



# The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

T. Lewis, M. Faubel, B. Winter, J. C. Hemminger\*

CO<sub>2</sub> Capture in an Aqueous Solution of an Amine: Role of the Solution Interface

Y. H. Kim, S. Banta\*

Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

A. W. Fay, M. A. Blank, C. C. Lee, Y. Hu,\* K. O. Hodgson,\* B. Hedman,\* M. W. Ribbe\*

Spectroscopic Characterization of a Precursor Isolated from NifEN of an Iron-Molybdenum Cofactor

V. Zinth, T. Dellmann, H.-H. Klauss, D. Johrendt\*
Recovery of a Parentlike State in Ba<sub>1-x</sub>K<sub>x</sub>Fe<sub>1.86</sub>Co<sub>0.14</sub>As<sub>2</sub>

P. G. Cozzi,\* A. Gualandi, E. Emer, M. G. Capdevila Highly Enantioselective  $\alpha$  Alkylation of Aldehydes with 1,3-Benzodithiolylium Tetrafluoroborate: A General Formal Organocatalytic  $\alpha$  Alkylation of Aldehydes by Carbenium Ions

I. Coin, M. H. Perrin, W. W. Vale, L. Wang\*

Photo-Cross-Linkers Incorporated into G-Protein-Coupled Receptors in Mammalian Cells: A Ligand Comparison C. Nilewski, N. R. Deprez, T. C. Fessard, D. Bo Li, R. W. Geisser, E. M. Carreira\*

Synthesis of Undecachlorosulfolipid A: Re-evaluation of the Nominal Structure

S. Kawamorita, H. Ohmiya, T. Iwai, M. Sawamura\*
Palladium-Catalyzed Borylation of Sterically Demanding Aryl
Halides with a Silica-Supported Compact Phosphane Ligand

R. A. Sanguramath, T. N. Hooper, C. P. Butts, M. Green,\* J. E. McGrady, C. A. Russell\*

Interaction of Gold(I) Cations with 1,3-Dienes

F. Freire, A. M. Almeida, J. D. Fisk, J. D. Steinkruger, S. H. Gellman\* Impact of Strand Length on the Stability of Parallel-β-Sheet Secondary Structure

K. A. B. Austin, E. Herdtweck, T. Bach\*
Intramolecular [2+2]-Photocycloaddition of Substituted
Isoquinolones: Enantioselectivity and Kinetic Resolution

Induced by a Chiral Template

O. V. Zenkina, E. C. Keske, R. Wang, C. Crudden\*

Double Single-Crystal-to-Single-Crystal Transformation and

Small-Molecule Activation in Rhodium NHC Complexes

## **Author Profile**

Stefan Hecht \_\_\_\_\_\_ 7218

# "What I look for first in a publication is a thrilling new concept.

The best stage in a scientist's career is when they can still do chemistry in the lab with their own hands  $\dots$ "

This and more about Stefan Hecht can be found on page 7218.

A. Corma



L. González



V. W.-W. Yam

### News



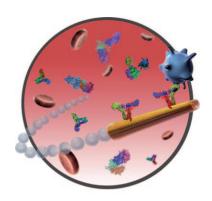
## Highlights

### Cancer Cells

W. Gao, O. C. Farokhzad\* \_ 7220 - 7221

Self-Propelled Microrockets to Capture and Isolate Circulating Tumor Cells

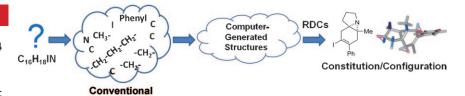
Ready for take-off: A self-propelled "microrocket" has been developed to capture and isolate circulating tumor cells from a cell mixture (see picture). This novel approach builds on the existing cell capture technologies whereby cell mixtures are exposed to antibody-functionalized surfaces to achieve binding-mediated cell capture. Self-propelled microrockets will facilitate a wide range of biomedical applications.



#### Structure Elucidation

R. R. Gil\* \_\_\_\_\_\_ 7222 - 7224

Constitutional, Configurational, and Conformational Analysis of Small Organic Molecules on the Basis of NMR Residual Dipolar Couplings



Nearly 50 years after its conception, the configurational and conformational analysis of small organic molecules on the basis of residual dipolar couplings (RDCs) was made possible by the development of alignment media compatible with organic

**NMR Spectroscopy** 

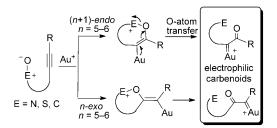
solvents. RDCs have now also been used to determine the chemical constitution of a synthetic organic compound whose structure could not be identified by conventional spectroscopic techniques (see picture).

### **Minireviews**

### Gold Catalysis

J. Xiao, X. Li\* \_\_\_\_\_\_ 7226-7236

Gold  $\alpha$ -Oxo Carbenoids in Catalysis: Catalytic Oxygen-Atom Transfer to Alkynes



Can't avoid carbenoids: Gold  $\alpha$ -oxo carbenoids are key intermediates generated from gold complexes, alkynes, and nucleophilic oxygen-atom donor groups (see scheme). These  $\alpha$ -oxo carbenoids can undergo nucleophilic attack by various

groups leading to the formation of C–E (E=C, N, S, or O) bonds and manipulation of the molecular skeleton. The scope of these reactions is examined for different nucleophilic oxygen-atom donors.

