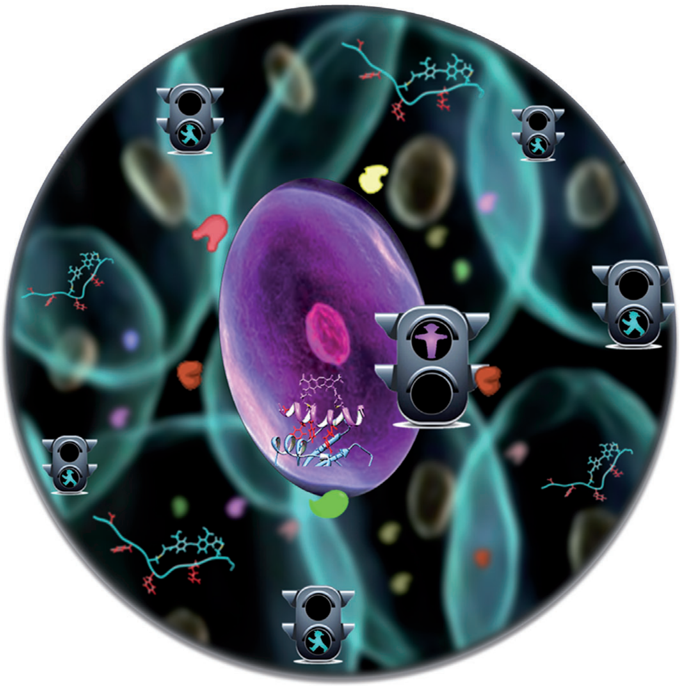
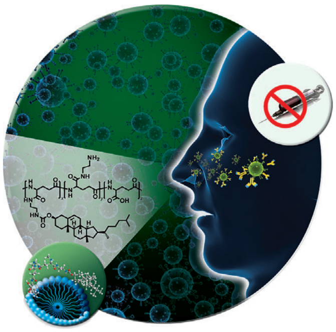
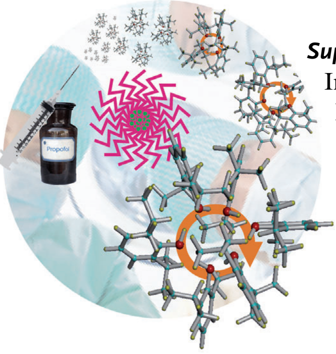
Remote control of membrane traffic …



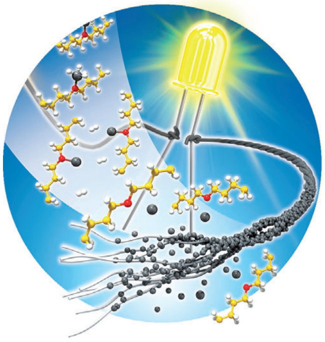
… is described by E. Giralt, P. Gorostiza, et al. in their Communication on page 7704 ff. Photoswitchable inhibitors of protein–protein interactions have been applied to photoregulate clathrin-mediated endocytosis in living cells. Traffic light peptides constitute a new tool to control cell signaling in spatiotemporally defined patterns and can be used to dissect the role of clathrin-mediated endocytosis in receptor internalization and in cell growth, division, and differentiation.



Nanomicelles
In their Communication on page 7684 ff., H. Poo, Y. T. Lim, et al. show that the intranasal administration of a mucosal vaccine system based on γ-PGA nanomicelles and viral antigens induces a high immune response.



Supramolecular Chemistry
In their Communication on page 7772 ff., J. A. Fernández et al. present a combination of spectroscopic techniques and high-level quantum-mechanical calculations for determining the structure of an inverse micelle.



Tailor-Made Electronics
In their Communication on page 7718 ff., H. M. Lee, S. H. Ko, et al. show that cotton or paper fibers can be coated with Al atoms from the precursor Al{O(C_4H_9)$_2$}. The materials can then be used in flexible and wearable electronics.

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DEUTSCHER CHEMIKER

Editorial

„... Many more metastable solids are waiting to be first identified—and identification is needed prior to exploring properties and function ...“
Read more in the Editorial by Claus Feldmann.

C. Feldmann* ______ **7610–7611**

Metastable Solids—Terra Incognita Awaiting Discovery

Service

Spotlight on Angewandte's Sister Journals ***7630–7633***

Author Profile

“What I look for first in a publication is the abstract and schemes.
The most important thing I learned from my parents is to work hard. …”
This and more about Janine Cossy can be found on page 7634–7635.

Janine Cossy ______ **7634–7635**

News


R. N. Zare


F. Besenbacher


G. Bellussi


C. W. Jones


E. V. Anslyn


T. Ogoshi

International Scientific and Technological Cooperation Award of the People's Republic of China:
R. N. Zare and F. Besenbacher ____ **7636**

Eugene J. Houdry Award:
G. Bellussi ____ **7636**

Paul H. Emmett Award:
C. W. Jones ____ **7636**

Awards at the International Symposium on Macrocyclic and Supramolecular Chemistry:
E. V. Anslyn and T. Ogoshi Honored ____ **7636**

Books

Acids and Bases　Brian G. Cox　*reviewed by R. A. Cox* ____ **7638**

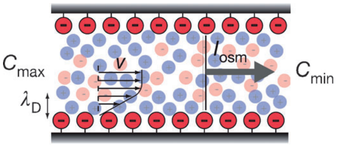
Highlights

Energy Harvesting

L. Zhang, X. Chen* ____ **7640 – 7641**

Nanofluidics for Giant Power Harvesting

Nanochannels for power generation: The confinement of fluid motion in a single boron nitride nanotube can provide an efficient means of power harvesting owing to the osmotically driven streaming current under a salt concentration difference (see picture). Devices based on this principle may open a new avenue in the exploration for new sources of renewable energy.



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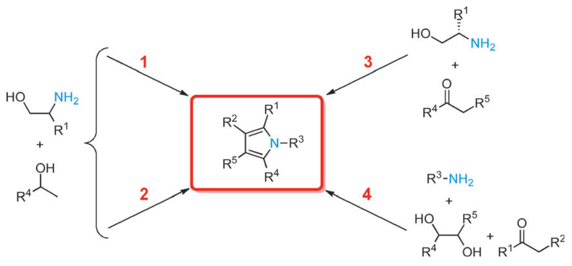


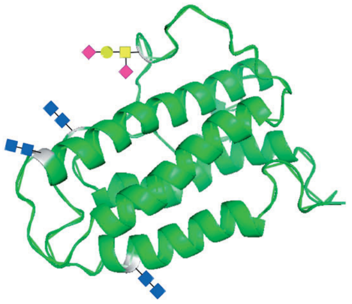
Heterocycles made green: New methodologies for the synthesis of pyrroles were recently developed based on domino Ir- and Ru-catalyzed amination and alkylations of alcohols. The concept provides a greener approach to interesting N-heterocyclic compounds.

