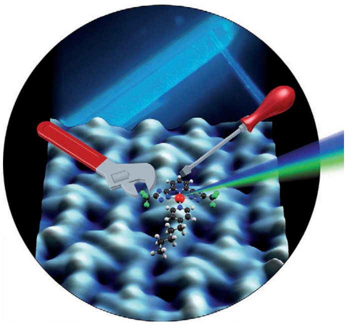
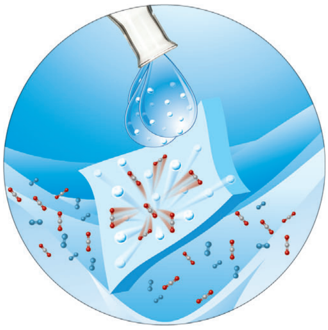
Sulfur monoxide …

… bears similarities to molecular oxygen, but unlike O_2, SO is unstable on Earth and only found in outer space. In their Communication on page 809 ff., D. W. Stephan and co-workers show that P/B frustrated Lewis pairs react with an *N*-sulfinylamine to form PNSOB linkages. These species can be regarded as phosphinimine–borane-stabilized sulfur monoxide complexes, and they act as sources of SO, effecting the oxidation of PPh_3 and delivering SO to various acceptors.

Scanning Tunneling Spectroscopy

D. Wegner, C. A. Strassert et al. describe in their Communication on page 786 ff. how scanning tunneling microscopy and spectroscopy can be used to visualize and measure the frontier orbitals of tridentate Pt^{II} complexes.



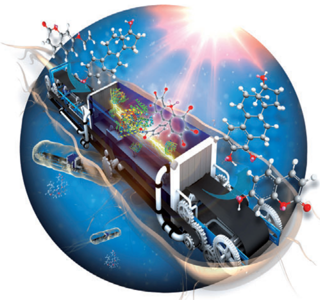


Porous Liquids

In their Communication on page 932 ff., S. Dai and co-workers show that porous liquids derived from the surface functionalization of hollow silica spheres have great potential in gas separation.

Biocatalysis

A platform for cofactor-free P450 biocatalysis is described by C.-H. Yun, K. J. Jeong, C. B. Park et al. in their Communication on page 969 ff. Instead of expensive cofactors, the use of a photosensitizer and visible light leads to a cost-effective process for P450-catalyzed reactions.



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Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

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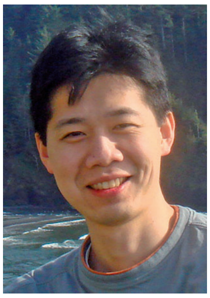


"In a spare hour, I like to read the news. My favorite quote is 'Ever tried. Ever failed. No matter. Try again. Fail again. Fail better.' (Samuel Beckett) …" This and more about Shih-Yuan Liu can be found on page 726.

News

S. S. Stahl

D. Enders

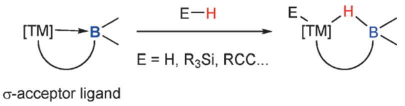
B. M. Stoltz

S. Yamaguchi

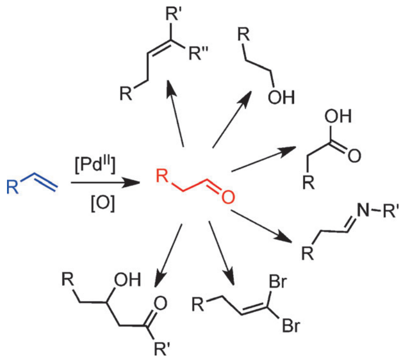
Books

Highlights

The presence of a Lewis acid, typically a borane, in the coordination sphere of transition metals (Ni, Fe, Pt) offers a new way to activate H_2 and strong H–E (E = Si, C) bonds.

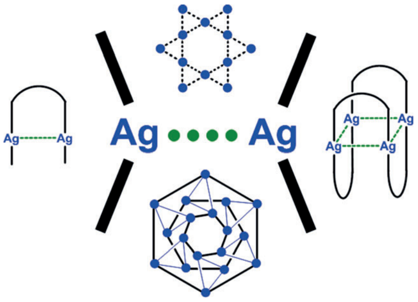


Minireviews



Out of wack: The Wacker–Tsuji reaction provides reliable access to methyl ketones from terminal alkenes under mild reaction conditions. Methods leading to a switch in the selectively of the reaction to provide the aldehyde product are desirable. Recent developments and mechanistic insights which offer promise in achieving the goal of a general method for anti-Markovnikov-selective olefin oxidation are discussed.

Reviews



Silver likes silver: Extensive evidence has accumulated in recent years that significant bonding interactions occur between seemingly closed-shell silver(I) centers of silver compounds. This argentophilic bonding appears to determine many structural details and important physical properties of silver(I) compounds in much the same way as aurophilic bonding is ubiquitously "at work" in gold chemistry.

For the USA and Canada:
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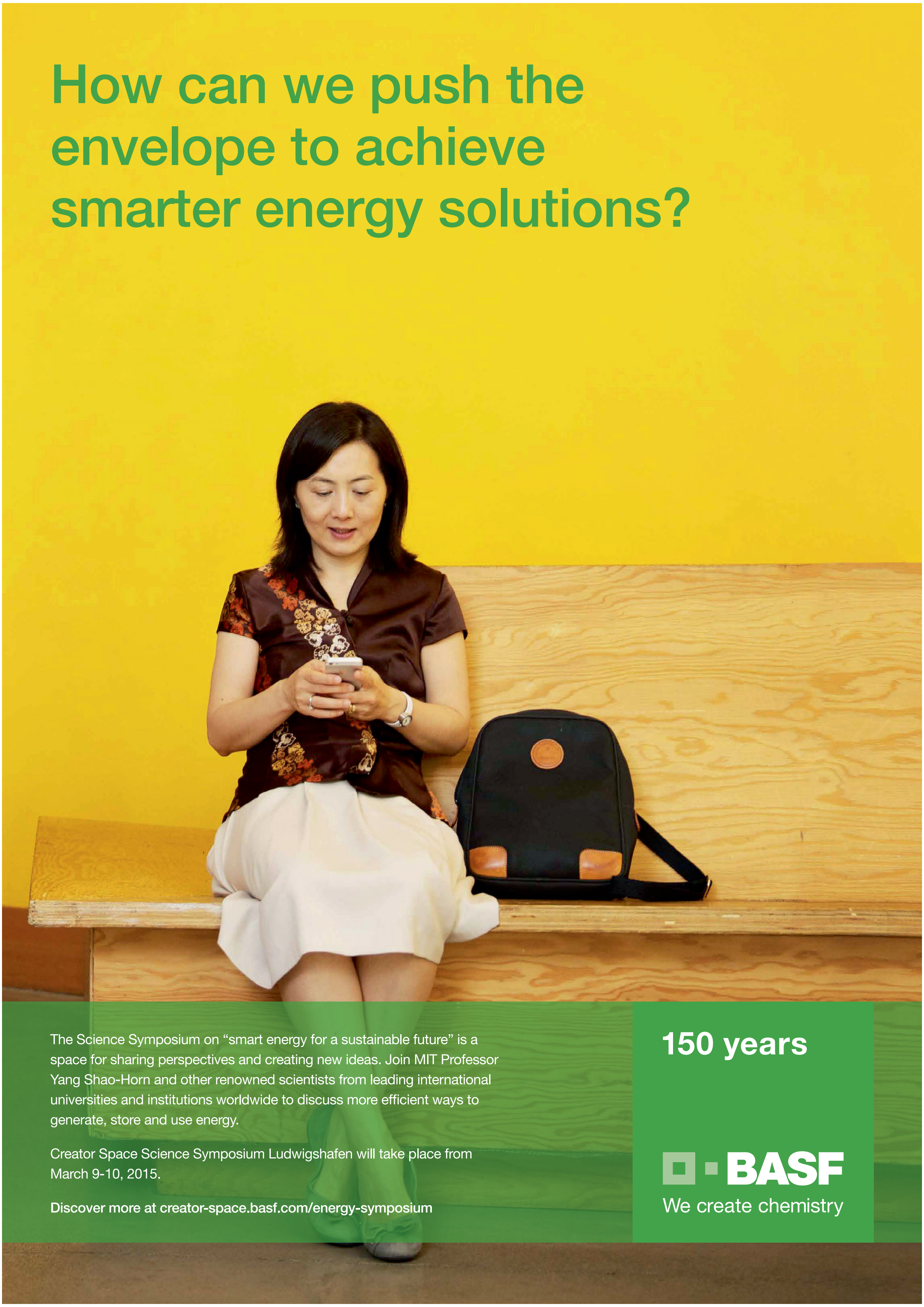

