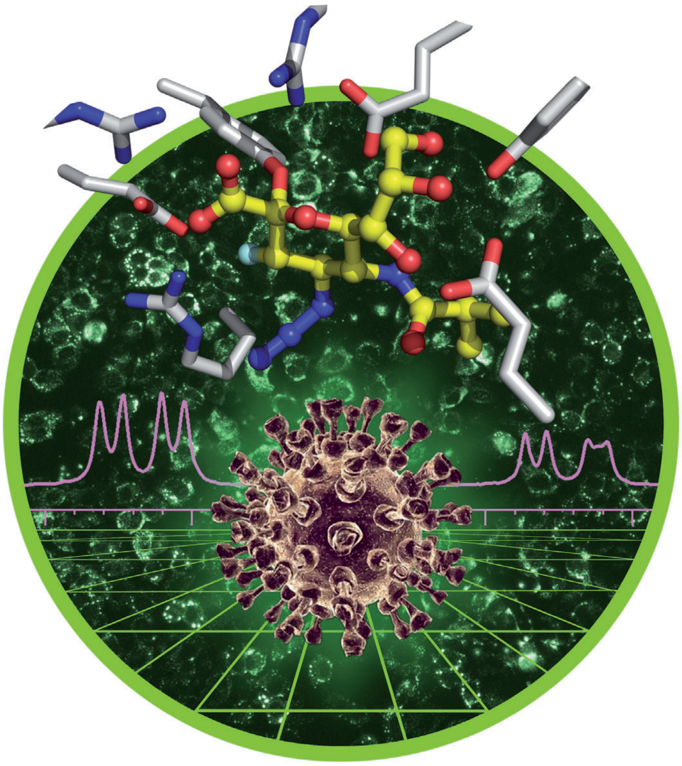
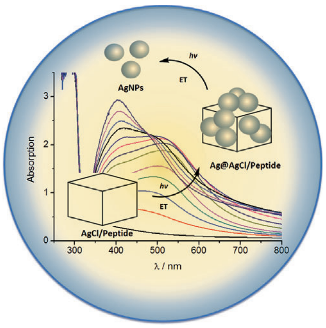
The human parainfluenza virus …

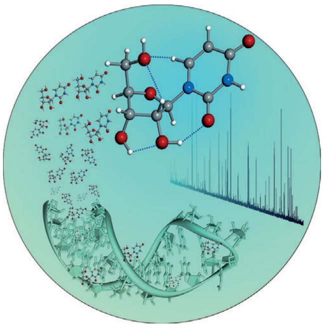


… type 3 (hPIV-3) is one of the leading causes of lower respiratory tract disease in children. In their Communication on page 2936 ff., M. von Itzstein, I. M. El-Deeb, P. Guillon, L. M. G. Chavas, and co-workers investigate the catalytic mechanism of hPIV-3 haemagglutinin-neuraminidase (HN) and determine that it is a retaining glycohydrolase. Moreover hPIV-3 HN utilizes a highly conserved tyrosine residue to form a transient covalent bond with the anomeric carbon of the substrate. Finally a novel sialic acid derivative showed potency in virus blockade assays.

Nanoparticles

K. M. Fromm, B. Giese et al. report in their Communication on page 2912 ff. how shielding effects prevent the formation of Ag nanoparticles from Ag$^+$–peptides. This problem was overcome by chloride ions first forming AgCl microcrystals.





Microwave Spectroscopy

In their Communication on page 2991 ff., J. L. Alonso et al. show that intramolecular hydrogen bonds involving uracil and ribose moieties play an important role in the stabilization of the nucleoside uridine.

Blood–Brain Barrier

In their Communication on page 3023 ff., W. Lu, C. Zhan, et al. identified a D-peptide ligand of nicotine acetylcholine receptors that is resistant to proteolysis and verified its superiority for brain-targeted drug delivery over the L-peptide ligand.

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Service

Author Profile

"I advise my students to see the world and keep an open mind.
My favorite quote is 'Never try to discourage thinking for you are sure to succeed' (Bertrand Russell) ..."
This and more about Todd B. Marder can be found on page 2882.

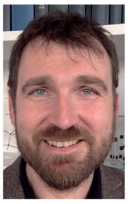
News


R. Sarpong


A. Doyle


M. S. Sigman


F. Glorius


D. Trauner


K. R. Liedl


A. Marx


D. Díaz Díaz


J. Groll


F. H. Schacher


S. Seiffert

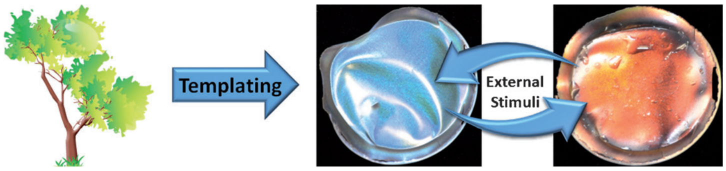
Books

Reviews

Liquid-Crystal Templates

M. Giese, L. K. Blusch, M. K. Khan,
M. J. MacLachlan* ________ **2888 – 2910**

Functional Materials from Cellulose-Derived Liquid-Crystal Templates



Out of the woods: Novel mesoporous and nanostructured materials can be generated by templating approaches based on cellulose-based liquid crystals derived from trees. This Review focuses on materials templated by cellulose nanocrystals, since their chiral nematic order allows their use in various optical applications such as optical filters, sensors, and optoelectronics.

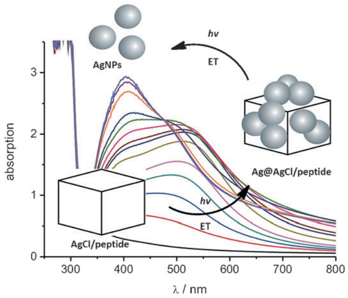
Communications

Nanoparticles

S. Kracht, M. Messerer, M. Lang,
S. Eckhardt, M. Lauz, B. Grobéty,
K. M. Fromm,* B. Giese* __ **2912 – 2916**

Electron Transfer in Peptides: On the Formation of Silver Nanoparticles

Frontispiece



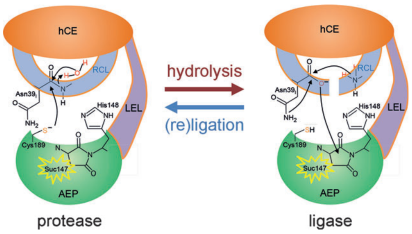
Interplay of peptides and silver: Shielding effects prevent the formation of Ag nanoparticles (AgNPs) from Ag^+-peptides. How can nature overcome this problem and synthesize AgNPs through electron transfer processes over long distances?

