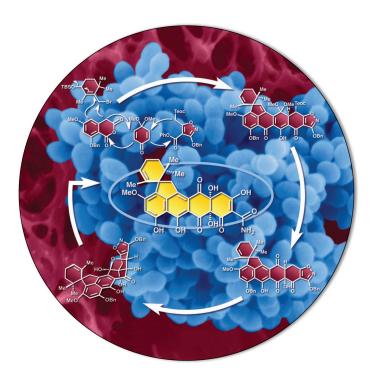
# The potent and complex antibiotic ...

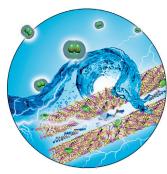




... viridicatumtoxin B is a member of the tetracycline family and exhibits impressive activity against a variety of Gram-positive bacterial strains, including methicillin-resistant *Staphylococcus aureus* (MRSA) and *Enterococcus faecalis* (shown in the background). In their Communication on page 8736 ff.,, K. C. Nicolaou et al. describe the total synthesis and structural revision of viridicatumtoxin B, thus paving the way for future molecular design, chemical syntheses, and biological investigations.

#### Electrocatalysis

In their Communication on page 8546 ff., S. H. Yu et al. report a Ni/NiO/CoSe<sub>2</sub> catalyst that is currently the best Pt-free electrocatalyst for the hydrogen evolution reaction in acidic medium.



# Sublimation Diffusion Adsorption

#### Room-Temperature Ice

Nano-sized graphene oxide flakes on graphite induce room-temperature ice growth on the substrate. In their Communication on page 8708 ff., K. P. Loh et al. show that crystal nucleation and growth can be studied in real time.

#### **Hollow Nanostructures**

X. W. Lou, Y. Xie, et al. describe in their Communication on page 8579 ff. the fabrication of complex hollow tube-in-tube nanostructures, which are promising materials for electrocatalysts and electrodes.



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8496 - 8498



"In a spare hour, I read outside chemistry.

If I could be any age I would be young again. ..."

This and more about George A. Olah can be found on page 8500.

**Author Profile** 

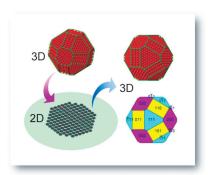
George A. Olah \_\_\_\_\_\_ 8500

Chemical Technology

Andreas Jess, Peter Wasserscheid

Books

reviewed by G. Rothenberg \_\_\_\_\_ 8501



No matter how you slice it: New insight into nanostructured materials is provided by a novel imaging technique, which reproduces the real three-dimensional (3D) fine structure of nanomaterials at the atomic level from two-dimensional (2D) projections (see scheme).

# Electon Tomography

Highlights

B. Zhang, D. S. Su\* \_\_\_\_\_ 8504-8506

Electron Tomography: Three-Dimensional Imaging of Real Crystal Structures at Atomic Resolution



#### Radical Enzymes

W. Buckel\* \_\_\_\_\_\_ 8507 - 8509

Bacterial Methanogenesis Proceeds by a Radical Mechanism

The thiyl radical of cysteine 272 (C272) in the C-P lyase adds to 5-phosphoribose-1-methylphosphonate to give a covalently bound thiophosphonate radical. Reaction with glycine 32 (G32) of the enzyme yields methane, a glycyl radical, and thiophosphate (see scheme). Intramolecular attack of the 2-OH group leads to 5-phosphoribose-1,2-cyclic-phosphate, whereas the glycyl radical oxidizes the liberated SH group back to the thiyl radical.

#### **Minireviews**

#### Organometallic Reactions

P. S. Hanley, J. F. Hartwig\* - 8510-8525

Migratory Insertion of Alkenes into Metal-Oxygen and Metal-Nitrogen Bonds

$$ML_n$$
 $X = OR, NR_2$ 

In the middle of things: Recent work has shown that the insertions of unactivated alkenes into the metal—oxygen and metal nitrogen bonds of metal alkoxo and metal amido complexes can occur as rapidly or

more rapidly than insertions into metal—alkyl bonds. Studies on catalytic and stoichiometric reactions occurring through this increasingly common class of organometallic reactions are reviewed.

#### Reviews

#### Oxygen Reduction Reaction

S. Guo, S. Zhang, S. Sun\* \_ 8526-8544

Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction



Efforts in searching for efficient nanoparticle catalysts for the oxygen reduction reaction (ORR) in fuel cells have led to various nanoparticle (NP) systems with precise control of size, shape, composition, and structure. Whereas the traditional Pt-based catalysts are still under heavy investigation, recent studies have led to the emergence of non-Pt systems. This Review highlights the recent efforts in developing Pt- and non-Pt-based NPs into advanced nanocatalysts for the ORR.