#### For the USA and Canada:

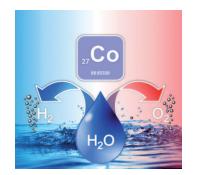
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals

postage paid at Jamaica, NY 11431. US POST-MASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 9442/8583 (valid for print and electronic / print or electronic delivery); for

individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



It's cobalt's turn: Splitting water with light appears to be a promising solution for the renewable production of a fuel such as hydrogen. Recent developments on cobalt-based catalysts for  $H_2$  or  $O_2$  evolution are discussed, along with how they can be coupled with photosensitizers, to generate light-driven systems, or immobilized onto conducting materials to form electrodes or photoelectrodes for integration in a photoelectrochemical cell.

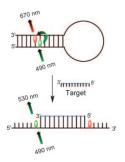


### Reviews

### Photocatalytic Water Splitting

V. Artero,\* M. Chavarot-Kerlidou,
M. Fontecave\* \_\_\_\_\_\_ 7238 – 7266

Splitting Water with Cobalt



**DNA** traffic lights for hybridization: An efficient energy transfer between thiazole orange and thiazole red in the DNA stem architecture yields a red fluorescence that changes to green emission upon binding to the target oligonucleotide sequence.

### **Communications**

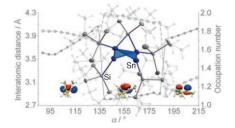
#### Molecular Beacons

C. Holzhauser,

H.-A. Wagenknecht\* \_\_\_\_\_ 7268 - 7272

In-Stem-Labeled Molecular Beacons for Distinct Fluorescent Color Readout





A small leak will sink a great ship: Treating Sn'Br with LiSi(SiMe<sub>3</sub>)<sub>3</sub> gives the polyhedral title cluster, a new member of the singlet biradicaloid species. Calculations show that the ligand orientation influences the bonding inside the cluster leading to a sudden transition between bonded and biradicaloid forms. The cluster could be an ideal model system to study this transition.

### Tin Clusters

C. Schrenk, A. Kubas, K. Fink,

A. Schnepf\* \_\_\_\_\_\_ 7273 – 7277

[Sn<sub>4</sub>Si{Si(SiMe<sub>3</sub>)<sub>3</sub>}<sub>4</sub>{SiMe<sub>3</sub>}<sub>2</sub>]: A Model Compound for the Unexpected First-Order Transition from a Singlet Biradicaloid to a Classical Bonded Molecule





**Alcohol and CO**: A new process for hydrogenating CO<sub>2</sub> to formic acid has been developed. Calorimetric studies were carried out to clarify the role of the alcohol solvent in the catalytic cycle. CO<sub>2</sub> hydrogenation is only thermodynamically feasi-

ble in the presence of hydrogen-bonding solvents. NMR spectroscopy indicates that catalytically active monocarbonyl complexes are formed when highly basic alkyl phosphine complexes are used as catalysts.

### CO<sub>2</sub> Hydrogenation

T. Schaub,\* R. A. Paciello\* \_ 7278 - 7282

A Process for the Synthesis of Formic Acid by CO<sub>2</sub> Hydrogenation: Thermodynamic Aspects and the Role of CO



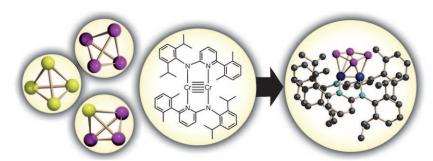
### Pnicogen Complexes

C. Schwarzmaier, A. Noor, G. Glatz, M. Zabel, A. Y. Timoshkin, B. M. Cossairt, C. C. Cummins, R. Kempe,\*

M. Scheer\* \_ 7283 - 7286



Formation of cyclo- $E_4^{2-}$  Units ( $E_4 = P_4$ , As<sub>4</sub>, AsP<sub>3</sub>) by a Complex with a Cr-Cr Quintuple Bond



White phosphorus, yellow arsenic, and AsP<sub>3</sub> have been successfully activated by a complex with a Cr-Cr quintuple bond in one step leading to the formation of rare terminally bound cyclo-P<sub>4</sub><sup>2-</sup>, cyclo-As<sub>4</sub><sup>2-</sup>,

and cyclo-AsP3 units. The subsequent reaction with an excess of [W(CO)<sub>5</sub>(thf)] leads to the coordination of one {W(CO)<sub>5</sub>} fragment in the thermodynamically most stable form according to DFT calculations.

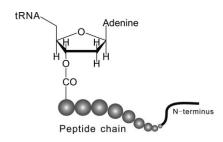
### Ribosomes

Y. Huang, M. Sprinzl\* \_\_\_\_\_ 7287 - 7289



Peptide Bond Formation on the Ribosome: The Role of the 2'-OH Group on the Terminal Adenosine of PeptidyltRNA and of the Length of Nascent Peptide Chain

The conformation of the 3'-terminal ribose is essential for peptide bond formation on the ribosome. The growing peptide chain (see picture) anchored in the ribosomal peptide exit tunnel stabilizes to required conformation and provides the frame for precisely positioning the peptidyl-tRNA and aminoacyl-tRNA. The 2'-OH group on the 3'-terminal adenosine of peptidyltRNA is not essential.