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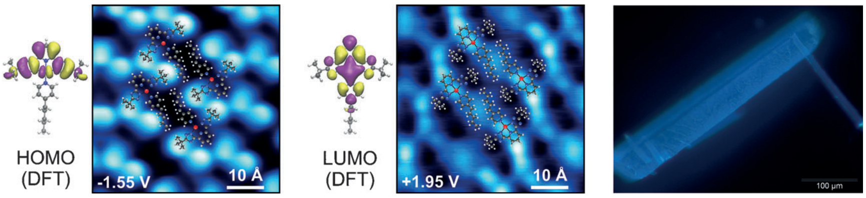
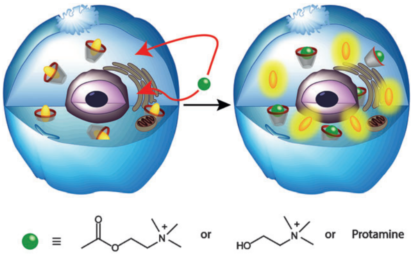
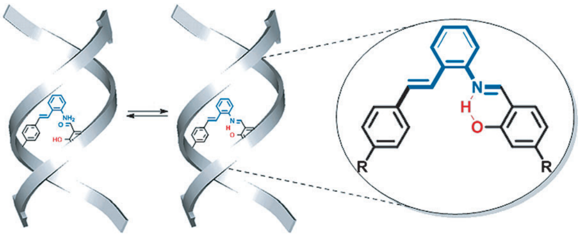
Communications



Seeing is believing: Frontier orbitals of Pt^{II} complexes have been visualized and measured by scanning tunneling spectroscopy. Moreover, they have been tuned with the aid of targeted synthetic strategies to yield a deep-blue triplet emitter. This approach of finding and tuning the right electronic set screws at the molecular level constitutes a new strategy to design and to realize tailored optoelectronic materials.



Live coverage: Macrocyclic host–dye complexes can be used to detect the presence of an analyte inside live cells through dye displacement. *p*-Sulfonatocalix[4]arene (CX4) and the fluorescent dye lucigenine (LCG, yellow) are both taken up into CHO and V79 cells to form a weakly fluorescent CX4–LCG complex in the cytoplasm. Subsequent addition of the corresponding analytes (acetylcholine, choline, and protamine; green) results in a clear increase in fluorescence.

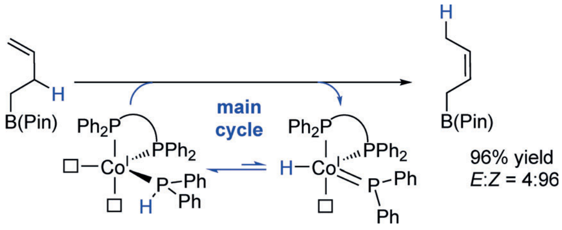


Reversible bond formation was used as a design principle to create a “post-it”-type cross-linking unit. The aldehyde–amine DNA cross-link endows DNA duplexes with a reversible but unusual high stability.

Synthetic Methods

A. Schmidt, A. R. Nödling,
G. Hilt* ———— **801 – 804**

An Alternative Mechanism for the Cobalt-Catalyzed Isomerization of Terminal Alkenes to (*Z*)-2-Alkenes

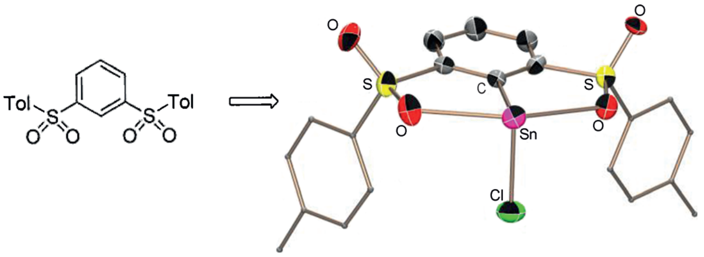


Hide the metal hydride: Generation of the thermodynamically less stable (*Z*)-2-alkenes at ambient temperatures by a cobalt-catalyzed selective isomerization of terminal alkenes is described. The reaction takes place by a new mechanism involving the transfer of a hydrogen atom from a Ph_2PH ligand to the starting material and the formation of a phosphenium complex, which recycles the Ph_2PH complex through a 1,2-H shift (Bpin = (pinacolato)boron).

Tin Pincer Complexes

M. El Ezzi, R. Lenk, D. Madec,*
J. M. Sotiropoulos, S. Mallet-Ladeira,
A. Castel ———— **805 – 808**

A Bis-Sulfonyl O,C,O Aryl Pincer Ligand and its Tin(II) Complex: Synthesis, Structural Studies, and DFT Calculations



Pinching tin: A heteroleptic tin(II) complex stabilized by intramolecular S=O coordination has been isolated using the deprotonated aryl bis-sulfone ligand $[2,6\text{-}\{(p\text{-tolyl})SO_2\}_2C_6H_3]^-$. The structure of the complex has been analyzed both computationally and by single-crystal X-ray diffraction analysis.

Small-Molecule Trapping

L. E. Longobardi, V. Wolter,
D. W. Stephan* ———— **809 – 812**

Frustrated Lewis Pair Activation of an *N*-Sulfinylamine: A Source of Sulfur Monoxide

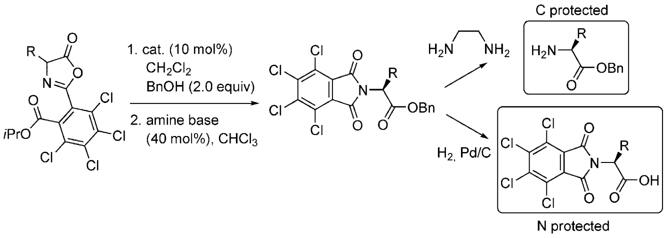
SO good: Inter- and intramolecular P/B frustrated Lewis pairs are shown to react with an *N*-sulfinylamine to form PNSOB linkages. These species can be regarded as phosphinimine–borane-stabilized sulfur monoxide complexes, and they indeed act as sources of SO, effecting the oxidation of PPh_3 and delivering SO to $[RhCl(PPh_3)_3]$ and N-heterocyclic carbenes.

Front Cover

Organocatalysis

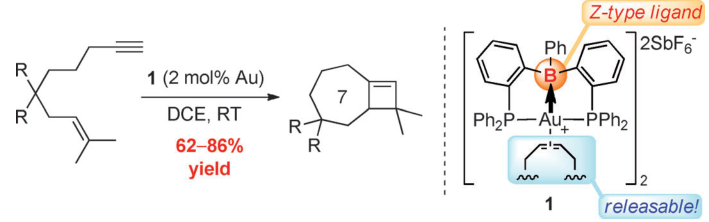
S. Tallon, F. Manoni,
S. J. Connon* ———— **813 – 817**

A Practical Aryl Unit for Azlactone Dynamic Kinetic Resolution: Orthogonally Protected Products and A Ligation-Inspired Coupling Process



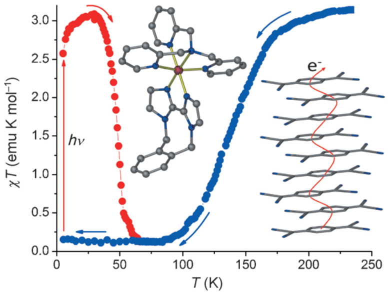
Squared away: A strategy for enantioselective azlactone dynamic kinetic resolution to generate orthogonally protected amino acids has been developed. In the presence of a squaramide-based catalyst, benzyl alcohol reacts with tetrachloroisopropoxycarbonyl-substituted azlactones to generate phthalimide products with excellent enantiocontrol. Removal of the phthalimide can be achieved in the presence of the ester and vice versa.

Synthetic Methods



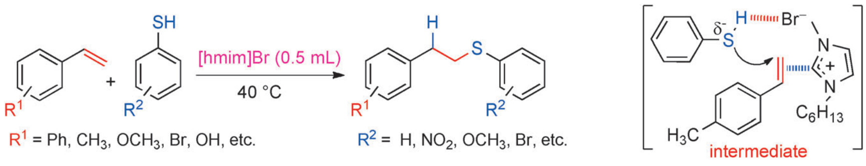
Z-shaped: The air-stable cationic Au$^{\mathrm{I}}$ complex **1** featuring a Z-type ligand was developed for elucidating the effect of the boron ligand in catalytic reactions. For an enyne cyclization in the presence of either **1** or an analogous complex without B ligand, it was shown that B promotes the reactivity of the neighboring gold center in the construction of five- to seven-membered rings.

