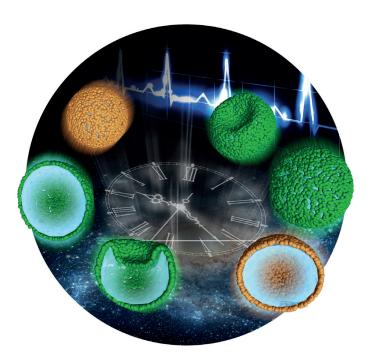
# Complex oscillatory behaviors ...

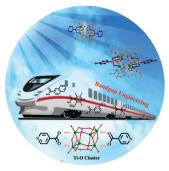


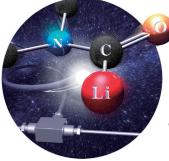


... of living cells are demonstrated by R. Yoshida, T. Ueki, and R. Tamate in their Communication on page 5179 ff. by using a biomimetic colloidosome composed of self-oscillating microgels that exhibit autonomous shape oscillations with buckling deformations driven by an oscillatory chemical reaction. The resulting oscillatory waveform profile becomes markedly more complex than that of conventional self-oscillating materials.

#### Cluster Chemistry

In their Communication on page 5160 ff., L. Zhang, J. Zhang et al. show that the labile coordination sites of a  $\{Ti_6\}$  cluster can be used to functionalize the surface of the  $\{Ti_6\}$  cluster with organic species and transition-metal ions.





#### Microreactors

In their Communication on page 5327 ff., J. Yoshida, A. Nagaki, and Y. Takahashi report the use of a flow microreactor system for the generation of unstable carbamoyl anions and their reaction with electrophiles to give various amides.

# Heterogeneous Catalysis

In their Communication on page 5215 ff., A. M. Beale, B. M. Weckhuysen et al. describe the use of a combination of operando X-ray techniques to gain insight into the nature of the Mo species on zeolite ZSM-5 during methane dehydroaromatization.



### How to contact us:

#### **Editorial Office:**

E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01-606-331
Telephone: (+49) 62 01-606-315

### Reprints, E-Prints, Posters, Calendars:

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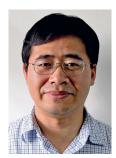
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"My favorite drink is Chinese black tea. My favorite reaction is natural DNA synthesis ..." This and more about Shu Wang can be found on page 5120.

# **Author Profile**

Shu Wang \_\_\_\_\_\_ 5120



D. Schade

Angew. Chem. Int. Ed. 2016, 55, 5103-5114



A. Koeberle



D. Hilvert



B. G. Davis

# News

GDCh Innovation Prize in Medicinal/ Pharmaceutical Chemistry: D. Schade and A. Koeberle \_\_\_ Feodor Lynen Lectureship: \_ 5121 D. Hilvert \_\_\_\_\_ Roy L. Whistler Award: B. G. Davis \_\_\_\_\_

Books

Graphene Madhuri Sharon, Maheshwar Sharon reviewed by S. Eigler\* \_\_



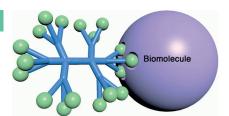


# **Minireviews**

#### Biomaterials

J. Wan, P. F. Alewood\* \_\_\_\_\_ 5124-5134

Peptide-Decorated Dendrimers and Their Bioapplications



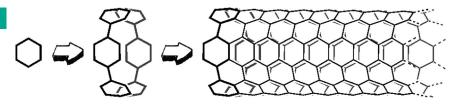
Decking out dendrimers: Peptide-decorated dendrimers (PDDs), a class of spherical polymers with peptides covalently attached to their surface, have found application in imaging and drug development. In addition to selected bioapplications, this Minireview also summarizes the development of PDD synthetic routes that employ diverse conjugation chemistry. Green ball = peptide; blue structure = dendrimer scaffold.

# Reviews

# **CNT Segments**

Y. Segawa,\* A. Yagi, K. Matsui,K. Itami\* \_\_\_\_\_\_ 5136 – 5158

Design and Synthesis of Carbon Nanotube Segments



The selective and predictable synthesis of structurally uniform carbon nanotubes (CNTs) represents a long-standing goal in both nanocarbon science and synthetic organic chemistry. This Review focuses on

the studies toward controlled synthesis of CNTs with single chirality through the organic synthesis of CNT segments and the organic template-assisted growth of CNTs.

