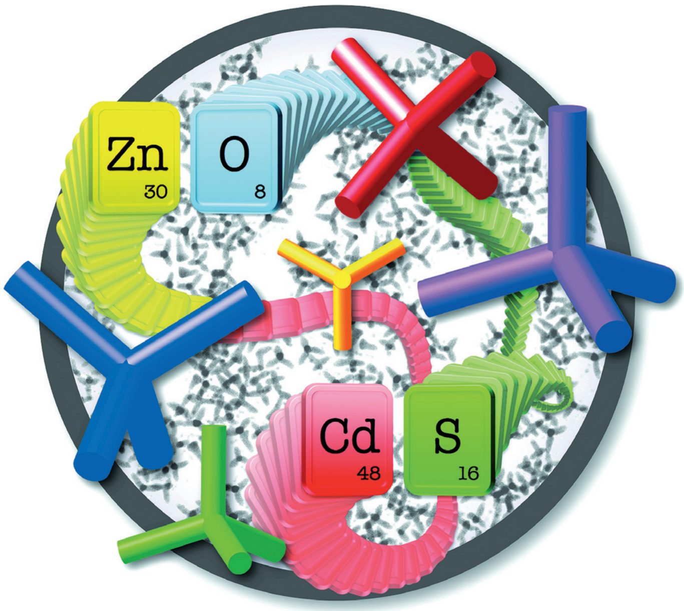
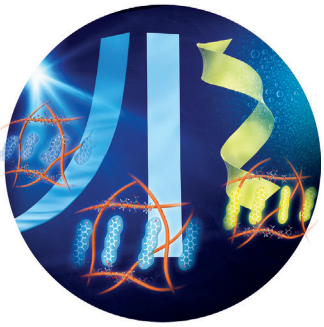
A total transformation process ...

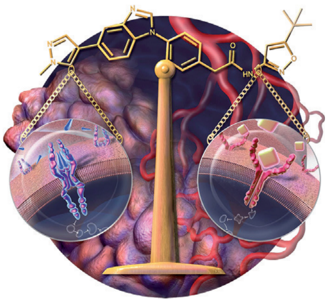


... fully decouples morphology and composition control in colloidal nanocrystal synthesis. In their Communication on page 8669 ff., R. E. Schaak et al. show how metal oxide nanocrystals can be transformed into chalcogenides of different metals using sequential anion and cation exchange reactions. The products retain the morphology of the starting material but contain entirely different constituent elements.

Smart Materials

A self-actuated composite material that responds to pH variations with a color change from colorless to yellow and a fluorescence shift from blue to yellow is described by P. Naumov and L. Zhang in their Communication on page 8642 ff.



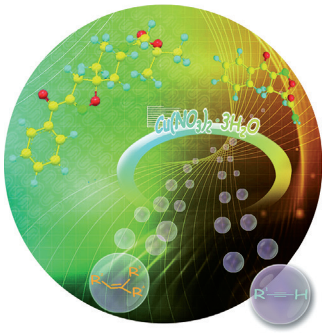


Polypharmacology

A dual RET/VEGFR2 inhibitor for the treatment of RET-driven malignancies was optimized through a medicinal chemistry/polypharmacology approach as described by H.-y. Li, M. Santoro, et al. in their Communication on page 8717 ff.

Cascade Reactions

An efficient copper nitrate mediated cascade reaction of simple alkynes and alkenes that leads to pharmacologically interesting polysubstituted Δ^2-isoxazolines is described by B. Xu and co-workers in their Communication on page 8795 ff.



How to contact us:

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Fax: (+49) 6201–606-331
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Service

Author Profile

“My not-so-secret passion is theater.
My favorite authors (fiction) are Jeanne Benameur, Guy de Maupassant, and Arto Paasilinna …”
This and more about Sylviane Sabo-Etienne can be found on page 8592.

News

L. Banci

M. A. Brimble

H. Lee

C. Nájera

R. Sessoli

Meeting Reviews

Thought-provoking for half a century: The famous Bürgenstock Conference recently celebrated its 50th anniversary, which was marked with outstanding science and vibrant discussions in a distinctively stimulating setting. In the Meeting Review, Christof Sparr summarizes the program of the 2015 conference.

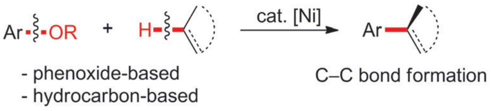
Obituaries

Gerhard Quinkert, emeritus professor at the University of Frankfurt, passed away on May 6, 2015. The chemistry community has lost a passionate teacher and a researcher with foresight, and independent, firm opinions who argued from early on that organic chemistry should open up to address questions in biology.

Books

Highlights

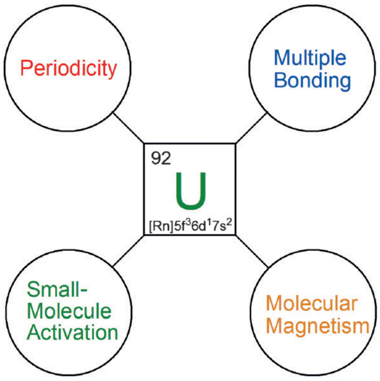
Cross-Coupling



Halides not required: Nickel-catalyzed C—O/C—H cross-couplings for the construction of C—C bonds have recently been disclosed. By carefully optimizing the nickel catalyst, new C—C bond-forming reactions were developed, and even quaternary stereogenic centers are now accessible in high yields from readily available phenoxide derivatives and hydrocarbons.

Reviews

Uranium Complexes



Rise like a phoenix? In the last several years, there has been a resurgence of non-aqueous uranium chemistry, in particular dealing with the development of new ligand classes and complexes with multiple bonding, single-molecule magnetism, and the activation of small molecules, such as N_2, CO_2, and alkanes. Owing to its unusual coordination properties, uranium is remarkably different from transition metals, but also from other actinides.

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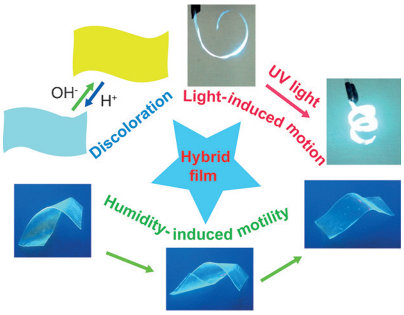
Smart Materials

L. Zhang, P. Naumov* ______ 8642 – 8647

Light- and Humidity-Induced Motion of an Acidochromic Film

Frontispiece

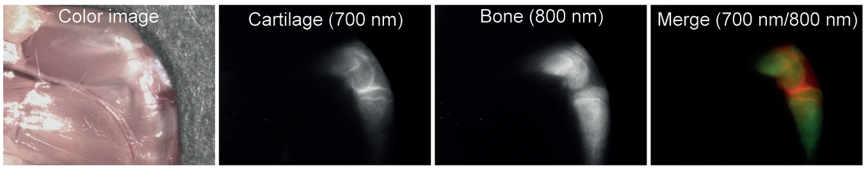


A composite self-actuated material is capable of a rapid response to pH variations with color changes from colorless to yellow and with a drastic shift in the fluorescence emission from blue to yellow. Furthermore, this smart acidochromic agarose-based film can harness the potentials of aerial-humidity gradients and light energy to convert them into mechanical work.