#### For the USA and Canada:

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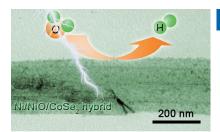
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## Communications

Not noble but effective: A novel Ni/NiO/CoSe<sub>2</sub> hybrid material has been synthesized as an efficient catalyst for the hydrogen evolution reaction (HER; see picture). This new catalyst has a cathodic onset potential at -0.03 V, a Tafel slope of 39 mV per decade, and represents currently the best Pt-free electrocatalyst for the HER in acidic medium.



#### Electrocatalysis

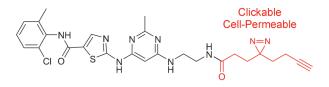
Y. F. Xu, M. R. Gao, Y. R. Zheng, J. Jiang, S. H. Yu\* \_\_\_\_\_\_ **8546-8550** 

Nickel/Nickel(II) Oxide Nanoparticles Anchored onto Cobalt(IV) Diselenide Nanobelts for the Electrochemical Production of Hydrogen



#### **Frontispiece**





Less is more: A minimalist "clickable" photo-crosslinker (see scheme) was incorporated with numerous small-molecule kinase inhibitors. The resulting probes were used for both in vitro (cell

lysates) and in situ (live cells) proteome profiling, for large-scale identification of their potential cellular kinase targets and shows improved outcomes over previous probes.

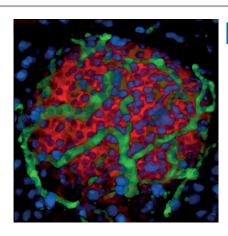
#### **Kinase Proteomics**

Z. Li, P. Hao, L. Li, C. Y. J. Tan, X. Cheng,
G. Y. J. Chen, S. K. Sze, H.-M. Shen,
S. Q. Yao\* \_\_\_\_\_\_\_ 8551 – 8556

Design and Synthesis of Minimalist Terminal Alkyne-Containing Diazirine Photo-Crosslinkers and Their Incorporation into Kinase Inhibitors for Cell- and Tissue-Based Proteome Profiling



Lighting up the pancreas: A pancreatic beta cell selective probe PiY (red, see picture) was developed which stains Langerhans islets in live animals without toxicity or side effects. Through tail-vein injection, PiY allowed for a comparison of the islets between healthy and diabetic mice. PiY also facilitated the isolation of healthy Langerhans islets by using a fluorescence-guided surgical procedure.

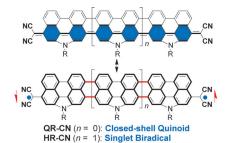


#### Fluorescent Probes

N.-Y. Kang, S.-C. Lee, S.-J. Park, H.-H. Ha, S.-W. Yun, E. Kostromina, N. Gustavsson, Y. Ali, Y. Chandran, H. S. Chun, M. A. Bae, J. H. Ahn, W. Han, G. K. Radda, Y.-T. Chang\*

Visualization and Isolation of Langerhans Islets by a Fluorescent Probe PiY





#### Biradicaloids based on quinoidal rylenes!

Soluble and stable tetracyanoquater-rylenequinodimethane (QR-CN) and tetracyanohexarylenequinodimethane (HR-CN) were synthesized. QR-CN has a closed-shell quinoidal structure in the ground state, whereas HR-CN has a singlet biradical ground state. Both compounds showed very strong one-photon and two-photon absorption in the NIR range.

#### Biradicaloids

Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, X. Zhu, Z. Sun, Y. Ni, R. D. Webster, R.-W. Li, J. T. López Navarrete,\* C. Chi,\* J. Ding,\* J. Casado,\* D. Kim,\* J. Wu\* \_\_\_\_\_\_\_ 8561 – 8565

Tetracyanoquaterrylene and Tetracyanohexarylenequinodimethanes with Tunable Ground States and Strong Near-Infrared Absorption

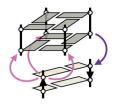


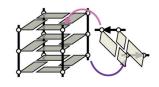
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**DNA Structures** 

K. W. Lim, A. T. Phan\* \_\_\_\_\_ 8566 - 8569

Structural Basis of DNA Quadruplex-**Duplex Junction Formation** 



Coaxial and orthogonal orientations of the helices (left and right illustration, respectively) in a quadruplex-duplex junction were realized by incorporating a duplex hairpin across the diverse geometries of

Stirred, not shaken: Single-line chains of 40 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles can be used as the world's smallest magnetic stir bars.

Their synthesis is facile and scalable. They

can be introduced into picoliter emulsion

droplets and turned effectively using a commercial magnetic stir plate. Because

of their small size, they can resist sed-

solution.

imentation under gravitational and magnetic forces, thus allowing them to remain suspended and stir all parts of the

a quadruplex. The modularity of the approach was validated through the simultaneous attachment of multiple duplex stems onto a G-quadruplex scaffold to generate a G-junction.