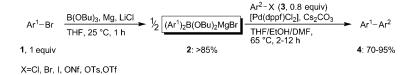


### Magnesium Diorganoboronates

B. A. Haag, C. Sämann, A. Jana, P. Knochel\* \_\_\_\_\_ 7290 - 7294



Practical One-Pot Preparation of Magnesium Di(hetero)aryl- and Magnesium Dialkenylboronates for Suzuki-Miyaura Cross-Coupling Reactions



Mg for B: An atom-economical one-pot synthesis by direct magnesium insertion in the presence of B(OBu)<sub>3</sub> and LiCl allows a broad range of functionalized (hetero)aryl and alkenyl bromides to be converted into magnesium diorganoboronates 2,

which undergo Suzuki-Miyaura crosscoupling reactions with various aryl (pseudo) halides (see scheme). Both aryl groups of 2 are transferred and furnish the products in good to excellent yields.

### Metallacycles

J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin,\* **7295 – 7299** 

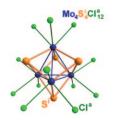
G. Jia\* \_\_\_\_\_

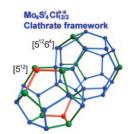


Conversion of Metallabenzynes into Carbene Complexes

Osmabenzynes are shown to rearrange to carbene complexes. This previously unknown reaction of metallabenzynes, in analogy to the well-known formation of cyclopentadienyl complexes from metallabenzenes, has thus now been achieved. A subtle change in the substituents in the metallacycle can have a drastic effect on the transformation, as seen by the relative thermal stability of 1 and 2 (see scheme).







Cluster-based clathrate: Mo<sub>4</sub>Si<sub>4</sub>Cla<sub>12</sub> inorganic building blocks (see picture, i = inner, a = apical) containing Mo<sub>4</sub> metal atom clusters assemble to yield an inorganic giant framework structurally related to type II clathrate. This compound is the

first member of a promising family of materials with a wide range of physical properties that combine the chemistry of metallic clusters characterized by delocalized electrons with that of inorganic clathrates.

#### Clathrates

M. A. Shestopalov, A. Y. Ledneva,

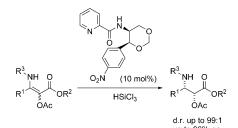
S. Cordier,\* O. Hernandez, M. Potel,

T. Roisnel, N. G. Naumov,

C. Perrin\* \_ 7300 - 7303

Tetrahedral Mo<sub>4</sub> Clusters as Building Blocks for the Design of Clathrate-Related Giant Frameworks





By design: A series of  $\alpha$ -acetoxy- $\beta$ -enamino esters 1 were synthesized and then subjected to catalytic asymmetric hydrosilylation. In the presence of a chiral Lewis base catalyst, the reactions proceeded smoothly to provide a wide range of chiral  $\alpha$ -acetoxy  $\beta$ -amino acid derivatives in high yields with good diastereoselectivities and enantioselectivities.

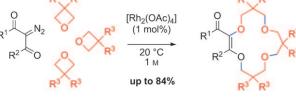
### Asymmetric Hydrosilylation

Y. Jiang, X. Chen, Y. Zheng, Z. Xue, C. Shu, W. Yuan, X. Zhang\* \_\_\_\_\_ 7304-7307

Highly Diastereoselective and Enantioselective Synthesis of  $\alpha$ -Hydroxy β-Amino Acid Derivatives: Lewis Base Catalyzed Hydrosilylation of α-Acetoxy β-Enamino Esters







Highly concentrated: The title reaction proceeds to afford a rare type of 15membered polyether macrocycle in up to 84 % yield ( $R^1 = alkyl$ , alkoxy, O-allyl,  $OCH_2CH_2Ph$ ;  $R^2 = alkyl$ , Ph;  $R^3 = H$ , Me,

Et). This nontemplated macrocyclization is performed in a single pot under high concentration and precludes the usual polymerization.

### Synthetic Methods

D. Rix, R. Ballesteros-Garrido, W. Zeghida, C. Besnard, J. Lacour\* \_\_\_\_\_ 7308-7311

Macrocyclization of Oxetane Building Blocks with Diazocarbonyl Derivatives under Rhodium(II) Catalysis



Good to excellent yields of aryl trifluoromethyl sulfides, which are an important class of compounds in both the pharmaceutical and agrochemical areas, can be

achieved under mild conditions by the Pdcatalyzed reaction of aryl bromides with a trifluoromethylthiolate nucleophile (see scheme).