Protein Modification

E. Dall, J. C. Fegg, P. Briza,
H. Brandstetter* ________ **2917 – 2921**

Structure and Mechanism of an Aspartimide-Dependent Peptide Ligase in Human Legumain

Peptide bond (bio)synthesis requires ATP as a coupling reagent. By contrast, human legumain ligase exploits an endogenous energy reservoir that results from the conversion of a conserved aspartate to a metastable succinimide. Legumain's protease activity recharges the succinimide. This functional duality may account for the generation of three-dimensional epitopes for MHC presentation through the cleavage and splicing of sequentially distant epitopes.



For the USA and Canada:
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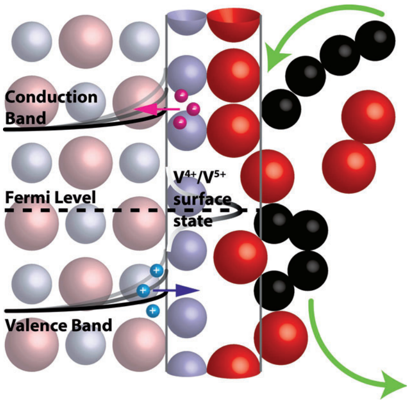
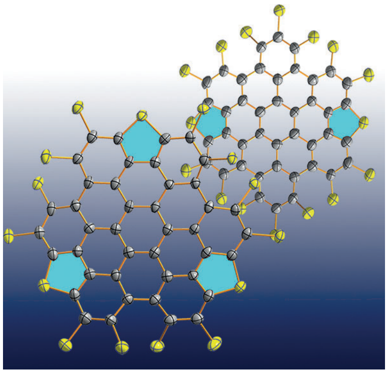


Decades-old concepts in semiconductor physics such as gas-phase-dependent band bending (see figure) could be proven in heterogeneous oxidation catalysis for selective alkane oxidation reactions on vanadium oxide based catalysts by near-ambient-pressure X-ray photoelectron spectroscopy. These "electronic factors" are discussed as descriptors for selective catalyst materials.

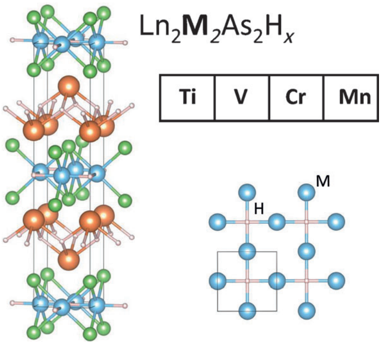
Heterogeneous Catalysis



Sulfur annulation: The unprecedented sulfur-annulated hexa-peri-hexabenzocoronenes were synthesized and unambiguously characterized by X-ray diffraction, revealing the distinct sulfur-annulated peripheral structure. Associated with DFT calculations, the strain minimization of the aromatic carbon skeleton should be responsible for the regioselective sulfur annulation at the bay positions.

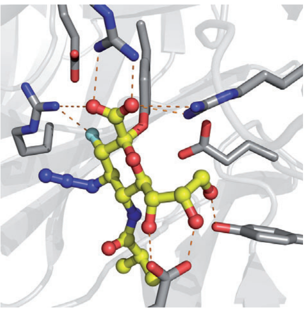
Heteroarenes

Using the strong donating nature of H$^-$, a new series of $La_2Fe_2Se_2O_3$-type layered mixed-anion arsenides, $Ln_2M_2As_2H_x$ (Ln = La or Sm, M = Ti, V, Cr, or Mn; $x \approx 3$), was synthesized. These contain an unusual M_2H square net, which has anti CuO_2 square net structures and strong metal–metal bonding with a distance of 2.80 Å confirmed in $La_2Ti_2As_2H_{2.3}$.



Metal Hydrides

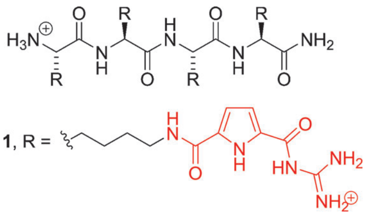
Antivirus update: 2,3-difluoro sialic acid derivatives were used to explore the catalytic mechanism of human parainfluenza type 3 haemagglutinin-neuraminidase. The enzyme is a retaining glycohydrolase and acts by a mechanism involving a covalent adduct formed between the key amino acid residue Tyr530 and the substrate. One sialic acid derivative showed potency in virus blockade assays and is thus a promising new lead in anti-parainfluenza virus inhibitor design.



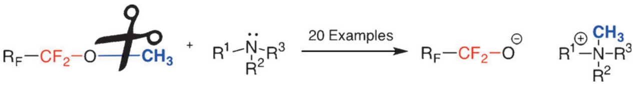
Parainfluenza Virus

Front Cover

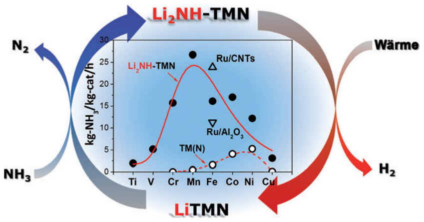
Gene Delivery



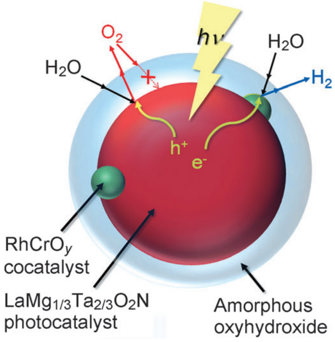
Perfluorinated Alkoxides



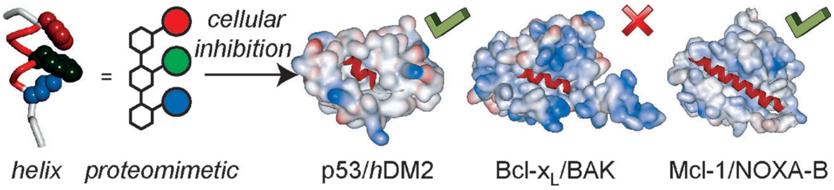
Ammonia Decomposition



Photocatalysis



Inside Cover

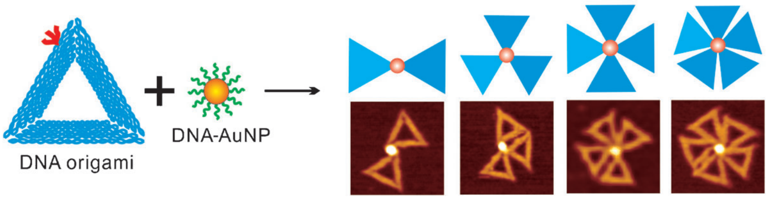


Inhibitors

A. Barnard, K. Long, H. L. Martin,
J. A. Miles, T. A. Edwards,
D. C. Tomlinson, A. Macdonald,*
A. J. Wilson* **2960 – 2965**

Selective and Potent Proteomimetic Inhibitors of Intracellular Protein–Protein Interactions

Picky mimics: Inhibition of protein–protein interactions represents a major challenge in chemical biology and drug discovery. By using a library of N-alkylated aromatic oligoamides, helix mimetics that reproduce their biophysical binding selectivity in a cellular context can be identified.