Nano Stir Bars



W. H. Chong, L. K. Chin, R. L. S. Tan, H. Wang, A. Q. Liu, H. Chen\* \_\_

Stirring in Suspension: Nanometer-Sized Magnetic Stir Bars



8570-8573

Stirring dye in water droplets

# PMP

Regiodivergent catalysis: Cobalt N-heterocyclic carbene (NHC) catalysts promote intramolecular olefin hydroarylation of indoles bearing an N-homoallyl or bis-(homoallyl) tether and a C3 aldimine

directing group to afford dihydropyrroloindoles and tetrahydropyridoindoles under mild conditions. The course of the cyclization is dependent on the tether, but can be controlled by the NHC ligand.

#### C-H Bond Functionalization

Z. Ding, N. Yoshikai\* \_\_\_\_\_ 8574-8578

Cobalt-Catalyzed Intramolecular Olefin Hydroarylation Leading to Dihydropyrroloindoles and Tetrahydropyridoindoles



Holes in holes: By using a modified colloidal crystal templating method, periodically ordered macroporous architectures with controllable dual porosity are fabricated (see picture). Taking BiVO<sub>4</sub> as an example, these unique structures provide a platform for a better understanding of the correlation between material geometrical features and charge migration for the photoelectrochemical water splitting process.

#### Solar Water Splitting

M. Zhou, H. B. Wu, J. Bao, L. Liang, X. W. Lou,\* Y. Xie\* \_\_\_\_\_ 8579 - 8583

Ordered Macroporous BiVO<sub>4</sub> Architectures with Controllable Dual Porosity for Efficient Solar Water Splitting



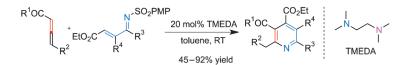


#### Heterocycles

Z. Shi, T. P. Loh\* \_\_\_\_\_\_ 8584 - 8587



Organocatalytic Synthesis of Highly Functionalized Pyridines at Room Temperature



Amines by all means: A unique aza-Rauhut—Currier/cyclization/desulfonation cascade reaction between allenoates and N-sulfonyl-1-aza-1,3-dienes, catalyzed by the readily available diamine TMEDA, has

been developed. This strategy provides facile access to a broad range of valuable highly functionalized pyridines in good yields under very mild reaction conditions.

#### Organocatalysis

J. Mo, L. Shen, Y. R. Chi\* \_\_ 8588-8591



Direct  $\beta$ -Activation of Saturated Aldehydes to Formal Michael Acceptors through Oxidative NHC Catalysis



Without detours: Oxidative catalysis mediated by N-heterocyclic carbenes (NHCs) enables the direct  $\beta$ -carbon functionalization of saturated aldehydes (see scheme). The reaction proceeds through two sequential oxidative steps to

generate  $\alpha$ , $\beta$ -unsaturated triazolium ester equivalents as formal Michael acceptors, which react with 1,3-diketones and  $\beta$ -ketone esters in an enantioselective manner.

#### Asymmetric Organocatalysis

J. Cheng, Z. Huang,

Y. R. Chi\* \_\_\_\_\_\_ 8592 – 8596



NHC Organocatalytic Formal LUMO Activation of  $\alpha$ , $\beta$ -Unsaturated Esters for Reaction with Enamides



R<sup>1</sup> R<sup>3</sup> R<sup>4</sup> lactam products typically 99% ee

An effective wake-up call: Stable  $\alpha,\beta$ -unsaturated esters were activated by the addition of a chiral N-heterocyclic carbene (NHC) organocatalyst, and the resulting reactive Michael acceptor intermediates reacted with enamide nucleophiles to

furnish optically pure products (see scheme; Ts = p-toluenesulfonyl). These products can be converted readily into bioactive  $\delta$ -lactams, piperidines, and their derivatives.

#### Asymmetric Catalysis

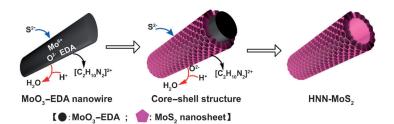
Y. Zhao, X. Jiang,

Y.-Y. Yeung\* \_\_\_\_\_\_ **8597 – 8601** 



Catalytic, Enantioselective, and Highly Chemoselective Bromocyclization of Olefinic Dicarbonyl Compounds Overriding preferences: An amine—thio-carbamate catalyst can mediate the facile, efficient, and highly enantioselective bro-mocyclization of olefinic 1,3-dicarbonyl compounds. In the presence of the bifunctional catalyst, the bromination occurs chemoselectively at the olefinic moiety rather than at the carbon atom in the  $\alpha\text{-position}$  to the carbonyl units.





Moving onward and outward: MoO<sub>3</sub>ethylenediamine (EDA) inorganic-organic hybrid nanowires were successfully transformed into hierarchical nanosheet-based MoS<sub>2</sub> nanotubes (HNN-MoS<sub>2</sub>) by anion

exchange with S2- anions at elevated temperature (see picture). The resulting nanotubes were highly active catalysts for photoelectrochemical hydrogen evolution by water splitting.

