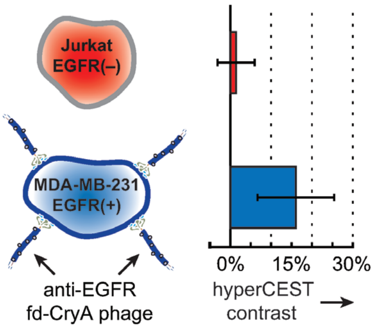


**Alternating copolymers** consisting of phenyl-capped bithiophene (red units) and oligo(ethylene glycol) hierarchically self-assemble into nanosheets through polymer folding in some organic solvents. The lateral size of the nanosheet is controllable by temperature and concentration of the solution. The nanosheet surface can be chemically modified by using copper-catalyzed Huisgen cycloaddition without disrupting the nanosheet structure.

## Xenon Biosensor

K. K. Palaniappan, R. M. Ramirez, V. S. Bajaj, D. E. Wemmer, A. Pines, M. B. Francis* ______ **4849 – 4853**

Molecular Imaging of Cancer Cells Using a Bacteriophage-Based $^{129}Xe$ NMR Biosensor

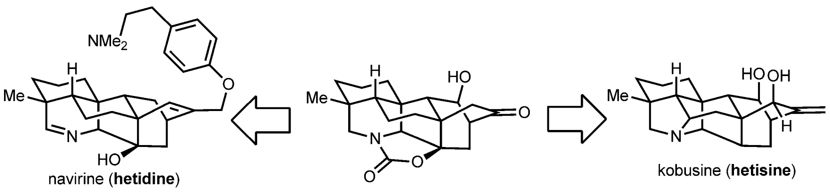


**NMR imaging**: Filamentous fd bacteriophage expressing antibodies recognizing the epidermal growth factor receptor (EGFR) were modified to incorporate cage-like xenon-binding molecules (CryA). The resulting contrast agent was shown to bind to an EGFR-positive cell line and detected by hyperpolarized $^{129}Xe$ NMR spectroscopy using chemical exchange saturation transfer (hyperCEST, see picture).

## Natural Product Synthesis

A. M. Hamlin, F. de J. Cortez, D. Lapointe, R. Sarpong* ______ **4854 – 4857**

Gallium(III)-Catalyzed Cycloisomerization Approach to the Diterpenoid Alkaloids: Construction of the Core Structure for the Hetidines and Hetisines

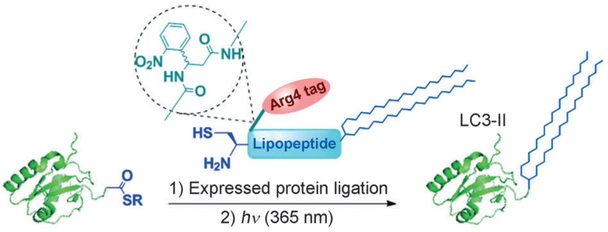


**A versatile core structure** has been prepared that should provide a foundation for the syntheses of the hetidine- and hetisine-type diterpenoid alkaloids. The synthesis of the caged polycyclic core structure, which features nine contiguous stereocenters, utilizes a $Ga^{III}$-catalyzed cycloisomerization of an alkynyl indene as well as a Michael/aldol sequence to build the bicyclo[2.2.2] framework.

## Protein Lipidation

Y.-C. Huang, Y.-M. Li, Y. Chen, M. Pan, Y.-T. Li, L. Yu, Q.-X. Guo, L. Liu* ______ **4858 – 4862**

Synthesis of Autophagosomal Marker Protein LC3-II under Detergent-Free Conditions

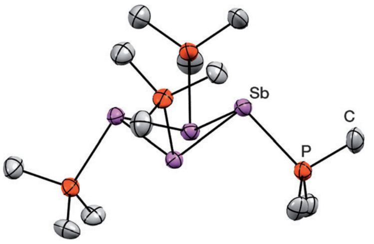


**Just add oil**: A new detergent-free method was developed to synthesize lipidated proteins using a light-activatable solubilizing side chain (in dashed circle, see scheme) to assist the ligation of the lipopeptides. This method allows the efficient preparation of a phosphatidylethanolamine-conjugated autophagosomal marker protein (LC3-II) as well as labeled derivatives of LC3-II, which can be used to study autophagy regulation.