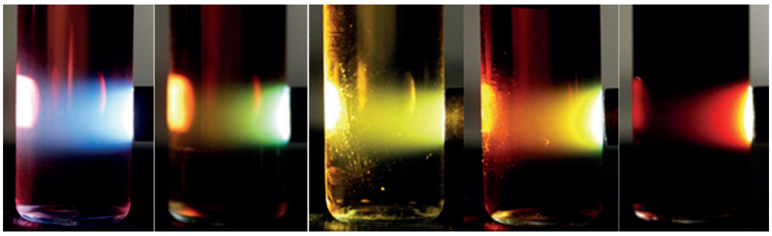


DNA Nanotechnology

G. Yao, J. Li, J. Chao, H. Pei, H. Liu,
Y. Zhao, J. Shi, Q. Huang, L. Wang,
W. Huang, C. Fan* **2966 – 2969**

Gold-Nanoparticle-Mediated Jigsaw-Puzzle-like Assembly of Supersized Plasmonic DNA Origami

Over the limit: A jigsaw-puzzle-like assembly strategy mediated by gold nanoparticles (AuNPs) is used to break the size limit of classic DNA origami. DNA-functionalized AuNPs are used as universal joints to assemble triangular DNA origami (see picture; red arrow denotes AuNP binding site) to form higher-order super-origami plasmonic nanostructures.

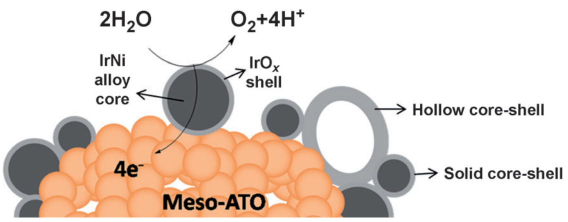


Carbon Dots

S. Hu,* A. Trinchi,* P. Atkin,
I. Cole **2970 – 2974**

Tunable Photoluminescence Across the Entire Visible Spectrum from Carbon Dots Excited by White Light

Color tuning: Carbon dots whose peak fluorescence emission wavelengths are tunable across the entire visible spectrum from 400 to 710 nm are synthesized by simple adjustment of reagents and synthesis conditions. They exhibit multicolor emission upon excitation with white light.



Electrochemistry

H. N. Nong, H. S. Oh, T. Reier,
E. Willinger, M. G. Willinger, V. Petkov,
D. Teschner,* P. Strasser* **2975 – 2979**

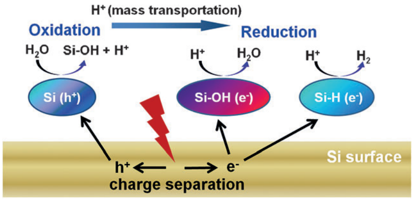
Oxide-Supported $IrNiO_x$ Core–Shell Particles as Efficient, Cost-Effective, and Stable Catalysts for Electrochemical Water Splitting

Water splitting: $IrNiO_x$ core–shell nanoparticles consisting of a thin IrO_x shell and an Ir-low/Ir-free core supported on mesoporous antimony doped tin oxide are demonstrated to provide substantial advances toward more efficient, stable, and less expensive electrolytic water splitting catalysts.

Photocatalysis

D. Liu, L. Li, Y. Gao, C. Wang, J. Jiang, Y. Xiong* ______ **2980 – 2985**

The Nature of Photocatalytic "Water Splitting" on Silicon Nanowires

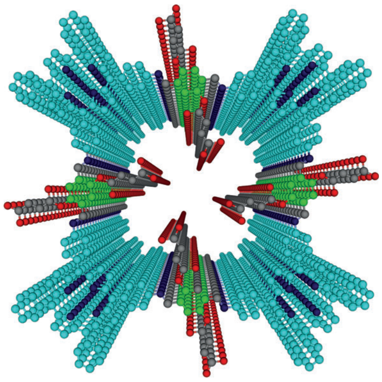


The production of hydrogen gas by photocatalytic water splitting on silicon nanowires was investigated. It occurs through cleavage of Si–H bonds and formation of Si–OH bonds; the surface dangling bonds have a great impact on charge separation.

Gas Adsorption

N. Huang, X. Chen, R. Krishna, D. Jiang* ______ **2986 – 2990**

Two-Dimensional Covalent Organic Frameworks for Carbon Dioxide Capture through Channel-Wall Functionalization



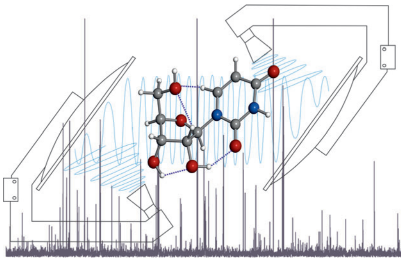
Efficient CO_2 capture is achieved by converting a conventional two-dimensional covalent organic framework (COF) to an outstanding CO_2 capture material with large capacity and high selectively. The nanopore walls are chemically engineered with functional groups in a controlled manner to enhance interactions with CO_2, leading to the development of a new general way to design COFs for gas storage and separation.

Microwave Spectroscopy

I. Peña, C. Cabezas, J. L. Alonso* ______ **2991 – 2994**

The Nucleoside Uridine Isolated in the Gas Phase

Inside Back Cover

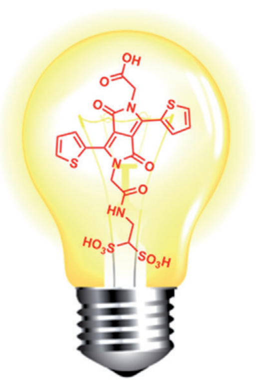


Intramolecular hydrogen bonds: The simplest nucleoside uridine has been placed in the gas phase by laser ablation and structurally characterized by Fourier transform microwave spectroscopy. Intramolecular hydrogen bonds involving uracil and ribose moieties (see picture) have been found to play an important role in the stabilization of the nucleoside.