### C-S Bond Formation

G. Teverovskiy, D. S. Surry, S. L. Buchwald\* 7312 - 7314

Pd-Catalyzed Synthesis of Ar-SCF<sub>3</sub> Compounds under Mild Conditions

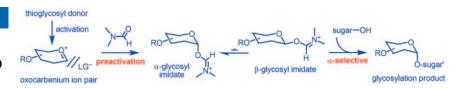


### Glycosylation

S.-R. Lu, Y.-H. Lai, J.-H. Chen, C.-Y. Liu, K.-K. T. Mong\* \_\_\_ \_ 7315 - 7320



Dimethylformamide: An Unusual Glycosylation Modulator



A simple solution: When N,N-dimethylformamide was used to direct the stereochemical course of glycosylation reactions, 1,2-cis glycosylation products were formed with excellent selectivity. A straightforward highly  $\alpha$ -stereoselective

glycosylation involving preactivation (see scheme) should find broad application and be especially useful for sequential glycosylation reactions to form oligosaccharides. LG = leaving group.

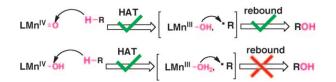
### Oxidation

S. Shi, Y. Wang, A. Xu, H. Wang, D. Zhu, S. B. Roy, T. A. Jackson, D. H. Busch,

G. Yin\* \_\_\_ \_\_\_ 7321 – 7324



Distinct Reactivity Differences of Metal Oxo and Its Corresponding Hydroxo Moieties in Oxidations: Implications from a Manganese(IV) Complex Having Dihydroxide Ligand



The  $M^{n+}$ —OH moiety in a manganese(IV) complex has more powerful electrontransfer capability than its corresponding  $M^{n+}=O$  moiety. An  $M^{n+}=O$  moiety can abstract hydrogen from a substrate, then rebind the OH group from its reduced

 $M^{(n-1)+}$ —OH form to the substrate radical. In contrast, the active center with an  $M^{n+-}$ OH cannot perform similar rebound from its reduced  $M^{(n-1)+}$ — $OH_2$  group (see scheme; HAT = hydrogen abstraction).

### Graphene Hydrogels

X. Yang, L. Qiu, C. Cheng, Y. Wu, Z.-F. Ma, \_\_\_\_\_ 7325 – 7328



Ordered Gelation of Chemically Converted Graphene for Next-Generation Electroconductive Hydrogel Films

Modified graphene can self-gel at the liquid-solid interface in a face-to-face manner to form an oriented conductive hydrogel film. This unusual gelation behavior enables a new generation of electroconductive hydrogels combining exceptional mechanical strength, high electrical conductivity, mechanical flexibility, and anisotropic responsive properties. Scale bar: 1 μm.





### Asymmetric Hydrogenation

J.-H. Xie,\* X.-Y. Liu, J.-B. Xie, L.-X. Wang, Q.-L. Zhou\* \_\_\_\_\_\_ 7329 – 7332



An Additional Coordination Group Leads to Extremely Efficient Chiral Iridium Catalysts for Asymmetric Hydrogenation of Ketones

$$R^{1} \stackrel{O}{\underset{\textbf{4}}{=}} R^{2} \stackrel{\text{[\{Ir(cod)Cl\}}_{2}] / (R) - \textbf{2g}}{\text{EtOH, KO} fBu, RT} \stackrel{OH}{\underset{\textbf{5}}{=}} R^{2}$$

$$R^{1} = \text{aryl, alkyl} \qquad 95 - 99\% \text{ yields}$$

88-99.9% ee

 $R^2$  = Me, Et, nBu

TON up to 4 550 000 (R)-2g  $(Ar = 3,5-(tBu)_2C_6H_3)$ 

What a turnover! An efficient chiral iridium catalyst that bears a tridentate spiro aminophosphine ligand catalyzes the asymmetric hydrogenation of ketones

with excellent enantioselectivities (up to 99.9% ee) and extremely high turnover numbers (TONs; as high as 4550000).



 $\mathsf{R}^1$ ,  $\mathsf{R}^2$  = cyclic, acyclic, aromatic amides, carbamates  $R^3 = CO_2R$ ,  $CONR_2$ , Ar

18 examples 51-81% yield

Functionalization of enamides under Heck conditions has been limited to those with unsubstituted vinyl groups. By tuning reaction parameters that allow for the balance between stability and reactivity of

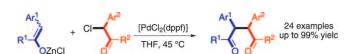
reactants, the oxidative Heck cross-coupling to produce highly substituted enamides in good to excellent yields was achieved (see scheme).

### Cross-Coupling

Y. Liu, D. Li, C.-M. Park\* \_\_\_\_ 7333 - 7336

Stereoselective Synthesis of Highly Substituted Enamides by an Oxidative Heck Reaction





Palladium can do it! A novel palladiumcatalyzed reaction between the bulky  $\alpha$ carbon centers of two ketones has led to the construction of 2,3-diaryl-1,4-diketones by employing  $\alpha$ -chloroketones as

electrophiles and zinc ketone enolates as nucleophiles (see scheme). This reaction allows the synthesis of bulky 1,4-diketones and is complementary with classic nucleophilic substitution reactions.

### C-C Coupling

C. Liu, Y. Deng, J. Wang, Y. Yang, S. Tang, \_ 7337 - 7341

Palladium-Catalyzed C-C Bond Formation To Construct 1,4-Diketones under Mild Conditions





The coordination mode of a monodentate phosphoroamidite ligand in a rhodium complex can be switched from equatorial

pseudo encapsulation (see scheme). The axial complex has higher activity and selectivity in the challenging asymmetric hydroformylation of internal alkenes.