#### Nanostructures

S. Zhuo, Y. Xu, W. Zhao, J. Zhang, B. Zhang\* \_\_ \_ 8602 - 8606

Hierarchical Nanosheet-Based MoS<sub>2</sub> Nanotubes Fabricated by an Anion-Exchange Reaction of MoO<sub>3</sub>-Amine Hybrid Nanowires



Enantioselectivity through H bonding: An unprecedented [4+3] annulation of enals with o-quinone methides catalyzed by N-heterocyclic carbenes (NHCs) to give benzo- $\epsilon$ -lactones is described. High to

excellent enantioselectivity was achieved by using a chiral triazolium NHC having a free OH group, which participates in a hydrogen-bonding interaction with the substrate.

#### Organocatalysis

H. Lv, W.-Q. Jia, L.-H. Sun, S. Ye\* \_ 8607 - 8610

N-Heterocyclic Carbene Catalyzed [4+3] Annulation of Enals and o-Quinone Methides: Highly Enantioselective Synthesis of Benzo-ε-Lactones



Easy peasy: The title reaction employs N-formylsaccharin, which is an easily accessible crystalline compound, as an effective CO source. The reactions proceed with a small excess of the CO source

Pd(OAc)<sub>2</sub> (1.5–3 mol%) dppb (Pd/P = 1:3) Et<sub>3</sub>SiH (1.3 equiv) Na<sub>2</sub>CO<sub>3</sub> DMF, 65–90 °C

at moderate temperatures and were successfully applied to a wide range of aryl bromides. DMF = N, N-dimethylformamide, dppb = 1,4-bis-(diphenylphosphino) butane.

#### Carbonylation

T. Ueda, H. Konishi, K. Manabe\* -8611-8615

Palladium-Catalyzed Reductive Carbonylation of Aryl Halides with N-Formylsaccharin as a CO Source



InternAl delivery: Organoaluminum reagents activate 1,4-dien-3-ones for Nazarov electrocyclization (see scheme), then transfer a substituent to the resulting cyclopentenyl cation with moderate to complete regioselectivity and diastereoselectivity.

#### Nazarov Reaction

Y. Kwon, R. McDonald, F. G. West\* \_ 8616-8619

Organoaluminum-Mediated Interrupted Nazarov Reaction





#### Drug Design

D. Ogasawara, Y. Itoh, H. Tsumoto,

T. Kakizawa, K. Mino, K. Fukuhara,

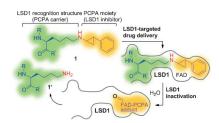
H. Nakagawa, M. Hasegawa, R. Sasaki,

T. Mizukami,\* N. Miyata,\*

T. Suzuki\* \_\_\_\_\_\_ 8620 – 8624



Lysine-Specific Demethylase 1-Selective Inactivators: Protein-Targeted Drug Delivery Mechanism Drug drop off: Given that lysine-specific demethylase 1 (LSD1) could be potently and selectively inactivated by delivering phenylcyclopropylamine (PCPA), a weak and nonselective LSD1 inhibitor, directly to the enzyme's active site, a novel series of LSD1 inactivators (1) were designed. Biological and mechanistic studies indicate that 1 inhibits LSD1 potently and selectively.



#### Silyl Complexes

C. Mitzenheim, T. Braun\* \_ 8625 - 8628



Si–Si and Si–O Bond Activation at Platinum: Stepwise Formation of a  $SiH_3$  Complex

The more, the better: Treatment of  $[Pt(H)_2(dcpe)]$  (dcpe=1,2-bis(dicyclohexylphosphino)ethane) with stoichiometric amounts of silane leads to the bis(silyl) complex  $[Pt\{Si(OMe)_3\}_2(dcpe)]$ , whereas the use of an excess silane results in hydrodealkoxylations by repetitive Si-O bond activation and the formation of  $SiH_3$  ligands (see scheme; Cy=cyclohexyl).

#### Fluorostannylation

H. Yoshida,\* R. Yoshida,

K. Takaki \_\_\_\_\_\_ 8629 – 8632



Synchronous Ar—F and Ar—Sn Bond Formation through Fluorostannylation of Arynes

An aryne insertion into the F-Sn bond of tributyltin fluoride leads to the synchronous formation of Ar-F and Ar-Sn bonds to afford diverse 2-fluoroarylstannanes

straightforwardly. The formal total synthesis of flurbiprofen by using a fluorostannylation product is also reported.