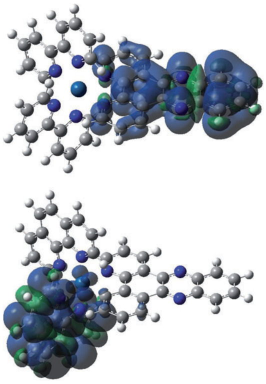
Imaging Agents

E. Heyer, P. Lory, J. Leprince, M. Moreau, A. Romieu,* M. Guardigli, A. Roda, R. Ziessel* ______ **2995 – 2999**

Highly Fluorescent and Water-Soluble Diketopyrrolopyrrole Dyes for Bioconjugation



All-in-one solution! A simple but very effective synthetic strategy to make diketopyrrolopyrrole (DPP) dyes water-soluble and highly fluorescent in aqueous media for bioconjugation to proteins is presented. Bovine serum albumin-DPP conjugates with unprecedentedly high quantum yields were obtained, thus enabling detection of minute amounts of fluorescent proteins through epifluorescence microscopy.



The same but different: Two new $\mathrm{Ir^{III}}$ complexes, with $\mathrm{Ir^{III}(NN)_2}$ moieties coordinated to either the DNA-intercalating ligand dipyridophenazine (dppz) or its cyclometalating analogue benzopyridophenazine (bppz), are reported. Experimental and computational studies show that the systems have very different excited states (see picture; dppz complex (top), bppz complex (bottom)) and both bind to DNA with affinities comparable to their $\mathrm{Ru^{II}}$ analogues.

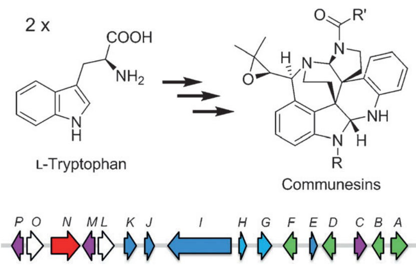
DNA Intercalators

S. Stimpson, D. R. Jenkinson, A. Sadler,
M. Latham, D. A. Wragg,
A. J. H. M. Meijer,
J. A. Thomas* ———— **3000 – 3003**

Tuning the Excited State of Water-Soluble $\mathrm{Ir^{III}}$-Based DNA Intercalators that are Isostructural with $[\mathrm{Ru^{II}(NN)_2(dppz)}]$ Light-Switch Complexes

---

Putting the whole family on the map: Communesins, a prominent class of complex indole alkaloids isolated from various *Penicillium* species, are shown to be biosynthesized from two different building blocks derived from L-tryptophan. The entire biosynthetic pathway was mapped by genetic inactivation studies, which led to the isolation of three new communesin analogues.

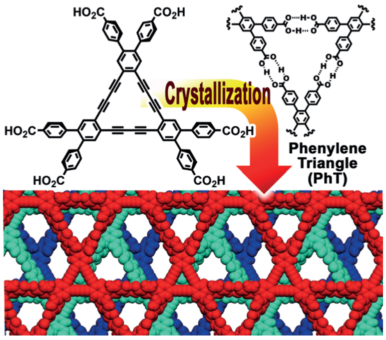


Alkaloid Biosynthesis

H.-C. Lin, G. Chiou, Y.-H. Chooi,
T. C. McMahon, W. Xu, N. K. Garg,*
Y. Tang* ———— **3004 – 3007**

Elucidation of the Concise Biosynthetic Pathway of the Communesin Indole Alkaloids

---



Construction of porous crystalline two-dimensional frameworks is achieved through non-interpenetrated stacking of a multiporous hexagonal network possessing three kinds of voids with different sizes and shapes. A cavity volume of up to 58% is obtained.

Supramolecular Chemistry

I. Hisaki,* S. Nakagawa, N. Tohnai,
M. Miyata* ———— **3008 – 3012**

A C_3-Symmetric Macrocycle-Based, Hydrogen-Bonded, Multiporous Hexagonal Network as a Motif of Porous Molecular Crystals

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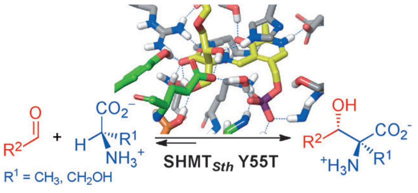


Quaternary stereocenters are obtained with a stereoselective biocatalyst. Chirally pure α,α-dialkyl-α-amino acid derivatives were synthetized through aldol addition of D-Ala and D-Ser to a variety of acceptor aldehydes. This reaction is catalyzed by the engineered pyridoxal-5′-phosphate dependent biocatalyst SHMT_{Sth} Y55T. (SHMT_{Sth} is the L-serine hydroxymethyltransferase from *Streptococcus thermophilus*).

Biocatalysis

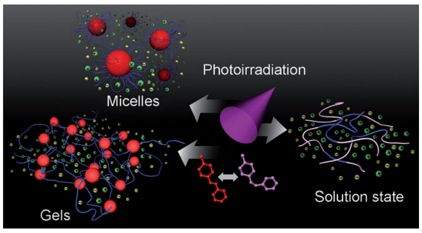
K. Hernandez, I. Zelen, G. Petrillo,
I. Usón, C. M. Wandtke, J. Bujons,
J. Joglar, T. Parella,
P. Clapés* ———— **3013 – 3017**

Engineered L-Serine Hydroxymethyltransferase from *Streptococcus thermophilus* for the Synthesis of α,α-Dialkyl-α-Amino Acids

Polymer Gels

T. Ueki, Y. Nakamura, R. Usui, Y. Kitazawa, S.-N. So, T. P. Lodge,* M. Watanabe* ________ **3018 – 3022**

Photoreversible Gelation of a Triblock Copolymer in an Ionic Liquid

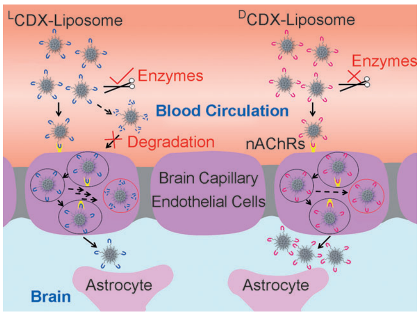


Make or break: The reversible micellization and gel-to-sol transition of an ionic liquid/ABA block copolymer solution triggered by a photostimulus is described. Photorheology is employed to monitor the light-induced viscoelastic property changes of the functional liquid resulting from hierarchical changes in the microscopic substructure of the macromolecular building blocks.