### Coordination Chemistry

R. Bellini, S. H. Chikkali, G. Berthon-Gelloz,\* I. N. H. Reek\* \_\_ 7342 - 7345

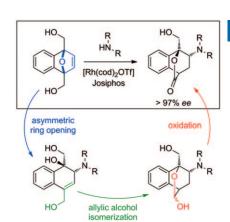
Supramolecular Control of Ligand Coordination and Implications in Hydroformylation Reactions



to axial by a unique supramolecular

Once, twice, three times a catalyst! A

novel domino rhodium(I)-catalyzed asymmetric transformation of substituted oxabicyclic alkenes into bicyclo-[2.2.2] lactones proceeded with good yields (up to 78 %) and excellent stereoselectivity (>97 % ee; see scheme; cod = 1,5-cyclooctadiene, Tf = trifluoromethanesulfonyl). Mechanistic investigations suggest that this process proceeds by rhodium-catalyzed asymmetric ring opening, allylic alcohol isomerization and oxidation.



### **Domino Reactions**

A. Boyer, M. Lautens\* \_\_\_\_\_ 7346-7349

Rhodium-Catalyzed Domino Enantioselective Synthesis of Bicyclo[2.2.2]lactones



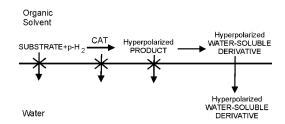
### Hyperpolarized Molecules

F. Reineri, A. Viale, S. Ellena, T. Boi, V. Daniele, R. Gobetto,

S. Aime\* \_\_\_\_\_\_ 7350 – 7353



Use of Labile Precursors for the Generation of Hyperpolarized Molecules from Hydrogenation with Parahydrogen and Aqueous-Phase Extraction



Hyperpolarization using parahydrogen can be more efficient when the reaction is carried out on a precursor that is then quickly transformed into the desired probe. The procedure was tested with

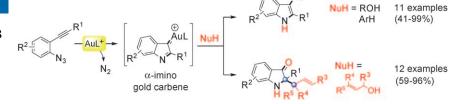
[1-13C]succinate prepared from hydrogenation with parahydrogen of maleic anhydride followed by hydrolysis. This method also allows the catalyst to be removed without polarization loss.

### Homogeneous Gold Catalysis

A. Wetzel, F. Gagosz\* \_\_\_\_\_ 7354-7358



Gold-Catalyzed Transformation of 2-Alkynyl Arylazides: Efficient Access to the Valuable Pseudoindoxyl and Indolyl Frameworks



An element of surprise: A series of functionalized 2-alkynyl arylazides has beed converted into 3-substituted indoles or 2,2-disubstituted indolin-3-ones in the presence of a gold (I) complex. Various oxygen or aryl nucleophiles can be used in

this process to trap the intermediate  $\alpha$ -imino gold carbene. The structural motifs of the products are found in a large variety of biologically active compounds and natural products.

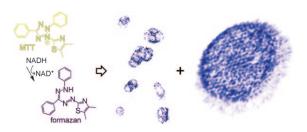
### Cell Imaging

Y. Zhang, X. Cai, Y. Wang, C. Zhang, L. Li, S.-W. Choi, L. V. Wang,\*

Y. Xia\* \_\_\_\_\_\_ 7359-7363



Noninvasive Photoacoustic Microscopy of Living Cells in Two and Three Dimensions through Enhancement by a Metabolite Dye

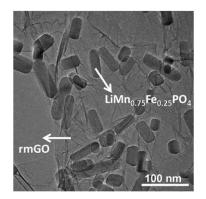


**Rich in contrast**: A new type of contrast agent, 1-(4,5-dimethyl-2-thiazolyl)-3,5-diphenylformazan (MTT formazan), is reported for nondestructive and nontoxic imaging of living cells by photoacoustic

microscopy (see picture). The contrast mechanism is general and can be applied to essentially all types of metabolically active cells, including stem cells and tumor cells.



A two-step solution-phase synthesis led to LiMn<sub>0.75</sub>Fe<sub>0.25</sub>PO<sub>4</sub> nanorods grown on graphene with superior electrical conductivity (see picture; rmGO = reduced mildly oxidized graphene oxide). The nanorod morphology is ideal for fast Li+ diffusion, with the diffusion path along the short radial direction (20-30 nm) of the nanorods. An ultrafast discharge performance for this hybrid cathode material is thus achieved.



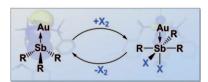
### Lithium Ion Batteries

H. Wang, Y. Yang, Y. Liang, L. Cui, H. Sanchez Casalongue, Y. Li, G. Hong, Y. Cui,\* H. Dai\* \_\_\_ \_\_\_\_\_ 7364 – 7368

LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> Nanorods Grown on Graphene Sheets for Ultrahigh-Rate-Performance Lithium Ion Batteries



A two-way street! The two-electron oxidation of a novel binuclear stibine gold compound induces an umpolung of the Sb-Au dative bond which switches from  $Sb \rightarrow Au$  in the reduced state to  $Sb \leftarrow Au$  in the oxidized state (see scheme). This reversible process can be triggered by the addition/elimination of a halogen-molecule equivalent.