Sustainable Chemistry

J. Schranck, A. Tlili,
M. Beller* ________ 7642 – 7644

More Sustainable Formation of C—N and C—C Bonds for the Synthesis of N-Heterocycles

Minireviews


Erythropoietin

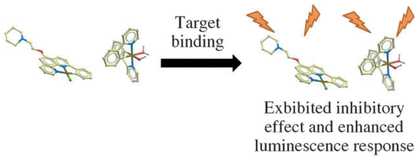
Going native: The total synthesis of a homogeneous erythropoietin, possessing the native amino acid sequence and chitobiose glycans at each of the three wild-type sites of N glycosylation, has been accomplished. Herein is an account of the decade-long research effort en route to this formidable target compound.

Total Synthesis

R. M. Wilson, S. Dong, P. Wang,
S. J. Danishefsky* ________ 7646 – 7665

The Winding Pathway to Erythropoietin Along the Chemistry–Biology Frontier: A Success At Last

Reviews



Metal-based theranostics: This Review highlights recent examples of biologically active luminescent metal complexes that can target and probe a specific biomolecule, and offers insight into the future potential of luminescent metal-based therapeutics for the investigation and treatment of human diseases.

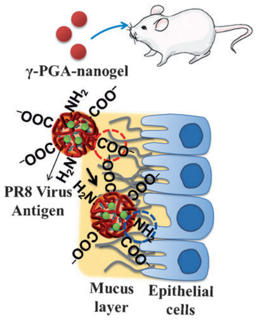
Bioorganometallic Chemistry

D.-L. Ma,* H.-Z. He, K.-H. Leung,
D. S.-H. Chan, C.-H. Leung _ 7666 – 7682

Bioactive Luminescent Transition-Metal Complexes for Biomedical Applications

Communications

Micelles for mucosal immunity: A mucosal vaccine system based on γ-PGA nanomicelles and viral antigens was synthesized. The intranasal administration of the vaccine system induces a high immune response both in the humoral and cellular immunity (see picture).

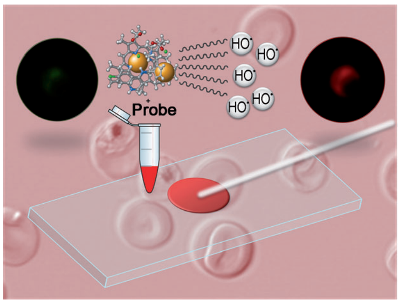


Bioorganic Chemistry

Y.-W. Noh, J. H. Hong, S.-M. Shim,
H. S. Park, H. H. Bae, E. K. Ryu,
J. H. Hwang, C.-H. Lee, S. H. Cho,
M.-H. Sung, H. Poo,*
Y. T. Lim* ________ 7684 – 7689

Polymer Nanomicelles for Efficient Mucus Delivery and Antigen-Specific High Mucosal Immunity

Frontispiece

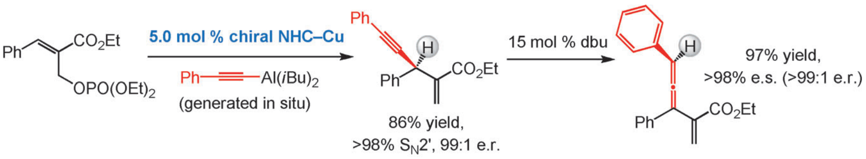


Metal health: Ferroquine is a ferrocene-based analogue of the antimalarial drug chloroquine. In addition to the primary mechanism of quinoline action, fluorescent probe studies in infected red blood cells show another mechanism is at work. It is based on the production of HO• in the acidic and oxidizing environment of the digestive vacuole of the malaria parasite and implies that, with ferroquine, reinvasion can be inhibited.

Bioorganometallics

F. Dubar, C. Slomianny, J. Khalife, D. Dive,
H. Kalamou, Y. Guérardel, P. Grellier,
C. Biot* ________ **7690 – 7693**

The Ferroquine Antimalarial Conundrum: Redox Activation and Reinvasion Inhibition

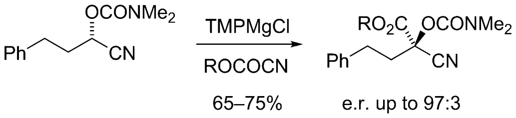


All-catalytic route to trisubstituted allenes: The first examples of catalytic enantioselective allylic substitution reactions that involve alkyne-based nucleophiles and lead to products having tertiary stereogenic centers are followed by an exceptionally stereospecific amine-catalyzed isomerization to trisubstituted allenes (see picture; NHC = N-heterocyclic carbene).

Enantioselective Catalysis

J. A. Dabrowski, F. Haeffner,
A. H. Hoveyda* ________ **7694 – 7699**

Combining NHC–Cu and Brønsted Base Catalysis: Enantioselective Allylic Substitution/Conjugate Additions with Alkynylaluminum Reagents and Stereospecific Isomerization of the Products to Trisubstituted Allenes

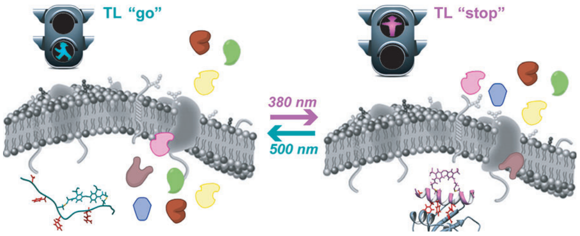


Quaternary stereocenters: Chiral α-magnesiated nitriles can be formed by deprotonation and are configurationally stable at low temperature, even for acyclic examples. These can be trapped with electrophiles to give enantiomerically enriched quaternary substituted products (see scheme; TMP = 2,2,6,6-tetramethylpiperidine).

Asymmetric Synthesis

G. Barker, M. R. Alshawish, M. C. Skilbeck,
I. Coldham* ________ **7700 – 7703**

Remarkable Configurational Stability of Magnesiated Nitriles



Control of membrane traffic: Photoswitchable inhibitors of protein–protein interactions were applied to photoregulate clathrin-mediated endocytosis (CME) in living cells. Traffic light (TL) peptides acting as "stop" and "go" signals for membrane traffic can be used to dissect the role of CME in receptor internalization and in cell growth, division, and differentiation.

Optopharmacology

L. Nevola, A. Martín-Quirós, K. Eckelt,
N. Camarero, S. Tosi, A. Llobet, E. Giralt,*
P. Gorostiza* ________ **7704 – 7708**

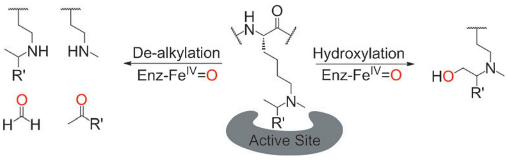
Light-Regulated Stapled Peptides to Inhibit Protein–Protein Interactions Involved in Clathrin-Mediated Endocytosis

Front Cover

Demethylases/Hydroxylases

R. J. Hopkinson, L. J. Walport, M. Münzel, N. R. Rose, T. J. Smart, A. Kawamura, T. D. W. Claridge, C. J. Schofield* ____ 7709 – 7713

Is JmjC Oxygenase Catalysis Limited to Demethylation?