Blood–Brain Barrier

X. Wei, C. Zhan,* Q. Shen, W. Fu, C. Xie, J. Gao, C. Peng, P. Zheng, W. Lu* ________ **3023 – 3027**

A D-Peptide Ligand of Nicotine Acetylcholine Receptors for Brain-Targeted Drug Delivery



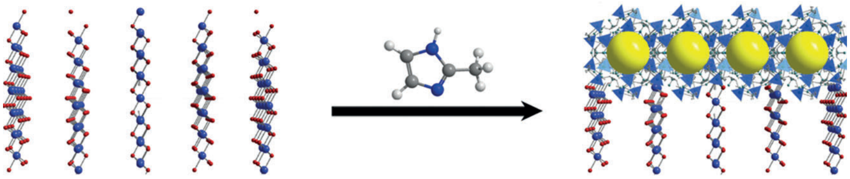
A D-peptide ligand of nicotine acetylcholine receptors (nAChRs), termed ^{D}CDX, was developed. The function of ^{D}CDX as a D-peptide antagonist of nAChRs was experimentally and computationally validated. ^{D}CDX exhibits exceptional stability during nAChRs-mediated transcytosis and in blood circulation, offering potential for brain-targeted drug delivery in the treatment of central nervous system diseases.

Back Cover

Gas Separation

Y. Liu,* J. H. Pan, N. Y. Wang, F. Steinbach, X. L. Liu, J. Caro* ________ **3028 – 3032**

Remarkably Enhanced Gas Separation by Partial Self-Conversion of a Laminated Membrane to Metal–Organic Frameworks

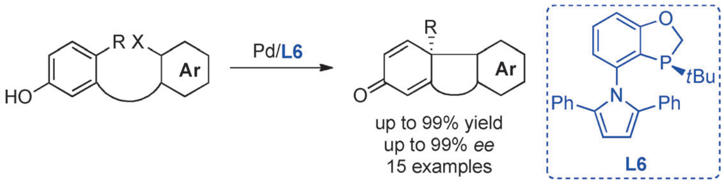


From LDH to MOF: The partial transformation of a ZnAl-NO_3 layered double hydroxide (LDH) membrane to a ZIF-8 metal–organic framework (MOF) top layer led to the formation of the composite membrane ZIF-8-ZnAl-NO_3 LDH. This membrane is characterized by remarkably enhanced H_2/CH_4 gas separation and H_2 permeance.

Asymmetric Cyclization

K. Du, P. Guo, Y. Chen, Z. Cao, Z. Wang, W. Tang* ________ **3033 – 3037**

Enantioselective Palladium-Catalyzed Dearomative Cyclization for the Efficient Synthesis of Terpenes and Steroids

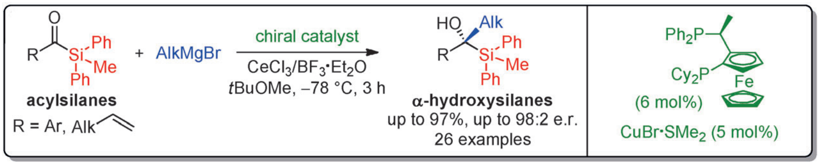


One, two, three: An enantioselective palladium-catalyzed dearomative cyclization was developed for the efficient construction of a series of chiral tricyclic phenanthrenone derivatives bearing all-carbon quaternary centers. This method was applied in highly efficient syntheses of a kaurene intermediate, the skeleton of the anabolic steroid boldenone, and the antimicrobial diterpene (−)-totaradiol.

Grignard Reactions

J. Rong, R. Oost, A. Desmarchelier, A. J. Minnaard, S. R. Harutyunyan* ______ 3038 – 3042

Catalytic Asymmetric Alkylation of Acylsilanes



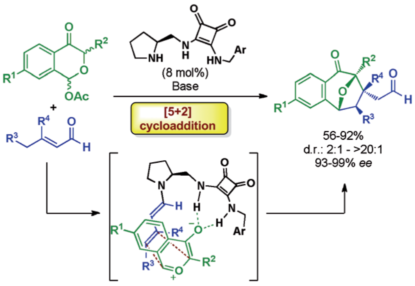
Chiral silanes: The highly enantioselective addition of Grignard reagents to acylsilanes is catalyzed by copper diphosphine complexes. This transformation affords α-silylated tertiary alcohols in up to 97% yield and 98:2 enantiomeric ratio.

Organocatalysis

A. Orue, U. Uria, E. Reyes,* L. Carrillo, J. L. Vicario* ______ 3043 – 3046

Catalytic Enantioselective [5+2] Cycloaddition between Oxidopyrylium Ylides and Enals under Dienamine Activation

By using all its powers of persuasion, a bifunctional secondary-amine/squaramide catalyst encouraged 1-acetoxyisochroman-4-ones to react as benzopyrylium ylides with α,β-unsaturated aldehydes in efficient [5+2] cycloaddition reactions with high diastereo- and enantioselectivity. The transformation proceeds by dienamine activation and involves β,γ-functionalization of the enal (see scheme).



Photocatalysis

S. Chen, S. Shen, G. Liu, Y. Qi, F. Zhang,* C. Li* ______ 3047 – 3051

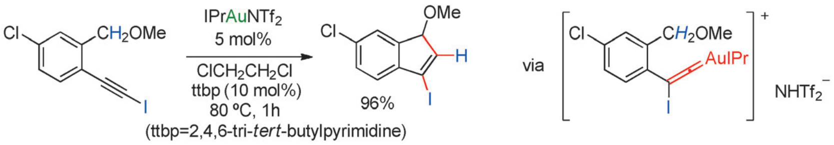
Interface Engineering of a CoO_x/Ta_3N_5 Photocatalyst for Unprecedented Water Oxidation Performance under Visible-Light-Irradiation

Hydrophilic interface modification of a CoO_x-modified Ta_3N_5 photocatalyst with a magnesia nanolayer significantly improves its water oxidation efficiency under visible light irradiation. The essential roles of the interface modification are proposed to enhance the interfacial coverage of the CoO_x/Ta_3N_5 photocatalyst and to decrease the defect density of Ta_3N_5 semiconductor. AQE = apparent quantum efficiency.