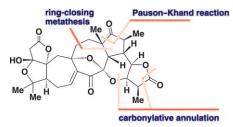


### Reversible Umpolung

C. R. Wade, F. P. Gabbaï\* \_\_ 7369 - 7372

Two-Electron Redox Chemistry and Reversible Umpolung of a Gold-Antimony Bond





schindilactone A

All together: A concise strategy for the first diastereoselective total synthesis of ( $\pm$ )-schindilactone A is reported. The synthesis features a ring-closing metathesis, a thiourea/cobalt-catalyzed

Pauson-Khand reaction, and a thiourea/ palladium-catalyzed carbonylative annulation reaction. The chemistry can be applied to the synthesis of structures related to schindilactone A.

### **Natural Products**

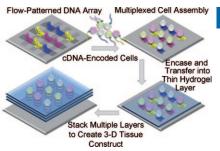
Q. Xiao, W.-W. Ren, Z.-X. Chen, T.-W. Sun, Y. Li, Q.-D. Ye, J.-X. Gong, F.-K. Meng, L. You, Y.-F. Liu, M.-Z. Zhao, L.-M. Xu, Z.-H. Shan, Y. Shi, Y. F. Tang,\* J.-H. Chen,\* Z. Yang\* \_\_\_ **—** 7373 – 7377

Diastereoselective Total Synthesis of ( $\pm$ )-Schindilactone A



#### Surface chemistry meets tissue engineer-

ing: A novel surface-patterning approach for creating arrays of DNA squares is combined with a unique method for DNAencoding of cells to construct dense arrays of distinct single cells. The cell patterns can be transferred from the substrate surface into thin hydrogel films, and these layers can be stacked to form 3D tissue constructs.



### Tissue Engineering

U. Vermesh, O. Vermesh, J. Wang, G. A. Kwong, C. Ma, K. Hwang, J. R. Heath\* \_\_\_\_ \_ 7378 - 7380

High-Density, Multiplexed Patterning of Cells at Single-Cell Resolution for Tissue Engineering and Other Applications

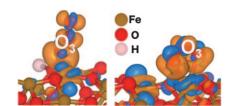


### Mesoporous Materials

T. Mathew,\* K. Suzuki,\* Y. Ikuta, Y. Nagai, N. Takahashi, H. Shinjoh \_\_\_\_ 7381 - 7384



Mesoporous Ferrihydrite-Based Iron Oxide Nanoparticles as Highly Promising Materials for Ozone Removal Ironing out ozone: Mesoporous two-line ferrihydrite is highly active for  $O_3$  removal owing to its abundance of surface unsaturated Fe sites.  $O_3$  can adsorb to both tricoordinate (see picture of charge transfer from blue to orange regions, left) and tetracoordinate sites (right). The less dense packing of oxygen around Fe sites with electrons more localized to the well-structured Fe 3d states of these mesoporous iron oxides obviously is advantageous for good  $O_3$  interaction.

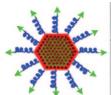


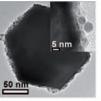
### **Multifunctional Nanoparticles**

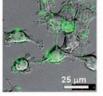
L. Cheng, K. Yang, Y. Li, J. Chen, C. Wang, M. Shao,\* S.-T. Lee, Z. Liu\* **7385 – 7390** 

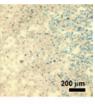


Facile Preparation of Multifunctional Upconversion Nanoprobes for Multimodal Imaging and Dual-Targeted Photothermal Therapy









Multimodal Imaging

Photothermal Therapy

Jack of all trades: A multifunctional nanoparticle (MFNP) integrates an upconversion nanoparticle (see picture, green), a layer of iron oxide nanoparticles (black), and a gold shell (red). The system can be used for in vitro targeted upcon-

version luminescence, magnetic resonance, and light scattering multimodal imaging of cells. The near-infrared optical absorption of MFNPs also enables photothermal destruction of cancer cells.

### Supercritical CO<sub>2</sub>

M. A. Méndez, P. Voyame,

H. H. Girault\* \_\_\_\_\_ 7391 - 7394



Interfacial Photoreduction of Supercritical  $CO_2$  by an Aqueous Catalyst



Not just a solvent anymore:  $CO_2$  reduction under supercritical conditions was achieved in a biphasic water–supercritical  $CO_2$  system using an aqueous soluble catalyst (see picture). The introduction of such an interface provides a suitable reaction medium where adsorption,  $CO_2$  binding, and protonation of intermediates are intimately linked.

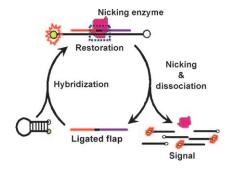
### **DNA** Detection

B. Zou, Y. Ma, H. Wu,

G. Zhou\* \_\_\_\_\_ 7395 - 7398



Ultrasensitive DNA Detection by Cascade Enzymatic Signal Amplification Based on Afu Flap Endonuclease Coupled with Nicking Endonuclease Hail CESA! Cascade enzymatic signal amplification (CESA) for DNA detection is achieved in three steps: invasive signal amplification by Afu endonuclease to generate amplified flaps, flap ligation by T4 ligase to form a nicking site, and nicking reaction by nicking endonuclease to produce amplified signals (see picture for last step). The sensitivity of CESA is as high as 1 fm DNA.