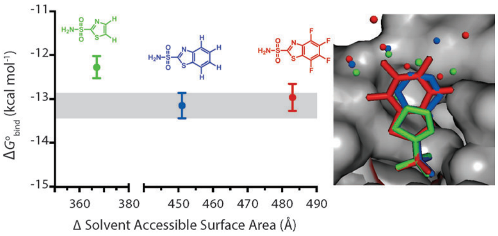


Jobs on the side: Substrate selectivity studies indicate that members of the biomedically important JmjC demethylase family of histone N^{ε}-methyllysine demethylases are capable of catalyzing the de-*N*-alkylation of groups other than *N*-methyl and can catalyze reactions that form stable hydroxylated products. The differences in binding preferences in this set of enzymes may be helpful in the design of selective inhibitors.

Protein–Ligand Binding

M. R. Lockett, H. Lange, B. Breiten, A. Heroux, W. Sherman, D. Rappoport, P. O. Yau, P. W. Snyder, G. M. Whitesides* ____ 7714 – 7717

The Binding of Benzoarylsulfonamide Ligands to Human Carbonic Anhydrase is Insensitive to Formal Fluorination of the Ligand



It's the water that matters. Pairs of benzo- and perfluorobenzoarylsulfonamide ligands bind to human carbonic anhydrase with a conserved binding geometry, an enthalpy-driven binding, and indistinguishable binding affinities (see picture). These data support the pervasive theory that the lock-and-key model disregards an important component of binding: the water, which fills the binding pocket of the protein and surrounds the ligand.

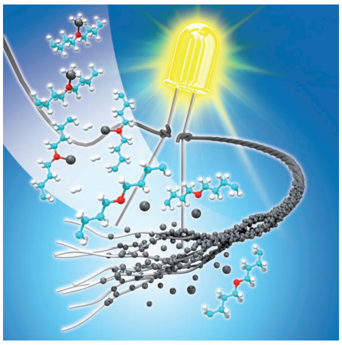
Conductive Fibrous Materials

H. M. Lee,* S.-Y. Choi, A. Jung, S. H. Ko* ____ 7718 – 7723

Highly Conductive Aluminum Textile and Paper for Flexible and Wearable Electronics

Back Cover

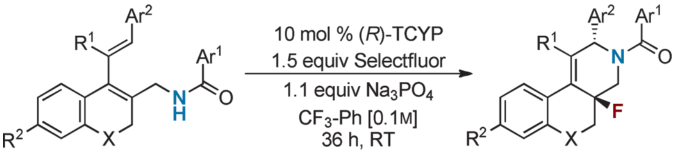
Light to wear: Aluminum coated fibrous materials with excellent electrical conductivity and mechanical endurance are fabricated at room temperature by a chemical solution process. The resulting aluminum-coated conductive papers and threads can be used in electric circuits for flexible and wearable electronics.



Asymmetric Fluorination

H. P. Shunatona, N. Früh, Y.-M. Wang, V. Rauniyar, F. D. Toste* ____ 7724 – 7727

Enantioselective Fluoroamination: 1,4-Addition to Conjugated Dienes Using Anionic Phase-Transfer Catalysis



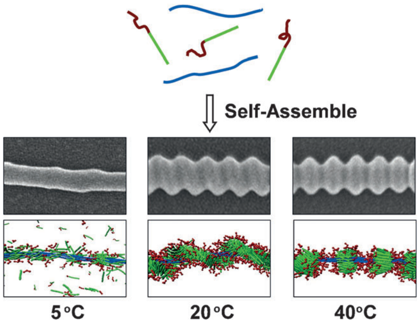
Chiral-anion phase-transfer catalysis (PTC) has been applied towards the enantioselective fluorocyclization reactions of 1,3-dienes. The method affords unprecedented fluorinated benz[*f*]isoquinoline and octahydroisoquinoline products in high yields and up to 96% *ee*. New fluorinated amine reagents outperformed Selectfluor in the desired transformation.

Where there's a wheel, there's a way: The terpyridine-based title system has been synthesized through a facile self-assembly process. Two tris(terpyridine) ligands possessing angles of either 120° or 60° between adjacent tpy units were mixed with a stoichiometric amount of Zn^{2+} (2:6:12) to generate the desired coordination-driven bicycle-like wheel (90% yield).

3D Metallomacrocycles

X. Lu, X. Li, Y. Cao, A. Schultz, J.-L. Wang,
C. N. Moorefield, C. Wesdemiotis,*
S. Z. D. Cheng,
G. R. Newkome* ———— **7728 – 7731**

Self-Assembly of a Supramolecular, Three-Dimensional, Spoked, Bicycle-like Wheel

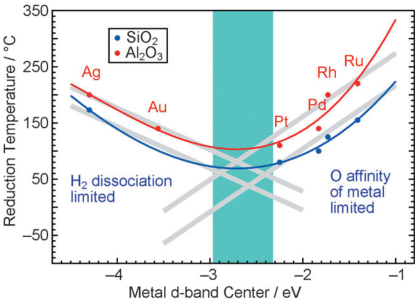


As you like it: The synthesis of supramolecular hierarchical nanostructures with designed morphologies has been realized through computer-simulation-guided multicomponent assembly of polypeptide-based block copolymers and homopolymers. By adjusting the attraction between hydrophobic polypeptide rods, as well as other parameters such as the molar ratio of copolymers and the rigidity of polymers, a variety of morphologies were obtained.

Hierarchical Assembly

C. Cai, Y. Li, J. Lin,* L. Wang, S. Lin,
X.-S. Wang,* T. Jiang ———— **7732 – 7736**

Simulation-Assisted Self-Assembly of Multicomponent Polymers into Hierarchical Assemblies with Varied Morphologies

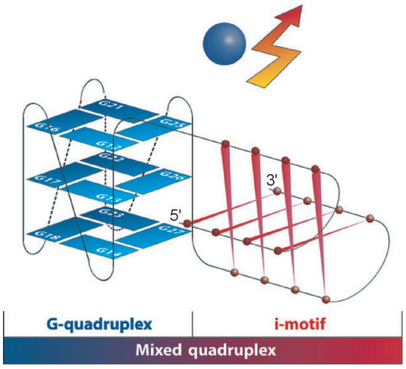


A correlation between ceria reducibility and the precious-metal d-band center is reported for ceria-supported precious-metal catalysts. The results could provide the missing link to fully explain the occurrence of strong metal–support interaction (SMSI) and hydrogen spillover in catalysts that consist of dispersed metals in contact with reducible metal oxides.

