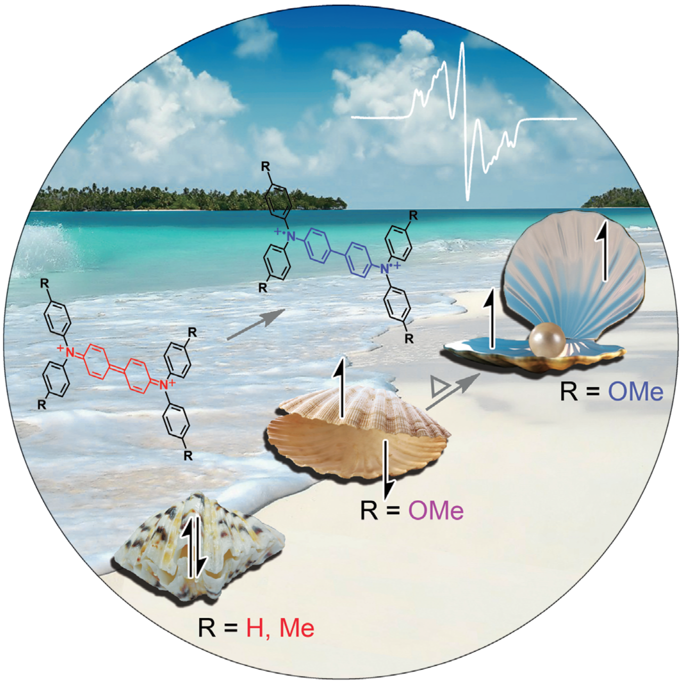
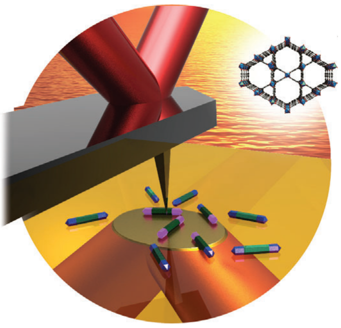
Tuning the ground states …

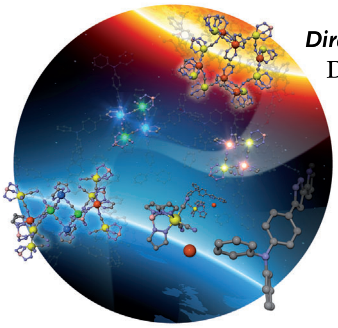


… of bis(triphenylamine)benzedine bipolarons through substituent effects is described by X. Wang et al. in their Communication on page 2857 ff. The ground-state structures of three bis(triphenylamine) dications, isolated by using weakly coordinating anions, were tunable through the donor substituents at the *para* positions of the triphenylamines. This gave rise to closed-shell singlets and a new and stable diradicaloid structure motif with an excited triplet state in the solid state.

Chemical Imaging of Materials

As shown by A. Centrone et al. in their Communication on page 2852 ff., by measuring the thermal expansion of metal–organic frameworks following absorption of IR light, an AFM tip maps the local chemical composition of such materials.



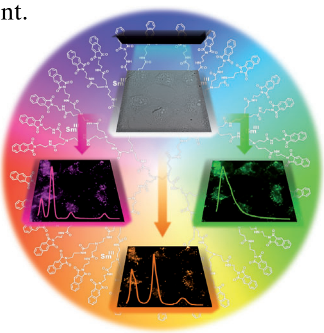


Directing self-assembly

Different cyanide-bridged clusters can be prepared form the same reaction mixture. H. Oshio and co-workers show in their Communication on page 2941 ff. the products are determined by a solution-state electron-transfer-coupled spin transition (ETCST) event.

Imaging

An Sm^{III}-functionalized dendrimer proved to be non-cytotoxic. S. V. Eliseeva, S. Petoud et al. show in their Communication on page 2927 ff. it functions as a bioprobe in both the visible or near-IR ranges in a live cell imaging experiment.



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Editorial

"... Public-funded applied research would be better managed by directors appointed for their proven ability to distinguish between innovative applied research and chronically nonproductive applied research. These directors should be delegated authority over, assume personal responsibility for, and held personally accountable for the outcomes of the projects they manage ..."
Read more in the Editorial by Adam Heller.

Service

Author Profile

"My greatest achievement has been exchanging the engine of a VW Beetle on a remote countryside road in Denmark, only equipped with a simple toolbox and the book Now I Help Myself.
My worst nightmare is sitting in the Festspielhaus in Bayreuth and suffering a Wagner opera ..."
This and more about Gernot Frenking can be found on page 2804.

News


A. H. Hoveyda

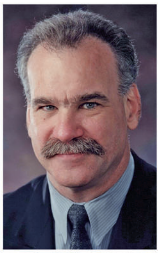

T. D. Tilley


S. H. Gellman


S. L. Schreiber


H. F. Schaefer III


D. P. Curran


S. E. Denmark

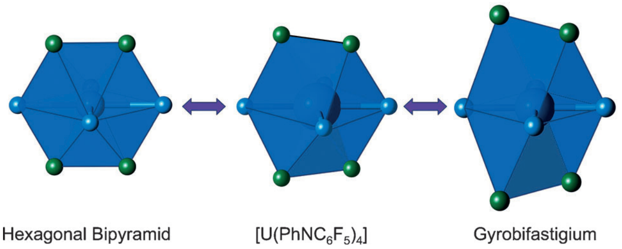

R. G. Bergman


S. J. Lippard

Books

Highlights

Fluorocarbon Coordination



Weak yet influential: Fluorocarbons, the least coordinating of all halocarbons, establish secondary coordinative interactions with f elements. These interactions affect the stereochemistry of the complexes and provide examples of coordination polyhedra along distortion paths not seen before (see graphic).

