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:

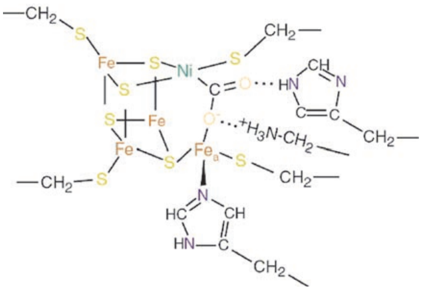
News

Books

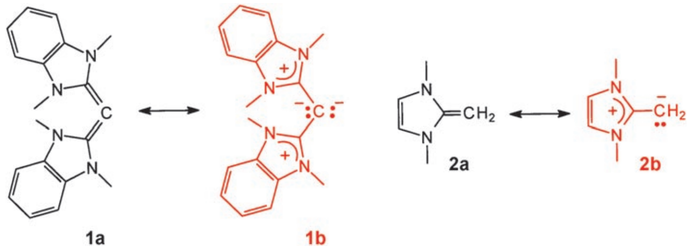
Highlights

Bioinorganic Chemistry

Seeing the C: Nickel-containing carbon monoxide dehydrogenases reversibly oxidize CO to CO$_2$ at a {[Fe$_3$S$_4$]:[Ni Fe$_a$]} active site known as the C-cluster. Recently reported structures of the enzyme by Jeoung and Dobbek, including those of CO$_2$-bound and OH-bound intermediates, shed new light on the enzyme's catalytic mechanism. This Highlight describes these developments and their implications.



Carbodicarbenes



Polarization of C=C bonds is the trick! A "push–push" polarization of the double bonds stabilized the nonlinear allene **1a** ($\sphericalangle_{C-C-C}$ 134.8(2)°), which can be described as carbodicarbene **1b**. A similar behavior has been observed for 1,3-dimethyl-2-methyleneimidazoline, which can be seen as an olefin **2a** or an ylide **2b**. Both compounds **1** and **2** act as interesting electron-rich η^1 ligands for transition metals.

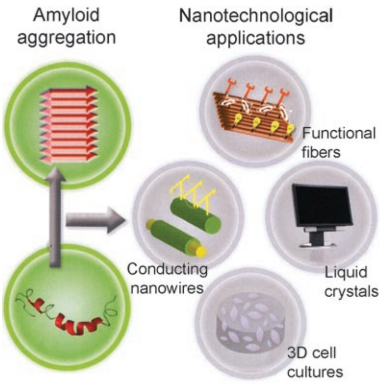
Minireviews

Protein Aggregates

I. Cherny, E. Gazit* ________ **4062 – 4069**

Amyloids: Not Only Pathological Agents but Also Ordered Nanomaterials

Domestication of amyloids: Amyloid structures, some beneficial, some detrimental, exist in nature. Now that these protein assemblies have been characterized and the amyloidogenic motifs identified, these types of structures will soon be utilized in a range of nanotechnological applications.



Reviews

Organic Electronics

S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf* ______ **4070 – 4098**

Organic Semiconductors for Solution-Processable Field-Effect Transistors (OFETs)

Part of the solution: Solution-processable organic semiconductor materials will take on a pivotal role in printed components of organic electronics (see photo; copyright Evonik). This Review gives an overview of the favored strategies for the solubilization of organic semiconductors and their synthetic conversion. Low molecular weight and oligomeric semiconductor materials as well as semiconductor polymers are discussed.

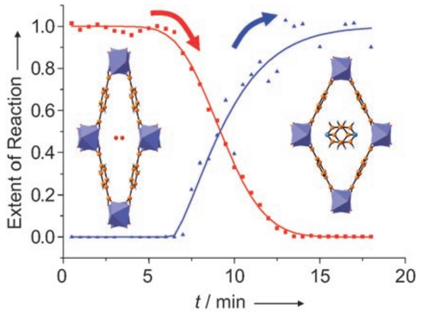
Communications

Metal–Organic Frameworks

F. Millange,* C. Serre, N. Guillou, G. Férey, R. I. Walton* ______ **4100 – 4105**

Structural Effects of Solvents on the Breathing of Metal–Organic Frameworks: An In Situ Diffraction Study

Breathing space: Time-resolved diffraction studies of the breathing of metal–organic frameworks in the presence of liquids reveal rapid exchange of one guest molecule by another. In some cases this occurs by direct exchange (as shown for water by pyridine), in others with the transient appearance of crystalline intermediates corresponding to partially expanded forms.