Synthetic Methods

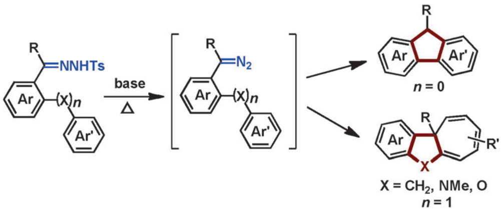
P. Morán-Poladura, E. Rubio, J. M. González* ______ 3052 – 3055

Intramolecular C–H Activation through Gold(I)-Catalyzed Reaction of Iodoalkynes



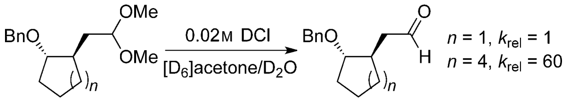
Golden dance: The cycloisomerization reaction of 1-(iodoethynyl)-2-(1-methoxyalkyl)arenes gives the corresponding 3-iodo-1-substituted-1*H*-indene. Gold(I) catalysis triggers a selective intramolecular carbon–carbon bond-forming event, which involves the insertion of benzylic C–H bonds in the catalytically assembled gold(I) iodovinylidene intermediate.

Carbenes



Transition-metal-free: The synthesis of fluorenes and [6,5,7]benzo-fused rings is achieved through a transition-metal-free protocol of intramolecular aromatic substitution and Büchner reaction. The new synthetic method uses readily available aromatic *N*-tosylhydrazones as the diazo compound precursors and shows wide substrate scope.

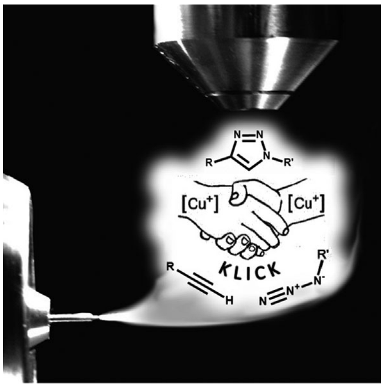
Carbohydrates



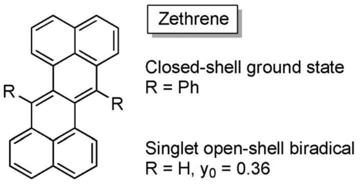
Making an approach: In contrast to observations with carbohydrates, alkoxy groups can accelerate acetal hydrolysis even though they are inductively electron withdrawing. The alkoxy group must be able to approach the acetal carbon atom without developing too much strain. The data are most consistent with the alkoxy group stabilizing the developing positive charge by electrostatic stabilization, not formation of a new covalent bond.

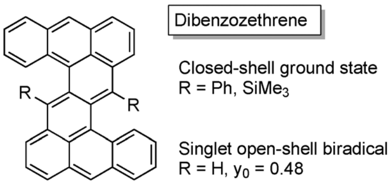
Reaction Intermediates

Mechanistic aspects of the CuAAC reaction have been clarified by electrospray ionization mass spectrometry (ESI-MS). Dinuclear copper intermediates have been detected for the first time and characterized. Neutral and ion-tagged reactants provided complementary evidence for the reaction catalytic cycle.



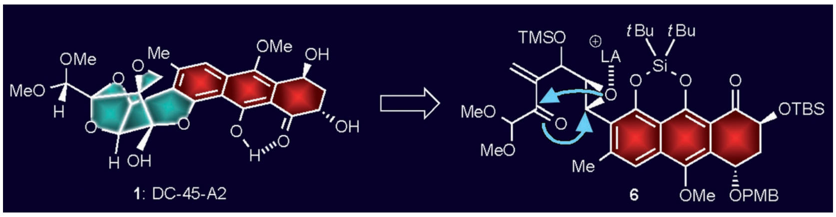
Macrocycles





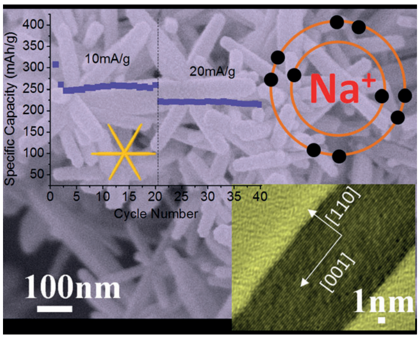
Shelling out: Substituents and π-conjugation remarkably affect the structures and properties of zethrene series. The parent dibenzozethrene and zethrene are both singlet open-shell biradicals, but the former has stronger biradical characteristics than the latter, as verified experimentally and theoretically, whereas all substituted derivatives have a closed-shell ground state.

Natural Product Synthesis



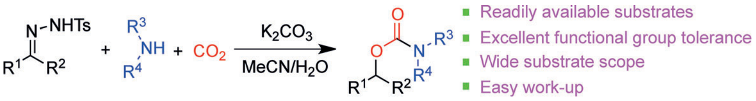
Zipping it all together: A monodentate Lewis acid was used to induce the stereoselective formation of the bicyclo[2.2.1]heptane structural motif of DC-45-A2 (**1**), the naturally occurring parent compound of the trioxacarcin class of antitumor agents.

Battery Electrodes



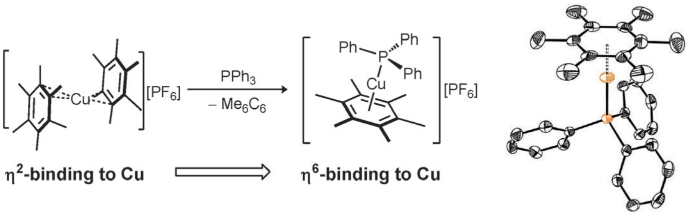
Fair of phase: A new wet-chemical method was developed for the facile preparation of phase-pure FeOF nanorod structures (see SEM image). The as-prepared FeOF nanorods demonstrated a high sodium-ion-storage capacity of approximately 250 mAh g^{-1} and excellent cycling and rate performance (see graph).

Multicomponent Reactions



Carbene intermediate? No! An unprecedented strategy for the synthesis of a range of organic carbamates through the coupling of carbon dioxide, amines, and *N*-tosylhydrazones is reported. The base-promoted reaction is proposed to proceed via a carbocation intermediate and is characterized by excellent functional group tolerance and a wide substrate scope.