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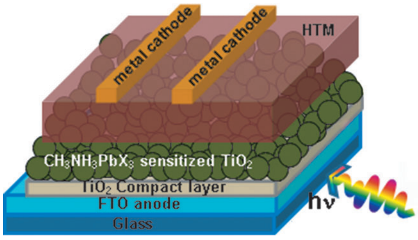
Minireviews

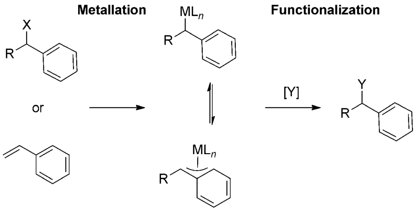
Perovskite Solar Cells

Wonder material: The use of perovskites as light absorber in photovoltaic cells has revolutionized the field. Light-to-electricity conversion efficiencies of 15 % have already been achieved, and even without additional hole transport layers efficiencies up to 8 % can be measured. The unique combination of high extinction coefficient along with their ambipolar nature gives perovskites an advantage over quantum-dot- and dye-sensitized solar cells.



Reviews

Dearomatization by Coordination

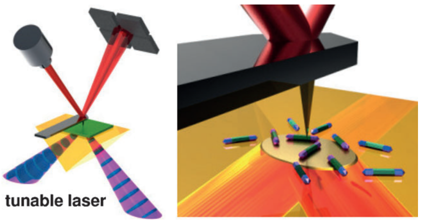


Transition metals bound to benzyl fragments exhibit a variety of binding patterns, including higher order hapticities with dearomatized arenes. Guided by these first discoveries, η^3-benzyl species have been proposed as catalytic intermediates. The synthesis of these complexes and catalytic reactions likely to proceed though the dearomatized intermediate from the past 50 years are discussed.

Communications

Chemical Imaging of Materials

Beaming with confidence: Mixed-linker metal–organic frameworks with either a homogeneous or a heterogeneous distribution of linkers were synthesized and characterized by PTIR, a novel technique that combines the lateral resolution of AFM with the chemical specificity of IR spectroscopy. By measuring the instantaneous thermal expansion following the absorption of IR light in the sample (see picture), an AFM tip maps the local chemical composition of these materials.



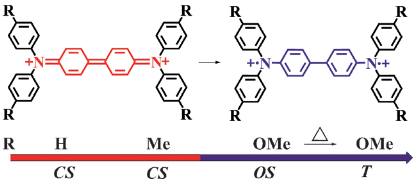
Frontispiece

Electronic Structures

Y. Su, X. Wang, X. Zheng, Z. Zhang,
Y. Song, Y. Sui, Y. Li,
X. Wang* ______ 2857 – 2861

Tuning Ground States of Bis(triarylamine) Dications: From a Closed-Shell Singlet to a Diradicaloid with an Excited Triplet State

Front Cover



Getting excited: The ground-state electronic structures of three bis(triarylamine) dications (R = H, Me, OMe), which were isolated using weakly coordinating anions and investigated experimentally and theoretically, were tunable by substituent effects. The work provides a new and stable diradicaloid structure motif with an excited triplet state. CS = closed-shell singlet, OS = open-shell singlet, T = excited triplet.

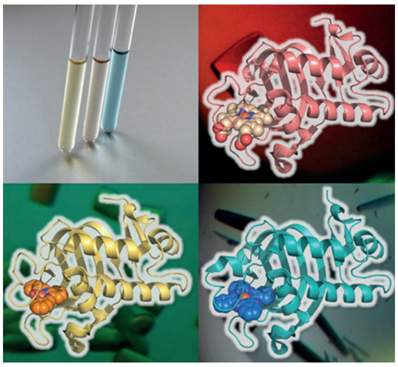
Heme Proteins

C. Shirataki, O. Shoji,* M. Terada,
S. Ozaki, H. Sugimoto, Y. Shiro,
Y. Watanabe* ______ 2862 – 2866

Inhibition of Heme Uptake in *Pseudomonas aeruginosa* by its Hemophore (HasA$_p$) Bound to Synthetic Metal Complexes

Inside Cover

Switching (t)heme: The *Pseudomonas aeruginosa* hemophore HasA$_p$ can bind a variety of synthetic metal complexes such as Fe–salophen (yellow), Fe–phthalocyanine (Fe–Pc; turquoise), and Fe–mesoporphyrin IX (pink). The crystal structures of HasA$_p$ bound to these metal complexes showed only small structural perturbations compared to that of heme-bound HasA$_p$. HasA$_p$ bound to Fe–Pc inhibits HasA$_p$-mediated heme acquisition in *P. aeruginosa*.

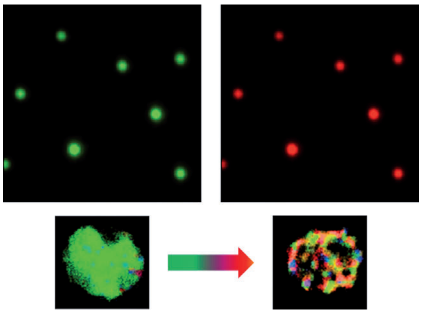


Nanoscale Critical Phenomena

J. G. Smith, Q. Yang,
P. K. Jain* ______ 2867 – 2872

Identification of a Critical Intermediate in Galvanic Exchange Reactions by Single-Nanoparticle-Resolved Kinetics

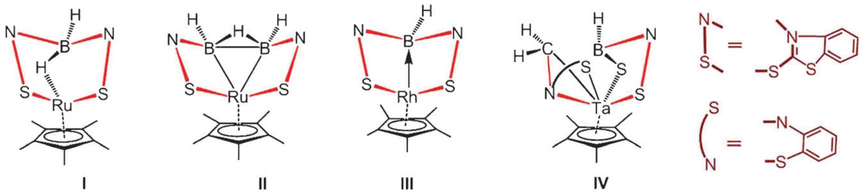
No two particles are alike: The probing of galvanic exchange with single-nanoparticle resolution (see picture) revealed a previously unknown critical phenomenon. The formation of a critical void of approximately 20 atomic vacancies in Ag nanoparticles drove rapid spontaneous galvanic exchange, which led to the formation of a Au/Ag nanocage.