For the USA and Canada:
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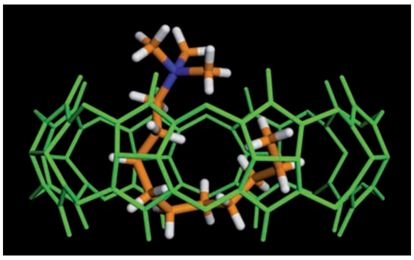
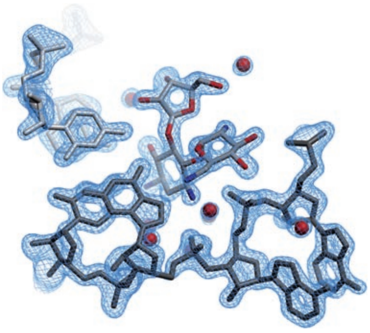
Taking it in turn: Despite the high internal strain, the long aliphatic chains of alkyltrimethylammonium ions buried deeply inside the cucurbit[8]uril (CB[8]) cavity adopt a U-shaped conformation (see X-ray structure), which is stabilized by electrostatic and van der Waals interactions with the carbonyl-laced portal and hydrophobic cavity of CB[8]. This conformation is similar to that of fatty acids bound to fatty acid binding proteins.



Host–Guest Chemistry

Y. H. Ko, H. Kim, Y. Kim,
K. Kim* ———— **4106–4109**

U-Shaped Conformation of Alkyl Chains Bound to a Synthetic Host

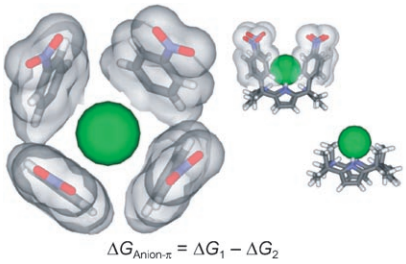


Targeting HIV RNA: High-resolution X-ray structures of the HIV-1 genomic RNA dimerization initiation site (DIS) extended duplex bound to several aminoglycoside antibiotics have been obtained (see ribostamycin complex as an example). They show the feasibility of targeting viral RNA with small drugs, and open up the possibility of structure-based rational drug design aimed against viral replication.

RNA Structures

S. Freisz, K. Lang, R. Micura, P. Dumas,
E. Ennifar* ———— **4110–4113**

Binding of Aminoglycoside Antibiotics to the Duplex Form of the HIV-1 Genomic RNA Dimerization Initiation Site

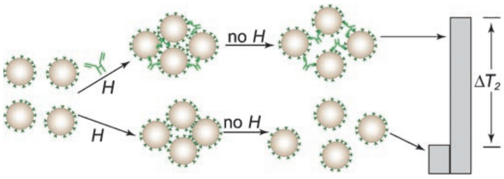


Anions included: A series of *meso*-tetraaryl calix[4]pyrrole receptors have been used as a model system to quantify chloride–π interactions in solution (see picture; green balls are chloride ions). The free energy values are generally indicative of a repulsive interaction; their magnitude depends on the substituent on the aromatic ring.