Copper Arenes

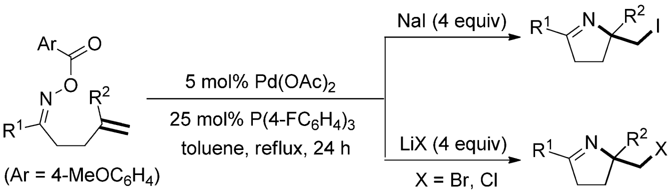


Addition of PR$_3$ (R = Ph or OPh) to [Cu(η^2-Me$_6$C$_6$)$_2$][PF$_6$] results in the formation of [(η^6-Me$_6$C$_6$)Cu(PR$_3$)][PF$_6$], the first copper–arene complexes to feature an unsupported η^6 arene interaction. DFT analysis shows that the preference for the η^6 binding mode is enforced by the steric clash between the methyl groups of the arene ligand and the phenyl rings of the phosphine co-ligand.

Heterocycle Synthesis

C. Chen, L. Hou, M. Cheng, J. Su, X. Tong* ______ 3092 – 3096

Palladium(0)-Catalyzed Iminohalogenation of Alkenes: Synthesis of 2-Halomethyl Dihydropyrroles and Mechanistic Insights into the Alkyl Halide Bond Formation



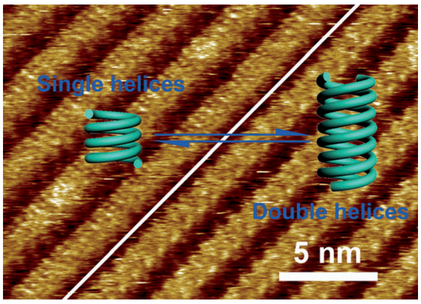
Eliminated: The use of electron-poor phosphine ligands proved to be crucial to promoting alkyl bromide and chloride reductive elimination in the title reaction with γ,δ-unsaturated oxime esters. Furthermore, $\mathrm{S_N}2$-type alkyl bromide and chloride reductive elimination has also been established.

Helical Superstructures

J. Y. Zhu, Z. Y. Dong,* S. B. Lei, L. L. Cao, B. Yang, W. F. Li, Y. C. Zhang, J. Q. Liu,* J. C. Shen ______ 3097 – 3101

Design of Aromatic Helical Polymers for STM Visualization: Imaging of Single and Double Helices with a Pattern of π–π Stacking

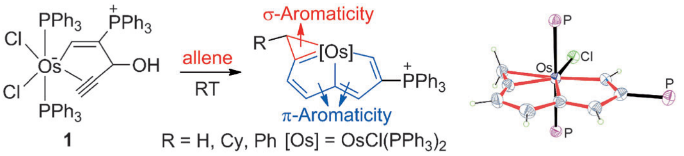
Seeing is believing: STM imaging of rationally designed helical polymers with a pattern of π–π stacking of the helical structures revealed single- and double-helical superstructures (see picture), including the smallest helical architecture observed to date, with a diameter of approximately 1.3 nm. The interconversion of single and double helices was further underpinned by experimental analyses.



Metallacycles

C. Zhu, X. Zhou, H. Xing, K. An, J. Zhu,* H. Xia* ______ 3102 – 3106

σ-Aromaticity in an Unsaturated Ring: Osmapentalene Derivatives Containing a Metallacyclopropene Unit

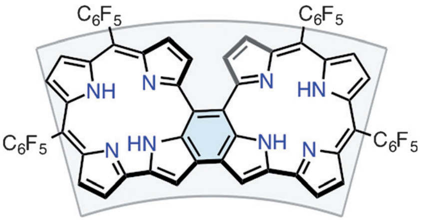


World of Os: A series of osmapentalene derivatives with a metallacyclopropene unit were synthesized by treatment of complex **1** with various allenes at room temperature. Experimental observations and theoretical calculations reveal that σ-aromaticity dominates in the unsaturated three-membered ring.

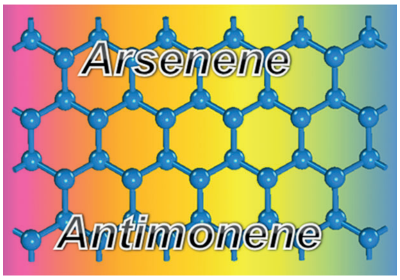
Conjugation

S. Ooi, T. Tanaka,* K. H. Park, S. Lee, D. Kim,* A. Osuka* ______ 3107 – 3111

Fused Corrole Dimers Interconvert between Nonaromatic and Aromatic States through Two-Electron Redox Reactions



Doubled up: A singly linked corrole dimer was synthesized and oxidized to a meso–meso and β–β doubly linked 2*H*-corrole dimer, which was interconvertible with an aromatic 3*H*-corrole dimer upon two-electron redox reactions. The nonaromatic 2*H*-corrole dimer was rather stable, probably because of the double direct connection between the corrole units.



Unlike black phosphorus, both arsenic and antimony are typical semimetals in their natural, layered bulk state. However, monolayered arsenene and antimonene are indirect wide-band-gap semiconductors, and under strain, they become direct band-gap semiconductors. Owing to these band-gap transitions, these materials could find applications in nano- and optoelectronic devices.

2D Semiconductors

S. Zhang, Z. Yan, Y. Li, Z. Chen,* H. Zeng* ______ **3112–3115**

Atomically Thin Arsenene and Antimonene: Semimetal–Semiconductor and Indirect–Direct Band-Gap Transitions

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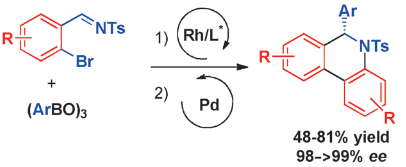

Retro-carbopalladation of aldimines in the presence of a suitable β-hydrogen atom is a key step in the Pd-catalyzed homocoupling reactions of *o*-bromobenzylamines, providing an expeditious synthetic route to 5,6-dihydrophenanthridine derivatives. A highly enantioselective synthesis procedure was also achieved in a one-pot manner by taking advantage of Rh and Pd catalysis.