Photomagnetic Semiconductors



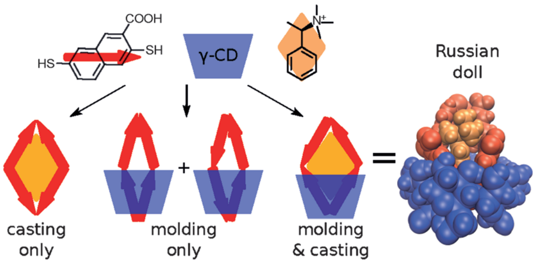
Multifunctional materials: Two cationic Fe$^{\mathrm{II}}$ complexes co-crystallized with partially charged TCNQ$^{\bullet\delta-}$ radical anions exhibit temperature- and light-induced conversion between the high-spin and low-spin states of the Fe$^{\mathrm{II}}$ ion, as well as semiconductivity propagated by the TCNQ stacks. The conductivity of these materials is among the highest for all reported spin-crossover semiconductors.

Click Chemistry



Linear thioethers are obtained by an atom-efficient thiol–ene "click" reaction in neutral [hmim]Br without the need for base or metal complexes. Detailed mechanistic studies using ^{1}H NMR spectroscopy and quadrupol time-of-flight electrospray ionization mass spectrometry showed that the "ambiphilic" character of the ionic liquid promotes the regioselective nucleophilic addition of thiol to styrene through an anti-Markovnikov pathway.

Systems Chemistry

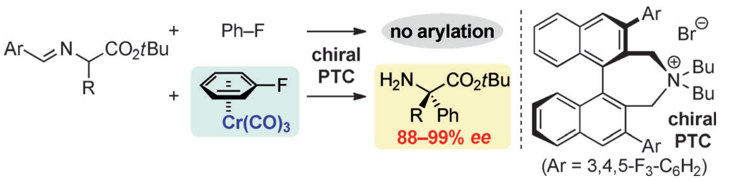


Mix and match: Using a dynamic combinatorial approach, two templates, γ-cyclodextrin (γ-CD) and an ammonium salt, were employed to simultaneously perform casting and molding of dynamic macrocycles (see picture). Binding of the templates by the macrocycle exhibits positive cooperativity forming a Russian-doll-like termolecular complex.

Organocatalysis

S. Shirakawa, K. Yamamoto, K. Maruoka* ———— 838 – 840

Phase-Transfer-Catalyzed Asymmetric $\mathrm{S_NAr}$ Reaction of α-Amino Acid Derivatives with Arene Chromium Complexes

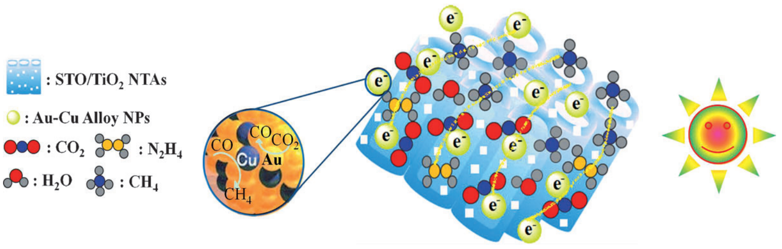


Increased substrate scope in phase-transfer-catalyzed asymmetric $\mathrm{S_NAr}$ reactions was achieved by the use of arene chromium complexes as electrophiles. An efficient asymmetric synthesis of α,α-disubstituted α-amino acids containing various aromatic substituents is shown. PTC = phase-transfer catalyst.

CO_2 Photoreduction

Q. Kang, T. Wang, P. Li, L. Liu, K. Chang, M. Li, J. Ye* ———— 841 – 845

Photocatalytic Reduction of Carbon Dioxide by Hydrous Hydrazine over Au–Cu Alloy Nanoparticles Supported on $SrTiO_3/TiO_2$ Coaxial Nanotube Arrays

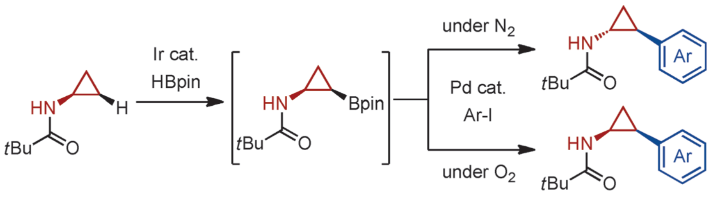


Alloy, alloy: Au–Cu alloy nanoparticles (NPs) supported on $SrTiO_3/TiO_2$ coaxial nanotube arrays are an efficient photocatalyst for the conversion of CO_2 into CO and hydrocarbons. $N_2H_4{\cdot}H_2O$ provides a reductive atmosphere for stabilizing the alloy NPs during the reaction. A CO yield of 3.77 mmol g^{-1} h^{-1} and total hydrocarbon of 725.4 μmol g^{-1} h^{-1} was realized on $Au_3Cu@SrTiO_3/TiO_2$ nanotube arrays.

Small Ring Systems

S. Miyamura, M. Araki, T. Suzuki, J. Yamaguchi,* K. Itami* ———— 846 – 851

Stereodivergent Synthesis of Arylcyclopropylamines by Sequential C–H Borylation and Suzuki–Miyaura Coupling

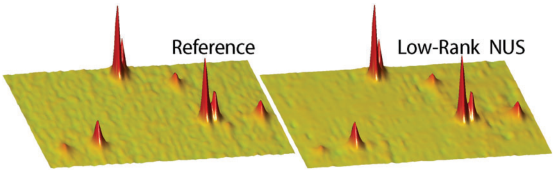


All about atmosphere: A step-economical synthesis of 2-arylcyclopropylamines through the title sequence has been developed. The iridium-catalyzed C–H borylation proceeds with *cis* selectivity, and the subsequent Suzuki–Miyaura coupling proceeds with retention of configuration at the carbon center bearing the Bpin group, and epimerization at the nitrogen-bound carbon atoms. Either isomer (*cis* or *trans*) can be accessed by simply changing the atmosphere (N_2 or O_2).

NMR Spectroscopy

X. Qu,* M. Mayzel, J. F. Cai, Z. Chen, V. Orekhov* ———— 852 – 854

Accelerated NMR Spectroscopy with Low-Rank Reconstruction



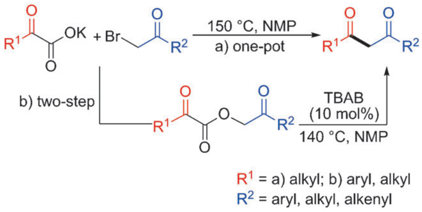
A low rank is an advantage: High-quality NMR spectra are reconstructed from a small number of non-uniformly sampled data points. Significant reduction in measurement time is obtained using the so far unexploited general property of NMR signal—its low rank (see picture; NUS = non-uniform sampling).

Decarboxylative Coupling

Z. He, X. Qi, S. Li, Y. Zhao, G. Gao,* Y. Lan,* Y. Wu, J. Lan, J. You* **855–859**

Transition-Metal-Free Formal Decarboxylative Coupling of α-Oxocarboxylates with α-Bromoketones under Neutral Conditions: A Simple Access to 1,3-Diketones

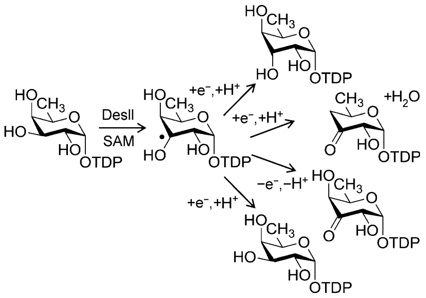
No metal needed: 1,3-Diketone compounds are synthesized from α-oxocarboxylates and α-bromoketones using a bromide-catalyzed, mild, neutral, and transition-metal-free procedure which tolerates a wide spectrum of functional groups. DFT calculations suggest a mechanism involving coupling followed by decarboxylation. NMP = *N*-methyl-2-pyrrolidone; TBAB = tetrabutylammonium bromide.