Imaging Agents

H. Hyun, E. A. Owens, H. Wada, A. Levitz, G. Park, M. H. Park, J. V. Frangioni, M. Henary,* H. S. Choi* ______ 8648 – 8652

Cartilage-Specific Near-Infrared Fluorophores for Biomedical Imaging

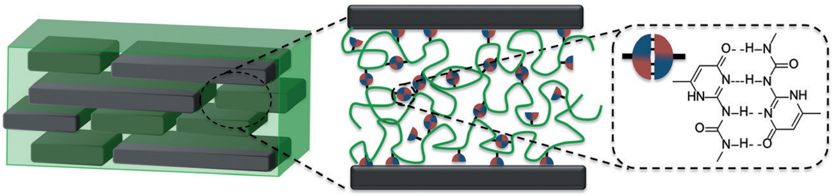


Seeing red: Near-infrared fluorophores specific for cartilage were synthesized and their performance tested in small and large animal models. These agents not only bind all types of cartilage in all species tested, but they can also be combined with other targeted near-infrared fluorophores, such as those specific to bone, to provide unprecedented biomedical optical imaging.

Bioinspired Nanocomposites

B. Zhu, N. Jasinski, A. Benitez, M. Noack, D. Park, A. S. Goldmann, C. Barner-Kowollik, A. Walther* ______ 8653 – 8657

Hierarchical Nacre Mimetics with Synergistic Mechanical Properties by Control of Molecular Interactions in Self-Healing Polymers

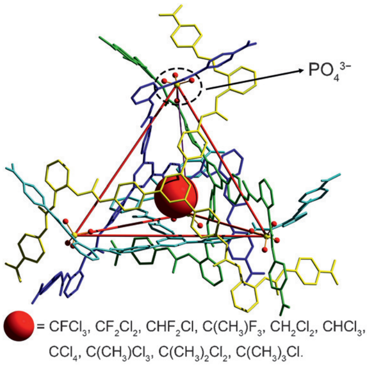


Molecular mortar: Dynamic, self-healing polymers with a low glass-transition temperature and bonded by fourfold ureidopyrimidinone hydrogen-bonding motifs were assembled with high-aspect-ratio synthetic nanoclays. This gives rise to transparent nacre mimetics with superbly defined mesostructure, and enable synergistic combinations of stiffness and toughness at intermediate density of supramolecular groups.

Anion Coordination

D. Yang, J. Zhao, Y. Zhao, Y. Lei, L. Cao, X.-J. Yang, M. Davi, N. d. S. Amadeu, C. Janiak, Z. Zhang, Y.-Y. Wang, B. Wu* ______ 8658 – 8661

Encapsulation of Halocarbons in a Tetrahedral Anion Cage

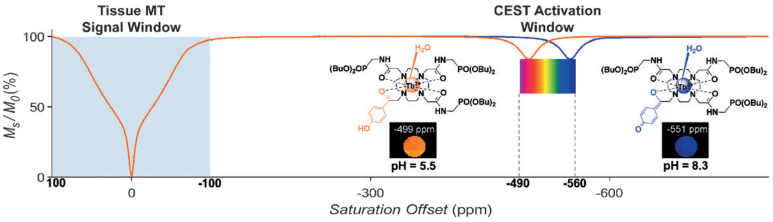


Caged supramolecular systems are promising hosts for guest inclusion, separation, and stabilization. The first examples of the inclusion chemistry of anion coordination in a tetrahedral cage are reported. A wide range of the harmful fluoro- und chlorocarbon guests were investigated (see picture).

Imaging Agents

X. Wang, Y. Wu, T. C. Soesbe, J. Yu,
P. Zhao, G. E. Kiefer,
A. D. Sherry* ______ 8662 – 8664

A pH-Responsive MRI Agent that Can Be Activated Beyond the Tissue Magnetization Transfer Window

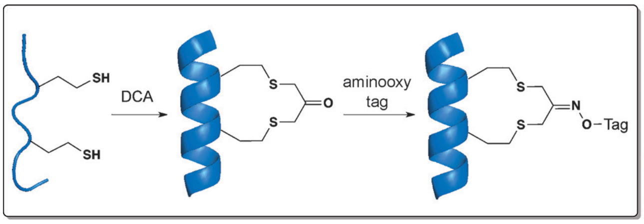


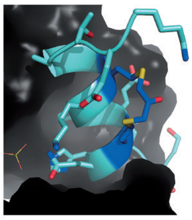
Imaging beyond the MT effect: A pH-responsive MRI contrast agent displays a water exchange peak near −550 ppm, well outside the magnetization transfer (MT) window. Additionally, the chemical shift of 56 ppm in this CEST peak is quite sensitive to changes in pH. These features enable direct imaging of pH in vivo with no masking effect from the inherent tissue MT signal.

Macrocyclization

N. Assem, D. J. Ferreira, D. W. Wolan,
P. E. Dawson* ______ 8665 – 8668

Acetone-Linked Peptides: A Convergent Approach for Peptide Macrocyclization and Labeling





Macrocyclizations are broadly applied for overcoming the intrinsically disordered nature of linear peptides. Dichloroacetone (DCA) enhances helical secondary structures when introduced between peptide nucleophiles, such as thiols, to yield an acetone-linked bridge. The ketone moiety embedded in the linker can be modified with diverse molecular tags by oxime ligation.

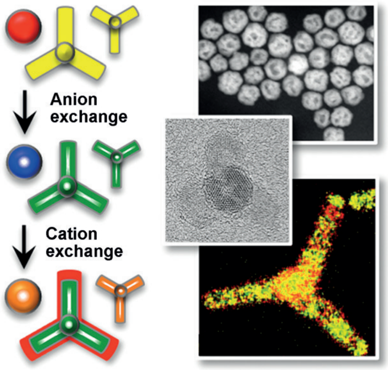
Nanoparticle Morphology

J. M. Hodges, K. Kletetschka, J. L. Fenton,
C. G. Read, R. E. Schaak* ___ 8669 – 8672

Sequential Anion and Cation Exchange Reactions for Complete Material Transformations of Nanoparticles with Morphological Retention

Front Cover

Complete transformation: Metal oxide nanocrystals can be transformed into chalcogenides of different metals using sequential anion and cation exchange reactions. The products retain the morphology of the starting material, but contain entirely different elemental components. Morphology and composition control in colloidal nanocrystal synthesis are thus fully decoupled.