#### 1,3-Dipolar Cycloaddition

W. Sun, G. Zhu, C. Wu, G. Li, L. Hong,\*
R. Wang\* \_\_\_\_\_\_ 8633 – 8637

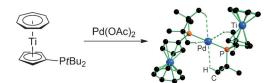


Organocatalytic Diastereo- and Enantioselective 1,3-Dipolar Cycloaddition of Azlactones and Methyleneindolinones

A simple route to complexity: An organocatalytic 1,3-dipolar cycloaddition between azlactones and methyleneindolinones provided spirooxindoles with high enantioselectivity (see scheme). This transformation takes advantage of the

nucleophilic C4 and electrophilic C2 atoms in the azlactone substrate. Bn = benzyl, HOBt = 1-hydroxy-1*H*-benzotriazole, MTBE = methyl *tert*-butyl ether, PG = protecting group, TMS = trimethylsilyl.





A picture of (non)innocence: Non-innocent and bulky phosphanes bearing a reducing cycloheptatrienyl-cyclopentadienyl titanium moiety swiftly convert Pd<sup>II</sup> into Pd<sup>0</sup> species at room temperature (see

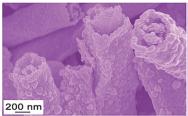
scheme). The resulting complex catalyzes the Suzuki-Miyaura coupling with fast conversion even of sterically hindered aryl bromides.

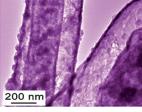
#### C-C Coupling

A. C. Tagne Kuate, S. Sameni, M. Freytag, P. G. Jones, M. Tamm\* \_\_\_\_ 8638 - 8642

Phosphane-Functionalized Cycloheptatrienyl-Cyclopentadienyl Titanium Sandwich Complexes: Phosphorus Ligands with an Integrated Reducing Agent for Palladium (0) Catalyst Generation







Tube in a tube: A general strategy for the fabrication of novel complex tube-in-tube nanostructures for many metal oxides has been developed. The method involves coating carbon nanofibers with a layer of

metal glycolate followed by calcination in air. The unique complex tubular structures of metal oxides are shown to exhibit promising properties for the title applications.

#### Hollow Nanostructures

G. Q. Zhang, B. Y. Xia, C. Xiao, L. Yu, X. Wang, Y. Xie, \* X. W. Lou\* 8643 - 8647

General Formation of Complex Tubular Nanostructures of Metal Oxides for the Oxygen Reduction Reaction and Lithium-Ion Batteries







Carbocyclic cage fight: The substratecontrolled total synthesis of vinigrol features a strategic oxidative dearomatization/Diels-Alder cycloaddition reaction and a subsequent palladium-catalyzed cyclization cascade to construct the

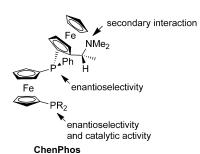
carbocyclic core. The C4, C9, and C12 stereocenters were installed using either reduction or oxidation reactions, and the diterpenoid core was unraveled by a ring fragmentation reaction.

#### Natural Products Synthesis

Q. Yang, J. T. Njardarson,\* C. Draghici, \_\_ 8648 - 8651

Total Synthesis of Vinigrol





These cats are purrfectionists: The Chen-Phos ligands (see structure) showed dramatically higher catalytic activity in the title reaction than their  $C_2$ -symmetric predecessor with two dimethylaminoethyl-substituted ferrocenyl(phenyl)phosphanyl groups. The ready accessibility, extreme air stability, and high enantioselectivity, activity, and productivity of these ligands make them very promising for a wide range of practical applications.

#### Ligand Design

W. Chen,\* F. Spindler, B. Pugin, U. Nettekoven \_\_\_\_\_\_ 8652 - 8656

ChenPhos: Highly Modular P-Stereogenic C<sub>1</sub>-Symmetric Diphosphine Ligands for the Efficient Asymmetric Hydrogenation of α-Substituted Cinnamic Acids





#### Radical C-H Oxidation

S. A. Moteki, A. Usui, T. Zhang, C. R. Solorio Alvarado,

K. Maruoka\* \_\_\_\_\_\_ 8657 - 8660



Site-Selective Oxidation of Unactivated  $C_{sp^3}$ —H Bonds with Hypervalent Iodine(III) Reagents

By design: The site-selective oxidation of unactivated secondary  $C_{sp^3}$ —H bonds was accomplished with hypervalent iodine(III) reagents and *tert*-butyl hydroperoxide (see scheme). The preparation and derivatization of the hypervalent iodine(III) reagent are simple, thus allowing the rational design of these reagents to optimize the site selectivity of the oxidation.

#### Sulfimides

J. Wang, M. Frings, C. Bolm\*

\_\_\_\_\_ 8661 – 8665



Enantioselective Nitrene Transfer to Sulfides Catalyzed by a Chiral Iron Complex Iron works: Enantioselective nitrene transfer to sulfide was accomplished by a chiral iron(III)/PyBOX catalyst (see scheme). Various sulfimides were thus obtained in high enantioselectivities and yields. Applications of this protocol to the syntheses of enantioenriched sulfoximines and an epoxide were also demonstrated.