Biosynthesis

Y. Ko, M. W. Ruszczycky, S.-H. Choi, H.-w. Liu* **860–863**

Mechanistic Studies of the Radical *S*-Adenosylmethionine Enzyme DesII with TDP-D-Fucose

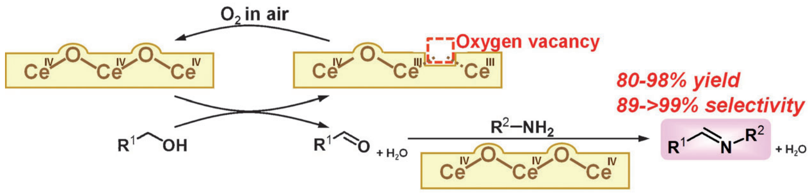


What dictates the substrate's fate? DesII is a radical *S*-adenosylmethionine (SAM) enzyme that can catalyze either deamination or dehydrogenation depending on the substitution pattern of its substrate. By altering the stereochemistry of the dehydrogenation substrate, however, dehydration also becomes possible. This supports a model in which the fate of the substrate radical depends on its binding configuration in the enzyme active site.

Direct Imine Formation

M. Tamura,* K. Tomishige **864–867**

Redox Properties of CeO_2 at Low Temperature: The Direct Synthesis of Imines from Alcohol and Amine



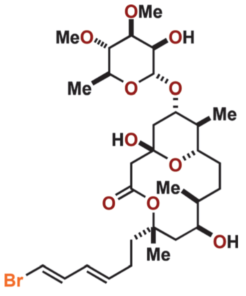
The amazing redox property of CeO_2 is utilized in the direct imine formation from alcohols and amines even at 303 K. The catalytic activity of CeO_2 is more than 38-fold higher than that of other simple metal oxides. CeO_2 is a reusable heterogeneous catalyst and can be applied to various alcohols and amines, resulting in high yields (75–98 %) and high selectivities (89–>99 %).

Natural Products

H. Fuwa,* Y. Okuaki, N. Yamagata, M. Sasaki **868–873**

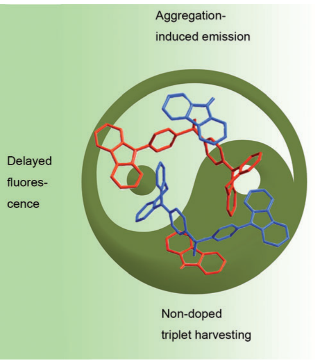
Total Synthesis, Stereochemical Reassignment, and Biological Evaluation of (−)-Lyngbyaloside B

What I can create, I understand: Total synthesis of the proposed structure of (−)-lyngbyaloside B, a cytotoxic macrolide glycoside of marine origin, showed that the original stereochemical assignment needed to be reconsidered. The correct structure of this natural product was reassigned on the basis of spectroscopic and molecular modeling considerations and ultimately established by means of total synthesis.



correct structure of
(−)-lyngbyaloside B

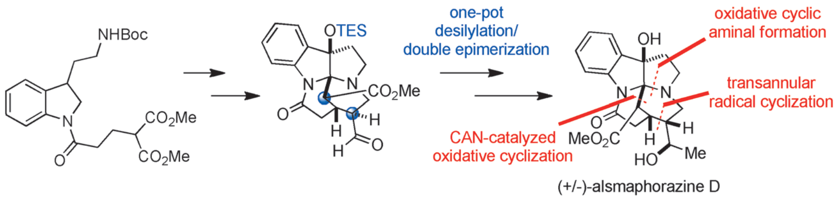
In a “scense”: A novel compound having an asymmetric structure exhibited aggregation-induced emission, delayed fluorescence, and mechanoluminescence simultaneously.



Materials Science

S. Xu, T. Liu, Y. Mu, Y. Wang, Z. Chi,* C. Lo, S. Liu, Y. Zhang,* A. Lien, J. Xu* ________ **874 – 878**

An Organic Molecule with Asymmetric Structure Exhibiting Aggregation-Induced Emission, Delayed Fluorescence, and Mechanoluminescence

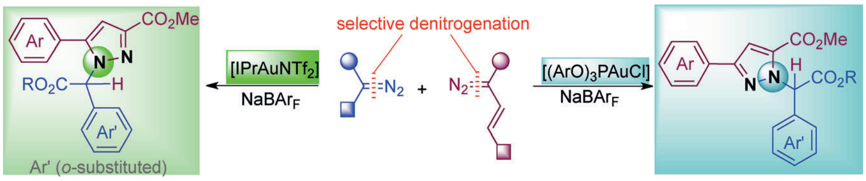


The total synthesis of (±)-alsmaphorazine D was achieved in a concise and efficient fashion. The key features of the strategy are based on a catalytic intramolecular oxidative cyclization, an oxidative cyclic aminal formation, a transannular radical cyclization, and a one-pot desilylation/double epimerization reaction. CAN = cerium(IV) ammonium nitrate.

Natural Product Synthesis

C. Zhu, Z. Liu, G. Chen, K. Zhang, H. Ding* ________ **879 – 882**

Total Synthesis of Indole Alkaloid Alsmaphorazine D

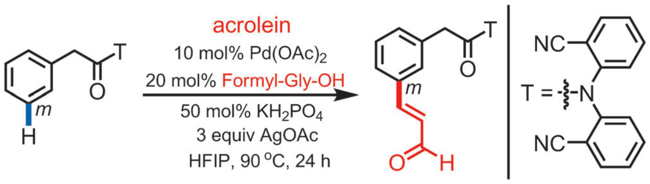


Old switcheroo: The title reaction proceeds through sequential denitrogenation and cyclization to afford N-substituted pyrazoles in a position-switchable mode. This novel transformation features selective decomposition of one diazo moiety and simultaneous preservation of the other one from two substrates. The choice of the ancillary ligand on the gold complex plays a pivotal role on the chemo- and regioselectivity of the reaction.

Cyclization

G. Xu, C. Zhu, W. Gu, J. Li, J. Sun* ________ **883 – 887**

Gold(I)-Catalyzed Diazo Cross-Coupling: A Selective and Ligand-Controlled Denitrogenation/Cyclization Cascade



It’s T time: The title reaction has been achieved using a commercially available nitrile-containing template. The identification of N-formyl-protected glycine as the ligand (Formyl-Gly-OH) was crucial for the development of this reaction. Versatility of the template approach in accommodating macrocyclopalladation processes with different ring sizes is demonstrated.

C–H Activation

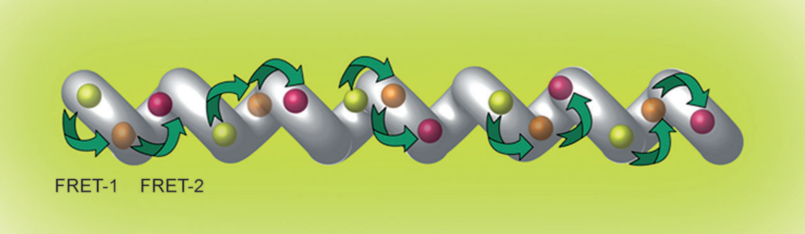
Y. Deng, J.-Q. Yu* ________ **888 – 891**

Remote *meta*-C–H Olefination of Phenylacetic Acids Directed by a Versatile U-Shaped Template

Light Harvesting

F. Pu, L. Wu, X. Ran, J. Ren,*
X. Qu* ________ **892 – 896**

G-Quartet-Based Nanostructure for Mimicking Light-Harvesting Antenna

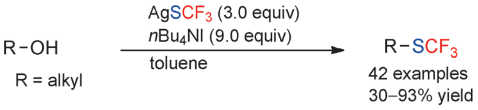


Curl up and dye: G-quartet-based hierarchical nanofibers generated from the self-assembly of guanosine 5′-monophosphate with Sr^{2+} ions have been developed to mimic natural light-harvesting antenna. Three dyes (yellow, orange, red spheres in picture) were confined simultaneously in the nanofibers and brought into proximity, thus allowing for a two-step FRET process. Photocurrent is generated upon irradiation with visible light.