Metal–Boron Complexes

R. S. Anju, D. K. Roy, B. Mondal,
K. Yuvaraj, C. Arivazhagan, K. Saha,
B. Varghese, S. Ghosh* ______ 2873 – 2877

Reactivity of Diruthenium and Dirhodium Analogues of Pentaborane(9): Agostic versus Boratrane Complexes

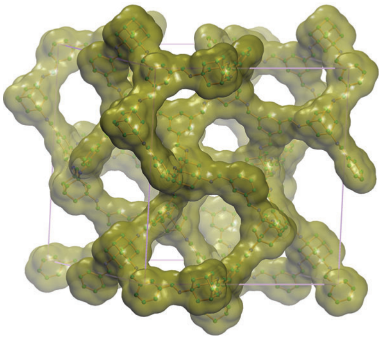


All in a bind of a different kind: Boron–transition-metal complexes with novel binding modes were synthesized efficiently from diruthenium and dirhodium analogues of pentaborane(9) without the use of preformed boron-containing ligands. The observed binding modes included an agostic interaction, a metalladiborane structure, and a boratrane (see structures **I**–**III**). A thioborane with a tantalum center (structure **IV**) is also described.

Covalent Organic Frameworks

Q. Fang, S. Gu, J. Zheng, Z. Zhuang,
S. Qiu, Y. S. Yan* ________ 2878 – 2882

3D Microporous Base-Functionalized Covalent Organic Frameworks for Size-Selective Catalysis



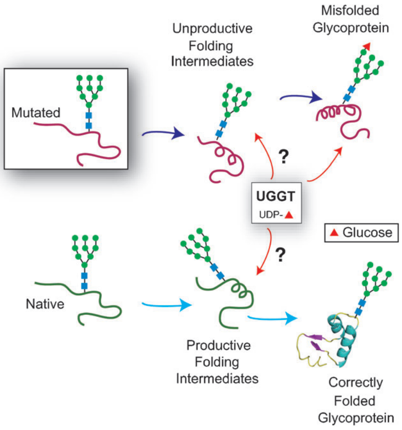
A nifty net: Two novel 3D microporous base-functionalized COFs (BF-COFs, see structure of one framework), were synthesized by the condensation of a tetrahedral alkyl amine with two planar triangular building units, and their catalytic properties were explored in the Knoevenagel condensation reaction. Both BF-COFs showed excellent catalytic activity with high conversion, excellent size selectivity, and good recyclability.

Molecular Recognition

S. Dedola, M. Izumi, Y. Makimura,
A. Seko, A. Kanamori, M. Sakono, Y. Ito,*
Y. Kajihara* ________ 2883 – 2887

Folding of Synthetic Homogeneous Glycoproteins in the Presence of a Glycoprotein Folding Sensor Enzyme

Folded up: A flexible model to reproduce in vitro folding of a glycoprotein in the presence of UDP-glucose:glycoprotein glucosyltransferase (UGGT) in a mixture containing correctly folded, folding intermediates, and misfolded glycoproteins is described. The data demonstrates that UGGT can re-glucosylate all intermediates, thus indicating that UGGT inspects not only final folded products, but also the glycoprotein folding intermediates.



Mesoporous Materials

B. Kong, J. Tang, Z. Wu, J. Wei, H. Wu,
Y. Wang, G. Zheng,*
D. Zhao* ________ 2888 – 2892

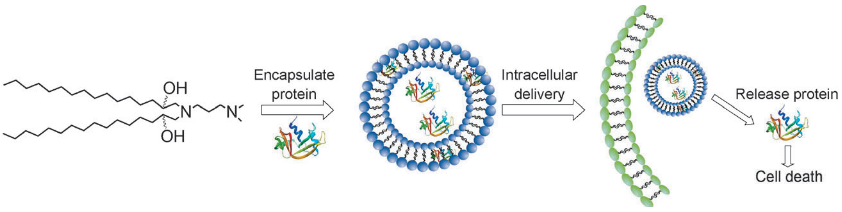
Ultralight Mesoporous Magnetic Frameworks by Interfacial Assembly of Prussian Blue Nanocubes

Ultralight: A method for the synthesis of three-dimensional iron oxide (3DMI) architectures that feature hierarchically porous frameworks, high surface area (ca. 117 $m^2 g^{-1}$), and ultralow density (ca. 6 $mg\,cm^{-3}$) has been developed. These 3DMI materials exhibit high superparamagnetism and tunable hydrophilicity and hydrophobicity, and can be cut and tailored into arbitrary shapes.

Protein Delivery

M. Wang, K. Alberti, S. Sun, C. L. Arellano,
Q. B. Xu* ________ 2893 – 2898

Combinatorially Designed Lipid-like Nanoparticles for Intracellular Delivery of Cytotoxic Protein for Cancer Therapy

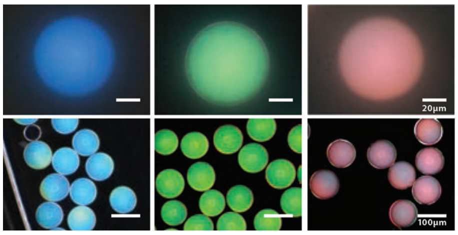


A protein delivery platform that combines a library of lipid-like nanoparticles and a reversible chemical protein modification approach is presented. With ribonuclease A (RNase A) and saporin as representative cytotoxic proteins, the nanoparticles deliver proteins into cancer cells and inhibit cell proliferation. A representative lipidoid protein nanoparticle formulation inhibits tumor cell proliferation in vitro and suppresses tumor growth.

Pigment Design

J.-G. Park, S.-H. Kim, S. Magkiriadou,
T. M. Choi, Y.-S. Kim,
V. N. Manoharan* ________ **2899 – 2903**

Full-Spectrum Photonic Pigments with Non-iridescent Structural Colors through Colloidal Assembly



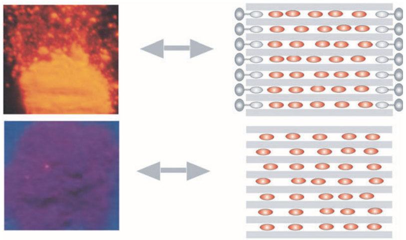
Coloration without colorants: A new colloidal assembly method is presented to fabricate "photonic pigments": microcapsules with non-iridescent structural colors. These pigments exhibit full-spectrum colors that are viewing angle independent.