Supported Catalysts

N. Acerbi,* S. C. E. Tsang,* G. Jones,
S. Golunski, P. Collier ———— **7737 – 7741**

Rationalization of Interactions in Precious Metal/Ceria Catalysts Using the d-Band Center Model



Peaceful coexistence: A double quadruplex composed of an i-motif and a G-quadruplex was constructed within one oligonucleotide strand (see picture). The defined double-quadruplex structure can serve as a NOTIF logic gate on the basis of the fluorescence of crystal violet.

Quadruplex Formation

J. Zhou, S. Amrane, D. N. Korkut,
A. Bourdoncle, H.-Z. He, D. Ma,
J. L. Mergny* ———— **7742 – 7746**

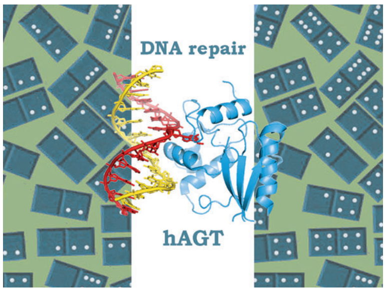
Combination of i-Motif and G-Quadruplex Structures within the Same Strand: Formation and Application

Biosensors

M. Tintoré, I. Gállego, B. Manning, R. Eritja, C. Fàbrega* ——— 7747 – 7750

DNA Origami as a DNA Repair Nanosensor at the Single-Molecule Level

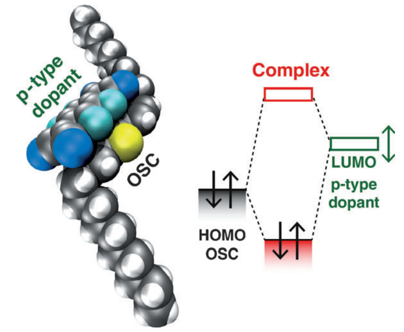
The folding of DNA molecules by DNA origami is used in a nanosensor to analyze enzymatic DNA repair activity of hAGT. The method uses conformational changes that condition α-thrombin interaction with DNA aptamers, and illustrates the use of DNA origami as a protein-recognition biosensor.



Organic Semiconductors

H. Méndez, G. Heimel,* A. Opitz, K. Sauer, P. Barkowski, M. Oehzelt, J. Soeda, T. Okamoto, J. Takeya, J.-B. Arlin, J.-Y. Balandier, Y. Geerts, N. Koch, I. Salzmann* ——— 7751 – 7755

Doping of Organic Semiconductors: Impact of Dopant Strength and Electronic Coupling

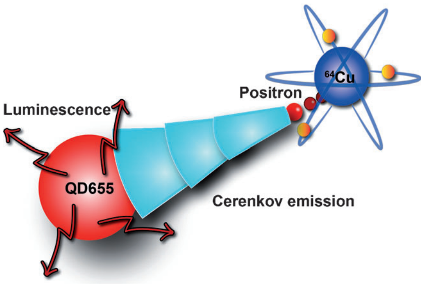


Molecular doping: The standard model for molecular p-doping of organic semiconductors (OSCs) assumes integer charge transfer between OSC and dopant. This is in contrast to an alternative model based on intermolecular complex formation instead. By systematically varying the acceptor strength it was possible to discriminate the two models. The latter is clearly favored, suggesting strategies for the chemical design of more efficient molecular dopants.

Luminescent Probes

N. Kotagiri, D. M. Niedzwiedzki, K. Ohara, S. Achilefu* ——— 7756 – 7760

Activatable Probes Based on Distance-Dependent Luminescence Associated with Cerenkov Radiation

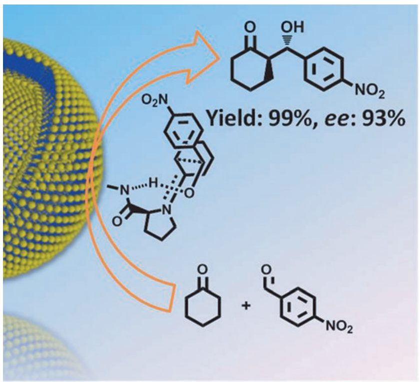


Let me get my nanoruler: Activatable probes based on radionuclide and quantum dots (QDs) were constructed using DNA as a linker. Cerenkov radiation from ^{64}Cu was used to excite the QDs in a distance-dependent manner. The luminescence was lowest nearest to the QD and increased with distance.

Supramolecular Catalysis

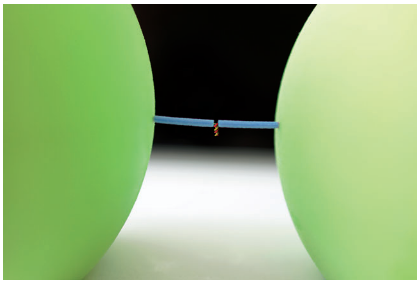
L. Qin, L. Zhang,* Q. X. Jin, J. L. Zhang,* B. X. Han, M. H. Liu* ——— 7761 – 7765

Supramolecular Assemblies of Amphiphilic L-Proline Regulated by Compressed CO_2 as a Recyclable Organocatalyst for the Asymmetric Aldol Reaction



Compressed CO_2 triggers the formation of amphiphilic proline supramolecular assemblies in water, which catalyze the asymmetric aldol reaction without any additives. Compressed CO_2 can dynamically regulate the size of the assemblies and subsequently the catalyst activity and selectivity. Furthermore, CO_2 provides the merit of easy separation and purification, making the process sustainable and recyclable.

Bridging the gap: Rigid DNA linkers (blue, see picture) between microspheres (green) for high-resolution single-molecule mechanical experiments were constructed using DNA origami. The resulting DNA helical bundles greatly reduce the noise generated in studies of conformation changes using optical tweezers and were applied to study small DNA secondary structures.



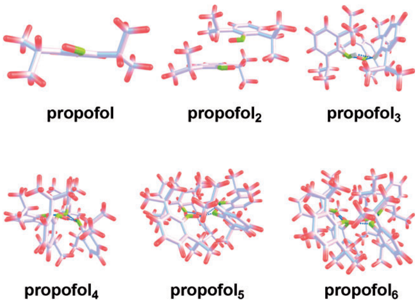
DNA Nanotechnology

E. Pfitzner, C. Wachauf, F. Kilchherr, B. Pelz, W. M. Shih, M. Rief, H. Dietz* ________ **7766 – 7771**

Rigid DNA Beams for High-Resolution Single-Molecule Mechanics

---

A subtle interplay: In the formation of a 1.6 nm micelle containing up to six molecules of propofol, a hydrogen-bond network is shown to influence the structure of the micelle, whereas the nonpolar groups arrange in such a way that the remaining noncovalent interactions are maximized. Such globular structures present a characteristic signature in the IR spectrum that will allow their identification in more complex media.