# **Communications**

### Cluster Chemistry

J. X. Liu, M. Y. Gao, W.-H. Fang, L. Zhang,\*
J. Zhang\* \_\_\_\_\_\_ 5160 - 5165

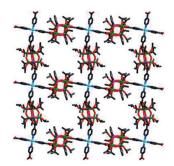


Bandgap Engineering of Titanium-Oxo Clusters: Labile Surface Sites Used for Ligand Substitution and Metal Incorporation



# **Frontispiece**

Organized titanium clusters: The labile coordination sites of a robust  $\{Ti_6\}$  cluster have been used to functionalize the surface of the  $\{Ti_6\}$  cluster with organic species and transition-metal ions (see picture). A bandgap engineering study indicates that both the electron-with-drawing effect of the organic ligands and the coordination environments of the incorporated metal ions tune the bandgap structures of the titanium—oxo clusters.

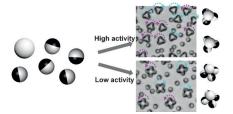


#### For the USA and Canada:

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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.





The journey matters: Self-propelled particles are induced to assemble into different chiral structures that rotate persistently in an electric field. Rather than energy preference, dynamic factors during the non-equilibrium assembly determine which structure is selected.

### Colloidal Motor

J. Zhang, J. Yan, S. Granick\* 5166 - 5169

Directed Self-Assembly Pathways of Active Colloidal Clusters



Dig this! Cyclization of silylenoletherynesulfonamides proceeds at ambient temperature under mild reaction conditions under silver catalysis. Bridged com-

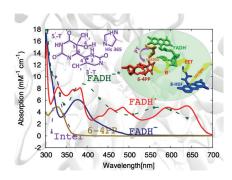
pounds were obtained exclusively through 7-exo-dig reactions. The protocol is applicable to a wide range of substrates, thus leading to azabicyclic frameworks.

### Heterocycle Synthesis

C. F. Heinrich, I. Fabre, L. Miesch\* \_\_\_ 5170 - 5174

Silver-Catalyzed 7-exo-dig Cyclization of Silylenolether-ynesulfonamides





QM/MM simulations were conducted to assign a specific molecular structure to the intermediate formed in the electroninduced repair of (6-4) photolesions (purple) detected previously in ultrafast transient absorption spectroscopy. The repair mechanism involves proton transfer from the protonated His365 to the N3' nitrogen of the lesion along an oxetanelike transition state.

#### **Photolesions**

S. Faraji,\* D. Zhong, A. Dreuw \_\_\_ 5175 - 5178

Characterization of the Intermediate in and Identification of the Repair Mechanism of (6-4) Photolesions by **Photolyases** 



Buckle up! A cell-like colloidosome composed of self-oscillating microgels that exhibits drastic shape oscillations in addition to swelling/deswelling oscillations was fabricated. The resulting oscillatory profile waveform became markedly more complex than a conventional one. Multiple buckling points were observed for larger colloidosomes, analogous to cell behavior.



# Artificial Cells

R. Tamate, T. Ueki,\*

R. Yoshida\* \_\_\_\_\_ \_ 5179 - 5183

Evolved Colloidosomes Undergoing Celllike Autonomous Shape Oscillations with Buckling



**Front Cove** 







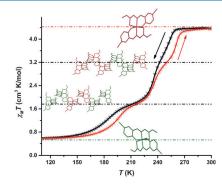
# Multistability

Z. Y. Li, H. Ohtsu, T. Kojima, J. W. Dai,\*
T. Yoshida, B. K. Breedlove, W. X. Zhang,
H. Iguchi, O. Sato,\* M. Kawano,

M. Yamashita\* \_\_\_\_\_ 5184 - 5189



Direct Observation of Ordered High-Spin–Low-Spin Intermediate States of an Iron(III) Three-Step Spin-Crossover Complex In quite a state: A neutral mononuclear  $Fe^{III}$  complex  $[Fe^{III}(H-5-Br-thsa-Me)] \cdot Farthsa-Me)] \cdot H_2O$  (thsa = 5-bromosalicylaldehyde methylthiosemicarbazone) exhibited a three-step spin crossover with symmetry breaking and a 14 K hysteresis loop owing to strong cooperativity (see picture). The intermediate spin states showed remarkable long-range 4 HS-2 LS and 2 HS-4 LS spin-state ordering (HS = high-spin, red; LS = low-spin, green).

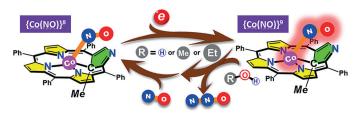


# Bioinorganic Chemistry

C.-H. Chuang, W.-F. Liaw,\*
C.-H. Hung\* \_\_\_\_\_\_ 5190 – 5194



Conversion of Nitric Oxide into Nitrous Oxide as Triggered by the Polarization of Coordinated NO by Hydrogen Bonding



**Alcohol can H···elp**: Water, methanol, or ethanol triggered the formation of a  $[N_2O_2]$ -bridged intermediate from a reduced cobalt–nitrosyl N-confused porphyrin to enable the conversion of NO

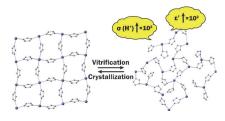
into  $N_2O$  (see scheme). Hydrogen-bonding interactions assisted N-N coupling and N-O bond cleavage in the intermediate to generate  $N_2O$ .