Anion–π Interactions

G. Gil-Ramírez, E. C. Escudero-Adán,
J. Benet-Buchholz,
P. Ballester* ———— **4114–4118**

Quantitative Evaluation of Anion–π Interactions in Solution

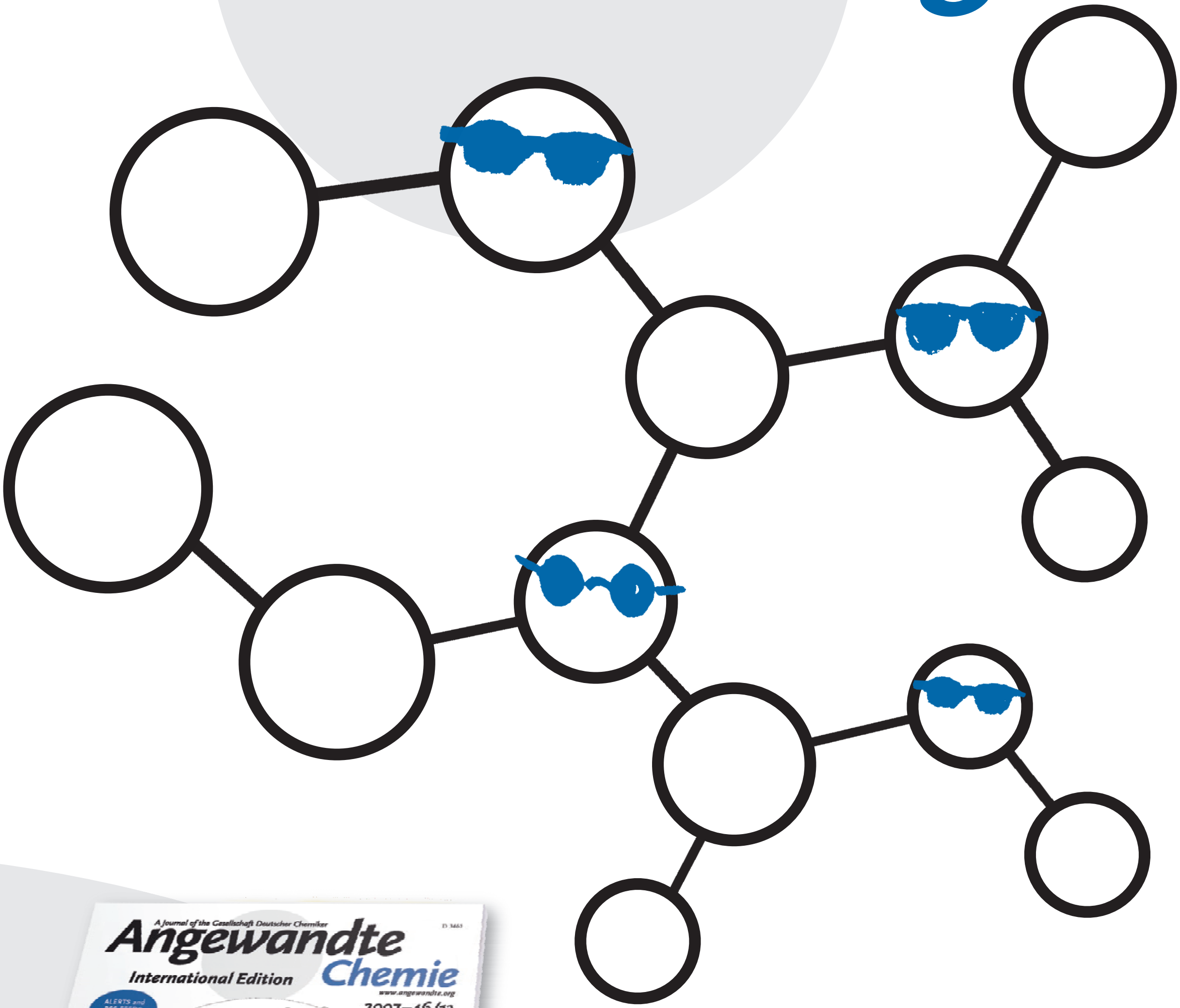


Catching the flu: Magnetic particle aggregation has been used to provide a highly sensitive, NMR-based sensor for detecting antibodies to an influenza virus. To achieve high sensitivity, a homogeneous magnetic field (H) was employed to enhance antibody-based cross-linking between particles suspended in solution (see scheme; ΔT_2: change in the transverse relaxation time).

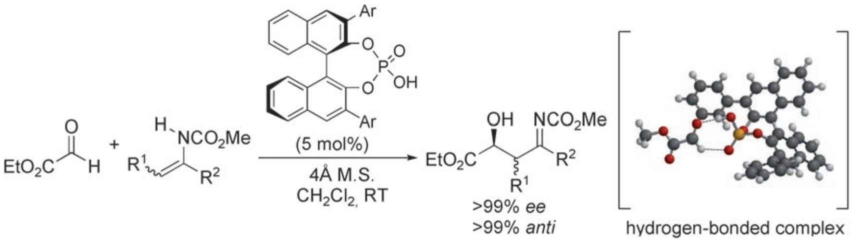
Biosensors

I. Koh, R. Hong, R. Weissleder,
L. Josephson* ———— **4119–4121**

Sensitive NMR Sensors Detect Antibodies to Influenza



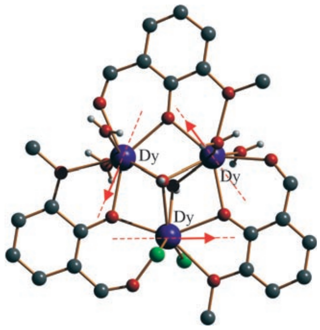
Organocatalysis



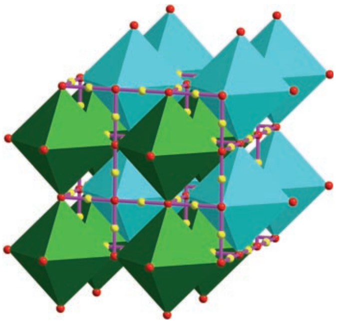
Double interaction does it: Highly enantio- and diastereoselective aza-ene-type reaction of glyoxylate with an enecarbamate is accomplished by using a binol-derived phosphoric acid catalyst (see scheme). DFT computational analysis revealed that two hydrogen bonds formed between the catalyst and the aldehyde are critical for the high enantioselectivity.

Molecular Magnetism

Triangular donuts: High-level ab initio calculations reveal a toroidal arrangement of local magnetizations at dysprosium sites in the ground state of triangular dysprosium complexes (see picture), an arrangement that explains their unusual magnetic properties.

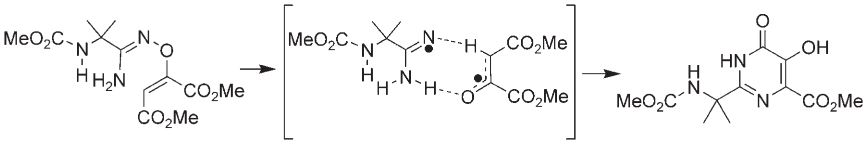


Metal–Organic Frameworks



Narrow pores for high selectivity: The ytterbium metal–organic framework PCN-17, which contains coordinatively (through SO_4^{2-} ions) linked, doubly interpenetrated (8,3)-nets (see picture), is stable up to 480 °C and exhibits selective adsorption of H_2 and O_2 over N_2 and CO.