#### Optoelectronics

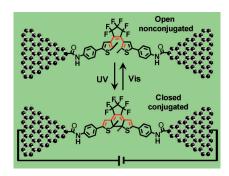
C. Jia, J. Wang, C. Yao, Y. Cao, Y.-W. Zhong, Z.-R. Liu, Z.-F. Liu,\*

X.-F. Guo\* \_\_\_\_\_\_ 8666 – 8670



Conductance Switching and Mechanisms in Single-Molecule Junctions

A molecular switch: The conductance of a new molecular device based on graphene—molecule junctions was reproducibly switched between open and closed states under irradiation of external light (see picture). Three photochromic diarylethene derivatives with different substituents were used as key elements of the molecular devices.



#### Non-Natural Polysaccharides

A. Pathigoolla,

K. M. Sureshan\* \_\_\_\_\_\_ 8671 - 8675



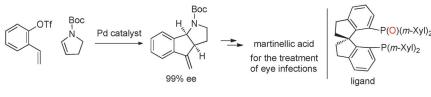
A Crystal-to-Crystal Synthesis of Triazolyl-Linked Polysaccharide



**Crystal sweets**: Polysaccharide synthesis is hampered by many factors. These problems can be circumvented by the crystal-to-crystal azide–alkyne cycloaddi-

tion polymerization of an unprotected monosaccharide, which gives a crystalline glycopolymer regiospecifically in quantitative yield.





**Domino cyclization**: Alkylpalladium intermediates in an asymmetric Heck reaction were intercepted by a second alkene to give tricyclic products with high enantioselectivity (see scheme; Boc = tert-butoxy-

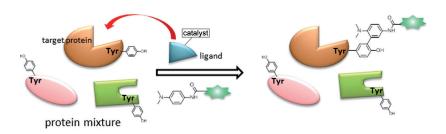
carbonyl). The method was applied to the asymmetric synthesis of a precursor of (—)-martinellic acid, a folk eye medicine in South America.

#### Heck Reaction

J. Hu, H. Hirao, Y. Li,
J. Zhou\* \_\_\_\_\_\_ 8676 – 8680

Palladium-Catalyzed Asymmetric Intermolecular Cyclization





A photocatalyst ( $[Ru(bpy)_3]^{2+}$ ) bound to a protein ligand was essential for the title method. Local single-electron transfer from the catalyst resulted in the formation of tyrosyl radicals. N'-Acetyl-N,N-

dimethyl-1,4-phenylenediamine was used as the tyrosyl radical trapping agent and used in a radical addition to afford selective modification of the target protein.

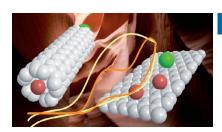
#### **Protein Modification**

S. Sato, H. Nakamura\* \_\_\_\_ 8681 - 8684

Ligand-Directed Selective Protein Modification Based on Local Single-Electron-Transfer Catalysis



Metallic impurities: Graphene oxide nanoribbons (GONRs) are commonly synthesized using carbon nanotubes (CNTs) as a precursor (see picture). The CNTs contain significant amounts of metallic impurities even after purification. These impurities persist after oxidative opening of the CNTS to GONRs and heavily influence the electrochemical behavior of the resulting material.



#### Graphene

C. H. A. Wong, C. K. Chua, B. Khezri, R. D. Webster, M. Pumera\* **8685 – 8688** 

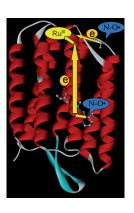
Graphene Oxide Nanoribbons from the Oxidative Opening of Carbon Nanotubes Retain Electrochemically Active Metallic Impurities



Inside Cover



Electron-transfer (ET) rates are measured by use of time-resolved EPR spectroscopy, involving photooxidation of nitroxyl radicals by a ruthenium bipyridyl complex. This permits acquisition of the fundamental characteristics of ET in solution. The method was used on two spin-labeled derivatives of bacteriorhodopsin, and is applicable to proteins, nucleic acids, and biological membranes.



#### Electron Transfer

T. Eliash, A. Barbon,\* M. Brustolon, M. Sheves, I. Bilkis,

L. Weiner\* \_\_\_\_\_\_ 8689 – 8692

Nitroxyl Radicals for Studying Electron Transfer



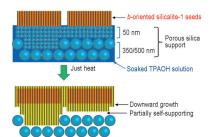


#### Mesoporous Materials

T. C. T. Pham, T. H. Nguyen, K. B. Yoon\* \_ 8693 - 8698



Gel-Free Secondary Growth of Uniformly Oriented Silica MFI Zeolite Films and Application for Xylene Separation



Zeolite membranes: A promising method is reported for the fabrication of oriented silica MFI zeolite films (see picture; TPAOH = tetrapropylammonium hydroxide). The films synthesized by using this method exhibit an outstanding performance for the separation of p- and o-xylene.