# **Coordination Polymers**

W. Chen, S. Horike,\* D. Umeyama,
N. Ogiwara, T. Itakura, C. Tassel, Y. Goto,
H. Kageyama, S. Kitagawa\* 5195 – 5200



Glass Formation of a Coordination Polymer Crystal for Enhanced Proton Conductivity and Material Flexibility Phase transitions: The glassy state of a two-dimensional (2D) Cd<sup>2+</sup> coordination polymer crystal was prepared by a solvent-free mechanical milling process. The coordination polymer shows an increased proton conductivity and an increased dielectric constant in the glassy state (see picture).





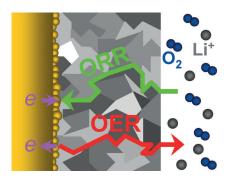
### Li-O, Batteries

J. Wang, Y. Zhang, L. Guo, E. Wang, Z. Peng\* \_\_\_\_\_\_\_ **5201 – 5205** 



Identifying Reactive Sites and Transport Limitations of Oxygen Reactions in Aprotic Lithium- $O_2$  Batteries at the Stage of Sudden Death

Direct conductivity measurement of an electrodeposited  $\text{Li}_2\text{O}_2$  film and an in situ SERS study on the  $\text{O}_2$  reduction reaction (ORR) using  $^{18}\text{O}_2$  for passivation and  $^{16}\text{O}_2$  for further discharging unveiled the origin of sudden death of aprotic Li- $\text{O}_2$  batteries. Both ORR and  $\text{O}_2$  evolution (OER) occur at the buried interface of cathode |  $\text{Li}_2\text{O}_2$ , and thus the Li- $\text{O}_2$  electrochemistry is limited by electron transport instead of Li+ and  $\text{O}_2$  transport.

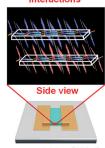






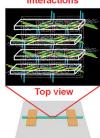
Molecular packing motifs play a key role in determining the charge-transport properties of molecular materials. Interlayer electronic couplings perpendicular to the current direction result in a drastic decrease of charge mobilities, shown by utilizing field-effect transistors.  $\alpha$ -Phase TiOPc crystals (see picture; left) show a maximum mobility  $\mu_{\text{max}}$  more than 250 times that of the  $\beta$ -phase.

No inter-layer interactions



$$\begin{split} \mu_{max} &= 26.8 \text{ cm}^2 \text{ V}^{\text{-}1} \text{ s}^{\text{-}1} \\ \mu_{ave} &= 10.6 \text{ cm}^2 \text{ V}^{\text{-}1} \text{ s}^{\text{-}1} \end{split}$$

Strong inter-layer interactions



$$\begin{split} \mu_{max} &= 0.1 \ cm^2 \ V^{\text{-}1} \, s^{\text{-}1} \\ \mu_{ave} &= 0.014 \ cm^2 \ V^{\text{-}1} \, s^{\text{-}1} \end{split}$$

### **Organic Semiconductors**

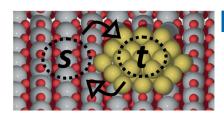
Z. P. Zhang, L. Jiang, C.L. Cheng, Y. G. Zhen,\* G. Y. Zhao, H. Geng, Y. P. Yi,\* L. Q. Li, H. L. Dong, Z. G. Shuai,

W. P. Hu\* \_\_\_\_\_\_ **5206 – 5209** 

The Impact of Interlayer Electronic Coupling on Charge Transport in Organic Semiconductors: A Case Study on Titanylphthalocyanine Single Crystals



The gains in catalytic activity that are achievable through bifunctional coupling by diffusion (between two sites s and t; see picture) are assessed using generic reaction schemes and a descriptor-based approach. The analysis predicts that only the coupling of different classes of materials, such as metals and oxides, can give rise to substantial gains.