Synthetic Methods

J.-B. Liu, X.-H. Xu, Z.-H. Chen,
F.-L. Qing* ________ **897 – 900**

Direct Dehydroxytrifluoromethylthiolation of Alcohols Using Silver(I) Trifluoromethanethiolate and Tetra-*n*-butylammonium Iodide



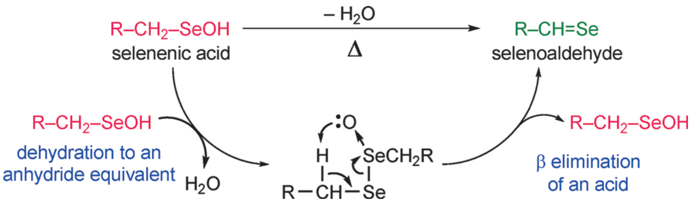
Silver bullet: A new strategy has been developed for the direct trifluoromethylthiolation of alkyl alcohols using $AgSCF_3$ and nBu_4NI. This protocol does not require the activation of alcohols in advance. A variety of alkyl alcohols bearing different functional groups were transformed into the corresponding alkyl trifluoromethyl sulfides in moderate to good yields.

Reaction Mechanisms

S. Sase, R. Kakimoto, K. Goto* **901 – 904**

Synthesis of a Stable Selenoaldehyde by Self-Catalyzed Thermal Dehydration of a Primary-Alkyl-Substituted Selenenic Acid

Inside Cover



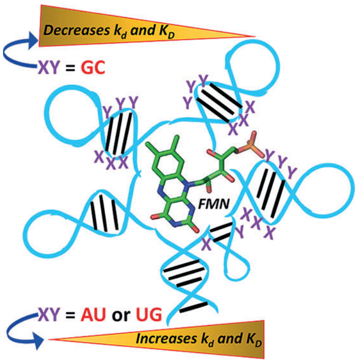
Selen' it: A stable selenoaldehyde was synthesized by thermal dehydration of a selenenic acid bearing a nanosized primary-alkyl group. Intrinsic properties of a selenenic acid play a key role in this self-catalyzed β dehydration of an organic acid involving formation of an anhydride equivalent and subsequent β elimination of an acid. The selenoaldehyde showed remarkable stability and was characterized by crystallographic analysis.

Riboswitch Tuning

A. B. Rode, T. Endoh,
N. Sugimoto* ________ **905 – 909**

Tuning Riboswitch-Mediated Gene Regulation by Rational Control of Aptamer Ligand Binding Properties

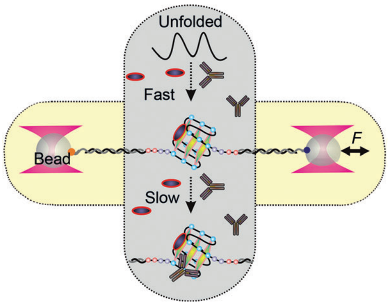
Interior tuning regions in riboswitch aptamers that modulate ligand binding kinetics and affinity were identified by comparative analysis of kinetic parameters of several natural and mutated riboswitch aptamers. An artificial riboswitch with modified tuning regions achieved 9.31-fold reduction of half-maximal effective concentration of flavin mononucleotide (FMN)-dependent suppression of gene expression in vitro relative to the parent aptamer riboswitch.



RNA Structures

P. M. Yangyuoru, M. Di Antonio, C. Ghimire, G. Biffi, S. Balasubramanian,* H. Mao* ———— **910–913**

Dual Binding of an Antibody and a Small Molecule Increases the Stability of TERRA G-Quadruplex

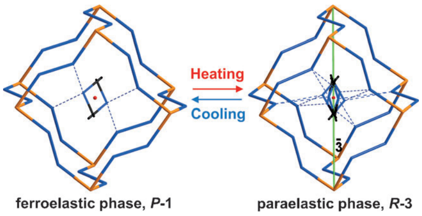


Quadruplex complex: Single-molecule mechanical unfolding experiments revealed that the small molecule carboxypyridostatin (cPDS; red and blue ovals) and the GQ-selective antibody BG4 simultaneously bind the human telomeric RNA (TERRA) G-quadruplex (GQ) in a process that involves conformational rearrangement. The resulting increased mechanical and thermodynamic stability could provide new leads for the design of more effective GQ-binding ligands.

Host–Guest Systems

Z.-Y. Du, T.-T. Xu, B. Huang, Y.-J. Su, W. Xue, C.-T. He, W.-X. Zhang,* X.-M. Chen ———— **914–918**

Switchable Guest Molecular Dynamics in a Perovskite-Like Coordination Polymer toward Sensitive Thermoresponsive Dielectric Materials

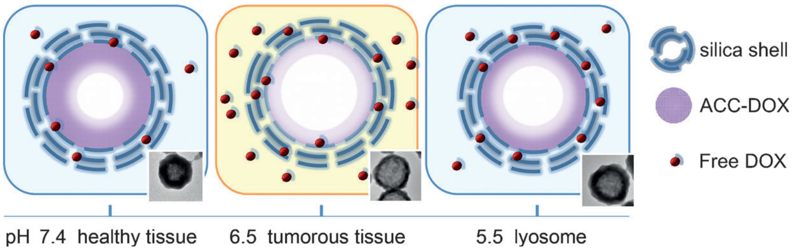


Flexible frameworks: A perovskite-like coordination polymer $[(CH_3)_2NH_2][Cd(N_3)_3]$ undergoes a ferroelastic-to-paraelastic phase transition as a result of the motion of the guest cation within the host framework (see picture), which itself undergoes a simultaneous deformation. This material acts as a thermoresponsive dielectric system owing to the well-controlled guest molecular dynamics in the confined space.

Drug Delivery

Y. Zhao, Z. Luo, M. Li, Q. Qu, X. Ma, S.-H. Yu,* Y. L. Zhao* ———— **919–922**

A Preloaded Amorphous Calcium Carbonate/Doxorubicin@Silica Nanoreactor for pH-Responsive Delivery of an Anticancer Drug

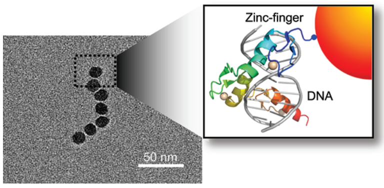


Precise release of doxorubicin (DOX) in the weakly acidic microenvironment of cancer cells has been achieved with an amorphous calcium carbonate/doxorubicin@silica (ACC–DOX@silica) nanoreactor. Only low drug leakage occurs in physiological and lysosomal/endosomal environments, but at pH 6.5 the drug is specifically released and results in efficient cell death.

Magnetic Nanoparticle Clusters

Y. Ryu, Z. Jin, J.-j. Lee, S.-h. Noh, T.-H. Shin, S.-M. Jo, J. Choi, H. Park, J. Cheon, H.-S. Kim* ———— **923–926**

Size-Controlled Construction of Magnetic Nanoparticle Clusters Using DNA-Binding Zinc Finger Protein



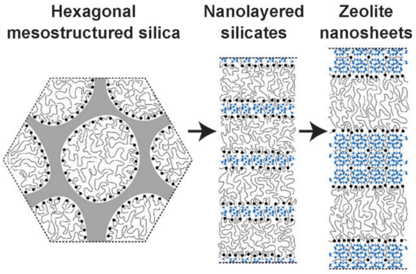
Bound by zinc fingers: Nanoparticle clusters were constructed in a size-controlled manner using the DNA-binding zinc finger protein and linear DNA templates. The number of magnetic nanoparticles (MNPs) bound to the DNA template was well coincident with the expected number of MNPs. This method can also be applied to other nanoparticles and might find applications in many areas.

Mesostructured Zeolites

R. J. Messinger, K. Na, Y. Seo, R. Ryoo,
B. F. Chmelka* ——— **927 – 931**

Co-development of Crystalline and Mesoscopic Order in Mesostructured Zeolite Nanosheets

Self-assembly of MFI-type crystal: The atomic and mesoscopic structural transformations that occur during hydrothermal syntheses of zeolite MFI nanosheets have been correlated and shown to proceed through initially mesostructured amorphous silica, followed by an intermediate nanolayered silicate phase. The results establish the transient processes by which coupled framework crystallization and surfactant self-assembly occur.

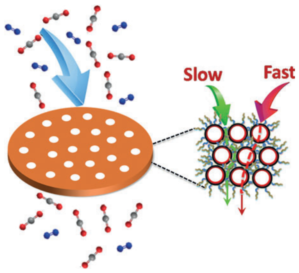


Gas Separation

J. Zhang, S. Chai, Z. Qiao, S. M. Mahurin,*
J. Chen, Y. Fang, S. Wan, K. Nelson,
P. Zhang, S. Dai* ——— **932 – 936**

Porous Liquids: A Promising Class of Media for Gas Separation

Inside Back Cover

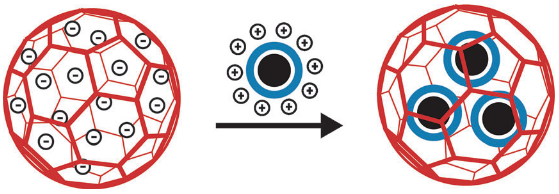


Perforated liquids: Functionalizing hollow silica spheres with suitable polymer species can produce a porous liquid containing empty silica cavities. Taking advantage of their liquid-like polymeric matrixes as the separation medium and the empty cavities as the gas transport pathway they can function as a promising candidates for gas separation.