Supramolecular Chemistry

P. Li, Y. Wang, H. Li,*
G. Calzaferri* ________ **2904 – 2909**

Luminescence Enhancement after Adding Stoppers to Europium(III) Nanozeolite L

Tales of the unexpected: A surprisingly large increase of the luminescence intensity of Eu^{3+}-β-diketonate complexes inside the channels of nanosized zeolite L was observed after modification with an imidazolium stopper molecule.

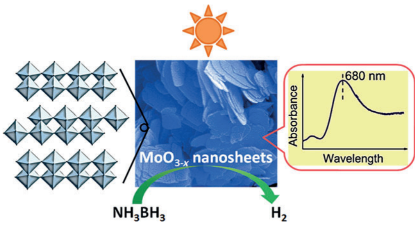


Plasmonic Nanocatalysts

H. Cheng, T. Kamegawa, K. Mori,
H. Yamashita* ________ **2910 – 2914**

Surfactant-Free Nonaqueous Synthesis of Plasmonic Molybdenum Oxide Nanosheets with Enhanced Catalytic Activity for Hydrogen Generation from Ammonia Borane under Visible Light

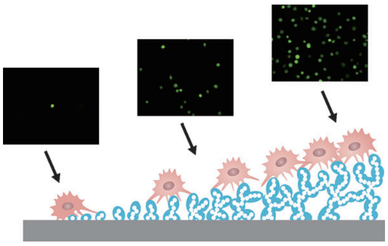
Making MoO_{3-x}, and hydrogen too: Well-defined molybdenum oxide nanosheets (MoO_{3-x}) were prepared by a facile surfactant-free nonaqueous process. With strong localized surface plasmon resonances, these MoO_{3-x} nanostructures could be used as highly efficient catalysts, and showed dramatically enhanced activity for hydrogen evolution from ammonia borane under visible-light irradiation.



Surface Topography

G. Yang, Y. Cao, J. Fan, H. Liu, F. Zhang,
P. Zhang, C. Huang, L. Jiang,
S. T. Wang* ________ **2915 – 2918**

Rapid Generation of Cell Gradients by Utilizing Solely Nanotopographic Interactions on a Bio-Inert Glass Surface

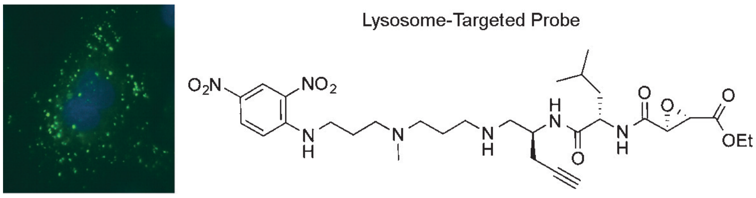


Making things stick: A nanotopographic gradient strategy was used to rapidly generate cell gradients on a glass surface solely by the introduction of gradient nanodendritic silica. This approach can generate cell gradients rapidly and without chemical modifications owing to the enhanced topographic interactions between the nanodendritic structures and nanoscaled filopodia of the cells.

Proteomics

S. D. Wiedner, L. N. Anderson,
N. C. Sadler, W. B. Chrisler, V. K. Kodali,
R. D. Smith, A. T. Wright* ___ **2919 – 2922**

Organelle-Specific Activity-Based Protein Profiling in Living Cells

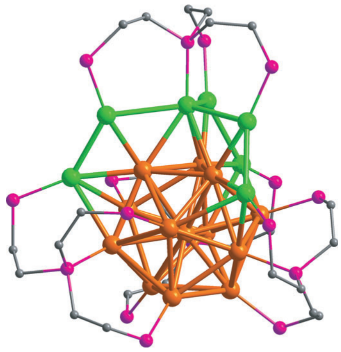


Basic targeting: Organelle-targeted chemoproteomics in live cells is possible through tuning the physicochemical properties of an activity-based probe. A weakly basic amine was used to target an activity-based probe to the lysosome. Analysis of in vivo labeled cells by LC–MS/MS showed good probe specificity for lysosome cysteine proteases. The probe was then used to measure the activity of these proteases during autophagy.

Gold Nanoclusters

X.-K. Wan, S.-F. Yuan, Z.-W. Lin,
Q.-M. Wang* ___ **2923 – 2926**

A Chiral Gold Nanocluster Au_{20} Protected by Tetradentate Phosphine Ligands



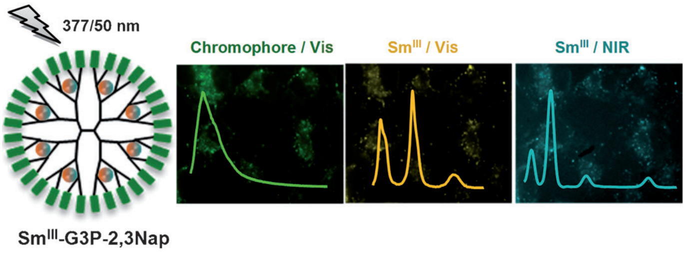
Gold with a twist: A chiral Au_{20} nanocluster has been prepared by the reduction of a gold(I)–tetraphosphine complex. The C_3 Au_{20} core can be viewed as the combination of an icosahedral Au_{13} (see picture, orange) and a helical Y-shaped Au_7 motif (green). This is the first structural determination of a gold nanocluster containing an intrinsic chiral inorganic core.

Combined Vis and NIR imaging

A. Foucault-Collet, C. M. Shade,
I. Nazarenko, S. Petoud,*
S. V. Eliseeva* ___ **2927 – 2930**

Polynuclear Sm^{III} Polyamidoamine-Based Dendrimer: A Single Probe for Combined Visible and Near-Infrared Live-Cell Imaging

Back Cover

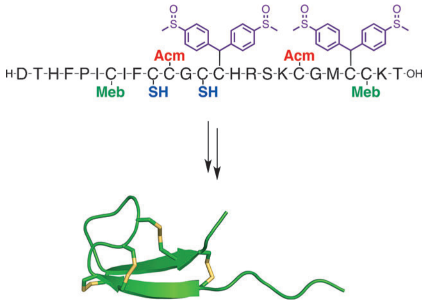


The good samarium: As a proof-of-principle, a generation-3 polyamidoamine dendrimer functionalized with thirty-two 2,3-naphthalimide moieties and incorporating eight Sm^{III} ions is used as a bioprobe for combined visible and near-infrared imaging.