## Main-Group Elements

S. S. Chitnis, Y.-Y. Carpenter, N. Burford,* R. McDonald, M. J. Ferguson ______ **4863 – 4866**

Assembly of a *cyclo*-Tetrastibinotetraphosphonium Tetracation by Reductive Elimination



$[(Me_3P)_4Sb_4]^{4+}$

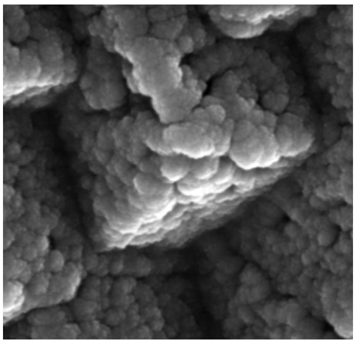
**Square deal**: Reactions of $SbF_3$ with $Me_3SiOSO_2CF_3$ produce $Sb^{3+}$ and $[Sb\text{-}F]^{2+}$ cations, which form complexes with two or three $Me_3P$ ligands. Subsequent reductive elimination of diphosphonium or fluorophosphonium cations from the complexes give the folded square *cyclo*-$[(Me_3P)_4Sb_4][OTf]_4$. Formation of the tetracation framework reveals new redox chemistry for Sb.

## Crystal Growth

A. Gal, W. Habraken, D. Gur, P. Fratzl, S. Weiner, L. Addadi* ______ **4867 – 4870**

Calcite Crystal Growth by a Solid-State Transformation of Stabilized Amorphous Calcium Carbonate Nanospheres in a Hydrogel

**An ugly duckling grows into a swan**: Many organisms grow their crystalline mineral phases through the secondary nucleation of nanospheres made of an amorphous precursor phase. Stable amorphous calcium carbonate biominerals were used to induce a similar transformation in vitro. The amorphous nanospheres underwent a solid-phase transformation that resulted in highly ordered calcite crystals composed of aggregated particles (see SEM image).

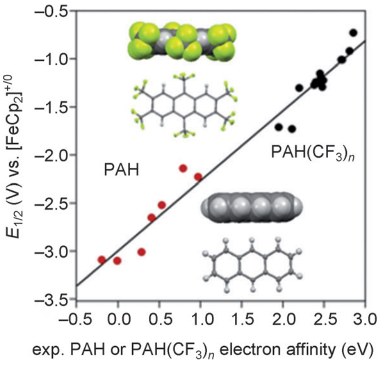


## Polycyclic Aromatic Hydrocarbons

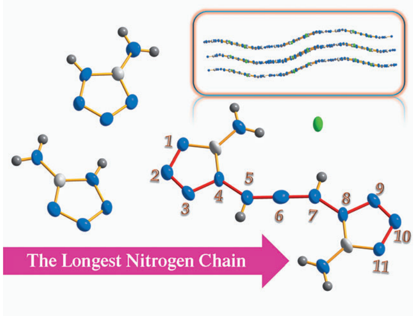
I. V. Kuvychko,* K. P. Castro, S. H. M. Deng, X.-B. Wang,* S. H. Strauss,* O. V. Boltalina* ______ **4871 – 4874**

Taming Hot $CF_3$ Radicals: Incrementally Tuned Families of Polyarene Electron Acceptors for Air-Stable Molecular Optoelectronics

**A regioselective, solvent-, and catalyst-free method** for the perfluoroalkylation of polycyclic aromatic hydrocarbons (PAHs) with $CF_3I$ was used to synthesize air-stable organic electron acceptors ($PAH(CF_3)_n$). The gas-phase electron affinities of these compounds correlate to the number of $CF_3$ groups. The number and orientation of the $CF_3$ groups also influenced the π–π stacking and crystalline morphologies of these compounds.