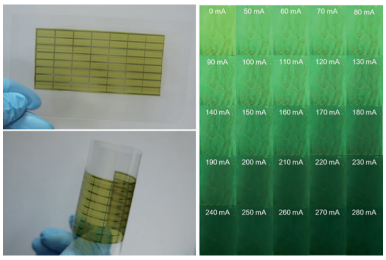
Supramolecular Chemistry

I. León, J. Millán, E. J. Cocinero, A. Lesarri, J. A. Fernández* ________ **7772 – 7775**

Shaping Micelles: The Interplay Between Hydrogen Bonds and Dispersive Interactions

Inside Back Cover

Making sense: A novel polyacetylene composite material with incorporated aligned carbon nanotubes shows rapid changes in both fluorescent intensity and color appearance in response to applied electric currents, and these electrochromatic transitions remain reversible even after a thousand cycles. The composite material is anticipated to be suitable for various other sensing applications.



Sensor Materials

X. Sun, Z. Zhang, X. Lu, G. Guan, H. Li, H. Peng* ________ **7776 – 7780**

Electric Current Test Paper Based on Conjugated Polymers and Aligned Carbon Nanotubes

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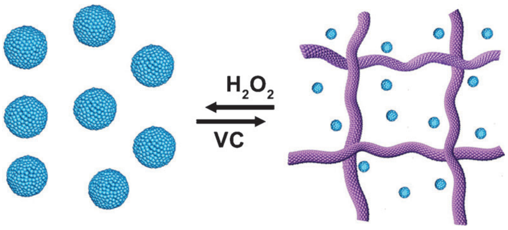


Mimicking nature: The reversible formation of self-assembled nanostructures of selenium-containing peptides can be controlled by redox triggers (see scheme, VC = vitamin C). As a consequence, the catalytic activity of these peptides is switchable. These results should lead to the development of nature-mimicking smart materials with promising properties.

Self-Assembly

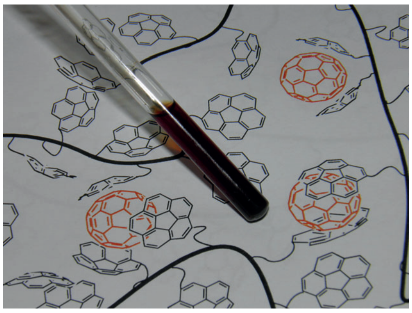
X. Miao, W. Cao, W. Zheng, J. Wang, X. Zhang, J. Gao, C. Yang, D. Kong,* H. Xu,* L. Wang, Z. Yang* _ **7781 – 7785**

Switchable Catalytic Activity: Selenium-Containing Peptides with Redox-Controllable Self-Assembly Properties

Polymer Receptors

M. C. Stuparu* ______ 7786 – 7790

Rationally Designed Polymer Hosts of Fullerene



A class of its own: A new class of fullerene C_{60} hosts—polymeric in nature—has been developed by careful design of the molecular structure of the polymer repeat unit and the mode of interaction between the repeat unit and C_{60} (see picture). As these hosts are synthesized by free-radical polymerization, polymer hosts with various chemical compositions and architectures can be constructed readily by appropriate design of the receptor monomer.

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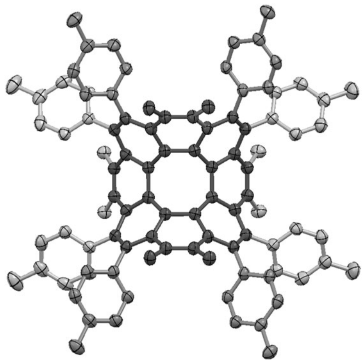
[8]Circulenes

C.-N. Feng, M.-Y. Kuo,
Y.-T. Wu* ______ 7791 – 7794

Synthesis, Structural Analysis, and Properties of [8]Circulenes

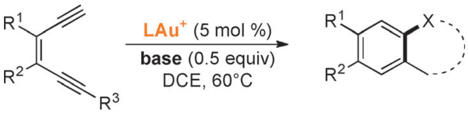
Polygons: [8]Circulenes were easily prepared by Pd-catalyzed annulations of tetraiodotetraphenylenes with alkynes. Their saddle-shaped structure with an [8]radialene character was identified by X-ray crystallography. Similar to 1,3,5,7-cyclooctatetraene, they have a tub-shaped eight-membered ring, but all of the bond lengths and bond angles are almost equal. Variable-temperature NMR investigations showed interesting dynamic behavior.



Homogeneous Catalysis

Y. Wang, A. Yepremyan, S. Ghorai, R. Todd, D. H. Aue,* L. Zhang* ______ 7795 – 7799

Gold-Catalyzed Cyclizations of *cis*-Enediynes: Insights into the Nature of Gold–Aryne Interactions

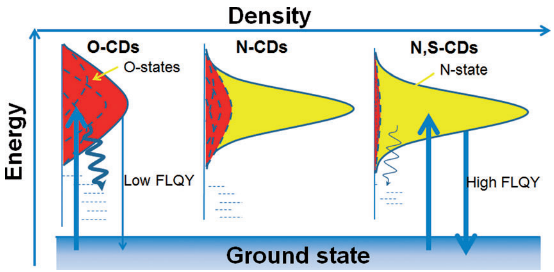


Golden aryne? Gold aryne complexes are inferred as transition states in dual gold-catalyzed cyclizations of *cis*-enediynes (see scheme; DCE = 1,2-dichloroethane). They are better described as *ortho*-aurophenyl cations, which react with weak nucleophiles and undergo facile intramolecular insertions into C(sp^3)−H bonds. Indanes, fused heteroarenes, and phenol derivatives are readily prepared using this method.

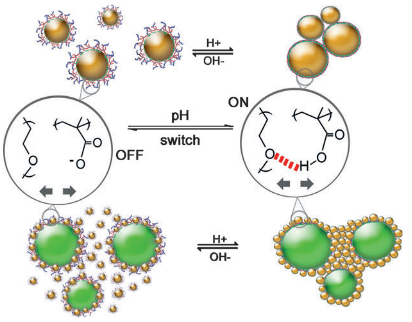
Quantum Dots

Y. Dong, H. Pang, H. B. Yang, C. Guo, J. Shao, Y. Chi, C. M. Li,*
T. Yu* ______ 7800 – 7804

Carbon-Based Dots Co-doped with Nitrogen and Sulfur for High Quantum Yield and Excitation-Independent Emission



Helpful elements: A facile bottom-up method using citric acid and L-cysteine as a precursor has been developed to prepare graphene quantum dots (GQDs) co-doped with nitrogen and sulfur. A new type and high density of surface state of GQDs arises, leading to high yields (more than 70%) and excitation-independent emission. FLQY = fluorescence quantum yield.