Host–Guest Systems

T. Beck, S. Tetter, M. Künzle,
D. Hilvert* ——— **937 – 940**

Construction of Matryoshka-Type Structures from Supercharged Protein Nanocages

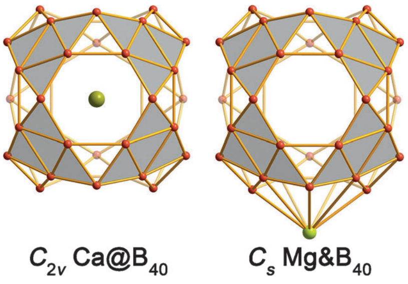


Cages within cages: By exploiting electrostatic interactions between two supercharged protein containers, namely supercharged lumazine synthase (red) and supercharged ferritin (blue) loaded with iron-oxide nanoparticles (black), nested Matryoshka-type structures were assembled. These cage-within-cage structures consist of two layers of protein surrounding iron oxide nanoparticles in a manner reminiscent of Russian dolls.

Boron Cage Clusters

H. Bai, Q. Chen, H. J. Zhai,*
S. D. Li* ——— **941 – 945**

Endohedral and Exohedral Metalloborospherenes: M@B_{40} (M = Ca, Sr) and M&B_{40} (M = Be, Mg)

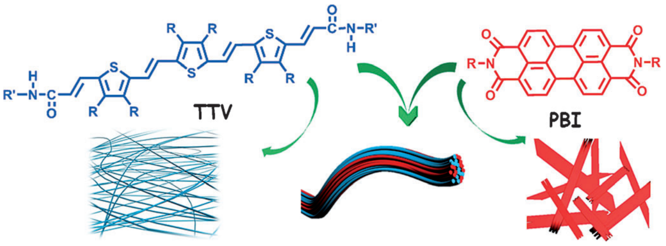


Into higher spheres: The recently observed B_{40} borospherene is predicted to be capable of hosting a metal atom inside (M@B_{40}; M = Ca, Sr) or coordinating one on its heptagonal surface (M&B_{40}; M = Be, Mg). Metalloborospherenes are charge-transfer $M^{2+}B_{40}^{2-}$ complexes, demonstrating the structural and electronic integrity of borospherene, akin to C_{60} buckyball.

Donor–Acceptor Systems

S. Prasanthkumar, S. Ghosh, V. C. Nair,
A. Saeki, S. Seki,
A. Ajayaghosh* ———— **946 – 950**

Organic Donor–Acceptor Assemblies form Coaxial p–n Heterojunctions with High Photoconductivity

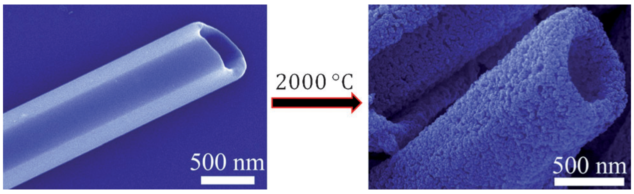


Self-assembled coaxial fibers: A thiophene-based p-type gelator (TTV) and an n-type perylene bisimide (PBI) self-sort at the molecular level and undergo self-assembly at the mesoscopic level to form bundled coaxial donor–acceptor fibers. These combined processes allow the formation of coaxial p–n heterojunctions with high photoconductivity.

Carbon Materials

L. K. Shrestha,* R. G. Shrestha,
Y. Yamauchi,* J. P. Hill, T. Nishimura,
K. Miyazawa, T. Kawai, S. Okada,
K. Wakabayashi, K. Ariga* ——— **951 – 955**

Nanoporous Carbon Tubes from Fullerene Crystals as the π-Electron Carbon Source

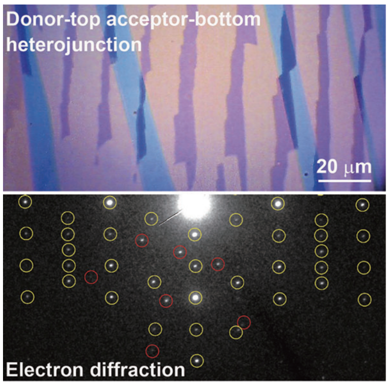


Thermal conversion of 1D fullerene (C_{60}) single-crystal nanorods and nanotubes gives nanoporous carbon materials with retention of the initial 1D morphology. The nanoporous carbon materials exhibit π-electron conjugation within the sp^2-carbon robust frameworks and show excellent electrochemical capacitance and superior sensing properties for aromatic compounds.

Heterojunctions

H. Y. Li,* C. C. Fan, W. F. Fu, H. L. Xin,
H. Z. Chen* ———— **956 – 960**

Solution-Grown Organic Single-Crystalline Donor–Acceptor Heterojunctions for Photovoltaics

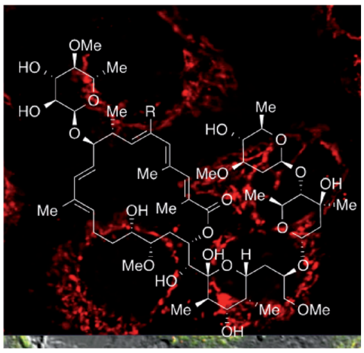


Ideal candidates for high-performance photovoltaics, organic single-crystalline heterojunctions are difficult to prepare. Now, extended single-crystalline heterojunctions with consistent donor-top and acceptor-bottom structure throughout the substrate can be obtained from a mixed solution of donor and acceptor through sequential crystallization. These heterojunctions exhibit a significant photovoltaic effect.

Polyketides

S. M. DeGuire, D. C. Earl, Y. Du,
B. A. Crews, A. T. Jacobs, A. Ustione,
C. Daniel, K. M. Chong, L. J. Marnett,
D. W. Piston, B. O. Bachmann,
G. A. Sulikowski* ———— **961 – 964**

Fluorescent Probes of the Apoptolidins and their Utility in Cellular Localization Studies



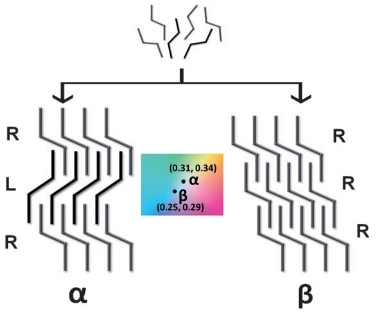
Pop in: Apoptolidins have been described among the top 0.1 % most-cell-selective cytotoxic agents to be evaluated in the NCI 60 cell line panel. Combined methods of genetic deletion, to manipulate the biosynthetic machinery, and chemical synthesis provides access to new fluorescent derivatives of the apoptolidins for biological study.

Photoluminescence

H.-L. Huang, S.-L. Wang* ____ **965 – 968**

Nanoribbon-Structured Organo Zinc Phosphite Polymorphs with White-Light Photoluminescence

Polymorphism: The first neutral organo zinc phosphites composed of 2.8 nm-wide one-dimensional ribbons, exhibiting interesting polymorphism, were prepared by the "mesitylene strategy". The S-shaped ribbons in R or L arrays display different stacking modes in the polymorphic phases. The different arrays exhibit distinct photoluminescence properties.

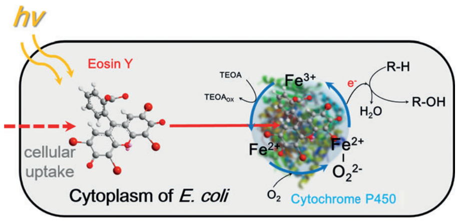


Biocatalysis

J. H. Park, S. H. Lee, G. S. Cha, D. S. Choi, D. H. Nam, J. H. Lee, J.-K. Lee, C.-H. Yun,* K. J. Jeong,* C. B. Park* ______ **969 – 973**

Cofactor-Free Light-Driven Whole-Cell Cytochrome P450 Catalysis

Back Cover



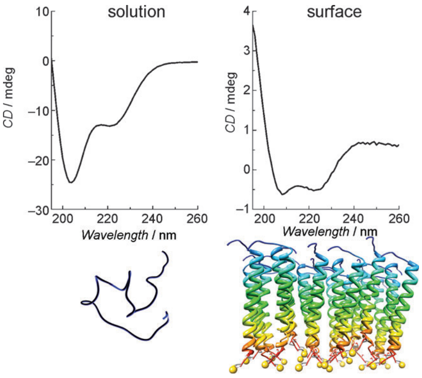
Eosin Y (EY) can bind specifically to the heme domain of cytochromes P450 expressed in the cytoplasm of *Escherichia coli*. The catalytic turnover is mediated by direct transfer of photoinduced electrons from photosensitized EY to the heme domain of P450 under visible light illumination. The photoactivation of P450 catalytic cycle is a new platform for cost-effective, cofactor-free, light-driven biocatalysis.