**A nitrogen-rich energetic salt** containing the longest reported nitrogen chain ($N_{11}$), was obtained by an azo coupling reaction from 1,5-diaminotetrazole. This is the first example of an azo reaction between an N–$NH_2$ diazonium salt and an amine derivative. The product structure was confirmed by X-ray crystallography, and its physical and explosive properties were characterized.



### Energetic Materials

Y. Tang, H. Yang,* B. Wu, X. Ju, C. Lu, G. Cheng* ______ 4875 – 4877

Synthesis and Characterization of a Stable, Catenated $N_{11}$ Energetic Salt

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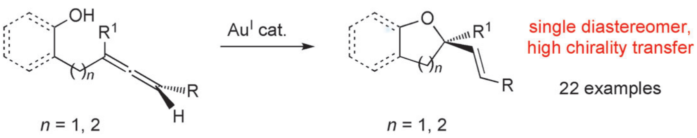

**'Ether' furan or pyran**: The *exo*-selective cyclization of enantioenriched allenols is accomplished with high chirality transfer using as little as 0.02 mol % of a gold catalyst. The new method is effective in the synthesis of a wide range of enantioenriched cyclic ethers, which are prepared in excellent yields in three steps from readily available propargylic phosphates.

### Asymmetric Synthesis

N. Cox, M. R. Uehling, K. T. Haelsig, G. Lalic* ______ 4878 – 4882

Catalytic Asymmetric Synthesis of Cyclic Ethers Containing an α-Tetrasubstituted Stereocenter

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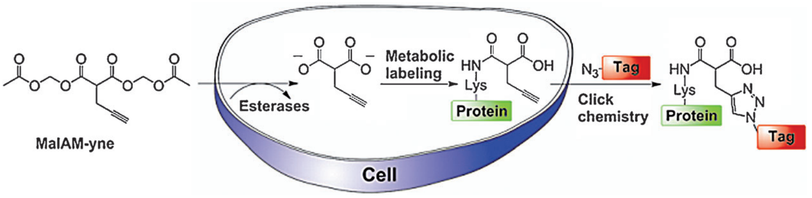

**Tag! You're it!** MalAM-yne is a chemical reporter for malonylation of lysines within proteins (see scheme), a newly identified posttranslational modification. MalAM-yne is cell-permeable and metabolically incorporated into proteins in living cells. Subsequent bioorthogonal tag conjugation allows the fluorescent visualization of cellular malonylation and profiling of malonylated proteins.

### Protein Modifications

X. Bao, Q. Zhao, T. Yang, Y. M. E. Fung,* X. D. Li* ______ 4883 – 4886

A Chemical Probe for Lysine Malonylation

**Back Cover**

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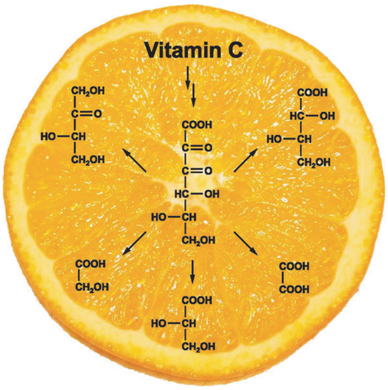
**Degradation mechanisms**: 75 % of the Maillard degradation pathways of ascorbic acid can be explained by oxidative α fragmentation (31 %), β cleavage (32 %), and decarboxylation from hydrate/hemiaminal intermediates (12 %), which lead to carbonyl and dicarbonyl compounds, carboxylic acids, and amide advanced glycation endproducts. The results are a major step forward in the understanding of changes occurring in systems containing vitamin C.