Controlled Peptide Folding

Z. Dekan, M. Mobli, M. W. Pennington,
E. Fung, E. Nemeth,
P. F. Alewood* ___ **2931 – 2934**

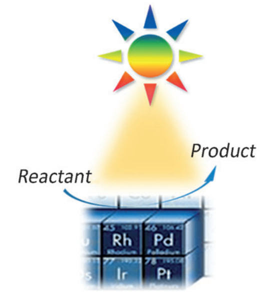
Total Synthesis of Human Hepcidin through Regioselective Disulfide-Bond Formation by using the Safety-Catch Cysteine Protecting Group 4,4′-Dimethylsulfinylbenzhydryl



Safety first: Native hepcidin, which contains four disulfide bonds, and an earlier proposed disulfide-bond isomer were synthesized with full regiocontrol by employing the safety-catch thiol protecting group 4,4′-dimethylsulfinylbenzhydryl (Msbh). With the synthetically confirmed connectivity, a high-resolution NMR structure of native hepcidin could be obtained. The Msbh group expands the scope of strategies for the regioselective synthesis of disulfide-rich molecules.

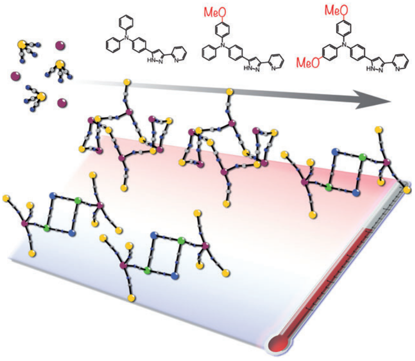
Nanoparticle Photocatalysts

An effective energy boost: Electrons in nonplasmonic transition-metal nanoparticles absorb light energy by interband absorption (see picture) and drive a wide range of well-established organic reactions with high efficiency at ambient temperatures.



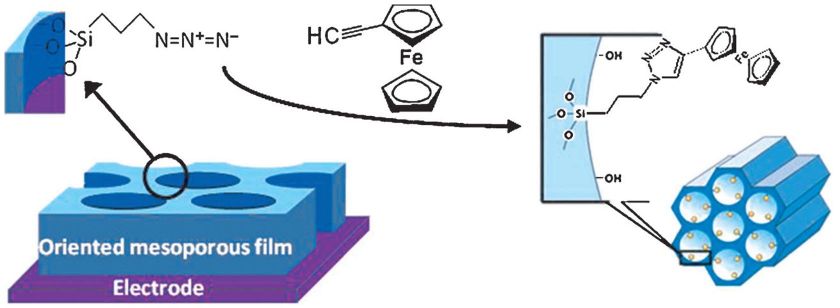
Self-Assembly

Inside Back Cover



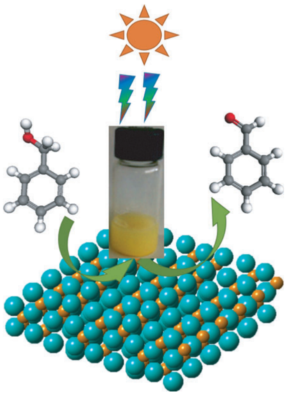
Spin offs: A bulky bidentate ligand stabilizes a $[Fe_8Co_6]$ cluster. Changing the ligand's electronic state by derivatization with one or two methoxy groups gave a homologous $[Fe_8Co_6]$ species and a $[Fe_8Co_4]$ complex, respectively. Reactions at low temperature allowed the isolation of the $[Fe_8Co_4]$ cluster with all three ligands through a solution-state electron-transfer-coupled spin transition (ETCST) which acts as a self-assembly directing process.

Functionalized Mesoporous Films



A combination of click chemistry with electrochemically assisted self-assembly enables highly ordered and vertically aligned mesoporous silica films to be generated. These can be derivatized with a variety of organic functional groups that remain active and easily accessible upon immobilization in the oriented matrix.

Photocatalysis

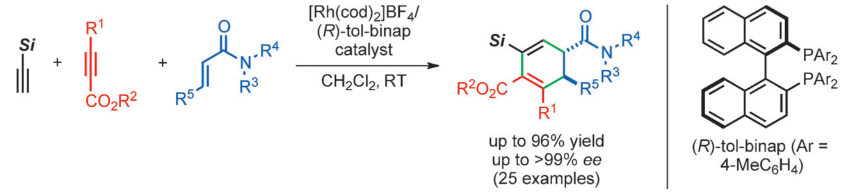


One layer is enough: Surface complexes between monolayer HNb_3O_8 and reactants help to remove the bandgap limitation for visible light photocatalysis. This catalyst exhibited exceptional performance for the selective oxidation of alcohols. This research provides proof-of-concept for the rational fabrication of visible light photocatalysts.

Asymmetric Catalysis

J. Hara, M. Ishida, M. Kobayashi, K. Noguchi, K. Tanaka* ____ **2956 – 2959**

Highly Chemo-, Regio-, and Enantioselective Rhodium-Catalyzed Cross-Cyclotrimerization of Two Different Alkynes with Alkenes

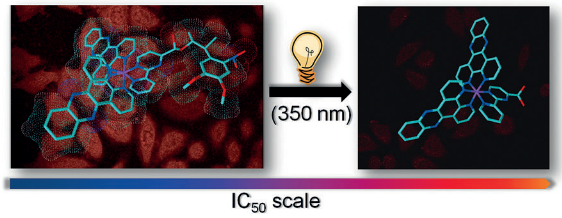


Cross-training: It has been established that a cationic rhodium(I)/(*R*)-tol-binap complex catalyzes the cross-cyclotrimerization of silylacetylenes, di-*tert*-butyl acetylenedicarboxylates, and acrylamides with excellent chemo-, regio-, and enantioselectivities. Unsymmetrical alkynoates can also be employed in place of di-*tert*-butyl acetylenedicarboxylate for this process, but with a reduced chemoselectivity. cod = cyclo-1,5-octadiene.