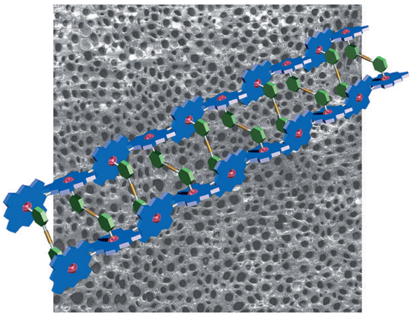


Polymeric Materials

K. Kose, J. Motoyanagi, T. Kusukawa,
A. Osuka,* A. Tsuda* ______ 8673 – 8678

Formation of Discrete Ladders and a Macroporous Xerogel Film by the Zipperlike Dimerization of Meso–Meso-Linked Zinc(II) Porphyrin Arrays with Di(pyrid-3-yl)acetylene

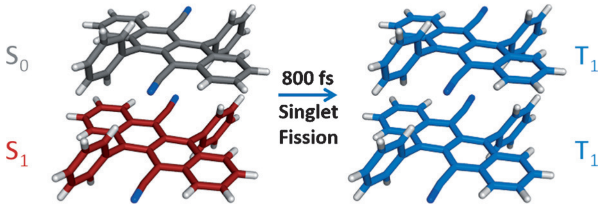
Porphyrin polymers linked in ladders: Meso–meso-linked zinc(II) porphyrin arrays underwent zipper-like dimerization upon complexation with di(pyrid-3-yl)-acetylene in chloroform to form discrete double-stranded porphyrin ladders (see picture). Similar dimerization of the corresponding poly(porphyrinylene) gave a thermoresponsive gel. In this case, the strong three-dimensional network enabled the formation of a macroporous xerogel film.



Singlet Fission

E. A. Margulies, Y.-L. Wu, P. Gawel,
S. A. Miller, L. E. Shoer, R. D. Schaller,
F. Diederich,*
M. R. Wasielewski* ______ **8679 – 8683**

Sub-Picosecond Singlet Exciton Fission in Cyano-Substituted Diaryltetracenes



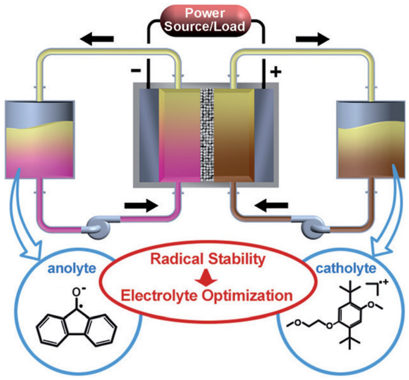
Divide and conquer: Transient absorption measurements reveal sub-picosecond singlet exciton fission in thin films of a cyano-substituted diaryltetracene. A triplet yield analysis of the transient absorption data set indicates the formation of 1.6 ± 0.3 triplet excitons per singlet exciton, as a result of rapid and efficient singlet fission.

Electrochemistry

X. Wei,* W. Xu, J. Huang, L. Zhang,
E. Walter, C. Lawrence , M. Vijayakumar,
W. A. Henderson, T. Liu, L. Cosimbescu,
B. Li, V. Sprenkle, W. Wang* **8684 – 8687**

Radical Compatibility with Nonaqueous Electrolytes and Its Impact on an All-Organic Redox Flow Battery

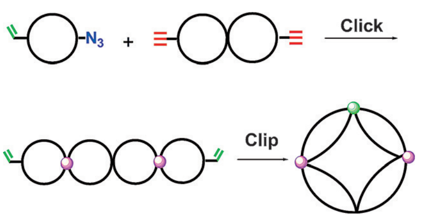
Picky radical redox species: The choice of both solvent and salt used in the supporting electrolyte is found to greatly affect the cycling stability of nonaqueous all-organic flow chemistry because of substantial variations in the chemical stability of the charged radical redox species. This mechanistic understanding articulates the significance of electrolyte optimization for achieving performance improvements for nonaqueous redox flow batteries.



Polymer Folding

H. Heguri, T. Yamamoto,
Y. Tezuka* ______ **8688 – 8692**

Folding Construction of a Pentacyclic Quadruply *fused* Polymer Topology with Tailored *kyklo*-Telechelic Precursors

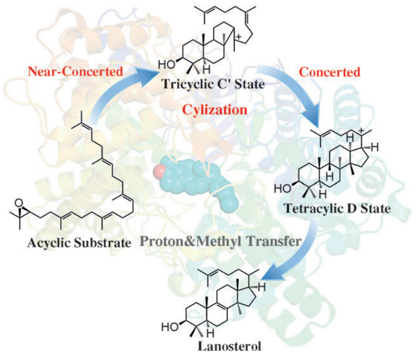


***Shippo* rings**: A pentacyclic quadruply *fused* polymer has been constructed for the first time by programmed polymer folding. Click and clip (olefin metathesis) reactions were used in conjunction with electrostatic self-assembly and covalent fixation.

Biosynthesis

N. Chen, S. Wang, L. Smentek,
B. A. Hess, Jr.,* R. Wu* ___ **8693 – 8696**

Biosynthetic Mechanism of Lanosterol: Cyclization

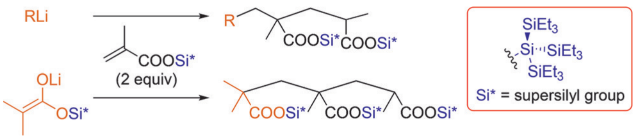


Biocyclization: Lanosterol is the precursor of all animal sterols and its biocyclization mechanism has been debated over half a century. Herein it has been elucidated by state-of-the-art simulations. The cyclization involves two concerted (or near-concerted) reactions through two metastable states and one stable intermediate under oxidosqualane cyclase enzyme catalysis.

Synthetic Methods

A. Izumiseki,*
H. Yamamoto* ________ 8697 – 8699

Selective Michael Reaction Controlled by Supersilyl Protecting Group



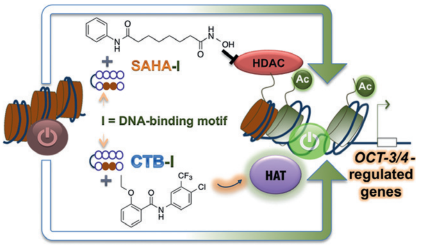
Bulky protecting group: A selective Michael reaction of organolithium reagents to supersilyl methacrylate is reported. The method can control whether a single or double Michael addition occurs. The successful termination of the process using the supersilyl protecting group allows for a controlled, chemoselective, and diastereoselective Michael reaction.