Mechanistic Studies



Break up to make up: Combined experimental and computational studies provide evidence that the key step in the synthesis of a novel anti-HIV drug involves an unprecedented stepwise radical pair rearrangement mechanism in which radical fragments are held together by strong electrostatic forces (see scheme); this is favored over alternative mechanisms involving concerted pericyclic rearrangement.

Hydrophobic Compounds

J. M. Mabry,* A. Vij,* S. T. Iacono,
B. D. Viers ______________ **4137 – 4140**

Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS)

Water-repellent: Fluorinated polyhedral oligomeric silsesquioxanes (POSS) are produced by facile, single-step, base-catalyzed condensation of trialkoxy silanes. The octameric fluorinated polyhedra are soluble, thermally stable, and hydrophobic, exhibiting static water contact angles up to 154°. The fluorodecyl POSS is believed to be the most hydrophobic crystalline solid known.

η^1-Silane Complex

J. Yang, P. S. White, C. K. Schauer,*
M. Brookhart* ______________ **4141 – 4143**

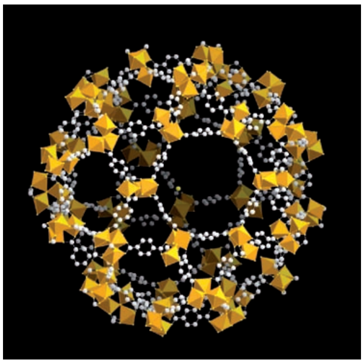
Structural and Spectroscopic Characterization of an Unprecedented Cationic Transition-Metal η^1-Silane Complex

No room for side-on: In the complex shown, Et$_3$SiH is bound to the cationic Ir^{III} center in an unprecedented end-on fashion through the Si—H bond with no appreciable metal–silicon interaction (white H, green Si, pink Ir, red O, orange P, gray C). The long Ir···Si distance of 3.346(1) Å is 0.97 Å greater than the sum of the covalent radii of Ir and Si. DFT studies indicate that the *t*Bu substituents on the bidentate phosphorus ligand dictate the coordination mode of the silane.

Porous Materials

Y. K. Hwang, D.-Y. Hong, J.-S. Chang,*
S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont,
M. Daturi, C. Serre,
G. Férey* ______________ **4144 – 4148**

Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation



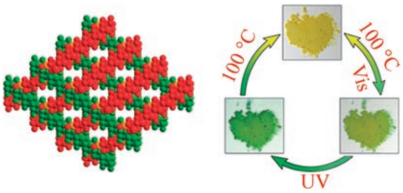
The coordinatively unsaturated sites in MIL-101, $Cr_3(F,OH)(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3\cdot nH_2O$ ($n \approx 25$), having zeotypic giant pores can be selectively functionalized in a way differing from that of mesoporous silica. Metal–organic frameworks, grafted with ethylenediamine or diethylenetriamine on the unsaturated Cr^{III} sites of MIL-101, exhibit remarkably high activities in the Knoevenagel condensation relative to that of the mesophase.

Open-Framework Materials

Z.-J. Zhang, S.-C. Xiang, G.-C. Guo,*
G. Xu, M.-S. Wang, J.-P. Zou, S.-P. Guo,
J.-S. Huang ______________ **4149 – 4152**

Wavelength-Dependent Photochromic Inorganic–Organic Hybrid Based on a 3D Iodoplumbate Open-Framework Material

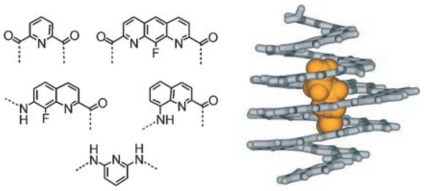
Plumb pudding: A 3D iodoplumbate inorganic–organic hybrid built from purely octahedral units, obtained through in situ solvothermal synthesis, belongs to a new structural subclass of organically templated inorganic open-framework materials. It exhibits the properties of its 1D incomplete-cubane-chain building block and shows ordered and periodic quantum-wire behavior, as well as a wavelength-dependent photochromic response.



Oligoamide Foldamers

C. Bao, B. Kauffmann, Q. Gan, K. Srinivas, H. Jiang, I. Huc* ________ **4153 – 4156**

Converting Sequences of Aromatic Amino Acid Monomers into Functional Three-Dimensional Structures: Second-Generation Helical Capsules

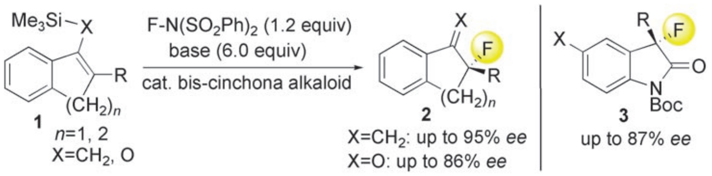


New codes for sequence–structure–function relationships can be elaborated in aromatic oligoamide foldamers upon varying main-chain components. Each monomer carries its own structural and functional features and enables oligomeric sequences to be designed to encapsulate specific guests.