### Vitamin C Degradation

M. Smuda, M. A. Glomb* ______ 4887 – 4891

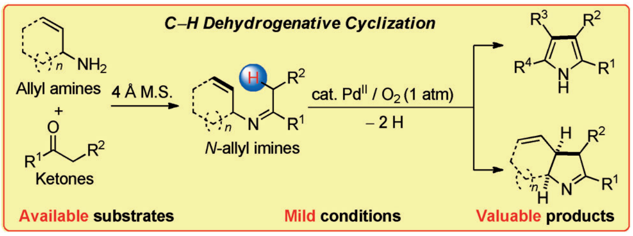
Maillard Degradation Pathways of Vitamin C

**Front Cover**

## Synthetic Methods

Z. Shi, M. Suri, F. Glorius* **4892 – 4896**

### Aerobic Synthesis of Pyrroles and Dihydropyrroles from Imines: Palladium(II)-Catalyzed Intramolecular C–H Dehydrogenative Cyclization

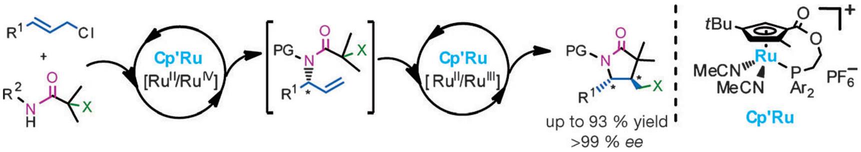


**sp³ectacularly mild!** An efficient Pd$^{II}$-catalyzed intramolecular dehydrogenative cyclization of imines affords (dihydro)pyrrole products using molecular oxygen as the sole oxidant. This mild formal sp$^3$-C–H functionalization allows rapid and atom-economical assembly of (dihydro)pyrrole rings from inexpensive and readily available allylamines and ketones. A broad range of functional groups are tolerated.

## Asymmetric Auto-Tandem Catalysis

N. Kanbayashi, K. Takenaka, T. Okamura,* K. Onitsuka* **4897 – 4901**

### Asymmetric Auto-Tandem Catalysis with a Planar-Chiral Ruthenium Complex: Sequential Allylic Amidation and Atom-Transfer Radical Cyclization

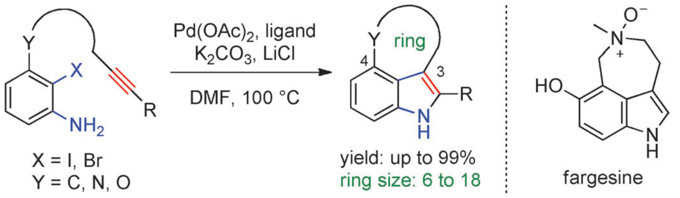


**Ru does it all**: A novel example of an asymmetric auto-tandem reaction catalyzed by a planar-chiral cyclopentadienyl–ruthenium complex is described. The reaction of allylic chloride with α-haloamides provides synthetically useful, diastereomerically and enantiomerically enriched γ-lactams with multiple stereogenic centers through one-pot sequential allylic amidation/atom-transfer radical cyclization. PG = protecting group.

## Synthetic Methods

D. Shan, Y. Gao, Y. Jia* **4902 – 4905**

### Intramolecular Larock Indole Synthesis: Preparation of 3,4-Fused Tricyclic Indoles and Total Synthesis of Fargesine

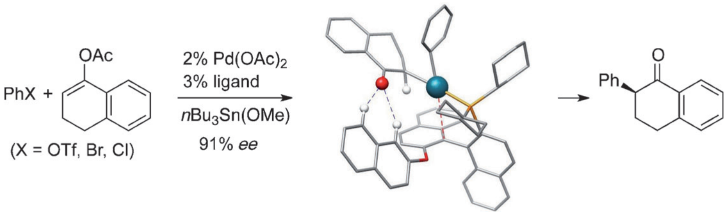


**Core strength**: A new and general strategy for the construction of 3,4-fused tricyclic indoles, which are the core structure of numerous natural products and bioactive molecules, has been developed. The method involves a one-step intramolecular Larock indolization and was successfully applied to the first total synthesis of fargesine.