Epigenetics

L. Han, G. N. Pandian, A. Chandran,
S. Sato, J. Taniguchi, G. Kashiwazaki,
Y. Sawatani, K. Hashiya, T. Bando, Y. Xu,
X. Qian, H. Sugiyama* ____ 8700 – 8703

A Synthetic DNA-Binding Domain Guides Distinct Chromatin-Modifying Small Molecules to Activate an Identical Gene Network

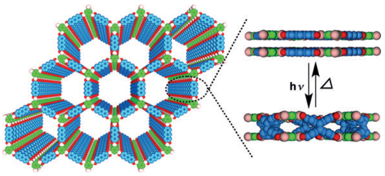
Same difference: Conjugation of a selective pyrrole–imidazole polyamide (PIP) DNA-binding domain "I" to the histone acetyltransferase (HAT) activator CTB yielded an epigenetic switch with identical bioactivity to that of I conjugated to the histone deacetylase (HDAC) inhibitor SAHA. Unconjugated CTB and SAHA, on the other hand, show distinct patterns of biological activity.



Smart Materials

N. Huang, X. Ding, J. Kim, H. Ihee,
D. Jiang* ________ 8704 – 8707

A Photoresponsive Smart Covalent Organic Framework



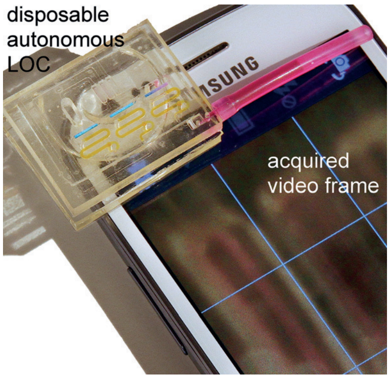
Smart sheets: A "smart" covalent organic framework that is responsive to external stimuli is described. The anthracene-based framework is reversibly switchable between two-dimension sheets and concavo-convex skeletons upon irradiation and thermal stimuli. The structural transformation is accompanied by profound changes in porosity and π-electronic functions, demonstrating the usefulness of organic frameworks in exploring smart materials.

Lab-on-a-Chip

G. Comina, A. Suska,
D. Filippini* ________ 8708 – 8712

Autonomous Chemical Sensing Interface for Universal Cell Phone Readout

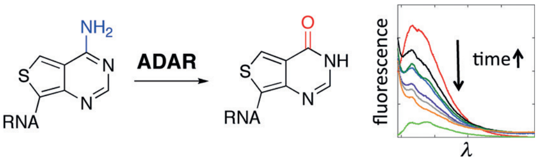
Smart solution: An autonomous disposable device for quantitative chemical glucose sensing on cell phones was developed. It can operate without permanent accessories, integrates all necessary reagents, calibration and actuation elements, and entails a single design conceived to universally couple to any cell phone.



Fluorescent Nucleosides

R. A. Mizrahi, D. Shin, R. W. Sinkeldam, K. J. Phelps, A. Fin, D. J. Tantillo, Y. Tor,* P. A. Beal* ________ **8713 – 8716**

A Fluorescent Adenosine Analogue as a Substrate for an A-to-I RNA Editing Enzyme



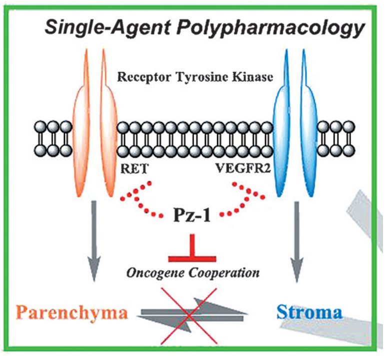
The reactivity of ADAR2 enzyme with RNA containing the emissive adenosine analogue thieno[3,4-d]-6-aminopyrimidine (thA) was investigated. thA is recognized by AMV reverse transcriptase as A, and is deaminated rapidly by human ADAR2 to give thI. The ADAR reaction progress can be monitored by following the deamination-induced change in fluorescence of the thA-modified RNA.

Polypharmacology

B. Frett, F. Carlomagno, M. L. Moccia, A. Brescia, G. Federico, V. De Falco, B. Admire, Z. Chen, W. Qi, M. Santoro,* H.-y. Li* ________ **8717 – 8721**

Fragment-Based Discovery of a Dual pan-RET/VEGFR2 Kinase Inhibitor Optimized for Single-Agent Polypharmacology

Inside Back Cover

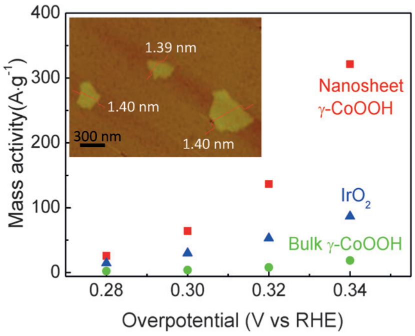


Dual inhibition: A kinase-directed fragment-based screen identified a novel active pharmacophore for the RET tyrosine kinase (RET = rearranged during transfection). In a medicinal chemistry/polypharmacology approach, Pz-1 was found to be a dual pan-RET/VEGFR2 inhibitor and able to simultaneously treat the parenchyma (RET) and stroma (VEGFR2) of RET-driven tumors in cell and xenograft models.

Electrocatalysis

J. H. Huang, J. T. Chen, T. Yao, J. F. He, S. Jiang, Z. H. Sun, Q. H. Liu,* W. R. Cheng, F. C. Hu, Y. Jiang, Z. Y. Pan,* S. Q. Wei* ________ **8722 – 8727**

CoOOH Nanosheets with High Mass Activity for Water Oxidation

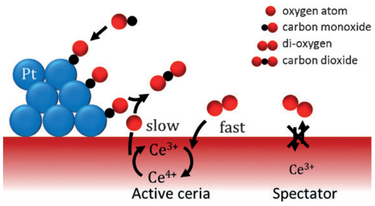


Half-metallic γ-CoOOH nanosheets were synthesized showing high electrical conductivity and low activation energy in electrocatalytic water oxidation. Their mass activity in water oxidation is 20 times higher than that of γ-CoOOH bulk and 2.4 times higher than that of the state-of-the-art IrO_2 electrocatalyst.