Fluorination

T. Ishimaru, N. Shibata,* T. Horikawa, N. Yasuda, S. Nakamura, T. Toru, M. Shiro ________ **4157 – 4161**

Cinchona Alkaloid Catalyzed Enantioselective Fluorination of Allyl Silanes, Silyl Enol Ethers, and Oxindoles

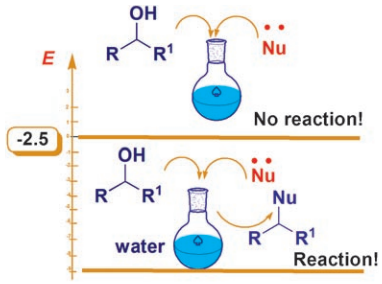


Catalytic variant: Allyl silanes and silyl enol ethers **1** are good substrates for the catalytic highly enantioselective fluorodesilylation using a combination of a bis-cinchona alkaloid, *N*-fluorobenzenesulfonimide (NFSI), and base (see scheme). Pharmaceutically attractive 3-aryl-3-fluorooxindoles such as **3** can also be synthesized with high enantioselectivity.

Heterogeneous Reactions

P. G. Cozzi,* L. Zoli ________ **4162 – 4166**

A Rational Approach towards the Nucleophilic Substitutions of Alcohols “on Water”

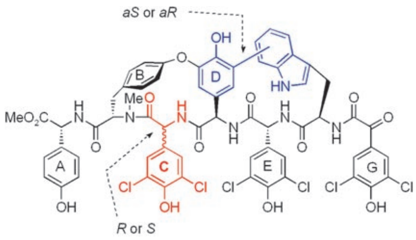


Walking on water: Which alcohols react with nucleophiles on the surface of water? The correlations introduced by Mayr et al., in which electrophiles are characterized by the parameter *E*, gives practical indications about the reactivity of alcohols with nucleophiles in pure water. Stable carbocations generated from the alcohols and characterized by $E < -2.5$ readily react with nucleophiles in pure water at 80 °C, without added Brønsted or Lewis acids.

Asymmetric Synthesis

Y. Jia, M. Bois-Choussy, J. Zhu* ________ **4167 – 4172**

Synthesis of Diastereomers of Complestatin and Chloropeptin I: Substrate-Dependent Atropstereoselectivity of the Intramolecular Suzuki–Miyaura Reaction



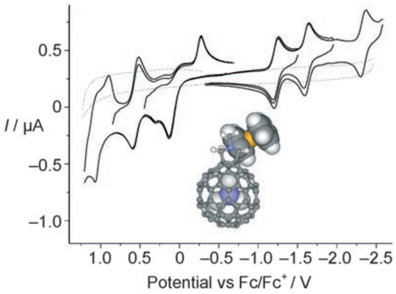
See the effect of C: Atropisomers as well as C_{C2} epimers of complestatin and chloropeptin I (see picture) are readily synthesized through an intramolecular S_NAr reaction and the Suzuki–Miyaura reaction. The absolute configuration of amino acid C (red) was found to determine the atropselectivity of the aryl–aryl (blue) bond-forming reaction.

Metallofullerenes

J. R. Pinzón, M. E. Plonska-Brzezinska, C. M. Cardona, A. J. Athans, S. S. Gayathri, D. M. Guldi,* M. Á. Herranz, N. Martín,* T. Torres,* L. Echegoyen* ____ **4173–4176**

Sc$_3$N@C$_{80}$-Ferrocene Electron-Donor/Acceptor Conjugates as Promising Materials for Photovoltaic Applications

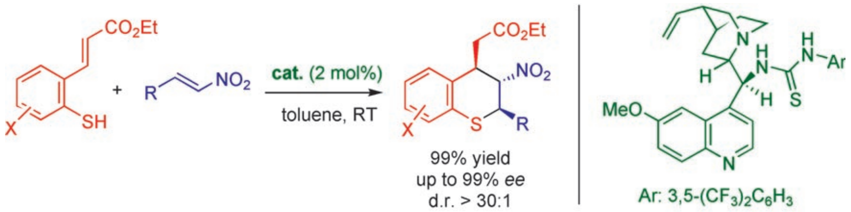
Intriguing materials for photovoltaics: The first trimetallic nitride endohedral metallofullerene covalently connected to a donor group is efficiently synthesized in a 1,3-dipolar cycloaddition reaction. Exclusive formation of the [5,6]-regioisomer in the isolated *N*-methyl-2-ferrocenyl-I_h-Sc$_3$N@C$_{80}$-fulleropyrrolidine is confirmed by NMR spectroscopy and electrochemistry (see picture).