The stacking order and distance in columnar phases of triindole-based liquid crystals is controlled by an ethynyl linker (see picture; orange rod) between the central triindole core (green) and the peripheral flexible chains of a discotic mesogen. Hole (h) mobility is very high even if the stacking distances is not very short and the conjugated system is not particularly extended.

### Liquid Crystals

E. M. García-Frutos, U. K. Pandey,

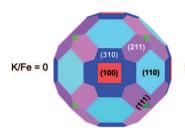
R. Termine, A. Omenat, J. Barberá,

J. L. Serrano, A. Golemme,\*

B. Gómez-Lor\* \_\_\_\_\_ 7399 - 7402

High Charge Mobility in Discotic Liquid-Crystalline Triindoles: Just a Core Business?







with abundant highly active facets (see picture). This finding opens a new perspective for understanding the promotion effect and for designing efficient catalysts with controllable surface structures.

### Heterogeneous Catalysis

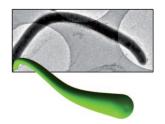
C.-F. Huo,\* B.-S. Wu, P. Gao, Y. Yang, Y.-W. Li, H. Jiao\* \_\_\_\_\_\_ **7403 – 7406** 

The Mechanism of Potassium Promoter: Enhancing the Stability of Active Surfaces



How do your crystallites grow? DFT calculations and experiments show that potassium promoter ( $K_2O$ ) modifies the crystallographic orientation in catalysts in favor of the formation of Fe crystallites

Self-assembled nanowires are obtained in aqueous solution (see picture) from cyclodextrin- and adamantane-modified calcein. A combination of scanning electron microscopy, laser scanning microscopy, and differential scanning calorimetry were performed, showing the stability and resistance towards disassembly of these wires.



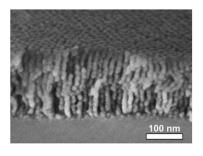
### Self-Assembled Nanowires

I. Böhm, K. Isenbügel, H. Ritter,\*

R. Branscheid, U. Kolb \_\_\_\_\_ **7407 – 7409** 

Fluorescent Nanowires Self-Assembled through Host-Guest Interactions in Modified Calcein





Pointing in the right direction: Uniform mesoporosity oriented vertically to the substrate is created among  $\gamma$ -alumina nanowires after the conversion from a cage-type  $Im\bar{3}m$  mesostructure. Highly stable  $\gamma$ -alumina films with vertical mesoporosity (see picture) are useful in a wide range of applications, such as highly sensitive sensors and highly reactive catalyst supports.

### Mesoporous Films

H. Oveisi, X. Jiang, M. Imura, Y. Nemoto, Y. Sakamoto, Y. Yamauchi\* \_ **7410-7413** 

A Mesoporous  $\gamma$ -Alumina Film with Vertical Mesoporosity: The Unusual Conversion from a  $Im\bar{3}m$  Mesostructure to Vertically Oriented  $\gamma$ -Alumina Nanowires

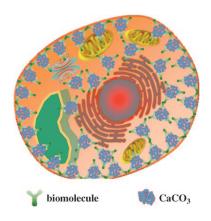


### Biosynthesis

X. M. Ma, H. F. Chen, L. Yang,\* K. Wang, Y. M. Guo, L. Yuan \_\_\_\_\_\_\_ **7414-7417** 



Construction and Potential Applications of a Functionalized Cell with an Intracellular Mineral Scaffold



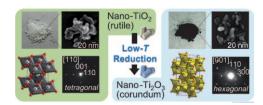
**Growing within:** The reaction of added  $Ca^{2+}$  ions with the  $CO_2$  produced by respiration results in the endogenous production of a  $CaCO_3$  scaffold in functionalized cells (see picture). These cells act as anticancer drug carriers with pH-sensitive release, and can enhance the cytotoxicity of drugs by increasing the cellular uptake. The functionalized cells also have potential applications in heavymetal extraction.

### Nanomaterials

S. Tominaka,\* Y. Tsujimoto,\*
Y. Matsushita, K. Yamaura \_ **7418-7421** 



Synthesis of Nanostructured Reduced Titanium Oxide: Crystal Structure Transformation Maintaining Nanomorphology



Reduction without particle growth:  $Ti_2O_3$  nanoparticles of corundum structure were synthesized by reducing  $TiO_2$  nanoparticles of rutile structure with  $CaH_2$  powder at a low temperature of 350 °C. The

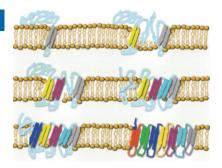
morphology of the reduced oxide was the same as that of the precursor, though the crystal structure was transformed from the tetragonal to the hexagonal system (see picture).