CO Oxidation

R. Kopelent, J. A. van Bokhoven, J. Szlachetko, J. Edebeli, C. Paun, M. Nachtegaal, O. V. Safonova* ________ **8728 – 8731**

Catalytically Active and Spectator Ce^{3+} in Ceria-Supported Metal Catalysts

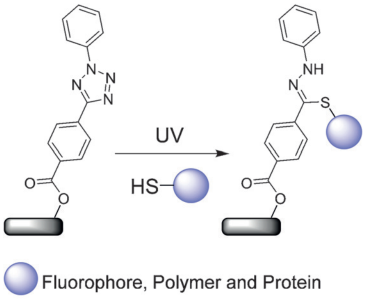


Short-lived Ce^{3+} is the active and kinetically relevant intermediate during catalytic CO oxidation on a ceria-supported metal catalyst, whereas long-lived Ce^{3+} species are inactive spectators. This was shown by in situ resonant X-ray emission spectroscopy and quantitative correlation between the initial rate of Ce^{3+} formation under transient conditions and the overall CO oxidation rate.

Photochemistry

W. Feng, L. Li, C. Yang, A. Welle, O. Trapp, P. A. Levkin* ________ 8732 – 8735

UV-Induced Tetrazole-Thiol Reaction for Polymer Conjugation and Surface Functionalization

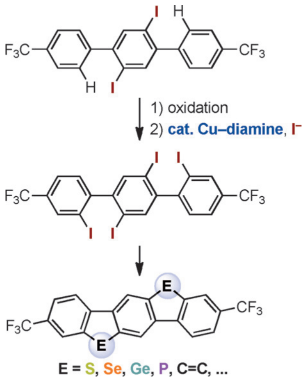


Without catalyst: A UV-induced tetrazole-thiol reaction is reported. This reaction proceeds rapidly at ambient temperature under UV light in different solvents including water with high yield and without a catalyst. The reaction has been demonstrated for small-molecule and polymer–polymer conjugation, as well as for rapid site-selective surface functionalization and patterning.

Iodination Reaction

B. Wu, N. Yoshikai* ________ 8736 – 8739

Conversion of 2-Iodobiaryls into 2,2′-Diiodobiaryls via Oxidation-Iodination Sequences: A Versatile Route to Ladder-Type Heterofluorenes

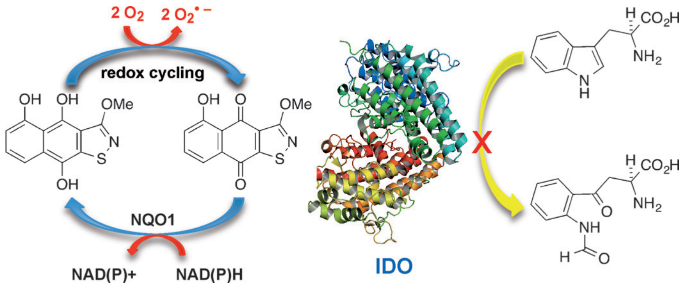


Biaryl iodination: 2-Iodobiaryls can be readily converted to 2,2′-diiodobiaryls through an initial oxidation to form cyclic diaryliodonium salts, followed by a copper/diamine-catalyzed iodinative ring-opening under mild conditions. The versatility of this two-step protocol is demonstrated by the preparation of hitherto unexplored tetraiodoteraryls and their conversion into ladder-type π-conjugated systems.

Quinones

C. E. Blunt, C. Torcuk, Y. Liu, W. Lewis, D. Siegel, D. Ross, C. J. Moody* ________ 8740 – 8745

Synthesis and Intracellular Redox Cycling of Natural Quinones and Their Analogues and Identification of Indoleamine-2,3-dioxygenase (IDO) as Potential Target for Anticancer Activity

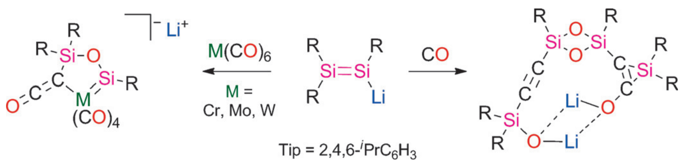


Aulosirazole, a structurally unique natural product, was synthesized for the first time and shown to target the immunoregulatory enzyme indoleamine-2,3-dioxygenase (IDO).

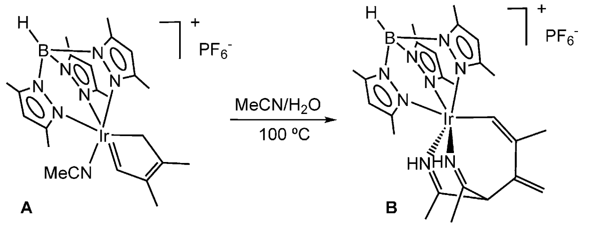
CO Reduction

M. Majumdar, I. Omlor, C. B. Yildiz, A. Azizoglu, V. Huch, D. Scheschkewitz* ________ 8746 – 8750

Reductive Cleavage of Carbon Monoxide by a Disilenide

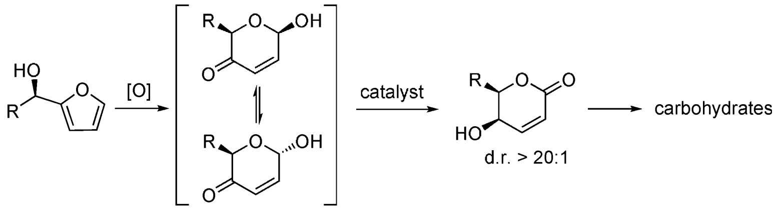


Hidden powers: Lithium disilenide reductively cleaves the strongest bond in chemistry, the C≡O bond of carbon monoxide, at room temperature. A key step in the Fischer–Tropsch process is reiterated by an anionic molecular main-group system with Si=Si bonds. The mechanism is elucidated by DFT calculations and model reactions with Group 6 hexacarbonyls.



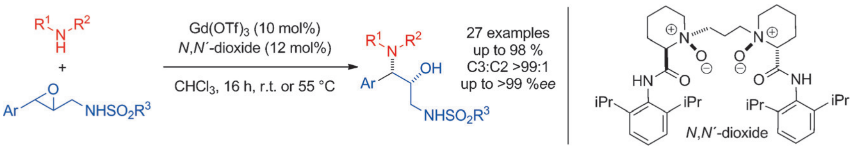
A barrel of iridium: A cationic iridacyclopentenylidene (**A**) was transformed to an iridabicyclic complex (**B**) under the catalytic action of water. The three-component reaction involved the C–C coupling of **A** with two coordinated MeCN molecules to the barrelene-like structure **B**.

Alkylidenes



Sweet isomerization: The highly stereoselective dynamic kinetic isomerization of hemiacetal intermediates through internal transfer hydrogenation (see scheme) provided straightforward access to a series of naturally occurring carbohydrates from simple furan derivatives. The synthetic method is amenable to the preparation of either enantiomer of a sugar target.