Cascade Reactions

J. Wang, H. Xie, H. Li, L.-S. Zu, W. Wang* ____ **4177–4179**

A Highly Stereoselective Hydrogen-Bond-Mediated Michael–Michael Cascade Process through Dynamic Kinetic Resolution

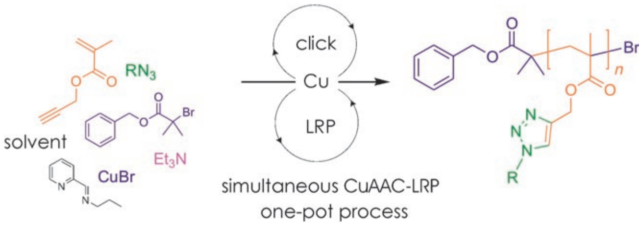


Oh Mickey, you're so fine: The title reaction, which is efficiently catalyzed by a cinchona alkaloid thioure affords direct access to thiochromanes in high efficiency. The reaction features a new activation mode of organocatalytic dynamic kinetic resolution involving a Michael–retro-Michael–Michael–Michael cascade.

Living Polymerization

J. Geng, J. Lindqvist, G. Mantovani,* D. M. Haddleton* ____ **4180–4183**

Simultaneous Copper(I)-Catalyzed Azide–Alkyne Cycloaddition (CuAAC) and Living Radical Polymerization



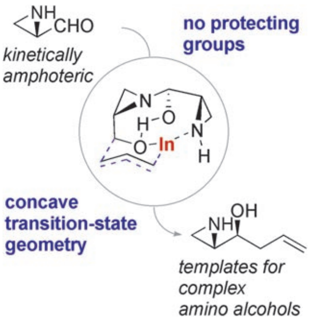
All in one: CuBr/iminopyridine systems can catalyze simultaneously both copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC, "click") and living radical polymerization (LRP) processes (see scheme). The relative rate of the two processes can be tailored by a judicious choice of the reaction conditions (solvent, temperature, [CuBr]$_0$) leading to the development of a potentially very efficient synthetic route to well-defined functional polymers.

C−H Bond Activation

W. Tu, L. Liu, P. E. Floreancig* ____ **4184–4187**

Diastereoselective Tetrahydropyrone Synthesis through Transition-Metal-Free Oxidative Carbon–Hydrogen Bond Activation

C−C bonds from C−H bonds: Tethering nucleophilic groups to benzylic and allylic ethers allows cyclization reactions by DDQ-mediated oxidative carbon–hydrogen bond activation (see scheme; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone). The method is operationally simple, proceeds with a wide range of ether groups, is tolerant of functional groups, and is highly stereoselective.



Apples and oranges: The term “amphoteric” is derived from the Greek “amphoteros”, which literally means “both of two”. Amphoteric amino aldehydes are counterintuitive molecules in that they contain both electrophilic and nucleophilic centers. These small but powerful reagents can be used for the streamlined construction of complex amino alcohol scaffolds (see scheme). Their premature self-destruction is prevented on kinetic grounds.

Synthetic Methods

R. Hili, A. K. Yudin* ______ **4188 – 4191**

Amphoteric Amino Aldehydes Enable Rapid Assembly of Unprotected Amino Alcohols

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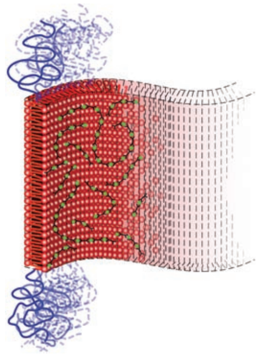

Concerted effects: Triblock peptide copolymers, organic multidentate ligands, and Zn^{2+} ions associate spontaneously into well-defined nanoribbons when dissolved at proper ratios in water at moderate pH values. These nanofibers are stabilized by an extraordinary concerted effect of distinct noncovalent interactions: metal–ligand complexation, hydrogen bonding, hydrophobic interaction, and polyelectrolyte complexation between coordination polymers and the charged blocks of the peptide copolymers.

Polypeptides

Y. Yan,* A. A. Martens, N. A. M. Besseling, F. A. de Wolf, A. de Keizer, M. Drechsler, M. A. Cohen Stuart* ______ **4192 – 4195**

Nanoribbons Self-Assembled from Triblock Peptide Polymers and Coordination Polymers

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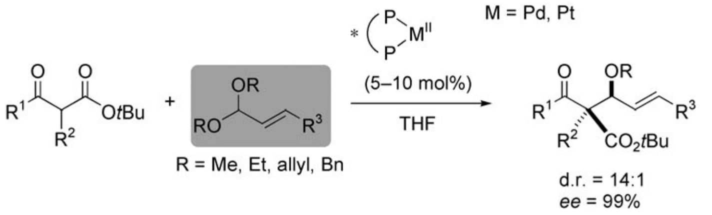

Two activations, one catalyst: By using cationic Pd and Pt complexes, a catalytic enantioselective aldol-type reaction of β-ketoesters with acetals has been developed (see scheme). The formation of metal enolates occurs under acidic conditions to allow the use of acetals as electrophiles to give the desired aldol products in high diastereoseletivity and enantioselectivity.