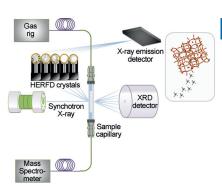
#### Reaction Mechanisms

M. Andersen, A. J. Medford, J. K. Nørskov, K. Reuter\* \_\_\_\_\_\_ 5210 – 5214

Analyzing the Case for Bifunctional Catalysis



"Watch" and learn: Combined high-resolution fluorescence detection X-ray absorption near-edge spectroscopy (HERFD-XANES), X-ray diffraction (XRD), and X-ray emission spectroscopy under real operando conditions provided detailed insight into the nature of the Mo species on zeolite ZSM-5 during methane dehydroaromatization, demonstrating the importance in controlling Mo speciation to influence selectivity towards light olefins and/or aromatic species.



# Heterogeneous Catalysis

I. Lezcano-González, R. Oord, M. Rovezzi,

P. Glatzel, S. W. Botchway,

B. M. Weckhuysen,\*

A. M. Beale\* \_\_\_\_\_\_ **5215 – 5219** 

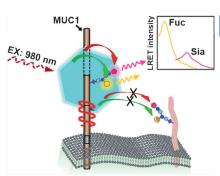
Molybdenum Speciation and its Impact on Catalytic Activity during Methane Dehydroaromatization in Zeolite ZSM-5 as Revealed by Operando X-Ray Methods



Back Cover



Using upconversion luminescent nanoparticles (UNPs) as a polychromatic emission donor, a single-excited duplexed luminescence resonance energy transfer (D-LRET) system was developed on a cell surface for in situ duplexed imaging and relative quantification of two kinds of sugars on a specific protein using mucin 1 (MUC1) as the model. The strategy also enables monitoring of the expression of the fucosylated and sialylated terminal on MUC1.



### **Duplexed Imaging**

N. Wu, L. Bao, L. Ding,\* H. Ju\* \_\_\_\_\_\_ **5220 – 5224** 

A Single Excitation-Duplexed Imaging Strategy for Profiling Cell Surface Protein-Specific Glycoforms







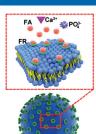


#### Biomineralization

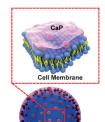
R. Zhao, B. Wang, X. Yang, Y. Xiao, X. Wang, C. Shao, R. Tang\* **5225 – 5229** 



A Drug-Free Tumor Therapy Strategy: Cancer-Cell-Targeting Calcification



Cancer Cell



Calcified Cell

Anticancer mineralization: Cancer-cell-targeting calcification can convert tumors into calcified tissues by using folic acid (FA), calcium, and the folate receptor (FR) resulting in cancer cell growth and metastatic inhibition without any drugs. These results suggest cancer cells can be selectively targeted using biomineralization methods.

# Singlet Fission

D. Kato, H. Sakai, N. V. Tkachenko,\*
T. Hasobe\* \_\_\_\_\_\_ **5230 – 5234** 



High-Yield Excited Triplet States in Pentacene Self-Assembled Monolayers on Gold Nanoparticles through Singlet Exciton Fission Split the difference: A series of 6,13-bis(triisopropylsilylethynyl)pentacene—alkanethiolate monolayer protected gold nanoparticles with different particle sizes and alkane chain lengths were synthesized. These systems were employed for the efficient generation of excited triplet states on the pentacene molecules by using singlet exciton fission to suppress energy transfer to the Au surface.





### Transition-State Theory

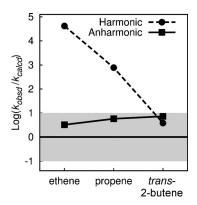


G. Piccini, M. Alessio, J. Sauer\*





Ab Initio Calculation of Rate Constants for Molecule–Surface Reactions with Chemical Accuracy



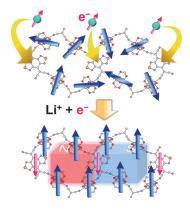
A new strategy enables accurate quantum-mechanical ab initio predictions for the methylation of small alkenes over zeolite catalysts. The calculated reaction rate constants (free energies), pre-exponential factors (entropies), and enthalpy barriers show that this computational strategy yields results that agree with experiment within chemical accuracy limits.

# Donor-Acceptor Systems

K. Taniguchi,\* K. Narushima, J. Mahin, W. Kosaka, H. Miyasaka\* — 5238 – 5242

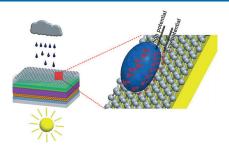


Construction of an Artificial Ferrimagnetic Lattice by Lithium Ion Insertion into a Neutral Donor/Acceptor Metal-Organic Framework



A ferrimagnetic order lattice has been artificially constructed by electron doping by lithium ion insertion from a magnetically disordered ground state in a neutral donor/acceptor metal—organic framework (D/A-MOF). The stability of the magnetically ordered lattice depends on the equilibrium potential of the D/A-MOF cathode. The results suggest a new strategy and direction for the design of molecule-based magnets.