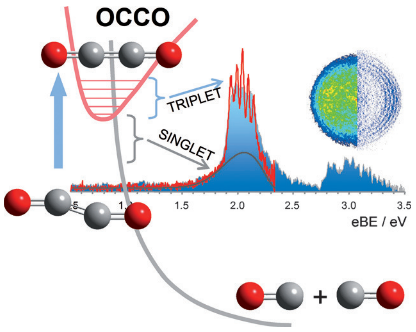
Carbohydrate Synthesis



A sulfonamide-directed highly enantioselective aminolysis of 2,3-epoxy amines derivatives with Gd-*N*,*N*′-dioxide as catalyst was developed. The reaction provides various tosyl- and (2-trimethylsilyl)ethanesulfonyl-protected 3-amino-3-phenylpropan-2-olamines with complete regiocontrol.

Asymmetric Catalysis

For over a century, the mysterious compound OCCO has been pursued by chemists, but all past studies have failed to provide conclusive experimental evidence for its existence. The quasi-bound triplet and dissociative singlet states of OCCO were now observed and spectroscopically characterized for the first time using anion photoelectron spectroscopy (eBE = electron binding energy).



Diradicals

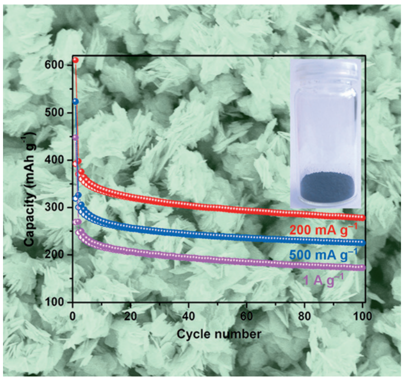
Inside Cover

Battery Materials

Y. Xu, M. Zhou, X. Wang, C. L. Wang, L. Y. Liang, F. Grote, M. Wu, Y. Mi, Y. Lei* ———— **8768 – 8771**

Enhancement of Sodium Ion Battery Performance Enabled by Oxygen Vacancies

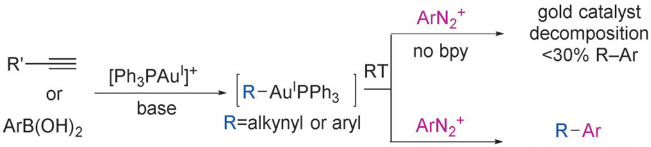
The benefits of oxygen vacancies on sodium ion battery performance were demonstrated by using ultrathin Al_2O_3-coated MoO_{3-x} nanosheets as anodes. Owing to the increased electric conductivity and sodium ion diffusion coefficient as well as the reduced solid–electrolyte interphase at deep-discharge conditions, the anodes exhibited high reversible capacity and great rate capability over long-term cycling.



Redox Gold Catalysis

R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen,* X. Shi* ———— **8772 – 8776**

Ligand-Assisted Gold-Catalyzed Cross-Coupling with Aryldiazonium Salts: Redox Gold Catalysis without an External Oxidant



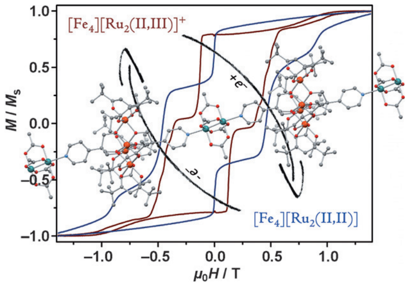
I to III: Gold-catalyzed C(sp)–C(sp^2) and C(sp^2)–C(sp^2) cross-coupling reactions are accomplished with aryldiazonium salts as the coupling partner. With the assistance of the bpy ligand, gold(I) species were oxidized to gold(III) by diazonium without any external oxidants. Monitoring the reaction with NMR and ESI-MS provided strong evidence for the nitrogen extrusion followed by Au^{III} reductive elimination as the key step.

Single-Molecule Magnets

A. Nava, L. Rigamonti, E. Zangrando, R. Sessoli, W. Wernsdorfer, A. Cornia* ———— **8777 – 8782**

Redox-Controlled Exchange Bias in a Supramolecular Chain of Fe_4 Single-Molecule Magnets

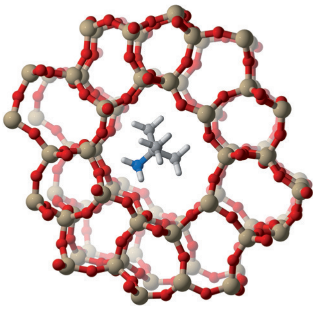
One electron makes the difference: Functionalized single-molecule magnets (SMMs) can be lined up into infinite chains by diruthenium(II,II) or (II,III) paddlewheel complexes. Whereas the reduced dimer ($s=1$) allows no magnetic communication between adjacent SMMs, the mixed-valent dimer ($s=3/2$) affords weak intrachain coupling (see hysteresis loops).



Heterogeneous Catalysis

W. Dai, C. Wang, X. Yi, A. Zheng, L. Li,* G. Wu, N. Guan, Z. Xie,* M. Dyballa, M. Hunger* ———— **8783 – 8786**

Identification of *tert*-Butyl Cations in Zeolite H-ZSM-5: Evidence from NMR Spectroscopy and DFT Calculations

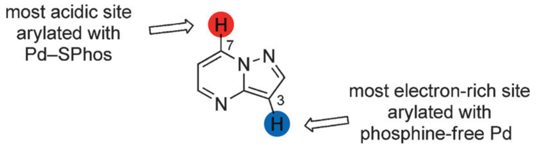


Captured and characterized: The intermediacy of *tert*-butyl cations in the acid-catalyzed conversion of isobutene on zeolite H-ZSM-5 was confirmed by their capture with ammonia. The resulting stable surface compounds were characterized by $^1H/^{13}C$ MAS NMR spectroscopy and analyzed by density functional theory (DFT) calculations.

C–H Activation

R. B. Bedford,* S. J. Durrant, M. Montgomery ———— **8787 – 8790**

Catalyst-Switchable Regiocontrol in the Direct Arylation of Remote C–H Groups in Pyrazolo[1,5-*a*]pyrimidines

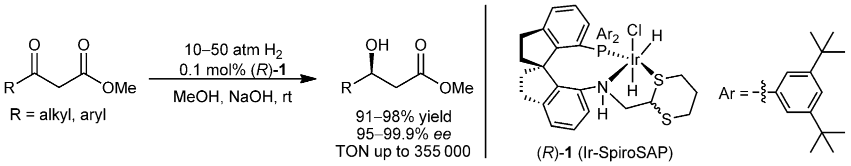


Remote control: Switching the regioselectivity of C–H arylation between remote sites on pyrazolo[1,5-*a*]pyrimidine can be achieved by tuning the structure of the catalyst. The control appears to be due to a change in mechanistic pathways between electrophilic palladation and base-assisted deprotonation.