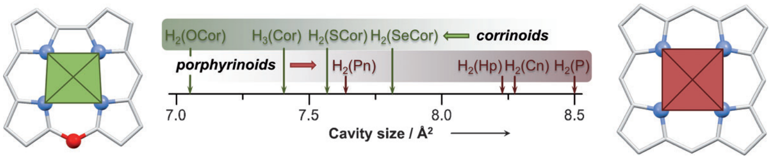
## Cross-Coupling

Z. Huang, L. H. Lim, Z. Chen, Y. Li, F. Zhou, H. Su, J. Zhou* **4906 – 4911**

### Arene CH–O Hydrogen Bonding: A Stereocontrolling Tool in Palladium-Catalyzed Arylation and Vinylation of Ketones



**Weak is powerful**: For the arylation of tin enolates, the palladium catalyst engages in weak CH–O hydrogen bonds to control stereoselectivity (see scheme). Similar catalysts capable of NH–O hydrogen bonding also works well.

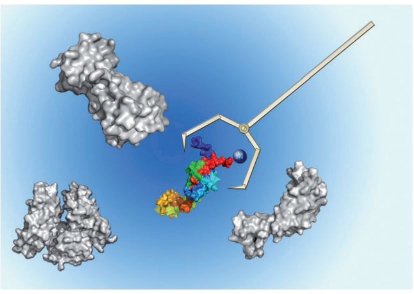


**A homologous series** of ring-contracted corrinoids, the 10-heterocorroles $H_2(XCor)$, is now available as the free-base ligand set. While the higher homologues, 10-thia- and 10-selenacorrole, show a porphyrin-like spectroscopic behavior, 10-oxacorrole displays lower aromatic character and has the smallest $N_4$ cavity of all free-base porphyrinoids synthesized so far, smaller even than those of corrole and porphycene ligands (see picture).

## *Contracted Porphyrinoids*

D. Sakow, B. Böker, K. Brandhorst, O. Burghaus, M. Bröring* **4912 – 4915**

10-Heterocorroles: Ring-Contracted Porphyrinoids with Fine-Tuned Aromatic and Metal-Binding Properties



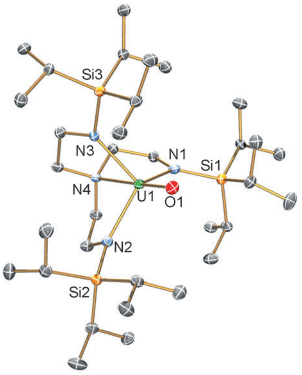
**Metal detector**: The title strategy provides a new way for rapid profiling of the metal-associated proteins on a proteome- and metallome-wide scale. The technique was applied to identify protein targets of a bismuth-based drug in *Helicobacter pylori* and to study the metal binding of the protein SlyD, which is a member of the FK506-binding protein family, in *E. coli*.

## *Metallomics*

L. Hu, T. Cheng, B. He, L. Li, Y. Wang, Y.-T. Lai, G. Jiang, H. Sun* **4916 – 4920**

Identification of Metal-Associated Proteins in Cells by Using Continuous-Flow Gel Electrophoresis and Inductively Coupled Plasma Mass Spectrometry

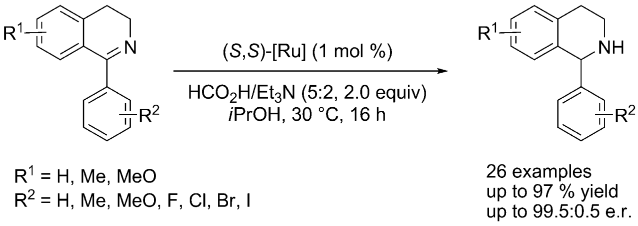
**Single-molecule magnets**: Straightforward oxidation of a triamidoamine uranium(III) complex with trimethyl-*N*-oxide affords a uranium(V) terminal mono-oxo complex which is the first clear-cut example of a uranium(V) single-molecule magnet (SMM). This monometallic complex unambiguously shows that a strongly axially ligated and thus anisotropic ligand field can be used to overcome the limited magnetic anisotropy of uranium(V).