Particle get-together: Surface functionalization with a branched copolymer surfactant is used to create responsive inorganic particles that can self-assemble in complex structures. The assembly process is triggered by a pH switch that reversibly activates multiple hydrogen bonds between ceramic particles (see picture; yellow) and soft templates (*n*-decane; green).

Complex Ceramic Structures

E. Garcia-Tunon,* S. Barg, R. Bell,
J. V. M. Weaver, C. Walter, L. Goyos,
E. Saiz ________ **7805 – 7808**

Designing Smart Particles for the Assembly of Complex Macroscopic Structures

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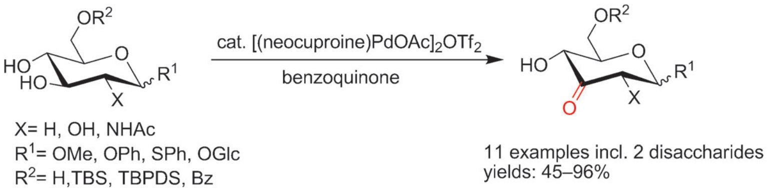
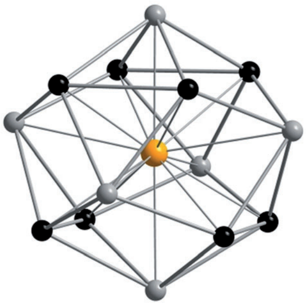


Discrimination among equals: A catalytic method for the selective oxidation of unprotected glycosides, both monosaccharides and disaccharides, has been developed. The resulting ketosaccharides are isolated in moderate to excellent yields. This approach provides a basis for protecting-group-free synthetic transformations of carbohydrates.

Synthetic Methods

M. Jäger, M. Hartmann, J. G. de Vries,*
A. J. Minnaard* ________ **7809 – 7812**

Catalytic Regioselective Oxidation of Glycosides

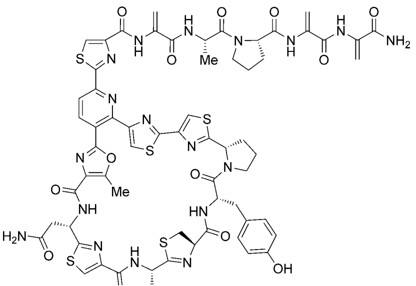


Heart of gold (or silver): The pseudo-D_{2d} distorted MPd$_{14}$ cubic kernel of $[(\mu_{14}\text{-M})Pd_{22}(CO)_{20}(PEt_3)_8]^+$ cations, with M = Au (**1**), Ag (**2**), has an encapsulated M atom (see picture; yellow) coordinated to eight cubic corner (black) and six face-capping Pd atoms (gray). Compounds **1** and **2** were obtained (28–60% yields) from two-step/one-pot reactions of a Pd$_{10}$ precursor with CF_3CO_2H followed by coinage-metal ion exchange of protons.

Metal Clusters

E. G. Mednikov,*
L. F. Dahl* ________ **7813 – 7817**

Ion Exchange of Protons by Coinage Metals to Give Gold and Silver Encapsulation within a Pseudo-D_{2d} Distorted Face-Capped Pd$_{14}$ Cubic Kernel: $[(\mu_{14}\text{-M})Pd_{22}(CO)_{20}(PEt_3)_8]^+$ (M = Au, Ag)



Baringolin

The thiopeptide antibiotic baringolin has been synthesized, and its structure and stereochemistry have been confirmed. The use of a strategy based on palladium-catalyzed cross-couplings permitted a modular construction of this natural product.

Natural Products

X. Just-Baringo, P. Bruno, L. K. Ottesen,
L. M. Cañedo, F. Albericio,*
M. Álvarez* ________ **7818 – 7821**

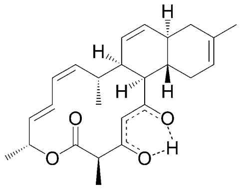
Total Synthesis and Stereochemical Assignment of Baringolin

Natural Products

K. H. Jang, S.-J. Nam, J. B. Locke, C. A. Kauffman, D. S. Beatty, L. A. Paul, W. Fenical* ______ **7822 – 7824**

Anthracimycin, a Potent Anthrax Antibiotic from a Marine-Derived Actinomycete

Licensed to kill: A new antibiotic, anthracimycin (see scheme), produced by a marine-derived actinomycete in saline culture, shows significant activity toward *Bacillus anthracis*, the bacterial pathogen responsible for anthrax infections. Chlorination of anthracimycin gives a dichloro derivative that retains activity against Gram-positive bacteria, such as anthrax, but also shows activity against selected Gram-negative bacteria.

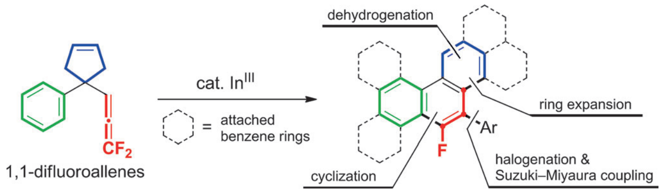


Anthracimycin

Arenes

K. Fuchibe, Y. Mayumi, N. Zhao, S. Watanabe, M. Yokota, J. Ichikawa* ______ **7825 – 7828**

Domino Synthesis of Fluorine-Substituted Polycyclic Aromatic Hydrocarbons: 1,1-Difluoroallenes as Synthetic Platforms

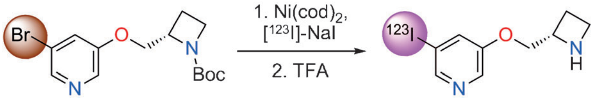


Rather crafty: 1,1-Difluoroallenes bearing an aryl group and a cyclopentene moiety undergo indium(III)-catalyzed Friedel–Crafts-type cyclization with subsequent ring expansion and dehydrogenation to afford fluorinated polycyclic aromatic hydrocarbons in high yields. The introduction of an Ar group was effected by in situ halogenation of the intermediary indium species and a subsequent Suzuki–Miyaura reaction.

Radiochemistry

A. A. Cant, S. Champion, R. Bhalla, S. L. Pimlott, A. Sutherland* ______ **7829 – 7832**

Nickel-Mediated Radioiodination of Aryl and Heteroaryl Bromides: Rapid Synthesis of Tracers for SPECT Imaging

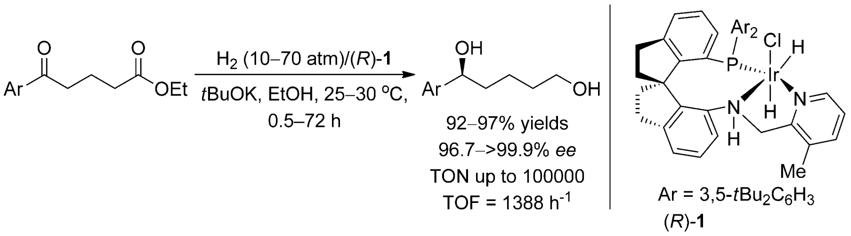


Rapid and efficient radioiodination of aryl and heteroaryl bromides has been achieved using a nickel(0)-mediated halogen-exchange reaction. This transformation gives direct access to [^{123}I]- and [^{125}I]-imaging agents for single photon emission computed tomography (SPECT), such as 5-[^{123}I]-A85380 (see scheme, Boc = *tert*-butyloxycarbonyl, cod = 1,5-cyclooctadiene, TFA = trifluoroacetic acid).