Prodrugs

T. Joshi,* V. Pierroz, C. Mari, L. Gemperle, S. Ferrari, G. Gasser* ____ **2960 – 2963**

A Bis(dipyridophenazine)(2-(2-pyridyl)pyrimidine-4-carboxylic acid)ruthenium(II) Complex with Anticancer Action upon Photodeprotection

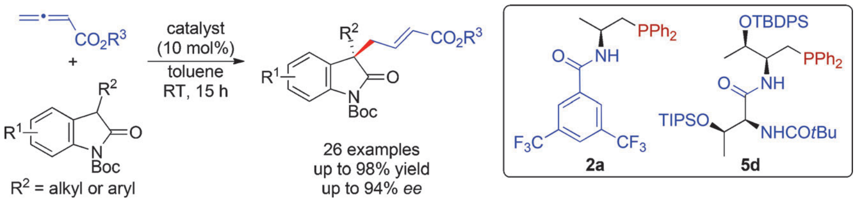


Light, ruthenium, anticancer action! Modifying substitutionally inert $[Ru(dppz)_2(CppH)]^{2+}$ to become a 3-(4,5-dimethoxy-2-nitrophenyl)-2-butyl ester renders it inactive to both cancerous (HeLa and U2OS) and non-cancerous (MRC-5) cells. Cytotoxic effects of the complex can be unleashed upon illumination. CppH = 2-(2-pyridyl)pyrimidine-4-carboxylic acid; dppz = dipyrido[3,2-*a*:2′,3′-c]phenazine.

Phosphine Catalysis

T. Wang, W. Yao, F. Zhong, G. H. Pang, Y. Lu* ____ **2964 – 2968**

Phosphine-Catalyzed Enantioselective γ-Addition of 3-Substituted Oxindoles to 2,3-Butadienoates and 2-Butynoates: Use of Prochiral Nucleophiles

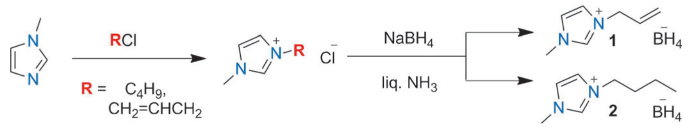


Oxindoles and allenoates: The phosphine-catalyzed γ-addition of allenoates to oxindoles enabled the synthesis of oxindole derivatives that bear an all-carbon quaternary stereogenic center at the 3-position in high yields and with excellent enantioselectivity. The synthetic potential of the addition products was demonstrated by the formal total synthesis of two natural products.

Hypergolic Ionic Liquids

S. Li, H. Gao,* J. M. Shreeve* ____ **2969 – 2972**

Borohydride Ionic Liquids and Borane/Ionic-Liquid Solutions as Hypergolic Fuels with Superior Low Ignition-Delay Times



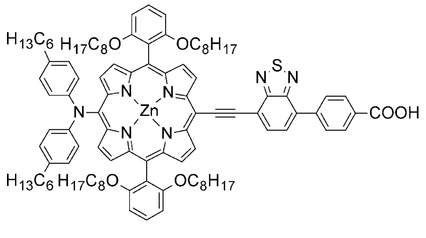
No more delay: Boron hydrides show marked potential in accelerating the ignition of hypergolic liquid fuels. The borohydride-based ionic liquids (IL) **1** and **2** were investigated along with borane additives. IL **1** exhibited the shortest ignition-delay time of any known hypergolic ILs, and the triethylamine–borane complex is the most efficient hypergolic additive examined to date.

Porphyrin Sensitizers

A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh,* M. Grätzel* ________ 2973 – 2977

Molecular Engineering of Push–Pull Porphyrin Dyes for Highly Efficient Dye-Sensitized Solar Cells: The Role of Benzene Spacers

Not just to fill a gap: Porphyrins are promising sensitizers owing to the large absorption coefficients of their Soret and Q bands in the visible region. The incorporation of a 2,1,3-benzothiadiazole moiety in a donor–acceptor zinc porphyrin as a π-conjugated linker between the anchoring group and the chromophore (see structure) broadened the absorption spectra to fill the valley between the Soret and Q bands and led to efficient power conversion.

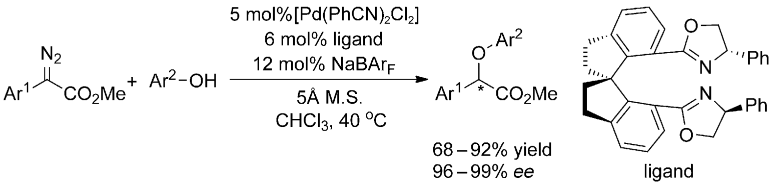


GY50

Asymmetric Catalysis

X.-L. Xie, S.-F. Zhu,* J.-X. Guo, Y. Cai, Q.-L. Zhou* ________ 2978 – 2981

Enantioselective Palladium-Catalyzed Insertion of α-Aryl-α-diazoacetates into the O–H Bonds of Phenols

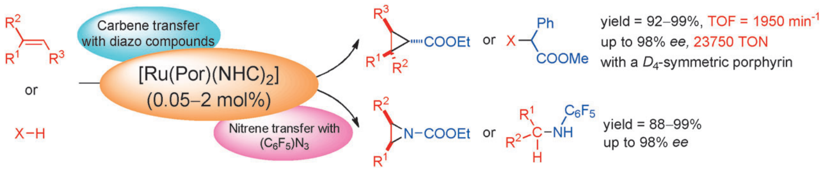


Things and Ar–OHs: A palladium-catalyzed asymmetric O–H insertion of α-aryl-α-diazoacetates into phenols was developed. As well as giving high yields and excellent enantioselectivity, this reaction exhibits a broad substrate scope under mild reaction conditions, thus providing an efficient method for the preparation of synthetically useful optically active α-aryl-α-aryloxyacetates.