## *Single-Molecule Magnets*

D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes,* S. T. Liddle* **4921 – 4924**

Single-Molecule Magnetism in a Single-Ion Triamidoamine Uranium(V) Terminal Mono-Oxo Complex



**Give me an H! Give me another H!** The first general and highly enantioselective Ru-catalyzed transfer hydrogenation of a wide range of 1-aryl-substituted 1,2,3,4-dihydroisoquinolines is described. This atom-economic reaction proceeds under mild conditions, allowing rapid access to the corresponding biologically relevant 1-aryl-tetrahydroisoquinoline derivatives, in high yields and enantioselectivities of up to 99%.

## *Asymmetric Transfer Hydrogenation*

Z. Wu, M. Perez, M. Scalone,* T. Ayad,* V. Ratovelomanana-Vidal* **4925 – 4928**

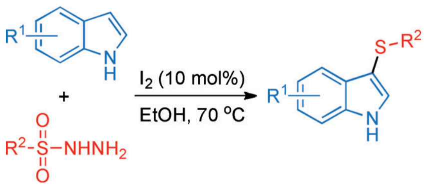
Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of 1-Aryl-Substituted Dihydroisoquinolines: Access to Valuable Chiral 1-Aryl-Tetrahydroisoquinoline Scaffolds

## Synthetic Methods

F.-L. Yang, S.-K. Tian* ______ 4929 – 4932

Iodine-Catalyzed Regioselective Sulfenylation of Indoles with Sulfonyl Hydrazides

**New S in town**: Sulfonyl hydrazides smoothly undergo sulfenylation with indoles in the presence of 10 mol% $I_2$ to give structurally diverse indole thioethers in moderate to excellent yields with extremely high regioselectivity. This study paves the way for the use of sulfonyl hydrazides as unique sulfur electrophiles in chemical synthesis.



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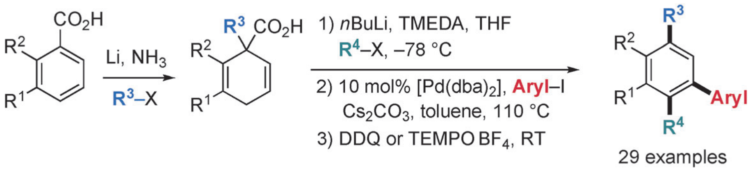
## Arene Functionalization

E. Koch, A. Studer* ______ 4933 – 4936

Regioselective Threefold Aromatic Substitution of Benzoic Acid Derivatives by Dearomatization, Regioselective Functionalization, and Rearomatization



***Ipso, meta, and para***: Benzoic acid derivatives can be highly regioselectively substituted at the *ipso*, *meta*, and *para* positions. The reaction sequence comprises an alkylative Birch reduction, a 4-alkylation, a palladium-catalyzed γ-arylation, and an oxidative rearomatization (see scheme). All the reactions are robust and experimentally easy to conduct.

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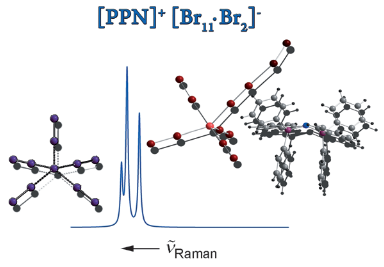
## Polyhalogen Anions

H. Haller, J. Schröder,
S. Riedel* ______ 4937 – 4940

Structural Evidence for Undecabromide $[Br_{11}]^-$



**Spreading the charge**: Besides iodine, few of the polyhalogen anions have been structurally characterized. Remarkably, the highest known ratio of elements-to-charge has now been found in the undecabromide $[Br_{11}]^-$. This new polybromide monoanion has been prepared in pure halogen and was structurally characterized by single-crystal X-ray diffraction, Raman spectroscopy (see picture), and quantum-chemical methods.