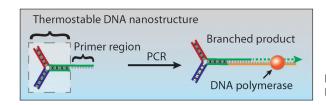
#### **DNA Nanostructures**

M. R. Hartman, D. Yang, T. N. N. Tran, K. Lee, J. S. Kahn, P. Kiatwuthinon, K. G. Yancey, O. Trotsenko, S. Minko,

D. Luo\* \_ \_\_ 8699 - 8702



Thermostable Branched DNA Nanostructures as Modular Primers for Polymerase Chain Reaction





Chemical cross-linking was used to prepare DNA nanostructures with enhanced thermal stability. These thermostable DNA nanostructures were then utilized as modular primers in the polymerase chain

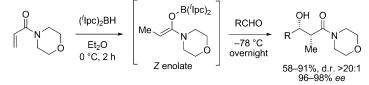
reaction (PCR; see picture), thus enabling the production of multifunctionalized and branched PCR products for multiplexed detection and hydrogel formation.

#### **Reductive Aldol Reaction**

P. Nuhant, C. Allais, W. R. Roush\* \_\_ 8703 - 8707



Diisopinocampheylborane-Mediated Reductive Aldol Reactions: Highly Enantio- and Diastereoselective Synthesis of syn Aldols from N-Acryloylmorpholine



Cutting costs, cutting corners: In an inexpensive and straightforward synthesis of syn-propionamide aldols, formation of the Z enolborinate by the hydroboration of 4-acryloylmorpholine with diisopinocampheylborane ((Ipc)2BH) was followed by

aldol reactions with achiral and chiral aldehydes to provide syn- $\alpha$ -methyl- $\beta$ hydroxymorpholinecarboxamides with excellent enantio- and diastereoselectivity (see scheme; R = alkyl, alkenyl, aryl, heteroaryl).

#### Self-Assembly

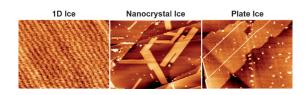
Y. Zheng, C. Su, J. Lu, K. P. Loh\* \_\_\_ 8708 - 8712



Room-Temperature Ice Growth on Graphite Seeded by Nano-Graphene Oxide

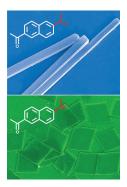


Inside Back Cover



Ice to see you: The Stenocara beetle in the Namib Desert collects drinking droplets from the morning mist using its waxy wings, which are tailored with sub-millimeter hydrophilic humps. Superhydrophilic graphene oxide nanoflakes are biomimetic analogues of these humps and can seed ice nucleation on hydrophobic graphite. Various ice solids can thus be grown at ambient conditions (see images).





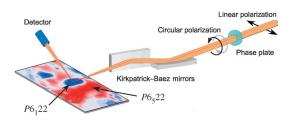
Exploring the stacks: Two different but related naphthalene compounds were shown to form different nanostructures (see picture) depending on the  $\pi$ – $\pi$ stacking and hydrogen bonding of the molecules. These nanostructures had unique photonic confinement and lightpropagation characteristics, which show potential for nanophotonic circuits.

#### Organic Nanophotonics

W. Yao, Y. Yan, L. Xue, C. Zhang, G. Li, Q. D. Zheng, Y. S. Zhao,\* H. Jiang,\* J. N. Yao\* \_\_\_\_\_ \_\_ 8713 - 8717

Controlling the Structures and Photonic Properties of Organic Nanomaterials by Molecular Design





Imaging of chirality domains: Resonant circularly polarized X-ray diffraction distinguishes crystalline enantiomers (see picture). Control of the penetration depth and microfocusing of X-rays leads to

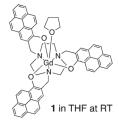
a new visualization technique of the threedimensional chirality-domain morphology, providing support to the increasing demand for the improvement of inorganic chiral crystal engineering.

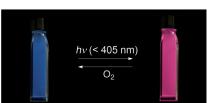
#### Chirality

H. Ohsumi, \* A. Tokuda, S. Takeshita, M. Takata, M. Suzuki, N. Kawamura, Y. Kousaka, J. Akimitsu, T. Arima \_\_\_\_ 8718 - 8721

Three-Dimensional Near-Surface Imaging of Chirality Domains with Circularly







From blue to red: The structure and luminescence properties of the gadolinium(III) complex 1 were investigated. Reversible switching of the luminescence of 1 in THF at room temperature by alternating light irradiation and O2 exposure is presented, during which the emission color changes as shown in the picture. Light-induced phosphorescence of 1 plays a key role in this behavior.