A flexible solar cell that can be excited by sunlight and raindrops is presented. The solar-to-electric conversion efficiency is created by complicated photoelectrochemical reactions, while electric signals, produced by dropping raindrops on rGO film, arise from  $\pi$ -electron cation pseudocapacitance at the rGO/raindrop interface. This work could guide the design of all-weather solar cells.

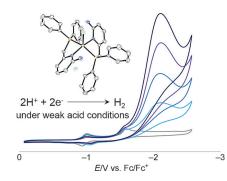
# **Energy Conversion**

Q. Tang, \* X. Wang, P. Yang, 5243 - 5246

A Solar Cell That Is Triggered by Sun and



A nickel(II) complex  $[Ni(L)_2Cl]Cl$  (L= 6-((diphenylphosphino) methyl) pyridin-2amine), having an amine base as a proton-transfer site, was synthesized and used as a hydrogen-production catalyst. Electrochemical measurements with the complex show that a higher rate of H<sub>2</sub> production (turnover frequency = 8400 s<sup>-1</sup>) can be achieved under weak acid conditions using acetic acid as a proton source.



### Electrocatalysis

R. Tatematsu, T. Inomata, T. Ozawa, H. Masuda\* \_\_\_\_\_\_ 5247 - 5250

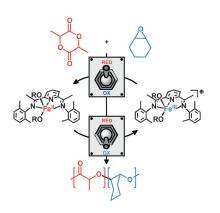
Electrocatalytic Hydrogen Production by a Nickel(II) Complex with a Phosphinopyridyl Ligand



Inside Cover



The redox-controlled block copolymerization of cyclohexene oxide and lactide capitalizes on the ability for a bis-(imino) pyridine iron bisalkoxide complex to polymerize lactide in the iron(II) oxidation state and epoxide in the iron(III) state, but not vice versa. Diblock copolymers were synthesized with both monomers present starting with either the iron(II) or iron(III) catalyst and using an in situ redox switch.

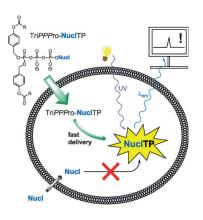


# **Block Copolymers**

A. B. Biernesser, K. R. Delle Chiaie, J. B. Curley, J. A. Byers\* \_\_\_\_ **5251 – 5254** 

Block Copolymerization of Lactide and an Epoxide Facilitated by a Redox Switchable Iron-Based Catalyst





**NTP drugs go pro**: The Tri*PPP*ro-approach was used to synthesize a series of nucleoside triphosphate analogues. The TriPPPro-compounds displayed anti-HIV activity and cellular uptake. In some cases, even inactive parent nucleosides were converted into powerful antiviral compounds. These results could thus aid the development of future nucleoside prodrugs.

### **Nucleotide Prodrugs**

T. Gollnest, T. Dinis de Oliveira, A. Rath,

I. Hauber, D. Schols, J. Balzarini,

C. Meier\* \_\_\_ \_\_\_\_\_ 5255 – 5258

Membrane-permeable Triphosphate Prodrugs of Nucleoside Analogues



5109



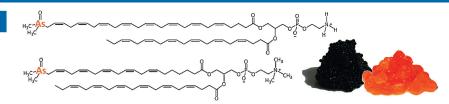


#### Arsenolipids

S. A. Viczek, K. B. Jensen,\*
K. A. Francesconi \_\_\_\_\_\_ 5259 – 5262



Arsenic-Containing Phosphatidylcholines: A New Group of Arsenolipids Discovered in Herring Caviar



A complex delicacy: Arsenic-containing phosphatidylcholines and an arsenic-containing phosphatidylethanolamine have been identified in fish roe. The incorpo-

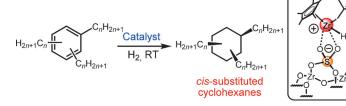
ration of the arsenic group into typical membrane lipids might impart particular properties to the molecules not displayed by their non-arsenic analogues.

# Stereoselective Hydrogenation

M. M. Stalzer, C. P. Nicholas,
A. Bhattacharyya, A. Motta, M. Delferro,\*
T. J. Marks\* \_\_\_\_\_\_\_ 5263 – 5267



Single-Face/All-cis Arene Hydrogenation by a Supported Single-Site  $d^0$ Organozirconium Catalyst



**Stereocontrol is on**: A single-site supported organozirconium catalyst exhibits unprecedented all-*cis* stereo/face-selective hydrogenation of substituted alkylarenes

under mild reaction conditions. The resulting stereopure cycloalkanes offer new building blocks for value-added fine chemicals.