Coordination Chemistry

K.-H. Chan, X. Guan, V. K.-Y. Lo,* C.-M. Che* ________ 2982 – 2987

Elevated Catalytic Activity of Ruthenium(II)–Porphyrin-Catalyzed Carbene/Nitrene Transfer and Insertion Reactions with N-Heterocyclic Carbene Ligands

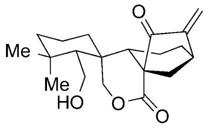


Por complexes, working like crazy: Bis(N-heterocyclic carbene) (NHC) ruthenium(II) porphyrin (Por) complexes showed unprecedentedly high catalytic activity toward alkene cyclopropanation (see scheme; TOF/TON = turnover frequency/number), carbene C–H, S–H, N–H, and O–H insertion, alkene aziridination, and nitrene C–H insertion. Highly enantioselective carbene and nitrene C–H insertion and addition to C=C bonds was also possible.

Natural Product Synthesis

B. J. Moritz, D. J. Mack, L. Tong, R. J. Thomson* ________ 2988 – 2991

Total Synthesis of the *Isodon* Diterpene Sculponeatin N



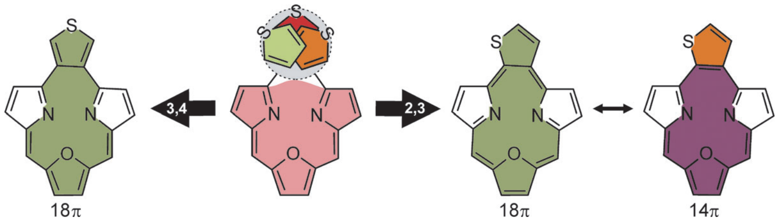
Sculponeatin N

Sculpting sculponeatin: The total synthesis of sculponeatin N, a bioactive polycyclic diterpene isolated from *Isodon sculponeatus*, is reported. Key features of the synthesis include diastereoselective Nazarov and ring-closing metathesis reactions, and highly efficient formation of the bicyclo[3.2.1]octane ring system by a reductive radical cyclization.

Triphyrins(n.1.1)

M. Pawlicki,* K. Hurej, L. Szterenberg,
L. Latos-Grażyński* 2992 – 2996

Synthesis and Switching the Aromatic Character of Oxatriphyrins(2.1.1)

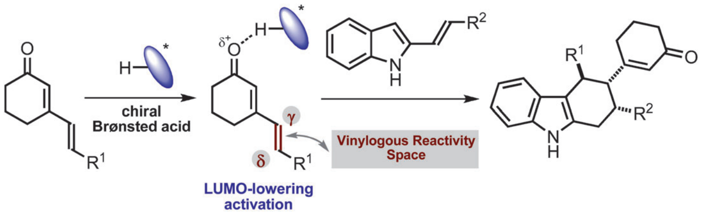


Going for a spin: The precisely crafted thiophene-fused oxatriphyrins(2.1.1) show an aromatic character consistent with 14π or 18π delocalization pathways. The aromaticity is strongly dependent on a thiophene incorporation mode and can be switched to anti-aromatic (16π electrons) or non-aromatic by reduction with a zinc amalgam. Both reduced structures are stable as boron(III) complexes.

Synthetic Methods

X. Tian, N. Hofmann,
P. Melchiorre* 2997 – 3000

Asymmetric Vinylogous Diels–Alder Reactions Catalyzed by a Chiral Phosphoric Acid

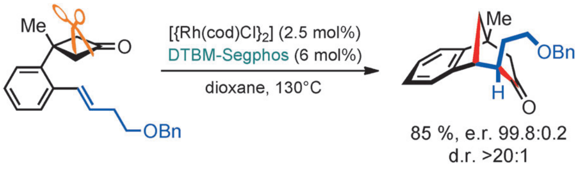


Further and further: A vinylogous Diels–Alder reaction that is catalyzed by a commercially available chiral phosphoric acid has been developed. A range of structurally diverse complex tetrahydrocarbazoles were obtained in high chemical yields and with excellent stereoselectivity. It was thus demonstrated that the synthetic utility of the Diels–Alder reaction can be extended to include a vinylogous reactivity space.

C–C Activation

L. Souillart, E. Parker,
N. Cramer* 3001 – 3005

Highly Enantioselective Rhodium(I)-Catalyzed Activation of Enantiotopic Cyclobutanone C–C Bonds



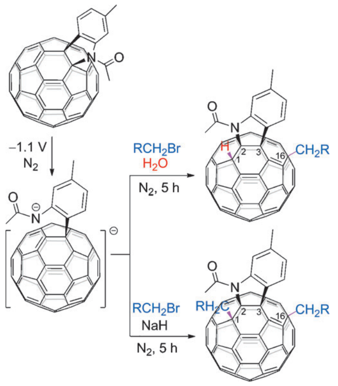
All in (cyclobutan)one: The enantioselective direct C–C activation of cyclobutanones was achieved by using chiral rhodium(I) catalysts. The intermediate rhodacyclopentanone reacts with a wide variety of tethered olefins to deliver complex bicyclic ketones in high yield. Despite operating at 130 °C, the process is characterized by outstanding enantioselectivity with the e.r. generally greater than 99.5:0.5.

Fullerene Chemistry

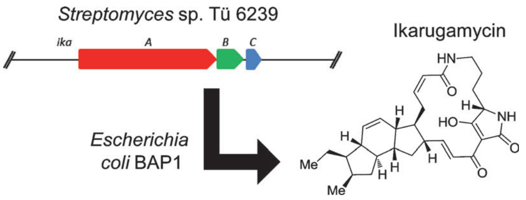
Y. Xiao, S.-E Zhu, D.-J. Liu, M. Suzuki,
X. Lu,* G.-W. Wang* 3006 – 3010

Regioselective Electrosynthesis of Rare 1,2,3,16-Functionalized [60]Fullerene Derivatives

Exercizing control: The highly regioselective reaction of dianionic fullerene species, generated by electroreduction of a fulleroindoline, with benzyl bromide or ethyl bromoacetate affords the rare 1,2,3,16-adducts of C_{60} (see scheme). Intriguingly, either one or two alkyl groups can be selectively introduced onto the fullerene surface in the absence or presence of sodium hydride. The high regioselectivity is governed by both the charge distribution and steric factors.