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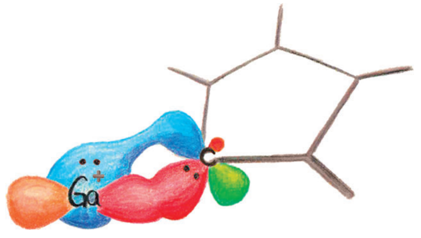
## Carbene Complexes

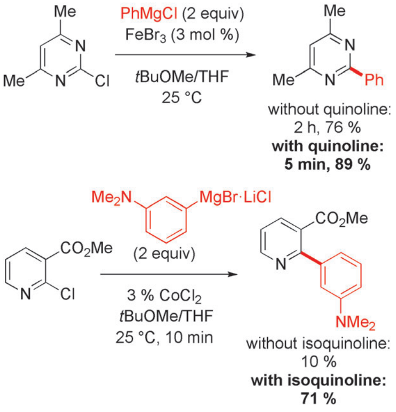
A. Higelin, S. Keller, C. Göhringer,
C. Jones,* I. Krossing* ______ 4941 – 4944

Unusual Tilted Carbene Coordination in Carbene Complexes of Gallium(I) and Indium(I)

**Ga,In insights**: A general explanation for the unusual tilted coordination mode of undisturbed gallium(I) and indium(I) carbene complexes of the weakly coordinating anion $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) is given, which is based on the experimental structures. The results are supported by extensive DFT studies.



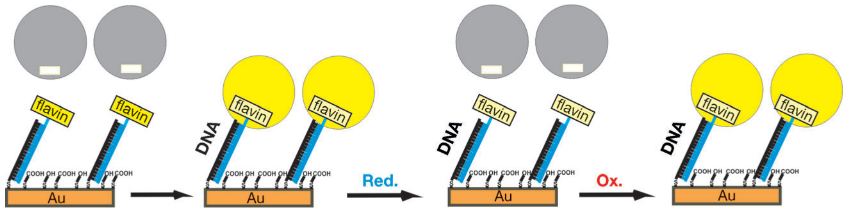
**Quinoline and isoquinoline** dramatically increase the rate and yield of Fe- and Co-catalyzed cross-coupling reactions. This new catalytic process extends the scope of such cross-coupling reactions to include complex functional groups and allows heteroaryl–heteroaryl bond formation to occur.



### Cross-Coupling

O. M. Kuzmina, A. K. Steib,
J. T. Markiewicz, D. Flubacher,
P. Knochel* ———————— **4945 – 4949**

Ligand-Accelerated Iron- and Cobalt-Catalyzed Cross-Coupling Reactions between N-Heteroaryl Halides and Aryl Magnesium Reagents



**Flavin away**: Dodecin binds oxidized flavins, whereas reduction of the bound flavin induces dissociation of the holoprotein into apododecin and free flavins. The stepwise reconstitution of dodecin on flavin-terminated ds-DNA monolayers showed that although electrochemical flavin reduction (i.e. electron transfer through DNA) was not possible, apododecin (gray circles) could be released by chemical reduction (see scheme).

### Electron Transfer

Y. Yu, B. Heidel, T. L. Parapugna,
S. Wenderhold-Reeb, B. Song,
H. Schönherr, M. Grininger,
G. Nöll* ———————— **4950 – 4953**

The Flavoprotein Dodecin as a Redox Probe for Electron Transfer through DNA

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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This article is accompanied by a cover picture (front or back cover, and inside or outside).

## Angewandte Corrigendum

The assignment of the formaldehyde protective group to W203 as given throughout the text and also in the Supporting Information is wrong, it rather should have been W105. Conclusions and discussion are not affected by this error, however, since both residues, W105 and W203, are located close to each other at the periphery of the molecule.

Reconstitution of the Catalytic Core of F-ATPase $(\alpha\beta)_3\gamma$ from *Escherichia coli* Using Chemically Synthesized Subunit γ

F. Wintermann,*
S. Engelbrecht* ———————— **1309–1313**

*Angew. Chem. Int. Ed.* **2013**, *52*

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