Peptide Monolayers

S. J. White, S. D. Johnson,* M. A. Sellick, A. Bronowska, P. G. Stockley, C. Wälti* ________________ **974 – 978**

The Influence of Two-Dimensional Organization on Peptide Conformation

Collective action: Molecular crowding in the high-molecular density environment of a 2D peptide monolayer is shown to govern peptide conformation and function. The results show that these collective interactions need to be accounted for in the design and interpretation of experimental studies involving surface-immobilized molecular systems.

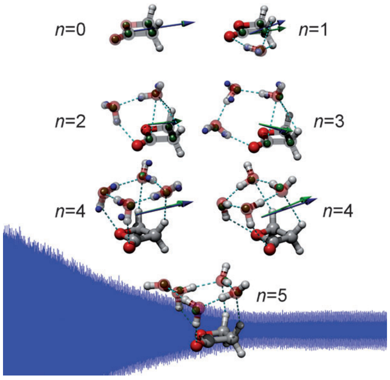


Microsolvation

C. Pérez, J. L. Neill, M. T. Muckle, D. P. Zaleski, I. Peña, J. C. Lopez, J. L. Alonso, B. H. Pate* _____ **979 – 982**

Water–Water and Water–Solute Interactions in Microsolvated Organic Complexes

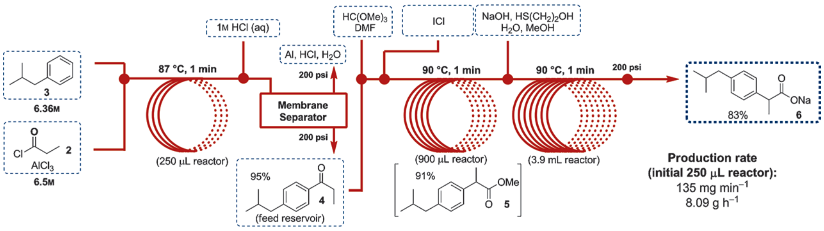
Water clusters: The microsolvated structures of BPL–$(H_2O)_n$ ($n = 1$–5; BPL = β-propiolactone) have been measured by chirped-pulse Fourier transform microwave spectroscopy. A delicate trade-off is found between maximizing the number of solute–H_2O interactions and the minimum-energy structures of isolated clusters. The calculated and the experimentally derived dipole moments are shown by blue and green arrows, respectively (see picture).



Continuous Flow

D. R. Snead, T. F. Jamison* ___ **983 – 987**

A Three-Minute Synthesis and Purification of Ibuprofen: Pushing the Limits of Continuous-Flow Processing

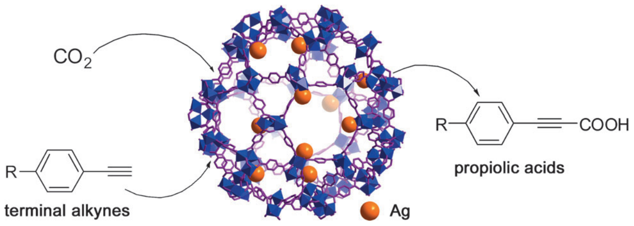


Within three minutes, ibuprofen was assembled from its elementary building blocks with an average yield of above 90% for each step. The process featured a Friedel–Crafts acylation run under neat conditions and promoted by $AlCl_3$, an exothermic in-line quench of flocculation-prone concentrated $AlCl_3$, liquid–liquid separations run at or above 200 psi to give solvent-free product, and the continuous pumping of a neat aggressive oxidant.

Carbon Dioxide Fixation

X.-H. Liu, J.-G. Ma,* Z. Niu, G.-M. Yang, P. Cheng* ___ **988 – 991**

An Efficient Nanoscale Heterogeneous Catalyst for the Capture and Conversion of Carbon Dioxide at Ambient Pressure

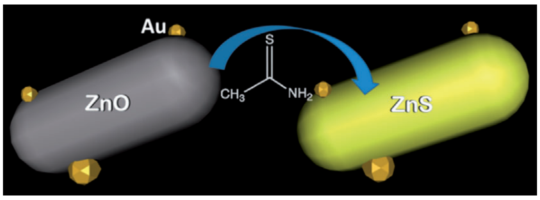


Silver nanoparticles were supported on the zeolite-type metal–organic framework MIL-101 by a simple liquid impregnation method to yield Ag@MIL-101. CO_2 and terminal alkynes could be converted into propiolic acids in the presence of the very active Ag@MIL-101 catalyst at atmospheric pressure and low temperature (50 °C).

Zinc Oxide

M. Behl, P. K. Jain* ___ **992 – 997**

Catalytic Activation of a Solid Oxide in Electronic Contact With Gold Nanoparticles

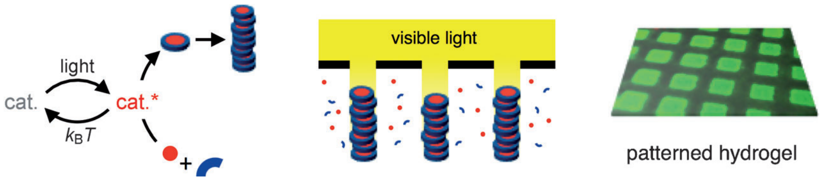


Nanoscale gold particles, which are commonly used for the activation of small molecules, have been found to catalytically activate an extended solid oxide. The oxide thus becomes more reactive for solid-state transformations and reactive adsorption processes of relevance in pollutant removal and hydrocarbon processing.

Photochemistry

C. Maity, W. E. Hendriksen, J. H. van Esch,* R. Eelkema* ___ **998 – 1001**

Spatial Structuring of a Supramolecular Hydrogel by using a Visible-Light Triggered Catalyst

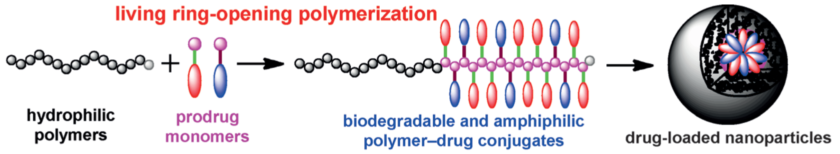


Lighting the way: The spatial distribution and mechanical properties of a low-molecular-weight hydrogel can be controlled by using a photoswitchable catalyst for in situ gelator formation. Upon light irradiation, the photochromic compound temporarily lowers the pH of the solution, thereby catalyzing the formation of the of the hydrazone gelator. Spatial control over gel formation is accomplished by using a simple photomask to give local catalyst activation.

Polymer–Drug Conjugates

J. Liu, W. Liu, I. Weitzhandler, J. Bhattacharyya, X. Li, J. Wang, Y. Qi, S. Bhattacharjee, A. Chilkoti* ______ **1002 – 1006**

Ring-Opening Polymerization of Prodrugs: A Versatile Approach to Prepare Well-Defined Drug-Loaded Nanoparticles

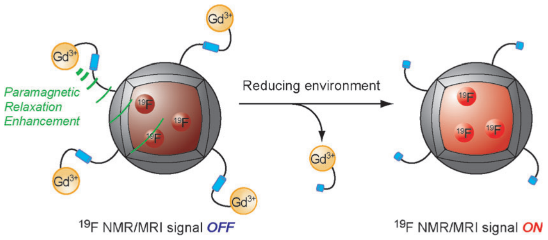


Conjugates: Biodegradable polymer–drug conjugates were synthesized through living ring-opening polymerization of prodrug monomers consisting of a cyclic polymerizable group that is attached to a drug through a cleavable linker. The polymer–drug conjugates are designed to self-assemble into nanoparticles and release the drug in response to a physiologically relevant stimulus.