Asymmetric Catalysis

N. Umebayashi, Y. Hamashima, D. Hashizume, M. Sodeoka* ______ **4196 – 4199**

Catalytic Enantioselective Aldol-type Reaction of β-Ketosters with Acetals

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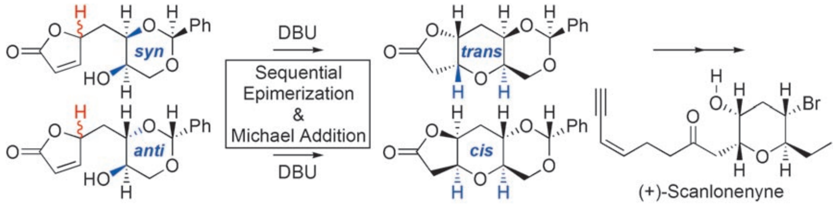


A synthetic three-ring circus: The asymmetric total synthesis of (+)-scanlonenyne includes a sequential epimerization and intramolecular hetero-Michael addition for the construction of pyrano-γ-lactones (see scheme; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene), a highly efficient one-carbon homologation/bromination strategy, and a Weinreb ketone synthesis/cross-metathesis protocol for the elaboration of a sensitive side chain.

Natural Product Synthesis

H. Lee, K. W. Kim, J. Park, H. Kim, S. Kim, D. Kim,* X. Hu, W. Yang, J. Hong ______ **4200 – 4203**

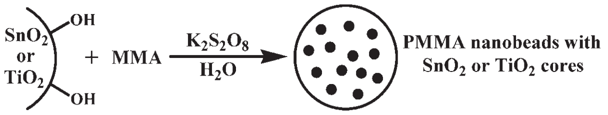
A General Strategy for Construction of Both 2,6-*cis*- and 2,6-*trans*-Disubstituted Tetrahydropyrans: Substrate-Controlled Asymmetric Total Synthesis of (+)-Scanlonenyne

Contents

Nanostructured Enrichment Materials

H.-M. Xiong, X.-Y. Guan, L.-H. Jin,
W.-W. Shen, H.-J. Lu,*
Y.-Y. Xia* **4204 – 4207**

Surfactant-Free Synthesis of SnO_2@PMMA and TiO_2@PMMA Core–Shell Nanobeads Designed for Peptide/Protein Enrichment and MALDI-TOF MS Analysis

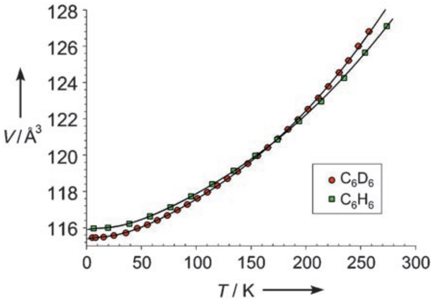


Extremely low concentrations of peptides and proteins can be enriched from complex solutions by SnO_2@PMMA and TiO_2@PMMA core–shell nanobeads with controlled size and composition (see picture for schematic synthesis), and their MALDI-TOF MS signal intensities and signal-to-noise ratios are also significantly improved. These effects are ascribed to the physical properties and structure of the nanobeads. PMMA = poly(methyl methacrylate).

Deuterium Isotope Effects

J. D. Dunitz,*
R. M. Ibberson* **4208 – 4210**

Is Deuterium Always Smaller than Protium?

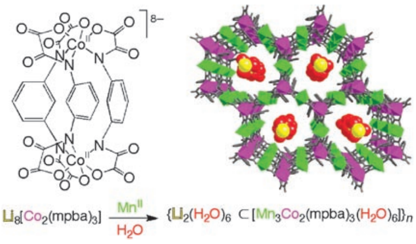


A question of size: At low temperatures the molecular volume in crystalline deuterated benzene is smaller than in the hydrogen isotopologue; above 170 K, however, the reverse is true (see graph).

Molecular Magnets

E. Pardo, D. Cangussu, M. C. Dul,
R. Lescouëzec, P. Herson, Y. Journaux,*
E. F. Pedroso, C. L. M. Pereira,
M. C. Muñoz, R. Ruiz-García, J. Cano,
P. Amorós, M. Julve,
F. Lloret* **4211 – 4216**

A Metallacryptand-Based Manganese(II)–Cobalt(II) Ferrimagnet with a Three-Dimensional Honeycomb Open-Framework Architecture

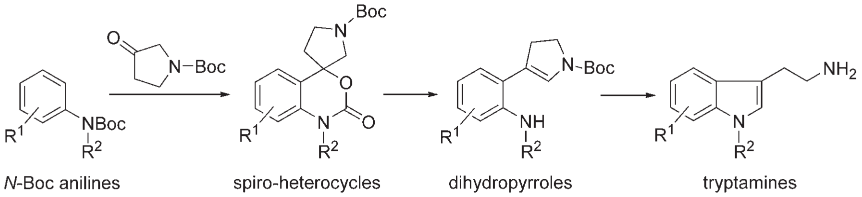


Building a three-dimensional magnet: The manganese(II)-mediated self-assembly of a ferromagnetically coupled dicobalt(II) metallacryptand provides the first example of an oxamato-bridged heterobimetallic ferrimagnet with a three-dimensional honeycomb open-framework structure hosting linear arrays of water-bridged lithium(I) guests (see picture; mpba = 1,3-phenylenebis(oxamato)).