# Homogeneous Catalysis

T. Jia, C. Zhao, R. He, H. Chen,\*
C. Wang\* \_\_\_\_\_\_ 5268 – 5271



Iron-Carbonyl-Catalyzed Redox-Neutral [4+2] Annulation of N-H Imines and Internal Alkynes by C-H Bond Activation

**Double dose of iron**: The titled redoxneutral [4+2] annulations to furnish cis3,4-dihydroisoquinolines were achieved by using iron catalysis. Mechanistic studies show the synergy of dinuclear iron in the

C—H bond activation and turnover-limiting hydrogen-transfer steps. The reaction demonstrates excellent atom economy and exclusive *cis* stereoselectivity.

# Cross-Coupling

K. Matsumoto, M. Yoshida,

M. Shindo\* \_\_\_\_\_ 5272 – 5276



Heterogeneous Rhodium-Catalyzed Aerobic Oxidative Dehydrogenative Cross-Coupling: Nonsymmetrical Biaryl Amines

$$NR_2$$
 +  $H$  Ar  $Rh/C$   $Rh/C$   $NR_2$ 

A jab-cross move: A heterogeneously catalyzed oxidative dehydrogenative cross-coupling of aryl amines is reported. Aryl amines were treated with various arenes using a heterogeneous Rh/C catalyst under mild aerobic conditions to

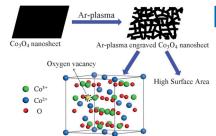
• yields up to 99%
• high selectivities

selectively afford cross-coupled products, and provides an efficient synthetic method for the preparation of nonsymmetrical biaryl amines by oxidative C—H activation.





Less is more: A highly efficient  $\text{Co}_3\text{O}_4$ -based electrocatalyst for the oxygen evolution reaction has been designed. The electrocatalyst, which features oxygen vacancies and a high surface area, was formed by an argon plasma-engraving strategy.



# Oxygen Vacancies

L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang,\* L. Dai \_\_\_\_\_\_\_ **5277 – 5281** 

Plasma-Engraved Co<sub>3</sub>O<sub>4</sub> Nanosheets with Oxygen Vacancies and High Surface Area for the Oxygen Evolution Reaction



**Ugi for real**: Reaction of isonitriles **(A)** with 3-(arylamino) isobenzofuran-1 (3*H*)-ones **(B)** in the presence of a catalytic amount of chiral phosphoric acid (CPA) afforded 3-oxo-2-arylisoindoline-1-carbox-

amides (C) in high yields with good to high enantioselectivities. An enantioselective Ugi multicomponent reaction of D, E, and A was subsequently developed for the synthesis of the same heterocycle C.

# Synthetic Methods

Y. Zhang, Y.-F. Ao, Z.-T. Huang, D.-X. Wang,\* M.-X. Wang,\* J. Zhu\* \_\_\_\_\_\_\_\_ **5282 – 5285** 

Chiral Phosphoric Acid Catalyzed Asymmetric Ugi Reaction by Dynamic Kinetic Resolution of the Primary Multicomponent Adduct



$$R^{1} \stackrel{\text{I}}{ \downarrow \downarrow} O + = R^{2} \stackrel{\text{Cui/L*}}{ 2.4.6 \text{-collidine} \atop \text{toluene, } 30 \text{ °C} } R^{1} \stackrel{\text{HO}}{ \downarrow \downarrow} O \\ R^{2} = \text{alkyl, aryl} \qquad \qquad R^{2} = \text{alkyl, aryl} \qquad \qquad R^{2} \stackrel{\text{Cui/L*}}{ 89-97\% \text{ ee} } R^{2} \qquad \qquad R^{2} \stackrel{\text{R}^{2}}{ \downarrow \downarrow} O \\ R^{2} \stackrel{\text{Cui/L*}}{ \downarrow \downarrow} O + \stackrel{\text{R}^{2}}{ \downarrow} O + \stackrel{\text{R}^$$

Active duty: Asymmetric alkynylation of isatins was achieved by a new bifunctional chiral guanidine ligand in combination with CuI under mild reaction conditions. Good levels of reactivity and excellent

enantioselectivities were achieved with diverse alkyl- and aryl-substituted terminal alkynes and various substituted isatins, thus generating bioactive 3-alkynyl-3-hydroxyindolin-2-ones.

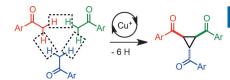
### Asymmetric Catalysis

Q. G. Chen, Y. Tang, T. Y. Huang, X. H. Liu,\* L. L. Lin, X. M. Feng \_\_\_\_\_\_\_\_ **5286 – 5289** 

Copper/Guanidine-Catalyzed Asymmetric Alkynylation of Isatins



Give it a tri: Copper-catalyzed oxidative [1+1+1] cyclotrimerization of acetophenone derivatives under mild reaction conditions and with a broad reaction scope has been developed. This transformation is a radical cascade process that allows saturated carbocycles to be obtained by cyclotrimerization through functionalization of  $C(sp^3)$ —H bonds.