#### Membrane Proteins

M. Damaghi, S. Köster, C. A. Bippes, Ö. Yildiz, D. J. Müller\* \_\_\_\_\_\_ 7422 – 7424



One  $\beta$  Hairpin Follows the Other: Exploring Refolding Pathways and Kinetics of the Transmembrane  $\beta\textsc{-Barrel}$  Protein OmpG



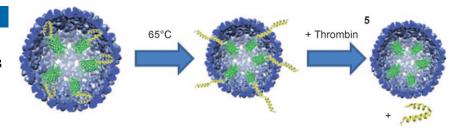
One by one: The  $\beta$ -barrel-forming outermembrane protein G (OmpG) from *E. coli* can be folded into the native lipid membrane by using single-molecule force spectroscopy. Surprisingly, single  $\beta$  strands do not refold individually but as  $\beta$  hairpins that refold consecutively until the entire  $\beta$ -barrel membrane protein is refolded (see picture). This mechanism significantly advances the understanding of current folding models of  $\beta$ -barrel proteins.

### In Vivo Encapsulation

A. O'Neil, C. Reichhardt, B. Johnson, P. E. Prevelige, T. Douglas\* 7425 – 7428



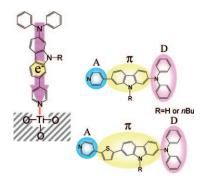
Genetically Programmed In Vivo Packaging of Protein Cargo and Its Controlled Release from Bacteriophage P22



Packed and ready to go: A scaffold protein (SP) aids the assembly of Salmonella typhimuriam bacteriophage P22 into a capsid, with encapsulation of the SP. This natural process was exploited by using an engineered molecular system to fuse a

fluorescent protein cargo (green in the picture) to a portion of the SP (yellow), which templated accurate spontaneous assembly. Heating of the capsids and treatment with thrombin released the SP but not the cargo.





Firmly attached: The short-circuit photocurrent density and conversion yields of solar cells based on pyridine-containing donor–acceptor  $\pi$ -conjugated (D- $\pi$ -A) dyes (see scheme) are greater than those for conventional D- $\pi$ -A dye sensitizers that bear a carboxy group as the electronwithdrawing anchoring group. The dyes are attached to the surface by coordinate bonding with the Lewis acid sites of TiO2.

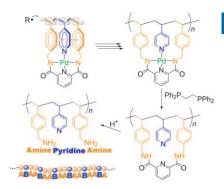
#### Solar Cells

- Y. Ooyama, S. Inoue, T. Nagano,
- K. Kushimoto, J. Ohshita, I. Imae,
- K. Komaguchi, Y. Harima\* \_ 7429 7433

Dye-Sensitized Solar Cells Based On Donor-Acceptor π-Conjugated Fluorescent Dyes with a Pyridine Ring as an Electron-Withdrawing Anchoring Group



Two is better than one: Repetitive ABA sequences in copolymers were obtained by a palladium-templated monomer. Crucial in the polymerization were  $\pi$ – $\pi$ stacking interactions between aromatic side groups to array three vinyl groups (see picture). Because of the interactions double cyclopolymerization at the palladium-templated monomer was possible. Removal of the template led to sequenceregulated copolymers.

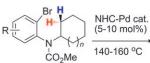


### Sequence-Regulated Polymers

Y. Hibi, M. Ouchi,\* M. Sawamoto\* \_

Sequence-Regulated Radical Polymerization with a Metal-Templated Monomer: Repetitive ABA Sequence by Double Cyclopolymerization





12 examples

up to 94% yield, 95% ee

CO<sub>2</sub>Me

Selectivity at high temperatures: Bulky, thermally stable, chiral palladium complexes generated from N-heterocyclic carbenes (NHCs; see picture) were successfully applied to the synthesis of highly

enantioenriched trans-fused indolines. Remarkably, this reaction occurs at elevated temperatures with excellent asymmetric recognition of an enantiotopic C-H bond in an unactivated methylene unit.

NHC-HI

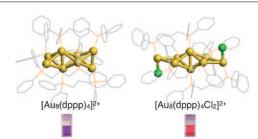
### C-H Activation



M. Nakanishi, D. Katayev, C. Besnard, E. P. Kündig\* \_\_\_ \_\_\_\_\_ 7438 – 7441

Fused Indolines by Palladium-Catalyzed Asymmetric C-C Coupling Involving an Unactivated Methylene Group





Cores and effect: A post-synthetic approach using a diphosphine ligand gave two Au<sub>8</sub> clusters with unique core geometries based on edge-shared gold tetrahedron motifs (see picture). Although the

clusters have isomeric cores, they have different colors and different optical properties. These differences are shown to depend on the core geometries.

### **Gold Clusters**

Y. Kamei, Y. Shichibu,

K. Konishi\* 7442 - 7445

Generation of Small Gold Clusters with Unique Geometries through Cluster-to-Cluster Transformations: Octanuclear Clusters with Edge-sharing Gold Tetrahedron Motifs





Supporting information is available on www.angewandte.org (see article for access details).



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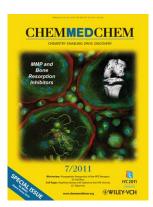
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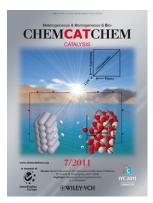
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