Heterocycles

K. C. Nicolaou,* A. Krasovskiy,
V. É. Trépanier,
D. Y.-K. Chen* **4217 – 4220**

An Expedient Strategy for the Synthesis of Tryptamines and Other Heterocycles

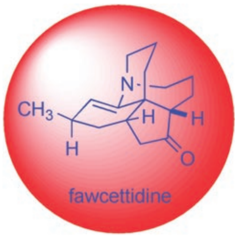


Making many from one: N-Boc-protected anilines are converted into an array of useful N-heterocycles and tryptamines through an expedient, cascade-based synthetic sequence involving *ortho* metalation and subsequent coupling with N-Boc-pyrrolidin-3-one (see scheme).

Alkaloid Synthesis

J. A. Kozak, G. R. Dake* ____ 4221 – 4223

Total Synthesis of (+)-Fawcettidine

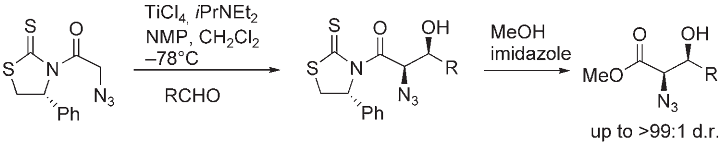


Alkaloids alchemy: A synthesis of the *Lycopodium* alkaloid (+)-fawcettidine (see structure) has been developed which requires 16 steps from (*R*)-(+)-pulegone as the chiral starting material. Key steps include a platinum(II)-catalyzed annulation reaction of a functionalized enamide and a one-pot Ramberg–Bäcklund process.

Synthetic Methods

J. Patel, G. Clavé, P.-Y. Renard,
X. Franck* ____ 4224 – 4227

Straightforward Access to Protected *syn* α-Amino-β-hydroxy Acid Derivatives

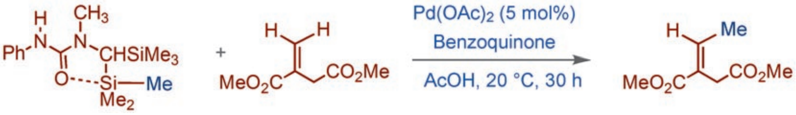


Titanium stability: *syn* α-Amino-β-hydroxy acid derivatives were prepared in excellent diastereoselectivities by an aldol reaction with chiral *N*-(azidoacetyl)thiazolidin-2-thione derivatives (see scheme; NMP = *N*-methylpyrrolidinone). Titanium enolates of these derivatives are stable and provide a new and efficient method to access chiral amino acids.

Intermolecular Heck Methylations

W. Rauf, J. M. Brown* ____ 4228 – 4230

Catalytic Amide-Mediated Methyl Transfer from Silanes to Alkenes in Fujiwara–Moritani Oxidative Coupling

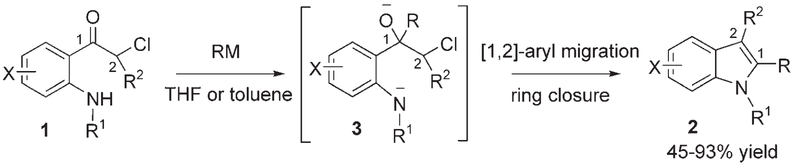


Intramolecular assistance: Carbon-bound trimethylsilyl groups are activated intramolecularly by a carbonyl group and can participate in Heck reactions under oxidative conditions. Good stereoselectivities are obtained for a range of di- and trisubstituted alkenes (see example).

Synthetic Methods

T. Pei,* C.-Y. Chen,* P. G. Dormer,
I. W. Davies ____ 4231 – 4233

Expanding the [1,2]-Aryl Migration to the Synthesis of Substituted Indoles



Closing in on the product: A range of 2- and 2,3-substituted indoles **2** have been synthesized in moderate to excellent yields by the addition of carbon nucleophiles (organometallic reagents, RM) to readily accessible 1-(2-aminophenyl)-2-chloroethanones of type **1** under mild conditions (see scheme). A mechanism has been proposed that involves a unique [1,2]-aryl migration of intermediate **3**.

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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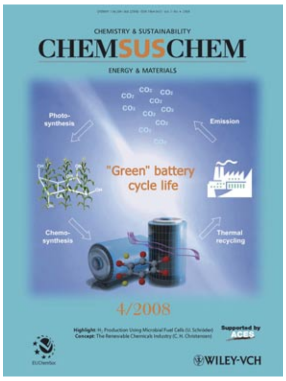

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Corrigendum

Medicinal Chemistry: F. von Nussbaum Honored Solid-State Chemistry: Prize to T. Loiseau Literature: 100 Years of CAS

____ **3086–3086**

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The last sentence in the news item in Issue 17 was incorrect. It should read: “CAS Director Robert Massie (right) presented an accolade to Dr. Reinhard Neudert on behalf of Wiley-VCH in recognition of the many years of collaboration.”