# Cyclotrimerization



S. Manna,

A. P. Antonchick\* \_\_\_\_\_\_ 5290 - 5293

[1+1+1] Cyclotrimerization for the Synthesis of Cyclopropanes





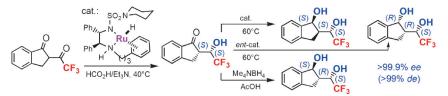


# Asymmetric Catalysis

A. E. Cotman, D. Cahard,
B. Mohar\* \_\_\_\_\_\_ **5294 – 5298** 



Stereoarrayed CF<sub>3</sub>-Substituted 1,3-Diols by Dynamic Kinetic Resolution: Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation



**Doubling up**: A double dynamic kinetic resolution is described for the ansaruthenium(II)-catalyzed asymmetric transfer hydrogenation of diketones in formic acid/triethylamine to yield the title

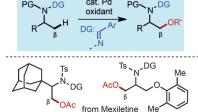
compounds, displaying a stereotriad, in excellent stereopurity. The intermediate mono-reduced alcohols were isolated in very high enantiopurity by using milder reaction conditions.

### Synthetic Methods

- Z. Huang, C. Wang,
- G. Dong\* \_\_\_\_\_ 5299 5303



A Hydrazone-Based  $\textit{exo}\textsc{-}\mathsf{Directing}\textsc{-}\mathsf{Group}$  Strategy for  $\beta$  C-H Oxidation of Aliphatic Amines



from Rimantadine

Ts 
$$^{\text{DG}}$$
  $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{SPh}}$   $^{\text{SPh}}$   $^{\text{SPh}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{R}}$   $^{\text{DG}}$   $^{\text{SPh}}$   $^{\text{SPh}}$   $^{\text{SPh}}$   $^{\text{OPh}}$ 

All about the DGs: A hydrazone-based exo-directing group (DG) strategy is developed for the functionalization of unactivated primary  $\beta$  C—H bonds of aliphatic amines. The hydrazone DGs can be conveniently installed and removed, and promote  $\beta$ -acetoxylation and tosyloxylation via a five-membered exo-palladacycle. PG = protecting group, Ts = 4-toluenesulfonyl.

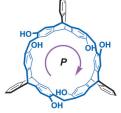
# Host-Guest Chemistry

G.-W. Zhang, P.-F. Li, Z. Meng, H.-X. Wang, Y. Han,

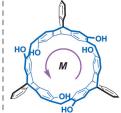
C.-F. Chen\* \_\_\_\_\_\_ 5304 – 5308



Triptycene-Based Chiral Macrocyclic Hosts for Highly Enantioselective Recognition of Chiral Guests Containing a Trimethylamino Group



**Go nuts!** A novel triptycene-based chiral macrocyclic host with a hex-nut-like structure and highly fixed conformation was synthesized. Efficient resolution was achieved through the introduction of



chiral auxiliaries to give a couple of enantiopure macrocycles, which exhibited highly enantioselective recognition of three pairs of chiral compounds containing a trimethylamino group.

# Asymmetric Catalysis

H. Huang, X. Liu, L. Zhou,\* M. Chang,\*
X. Zhang \_\_\_\_\_\_\_ 5309 – 5312

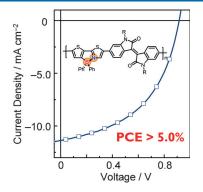
Direct Asymmetric Reductive Amination for the Synthesis of Chiral  $\beta$ -Arylamines

Asymmetric reductive coupling of a ketone and an amine is a straightforward and atom-economic approach for preparing optically enriched amines. The highly efficient and direct asymmetric reductive amination of arylacetones, catalyzed by an

iridium complex, supplies enantiomerically pure  $\beta$ -arylamines. The new phosphoramidite ligands reported show superb reactivity and enantioselectivity in this reductive coupling. M.S. = molecular sieves, TFA = trifluoroacetic acid.



From giver to taker: Incorporation of  $B \leftarrow N$  units into polymer electron donors has resulted in a series of polymer electron acceptors. Extending the length of the repeating units of the conjugated polymers alleviates the effect of steric hindrance from the pendant groups and promotes the  $\pi$ - $\pi$  stacking of the polymer backbones. The all-polymer solar-cell device shows a power conversion efficiency (PCE) exceeding 5.0%.