β-Carbon Elimination

J. Ye, A. Limouni, S. Zaichuk, M. Lautens* ______ **3116–3120**

Synthesis of Enantioenriched 5,6-Dihydrophenanthridine Derivatives through retro-Carbopalladation of Chiral *o*-Bromobenzylamines

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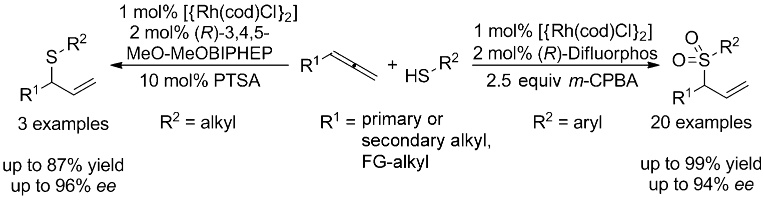

All about S: The rhodium-catalyzed enantioselective hydrothiolation of terminal monosubstituted allenes with aromatic and functionalized aliphatic thiols permits the atom-economic synthesis of valuable branched allylic thioethers and sulfones in high regio- and enantioselectivity. By varying the ligand and reaction conditions both aromatic and aliphatic thiols were tolerated.

Asymmetric Catalysis

A. B. Pritzius, B. Breit* ______ **3121–3125**

Asymmetric Rhodium-Catalyzed Addition of Thiols to Allenes: Synthesis of Branched Allylic Thioethers and Sulfones

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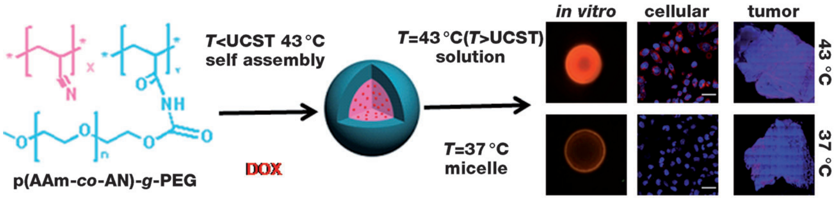


Smart device: Poly(AAm-*co*-AN)-*g*-PEG micelles were used as a temperature-triggered drug delivery system based on their upper critical solution temperature. The polymeric micelles displayed a good drug release profile both in vitro and in vivo. Additionally, an excellent antitumor efficiency was achieved. DOX = doxorubicin.

Drug Delivery

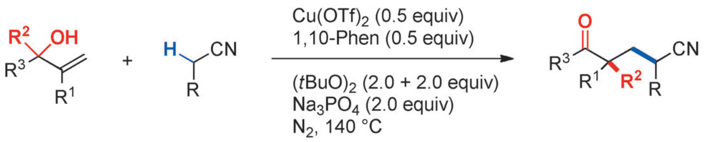
W. S. Li, L. W. Huang, X. Ying, Y. Jian, Y. Hong, F. Q. Hu, Y. Z. Du* **3126–3131**

Antitumor Drug Delivery Modulated by A Polymeric Micelle with an Upper Critical Solution Temperature

Synthetic Methods

A. Bunescu, Q. Wang,
J. Zhu* ________________ 3132 – 3135

Copper-Catalyzed Cyanomethylation of Allylic Alcohols with Concomitant 1,2-Aryl Migration: Efficient Synthesis of Functionalized Ketones Containing an α-Quaternary Center

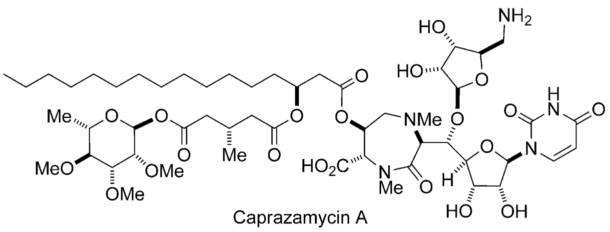


A shift in gear: Ketones with an α-quaternary center were synthesized by the title copper triflate catalyzed alkylation of alkenes with non-activated alkyl nitriles (see scheme; 1,10-Phen = 1,10-phenanthroline). The reaction involves the copper-catalyzed formation of an alkyl nitrile radical, its addition to the alkene, and the migration of a vicinal aryl group with the concomitant generation of a carbonyl functionality.

Natural Product Synthesis

H. Nakamura, C. Tsukano, M. Yasui,
S. Yokouchi, M. Igarashi,
Y. Takemoto* ________________ 3136 – 3139

Total Synthesis of (−)-Caprazamycin A



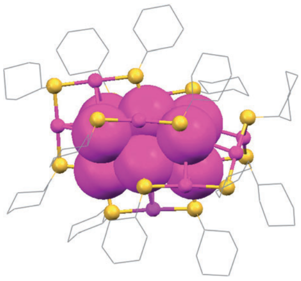
Abra‘capraza’: Caprazamycin A has significant antibacterial activity against *Mycobacterium tuberculosis* (TB). The first total synthesis is herein reported and features the scalable preparation of the *syn*-β-hydroxy amino acid with a thiourea-catalyzed diastereoselective aldol reaction, construction of a diazepanone with an unstable fatty-acid side chain, and global deprotection by hydrogenation.

Gold Clusters

A. Das, C. Liu, H. Y. Byun, K. Nobusada,*
S. Zhao, N. L. Rosi, R. Jin* _ 3140 – 3144

Structure Determination of $[Au_{18}(SR)_{14}]$

Heart of gold: A decade after the first report of the $[Au_{18}(SR)_{14}]$ cluster, its structure is finally obtained (see picture, gold pink, sulfur yellow, cyclohexyl groups as wire frame). It has a bi-octahedral (or hexagonal closing packing) Au_9 kernel protected by staple-like surface motifs.

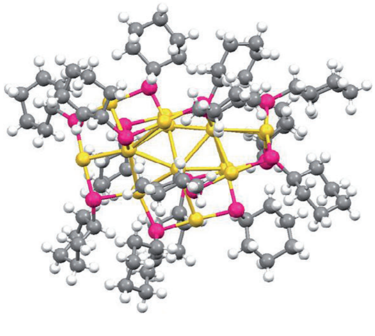


Gold Clusters

S. Chen, S. Wang, J. Zhong, Y. Song,
J. Zhang, H. Sheng, Y. Pei,*
M. Zhu* ________________ 3145 – 3149

The Structure and Optical Properties of the $[Au_{18}(SR)_{14}]$ Nanocluster

Gold mine: The X-ray crystallographic structure of cyclohexylthiolate-protected $[Au_{18}(SR)_{14}]$ nanocluster shows it has a Au_9 bi-octahedral kernel (Au gold, S pink, C gray). This Au_9 core is formed by two octahedral Au_6 units sharing one triangular face. A gold atom in the Au_9 core, which can also be considered as part of the $Au_4(SR)_5$ staple motif offering new insight into the evolution from Au^I complexes to larger Au nanoclusters.



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