Asymmetric Catalysis

D.-H. Bao, H.-L. Wu, C.-L. Liu, J.-H. Xie,* Q.-L. Zhou* ———— **8791 – 8794**

Development of Chiral Spiro P-N-S Ligands for Iridium-Catalyzed Asymmetric Hydrogenation of β-Alkyl-β-Ketoesters

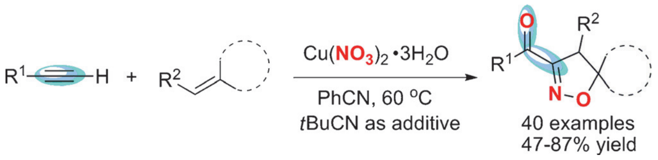


Bulkyness is the key: New chiral tridentate spiro P-N-S ligands (SpiroSAP) bearing a conformationally constrained 1,3-dithiane moiety were developed. Their iridium catalysts showed excellent enantioselectivities and activity (TON up to 355 000) for asymmetric hydrogenation of β-alkyl-β-ketoesters.

Cascade Reactions

M. Gao, Y. Li, Y. Gan, B. Xu* **8795 – 8799**

Copper Nitrate Mediated Regioselective [2+2+1] Cyclization of Alkynes with Alkenes: A Cascade Approach to Δ^2-Isoxazolines



From simple to complex: An efficient regioselective synthesis of valuable polysubstituted Δ^2-isoxazolines is based on a copper-mediated transformation of simple alkynes and alkenes. The overall process involves the formation of four chemical bonds, and simple and inexpensive copper nitrate trihydrate is employed as a novel precursor to nitrile oxides.

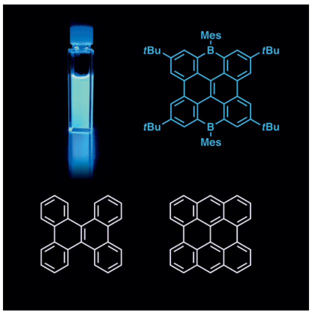
Back Cover

Polycyclic Aromatic Hydrocarbons

V. M. Hertz, M. Bolte, H.-W. Lerner, M. Wagner* ———— **8800 – 8804**

Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores

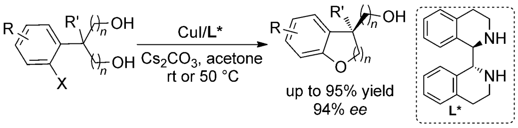
Desirable deficiency: A modular synthesis approach provides access to extended polycyclic aromatic hydrocarbons containing electron-deficient boron atoms (see picture). The compounds obtained are air- and water-stable, bright blue luminophores and show reversible redox behavior.



Asymmetric Catalysis

W. Yang, Y. Liu, S. Zhang,
Q. Cai* 8805–8808

Copper-Catalyzed Intramolecular Desymmetric Aryl C–O Coupling for the Enantioselective Construction of Chiral Dihydrobenzofurans and Dihydrobenzopyrans

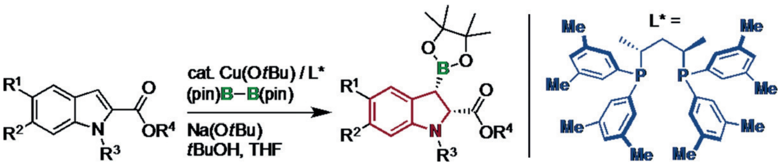


O-Heterocyclic structures such as chiral dihydrobenzofurans can be formed enantioselectively through a copper-catalyzed desymmetrization strategy with a chiral cyclic 1,2-diamine ligand. A broad range of substrates is compatible with this Cu^{I}-diamine catalytic system and afford the desired coupling products with chiral tertiary or quaternary carbon centers in high yields and good to excellent enantioselectivities under mild conditions.

Dearomatization

K. Kubota, K. Hayama, H. Iwamoto,
H. Ito* 8809–8813

Enantioselective Borylative Dearomatization of Indoles through Copper(I) Catalysis

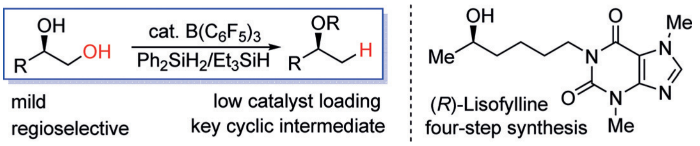


Chiral 3-borylindoline derivatives were obtained with excellent regio-, diastereo-, and enantioselectivities through the enantioselective borylative dearomatization of methyl indole-2-carboxylate using a copper(I) catalyst and a diboron reagent. The products of this reaction could be transformed to the corresponding chiral 1,2-aminoalcohol with high stereospecificity. pin = pinacolato.

Selective Reduction

N. Drosos, B. Morandi* 8814–8818

Boron-Catalyzed Regioselective Deoxygenation of Terminal 1,2-Diols to 2-Alkanols Enabled by the Strategic Formation of a Cyclic Siloxane Intermediate

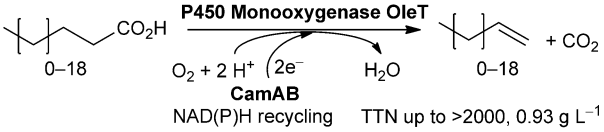


Pick the right one! A highly active and selective boron-based catalytic system enables the selective deoxygenation of terminal 1,2-diols at the primary position via the transient formation of a cyclic siloxane. The utility of this method for the preparation of synthetically challenging chiral 2-alkanols was illustrated by a short synthesis of the anti-inflammatory drug (*R*)-lisofylline.

Biocatalysis

A. Dennig, M. Kuhn, S. Tassoti,
A. Thiessenhusen, S. Gilch, T. Bülter,
T. Haas, M. Hall, K. Faber* 8819–8822

Oxidative Decarboxylation of Short-Chain Fatty Acids to 1-Alkenes

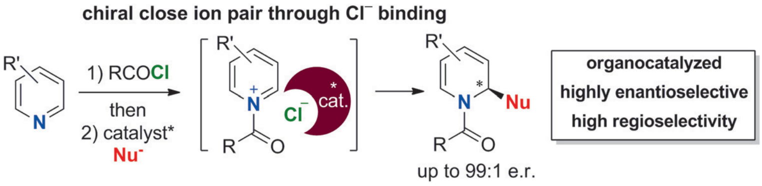


Biocatalysis: The oxidative decarboxylation of fatty acids using the P450 monooxygenase OleT in combination with the CamAB electron-transfer system and NAD(P)H recycling gave terminal alkenes (e.g., propene, 1-butene) with excellent conversion. The reaction may become applicable to the transformation of biomass into chemical compounds for organic synthesis.