Asymmetric Catalysis

X.-H. Yang, J.-H. Xie,* W.-P. Liu, Q.-L. Zhou* ______ **7833 – 7836**

Catalytic Asymmetric Hydrogenation of δ-Ketoesters: Highly Efficient Approach to Chiral 1,5-Diols

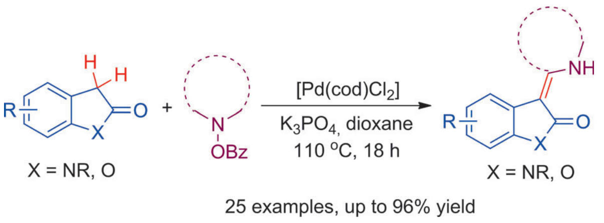


High turnover: An highly efficient catalytic asymmetric hydrogenation of δ-aryl-δ-ketoesters has been realized by using the chiral spiroiridium catalyst (*R*)-**1**. Chiral 1,5-diol products are obtained with excellent enantioselectivity and turnover numbers (TONs) as high as 100 000. TOF = turnover frequency.

Oxidative Cross-Coupling

G. Li, S. Qian, C. Wang,
J. You* ________________ **7837 – 7840**

Palladium(II)-Catalyzed Dehydrogenative Cross-Coupling between Two C_{sp^3}–H Bonds: Unexpected C=C Bond Formation

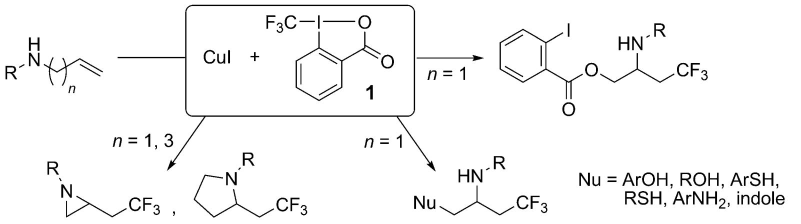


C=C bond construction: A palladium-catalyzed oxidative C_{sp^3}–H/C_{sp^3}–H cross-coupling is shown to forge C=C bonds rather than C_{sp^3}–C_{sp^3} bonds through reactions of indolin-2-ones or benzofuran-2-ones with *O*-benzoyl hydroxylamines in the absence of an added oxidant.

Trifluoromethylation

H. Egami, S. Kawamura, A. Miyazaki,
M. Sodeoka* ________________ **7841 – 7844**

Trifluoromethylation Reactions for the Synthesis of β-Trifluoromethylamines

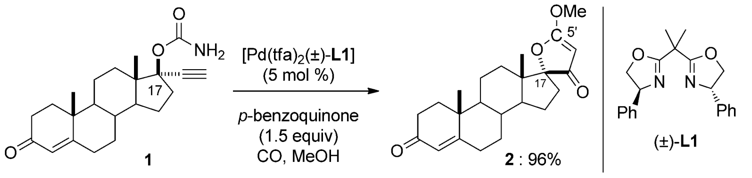


A multitalented system: *N*-Migratory oxytrifluoromethylation and one-pot three-component reactions of allylamines as well as the aminotrifluoromethylation of alkenyl amines all proceeded efficiently in the presence of the Togni reagent (**1**) and CuI to afford a variety of β-trifluoromethylamine derivatives (see scheme).

Synthetic Methods

T. Kusakabe, T. Takahashi, R. Shen,
A. Ikeda, Y. D. Dhage, Y. Kanno, Y. Inouye,
H. Sasai, T. Mochida,
K. Kato* ________________ **7845 – 7849**

Carbonylation of Propargyl Carbamates with Palladium(II) Bisoxazoline Catalysts: Efficient Synthesis of 5-Methoxy-3(2*H*)-furanones

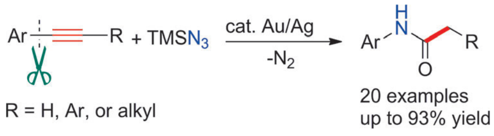


Palladium and CO: Carbonylation of **1** with [Pd(tfa)$_2$(±)-**L1**] (tfa = trifluoroacetate) affords the spirofuranone **2** with inversion of the stereochemistry at C17 in 96% yield. C17-*epi*-**1** also gave the same product **2** with retention of the stereochemistry at C17. Labelling studies show that ^{13}CO was incorporated into the C5′ position of the furanone ring. The first asymmetric version of this new reaction was achieved.

C–C Bond Cleavage

C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang,
N. Jiao* ________________ **7850 – 7854**

Selective C_{sp^2}–C_{sp} Bond Cleavage: The Nitrogenation of Alkynes to Amides

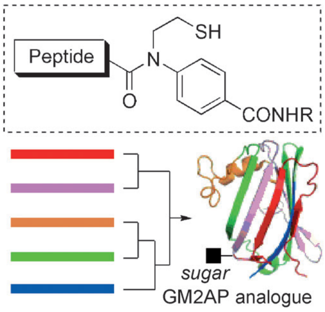


Breakthrough: A novel catalyzed direct highly selective C_{sp^2}–C_{sp} bond functionalization of alkynes to amides has been developed. Nitrogenation is achieved by the highly selective C_{sp^2}–C_{sp} bond cleavage of aryl-substituted alkynes. The oxidant-free and mild conditions and wide substrate scope make this method very practical.

Synthesis Design

K. Sato, A. Shigenaga, K. Kitakaze,
K. Sakamoto, D. Tsuji, K. Itoh,
A. Otaka* ________ 7855 – 7859

Chemical Synthesis of Biologically Active Monoglycosylated GM2-Activator Protein Analogue Using *N*-Sulfanylethylanilide Peptide



Going to SEA(lide): Total chemical synthesis of a 162-residue glycoprotein analogue of the monoglycosylated human GM2-activator protein (GM2AP) was achieved. Key steps were the use of *N*-sulfanylethylanilide (SEAlide) peptides in the kinetic chemical ligation synthesis of a large peptide fragment, and a convergent native chemical ligation for final fragment assembly.