#### Photochromism

Polarized X-rays

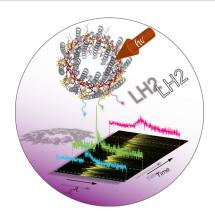
H. Nakai,\* K. Kitagawa, H. Nakamori, T. Tokunaga, T. Matsumoto, K. Nozaki,

S. Ogo \_\_\_\_\_\_ 8722 - 8725



Reversible Switching of the Luminescence of a Photoresponsive Gadolinium(III) Complex

Sequences of high resolution low-temperature emission spectra from individual light-harvesting 2 (LH2) complexes from Rhodopseudomonas acidophila reveal a much larger variety of the emission profiles than previously observed. The results provide direct evidence for substantial variations in electron-phonon coupling and concomitantly of exciton (de)localization within single pigmentprotein complexes.



#### **Excitons in Photosynthesis**

R. Kunz, K. Timpmann, J. Southall, R. J. Cogdell, A. Freiberg, J. Köhler\* \_\_\_\_\_ 8726-8730

Fluctuations in the Electron-Phonon Coupling of a Single Chromoprotein





#### **Dye-Sensitized Solar Cells**

N. Ashari Astani, J. Teuscher, R. Scopelliti, P. Gao, S. Mathew, J.-E. Moser, I. Tavernelli, U. Rothlisberger, M. Grätzel,



Towards Compatibility between Ruthenium Sensitizers and Cobalt Electrolytes in Dye-Sensitized Solar Cells

Ruthenium and Co: Ruthenium(II) complexes remain prime candidates for dyesensitized solar applications; however, current ruthenium sensitizers are not compatible with cobalt(II/III) electrolytes. Herein, the effect of surface insulation on device efficiency is studied by comparing two cyclometalated tris-heteroleptic ruthenium(II) complexes. This approach demonstrates a general principle that leads to unprecedented efficiency for a ruthenium(II) sensitizer used in combination with a cobalt electrolyte.

#### **Total Synthesis**

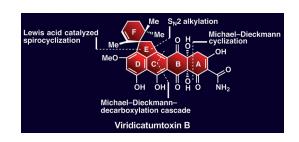
K. C. Nicolaou,\* C. Nilewski, C. R. H. Hale, H. A. Ioannidou, A. ElMarrouni, L. G. Koch \_ 8736-8741



Total Synthesis and Structural Revision of Viridicatumtoxin B



Front Cover



Will the real viridicatumtoxin B please stand up: The total synthesis of viridicatumtoxin B resulted in its structural revision and opens the way for analogue construction and biological evaluation of

this complex tetracycline-like antibiotic. The highly convergent strategy employed allows for swift construction of the entire carbocyclic framework of the molecule.

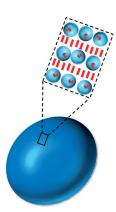
#### Self-Assembly

J. Düring, A. Hölzer, U. Kolb, R. Branscheid, F. Gröhn\* \_\_ 8742 - 8745

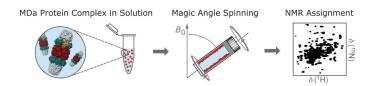


Supramolecular Organic-Inorganic Hybrid Assemblies with Tunable Particle Size: Interplay of Three Noncovalent Interactions

Gold or CdS nanoparticles and ionic dye molecules can form supramolecular assemblies with a defined size between 100 to 300 nm when using a macro-ion as template and connector. The picture shows the arangement of gold, dendrimer, and dye in the hybrid assembly (blue sphere: dendritic macro-ion, red spheres: gold, red bars: ionic dye).







Bigger is better: Sequential backbone assignments are obtained by NMR spectroscopy for a 1 MDa proteasome complex. The method relies on immobilization of a soluble protein complex by magicangle spinning. Deuteration and proton

detection of exchangeable sites and paramagnetic relaxation enhancement enables exploration of structural and dynamic properties of supramolecular assemblies at atomic resolution.

#### Protein NMR Spectroscopy

A. Mainz, T. L. Religa, R. Sprangers,R. Linser, L. E. Kay, B. Reif\* 8746 – 8751

NMR Spectroscopy of Soluble Protein Complexes at One Mega-Dalton and Beyond



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

In this Commumnication, the authors have accidentally omitted an important reference in their description of the state of the art in cyclobutanone functionalizations. The report by J. Rodriguez, Y. Coquerel, and co-workers, entitled "Enantioselective Organocatalytic Michael Addition of Cyclobutanones to Nitroalkenes" [1] should be referenced in the first paragraph on page 6718. The authors regret this oversight and thank Professor Rodriguez for bringing this to their attention.

[1] D. Mailhol, M. del Mar Sanchez Duque, W. Raimondi, D. Bonne, T. Constantieux, Y. Coquerel, J. Rodriguez, *Adv. Synth. Catal.* **2012**, *354*, 3523–3532.

Enantioselective Construction of  $\alpha$ -Quaternary Cyclobutanones by Catalytic Asymmetric Allylic Alkylation

C. M. Reeves, C. Eidamshaus, J. Kim, B. M. Stoltz\* \_\_\_\_\_\_ **6718–6721** 

Angew. Chem. Int. Ed. 2013, 52

DOI: 10.1002/anie.201301815

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