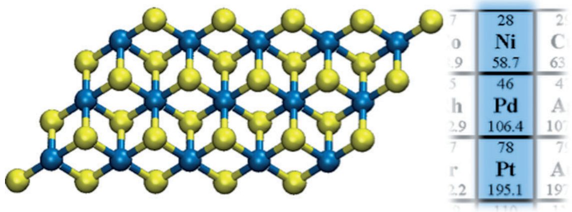


Natural Product Biosynthesis



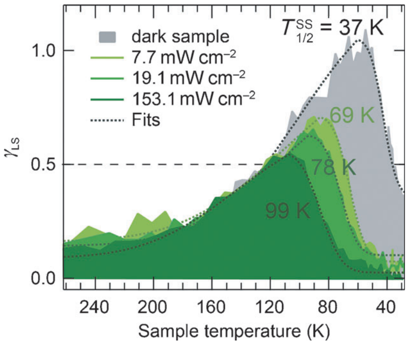
Small cluster, big molecule: Polycyclic tetramate macrolactams (PTMs) are a family of structurally diverse, bioactive natural products. Valuable insight into the compact biosynthesis of PTMs has been obtained by heterologous expression of the newly identified ikarugamycin biosynthetic gene cluster in *E. coli*. The heterologous production of PTMs with the established method will allow many cryptic PTM gene clusters to be chemically unlocked in the future.

Noble 2D Materials



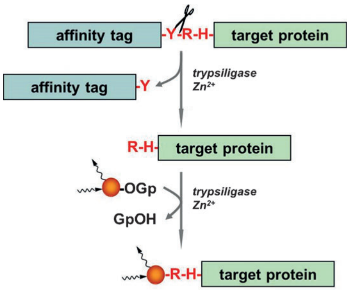
Show you're metal: The structure and electronic structure of layered noble-transition-metal dichalcogenides MX_2 with metals M (Pt and Pd) and chalcogenides X (S, Se, and Te) have been investigated with periodic density functional theory calculations. The MS_2 monolayers are indirect band-gap semiconductors whereas the MSe_2 and MTe_2 analogues show a significant decrease in their band-gaps and can even become semimetallic or metallic materials.

Spin-Crossover Films



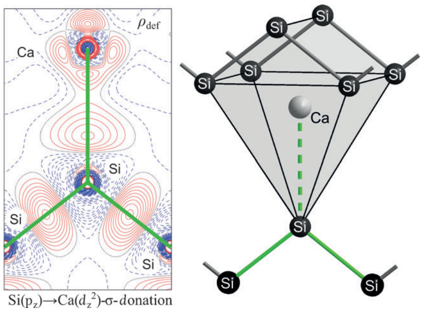
Spin-state switching in ultrathin films of a Fe^{II} spin crossover complex deposited on Au(111) is achieved by irradiation with visible and vacuum-UV light. The electronic structure of the complex is determined by UPS, which allows the thermal as well as light-induced transition between the high-spin (HS) and the low-spin (LS) form to be monitored.

Covalent Protein Modification



Trypsiligase catalyzes the selective modification of proteins with the substrate-mimetic 4-guanidino phenyl ester (OGp). Modification proceeds with quantitative product yields under native (aqueous) conditions. The variant possesses a disordered zymogen-like activation domain, effectively suppressing the hydrolysis reaction, which is converted to an active conformation in the presence of appropriate substrates.

Main-Group Compounds



Over-Zintl-ified? The nature of chemical bonding in the Zintl phase CaSi has been analyzed by experimental and theoretical charge density analyses. The presence of covalent Si–Si interactions supports this fundamental bonding concept. Now however, clear experimental evidence is provided that the cation–polyanion interaction cannot be solely described as purely ionic, a potential explanation of the unexpected metallic behavior.

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

Probing the Intracellular Glutathione Redox Potential by In-Cell NMR Spectroscopy

S. Y. Rhieu,* A. A. Urbas, D. W. Bearden, J. P. Marino, K. A. Lippa, V. Reipa* ______ **447–450**

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

DOI: 10.1002/anie.201308004

In this Communication, the numbers on the *y* axis of Figure 3 b were incorrect. The corrected version is shown below. The authors apologize for any confusion or inconvenience this error may have caused.

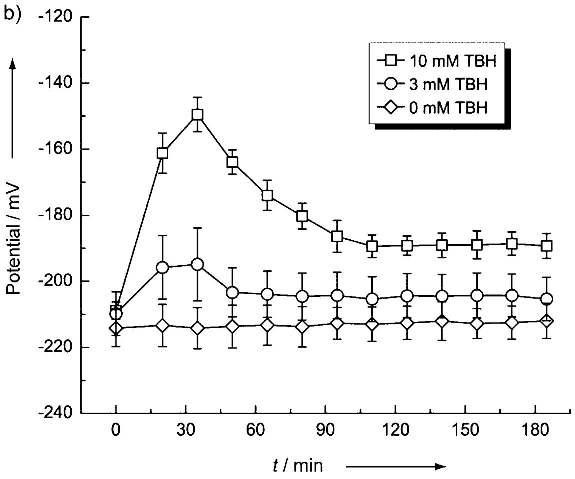

Figure 3. Monitoring of the intracellular glutathione redox potential. … b) Cellular concentrations of GSH* and GSSG* were calculated based on the calibration derived from cell samples examined by NMR spectroscopy and measured externally by the DTNB-GSSG reductase recycling assay (DTNB: 5,5′-dithiobis(2-nitrobenzoic acid); see the Supporting Information, Figure S3). The intracellular glutathione redox potential was calculated by using the Nernst equation with a standard redox potential ($E^{0'}_{GSSG/2GSH}$) of −240 mV at pH 7.0 and an average cell volume of 11.74 fL. Data represent the mean ± the standard deviation from three independent experiments.