Magnetic Resonance Imaging

T. Nakamura, H. Matsushita, F. Sugihara, Y. Yoshioka, S. Mizukami, K. Kikuchi* ______ **1007 – 1010**

Activatable ^{19}F MRI Nanoparticle Probes for the Detection of Reducing Environments

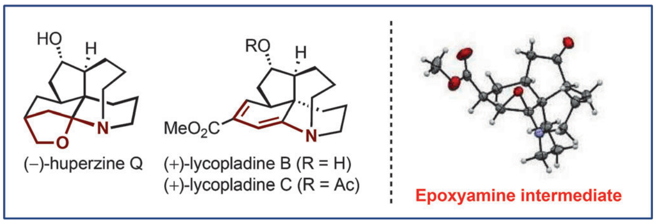


Redox-sensitive MRI agents: Reducing-environment-responsive ^{19}F magnetic resonance imaging (MRI) probes were developed. The ^{19}F NMR/MRI signals of the probes are quenched by the paramagnetic relaxation enhancement effect of the Gd^{3+} complexes. A reductive reaction induced high signal enhancement of the probes (see picture).

Alkaloids

B. Hong, H. Li, J. Wu, J. Zhang, X. Lei* ______ **1011 – 1015**

Total Syntheses of (−)-Huperzine Q and (+)-Lycopladines B and C



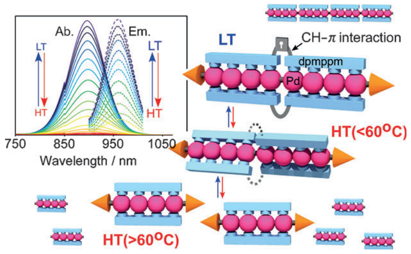
An enamine bromofunctionalization strategy has been utilized in the total syntheses of (−)-huperzine Q and (+)-lycopladines B and C. Other notable features of the syntheses include an ethylene-accelerated carbonyl–olefin metathesis, an unprecedented X-ray crystal structure of an unusual epoxyamine intermediate, and its first synthetic application in natural product synthesis.

Self-Alignment of Pd_8 Chains

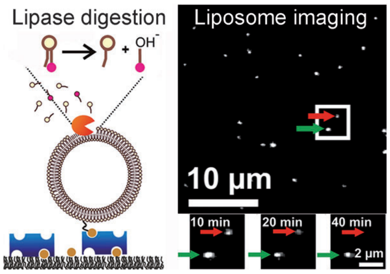
K. Nakamae, Y. Takemura, B. Kure, T. Nakajima, Y. Kitagawa, T. Tanase* ______ **1016 – 1021**

Self-Alignment of Low-Valent Octanuclear Palladium Atoms

Linear Pd_8 chains were synthesized through self-alignment. Discrete molecules of $[Pd_8(\mu\text{-dpmppm})_4](BF_4)_4$ (**1**) and $[Pd_8(\mu\text{-dpmppm})_4L_2](BF_4)_4$ [L = XylNC (**2**), acetonitrile (**3**), and dmf (**4**)] are stable in solution and exhibit interesting temperature-dependent photochemical properties in the near IR region. dpmppm = *meso*-bis[(diphenylphosphinomethyl)phenylphosphino]methane), XylNC = 2,6-xylyl isocyanide, dmf = *N*,*N*-dimethylformamide.



The power of statistical analysis: The kinetics of the phospholipase A2 digestion of individual liposomes composed of dye-modified lipids was measured by total internal reflection fluorescence imaging (see picture). In this way both k_{cat} and K_{m} could be extracted without the need to vary the initial concentration of the phospholipid substrate. This approach based on single liposomes and single enzyme molecules may give information on the effect of membrane morphology on reaction kinetics.



Enzyme Catalysis

M. Rabe, S. R. Tabaei, H. Zetterberg,
V. P. Zhdanov, F. Höök* 1022–1026

Hydrolysis of a Lipid Membrane by Single Enzyme Molecules: Accurate Determination of Kinetic Parameters

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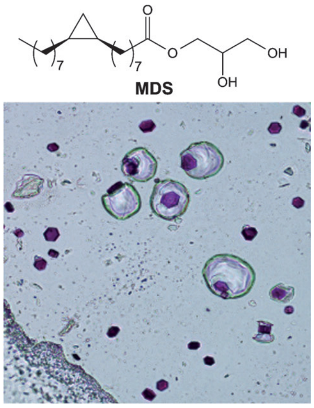
Membrane proteins: Lipidic cubic phases (LCPs) have been used as membrane-mimetic matrices to crystallize membrane proteins. A novel lipid, monodihydrosterculin (MDS; see picture) was designed and synthesized and its lipid molecular structure was correlated with the phase behavior of the ensuing mesophases. A particularly stable *Pn*3*m* cubic phase at low temperature was used to crystallize bacteriorhodopsin at 4 °C.



Lipid Synthesis

L. Salvati Manni, A. Zabara,
Y. M. Osornio, J. Schöppe, A. Batyuk,
A. Plückthun, J. S. Siegel,* R. Mezzenga,*
E. M. Landau* 1027–1031

Phase Behavior of a Designed Cyclopropyl Analogue of Monoolein: Implications for Low-Temperature Membrane Protein Crystallization

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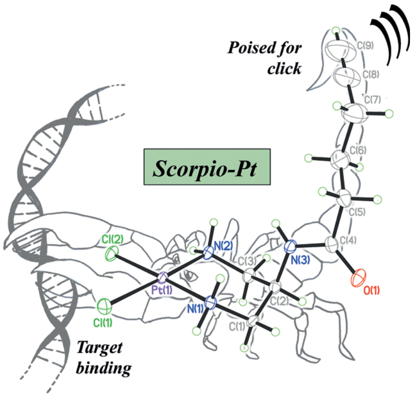
Poised for click: The alkyne-functionalized probe Scorpio-Pt, developed to investigate the cellular interactions of Pt-based therapeutics, exhibits no Pt–alkyne interactions and binds readily to DNA. Subsequent click reactivity with fluorogenic dansyl azide results in a 70-fold fluorescence increase. The Pt$^{\text{II}}$ compound exhibits an unusual solid-state arrangement, with CH/π(C$\equiv$C) interactions, Pt–Pt bonding, and NH:O/NH:Cl hydrogen bonds.



Bioorthogonal Chemistry

J. D. White, L. E. Guzman, L. N. Zakharov,
M. M. Haley, V. J. DeRose* 1032–1035

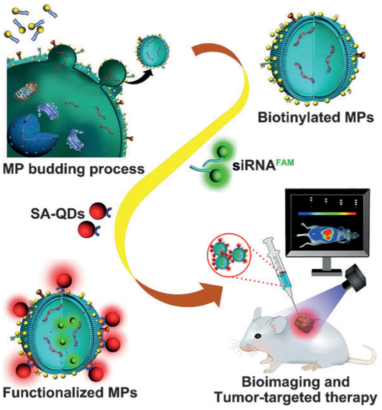
An Alkyne-Appended, Click-Ready Pt$^{\text{II}}$ Complex with an Unusual Arrangement in the Solid State

Traceable Biogenic Nanovectors

G. Chen, J. Y. Zhu, Z. L. Zhang, W. Zhang, J. G. Ren, M. Wu, Z. Y. Hong, C. Lv, D. W. Pang,* Y. F. Zhao* ___ **1036 – 1040**

Transformation of Cell-Derived Microparticles into Quantum-D'ot-Labeled Nanovectors for Antitumor siRNA Delivery

Illuminating biogenic microparticles: Cell-derived microparticles (MPs) are transformed to functionalized nanovectors by combining quantum dot (QD) labeling and efficient siRNA loading. This strategy not only reliably conferred excellent traceability and therapeutic potential on MPs, but also preserved their natural properties, thus facilitating the identification and further application of biogenic MPs. SA = streptavidin.



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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Angewandte Retraction

A Mechanochemical Approach to Deracemization

K. M. Wiggins,
C. W. Bielawski* ___________ **1640–1643**

Angew. Chem. Int. Ed. **2012**, *51*

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This Communication, first published online on January 4, 2012 in Wiley Online Library (www.wileyonlinelibrary.com), has been retracted by agreement between the corresponding author, the journal Editor in Chief, Peter Gölitz and Wiley-VCH Verlag GmbH & Co. KGaA . The retraction has been agreed since at least some of the data presented are unreliable. As part of an inquiry, a former research group member admitted to falsifying and/or fabricating data affecting this article. The action prompted a formal investigation by the Office of Research Integrity at the University of Texas at Austin, which later determined that scientific misconduct had occurred.