Asymmetric Catalysis

O. García Mancheño,* S. Asmus,
M. Zurro, T. Fischer ______ **8823 – 8827**

Highly Enantioselective Nucleophilic Dearomatization of Pyridines by Anion-Binding Catalysis

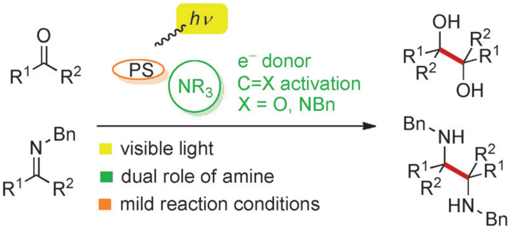


Direct metal-free access: For the asymmetric dearomatization of pyridines, only efficient metal-catalyzed reactions have been available to date. The first organocatalytic approach with a triazole-based H-donor catalyst is now presented. The catalyst induces a high enantioselectivity by forming a chiral ion-pair complex with the *N*-acyl pyridinium intermediate (see picture).

Photoredox Catalysis

M. Nakajima, E. Fava, S. Loescher,
Z. Jiang, M. Rueping* ______ **8828 – 8832**

Photoredox-Catalyzed Reductive Coupling of Aldehydes, Ketones, and Imines with Visible Light



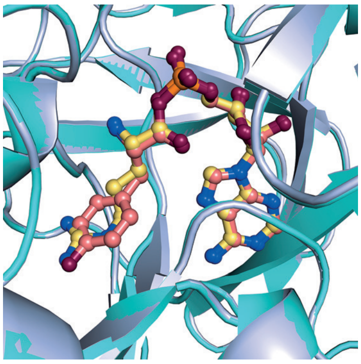
Overcoming the redox barrier with the amine playing a dual role: The photoredox-catalyzed reductive coupling of aldehydes, ketones, and imines was achieved with low catalyst loading, under mild reaction conditions, and wide functional-group tolerance (see scheme; PS = photosensitizer).

Substrate Recognition

H. Kaljunen, S. H. H. Schiefelbein,
D. Stummer, S. Kozak, R. Meijers,
G. Christiansen,*
A. Rentmeister* ______ **8833 – 8836**

Structural Elucidation of the Bispecificity of A Domains as a Basis for Activating Non-natural Amino Acids

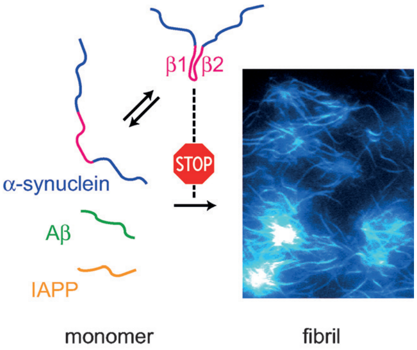
In good shape: The structural basis for the bispecificity of an adenylation domain for the two contrasting substrates arginine and tyrosine was revealed by crystal structure analysis. It was found that in the active site, the arginine side chain takes up a conformation that mimics the shape of the tyrosine ring. Three residues in the active site were identified to be critical for substrate recognition and were substituted to switch the specificity.



Protein Aggregation

H. Shaykhalishahi, A. Gauhar,
M. M. Wördehoff, C. S. R. Grüning,
A. N. Klein, O. Bannach, M. Stoldt,
D. Willbold, T. Härd,
W. Hoyer* ______ **8837 – 8840**

Contact between the β1 and β2 Segments of α-Synuclein that Inhibits Amyloid Formation



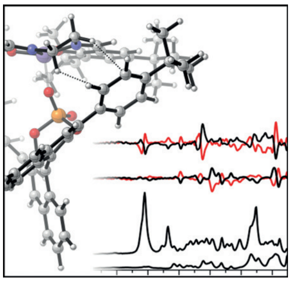
A stable intramolecular contact between the β1 and β2 sequence segments of the intrinsically disordered protein α-synuclein is established by disulfide engineering. The resulting protein does not form oligomers or amyloid fibrils, and inhibits aggregation and toxicity of the amyloidogenic proteins α-synuclein, amyloid-β, and islet amyloid polypeptide. Tertiary interactions in the β1–β2 region of α-synuclein interfere with amyloid formation.

Induced Chirality

C. Merten,* C. H. Pollok, S. Liao,
B. List* ________ 8841 – 8845

Stereochemical Communication within a Chiral Ion Pair Catalyst

Chiral up? VCD spectroscopy was used to study the transmission of stereochemical information in a chiral ion pair based catalyst. Spectral features indicative of chirality transfer from the chiral anion to the achiral cation can be correlated with the enantioselectivity of the catalyst.



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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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

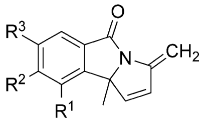
Chemoselective Benzylic C–H Activations for the Preparation of Condensed N-Heterocycles

H. Ren, P. Knochel* ________ 3462–3465

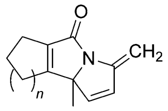
Angew. Chem. Int. Ed. **2006**, *45*

DOI: 10.1002/anie.200600111

In Scheme 4 of this Communication, the chemical structures of compounds **14a–c** and **16a–c** were drawn incorrectly. The correct structures are shown below.



14a: $R^1 = R^2 = R^3 = H$; 75 %
14b: $R^1 = R^2 = H$; $R^3 = OMe$; 80 %
14c: $R^1 = R^2 = R^3 = OMe$; 81 %



16a: $n = 1$; 80 %
16b: $n = 2$; 85 %
16c: $n = 3$; 74 %

Angewandte Corrigendum

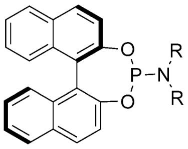
Palladium-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Michael Acceptors: Construction of Vicinal Quaternary Stereocenters

A. Khan, L. Yang, J. Xu, L. Y. Jin,
Y. J. Zhang* ________ 11257–11260

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201407013

In Table 1 of this Communication, the ligand **L1–L7** was inadvertently displayed as *S* enantiomer whereas the *R*-configured ligand (shown below) was used throughout. Therefore, the proposed stereochemical outcome (Figure 2, and the second sentence in right column in the page 11259) is incorrect. The absolute configuration of C4 of the cyclized products **3** and **5** should be opposite to that of the cycloaddition products from vinylethylene carbonates with formaldehyde in previous work by the authors (cited as Ref. [7]).



L1–L7

The authors sincerely apologize for these mistakes which do not affect any conclusions of this Communication.