Photoredox Catalysis

X. Wang,* G. D. Cuny,*
T. Noël* ________ 7860 – 7864

A Mild, One-Pot Stadler–Ziegler Synthesis of Arylsulfides Facilitated by Photoredox Catalysis in Batch and Continuous-Flow

$$\text{R-SH} + \text{Ar-NH}_2 \xrightarrow[t\text{BuONO, acid (cat.), MeCN, RT}]{\text{photoredox catalyst, visible light}} \text{R-S-Ar}$$

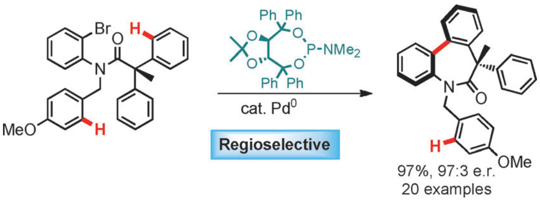
– Minimum formation of diazosulfide
– In continuous-flow: 15 s to completion

Visible advance: A mild, one-pot Stadler–Ziegler process for C–S bond formation has been developed. The method employs the photoredox catalyst $[\text{Ru(bpy)}_3\text{Cl}_2]\cdot 6\,\text{H}_2\text{O}$ irradiated with visible light. A variety of aryl–alkyl and diaryl sulfides were prepared from readily available arylamines and aryl/alkylthiols in good yields. The use of a photo microreactor led to a significant improvement with respect to safety and efficiency.

C–H Activation

T. Saget, N. Cramer* ________ 7865 – 7868

Enantioselective C–H Arylation Strategy for Functionalized Dibenzazepinones with Quaternary Stereocenters

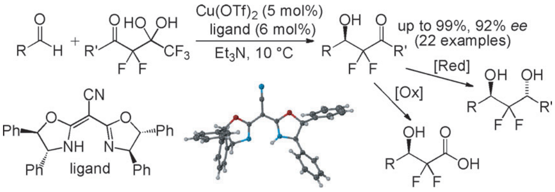


Tada! Highly functionalized chiral dibenzazepinones are obtained by a mild palladium(0)-catalyzed enantioselective C–H arylation with excellent selectivities by using simple taddol phosphoramidite ligands. The amide tether allows exclusive regioselectivity through a rare eight-membered palladacycle intermediate.

Asymmetric Catalysis

P. Zhang, C. Wolf* ________ 7869 – 7873

Catalytic Enantioselective Difluoroalkylation of Aldehydes



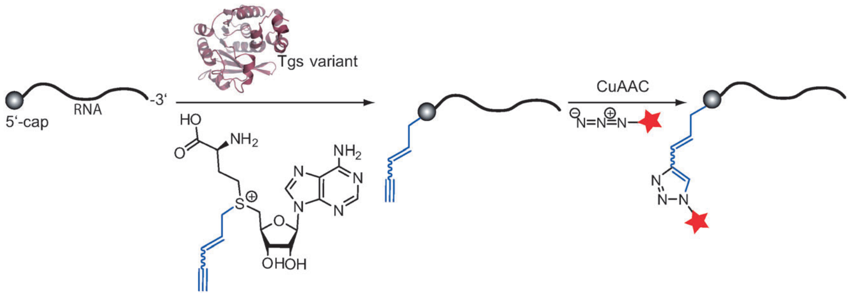
Copper-catalyzed bond scission of pentafluorobutane-1,3-diones generates difluoroenolates that react with aldehydes to give a wide range of chiral α,α-difluoro-β-hydroxy ketones within a few hours in up to 99% yield and 92% *ee*. The synthetic utility of this reaction is demonstrated with the stereoselective synthesis of a chiral *anti*-1,3-diol exhibiting a central difluoromethylene unit and efficient conversion to a 2,2-difluoro-3-hydroxy carboxylic acid.

Messenger RNA

D. Schulz, J. M. Holstein,
A. Rentmeister* ________ 7874 – 7878

A Chemo-Enzymatic Approach for Site-Specific Modification of the RNA Cap

Inside Cover

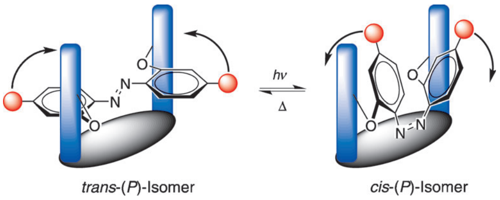


Capped and gowned: A two-step approach can be used to site-specifically modify the 5′-cap of eukaryotic mRNAs. First, a trimethylguanosinesynthase variant recognizes the m^7G cap structure and introduces bioorthogonal groups using *S*-adenosyl-L-methionine-based cosubstrates. Then, the enzymatically introduced reporter groups are further modified by thiol–ene or CuAAC click chemistry (see scheme).

Molecular Switches

G. Haberhauer,* C. Kallweit, C. Wölper,
D. Bläser ________ 7879 – 7882

An Azobenzene Unit Embedded in a Cyclopeptide as a Type-Specific and Spatially Directed Switch

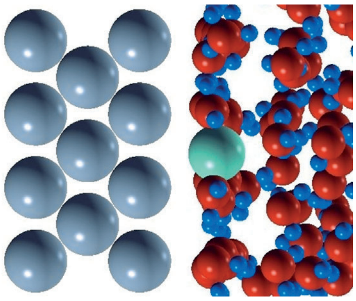


By embedding an azobenzene unit into a chiral scaffold, switching of azobenzene from the *trans*-(P) isomer to the *cis*-(P) isomer and back was achieved (black arrows in picture). The embedding leads to a flipping process in which the phenyl rings can only move directly towards one another in the switching process.

Electrochemistry

L. M. C. Pinto, E. Spohr, P. Quaino,
E. Santos, W. Schmickler* __ 7883 – 7885

Why Silver Deposition is so Fast: Solving the Enigma of Metal Deposition



A perfect match: Silver deposition is one of the fastest electrochemical reactions, even though the Ag^+ ion loses more than 5 eV solvation energy in the process. This phenomenon, an example of the enigma of metal deposition, was investigated by a combination of MD simulations, DFT, and specially developed theory. At the surface, the Ag^+ ion experiences a strong interaction with the sp band of silver, which catalyzes the reaction.

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 Corrigendum

Dendritic Luminescent Gold(III) Complexes for Highly Efficient Solution-Processable Organic Light-Emitting Devices

M.-C. Tang, D. P.-K. Tsang,
M. M.-Y. Chan,* K. M.-C. Wong,
V. W.-W. Yam* ______ **446–449**

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

DOI: 10.1002/anie.201206457

In the fourth paragraph of this Communication, the reduction potentials for the alkynylgold(III) complexes **1–3** in dichloromethane (0.1 mol dm^{-3} nBu$_4$NPF$_6$) were incorrectly given as +0.94 V, +1.05 V, and +1.12 V, respectively, versus saturated calomel electrode (SCE). The correct values are +0.83 V, +0.94 V, and +1.06 V versus SCE, which are given correctly in the fifth paragraph. This error does not affect the results and conclusions in the manuscript.