### **Electron Acceptor**



R. Zhao, C. Dou,\* Z. Xie,\* J. Liu,\* L. Wang \_\_\_\_\_\_\_ **5313 – 5317** 

Polymer Acceptor Based on B←N Units with Enhanced Electron Mobility for Efficient All-Polymer Solar Cells





The Binder Age: The organic binder in hybrid materials was used as a platform for grafting to preserve the high double-layer capacitance and the low ionic resistance of porous carbons. This binder

allowed minimizing the loading of inactive material in the electrode, while improving its capacitance and reducing its ionic resistance, mainly owing to a better wettability of the porous carbon.

### **Pseudocapacitors**

C. Benoit, D. Demeter, D. Bélanger,\*
C. Cougnon\* \_\_\_\_\_\_ 5318 - 5321

A Redox-Active Binder for Electrochemical Capacitor Electrodes





**Continuum split**: The isolation and systematic structural analysis of non-anchored indole–palladium(II) complexes revealed that there is a  $\sigma$ - $\pi$  continuum for

heteroarene—metal complexes. These findings may provide insights into key catalytic intermediates of metal-catalyzed heteroarene transformations.

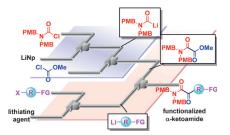
### **Coordination Modes**

K. Yamamoto, S. Kimura,

T. Murahashi\* \_\_\_\_\_\_ 5322 – 5326

 $\sigma\text{--}\pi \text{ Continuum in Indole-Palladium(II)}$  Complexes





Go with the flow: Using a flow microreactor system, carbamoyllithium compounds were successfully generated and used to react with electrophiles to give various amides, including  $\alpha$ -ketoamides. The method was applied to the three-component synthesis of functionalized  $\alpha$ -ketoamides using a carbamoyllithium compound, methyl chloroformate, and a functionalized organolithium reagent. PMB = p-methoxybenzyl; FG = functional group.

# <u>Microreactors</u>

A. Nagaki,\* Y. Takahashi,

J. Yoshida\* \_\_\_\_\_\_ 5327 – 5331

Generation and Reaction of Carbamoyl Anions in Flow: Applications in the Three-Component Synthesis of Functionalized  $\alpha$ -Ketoamides



Inside Back Cover



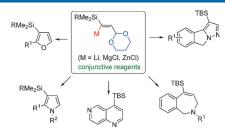


### Conjunctive Reagents

Z.-L. Shen, V. Dhayalan, A. D. Benischke, R. Greiner, K. Karaghiosoff, P. Mayer, P. Knochel\* \_\_ 5332 - 5336



Polyfunctional Lithium, Magnesium, and Zinc Alkenyl Reagents as Building Blocks for the Synthesis of Complex Heterocycles Versatile conjunctive reagents: New conjunctive β-silylated organometallic reagents of Li, Mg, and Zn have been prepared and used for an expeditive construction of various polyfunctionalized 5-, 6-, and 7-membered heterocycles, such as furans, pyrroles, quinolines, benzo-[b]thieno-[2,3-b]pyridine, naphthyridines, fused pyrazoles, and 2,3-dihydrobenzo-[c]azepines.





#### Genetic Code

T. Mukai, M. Englert, H. J. Tripp, C. Miller, N. N. Ivanova, E. M. Rubin,

N. C. Kyrpides, D. Söll\* \_\_\_\_ 5337 - 5341



Facile Recoding of Selenocysteine in Nature

Stop making sense: Selenocysteine is encoded by UGA, a stop codon reassigned by a Sec-specific elongation factor and a distinctive RNA structure. Analysis of 6.4 trillion base pairs of metagenomic sequences and about 25 000 genomes revealed tRNASec species that recognize the stop codons UAG and UAA, and ten sense codons. Thus the genetic code is much more flexible than previously thought.

Selenocysteine codons



major

AGA

minor expected

less expected

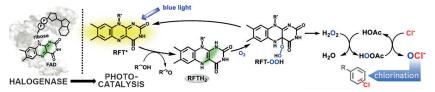
**GGA** 

### **Oxidative Chlorination**

T. Hering, B. Mühldorf, R. Wolf,\* B. König\* -\_ 5342 - 5345



Halogenase-Inspired Oxidative Chlorination Using Flavin Photocatalysis



Chlorination of arenes with chloride anions: The photochemical analogue of the enzymatic chlorination of Flavin-adenine dinucleotide (FAD)-dependent halo-

genases is possible in the presence of riboflavin, air, acetic acid, and blue light (see scheme; RFT = riboflavin tetraacetate).



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



This article is accompanied by a cover picture (front or back cover, and inside or outside).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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